DECARBOXYLATION OF SUBSTITUTED SODIUM PHENYLPROPIOLATES

KINETIC STUDY OF THERMAL DECARBOXYLATION OF SUBSTITUTED SODIUM PHENYLPROPIOLATES

by

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SCOPE AND CONTENTS:

The kinetics of the thermal decarboxylation of a series of substituted sodium phenylpropiolates were studied in detail. The reaction proceeded without formation of significant amounts of side products: its rate was independent of hydrogen ion concentration. The relative rates of decarboxylation are in the order: $\underline{p}\text{-NO}_2 > \underline{m}\text{-NO}_2 > \underline{m}\text{-CF}_3 > \underline{m}\text{-Cl} > \underline{p}\text{-Cl} > \text{H} > \underline{m}\text{-CH}_3$, and the entropies of activation are large and positive. The results were discussed in terms of the unimolecular (S_E1) mechanism.

A quantitative study of effects of substituents on the decarboxylation rates was made by the application of the Hammett free energy relationship. The ρ value of the Hammett plot was 0.886 ± 0.013. Deviation of *para* substituted compounds from the Hammett relationship were discussed in terms of *para* interaction or conjugation effects in the initial or the transition states.

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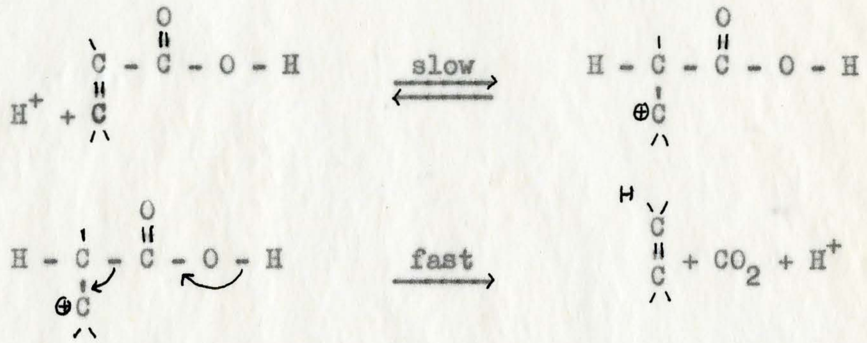
GENERAL INTRODUCTION

Almost any carboxylic acid can be decarboxylated by appropriate means and organic chemists were early in recognizing the synthetic and degradative value of this reaction. Furthermore, the frequent occurrence of decarboxylation in biological processes and the role which it has played in the development of theories of unimolecular reactions and of kinetic isotope effects testify to its great importance.

Kinetic studies of the decarboxylations of a wide variety of organic acids have shown that, with respect to the rate-determining step, the reaction may proceed by either a unimolecular or bimolecular mechanism. Since the overall process involves the replacement of a carboxyl group by a proton, the reactions are of the electrophilic type and, in terms of the symbolism developed by Hughes and Ingold, the two mechanisms may therefore be designated as S_E1 and S_E2, respectively.

Reactions proceeding by the bimolecular mechanism generally take place in strongly acidic media and involve organic acids in which the carboxyl group is attached to a carbon atom which is part of an unsaturated system, for example, α, β-ethylenic and acetylenic acids, and aromatic acids. The reaction is considered to proceed by the initial attack of a proton on the α-carbon atom giving a carbonium ion intermediate which, in a subsequent step, undergoes carbon-carbon bond fission.

S_E2

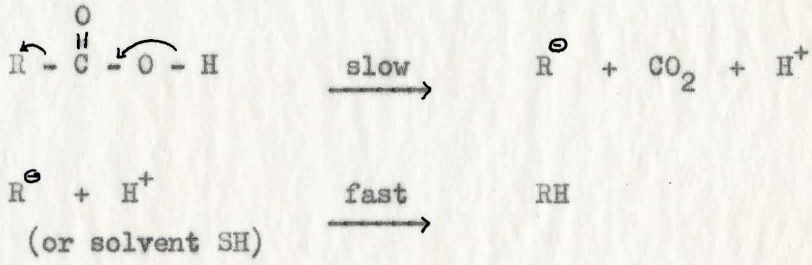


$$H^+ + C{=}C{-}C(=O){-}O{-}H \xrightleftharpoons{\text{slow}} H{-}C(C^{\oplus}){-}C(=O){-}O{-}H$$

$$H{-}C(C^{\oplus}){-}C(=O){-}O{-}H \xrightarrow{\text{fast}} C{=}C + CO_2 + H^+$$

