A STUDY OF THE THERMAL DECOMPOSITION
OF ESTERS OF OXALIC ACID

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OF ESTERS OF OXALIC ACID

by

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SCOPE AND CONTENTS:

This work was initiated with a view to elucidating the hitherto little-studied thermolysis of esters of oxalic acid.

A number of symmetrical diesters were synthesized and several were investigated thoroughly by use of product studies, kinetic methods and kinetic isotope-effect measurements. Both preparative and pyrolytic procedures and results are recorded.

The literature regarding previous studies of the effect of heat on oxalate esters is surveyed, and a review of the principles and uses of the investigative methods employed is presented.

The results are discussed in the light of more recent work and both general and specific mechanisms for oxalate thermolysis are suggested.

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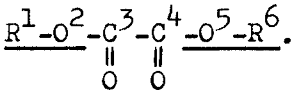
General Introduction

When symmetrical esters of oxalic acid are heated, either neat or in an inert solvent, they decompose to give a variety of products. Among the products resulting most frequently from this type of reaction are carbon monoxide, carbon dioxide, olefins and formates[1-7,94]. The product distribution often varies widely with changes in the conditions of the reaction, particularly with changes in temperature. For example, diethyl oxalate yields ethylene and carbon dioxide in all cases, but variable amounts of carbon monoxide, formic acid, ethyl formate and water may also be produced[1-5]. Other oxalates give rise to carbonates[6,7], aldehydes[7,11], alcohols[11,17], ethers[11] or substituted acetates[17].

(1) Possible Mechanisms for Decomposition of an Oxalate



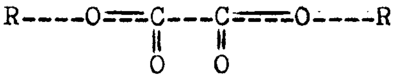
$\underline{R^1\text{-}O^2}\text{-}\underset{\underset{O}{\|}}{C^3}\text{-}\underset{\underset{O}{\|}}{C^4}\text{-}\underline{O^5\text{-}R^6}.$

In the following paragraphs are considered possible mechanisms of decomposition of an oxalate, together with the products that might be expected from each. The objective of this survey is to disclose differences which can be used to infer mechanism or at least to exclude particular mechanisms in certain cases.

a) Homolytic bond cleavage.

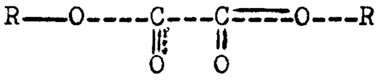
It is possible to conceive of homolytic bond cleavage occurring at the 1-2, 2-3 and 3-4 bonds, to yield free radicals of different degrees of stability. The nature of the products suggests that all three types of bonds may be broken. It therefore becomes of interest to determine whether bond breaking is concerted or, if not, the order of cleavage and the identity of the rate determining step.

Concerted decompositions could proceed via transition states such as I, II, III and IV. Non-concerted mechanisms could involve initial cleavage of one of the bonds 1-2, 2-3 or 3-4, followed by further reaction of the fragments produced, e.g., V, VI and VII.



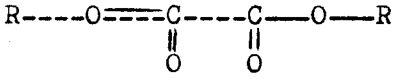
$$\mathrm{R{\cdots}O\overset{\cdots}{=}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}\overset{\cdots}{=}O{\cdots}R}$$

I



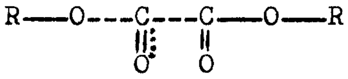
$$\mathrm{R{-}O{\cdots}\underset{\underset{O}{\vdots\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}\overset{\cdots}{=}O{\cdots}R}$$

II



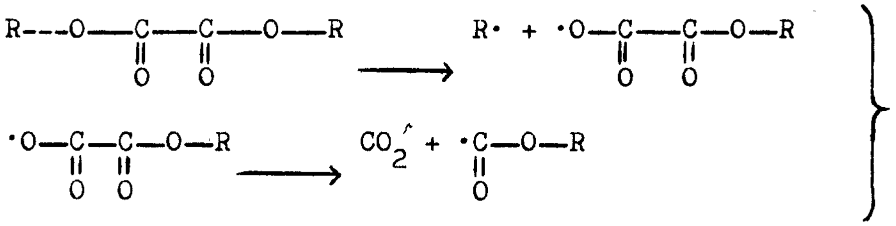
$$\mathrm{R{\cdots}O\overset{\cdots}{=}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

III



$$\mathrm{R{-}O{\cdots}\underset{\underset{O}{\vdots\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

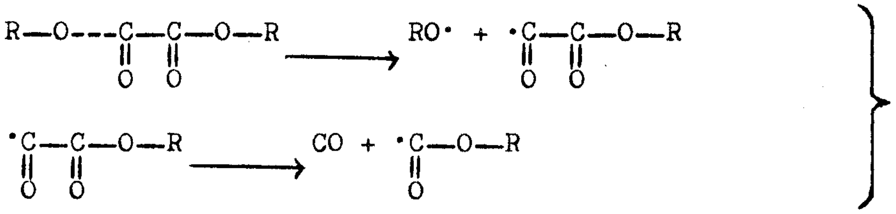
IV



$$\mathrm{R{\cdots}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R\cdot + \cdot O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

$$\mathrm{\cdot O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow CO_2 + \cdot\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

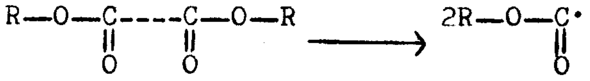
V



$$\mathrm{R{-}O{\cdots}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow RO\cdot + \cdot\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

$$\mathrm{\cdot\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow CO + \cdot\underset{\underset{O}{\|}}{C}{-}O{-}R}$$

VI



$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow 2R{-}O{-}\underset{\underset{O}{\|}}{C}\cdot}$$

VII

Transition state I would lead directly to two molecules of CO_2 and two $R\cdot$ radicals, while II would lead to one molecule of CO_2 and one of CO, together with the radicals $RO\cdot$ and $R\cdot$. Transition states III and IV, for partially concerted mechanisms, would lead to the radical $R\text{-}O\text{-}\dot{C}{=}O$. The fate of radicals such as $R\text{-}O\cdot$, $R\text{-}O\text{-}\dot{C}{=}O$ and $R\cdot$ would depend critically on the nature of R[18].

Where R is a simple alkyl group, $RO\cdot$ could either abstract a labile hydrogen atom to yield the corresponding alcohol, or it could itself undergo abstraction of an α-hydrogen atom, by another radical, to form a carbonyl compound. For long-lived $R\text{-}O\cdot$, coupling with another radical would be an alternative fate[18]. A tertiary alkoxy radical may undergo cleavage of a carbon-carbon bond to yield a carbonyl compound and another radical. The tertiarybutoxy radical, for example, may decompose to acetone and a methyl radical[18,32].

The radical $R\text{-}O\text{-}\dot{C}{=}O$ could abstract a hydrogen atom from a suitable donor, thus producing a formate, or alternatively it could decompose by decarbonylation or decarboxylation to yield, respectively, carbon monoxide and $RO\cdot$, or carbon dioxide and $R\cdot$. Long-lived $R\text{-}O\text{-}\dot{C}{=}O$ might couple with other radicals, yielding products such as $R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R$ or $R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R$. Decompositions involving formation of $R\text{-}O\text{-}\dot{C}{=}O$ radical pairs could conceivably set up equilibrium between caged radicals and parent oxalate.

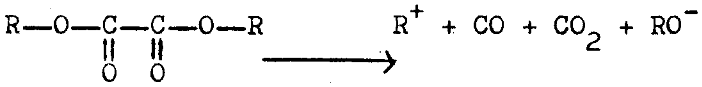
The radical $R\cdot$ also could undergo coupling or it could undergo disproportionation to yield an alkane and an alkene when a β-hydrogen atom is available. Both of these processes occur for a caged pair of 2-cyano-2-propyl radicals (the latter to a small extent)[19].

A priori, one might favour a primary cleavage of the central, 3-4 bond as in mechanism VII, since this bond is weakened by the mutual repulsion between the positive ends of the carbonyl dipoles.

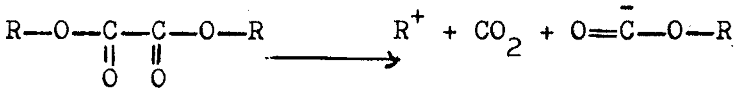
b) Ionic mechanisms.

Several conceivable rate-determining steps for ionic decomposition of an oxalate are written below. Mechanisms involving formation of $R\text{-}O^+$ are too unlikely to be worthy of consideration.

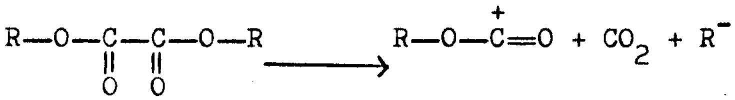
$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R^+ + 2CO_2 + R^- \qquad 1$$



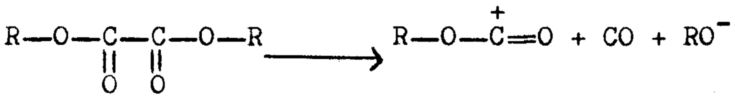
$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R^+ + CO + CO_2 + RO^- \qquad 2$$



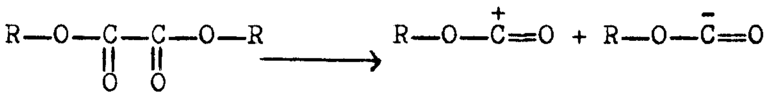
$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R^+ + CO_2 + O{=}\overset{-}{C}{-}O{-}R \qquad 3$$



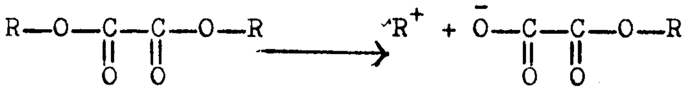
$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R{-}O{-}\overset{+}{C}{=}O + CO_2 + R^- \qquad 4$$



$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R{-}O{-}\overset{+}{C}{=}O + CO + RO^- \qquad 5$$



$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R{-}O{-}\overset{+}{C}{=}O + R{-}O{-}\overset{-}{C}{=}O \qquad 6$$



$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \longrightarrow R^+ + \overset{-}{O}{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \qquad 7$$

Examination of the consequences of these steps reveals the following relationships:

(i) Only 1, 3, 4, 6 and 7 can lead to formation of 2 moles of CO_2 per mole of ester and, of these, only 1 necessarily requires that stoichiometry.

(ii) Carbonate can be formed only through 5 and 6 and can only arise along with CO.

(iii) Cage recombination should lead to some R-O-R from mechanism 2 and to RCOOR from 3 or 4. The mechanisms 6 and 7 could also lead to these products after further steps.

(iv) Formate could be produced via 3, 4, 5, 6 and 7, but not through 1 or 2.

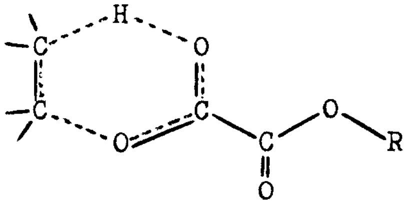
The most likely processes for production of formate are hydride transfer to $R\text{-}O\text{-}\overset{+}{C}\text{=}O$ or proton transfer to $R\text{-}O\text{-}\overset{-}{C}\text{=}O$. Possible hydride donors are $R\text{-}O^-$, R^- or certain solvents and, of these, $R\text{-}O^-$ is the most likely; hence aldehyde or ketone should also be found when formate is produced by such a process. Proton transfer could occur from R^+ or solvent.

Alkanes (R-H and R-R), alkenes and alcohols might be expected as additional products in the general case where R = alkyl. These should arise from ultimate destruction of R^+, R^- and $R\text{-}O^-$ in schemes where these entities occur, and aromatic solvents might undergo substitution by R^+.

It is clear that if a given oxalate decomposition were shown to be ionic in character, it would be possible to obtain additional mechanistic information from product studies. Kinetic isotope effects (C^{13} and O^{18}) might serve to distinguish, for example, 1 from 6 and 7 for these could give identical products.

c) Molecular mechanisms.

The first step in the decomposition of oxalates containing a β-hydrogen atom could be an elimination to the monoester and olefin, via a cyclic transition state. The observed products could be derived from the monoester[13-16,78]. The transition state IX could have considerable charge development and in fact Karabatsos[94] has produced evidence in agreement with this idea.

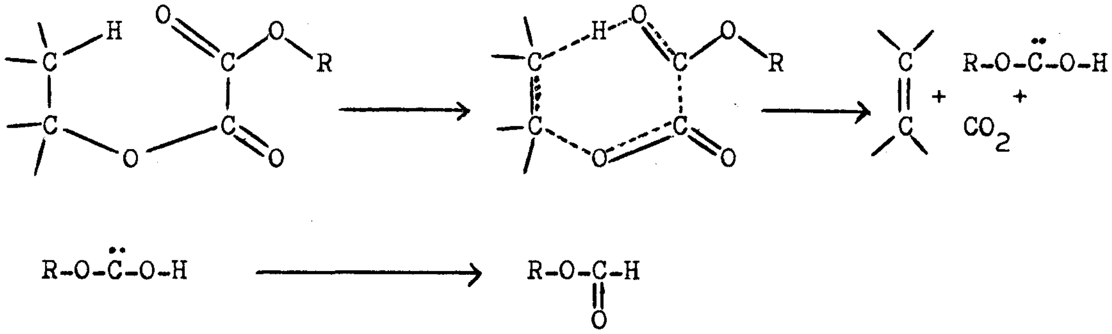


IX

Since esters lacking β-hydrogen atoms undergo thermal decomposition[11,17] this mechanism could not be general.

A cyclic, carbenoid mechanism may be possible for the formation of the formate.

i.e.



(2) Methods Used to Determine Mechanisms.

a) Product studies.

The nature of the products of a reaction often sheds light upon some or all of the steps leading to their formation. For example, the isolation of products such as RCOOR[17] and R-O-$\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}$H[1-5,17] would show that the integrity of the R-O-$\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}$-bond system is maintained sufficiently long for capture of the intermediate to take place, so that mechanisms involving simultaneous cleavage of the 1-2 and 5-6, the 1-2 and 4-5, or the 2-3 and 4-5 bonds, e.g. I and II section (1) a), would be eliminated from consideration.

If no carbonate is found when an oxalate is incompletely decomposed, it is almost certainly not formed at all and hence mechanisms such as 5 (section 1b) would be unlikely. (The results of Ritchie[84] suggest very strongly that dialkyl carbonates should survive conditions sufficiently stringent to decompose the corresponding oxalate.)

Formation of formate has no very strong mechanistic implications since homolytic, ionic and molecular mechanisms can be conceived. However, in the event that its production is unaccompanied by carbonate or CO, a free radical or cyclic mechanism would be indicated.

Changes in product distribution which accompany changes in reaction conditions may also be significant.

Variation of the solvent or of the ionic strength of the medium can change the products of a reaction, but such changes are frequently difficult to interpret with certainty unless solvent-derived species can be identified. The effect of solvation changes on the course of a reaction is often known only qualitatively, if indeed it is understood at all.

The effect of added compounds on the distribution of products in a reaction can often shed light on the mechanism. The presence of reactive intermediates such as ions and radicals can frequently be inferred from the products obtained when a trapping compound is present in the reaction mixture. Carbonium ions often reveal their presence by coupling with the anions from inorganic salts, the addition of which scarcely affects the reaction in any other way, and carbanions are frequently detected by their ability to abstract a deuteron from a suitably labelled solvent. Such "scavenging" compounds have found much use in the investigation of free-radical reactions[20-22]. For reactions in solution it is sometimes found that the addition of a radical scavenger in low concentration reduces the yields of a product to a level that remains constant over a considerable range of larger scavenger concentrations. Such behaviour is the result of the formation of free radicals in pairs. A fraction of such "caged" radicals will be separated by diffusion and it is these which are scavengeable. Geminate coupling in the cage, on the other hand, is not affected, to a first approximation, by low concentrations of scavengers[20]. This phenomenon is known as the "Cage Effect"[23] and has been discussed in some detail by several authors, in particular by Noyes[24,25].

Alkoxy radicals can frequently be trapped if they are generated in the presence of a compound with a readily abstractable hydrogen atom. For example, the occurrence of $(CH_3)_3C\text{-}OH$ as a product of the decomposition of a tertiarybutyl perester in cumene is evidence for the presence of the $(CH_3)_3C\text{-}O\cdot$ radical, especially since bicumyl is also formed (cf. 32 and subsequent papers of that series).

b) Kinetic investigations.

(i) Activation parameters.

The parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are obtained from the fundamental equation (1) of transition state theory[26].

$k = (KT/h) \exp(-\Delta F^{\neq}/RT)$ (1), in which k = rate constant, K = Boltzman constant, T = absolute temperature, h = Planck constant, $\Delta F^{\neq}$ = free energy of activation, R = gas constant.

Since $\Delta F^{\neq} = \Delta H^{\neq} - T.\Delta S^{\neq}$, where $\Delta H^{\neq}$ = enthalpy of activation, and $\Delta S^{\neq}$ = entropy of activation, (1) may be rewritten as (2).

$$k = (KT/h) \exp(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R) \tag{2}$$

Hence by measurement of the rate constant at two or more temperatures the activation parameters may be determined. The current controversy[27-31] regarding the significance of empirical relationships between the activation parameters for a series of related reactions is beyond the scope of the present work. It is possible, however, to discuss activation parameters in a general way and more specific relationships may be established in certain cases[32]. When $\Delta S^{\neq}$ is negative the entropy has decreased during passage from the ground state to the transition state, and this may be a result of a restrictive steric requirement in which the number of possible orientations or degrees of freedom of the molecule has been decreased. For example, reactions passing through a cyclic transition state[79] or possessing bond rotations which are restricted at the transition state relative to the ground state[32], would be expected to have negative $\Delta S^{\neq}$ parameters in the absence of other effects.

Reactions which may proceed only by breaking a relatively strong bond will be expected to have a high enthalpy of activation.

Thus it is not surprising that the thermal cracking of hydrocarbons requires greatly elevated temperatures in order to break the carbon-carbon bonds.

Solvation changes often have a powerful influence on the activation parameters for a reaction in solution, and sometimes this operates in unexpected directions[27,61,62]. It might be predicted that, because of electrostatic considerations, a reaction which developed a polar transition state from non-polar reactants should have a lower activation enthalpy and hence a greater rate, the more polar the solvent. However, Leffler[27] quotes the example of a Menschutkin reaction which, while indeed faster in more polar solvent, owes rate enhancement to a much increased entropy of activation which overcomes an actual increase in the activation enthalpy. Great caution then is required in the interpretation of activation parameters for reactions in solution and, where the changes in these parameters for a series of reactions are of the same order of magnitude as the experimental errors in the values, no quantitative significance whatever can be attached to them[28].

(ii) The Hammett equation - a linear free-energy relationship.

Linear free-energy relationships are expressions of empirical facts such as that noted by Hammett[35], that a plot of log K for the saponification of m- or p-substituted ethyl benzoates against log K_a for the ionization of the corresponding benzoic acids is approximately linear. This result suggests a relationship between the effects of the substituents on the extent of ionization and their effects on saponification rates, and the observation can be expressed mathematically as (3).

$$\log k = a \log K_a + \text{const.} \tag{3}$$

From (1) $\log k = -\Delta F^{\neq}/_{2.303RT} + \log(^{KT}/_{h})$,

and $\log K_a = -\frac{\Delta F}{2.303RT}$,

so that (3) may be written as (4).

$$\frac{-\Delta F^{\neq}}{2.303RT} = a(-\Delta F)/2.303RT - \log\frac{KT}{h} + \text{const.} \tag{4}$$

At constant temperature (4) becomes (5), which is a linear free-energy relationship.

$$\Delta F^{\neq} = a(\Delta F) + \text{const.} \tag{5}$$

Such relationships have been found to apply to both rate and equilibrium constants for many types of reaction series[53]. In particular, the effects of meta- and para-substituents on the rate and equilibrium constants for side-chain reactions of benzene derivatives have, in many cases, been correlated by the Hammett equation (6);

$$\log\left(\frac{k}{k_o}\right) = \rho\sigma \tag{6}$$

where k is the rate or equilibrium constant for a reaction of a meta- or para-substituted benzene derivative, and k_o is that for the corresponding reaction of the unsubstituted compound. The constant σ is characteristic only of the substituent and its position on the ring, and ρ is a constant characteristic of the reaction series and is not dependent on the particular substituent.