The unimolecular mechanism, which is the most frequently encountered mode of decarboxylation, involves in the rate-determining step a heterolytic fission of the carbon-carbon bond with the production of a carbanion. Kinetic investigations have shown that organic acids may decarboxylate unimolecularly in two distinct forms:

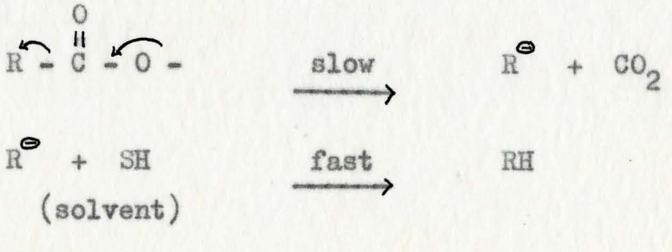
(1) free acid form



$$R{-}C(=O){-}O{-}H \xrightarrow{\text{slow}} R^{\ominus} + CO_2 + H^+$$

$$R^{\ominus} + H^+ \text{ (or solvent SH)} \xrightarrow{\text{fast}} RH$$

(2) anionic form

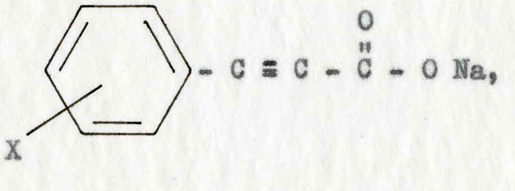


$$R{-}C(=O){-}O^- \xrightarrow{\text{slow}} R^{\ominus} + CO_2$$

$$R^{\ominus} + SH \text{ (solvent)} \xrightarrow{\text{fast}} RH$$

One of the classes of carboxylic acids which is most prone to decarboxylation is that of the acetylenic acids, $R - C \equiv C - COOH$ (where R can be a hydrogen, an alkyl, or an aryl group). Recently, the kinetics of the decarboxylation of salts of aliphatic acetylenic acids (where $R = H$, CH_3, $(CH_3)_3 - C$) in water and in other solvents (dioxane-water, ethanol-water, and methanol-water) have been investigated thoroughly by Halonen. On the basis of the observed positive entropies of activation and the relative decarboxylation rates ($HC \equiv C - CO_2Na > CH_3 - C \equiv C - CO_2Na > (CH_3)_3 - C \equiv C - CO_2Na$) it was concluded that the reaction proceeds by unimolecular decomposition of the carboxylate anion. The only other rate study of acetylenic acid decarboxylation has been made by Fairclough who observed first order kinetics and a positive entropy of activation for the decarboxylation of sodium phenylpropiolate in water.

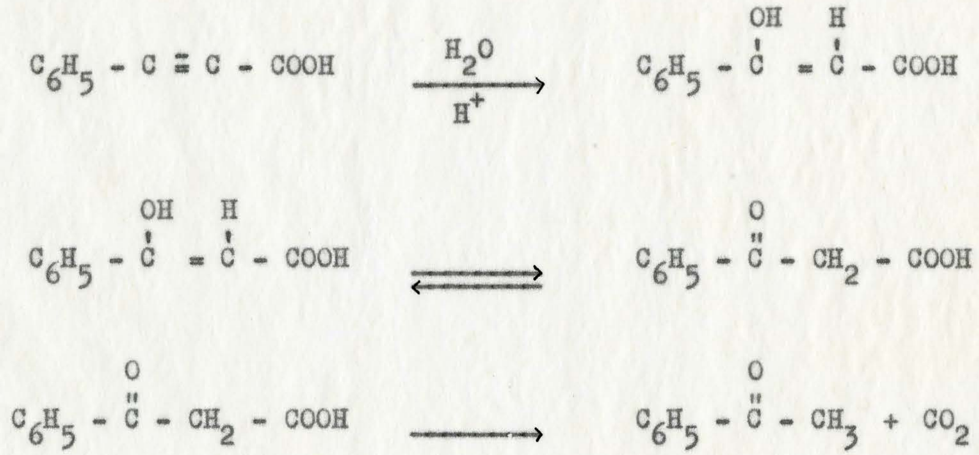
In the present investigation, the kinetics of the decarboxylation of a series of substituted sodium phenylpropiolates,



(where X = m-CH_3, m-Cl, p-Cl, m-NO_2, p-NO_2, m-CF_3, and H) have been studied in detail, with the objectives, first, of establishing unambiguously the unimolecular nature of the reaction and, second, of shedding light on the charge distribution in the transition state of the rate-determining step.

In seeking to establish the mechanism of the reaction, four factors have been examined.

(1) The Role of Triple Bond Hydration. - Phenylpropiolic acid is known to add a molecule of water in strongly acidic media to form benzoyl acetic acid which, like other β-keto-acids, is very prone to undergo decarboxylation. Furthermore, Fairclough has tentatively attributed the decrease in decarboxylation rate with time, which is observed in the kinetic studies at temperatures below 100°C, to an accumulation of the β-keto-acid.



$$C_6H_5 - C \equiv C - COOH \xrightarrow[H^+]{H_2O} C_6H_5 - \overset{OH}{\overset{|}{C}} = \overset{H}{\overset{|}{C}} - COOH$$

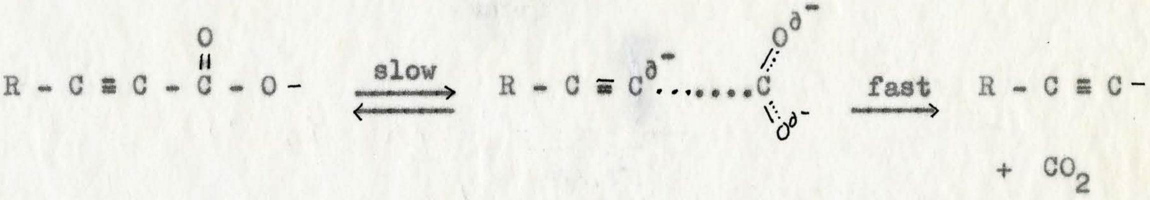
$$C_6H_5 - \overset{OH}{\overset{|}{C}} = \overset{H}{\overset{|}{C}} - COOH \rightleftharpoons C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_2 - COOH$$

$$C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_2 - COOH \longrightarrow C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_3 + CO_2$$

It was necessary, therefore, to establish that no significant portion of the decarboxylation, under the reaction conditions of the present studies, was proceeding by the way of the hydration mechanism. This was accomplished by product analyses since direct decarboxylation yields a phenylacetylene, whereas hydration/decarboxylation produces an acetophenone.

(2) The Effect of Hydrogen Ion Concentration. - The kinetics of the decarboxylations are usually carried out in media at pH about 8. At such a hydrogen ion concentration the substrate is essentially all in its anionic form and the reaction involving attack of a proton on this species would be approximately first order in hydrogen ion concentration while that involving proton attack on the free acid would be second order in this quantity. On the other hand, the unimolecular decomposition involving the anionic form would proceed at a rate independent of the concentration of hydrogen ions. To distinguish among these three possibilities, the rate of decarboxylation of sodium phenylpropiolate was studied over a range of 5 to 11 pH units.

(3) The Effect of Entropy of Activation. - Halonen has suggested that salts of the aliphatic acids decarboxylate unimolecularly in their anionic form as follows:



$$R - C \equiv C - \overset{\overset{\displaystyle O}{\|}}{C} - O^- \quad \underset{\longleftarrow}{\xrightarrow{\text{slow}}} \quad R - C \equiv C^{\partial^-} \cdots\cdots \overset{\overset{\displaystyle O^{\partial^-}}{\vdots}}{\underset{\underset{\displaystyle O^{\partial^-}}{\vdots}}{C}} \quad \xrightarrow{\text{fast}} \quad R - C \equiv C^- + CO_2$$

According to this mechanism, the carbon-carbon bond between the α-carbon atom and the carboxylate group is extended more in the transition state than the initial state and this implies a decreased order in the reacting molecule. Hence a positive entropy of activation would be expected to be associated with the process. Furthermore, the negative charge, which is localized on the carboxylate group in the initial state becomes dispersed over more of the molecule in the transition state. As a consequence, the assumption of the transition state configuration will result in a less precise orientation of solvent molecules around solute species, with an accompanying increase in the entropy of the system. This factor will therefore also contribute to the positive entropy of activation for the unimolecular reaction. In the S_E2 mechanism, however, the transition state leading to the carbonium intermediate is more rigidly orientated than the reactants and this implies an increased order in the reacting molecule. As a consequence, a negative entropy of activation would be expected to be associated with this process.