The σ parameter is defined by the relationship (7);

$$\sigma = \log K - \log K_o \qquad (7)$$

where K and K_o and the dissociation constants for, respectively, a meta- or para-substituted benzoic acid and for unsubstituted benzoic acid, in water at 25° C. This relation defines the value ρ = 1.0 for the dissociation of meta- and para-substituted benzoic acids under these conditions. Sigma values are usually considered to be representative of the electronic effects of meta- or para-substituents. Electron attracting groups have positive sigma values since they increase the strength of benzoic acids; conversely, since electron releasing groups decrease the strength of benzoic acids, they have negative sigma values.

The rho value is indicative of the susceptibility of the particular reaction series to the electronic influence of meta- or para-substituents. A positive value of ρ implies that the reaction is accelerated or the equilibrium is shifted to the right, by electron attracting substituents. The reverse effect is indicated by a negative rho value. The magnitude of rho is a measure of the sensitivity of the reaction to electronic effects, a high value indicating high susceptibility.

When the reaction site is insulated from the benzene ring, for example by methylene groups, then the substituents should have little or no effect on the change in resonance energy on moving from the ground to the transition state, and the effect of substituents may be considered to result from the change which they induce in electron density at the reaction site. When, however, the reaction site is not insulated from the benzene ring the differences in resonance energy between ground and transition states must also be considered.

Since there is, in general, a lack of precise information regarding the structures and energies of transition states and, in addition, a detailed discussion would have to deal separately with each reaction series, the assumption is customarily made[36] that reactivity depends on the electron distribution in a molecule. This assumption has been formalized and justified by R. D. Brown[38] in his "non-crossing" rule, which says that predictions of reactivities from electron densities will usually, but not necessarily, parallel predictions made from structural considerations or from calculations of the energies of transition states. This rule appears to hold widely for reactions of benzene derivatives[36] and its validity will thus be assumed for the purposes of this work.

Hammett assumed[39] that substituent effects were almost exclusively electrostatic in nature, but this view has been challenged by later workers[40]. Attempts to interpret substituent constants on the basis of purely electrostatic effects have given only fair correlations with experiment[41-44], and similar interpretation of reaction constants has given even poorer results[45].

Jaffe has shown[46-48] that substituent constants can be correlated with changes in electron density induced by the substituents, as calculated by molecular orbital methods, and has demonstrated that both inductive and resonance effects must be considered in order to obtain a satisfactory correlation. He has also had some success in calculating relative reaction constants from a consideration of molecular orbitals involving both inductive and resonance contributions[49].

The electronic influences of two or more substituents appear to be additive[50] in the absence of interfering steric effects, so that the Hammett equation could be expressed as

$$\log \left(\frac{k}{k_o}\right) = \rho \sum \sigma \tag{8}$$

In those instances where $\Delta S^{\neq}$ is essentially constant within a reaction series, rho is inversely related to temperature.

$$\text{Since } \log \left({}^{k}/_{k_o}\right) = (\Delta H_o^{\neq} - \Delta H^{\neq})/_{2.303RT} = \rho\sigma ,$$

$$\text{then } \rho = \left[(\Delta H_o^{\neq} - \Delta H^{\neq}) \ /2.303R\sigma\right] \ ({}^{1}/_{T}) \tag{9}$$

Since $\Delta H^{\neq}$ and σ are independent of temperature to a first approximation[36], then it follows from (9) that $\rho \propto {}^{1}/_{T}$. Hence the variation of rho with temperature should be investigated before any deductions can be made regarding the significance of the magnitude of rho, a precaution particularly necessary when rho is small.

Some strongly electron-releasing groups require special sigma constants for the para position when strong carbonium ion character is developing at the α-carbon in the transition state. H. C. Brown[52] has evaluated a number of these σ^{+} values by using the solvolysis of para-substituted cumyl chlorides as a standard reaction, with $\rho = -4.54$, and has shown that the modified Hammett equation $\log \left(\frac{k}{k_o}\right) = \rho\sigma^{+}$ gives good correlations of experimental data for rates and equilibria of a number of "electrophilic", side-chain reactions.

Similarly, certain strongly electron-withdrawing groups require a special σ^{-} value for reactions of aniline and phenol derivatives, and for nucleophilic substitution at ring positions[36,51].

Bunnett[53] has pointed out that the above considerations mean that the substituent constant is not really a constant at all but is a function of the electronic demands of the reaction series, and that it is surprising that most reaction series give reasonably good correlations without the necessity of introducing further parameters.

Other workers[54,55] have proposed modified treatments which yield a "spectrum" of σ-values. Such methods give good empirical correlations but deprive the σ-values of most of the theoretical significance with which they have been invested.

Taft[56,57] has extended the Hammett equation to deal with ortho-substituted benzene derivatives and aliphatic compounds. His treatment takes account of steric, resonance and inductive effects, and he was able to separate σ_m and σ_p values into their mesomeric and inductive components.

Many homolytic decompositions follow the Hammett relationship. For example the thermal decomposition of some peroxy compounds[36] and the dissociation equilibria of certain substituted tetrazanes[58], have negative rho values in the range -0.3 to -2.4 which is in accordance with the idea that some electrophilic character is associated with the radical center at the transition state, so that the reaction is accelerated by electron-donating substituents. However, other homolytic reactions are not well correlated by the conventional Hammett relationship[33,34], and no general picture of the nature of the transition state of such reactions has as yet emerged, if indeed a general view is applicable.

(iii) Kinetic isotope effects.

Since treatments of the theory of kinetic isotope effects from the points of view of the physical chemist[72], and of the organic chemist[73,74], are available in the literature, it would be superfluous to present a mathematical discussion of the subject here.

Kinetic isotope effects are usually considered to arise from a difference in the zero-point vibrational energy between bonds to different isotopes. The vibrational energy levels for a diatomic molecule A-B are given by (11),

$$E = h(n + \tfrac{1}{2})\nu \qquad (11)$$

where h is the Planck constant, ν is the vibrational frequency and n is the vibrational quantum number. At ordinary temperatures most molecules will be in their lowest (n = 0) energy level and will have the zero-point energy $\tfrac{1}{2}h\nu$. If A-B is regarded as a simple harmonic oscillator, its frequency is given by (12)

$$\nu = (1/2\pi)\,({}^{k}/_{\mu})^{\frac{1}{2}} \qquad (12)$$

where k is the force constant which measures the "stiffness" of the bond and μ is the reduced mass of A and B. Hence if B is replaced by a heavier isotope B*, μ will be increased and ν will be decreased since k is essentially constant. Thus the zero-point energy for A-B* is less than that for A-B. Assuming that, to a first approximation, the bonds A-B and A-B* are completely broken in the transition state, then the product fragments will possess only translational energy which should be identical for both A - B and A - B*. Since A-B starts from a higher level than A-B* it will require less energy for complete dissociation than will A-B* and the rate of bond breaking will be greater.

Various approximations are implicit in the simple theory above. It is assumed that only the bond A-B is affected by isotopic substitution, that the effect of changes in mass on the velocity of passage over the energy barrier is negligible and that there is no "tunneling", i.e. non-classical penetration of the energy barrier. If the bond A-B is not completely broken at the transition state then the assumption of equal energies for the isotopic transition states is not valid and for hydrogen, in some cases, the disregarding of bending modes may be unjustified[75].

Decarboxylation reactions are the most thoroughly studied with respect to carbon isotope effects, in particular the decarboxylation of malonic acid[76]. The case of polybasic acids must be approached with care since statistical considerations may dictate changes in methods of calculation of isotope effects from experimental data[17,73,74].

It is possible to calculate an approximate maximum value for the isotope effect if the stretching frequency of the bond being broken is known[72]. For the case of a symmetrical oxalate, such as benzhydryl oxalate, the following calculation applies[72]. The basic equation is (13),

$$\frac{k_{12}}{nk_{13}} = \left(\frac{\nu^{\neq}_{12}}{\nu^{\neq}_{13}}\right) \left(1 + G(u_1)\cdot\Delta u_1\right) \tag{13}$$

where k_{12} and k_{13} are the rate constants for the two isotopic species and n is a statistical factor. The term $\left(\frac{\nu^{\neq}_{12}}{\nu^{\neq}_{13}}\right)$ is the ratio, in the transition state, of the fundamental vibrations of the rupturing bonds, to the two isotopic species, and this is assumed to be equal to the corresponding ratio in the ground state $\left(\frac{\nu_{12}}{\nu_{13}}\right)$. The parameter u_1 is defined by the relation $u_1 = \frac{hc\nu_1}{KT}$, where ν_1 is the frequency of the bond being broken (in wave-numbers), h is the Planck constant, c is the velocity of light, K is the Boltzman constant and T is the absolute temperature.

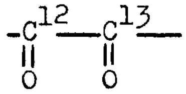
The terms $G(u_1)$ and Δu are defined by the relations (14) and (15),

$$G(u_1) = \frac{1}{2} - \frac{1}{u_1} + \frac{1}{(e^{u_1}-1)} \qquad (14)$$

$$\Delta u_1 = \frac{hc}{KT} (\nu_{12} - \nu_{13}) \qquad (15).$$

The equation (16) is derived from the Slater approximation, which assumes that only the two atoms joined by the bond being broken determine the frequency of the vibration, hence

$$\left(\frac{\nu^{\neq}_{12}}{\nu^{\neq}_{13}}\right) = \left(\frac{\nu_{12}}{\nu_{13}}\right) = \left(\frac{m_1 m_2}{m_1+m_2} \cdot \frac{2m_1}{m_1^{2}}\right)^{\frac{1}{2}} \qquad (16)$$

In (16) $m_1 = 12$ and $m_2 = 13$ for the species  $-\overset{\displaystyle O}{\underset{}{}}$ $-\underset{\underset{\displaystyle O}{\|}}{C^{12}}-\underset{\underset{\displaystyle O}{\|}}{C^{13}}-$.

Taking the value of 1150 cm^{-1} for ν_1[77], placing $T = 500^{\circ}$ K, and combining the equations (13), (14), (15), and (16), the value of $\frac{k_{12}}{k_{13}}$ is determined to be 1.022. That is, the maximum carbon isotope effect expected at this temperature is 2.2%. Similarly the corresponding isotope effect for oxygen is calculated to be 2.7% using the value 1200 cm^{-1} for ν_1[17].

The Slater approximation gives surprisingly good answers[72] despite the many other gross simplifications made in the associated calculations.

When a maximum value is calculated for the kinetic isotope effect for a bond cleavage, it is often possible to make qualitative estimates of the amount of bond stretching at the transition state by comparison of the experimental and the theoretical figures. In fact it is often tacitly assumed that there is a proportionality between the size of the isotope effect and the degree of bond stretching at the transition state.

There are exceptions to the above generalizations. For a three-centered, colinear transition state (e.g., proton transfer), Westheimer[96] has concluded that the isotope effect should pass through a maximum when plotted against the degree of bond stretching at the transition state. The maximum should occur when the central body is approximately equidistant from the other two at the transition state. This treatment does not apply to simple bond-breaking processes.

c) General mechanistic criteria.

In view of the many possible mechanisms for oxalate decomposition it is useful to consider what type of evidence may be used to distinguish between homolytic, heterolytic and molecular mechanisms. Although the criteria to be discussed may sometimes be ambiguous, a strong mechanistic indication may usually be obtained by consideration of a number of such pieces of evidence.

A reaction that is catalyzed by light, peroxides or metal ions and which is sensitive to oxygen, may well be suspected to be free-radical in nature. If, in addition, hydrogen atoms are abstracted from benzylic compounds or mercaptans, vinyl polymerization is initiated and reactive intermediates are scavengeable by stable free-radicals, then the homolytic nature of the reaction can scarcely be doubted. However, reactions may involve free-radical intermediates but may show few of the above characteristics. In such cases additional evidence may be obtained from the effect of solvent changes. Homolytic reactions are often relatively insensitive to changes in the solvent, in the ionic strength of the medium and in substituent groups in the substrate, whereas ionic reactions are usually strongly dependent on such factors.

The ratio of different isomers produced in aromatic substitution or in olefin formation often can be used to determine mechanisms (e.g., 94) and the known differences between ionic and homolytic mechanisms in this regard can usually be traced to the varying response to substituent effects already mentioned.

The characteristics of processes occurring by molecular mechanisms are usually less clear-cut and, as a result, there is frequently controversy regarding such reactions. Isomer ratios[94] and isotope effects have been used to detect such processes and substituent effects are often significant.

Historical

Until very recently, the thermal decomposition of esters of oxalic acid had never been systematically investigated, although data regarding the stability of individual compounds had been recorded, and some work had been done on the diethyl, and the glyceryl, esters[80].

Most of the published data concerns monoalkyl and dialkyl esters, and in most cases carbon monoxide and carbon dioxide are produced.

Grassi[1] noted that, when diethyl oxalate was passed through a red-hot tube, carbon dioxide, ethylene, formic acid and ethyl formate were produced, but no carbon monoxide was found. Senderens[2,3] found that, when the diethyl ester was passed over alumina at 360°, ethylene, carbon dioxide, carbon monoxide and water were produced. Other workers[4,5] found the same products when diethyl oxalate was heated in a sealed tube. It has been suggested[78] that formic acid is an intermediate in the decomposition of oxalic acid, and that carbon monoxide is produced only when the conditions are stringent enough to decompose formic acid. However, other modes of formation of carbon monoxide can be envisaged (see General Introduction).

Some cyclic, glycol oxalates were investigated by Tilicheiev[6,7] who found that, in addition to olefins, carbon monoxide and carbon dioxide, the corresponding carbonate was also produced. In one case[7] the corresponding straight-chain monoaldehyde and the parent glycol were also found.

The decomposition of some perchloroalkyl oxalates has been noted[8,9,10], but the production of phosgene and other acyl chlorides, in addition to carbon oxides, indicates the breaking of carbon-chlorine bonds. Since those products are most easily rationalized as arising by a free-radical abstraction mechanism they point to radical decomposition of the esters.

Upon being refluxed for six hours in the absence of solvent, dibenzyl oxalate was found[11] to yield benzaldehyde, benzyl alcohol and dibenzyl ether as involatile products. Presumably carbon oxides were also produced but the fate of the carbonyl fragments was not investigated. It had previously been reported, by Beilstein[12], that dibenzyl oxalate decomposes on attempted distillation at atmospheric pressure.

Mono-alkyl esters of oxalic acid are much less stable than the di-esters and many cannot be isolated in the free acid form. Mono-methyl oxalate disproportionates, on being heated in a sealed tube, to give oxalic acid and the dimethyl ester[13], and the mono-ethyl ester yields diethyl oxalate, carbon dioxide and ethyl formate when distilled at atmospheric pressure[13]. Mono-isopropyl oxalate disproportionates on storage to give di-isopropyl oxalate and oxalic acid, and on being distilled at atmospheric pressure it yields carbon oxides, di-isopropyl oxalate and isopropyl formate[13]. Mono-n-propyl oxalate disproportionates slowly on storage[13] and the mono-isopentyl derivative decomposes on heating to 100° [14]. Mono-*tert*-butyl oxalate was prepared with some difficulty since it disproportionates at room temperature to give the corresponding di-*tert*-butyl ester and oxalic acid and, on being warmed to 60°, it gives carbon dioxide and iso-butylene[15,16].

Chattaway[80], in attempting to explain the formation of allyl alcohol from a heated mixture of oxalic acid and glycerol, proposed a complicated reaction scheme involving mono-glyceryl oxalate and the 1,2-cyclic ester. His mechanism is based entirely on product studies and the details of individual steps were not established.

When a pure compound is pyrolyzed there is ample opportunity for bimolecular reactions to occur, particularly if the ester exists in the solid or liquid phase for an appreciable time at the reaction temperature, as is the case for the benzyl[11] and the α-cyanoisopropyl[17] esters. Also the pure compound is usually rather polar, and may promote an ionic decomposition mechanism. There is, in general, no reason to suppose that mechanisms deduced from the decomposition of a pure compound should apply to relatively dilute solutions of the compound in a high boiling solvent, and the only relevance of such "neat" decompositions have to solution studies is that they may help to identify products and suggest some paths that the solution reaction might take. In particular, the bimolecular mechanism proposed by Risinger and Mach[81] for the pyrolysis of benzyl and benzhydryl benzoates and acetates can probably not be extended to reactions in solution, and the interesting work of Ritchie[82] cannot be used as a model for the present investigation.

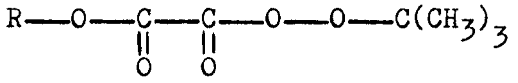
Very recently Karabatsos et al.[94] have investigated the pyrolysis of dialkyl oxalates, both in the neat state and in quinoline solutions. They found that the main reaction for oxalates of tertiary alcohols, at temperatures in the region of 140-160°, was elimination to oxalic acid and olefin in 80-100% yield. Oxalates of some cyclic tertiary and secondary alcohols underwent a similar reaction between 200° and 300°, with decrease in olefin yield. Formates were produced when the reaction temperature exceeded 210°. The oxalates of primary and secondary-acyclic alcohols were thermally stable below 325°.

Since the composition of the olefins obtained resembled that from acid- and dimethyl sulfoxide- catalyzed dehydration of alcohols (Saytzeff-type elimination) rather than that from ester and xanthate pyrolysis (Hofmann-type elimination), an ion-pair mechanism was suggested for the reaction.

The conclusion reached by Karabatsos is open to question, since he does not consider the possibility that the observed olefin ratios are composite values. The two alkyl residues in a dialkyl oxalate could eliminate in completely different ways. For example, there could be a primary, cyclic elimination to yield the monoalkyl oxalate, followed by ionic decomposition of this intermediate to yield further olefin together with oxalic acid. There are other reasons[17] for rejecting a simple ion-pair as a transition state or an intermediate in the decomposition of dialkyl oxalates, and these will be considered in the discussion of the experimental results of the present work.

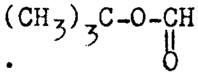
Much of the early work regarding the pyrolysis of oxalates is marred by the failure of the experimenters to exclude atmospheric oxygen from their reaction systems[78]. Oxygen could attack the α-position to form peroxycompounds by a chain mechanism and thus lead to carbonyl-containing products. This process might be expected to be more important when the α-position is also benzylic. Even some of the more recent workers[11,81,94] appear to have neglected this precaution, although Karabatsos et al. may be said to have justified the omission by the excellent yields of olefin which they obtained.

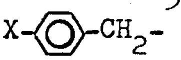
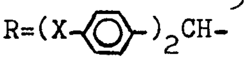
The work of Bartlett et al. on esters of monoperoxyoxalic acid[18,33,34] has some relevance to the question of a homolytic mechanism for the thermal decomposition of oxalates. He proposes that for esters of the type (A) there is a concerted, homolytic cleavage of the 3-4 and 5-6 bonds to give carbon dioxide and the radicals $(CH_3)_3C\text{-}O\cdot$ and $R\text{-}O\text{-}\dot{C}{=}O$. The subsequent fate of these radicals depends upon the nature of R and the presence or absence of scavengers. For $R{=}(CH_3)_3C\text{-}$ (in cumene; temperature range 25-56°) the products are CO_2 and di-*tert*-butyl carbonate together with C_4 hydrocarbons and $(CH_3)_3C\text{-}OH$. The effect of carrying out the reaction in the presence of the free-radical scavenger galvinoxyl[22,60] is to reduce the yield of CO_2 from 1.6 to 1.0 moles per mole of starting material and to prevent the production of materials of low molecular weight, other than di-*tert*-butyl carbonate the yield of which is unaffected. This evidence is consistent with the concerted cleavage described above, followed by cage recombination of most of the radicals $R\text{-}O\text{-}\dot{C}{=}O$ and $(CH_3)_3C\text{-}O\cdot$ to yield di-*tert*-butyl carbonate. In the absence of scavenger, a small fraction of the $(CH_3)_3C\text{-}O\cdot$ radicals is converted to $(CH_3)_3C\text{-}OH$ by abstraction of hydrogen from solvent, while a similar fraction of the $(CH_3)_3C\text{-}O\text{-}\dot{C}{=}O$ radicals is decarboxylated, giving rise to CO_2, isobutane and a little isobutene. With galvinoxyl present, the above processes are prevented

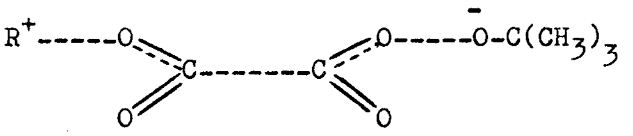


$$R\text{—}O\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}O\text{—}O\text{—}C(CH_3)_3 \qquad (A)$$

by efficient capture of radicals which escape cage coupling.

It is worthy of note that, in spite of the undoubted radical nature of the reaction, no  $(CH_3)_3C\text{-}O\text{-}\underset{\underset{O}{\|}}{C}H$ was produced. This implies that the radical $(CH_3)_3C\text{-}O\text{-}\dot{C}{=}O$ does not abstract a hydrogen atom from the solvent, since the formate is surely stable under the reaction conditions. This observation is consistent with general experimental experience which shows that carbon-radicals abstract hydrogen less readily than oxy-radicals so that other modes of radical destruction predominate.

For R = [33] and R= [34] in compounds of the type (A), vide supra, product studies show that the 1-2 bond is not involved in the rate-determining step so that any effect of the para-substituent must be exerted on the central 3-4 bond. Since this is too far away for direct resonance interaction, Bartlett proposes that the 8-fold accelerating effect of p-CH_3O over p-H may be due to the existence of a channel in the transition state for the cationic stability of the group R to set up the contributing ionic structure (B).


(B)

The fact that, for monoperoxyoxalates of the type (A), the rate for R=C_2H_5- falls between those for R=pCH_3O-C_6H_4-CH_2- and R=C_6H_5-CH_2-, supports the conclusion that the stabilization is electrostatic in origin. Bartlett further proposes that the R-O bond is not stretched anywhere near the point of no return, as must be the C-C and O-O bonds, and in fact does not break until a subsequent step[18,33]. Such a transition state is not directly applicable to the symmetrical case $R-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OR$ however, since whatever stabilization is gained by locating a partial positive charge on R at one end of the molecule would be cancelled by the loss in stabilization caused by locating a partial negative charge on R at the other end.

An example of a homolytic, thermal decomposition reaction, which is correlated by the Hammett equation using σ^+ parameters, is the decomposition of compounds of the type $pX-C_6H_4-NH-\underset{\underset{O}{\|}}{C}O-OC(CH_3)_3$[63]. In this case rho has the value -2.2, and the appreciable deviation of the para nitroderivative from the Hammett line is explained as an example of a special resonance "exaltation" effect, applicable to free-radical reactions, which is derived from the ability of the nitro group to locate some of the radical character on its oxygen atoms at the transition state.

The thermal decomposition of oxalates can probably occur by several mechanisms, the critical factor being the nature of the organic group attached. In the case where this is an alkoxy-group, and consequently the ester is a peroxy compound, the reaction is undoubtedly homolytic. However, for other cases, particularly in the absence of solvent, the mechanism may be ionic or it may involve a cyclic transition state. It may well be that the mechanism followed is a function not only of structural features in the substrate, but also of the experimental conditions.

Experimental Section

(1) General Discussion.

Since the historical evidence suggested that there might be several mechanisms for thermal decomposition of oxalates, it was decided to survey, briefly, a number of representative oxalates and to then select one system for more detailed investigation.

A number of previously unreported esters were synthesized and, in one case, an improved preparative method was developed for a carbonate, which was suspected to be an intermediate in the decomposition of the corresponding oxalate.

A cursory study of the products of pyrolysis of the following oxalates (RO_2CCO_2R) was carried out in order to probe for common features, if any: $R=(CH_3)_2C\text{-}CN$, $(CH_3)_3C\text{-}CH_2$, C_6H_5, $C_6H_5CH_2$, $(C_6H_5)_2CH$. The dibenzhydryl ester was selected as most amenable to further study. The thermolysis of this ester was investigated by kinetic methods, including the rate dependence on para-substituents and on changes in solvent and temperature. The kinetic isotope effects for carbon and oxygen in the carboyxlate groups were also determined.

(2) Solvent Purification.

Diphenyl ether, diphenylmethane and α-chloronaphthalene were obtained as practical or reagent grade chemicals from the Eastman, Fisher or Aldrich companies. They were purified by shaking, first with small portions of concentrated sulfuric acid until the acid layer no longer became coloured and then, successively, with distilled water, 10% sodium hydroxide, distilled water, saturated sodium bicarbonate solution (to remove all traces of strong base) and distilled water. After standing over Analar calcium chloride the solvents were then fractionated through a 2-ft. Vigreux or a 1½-ft. steel-pot-scrubber-packed column[90] at atmospheric pressure. The boiling ranges of the fractions used were: diphenyl ether, 251-254°; diphenylmethane, 259-263°; α-chloronaphthalene, 258-262°; all uncorrected. Diphenylmethane was further purified by passage through chromatographic alumina (10 x 1 cm column per 50 ml portion) immediately before use in order to remove possible peroxides. A faint yellow band was usually observed near the top of the column as a result of this procedure.

Passage through alumina did not appear to improve the quality of diphenyl ether or α-chloronaphthalene and in fact no change in rate was observed in any of the solvents for runs for which this procedure had been omitted.

Solvents for chromatography were bulk chemicals from various sources and were fractionated before use.

(3) Preparation of Compounds

All melting and boiling points are uncorrected. Melting points were determined using a Gallenkamp block apparatus or a simple oil-bath.

Infra-red spectra were measured on a Beckman I.R.5 spectrometer using sodium chloride cells or potassium bromide wafers. Ultraviolet and visible spectra were measured on a Perkin-Elmer Spectracord instrument and nuclear magnetic resonance spectra were measured on a Varian A.60

spectrometer. The N.M.R. samples were scanned in deuterochloroform or carbon tetrachloride solution with tetramethylsilane as internal standard.

Petroleum ether refers to the fraction boiling between 65-110° unless otherwise stated.

Pyridine (British Drug Houses Ltd., Analar grade) and oxalyl chloride (Fisher Scientific Co., Laboratory Chemical grade) were used as supplied.

Microanalyses were performed by Alfred Bernhardt, Max-Planck Institut, Mülheim, Germany.

Preparation of Di-(α-cyanoisopropyl) Oxalate

Acetone cyanohydrin, (Matheson Practical grade) was fractionated before use, b.p. 81-83°/15 mm.

Acetone cyanohydrin (38.5 g, 0.44 mole) was dissolved in 150 ml pyridine in a three-necked flask equipped with a dropping-funnel, a "Teflon Gland" stirrer and a reflux condenser fitted with a calcium chloride drying-tube.

The flask was cooled in an ice bath and stirred vigorously while oxalyl chloride (30.0 g, 0.23 mole) was added dropwise. When addition was complete the mixture was heated on a steam bath for 2 hours before it was cooled and poured, with stirring, into excess, ice-cold, 5% HCl. The resulting suspension was filtered by suction and the solid was washed on the filter with 5% HCl, distilled water, 5% sodium bicarbonate and distilled water. The damp, white material was crystallized twice from acetone to yield 40.5 g (82.1%) white crystals, m.p. 193-194°, slightly soluble in chloroform, acetone and ethanol and insoluble in most other solvents.

Anal. Found: C, 53.29; H, 5.44; N, 13.2

Calc. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.5

Preparation of Di-(α-cyanoisopropyl) Carbonate[84]

Acetone cyanohydrin (21.3 g, 0.25 mole) was dissolved in 100 ml pyridine in a flask equipped with a magnetic stirrer. The flask and contents was weighed, then cooled in an ice bath, and the solution was stirred while phosgene (Matheson) was bubbled gently through it.

When, after about ten minutes, the mixture turned bright red the passage of phosgene was discontinued and the flask was reweighed. It was found that the gain in weight was slightly greater than the theoretical amount (12.5 g, 0.125 mole).

The mixture was heated for 2 hours on a steambath before it was cooled and poured, with stirring, into ice-cold, 5% HCl.

The oily suspension resulting was extracted with ether and the solvent was evaporated to yield an oil, which was distilled under reduced pressure to remove a trace of α-chloroisobutyronitrile (b.p. 55°/10 mm). The slightly-discoloured residue (20.1 g, 82.4%) solidified on cooling. Two crystallizations from ethanol/water yielded pure white material m.p. 90-91.2° (lit.[84] m.p. 76-77°).

Anal. Found: C, 55.09; H, 6.17; N, 14.28

Calc. for $C_9H_{12}N_2O_3$: C, 54.61; H, 6.16; N, 14.36

The N.M.R. spectrum showed a single peak at 8.18τ.

Preparation of Di-(α-cyanocyclohexyl) Oxalate

Cyclohexanone cyanohydrin was prepared by the method of Lapworth et al.[85] It was obtained as an oil, b.p. 138-139°/23 mm, which solidified at about 15°.

Cyclohexanone cyanohydrin (18.0 g, 144 m.mole) was dissolved in 25 ml dry pyridine and a solution of oxalyl chloride (8.9 g, 71 m.mole), in dry ether was added dropwise to the cooled, stirred solution. The resulting suspension was diluted with pentane; the precipitate was filtered and washed on the filter with dilute HCl and distilled water. The yield was 5.5 g (25%). After four crystallizations from benzene/petroleum ether, the material had m.p. 135.2-135.9°.

Anal.	Found:	C, 63.14; H, 6.53; N, 9.43
	Calc. for $C_{16}H_{20}N_2O_4$:	C, 63.14; H, 6.52; N, 9.21

A greater yield would probably have been obtained in the absence of ether. Unlike the α-cyanoisopropyl analogue this compound is appreciably soluble in ether.

Preparation of Dineopentyl Oxalate

Neopentyl alcohol (Aldrich; 17.6 g, 0.2 mole) was dissolved in 30 ml pyridine and the flask was cooled in an ice bath. Oxalyl chloride (12.7 g, 0.1 mole), in dry petroleum ether (b.p. 30-45°), was added dropwise with stirring. When addition was complete a further 50 g pyridine was added to assist in dissolving the pyridine-oxalyl chloride complex. The yellow suspension was refluxed for 1 hour during which time it turned green. It was then stored at room temperature for three days.

The pH of the solution was adjusted to 5-6 by addition of cold, 10% HCl and the mixture was extracted with ether. The ether extract was washed once with 10% HCl, twice with 10% K_2CO_3 and twice with distilled water, after which it was dried over sodium sulfate and evaporated to yield an oil. The oil was warmed with petroleum ether and the solution was cooled in a refrigerator overnight to yield 16.8 g (81.6%) of large, transparent, plate-like crystals. Recrystallization from petroleum ether yielded a crystalline solid m.p. 32-33°.

Anal. Found: C, 62.49; H, 9.53

Calc. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63

The N.M.R. spectrum showed a singlet at 9.16 τ and a singlet at 6.05 τ, area ratio 5:1 (theoretical ratio 4.5:1).

Preparation of Dibenzyl Oxalate[70]

Benzyl alcohol (32.5 g, 0.30 mole) was placed in a flask equipped with a dropping-funnel, a magnetic stirrer and a reflux condenser protected by a drying tube. To the stirred alcohol was added dropwise oxalyl chloride (19.0 g, 0.15 mole) with occasional external cooling to moderate the reaction. Some oxalyl chloride was lost through the reflux condenser owing to local overheating. When addition was complete the mixture was allowed to cool to a white, crystalline mass which was recrystallized from ethanol to yield 20.6 g (51.5%) of white crystals m.p. 79.5-80° (lit.[70] m.p. 80.5-81.5°).

Preparation of Diphenyl Oxalate

Phenol (28.2 g, 0.3 mole) was dissolved in 100 ml pyridine and was added to the suspension formed by treating oxalyl chloride (19.1 g, 0.15 mole) with excess pyridine. The mixture was heated on a steam-bath for 2 hours, during which time it turned green, and was then poured, with stirring, into excess, ice-cold, 5% HCl. The suspension was filtered, the solid was washed on the filter with distilled water and sucked dry. The crude brown material was crystallized from benzene/petroleum ether to give 27.1 g (74.8%) of pale-yellow crystals, m.p. 134-136° (lit.[86] m.p. 134°). Two crystallizations from chloroform/petroleum ether gave white material (22.7 g, 83% recovery).

Preparation of Dibenzhydryl Oxalate[67]

Benzhydrol was Eastman Reagent grade and was used as supplied. The method used was that reported for di-(α-cyanoisopropyl) oxalate and the yield was usually about 85-100%. Recrystallization from chloroform/petroleum ether gave white crystals m.p. 142-143° (lit.[67] m.p. 142-143°).

Anal. Found: C, 80.23; H, 5.43

Calc. for $C_{28}H_{22}O_4$: C, 79.60; H. 5.25

Preparation of Bis-(4,4'-dichlorobenzhydryl) Oxalate

p-Chlorobenzaldehyde was Practical grade from Eastman, p-bromochlorobenzene was Reagent grade from Eastern Chemical Co., chlorobenzene was Reagent grade from Fisher, carbon disulfide was Fisher Certified reagent, carbon tetrachloride was Analar from Mallinkrodt as was aluminum chloride, lithium aluminum hydride was from Metal Hydrides Corporation.

Two methods were used for the synthesis of 4,4'-dichlorobenzhydrol because p-bromochlorobenzene became unavailable during the course of this work.

Preparation of 4,4'-Dichlorobenzhydrol

Method (i), Grignard Synthesis.

p-Bromochlorobenzene (48.0 g, 0.25 mole) was dissolved in 250 ml anhydrous ether and magnesium turnings (6.1 g, 0.25 mole) were added.

The mixture was stirred and refluxed in the absence of moisture till no more metal would dissolve (about one hour), then a solution of p-chlorobenzaldehyde (35.1 g, 0.25 mole) in anhydrous ether was added at a rate sufficient to maintain reflux. When the addition was complete the mixture was refluxed for 11 hours before it was cooled and poured into an excess of cold, saturated ammonium chloride solution. The mixture was stirred until no further reaction occurred and the layers were separated. The aqueous layer was extracted further with ether and the ether extract was washed with distilled water, dried over sodium sulfate and filtered through a pad of celite. The filtrate was concentrated, petroleum ether was added and the mixture was allowed to crystallize.

The yield was usually 37-47 g (60-70%).

Method (ii), Friedel-Crafts Synthesis, Followed by Reduction[68].

Preparation of 4,4'-Dichlorobenzophenone.

Aluminum chloride (135 g. 1.0 mole), carbon tetrachloride

(77.0 g, 0.5 mole) and 250 ml carbon disulfide were mixed at room temperature and chlorobenzene (114.5 g, 1.0 mole) was added with stirring. Stirring was continued for 3 hours before crushed ice was added cautiously with external cooling. Steam was bubbled through the solution for 2-3 hours to remove most of the carbon disulfide and to hydrolyze the dichloride intermediate. The mixture was extracted with chloroform and the extract was dried over sodium sulfate, warmed with decolourizing carbon and filtered through celite. Concentration of the filtrate gave 86.6 g (35%) of light yellow leaflets m.p. 144-145°. Some unhydrolyzed dichloride was also obtained.

Reduction of 4,4'-Dichlorobenzophenone

The ketone (86.6 g, 0.345 mole) was suspended in anhydrous ether (in which it is sparingly soluble) and the slurry was added to a stirred suspension of lithium aluminum hydride (4.0 g, 0.105 mole) in dry ether. The mixture was refluxed for 11 hours before water was added dropwise till no further reaction was visible. Sufficient 10% sulfuric acid was added to dissolve lithium salts and the layers were separated. The aqueous layer was extracted further with ether and the total ether extract was dried over sodium sulfate. The solution was concentrated to 200 ml, boiled with charcoal, and filtered through celite. The filtrate was diluted with 150 ml petroleum ether, concentrated to 150 ml and allowed to crystallize. The resulting suspension was vacuum-filtered and the solid was washed with a little petroleum ether to remove a yellow contaminant.

The yield of pure material was 33.2 g (38%). Additional, less pure material was worked up with subsequent preparations of the same compound.

The low yield largely results from the low solubility of the ketone in ether since, although a deficiency of lithium aluminum hydride was employed, some remained unreacted at the end of 11 hours reflux.

Preparation of Bis-(4,4'-dichlorobenzhydryl) Oxalate

The oxalate could be made by the same method as was used for the di-(α-cyanoisopropyl) ester, but pyridine adheres very strongly to the product and is not readily removed by washing with dilute hydrochloric acid. As a result, the crude material had to be chromatographed on specially deactivated alumina.

The alumina was deactivated by pre-treatment with 20% diethyl oxalate in refluxing benzene for twelve hours, followed by washing with chloroform and petroleum ether.

The recovery after chromatography and one crystallization from chloroform/petroleum ether was 86%. The hard, granular material had m.p. 143.8-144.8°.

Anal. Found: C, 59.71; H, 3.57; Cl, 26.76

Calc. for $C_{28}H_{18}Cl_4O_4$: C, 60.02; H, 3.24; Cl, 25.32

The following alternative method avoids a large excess of pyridine and removes the necessity for chromatography.

4,4'-Dichlorobenzhydrol (33.2 g, 0.13 mole) was dissolved in 150 ml anhydrous ether and pyridine (11.2 g, 0.14 mole) was added. To the cooled, stirred solution was added a solution of oxalyl chloride

(9.0 g, 0.07 mole) in 50 ml anhydrous ether. The mixture turned milky-white immediately and, after being refluxed for four hours, it was treated with sufficient 1 M HCl to remove the smell of pyridine. Water and chloroform were then added to dissolve all solid (the oxalate is sparingly soluble in ether) and the layers were separated. The aqueous layer was further extracted with chloroform and the total chloroform extract was dried over sodium sulfate. The solution was filtered through celite, concentrated to 120 ml, then diluted with 100 ml petroleum ether and allowed to crystallize.

The yield of oxalate was 32.0 g (88%).

Preparation of Bis-(4,4'-dimethylbenzhydryl) Oxalate

Preparation of 4,4'-Dimethylbenzhydrol.

The Grignard synthesis (as for 4,4'-dichlorobenzhydrol) was used. p-Tolualdehyde and p-bromotoluene were Columbia Organic Chemicals Co., Reagent grade materials. Yields were in the range 40-50%.

Preparation of Bis-(4,4'-dimethylbenzhydryl) Oxalate

When the method employed for the di-(α-cyanoisopropyl) ester was used a grey, elastic gum was obtained which was eventually purified by chromatography on alumina (pre-treated as for bis-(4,4'-dichlorobenzhydryl) oxalate.

The yield of pure compound was only 14.3% since losses were incurred during attempts to purify the gum by crystallization. The pure material was a white powder of m.p. 122.5-124.5°.

<u>Anal</u>. Found: C, 79.40; H, 6.28

Calc. for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32

When the alternative method, developed for the bis-(4,4'-dichlorobenzhydryl) ester, was employed (without the acid-washing step) a yield of 89.6% was obtained.

Attempted Preparation of Bis-(4,4'-Dimethoxybenzhydryl) Oxalate

Preparation of 4,4'-Dimethoxybenzhydrol.

p-Bromoanisole and p-anisaldehyde were Eastman White Label reagents. The aldehyde was discoloured and was fractionated through a 10 x 1 cm column packed with glass helices, b.p. 247-249°. The Grignard synthesis was employed but great care had to be taken to prevent the substituted benzhydrol from undergoing acid-catalyzed disproportionation[69].

When attempts were made to prepare the desired oxalate by the method which had been successful for the other substituted benzhydrols an oil was produced, the infrared spectrum of which lacked carbonyl absorption bands. Its spectral properties indicated that it was probably bis-(4,4'-dimethoxybenzhydryl)ether or 4,4'-dimethoxydiphenylmethane, both of which occur in the decomposition of this labile benzhydrol[69]. The alcohol apparently does not survive the conditions of the preparation long enough for an appreciable quantity of the ester to be produced.

Preparation of Di(4-methoxybenzhydryl) Oxalate

Preparation of 4-Methoxybenzhydrol.

Magnesium metal turnings (12.1 g, 0.5 mole) was covered with 50 ml anhydrous ether in a three-necked flask which was equipped with a mechanically driven "Teflon Gland" stirrer, a reflux condenser with drying tube and a dropping-funnel.

The flask was cooled to 5° in a water-bath before bromobenzene (86.4 g, 0.55 m.mole, Fisher Certified reagent) in 100 ml anhydrous ether was added dropwise with efficient stirring at a rate sufficient to maintain reflux. When the addition was complete the mixture was refluxed on a steam-bath for ½ hour to complete the formation of the Grignard reagent. p-Anisaldehyde (68.0 g, 0.5 mole) in anhydrous ether was added to the cooled, stirred solution at a rate sufficient to maintain gentle reflux.

When the addition was complete the mixture was immediately neutralized with 125 ml saturated ammonium chloride solution and stirred at room temperature overnight. The suspension was diluted with water and ether till all solid had dissolved and the layers were separated. The aqueous layer was extracted once more with ether and the combined extract was dried, concentrated, diluted with petroleum ether and allowed to crystallize. The yield of white, powdery material was 100.6 g (94.0%).

Preparation of Di-(4-methoxybenzhydryl) Oxalate.

The alternate method used for bis-(4,4'-dichlorobenzhydryl) oxalate was employed and the yield was 30.9 g (51.3%) from 53.5 g of alcohol. The material was slightly sticky and, when attempts were made to recrystallize it in the usual way, much decomposition occurred and a white precipitate appeared. It seemed probable that traces of moisture in the solvents used were sufficient to cause rapid hydrolysis of the compound at the boiling point of the solvent mixture with the precipitation of oxalic acid or other decomposition products. The material was eventually purified by fractional evaporation using a rotary evaporator, and the precipitate was washed with ether in which it is sparingly soluble. Recovered material weighed 6.0 g (20% recovery in purification) and the white powder had m.p. 117.5 - 118.7°.

Anal. Found: C, 73.38; H, 5.00

Calc. for $C_{30}H_{26}O_6$: C, 75.22; H, 5.45

This analytical result would be more disturbing were it not for the knowledge[17,94] that impurities have little or no effect on the decomposition of oxalates, and that, in particular, there is no evidence that the reaction is autocatalytic.

(4) Product Studies.

Measurement of Gaseous Products.

In order to estimate the yields of gases produced in the thermal decomposition of various oxalates a section of a vacuum line was calibrated by releasing into it known quantities of air and measuring the pressure produced.

It was found that, for pressures in the range 10-600 mm, carbon monoxide, carbon dioxide and hydrogen cyanide could be fractionated by selective freezing with different freezing mixtures. Carbon monoxide was not condensible at liquid air temperature, carbon monoxide and carbon dioxide were not condensible at dry-ice/acetone temperature and all three gases were non-condensible at ice/salt bath temperature.

The gases were measured by connecting the reaction tube to the vacuum line, freezing the tube successively in liquid air, dry-ice/acetone and ice/salt and releasing the non-condensible gases into the previously-evacuated, calibrated portion of the line.

Some inaccuracy was introduced by the inability of the ice-salt bath to totally condense volatile organic compounds, and by the non-uniform temperature in the vicinity of the freezing mixture. However, the yields could be determined with an accuracy of probably a few per cent, and the technique has been used successfully by Bartlett[32,102].

Unless otherwise stated, per cent yields are expressed as (moles product/moles oxalate) x 100.

Thermal Decomposition of Di-(α-cyanoisopropyl) Oxalate in Chlorobenzene

The oxalate (0.264 g, 1.2 m.mole) was dissolved in 40 ml reagent grade chlorobenzene in a heavy-walled glass tube and the solution was degassed by pumping during freeze-thaw cycles. The tube was sealed and heated at 180-190° for a week. It was then connected to the calibrated vacuum line through a side-arm fitted with a break-seal and a standard-taper joint and the line was evacuated. The solution in the tube was cooled in liquid air, then the break-seal was broken so that the non-condensible gas entered the calibrated section of the line. The tube was then isolated from the line by closing a stopcock. It was allowed to warm up till the solution was thawed, then refrozen with liquid air and re-opened to the line. This procedure was repeated till no further change in pressure was noted; then the pressure of the gas was recorded.

Similar determinations were carried out using first a dry-ice/acetone bath, then an ice-salt freezing mixture. The volume of the space in the tube above the solution was measured in a subsequent experiment. Mass spectrometric examination of the gaseous mixture showed that it was mainly carbon monoxide, carbon dioxide and hydrogen cyanide together with traces of water and acetone. The per cent yields of the gases were CO, 31; CO_2, 35; HCN, 27. The value obtained for the yield of hydrogen cyanide does not include that portion of the gas which was fixed in the form of acetone cyanohydrin.

The solution was fractionated through a 10 x 1 cm column, packed with glass helices, to yield a small fore-run, boiling below 130°, and chlorobenzene. Gas chromatographic studies using a 4 foot didecyl phthalate column at 115° showed that there were four components in the fore-run besides chlorobenzene. Two of these were identified as acetone and methacrylonitrile on the basis of retention times and the spectra of the mixture. By comparison of retention times with authentic samples it was shown that water, formic acid, isobutyronitrile and acetone cyanohydrin were not among the volatile products. Hydrogen cyanide was masked by the "air-peak" produced with the Fisher-Gulf micropipet injection system, but was readily detected by its odor.

Approximate infra-red measurements, made on the residual solid after removal of solvent, suggested that less than twenty per cent of the starting material remained, so that some of the oxalate carbonyl groups remained to be accounted for. The infra-red determination was carried out by reference to a calibration curve constructed by measurement of the height of the carbonyl peak at 1750 cm^{-1} for standard solutions in chloroform and 1,2-dichloroethane. The same curve was used in later determinations.

Thermal Decomposition of Di-(α-cyanoisopropyl) Oxalate in Diphenyl Ether

The oxalate (4.048 g, 18.1 m.mole) was dissolved in freshly distilled diphenyl ether in a heavy-walled glass tube and the solution was degassed during freeze-thaw cycles. The tube was sealed off and heated at 180-240° for 182 hours. After the tube had been opened the solution was fractionally distilled under nitrogen, at atmospheric pressure, to separate low boiling products from the bulk of the solvent. The low boiling material was investigated by vapour phase chromatography using a 20 foot x 3/8 inch SE.30 silicone gum-rubber column at 200° in an Aerograph A700 instrument. Eight components, other than solvent, were collected, but when these were rechromatographed using the same column at 160° only three were obtained in sufficient quantity for further investigation.

Component A: The infra-red spectrum suggested that this material might be an ester and the N.M.R. spectrum showed a singlet at 2.02 and a singlet at 8.20τ, ratio of areas = 1:6. By comparison of the infra-red spectrum with that of an authentic sample isolated in a later experiment, this component was shown to be α-cyanoisopropyl formate.

Component B: This material was present in only very small quantity and infra-red evidence for the presence of a carbonyl group was the only information obtained.

Component C: Although the infra-red spectrum of this material was almost superimposable on that of methacrylonitrile, gas chromatography and the N.M.R. spectrum clearly showed that it was not methacrylonitrile or a mixture containing that compound. The N.M.R. (CCl_4 solution; internal standard tetramethylsilane : relative areas in brackets) showed a doublet at 4.13τ (2), a complex multiplet centered at 7.49τ (3), a triplet at 8.12τ (2) and a doublet at 8.61τ (3). Relative areas are approximate only since the sample available was very small. The presumed unsaturated nitrile C was consumed in an unsuccessful attempt to hydrogenate it to the corresponding amine. Attempts to rationalize a structure for C, in keeping with the spectral evidence and with the structure of the starting material, were unsuccessful.

Identification of the volatile products of this reaction was hampered by the fact that they totalled less than 10% of the calculated yield from 4.05 g of oxalate.

Thermal Decomposition of Di-(α-cyanoisopropyl) Oxalate Without Solvent

The oxalate (2.17 g, 9.7 m.mole) was placed in a tube equipped for gas measurements and the tube was evacuated and sealed. It was heated at 205 ± 2° in an air-bath for 22 hours and the product gases were estimated by the calibrated-vacuum-line technique described previously. The per cent yields of the gases were CO, 58; CO_2, 51; HCN, 35.

The liquid fraction was decanted and fractionated by gas chromatography. It was found to consist of HCN, acetone, methacrylonitrile and a high boiling liquid whose infra-red spectrum showed it to be an ester. The N.M.R. spectrum of this material showed a singlet at 2.02τ and a singlet at 8.20τ with areas in the ratio 1:6. The compound was rechromatographed and analyzed.

Anal. Found: C, 53.03; H, 6.31; N, 12.27
Calc. for $C_5H_7NO_2$: C, 53.09; H, 6.24; N, 12.38

This material was different from an authentic sample of dimethylcyanoacetic acid and the singlet at 2.02τ in the N.M.R. is indicative of a formate[94], so that the material is probably α-cyanoisopropyl formate. All attempts to prepare an authentic sample of this material, by various alternative approaches, were unsuccessful.

The approximate per cent yields of the liquid products were HCN, 26; acetone, 48; methacrylonitrile, 79; α-cyanoisopropyl formate, 53. About 10 per cent of dissolved CO and CO_2 was also observed. The yields were obtained on the assumption that the gas-chromatographic peak-area ratios are directly proportional to the mole ratios of the products.

The black residue remaining after removal of the liquid fraction was extracted with hot chloroform and the resulting infra-red spectrum showed, by reference to the calibration curve already mentioned, that it contained less than 5% of the starting material.

The residue (0.133 g, 6%) gave negative tests for oxalic acid with the resorcinol, manganous sulfate and aniline-blue probes[87], and upon attempted sublimation, at 180°/0.001 mm for 8 hours, no sublimate was obtained. Both tetramethylsuccinonitrile and starting material were shown to sublime under much less stringent conditions and it is probable that this is true also of other possible products such as the corresponding carbonate and α-cyanoisopropyl dimethylcyanoacetate. The infra-red spectrum of the residue was unchanged by boiling the material with aqueous sodium carbonate or by the prolonged, attempted sublimation. Thin layer chromatography on alumina showed at least three components to be present, and the retention times for these were different from those of the oxalate, the carbonate, oxalic acid, and polymerized hydrogen cyanide.

Thermal Decomposition of Di-(α-cyanoisopropyl) Oxalate in Diphenyl Ether/Tetralin

The oxalate (2.604 g, 11.6 m.mole) was dissolved in 100 g purified diphenyl ether containing 63.2 g (478 m.mole) tetralin (b.p. 81-84°/14 mm, purified as was diphenyl methane - see Experimental Section, Solvent Purification). The solution was placed in a heavy-walled glass tube equipped for gas measurement and was degassed in the usual way. The tube was sealed and heated in an air bath at 246-275° for 24 hours.

A white sublimate which appeared in the neck of the tube showed a carbonyl peak in its infra-red spectrum around 1660 cm^{-1} but had no ester/ether band. This material was so volatile that it was swept away upon attempted sublimation at 80° and 0.6 mm.

Gas measurements were made by the usual technique and the per cent yields were CO, 148; CO_2, 79; HCN, 31.

Vapour phase chromatographic investigations using the S.E.30 silicone gum rubber column at temperatures between 100° and 200° showed that neither isobutyronitrile nor α-cyanoisopropyl formate was present in appreciable quantity. Using bromobenzene as an internal standard, and having reference to a calibration curve prepared by analysis of standard mixtures, the per cent yields of acetone and methacrylonitrile were determined to be 37 and 19 respectively. An additional trace component was recorded.

Attempted Thermal Decomposition of Dibenzyl Oxalate in Diphenyl Ether

Dibenzyl oxalate (2.016 g, 7.46 m.mole) was dissolved in diphenyl ether and the solution was degassed in the usual way. After 11 hours at 236-245° the yields of gas were found to be: CO, zero; CO_2, 3.4. The solvent was distilled off at 119°/2 mm and vapour phase chromatographic investigations showed that there were no appreciable volatile products. The solid residue was recrystallized from petroleum ether/benzene to give white crystals m.p. 82-83°. The infra-red spectrum of this material was identical with that of the starting material and the total recovery was 1.69 g (84%).

Thermal Decomposition of Diphenyl Oxalate in Diphenyl Ether

A solution of diphenyl oxalate (2.379 g, 9.83 m.mole) in 101.5 g diphenyl ether was degassed and sealed in a gas measuring tube. The tube was heated at 230° for 76.5 hours and the per cent gas yields were determined to be: CO, 13; CO_2, 9. Extraction of the mixture with dilute aqueous sodium hydroxide yielded a dark, phenolic oil which resisted efforts toward purification by chromatography and crystallization.

Thermal Decomposition of Dineopentyl Oxalate in Diphenyl Ether

The oxalate (2.19 g, 9.53 m.mole) was dissolved in 100 ml diphenyl ether and the solution was heated in a sealed, gas-measuring tube, in the absence of air, for 90 hours at 360°. The per cent gas yields were measured as before but an experimental mishap prevented accurate measurement of the CO_2 yield: the CO yield was 80%.

No materials could be distilled from the solution at room temperature to a bulb held at -78° indicating the absence of condensible, volatile materials.

Thermal Decomposition of Dibenzhydryl Oxalate in Diphenyl Ether (#1)

The oxalate (2.953 g, 7.00 m.mole) was dissolved in diphenyl ether in a gas-measuring tube and the solution was degassed. The tube was sealed and heated at 236-245° for 11 hours, after which time the gas yields were measured (CO, zero; CO_2, 115).

Gas chromatographic analysis showed that there were no materials present more volatile than diphenyl ether, so the solvent was removed at reduced pressure (b.p. 122-123°/3 mm), and the residue was crystallized from benzene/petroleum ether, m.p. 139-141°. The infra-red spectrum had similarities to that of diphenyl ether and the N.M.R. spectrum showed a complex multiplet centered around 2.84τ and a singlet at 4.49τ, area ratio 19:1. After a further crystallization from petroleum ether the material was analyzed.

Anal. Found: C, 88.36; H, 6.02

Calc. for $C_{25}H_{20}O$: C, 89.25; H, 5.99

This material is probably 4-phenoxytriphenylmethane (lit.[71] m.p. 136°) which is formed by substitution on diphenyl ether by a benzhydryl moiety.

Thermal Decomposition of Dibenzhydryl Oxalate in Diphenyl Ether (#2)

Two tubes were prepared as before, one containing 2.60 g (6.16 m.mole) oxalate and the other 2.78 g (6.58 m.mole) oxalate in diphenyl ether. The first was heated for 2.6 hours at 223° and the second for 6.2 hours at 228° and the per cent gas yields were measured for both. No CO was found but the CO_2 yields were, respectively, 126 and 153 per cent.

The solvent was removed by vacuum distillation and the residue was recrystallized from petroleum ether to yield white crystals, m.p. 209-211.5°, mixed m.p. with authentic 1,1,2,2-tetraphenylethane 207.5-210.5°. The infra-red spectrum showed signs of contamination with 4-phenoxytriphenylmethane.

Attempted Alkylation of Diphenyl Ether With 1,1,2,2-Tetraphenylethane

Tetraphenylethane (2.8 g, 8.4 m.mole) was dissolved in diphenyl ether in a heavy-walled glass tube and the solution was degassed. The tube was sealed and heated at 230-270° for 16 hours and the solvent was removed by distillation at 93-97°/0.5 mm. The residue was fractionally crystallized from petroleum ether/chloroform. A total of 2.3 g (83%) of material was obtained which was shown by its infra-red spectrum and melting point to be recovered tetraphenylethane. Hence it is unlikely that the benzhydryl moiety responsible for the production of 4-phenoxytriphenylmethane arises from dissociation of tetraphenylethane.

Thermal Decomposition of Dibenzhydryl Oxalate, In Diphenylmethane, In the Presence of Chloranil

The oxalate (0.842 g, 1.99 m.mole) and chloranil (0.504 g, 2.05 m.mole) were dissolved in 44.4 g diphenyl methane. The solution was degassed and was heated under nitrogen for 17 hours at 223.6°

(during which time the rate of gas evolution was measured). When the reaction flask was opened the smell of hydrogen chloride was immediately apparent. The solvent was removed by distillation (b.p. 110°/2.5 mm) and the solid residue was crystallized from petroleum ether to yield two crops of crystals.

Crop I (1.0 g). Upon recrystallization from petroleum ether white needles were obtained, m.p. 210-211.2°. The N.M.R. spectrum showed a singlet with slight splitting at 3.02τ and a singlet at 5.38τ, the area ratio being 12:1, approximately. The material was recrystallized once more from petroleum ether and then analyzed.

Anal. Found: C, 93.21; H, 6.76

Calc. for $C_{26}H_{22}$: C, 93.37; H, 6.63

This material was 1,1,2,2-tetraphenylethane. The yield of 164% indicates that some of the material arises from the solvent.

Crop II (0.1 g). This material was crystallized from chloroform-petroleum ether to yield a light yellow material, m.p. 184.5-186°, which had quinonoidal spectral characteristics. In particular, the ultraviolet spectrum of a solution in pentane had peaks at 268 mμ, 271 mμ, and 321 mμ while the visible spectrum had a peak at 730 mμ. The infra-red spectrum had many similarities to that of chloranil itself. The material was crystallized again from petroleum ether-chloroform.

Anal. Found: C, 85.54; H, 5.82; Cl, 5.76

Calc.: C, 86.50; H, 5.82; Cl, 5.88, for a mixture of $C_{26}H_{22}$ and $C_{19}H_{11}Cl_3O_2$ in the proportions 81.1:18.9. Thin layer chromatography showed that the material was a mixture of 1,1,2,2-tetraphenylethane and a single yellow component. The evidence suggests that the yellow component was benzhydryltrichloroquinone.

Thermal Decomposition of Dibenzhydryl Oxalate in Diphenyl Ether

When solutions resulting from kinetic investigation of the decomposition of the oxalate in diphenyl ether at 240.6° were combined and examined, only 1,1,2,2-tetraphenylethane was obtained as a non-gaseous product. However, when the combined solutions from similar experiments at lower temperatures were investigated, evidence of another product was found.

The reaction mixtures from decomposition of dibenzhydryl oxalate in diphenyl ether at temperatures between 213.5° and 230.3° were combined, and the solvent was removed at 120-125°/14 mm. The solid residue was treated with hot, aqueous-ethanolic sodium hydroxide for twelve hours. The ethanol was then boiled off and the basic mixture was extracted with ether to remove residual solvent, tetraphenylethane and other materials. The solution was then acidified with 10% sulfuric acid and extracted again with ether. The ether extract was dried over sodium sulfate before evaporation of the ether. The resulting oil was crystallized from petroleum ether to yield slightly tinted crystals, m.p. 144.8-147.8°. The infra-red spectrum and the chemical properties suggest that this material is diphenylacetic acid (literature m.p. 148°), which probably arises from base hydrolysis of its benzhydryl ester.

Decomposition of Bis-(4,4'-dichlorobenzhydryl) Oxalate in α-Chloronaphthalene

The combined reaction mixture from a number of kinetic experiments, involving the decomposition of this oxalate in α-chloronaphthalene, was degassed in a large flask. Reaction was then carried to completion by heating at 248° under nitrogen for 1.5 hours. The solvent was removed by distillation at 114°/0.5 mm and the residue was diluted with chloroform and filtered to yield a golden-brown crystalline solid, which was washed with chloroform. The remainder of the residue was chromatographed on Baker alumina to yield twelve fractions which were combined, by reference to infra-red spectra, into four main groups.

Group I. These fractions consisted largely of residual solvent.

Group II. This material was combined with the golden-brown solid and crystallized twice from benzene before analysis.

Anal.	Found:	C, 65.90; H, 3.84; Cl, 29.94
	Calc. for $C_{28}H_{18}Cl_4$:	C, 66.10; H, 3.85; Cl, 30.06

The mass spectrum had strong peaks at m/e = 473 to 470, as well as at lower values, in agreement with expectation for 1,1,2,2-tetra-(p-chlorophenyl)-ethane.

The yield was 56.5%.

Group III. The material was recrystallized three times from petroleum ether to give white crystals m.p. 127.2 - 128.2°.

Anal.	Found:	C, 61.98; H, 3.57; Cl, 28.06
	Calc. for $C_{27}H_{18}Cl_4O_2$:	C, 62.06; H, 3.59; Cl, 28.04

The infrared and N.M.R. spectra were in agreement with expectation for the structure 4,4'-dichlorobenzhydryl di-(p-chlorophenyl)-acetate, (lit. m.p. 118° [88]). The yield was 9.5%.

Group IV. The material was recrystallized twice from petroleum ether to give white crystals (21.3%) of 4,4'-dichlorobenzhydrol.

Anal. Found: C, 61.36; H, 4.14; Cl, 27.84

Calc. for $C_{13}H_{10}Cl_2O$: C, 61.65; H, 3.99; Cl, 28.04

The infra-red spectrum was identical with that of an authentic specimen of 4,4'-dichlorobenzhydrol.

The other fractions contained traces of oils which were not identified.

(5) Kinetic Studies.

a) Rate determinations.

The decomposition of dibenzhydryl oxalate and its derivatives, in solution, was followed by monitoring the evolution of CO_2.

The apparatus was of the conventional type (Fig. 1) with a manually adjusted mercury reservoir. The gas burette, readable to ±0.05 ml, was calibrated by the National Bureau of Standards and was surrounded by a glass jacket through which was pumped thermostatted water from a Labline circulating bath. Capillary connecting tubing was used to minimize the non-thermostatted volume of the apparatus and the connected end of the manometer was wrapped with glass wool. A stopcock at the open end of the manometer permitted use of a "sealed-in" standard atmosphere when this was desired. The reaction flask consisted of a bulb, of heavy-walled glass, of about 50 ml capacity, having a neck which ended in a ball joint and had a right-angled bend. The flask was connected to the apparatus by a crank-type coupling made of capillary

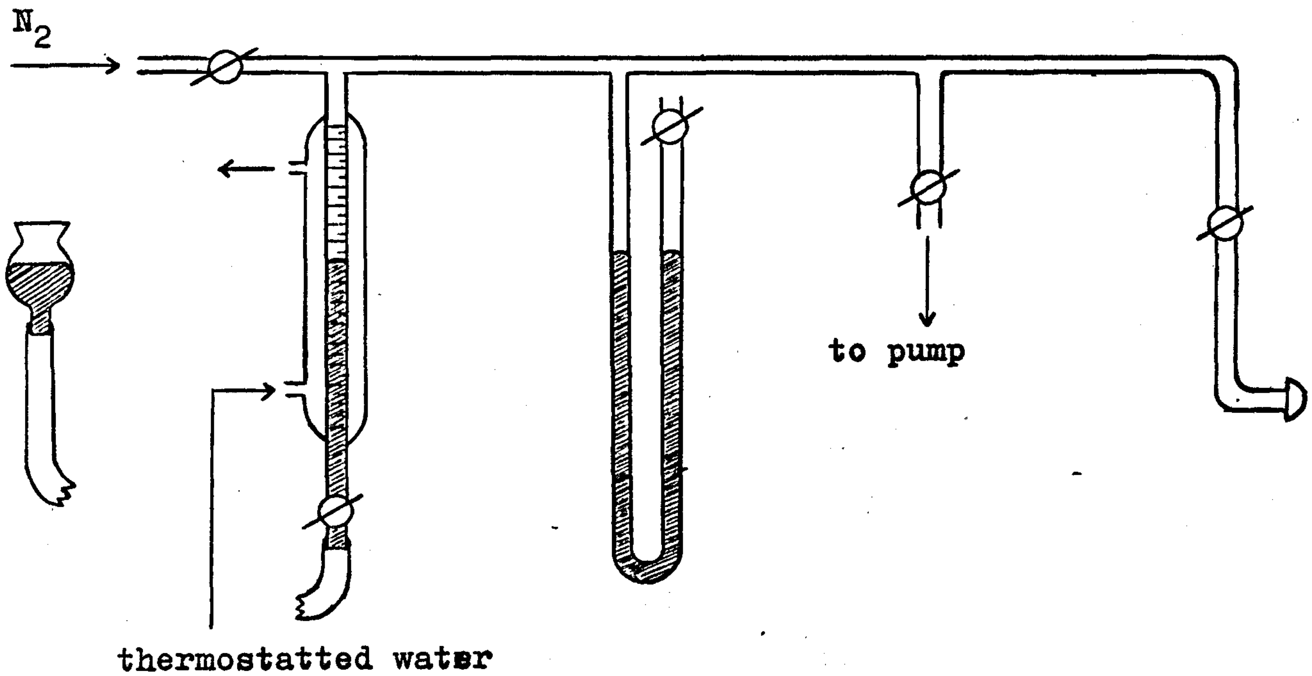


Fig.1. Apparatus for investigation of kinetics of gas evolution.

tubing and ball joints, which permitted smooth displacement of the reaction flask, from the degassing position beside the constant temperature bath to the reaction position in the heating medium, while maintaining gas-tight connection to the line. The apparatus was filled with nitrogen which was maintained at about atmospheric pressure throughout the experiment.

The heating fluid was a fused mixture of potassium nitrate, sodium nitrate and sodium nitrite in the proportions 40:7:53[64-66], which was heated by two glass-encased wire coils. One coil, which was of 30 ohms resistance, was connected to a variable transformer and was used as a base heater. The other, which was of 290 ohms resistance and gave an output of about 50 watts, was connected through a relay to a thermoregulator and was used to control the bath temperature. Temperature stability varied slightly from day to day but was always better than $\pm 0.2^{\circ}$. The temperature of the bath was measured with an Anschutz thermometer which had been calibrated by the Physical Chemistry Laboratory of the National Research Council of Canada.

Time was read with an accuracy of ±0.05 minutes.

Reaction solutions were made up by placing a weighed quantity of solid oxalate in a reaction flask and adding the calculated weight of solvent to attain the desired concentration. The flask was then connected to the apparatus and evacuated. Pumping was continued until all solid had dissolved and no further bubbles were observed on vigorous shaking. The system was then filled to one atmosphere pressure with nitrogen. The gas was purified by passage through two gasscrubbing bottles of Fieser's Solution[90], one of lead acetate solution and one of sulfuric acid, followed by a tube of potassium hydroxide pellets. The flask was shaken vigorously to saturate the contents with nitrogen in the last step of the deoxygenating cycle. After three such cycles the nitrogen pressure was adjusted to one atmosphere, the open end of the manometer was closed by the stopcock and the stopcock of the burette was opened. The flask was clamped in the constant temperature bath and the pressure in the system was rapidly adjusted to one atmosphere by lowering the mercury reservoir. Thereafter the internal pressure was never allowed to differ from one atmosphere by more than 2 mm of mercury. Readings were taken by adjusting the pressure to slightly less than one atmosphere and recording time and volume at the moment when the pressure equalled atmospheric again. Since the pressure differential was never more than 2 mm, error due to imperfect maintenance of liquid-vapour equilibrium should be small. This assumption was justified by the low standard deviation observed for the rate parameters in each run.

The effect of stirring the solution was investigated by the use of a larger flask which had an additional standard-taper, ground-glass neck. This could be equipped with a "Teflon Gland" stirrer connected to a motor by a speedometer cable.

The effect on the reaction of shaking the flask during a run was investigated using a modified flask (Fig. 2) with a stout, vertical extension which was attached to a motor-driven eccentric (not shown in Fig. 2). The flask could be shaken through an amplitude of about four centimeters at speeds between 150 and 450 cycles per minute, although

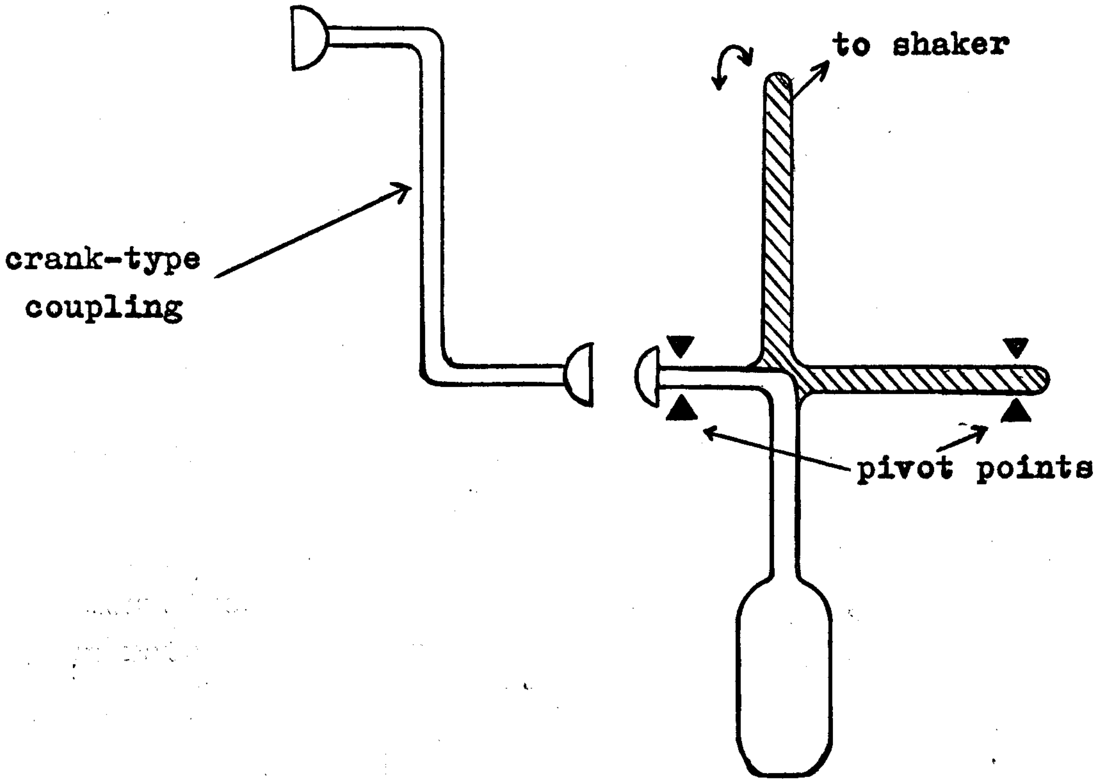


Fig.2. Reaction flask (adapted for shaking).

prolonged shaking at the higher speeds usually led to fracture of the extensions.

Glass beads were normally added to the mixture when the flask was to be shaken, in order to increase the churning effect. The beads were shown to have no effect in a static system.

The reaction followed very clean first-order kinetics and the standard deviation for the rate constant was usually 0.1-0.9%. However, the reproducibility of the rate constant for a series of determinations left much to be desired and values scattered over a range of ±25% were sometimes observed. The source of this scatter of values was not found, although no effort was spared in attempts to do so. The temperature control of both constant temperature baths was carefully checked and the deviations were found to be too small to produce effects of the observed magnitude. The solvents and the substrates were rigorously purified by repeated chromatography but no improvement in the spread of the rate constants was observed. Neither stirring nor the addition of glass beads made a detectable change in the variation but some improvement was noted when glass beads were added and the flask was shaken vigorously at speeds in excess of 200 cycles per minute. When this technique was employed the irregular "warm-up" period in the rate profile was shortened and smoothed out. These effects were probably due largely to a more rapid and consistent attainment of thermal equilibrium in the reaction mixture than could be achieved by convection alone.

To assess the importance of surface catalysis various methods of cleaning the flask between runs were investigated. Simple rinsing of the flask with chloroform gave the same results as were obtained after more thorough cleaning with chloroform, chromic acid and aqueous sodium bicarbonate or "Alconox" detergent, followed by washing with distilled water and drying at 180°.

The effect of oxygen on the reaction was investigated for a determination utilizing diphenylmethane as solvent and air in place of nitrogen in the reaction apparatus. The reaction was first order and had a normal rate constant, so that inefficient degassing was not the source of the poor reproducibility, unless traces of oxygen have an effect different from that of an excess. In spite of this result, degassing was still routinely carried out to avoid possible complication of the product mixture.

It was shown that there was no relation between the rate constants and the length of time during which the solution was exposed to fluorescent lights in the laboratory, and no trend was apparent when the rate constants for a particular set of conditions were plotted against the corresponding gas yields, which were also poorly reproducible.

According to Petersen[28], non-random error due to solvent vapour may contribute to poor reproducibility, though it seems unlikely that the effect could be as large as that observed here.

Reactions were normally followed for two to four half-lives and a large number of determinations were usually performed for each set of conditions.

b) Kinetic isotope effect determinations.

A convenient method for obtaining kinetic isotope effects is the examination of the isotopic distribution in gaseous products and this procedure was adopted here. The distribution of isotopic species in the starting material was determined by decomposing completely a sample of oxalate under conditions such that essentially all of the carboxyl groups were evolved as carbon dioxide. Too high a temperature, with concomitant increase in CO formation, was avoided and one of the criteria for the acceptability of mass-spectrometric results was that the ratio of CO to CO_2 should be small and the same for both sample and reference gases.

The isotopes monitored in this investigation were the naturally-occurring C^{13} and O^{18}, and these were detected and measured by a mass-spectrometric technique.

The mass spectrometer used for the analysis of the gas samples was specially built at McMaster University for the determination of ratios of the stable isotopes N^{15}/N^{14}, C^{13}/C^{12}, O^{18}/O^{16}, and S^{34}/S^{32}. It is a Nier-type, 90° instrument of 6" radius and is all metal. A potential of 1500 volts is applied for linear acceleration of the ions generated in the source.

The instrument is modified to permit the simultaneous collection and measurement, by means of a null method, of the ion currents due to the isotopic species related to the particular pair of isotopes under investigation. A potentiometer circuit permits the two ion currents to be balanced accurately and the balance point is recorded automatically on a moving chart.

A pair of valves enables the flow of gas into the mass spectrometer to be switched instantly from a standard reference sample of known isotopic composition to the unknown sample to be analyzed. From the resulting change in the balance point, the relative isotopic abundance of the unknown sample may be calculated.

For carbon dioxide samples, measurements of mass ratios 45:44 are converted into C^{13}/C^{12} ratios after applying a correction for the presence of O^{17}. A change in the focussing conditions allows mass 46 to be balanced against the sum of the masses 44 and 45 and measurements of this ratio are converted into O^{18}/O^{16} ratios after applying a correction for the presence of C^{13} and O^{17}.

The method allows the measurement of relative isotope ratios to ±0.01%.

Since the presence or absence of an isotope effect was the primary concern, and actual magnitudes were of secondary importance, a method was developed by which isotope effects might be measured very rapidly with moderate accuracy.

Samples of the oxalates were dissolved in diphenyl ether in tubes of the type shown in Fig. 3. The solutions were degassed and the tubes were sealed under vacuum. The tubes were immersed in the heating-bath and withdrawn after calculated extents of reaction had been reached. The lower parts of the tubes were cooled in ice water and the upper, gas-containing portions were sealed off and separated from the spent solution. Small droplets of solution which condensed in or near the break-seal were removed by cooling the lower end of the tube in liquid air and distilling down impurities by gentle warming of the break-seal area.

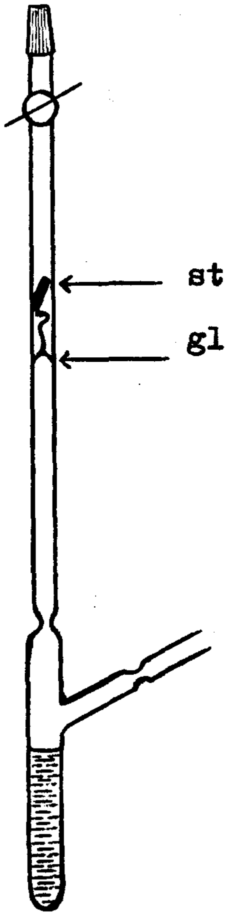


Fig.3.Reaction tube for isotope effect measurements.

The tubes were cooled in solid CO_2/acetone while the gas samples were being injected into the mass-spectrometer, so that volatile organic compounds were condensed. Admission of organic vapours into the spectrometer resulted in instability of the balance point and this variation often exhibited the characteristics of an exponential process. Such behaviour doubtless results from impurities reaching the ion-source and undergoing decomposition at the temperature encountered there.

The results of the mass spectrometric investigation indicate a small kinetic isotope effect for oxygen (0.4-1.0%) and a large effect for carbon (1.4-5.0%). The carbon isotope effects for the bis(4,4'-dichlorobenzhydryl) and the di(4-methoxybenzhydryl) oxalates (5.0% and 2.7% respectively) exceed the calculated maximum effect (2.2%) by a margin outside the estimated experimental error. Such behaviour has been observed before but has frequently been attributable to some type of experimental inaccuracy[72,76]. However, there may be other explanations[95] and these will be discussed later.

It was suggested[92] that an apparent excessive isotope effect, calculated from analyses of initial gas, might be attributed to a trace of an impurity which decomposed rapidly to yield isotopically-light carbon dioxide. An abnormal isotopic distribution arising from this source would be detectable only after a small extent of reaction and would be swamped by the larger quantity of isotopically normal gas as the reaction neared completion. This possibility was checked in two ways, as described below.

A sample of the bis(4,4'-dichlorobenzhydryl) oxalate was decomposed to a larger fraction of reaction than before, with only a slight decrease in the resulting isotope effect.

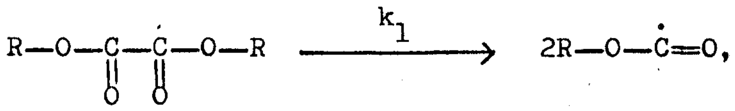
A quantity of dibenzhydryl oxalate was decomposed in the kinetic system (Fig. 1), under nitrogen, to twenty per cent of completion. The solution was then degassed and placed in sealed tubes of the type already described (Fig. 3). The isotope effects obtained from the samples prepared in this way were slightly more consistent than the others but showed no change in magnitude.

(6) Treatment of Results.

a) Kinetic measurements.

For a non-concerted or partly-concerted homolytic process giving the products described it may be shown that the rate of evolution of carbon dioxide is equal to the rate of rupture of the bond or bonds being broken in the first step of the reaction (since this must surely be the slowest step). The reaction cannot pass through a relatively stable intermediate since the over-all rate law observed for two consecutive first order processes with comparable rate constants is very different from that observed in this work. The first step cannot be appreciably reversible in view of the isotope effects observed (see below).

For a process illustrated by the following equations,



$$R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \xrightarrow{k_1} 2R{-}O{-}\dot{C}{=}O,$$

$$2R{-}O{-}\dot{C}{=}O \xrightarrow{k_2} RCOOR + CO_2,$$

$$2R{-}O{-}\dot{C}{=}O \xrightarrow{k_3} R{-}R + 2CO_2,$$

the quantity $2R{-}O{-}\dot{C}{=}O$ is regarded as an entity, since the radical pair is caged and the law of mass action does not apply.

Rate of formation of $CO_2 = k_2\left[2R\text{-}O\text{-}\dot{C}{=}O\right] + k_3\left[2R\text{-}O\text{-}\dot{C}{=}O\right]$.

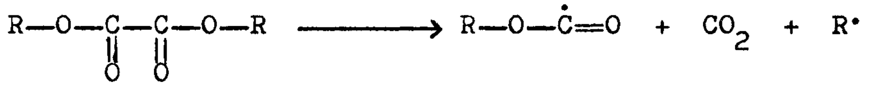
Application of the steady state hypothesis leads to the following equations

rate of formation of radicals = rate of destruction of radicals

$$\therefore\quad k_1\left[R\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R\right] = (k_2 + k_3)\left[2R\text{-}O\text{-}\dot{C}{=}O\right],$$

and therefore rate of formation of $CO_2 = k_1\left[R\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R\right]$.

Similar reasoning leads to an identical result for the case where the first step is



$$R{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R \longrightarrow R{-}O{-}\dot{C}{=}O + CO_2 + R^{\bullet}$$

Hence the conventional first order rate law[91] applies;

$$\text{i.e.,}\quad \log_e \frac{a}{a-x} = kt,$$

where a = initial concentration of oxalate,

x = concentration at time t,

k = rate constant.

Now, for a gas evolution reaction, the quantities a and x are proportional to V_∞ and V_t respectively, where V_∞ is the volume of gas evolved at infinite time, V_t is the volume of gas evolved at time t.

$$\text{Hence}\quad \log_e \frac{V_\infty}{V_\infty - V_t} = kt,$$

and the rate profile, that is the plot of V_t against t, should obey the relation $V_t = V_\infty (1 - \exp(-kt))$. However there is an irregular portion of the rate profile at the beginning of the run when factors such as the rapid thermal expansion of the flask, solution and nitrogen, and the attainment of thermal equilibrium, cause a deviation from the calculated curve. An additional parameter V_o is required to shift the origin of co-ordinates to take account of this "warm-up" period. From the modified rate law, $V_t = V_o + V_\infty (1 - \exp(-kt))$, it may be seen that V_o is the value of V_t at zero time, so that V_o represents the value of the intercept obtained when the smooth portion of the rate curve is extrapolated to zero time. Hence the value of V_∞ calculated from the expression is the true infinity volume and is directly proportional to the yield of gas.

The experimental data were fitted to the expression derived above using a non-linear, least-squares method which was applied by use of a program for the I.B.M. 7040 computer. This procedure obviated the necessity for measuring the infinity volume directly, thus removing a prime source of error, since the intervention of minor side reactions such as further decomposition of a product may introduce inaccuracies in the infinity volume which are magnified in the rate constant. In addition the program calculated the standard deviations for all parameters, so that this method is attractive both from the point of view of convenience and from that of accuracy. It may be regarded as a useful alternative to the Guggenheim method[83].

Since there were normally only a few values of the rate constant, for a particular set of conditions, which differed from the mean by as much as 15-25%, it was decided to discard these more extreme values so that a grossly deviant figure would not have a disproportionate effect on the standard mean. In order to establish a consistent basis for the rejection of seriously deviant values a computer program was used. The method extracted a mean value from the experimental rate constants and also the deviation of each experimental constant from the mean. Those constants having a deviation greater than the calculated standard deviation of the set of values were rejected and a new mean and standard deviation were calculated from the values remaining. It was the latter mean which was employed in further calculations. If it appeared that as many as thirty per cent of the values would be rejected, more runs were performed till the total rejected fell below this figure.

b) Calculation of activation parameters.

From transition state theory the relation

$$k = \frac{KT}{h} \exp.(- {}^{\Delta H^{\neq}}/_{RT} + {}^{\Delta S^{\neq}}/_{T})$$

is derived. The transmission factor is taken as unity and is omitted. Taking natural logarithms and rearranging one obtains

$$(R \log_e {}^{k}/_{T} - R \log_e {}^{K}/_{h}) = \Delta S^{\neq} + \Delta H^{\neq} (- {}^{1}/_{T}).$$

Now $R = 1.987$ cal/mole°C, and $R \log_e {}^{K}/_{h} = 47.217$, and hence a graph of $(1.987 \log_e {}^{k}/_{T} - 47.217)$ against $- {}^{1}/_{T}$ should be a straight line, the slope of which is $\Delta H^{\neq}$ in calories and the intercept of which is $\Delta S^{\neq}$ in entropy units. A computer program was employed which converted the experimental rate constants and the corresponding absolute temperatures to the functions above and performed a least-squares analysis on the resulting points. Assuming that the errors in the temperatures were negligible compared to the errors in the rate constants, the program calculated the errors in the activation parameters using the method of Petersen et al.[28]. The statistical expressions were not employed since there are insufficient points to justify such a procedure.

c) Correlation by means of the Hammett equation.

The Hammett equation was taken to be $\log_{10}\left(\frac{k}{k_o}\right) = \rho \sum^{n} \sigma$, where n is the number of groups influencing the bond being broken in the rate-determining step. That is, the sigma values were considered to be additive even though there is the possibility of cross-conjugation in the 4,4'-disubstituted benzhydryl group.

The data of Norris and Banta[97] for the solvolysis of substituted benzhydryl chlorides lend support to this assumption, since they are correlated by the Hammett equation using σ^{+} parameters, although they include both 4-substituted and 4,4'-disubstituted compounds.

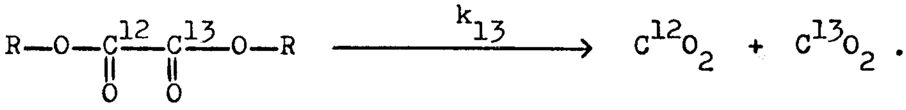
d) Calculation of kinetic isotope effects.

The oxalate decomposition is unique among decarboxylation reactions in that both carboxyl groups are evolved as carbon dioxide, and both of them may be involved in the bond breaking which leads to the production of an isotope effect. This feature invalidates the usual Bigeleisen equation[72,74] and necessitates the derivation of separate, modified equations for carbon and oxygen. The ratios of the rate constants for the breaking of the bonds between a light and a heavy isotopic species, and between two light ones, may then be calculated.

Derivation Of a Modified Bigeleisen Equation for Carbon.

Consider the decomposition of the two isotopic species

$$R{-}O{-}\underset{\overset{\|}{O}}{C^{12}}{-}\underset{\overset{\|}{O}}{C^{12}}{-}O{-}R \xrightarrow{k_{12}} 2C^{12}O_2 ,$$



$$R{-}O{-}\underset{\overset{\|}{O}}{C^{12}}{-}\underset{\overset{\|}{O}}{C^{13}}{-}O{-}R \xrightarrow{k_{13}} C^{12}O_2 + C^{13}O_2 .$$

Let s = concentration of symmetrical ester at time $t = 0$,

$s-x$ = " " " " at time $t = t$,

u = " " unsymmetrical " at time $t = 0$,

$u-x'$ = " " " " at time $t = t$.

$$\therefore \quad \log_e \frac{s}{s-x} = k_{12}t,$$

$$\log_e \frac{u}{u-x'} = k_{13}t.$$

Let $^u/_s = I = \dfrac{\text{unsymmetrical}}{\text{symmetrical}}$ molecules in the starting material.

$$\therefore \quad I = \frac{2(C^{13}O_2/C^{12}O_2)_\infty}{1-(C^{13}O_2/C^{12}O_2)_\infty} = \left(\frac{2C^{13}O_2}{C^{12}O_2-C^{13}O_2}\right)_\infty .$$

Let $^{x'}/_x = X$, where

x' = change in concentration of the unsymmetrical ester,

= half the resulting change in the concentration of carbon dioxide,

x = corresponding changes in concentration of symmetrical ester and of the resulting carbon dioxide.

Since one molecule of unsymmetrical ester gives

$$1 \text{ molecule } C^{12}O_2 \; + \; 1 \text{ molecule } C^{13}O_2,$$

$(C^{13}O_2)_t = x'$, and $(C^{12}O_2 - C^{13}O_2)_t$ measures the $C^{12}O_2$ produced by the symmetrical ester alone.

$$\therefore \; 1/2 \, (C^{12}O_2 - C^{13}O_2)_t = x,$$

$$\therefore \; X = \left(\frac{2C^{13}O_2}{C^{12}O_2 - C^{13}O_2}\right)_t$$

Let $\dfrac{x+x'}{u+s} = P = \dfrac{\text{total reacted oxalate}}{\text{total original oxalate}} = \dfrac{\text{Per cent reaction}}{100}$,

$$\therefore \; \frac{k_{12}}{k_{13}} = \frac{\log_e \frac{s}{s-x}}{\log_e \frac{u}{u-x'}} = \frac{\log_e(1+X) - \log_e(1+X-P(1+I))}{\log_e(1+{}^1/_X) - \log_e(1+{}^1/_X - P(1+{}^1/_I))} .$$

Let $(C^{13}O_2/C^{12}O_2)_t = R_t$ and $(C^{13}O_2/C^{12}O_2)_\infty = R_\infty$,

and substituting the values for X and I derived above,

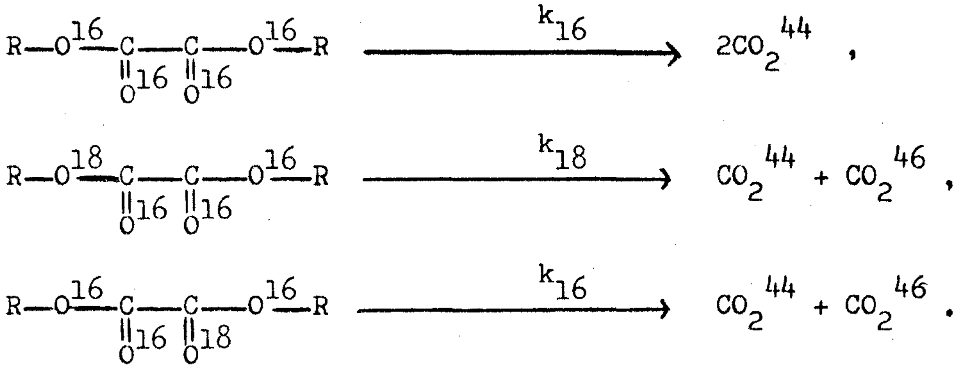
$$\frac{k_{12}}{k_{13}} = \frac{\log_e \left(\frac{1+R_t}{1-R_t}\right) - \log_e \left(\frac{1+R_t}{1-R_t} - P\left(\frac{1+R_\infty}{1-R_\infty}\right)\right)}{\log_e \left(\frac{1+R_t}{2R_t}\right) - \log_e \left(\frac{1+R_t}{2R_t} - P\left(\frac{1+R_\infty}{2R_\infty}\right)\right)} .$$

Since $R_t \sim R_\infty \ll 1$ the equation reduces to

$$\frac{k_{12}}{k_{13}} = \frac{\log_e (1+2R_t) - \log_e (1+2R_t - P(1+2R_\infty))}{\log_e \left(\frac{1+R_t}{2R_t}\right) - \log_e \left(\frac{1+R_t}{2R_t} - P\left(\frac{1+R_\infty}{2R_\infty}\right)\right)} .$$

Derivation Of a Modified Bigeleisen Equation For Oxygen.

Consider the decomposition of the following isotopic species:



$$R{-}O^{16}{-}\underset{\overset{\|}{O^{16}}}{C}{-}\underset{\overset{\|}{O^{16}}}{C}{-}O^{16}{-}R \xrightarrow{k_{16}} 2CO_2^{44} ,$$

$$R{-}O^{18}{-}\underset{\overset{\|}{O^{16}}}{C}{-}\underset{\overset{\|}{O^{16}}}{C}{-}O^{16}{-}R \xrightarrow{k_{18}} CO_2^{44} + CO_2^{46} ,$$

$$R{-}O^{16}{-}\underset{\overset{\|}{O^{16}}}{C}{-}\underset{\overset{\|}{O^{18}}}{C}{-}O^{16}{-}R \xrightarrow{k_{16}} CO_2^{44} + CO_2^{46} .$$

It will be assumed that the ratio of the concentrations of the two O^{18}-containing species is unity, since the difference between their concentrations must be small compared to the concentration of the species containing only O^{16}.

Let the fractional extent of reaction at time t be P,

$$\text{i.e.,} \quad P = \frac{\text{total reacted oxalate}}{\text{total original oxalate}} .$$

Let s = concentration of symmetrical ester at time $t = 0$,

$s-Ps$ = concentration of symmetrical ester at time $t = t$,

u = concentration of each unsymmetrical ester at time $t = 0$,

$u-Pu$ = concentration of ester containing O^{18} in one carbonyl group at time $t = t$,

$u-x'$ = concentration of ester containing O^{18} in one ether group at time = t,

$$\therefore \log_e \frac{s}{s-Ps} = k_{16}t = \log_e \frac{u}{u-Pu} ,$$

$$\log_e \frac{u}{u-x'} = k_{18}t .$$

Let $I = \frac{u}{s}$ = ratio of each unsymmetrical ester to the symmetrical ester in the starting material,

$$\therefore \quad I = 1/2 \quad \left(\frac{CO_2^{46}}{CO_2^{44} - CO_2^{46}}\right)_\infty \quad .$$

At time t = t the quantity of O^{18}-containing esters decomposed,

$$= \quad x' + Pu \, .$$

In the same time, the quantity of symmetrical ester decomposed,

$$= \quad Ps \, .$$

Let $X \;=\; \frac{x'}{Ps}$,

$$\therefore \quad X \;=\; \left(\frac{x'+Pu}{Ps} - I\right), \quad \text{and} \quad \frac{x'+Pu}{Ps} = \left(\frac{CO_2^{46}}{CO_2^{44} - CO_2^{46}}\right)_t \quad ,$$

$$\therefore \quad X \;=\; \left(\frac{CO_2^{46}}{CO_2^{44} - CO_2^{46}}\right)_t \;-\; 1/2\left(\frac{CO_2^{46}}{CO_2^{44} - CO_2^{46}}\right)_\infty \quad .$$

The difference between x' and Pu reflects an oxygen isotope effect and is small compared to Ps. Therefore we are justified in the assumption that P represents the fractional extent of total reaction.

$$\therefore \quad \frac{k_{16}}{k_{18}} \;=\; \frac{\log_e \frac{s}{s-Ps}}{\log_e \frac{u}{u-x'}} \;=\; \frac{\log_e(1+X) - \log_e(1+X - P(1+I))}{\log_e(1+{}^1/_X) - \log_e(1+{}^1/_X - P(1+{}^1/_I))}$$

Now $O^{18}/_{O^{16}} \;=\; {}^1/_2 \left(CO_2^{46}/CO_2^{44}\right)$ from statistical considerations.

Let $R_\infty \;=\; (O^{18}/_{O^{16}})_\infty$ and $R_t = (O^{18}/_{O^{16}})_t$.

Substituting the values of X and I derived above, and incorporating the definitions of R_∞ and R_t, the equation becomes

$$\frac{k_{16}}{k_{18}} = \frac{\log_e\left(1+\frac{2R_t}{1-2R_t} - \frac{1}{2}\,\frac{2R_\infty}{1-2R_\infty}\right) - \log_e\left(1+\frac{2R_t}{1-2R_t} - \frac{1}{2}\,\frac{2R_\infty}{1-2R_\infty} - P\left(1+\frac{1}{2}\,\frac{2R_\infty}{1-2R_\infty}\right)\right)}{\log_e\left(1+\frac{1}{\frac{2R_t}{1-2R_t} - \frac{1}{2}\,\frac{2R_\infty}{1-2R_\infty}}\right) - \log_e\left(1+\frac{1}{\frac{2R_t}{1-2R_t} - \frac{1}{2}\,\frac{2R_\infty}{1-2R_\infty}} - P\left(1+2\cdot\frac{1-2R_\infty}{2R_\infty}\right)\right)} .$$

Since $R_\infty \sim R_t \ll 1$, $2R_\infty$ may be neglected with respect to 1, but the equation does not reduce to the Bigeleisen equation as usually applied, since $\frac{1}{2R_t - R_\infty}$ is appreciably different from $^1/_{R_t}$.

The equation reduces to

$$\frac{k_{16}}{k_{18}} = \frac{\log_e\,(1+R_t) - \log_e(1+R_t - P(1+R_\infty))}{\log_e\left(1+\frac{1}{2R_t-R_\infty}\right) - \log_e\left(1+\frac{1}{2R_t-R_\infty} - P(1+{}^1/_{R_\infty})\right)} .$$

This equation specifically neglects isotopic fractionation due to partition of $Ar_2CH\text{-}O\text{-}\dot{C}{=}O$ between carbon dioxide and diarylmethyl diarylacetate.

The isotope effects were expressed in terms of the quantity $({}^{k_{16}}/_{k_{18}} - 1) \times 100\%$.

The experimental errors in the observed isotope effects were estimated from the observed scatter, and from the relative abundances of the various isotopic species, to be about ±0.2% for carbon and ±0.3% for oxygen.

Results and Discussion

In principle there are many possible mechanisms for the thermal decomposition of diesters of oxalic acid, and it is possible that, in some cases, more than one mechanism may be operative. The present discussion is concerned with two major aspects of such mechanisms; first, the nature of the intermediate species, and secondly, the nature of the transition states leading to these species. Although these topics may overlap to some degree it is proposed to consider them separately.

(1) Intermediate Species; Ions or Radicals?

The ion-pair mechanism for decomposition of dialkyl oxalates proposed by Karabatsos[94] cannot be general. This conclusion is reached by consideration of the thermal decomposition of several selected oxalates, in particular the di-(α-cyanoisopropyl)-, the dibenzyl- and the dineopentyl esters.

If the di-(α-cyanoisopropyl) oxalate were to decompose by an ion-pair mechanism it would probably do so very slowly, since the strongly electron-withdrawing cyano-group would destabilize a developing positive charge on the tertiary carbon atom. This effect would increase the energy required for formation of the ion-pair and thus retard the reaction. However, this oxalate decomposes under conditions comparable with those employed by Karabatsos[94] for oxalates of cyclic, secondary alcohols, as may be seen from the data presented in Tables I and II. (All per cent yields are expressed as (moles/mole oxalate) x 100 unless otherwise stated).

Table I

Decomposition of Di(α-cyanoisopropyl)Oxalate In Chlorobenzene

180 - 190° for 170 hours

Products	Per cent Yield
CO	31
CO_2	35
HCN[a]	27
Recovered starting material	20 (Infra-red determination)

Acetone and methacrylonitrile were observed (V.P.C.) but not measured.

[a] The yield of hydrogen cyanide does not include that part of the compound retained in the solution as acetone cyanohydrin.

Table II

Decomposition of Di-(α-cyanoisopropyl)Oxalate Without Solvent

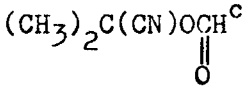
205 ± 2° for 22 hours

(A)

Gaseous Products	Per cent Yield
CO	58
CO_2	51
HCN	35 (Excluding acetone cyanohydrin)
Also	
Recovered starting material	5 (Infra-red determination)
Polymeric residue	6 (By weight)

(Table II continued on next page.)

(Table II continued)

(B) Liquid Products	Relative V.P.C. Peak Areas[a]	Approximate Per-Cent Yields[b]
Dissolved CO, CO_2	$\sim$ 0.2	$\sim$ 10
HCN	0.49	26
Acetone	0.91	48
$CH_2=C(CN)CH_3$	1.50	79
 $(CH_3)_2C(CN)O\underset{\underset{O}{\Vert}}{C}H$[c]	1.00	53

[a] Vapour Phase Chromatographic (V.P.C.) analysis was performed using a 20' x 3/8" S.E.30 silicone gum rubber on Chromosorb W (60-80 mesh) column, at 113°, in an Aerograph A700 instrument.

[b] Assuming (i) that the α-cyanoisopropyl groups are totally accounted for by the acetone, methacrylonitrile, α-cyanoisopropyl formate, recovered oxalate and polymeric solid, (ii) that the relative areas of the peaks observed are approximately proportional to the relative yields.

[c] This product also isolated from decomposition of the oxalate in diphenyl ether solution (see Experimental section).

The oxalates of acyclic, secondary alcohols, according to Karabatsos, are stable below 325° and it is difficult to believe that substitution of a cyanogroup for the secondary hydrogen atom would do other than retard decomposition via an ion-pair. The products in this case can be rationalized in terms of an ion-pair or of radicals and are thus of little significance with respect to the nature of the intermediate.

The decomposition of dineopentyl oxalate at 360° (Table III), while nearly complete, yielded no trace of volatile materials such as 2-methyl-2-butene and 2-methyl-1-butene, which would probably be produced if a positive charge appeared at the neopentyl carbon atom. The neopentyl carbonium ion undergoes extensive rearrangement by methyl migration to yield products of the 2-methyl-2-butyl cation, including olefins[108].

Table III

Decomposition of Dineopentyl Oxalate In Diphenyl Ether

360° for 90 hours

Products	Per cent Yield
CO	80
CO_2	Present, but not measured owing to experimental mishap.
Other Volatile Materials	None

If an ion-pair mechanism were operative, dibenzyl oxalate would be expected to undergo facile decomposition since the benzyl cation is stable relative to alkyl carbonium ions. However dibenzyl oxalate is quite stable at elevated temperatures (Table IV), and there is no evidence for appreciable aromatic substitution on solvent, which would be expected if the benzyl cation were present.

Table IV

Decomposition of Dibenzyl Oxalate In Diphenyl Ether

236 - 245° for 11 hours

Products	Per cent Yield
CO	None
CO_2	3.4
Recovered Starting Material	84

The decomposition of diphenyl oxalate under relatively mild conditions, although very slow (Table V), suggests that the ability to accommodate a positive charge on the carbon atom of the ether linkage is not the only consideration in determining ease of decomposition of a given oxalate.

Table V

Decomposition of Diphenyl Oxalate In Diphenyl Ether

230° for 76.5 hours

Products	Per cent Yield
CO	13
CO_2	9

An ion-pair with charges on the carbonyl groups, i.e., $R-O-\overset{-}{C}=O$, $R-O-\overset{+}{C}=O$, cannot be ruled out on the above evidence but can be discredited by reasonable arguments based on intuition and analogy. The ion $R-O-\overset{-}{C}=O$ would probably decompose readily to yield either carbon dioxide and R^-, or carbon monoxide and RO^-. Evidence for the carbanion R^- as an intermediate in oxalate decomposition is totally lacking, both in the present work and in the literature. For R = $(CH_3)_2C-CN$[17], where a carbanion R^- is stabilized both by resonance and induction, there was never found any $(CH_3)_2CHCN$, although a proton donor, HCN, was present under all conditions investigated. The carbonium ion $R-O-\overset{+}{C}=O$ could give rise to the formate R-O-CHO by abstraction of a hydride-ion from R^- or $R-O^-$. Abstraction of hydride from $R-O^-$ would lead to either a carbonyl compound or, less likely, a cyclic ether. However, neither of these products were observed by Karabatsos[94] although formate was formed under his conditions. The acetone produced in the case where R = $(CH_3)_2C-CN$[17] could not have been formed by a hydride abstraction process.

There are two reasonable alternative mechanisms for the decomposition of dialkyl oxalates. One possibility is a free radical process and the other is a cyclic modification of the Karabatsos ion-pair mechanism, adapted to accommodate the data presented above.

The free radical mechanism may intervene at higher temperatures in the decomposition of dialkyl oxalates[94] and is the most likely mechanism when the cyclic process is impossible (e.g., dibenzyl oxalate) or unfavourable (e.g., di-(α-cyanoisopropyl) oxalate).

It is proposed that the preferred mechanism for decomposition of oxalates possessing β-hydrogen atoms is a cyclic elimination process involving

a) strong polarization of the C-O bond, and

b) participation of a β-hydrogen atom, in the transition state.

This mechanism accounts for the reactivity series tertiary $>$ cyclic secondary $\gg$ acyclic secondary $\sim$ primary[94] and also for the thermal stability of dibenzyl oxalate[17].

Such a process has been considered in studies of the pyrolytic[99] and solvolytic[100] eliminations of cyclohexyl sulfonate esters but was rejected in both cases.

The primary product of elimination by this mechanism is the monoalkyl oxalate and the thermal decomposition of these compounds was reviewed in the Historical section. The principal products of thermolysis were shown to be the dialkyl ester and oxalic acid or the olefin and oxalic acid, depending on the conditions. The corresponding formate was also produced in some cases. The mechanism is thus in accord with the observed facts.

Oxalates lacking β-hydrogen cannot decompose by this mechanism and probably proceed by a free radical path. The absence of rearranged products in the decomposition of dineopentyl oxalate is also explained more readily by a radical process.

The data for di-(α-cyanoisopropyl)oxalate fit a free radical mechanism. This oxalate decomposes at a rate comparable to that for oxalates of cyclic secondary alcohols[94], yet it is really the ester of a cyano-substituted, acyclic, secondary alcohol. The apparent anomaly is explained if the mechanism involves not a cyclic process, but a free radical one, where the stability of the 2-cyano-2-propyl radical may contribute to the transition state. The stability of this radical is illustrated by the activation energies for the thermal decomposition of the azo-compounds R-N=N-R. The E_a values, in k.cal., are $R = (CH_3)_2CCN$, 31-33[104,105]; $R = C_6H_5$-CH-CH_3, 32.6[106]; $R = (C_6H_5)_2CH$, 27[107]. If these figures are accepted as a rough indication of the stabilities of the radicals produced, then the 2-cyano-2-propyl radical is at least as stable as the benzyl radical, though less stable than the benzhydryl radical. This reasoning suggests that the source of the more ready decomposition of the di-(α-cyanoisopropyl) ester, as compared to the benzyl ester, is to be found in the greater contribution that the 2-cyano-2-propyl radical can make to a radical-like transition state.

Further evidence of free radical intermediates in this thermolysis is provided by the presence of polymeric products (Table II). While polymerization may be induced by ionic intermediates or by heat alone, the observation of polymers is in agreement with the presence of radical intermediates.

The effect of added tetralin on the thermolysis in diphenyl ether solution (Table VI) supports the contention that free radicals are produced in the reaction. The greatly increased yield of carbon monoxide

Table VI

Decomposition of Di-(α-cyanoisopropyl)Oxalate In Diphenyl Ether/Tetralin

246 - 275° for 24 hours

Products	Per cent Yields	
CO	148	
CO_2	79	
HCN	31	Excluding acetone cyanohydrin.
Acetone	37	By gas chromatography.
$CH_2=C(CN)CH_3$	19	By gas chromatography.

may be rationalized as arising from an increased yield of the formate and the subsequent decomposition of the latter. There are two possible processes leading to formate, both of which involve hydrogen abstraction and would therefore be assisted by the presence of tetralin with its readily-abstractable, benzylic hydrogen atoms.

$$\text{a)}\quad R{-}O{-}\dot{C}{=}O \;+\; H{-}Z \longrightarrow R{-}O{-}CHO$$

$$\text{b)}\quad R{-}O{-}CO{-}CO{-}O{-}R \longrightarrow R{-}O{-}CO{-}CO_2\cdot \;+\; R\cdot$$

$$R{-}O{-}CO{-}CO_2\cdot \;+\; H{-}Z \longrightarrow R{-}O{-}CO{-}CO_2H$$

$$R{-}O{-}CO{-}CO_2H \longrightarrow ROCHO \;+\; CO_2$$

Process a) requires hydrogen abstraction by a carbon radical, which is less favourable, in the general case, than abstraction by an oxy-radical owing to the greater energy of the O-H bond as compared to the C-H bond. However, process b) requires the generation of the $R\text{-}O\text{-}CO\text{-}CO_2\cdot$ radical and its survival for long enough for hydrogen abstraction to take place. It is doubtful if such a radical would resist decarboxylation for very long and doubt is cast on its generation by analogy with the case of dibenzhydryl oxalate (vide infra). On balance, process a) is favoured, especially since hydrogen abstraction from benzylic compounds by alkyl radicals is known to occur[109].

The following mechanism is in accord with the evidence:

$$(CH_3)_2C(CN)OCOCO_2(CN)C(CH_3)_2 \longrightarrow 2(CH_3)_2C(CN)O\text{-}\dot{C}O \qquad (1),$$

$$2(CH_3)_2C(CN)O\dot{C}O \longrightarrow CH_2{=}C(CN)CH_3 + CO_2 + (CH_3)_2C(CN)OCHO \qquad (2),$$

$$(CH_3)_2C(CN)O\dot{C}O \longrightarrow (CH_3)_2C(CN)O\cdot + CO \qquad (3),$$

$$(CH_3)_2C(CN)O\dot{C}O \longrightarrow (CH_3)_2\dot{C}(CN) + CO_2 \qquad (4),$$

$$(CH_3)_2C(CN)O\cdot + (CH_3)_2C(CN)O\dot{C}O \longrightarrow (CH_3)_2C(CN)OH + CH_2{=}C(CN)CH_3 + CO_2 \qquad (5)$$

$$(CH_3)_2C(CN)OH \longrightarrow HCN + (CH_3)_2CO \qquad (6)$$

$$(CH_3)_2\dot{C}{-}CN + CH_2{=}C(CN)CH_3 \longrightarrow \text{Polymer} \qquad (7)$$

The process (2) and (5) must occur immediately following bond cleavage, e.g., in a solvent cage. Additional processes, such as cleavage of the oxalate molecule at other points, may also occur and the initial step may involve concerted loss of CO or CO_2 rather than the non-concerted reaction written above. The formate may decompose under sufficiently stringent conditions to yield further CO.

Dibenzhydryl oxalate and its para-substituted derivatives undergo decomposition by a homolytic mechanism. This conclusion was reached by consideration of the results of product studies and of the kinetic dependence on para-substituents and solvent.

The products obtained from decomposition of dibenzhydryl oxalate in diphenyl ether (Table VII) are consistent with the intervention of the benzhydryl radical. The formation of 4-phenoxytriphenylmethane is typical of an electrophilic attack on an electron-rich position of an aromatic ring. However, this product was not observed when the decomposition was carried out at a lower temperature and this fact is suggestive of free-radical, rather than cationic, substitution. Tetraphenylethane is readily accounted for as a product of coupling of two benzhydryl radicals and the absence of appreciable carbon monoxide mitigates against the intervention of the $R{-}O{-}\bar{C}{=}O$ anion. Although analogues are lacking, such an ion might be expected to undergo extensive decarbonylation to yield R-O$^-$.

Table VII

Decomposition of Dibenzhydryl Oxalate in Diphenyl Ether

Conditions	Products	Per cent Yields
236-245° for 11 hours	CO	None
	CO_2	115
	Substances boiling below solvent.	None[a]
	4-phenoxytriphenylmethane	163
223° for 2-6 hours	CO	None
	CO_2	126
	4-phenoxytriphenylmethane	Trace[b]
	1,1,2,2-Tetraphenylethane	Present[c]
228° for 6.2 hours	CO	None
	CO_2	153
	1,1,2,2-Tetraphenylethane	Present[c]

[a] Gas chromatographic analysis.

[b] Infra-red spectroscopy.

[c] Sample isolated and compared with authentic specimen, yield not determined.

In the presence of chloranil, products indicative of a free radical process were observed (Table VIII).

Table VIII

Decomposition of Dibenzhydryl Oxalate In Diphenylmethane in Presence of Chloranil

223-6° for 17 hours

Products	Per cent Yields	
HCl	91	(From volume measurement)
CO_2		
1,1,2,2-tetraphenylethane	164	
benzhydryltrichloroquinone(?)	3	

The high yield of 1,1,2,2-tetraphenylethane may be rationalized as arising from coupling of solvent-derived benzhydryl radicals. Formation of benzhydryltrichloroquinone is probably a radical substitution process which releases a chlorine atom. The chlorine atom then abstracts a hydrogen atom from the solvent to yield hydrogen chloride and a benzhydryl radical.

After a sample of dibenzhydryl oxalate had been heated in diphenyl ether solution at temperatures below 240°, base extraction of the reaction mixture led to the isolation of diphenylacetic acid. This product suggests that one molecule of carbon dioxide is ejected from the oxalate and that the remaining fragments recombine to form $Ph_2CHCO_2CHPh_2$, which is hydrolyzed by base to yield $Ph_2CH{\cdot}COOH$. This speculation was supported by the study of the products of decomposition of bis-(4,4'-dichlorobenzhydryl) oxalate in α-chloronaphthalene (Table IX).

Table IX

Decomposition of Bis-(4,4'-dichlorobenzhydryl) Oxalate In α-Chloronaphthalene

Partly spent reaction mixture equivalent to 3.335 g oxalate
was heated at 248° for 1.5 hours.

Products	Per cent Yields		Weights (g)
CO^a	10		0.017 (calcd.)
$CO_2{}^a$	200		0.520 (calcd.)
$[(pClC_6H_4)_2CH]_2$	56.5		1.587
$(pClC_6H_4)_2CHCO_2CH(pClC_6H_4)_2$	9.5		0.292
$(pClC_6H_4)_2CHOH^b$	21.3		0.320
Oils and Residues	5.3		0.176
		Total	2.912 (87.2% material balance)

[a] The relative yields of CO and CO_2 were determined by mass spectrometric analysis.

[b] Most, if not all, of the 4,4'-dichlorobenzhydrol probably arises from saponification of $Ar_2CH{\cdot}COOCHAr_2$ on the alumina of the chromatographic column. The inclusion of an equivalent amount of $(ClC_6H_4)_2CH{\cdot}COOH$ brings the material balance close to 100%.

The isolation of the ester $Ar_2CHCO_2CHAr_2$ is conclusive evidence of the intermediacy of a species in which the carbon-carbon bond of the oxalate has been broken, but which still retains the benzhydrylcarboxy system intact. The coupling of this species with a benzhydryl fragment is readily explainable in free radical terms. It is obvious, therefore, that we cannot write fully concerted processes for the decomposition of dibenzhydryl oxalates, whether ionic or radical in nature.

A concerted process, leading to Ar_2CH^- and $Ar_2CH\text{-}O\text{-}\overset{+}{C}O$ in the first step, is eliminated by the effect of para-substituents on the rate (Tables X, XI, XII, XIII, XIV, XV), since these would act principally on the developing carbanion at the transition rate.

Table X

Kinetic Data for Dibenzhydryl Oxalate (0.0196M solutions)

Solvent	Temperature °C	$k \times 10^2$ min^{-1} [a]	Average CO_2 Yield % [a,b]
Diphenylmethane	213.5	0.367 ± 0.056	69 ± 4
"	223.6	0.745 ± 0.125	79.4 ± 0.3
"	240.6	2.67 ± 0.20	98 ± 7
"	"	2.85	87.9 [c]
Diphenyl Ether	213.5	0.526 ± 0.016	65 ± 2
"	223.6	1.20 ± 0.23	82 ± 6
"	230.2	1.85 ± 0.14	80 ± 3
"	240.6	3.54 ± 0.61	90 ± 3
α-Chloronaphthalene	223.6	2.53 ± 0.16	92 ± 3
"	230.2	4.95 ± 0.09	110 ± 4
"	240.6	7.42 ± 0.34	92 ± 5

[a] Deviations quoted are standard deviations.

[b] CO_2 yields are based on the expectation of 2 moles CO_2 per mole oxalate.

[c] In presence of oxygen. Single run with initial concentration 0.0224M.

Table XI

Kinetic Data for Bis(4,4'-dichlorobenzhydryl) Oxalate (0.0196M)

Solvent	Temperature °C	$k \times 10^2$ min^{-1} [a]	Average CO_2 Yield % [a,b]
Diphenylmethane	230.2	1.17 ± 0.04	84.6 ± 0.6
"	240.6	2.12 ± 0.09	95 ± 2
Diphenyl Ether	230.2	1.51 ± 0.06	88 ± 1
"	240.6	2.74 ± 0.18	102 ± 2
α-Chloronaphthalene	213.5	1.16 ± 0.04	64 ± 2
"	229.1	2.74 ± 0.45	96 ± 4
"	240.6	6.02 ± 0.45	113 ± 8

[a] Deviations quoted are standard deviations.

[b] CO_2 yields are based on the expectation of 2 moles, CO_2 per mole oxalate.

Table XII

Kinetic Data for Bis(4,4'-dimethylbenzhydryl) Oxalate (0.0196M)

Solvent	Temperature °C	$k \times 10^2$ min^{-1} [a]	Average CO_2 Yield % [a,b]
Diphenylmethane	198.2	2.09 ± 0.05	54 ± 8
"	213.6	5.55 ± 0.75	74 ± 7
"	230.2	13.68 ± 0.01	110 ± 4
Diphenyl Ether	214.2	6.49 ± 0.28	72 ± 2
"	230.2	20.25 ± 0.02	112 ± 4
α-Chloronaphthalene	181.9	4.55 ± 0.01	41 ± 1
"	198.2	8.68 ± 0.65	57 ± 2
"	214.2	14.1 ± 0.8	94 ± 2

[a] Deviations quoted are standard deviations.

[b] CO_2 yields are based on the expectation of 2 moles, CO_2 per mole oxalate.

Table XIII

Kinetic Data for Di(4-methoxybenzhydryl) Oxalate (0.0196M solutions)

Solvent	Temperature °C	$k \times 10^2$ min^{-1} [a]	Average CO_2 Yield % [a,b]
Diphenylmethane	198.2	4.05 ± 0.14	63 ± 2
"	213.6	11.5 ± 0.1	94 ± 3
Diphenyl Ether	181.9	1.63 ± 0.17	56 ± 5
"	198.2	5.40 ± 0.18	55 ± 2
α-Chloronaphthalene	181.9	2.05 ± 0.12	78 ± 13
"	198.2	8.65 ± 0.68	75 ± 5

[a] All deviations quoted are standard deviations.

[b] CO_2 yields are based on the expectation of 2 moles, CO_2 per mole oxalate.

Table XIV

Variation In Rate Constant for Dibenzhydryl Oxalate with Initial Concentration

Solvent	Temperature °	Initial Concentration, M	$k \times 10^2$ min^{-1} [a]	$\%CO_2$ [a,b]
Diphenylmethane	223.6	0.0140	0.530	79.1
"	"	0.0196	0.745±0.124	79.4±0.3
"	"	0.0234	0.720	74.6
"	"	0.0450	0.96±0.08	81±1
Diphenyl Ether	"	0.0158	0.921	88.3
"	"	0.0196	1.20±0.23	82±6
"	"	0.0270	1.21	87.5
"	"	0.0529	1.40	78.3

Continued . . .

Table XIV - Continued

α-Chloronaphthalene	223.6	0.0180	2.64	98.1
"	"	0.0196	2.53±0.16	92±3
"	"	0.0320	2.42	89.3
Diphenyl Ether	240.6	0.0098	2.5±0.2	74.6
"	"	0.0183	4.44	85.1
"	"	0.0196	3.5±0.6	90±3
"	"	0.0225	4.11	81.2
"	"	0.0500	5.30	89.4
"	"	0.0600	4.74±0.03	82±2
α-Chloronaphthalene	"	0.0098	7.3±0.1	91±3
"	"	0.0196	7.42±0.31	92±5

[a] Error limits quoted are standard deviations and the figure listed is an average value from several runs. Figures without estimate of error are from single runs.

[b] CO_2 yields are based on the expectation of 2 moles of CO_2 per mole of oxalate.

Table XV

Variation of Rate Constant for Bis(4,4'-dichlorobenzhydryl) Oxalate With Concentration

Solvent	Temperature	Molarity	k x 10^2 min^{-1}	% CO_2 Yield [a]
α-Chloronaphthalene	240.6	0.00515	1.95 ± 0.9	122±22
"	"	0.00909	3.38	94.4
"	"	0.0196	6.02 ± 0.45	113±8
"	"	0.0228	5.81	107.4
"	"	0.0614	6.5 ± 0.6	114±1
"	"	0.0846	6.81	114.4

[a] The CO_2 yield is based on the expectation of 2 moles. CO_2 per mole of oxalate.

The alternative process, leading to Ar_2CH^+ and $Ar_2CH\text{-}O\text{-}\overset{-}{C}O$, would require us to believe that Ar_2CH^+ would not carry out aromatic substitution and that, for $Ar_2CH\text{-}O\text{-}\overset{-}{C}O$, the ratio of decarbonylation to decarboxylation would be small and independent of parasubstituents. That the latter is true may be seen from the mass spectrometric data (Table XVIII). In fact there appears to be a rough correlation between CO yield and extent of reaction, so that this may arise from decomposition of a product or from a slower, competing process.

A non-concerted, ionic cleavage of the central bond fails to accommodate the substituent effects. The relatively small acceleration with increasing solvent polarity is also more consistent with a homolytic mechanism than with an ionic process.

Although the evidence for radical character is not completely compelling, the results fit quite well. In particular, the fate of $Ar_2CH\text{-}O\text{-}\dot{C}O$ should be less dependent on para-substituents than that of the corresponding anion, so that it is easier to accept the near independence of the CO yield on substituents in terms of a radical process.

(2) The Nature of the Transition State.

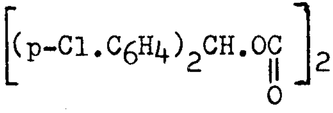
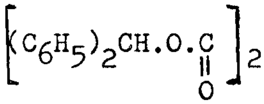
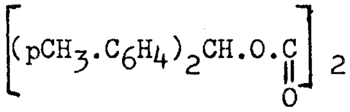
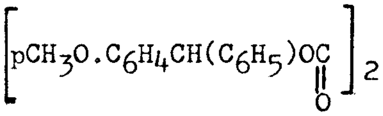
For dialkyl oxalates there is little evidence as to this question. The results of Karabatsos[94], supplemented by the data for dibenzyl and dineopentyl oxalates[17] suggest the participation of a β-hydrogen in the transition state together with strong polarization of the C-O bond. It is possible to speculate that the transition state resembles that for concerted, cyclic ester pyrolysis[79] with modifications to accommodate the conclusions above, however, more work is required to establish this. In particular, the effect of isotopic substitution of the β-hydrogen on the rate would be enlightening.

It is not possible to say, on the available evidence, whether di-(α-cyanoisopropyl) oxalate decomposes in a partially concerted or non-concerted process. A fully concerted process is excluded by the production of formate (Table II) and is, in any case, difficult to reconcile with the effect of added tetralin (Table VI). Analogy with the pyruvate system[93] and with the dibenzhydryl oxalate decomposition (vide infra) suggests that the central C-C bond is broken in the rate-determining step of the decomposition. The effect of the radical stability of the $(CH_3)_2C\text{-}CN$ group on the ease of decomposition of the oxalate is so marked when compared with simple, secondary alkyl oxalates, that it suggests that one of the C-O bonds may be breaking in concert with the C-C bond. However, there may be other ways for the 2-cyano-2-propyl group to exert an accelerating effect on the reaction[18] and this question must remain unsettled.

Dibenzhydryl oxalates probably decompose with two bonds breaking in concert. The entropies of activation are, for most such systems, large and negative (Table XVI). Although the errors are too large to

Table XVI

Activation Parameters For Para-substituted Dibenzhydryl Oxalates

Compound	Solvent	$\Delta H^{\neq}$ k.cal. mole^{-1}	$\Delta S^{\neq}$ e.u.
 $\left[(p\text{-}Cl.C_6H_4)_2CH.O\underset{\underset{O}{\Vert}}{C}\right]_2$	Diphenylmethane	28.5 ± 2.3	-20.0±4.5
"	Diphenylether	28.4 ± 5.3	-19.6±10.5
"	α-Chloronaphthalene	28.9 ± 2.0	-17.3±4.1
 $\left[(C_6H_5)_2CH.O.\underset{\underset{O}{\Vert}}{C}\right]_2$	Diphenylmethane	35.5 ± 2.9	-5.8±5.7
"	Diphenylether	33.8 ± 3.0	-8.5±6.1
"	α-Chloronaphthalene	30.1 ± 3.3	-14.2±6.4
 $\left[(pCH_3.C_6H_4)_2CH.O.\underset{\underset{O}{\Vert}}{C}\right]_2$	Diphenylmethane	26.7 ± 0.4	-18.5 ± 0.7
"	Diphenylether	33.7 ± 1.3	-4.0±2.6
"	α-Chloronaphthalene	14.5 ± 1.1	-41.9±2.3
 $\left[pCH_3O.C_6H_4CH(C_6H_5)O\underset{\underset{O}{\Vert}}{C}\right]_2$	Diphenylmethane	30.0 ± 1.2	-10.4±2.5
"	Diphenylether	30.4 ± 3.6	-8.9±7.7
"	α-Chloronaphthalene	36.7 ± 3.6	+5.5±7.8

make quantitative comparison with other systems possible, the results are at least in keeping with a concerted process. The entropy values indicate considerable loss of freedom at the transition state and this is probably a composite of solvation effects and restriction of internal degrees of freedom. For a given oxalate, changes in solvent are accompanied by changes in entropy of activation, but the errors are too large to make separation of the solvent contribution possible. The over-all rate variation with change of solvent (Table X) parallels the progression of increasing solvent polarity, and this order is consistent with a polar transition state.

There is no apparent trend in the activation parameters when the nature of the para-substituent is changed, and there can be no question of linear relationships between them when the errors are of the quoted magnitude.

The rates, at 230.2°, are correlated by the Hammett equation using σ^+ parameters (Table XVII, Fig. 4). The value of the rho parameter depends upon the number of groups considered to directly affect the bond or bonds breaking in the rate-determining step. In this case, if there is indeed a concerted cleavage of a C-O bond and the C-C bond, only the para-substituents on one of the benzhydryl groups should have an appreciable effect on the bond-breaking process. However, if there is a primary central cleavage then the substituents on both of the benzhydryl groups should influence the rate-determining process, presumably through a transition state analogous to that proposed for the esters of <u>tert</u>-butylperoxyoxalic acid[18,33,34]. Since the former situation

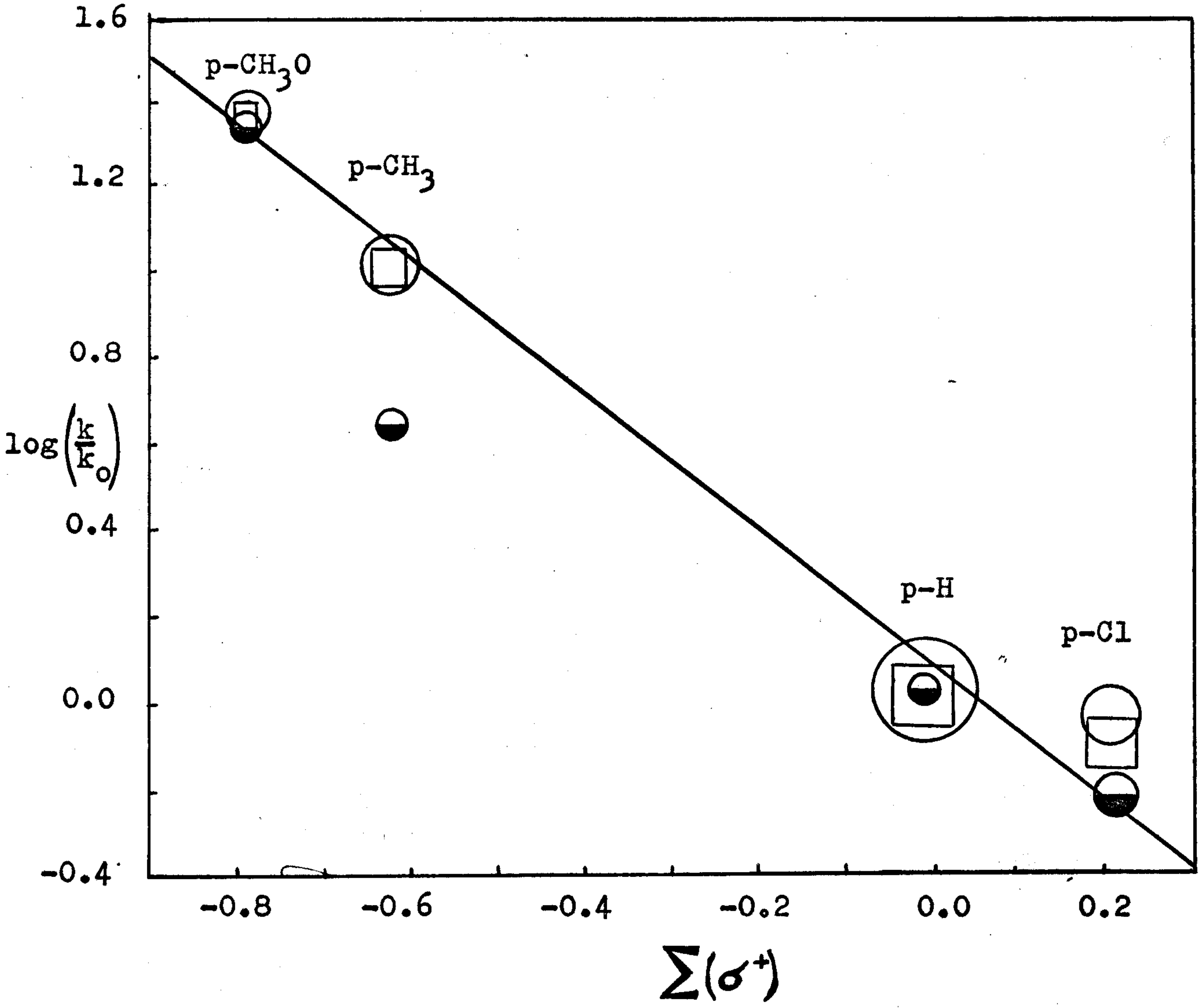


Fig.4. Hammett correlation of relative rates at 230.2° with σ^+ parameters.

○ -diphenylmethane solvent,

□ -diphenyl ether solvent,

◒ -α-chloronaphthalene solvent.

The vertical extent of each symbol represents the calculated error in $\log\left(\frac{k}{k_o}\right)$.

Table XVII

Data For Correlation Of Rate Ratios With The Hammett σ Parameters

X,Y[a]	Solvent	σ^{b}	σ^{+b}	$k\mathrm{x}10^{2}\,\mathrm{min}^{-1}$ [c]	k/k_o	$\log_{10}(k/k_o)$	Error in $\log_{10}(k/k_o)$ [d]
H,H	Diphenylmethane	0.00	0.00	1.30±0.15	1.000	0.000	0.110
"	Diphenyl Ether	0.00	0.00	1.85±0.14	1.000	0.000	0.066
"	α-Chloronaphthalene	0.00	0.00	4.95±0.09	1.000	0.000	0.016
Cl,Cl	Diphenylmethane	+0.46	+0.22	1.17±0.04	0.898	-0.047	0.065
"	Diphenyl Ether	+0.46	+0.22	1.51±0.06	0.816	-0.088	0.050
"	α-Chloronaphthalene	+0.46	+0.22	2.94±0.25	0.594	-0.226	0.045
CH_3,CH_3	Diphenylmethane	-0.34	-0.62	13.7±0.2	10.499	1.021	0.057
"	Diphenyl Ether	-0.34	-0.62	20.25±0.02	10.946	1.039	0.041
"	α-Chloronaphthalene	-0.34	-0.62	22.21±0.095	4.487	0.652	0.026
CH_3O,H	Diphenylmethane	-0.27	-0.78	31.50±0.01	24.175	1.383	0.050
"	Diphenyl Ether	-0.27	-0.78	44.90±0.02	24.270	1.385	0.033
"	α-Chloronaphthalene	-0.27	-0.78	15.8±0.3	23.394	1.369	0.023

[a] X,Y are groups at the para-positions of the benzhydryl group.

[b] The Hammett Equation is taken to be $\log_{10}(k/k_o) = \rho \sum^{n} \sigma$ with n = 2 (n = 1 for CH_3O).

[c] Rates are measured at 230.2° and where necessary the activation parameters have been used to obtain a value of k at this temperature.

[d] The error in log (k/k_o) is calculated by assuming that it is adequately represented by the quantity, $\frac{1}{2}\left[(\log k/k_o)_{max} - (\log k/k_o)_{min}\right]$, which is obtained when the errors in the rate constants are suitably incorporated.

Solvent	Rho Value (σ^+ correlation)
Diphenylmethane	-1.54
Diphenyl Ether	-1.62
α-Chloronaphthalene	-1.68

Estimated Error ±0.2

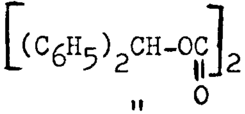
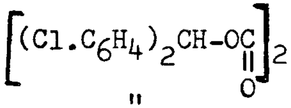
Average value -1.6 ± 0.2

is believed to apply, the rho value is calculated to be -1.6 ± 0.2; in the second case the value would be -0.8 ± 0.2. A rho value of this magnitude, at such a high temperature, suggests very strong interaction of the para-substituent with the reaction center, a feature more in keeping with a concerted rather than a non-concerted reaction. Reactions possessing similar rho values are the photobromination of substituted toluenes using N-bromosuccinimide ($\rho = -1.8$) and bromine ($\rho = -1.4$)[110,36]. The correlation with the σ^+ parameters suggests that there is development of positive charge on the benzhydrylic carbon atom at the transition state of the rate-determining step. This does not demand an ionic mechanism, since ionic contributions to the transition state of a homolytic cleavage are quite well established in the perester series[18,33,34]. Neither is a concerted mechanism necessarily indicated since, as has already been mentioned, Bartlett[18] has proposed a mechanism by which para-substituents can affect bonds quite remote from the benzylic carbon. However, Bartlett's suggestion has received no further support since that time and the σ^+-dependence is much more readily understood on the basis of carbon-oxygen bond cleavage in the rate-determining step.

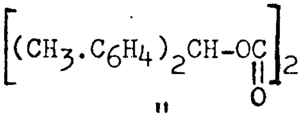
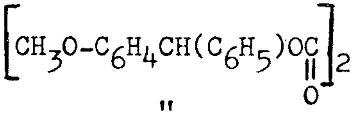
The kinetic isotope effects (Tables XVIII and XIX) show conclusively that the central carbon-carbon bond is breaking in the rate-

Table XVIII

Isotopic Ratios And Isotope Effects In Diphenyl Ether Solution

Compound	Temp. °C	P^a	$C^{13}/C^{12} \times 10^2$	$O^{18}/O^{16} \times 10^3$	% CO^b	$(k^{12}/k_{13}-1)\times 100\%$	$(k^{16}/k_{18}-1)\times 100\%$
 $[(C_6H_5)_2CH\text{-}OC(=O)]_2$	181.9	0.02	1.11009	2.0222	3.5	2.02	0.9
"	198.2	0.05	1.11589	2.0263	4.1	1.51	0.0
"	"	0.08	1.11853	2.0377	4.3	1.29	-0.1
"	248	1.00	1.13232	2.0260	3.5	-	-
"	228.4^c	0.10	1.11962	2.0320	12.9	1.94	0.3
"	" ^{c}	0.20	1.12104	2.0339	11.2	1.97	0.2
"	" ^{c}	0.30	1.12795	2.0320	9.4	1.30	0.4
"	" ^{c}	0.40	1.12401	2.0319	10.7	1.90	0.5
"	245 ^{c}	1.00	1.14014	2.0355	12.3	-	-
 $[(Cl.C_6H_4)_2CH\text{-}OC(=O)]_2$	198.2	0.02	1.10215	2.0168	5.6	4.83	0.8
"	"	0.05	1.09937	2.0169	2.6	5.18	1.0
"	"	0.08	1.10217	2.0199	-	4.98	0.8
"	228.4	0.30	1.11639	2.0326	5.0	4.14	-0.3
"	250	1.00	1.15485	2.0297	6.8	-	-
"	"	1.00	1.16359	2.0274	19.8	-	-

Continued . . . .

 $\left[(CH_3.C_6H_4)_2CH\text{-}O\underset{\underset{O}{\|}}{C}\right]_2$	181.9	0.02	1.10205	2.0257	0.6	1.71	0.7
"	181.9	0.05	1.11105	2.0238	1.2	1.36	1.2
"	181.9	0.08	1.11389	2.0260	-	1.11	1.1
"	248	1.00	1.12575	2.0374	3.8	-	-
 $\left[CH_3O\text{-}C_6H_4CH(C_6H_5)O\underset{\underset{O}{\|}}{C}\right]_2$	181.9	0.02	1.12153	2.0495	5.5	2.82	0.4
"	181.9	0.05	1.13204	2.0552	4.5	1.89	0.1
"	181.9	0.08	1.12479	2.0503	4.4	2.60	0.7
"	250	1.00	1.15288	2.0558	-	-	-

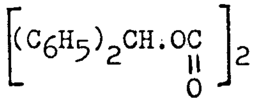
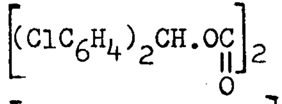
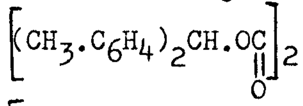
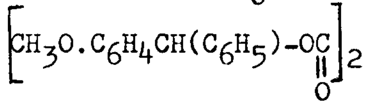
[a] P is the fractional extent of reaction.

[b] After correcting for carbon monoxide produced in the mass spectrometer from carbon dioxide.

[c] First 20% of product gases was discarded.

Table XIX

Average Isotope Effects

Compound	Temperature	Carbon Isotope Effect	Oxygen Isotope Effect
 $\left[(C_6H_5)_2CH.O\underset{\underset{O}{\|}}{C}\right]_2$	228.4	1.94 ± 0.03 [a]	0.35 ± 0.15
 $\left[(ClC_6H_4)_2CH.O\underset{\underset{O}{\|}}{C}\right]_2$	198.2	5.0 ± 0.2	0.9 ± 0.1
 $\left[(CH_3.C_6H_4)_2CH.O\underset{\underset{O}{\|}}{C}\right]_2$	181.9	1.4 ± 0.3	1.0 ± 0.2
 $\left[CH_3O.C_6H_4CH(C_6H_5)\text{-}O\underset{\underset{O}{\|}}{C}\right]_2$	181.9	2.7 ± 0.1	0.4 ± 0.3

[a] The deviations quoted are approximated standard deviations. The estimated deviations in the determination are higher; viz. ±0.2% for carbon and ±0.3% for oxygen.

determining step. The rather small oxygen isotope effects are somewhat ambiguous since a small oxygen isotope effect might arise from the fractionation of $Ar_2CH\text{-}O\dot{C}O$ radicals between decarboxylation and coupling to form $Ar_2CH.COOCH.Ar_2$. The following reasoning suggests that any oxygen isotope effect arising from this source is negligible. Decarboxylation of the radical $R\text{-}O\text{-}\dot{C}{=}O$ should be fast at this temperature and should have an enthalpy of activation close to zero so that, by the Hammond Postulate[103], there should be little bond stretching at the transition state and, consequently, a negligible oxygen isotope effect. A priori, there is no reason why the amount of bond stretching at the transition state, or the isotope effects, should be the same for the carbon-carbon bond as for the carbon-oxygen bond, in the event of a concerted bond cleavage. The small oxygen isotope effect can therefore be rationalized in terms of a concerted process.

(3) Other comments.

The limitations of product studies in these systems from a quantitative viewpoint are obvious from the poor material balances obtained in most cases, and the difficulty of obtaining reproducible kinetic results was mentioned during the discussion of experimental techniques used in attempts to correct this situation. However, some aspects of the numerical results require further comment.

The data of Tables XIV and XV show that while the rate constant for decomposition of dibenzhydryl oxalates was essentially independent of initial concentration over a moderate range, it appeared to fall off at low concentrations. The retardation observed for such concentrations may be, in part, an artifact of the experimental procedure, since the gas evolution method loses reliability when used for small quantities of gas in a large system.

The anomalous nature of the activation parameters for bis-(4,4'-dimethylbenzhydryl) oxalate (Table XVI) is noteworthy. The figures for solutions in α-chloronaphthalene would be scarcely credible were they not based on measurements at three temperatures. It is possible that a change in mechanism is occurring under these conditions, although such a change would be less surprising if it occurred with di-(4-methoxybenzhydryl) oxalate.

A number of isotope effect measurements were performed in order to investigate the possibility[92] that a small quantity of impurity was giving rise to an abnormal isotopic distribution in the products obtained at an early stage of the reaction. The results of these experiments (Table XVIII), in which the reaction was carried to a larger fraction of completion or else the first 20% of products was discarded, show that this effect is small. A trace impurity of the type proposed could account for the irregularities in the sets of values from different samples but could not explain the excess of the experimental, over the theoretical, isotope effects in two cases: neither are these large values explicable in terms of experimental error alone. It has been shown[95] that the occurrence of hydrogen/deuterium isotope effects larger than the calculated maximum, in the abstraction of hydrogen atoms from hydrocarbons by methyl radicals, may be explained by taking into account changes in the bending frequencies of the bond being broken. Since the radical $\mathrm{Ar{-}O{-}\dot{C}{=}O}$ can gain resonance stability only if the $\mathrm{{-}O{-}\dot{C}{=}O}$ system is linear, and the incipient molecule of carbon dioxide might be nearly linear in the transition state, it may be deduced that the bending frequency of the carbon-carbon bond would be decreased considerably in passing from the ground-, to the transition state, and might approach zero. The inclusion of this factor in the calculation of the maximum isotope effect might account for the observed discrepancies.

Summary

A number of symmetrical diesters of oxalic acid were synthesized and the thermal decomposition of several of these was investigated by a variety of techniques.

It is suggested that the recently-proposed ion-pair mechanism for the pyrolytic elimination reaction of dialkyl oxalates should be modified to include participation of a β-hydrogen atom in the transition state. This modification is suggested on the basis of the pyrolytic behaviour of dibenzyl oxalate and dineopentyl oxalate, which lack β-hydrogen. Further, the ready but complex fragmentation of di-(α-cyanoisopropyl) oxalate suggests radical rather than ionic character and supports the contention that an ion-pair mechanism cannot be general for oxalate decomposition.

Dibenzhydryl oxalate and certain of its derivatives probably decompose by a mechanism involving a polar transition state, with concerted cleavage of two bonds, to yield free radicals in the first step. This conclusion is drawn from the σ^+ rate-dependence on para-substituents, from the carbon- and oxygen-isotope effects and from the product composition.

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