(4) The Effect of Substituents on Reaction Rate. - Reactions proceeding by the bimolecular mechanism will be favored by electron-releasing substituents since these will provide stabilization of the transition state leading to the carbonium ion intermediate. On the other hand, the opposite effect is to be expected for the S_E1 mechanism since the electron-withdrawing groups would make it easier for the carbon-carbon bond between the carboxylate group and the α-acetylenic carbon to undergo fission. The direction of substituent effects on reaction rate therefore provides a criterion for distinguishing between the two mechanisms.

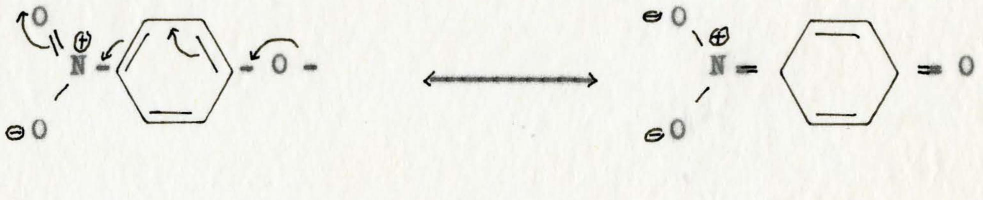
The major objective of the present investigation has been to obtain, through a quantitative correlation of structure with reaction rates, information on the electron distribution in the transition state of the decarboxylation reaction. It is well known that the effect of meta and para substituents on rate and equilibrium constants for a wide variety of reactions of benzene derivatives are described to a remarkable precision by an equation proposed by Hammett over twenty years ago and bearing his name:

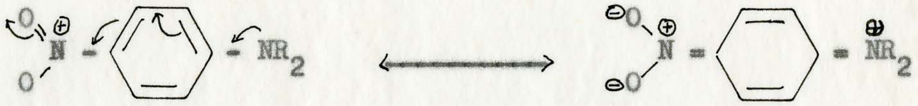
$$\log k/k_o = \rho\sigma$$

In this expression, k_o and k are, respectively, equilibrium or rate constants for the unsubstituted and substituted compounds, ρ is the reaction constant which is characteristic of the reaction under consideration, and σ is a substituent constant defined in terms of the effect of the substituent in question on the ionization constant of benzoic acid

$$\left(\sigma = \log \frac{K_{X-C_6H_4COOH}}{K_{C_6H_5COOH}} \right)$$

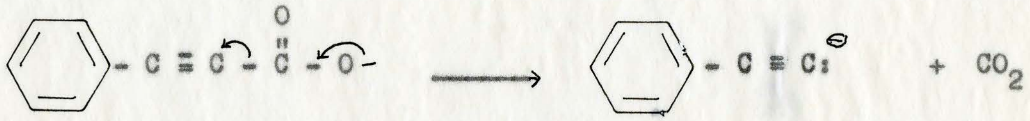
It was found very early in the application of the Hammett relationship that the σ values based on the ionization of substituted benzoic acids were inadequate in describing the effect of such para substituents as NO_2, CN, COOH, etc. on the ionization constants of phenols and anilinium ions. This is because the powerful conjugation of the substituents with the reaction centre in the phenoxide ion or the free amine



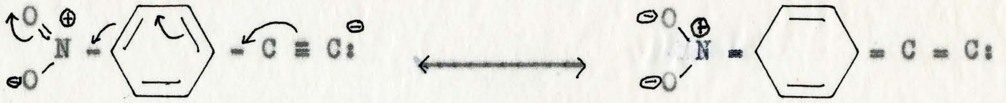


produces a stabilization of the base relative to the acid which is not present in the benzoic acid series. The exalted σ values which are required to fit such substituent effects to a Hammett plot in reactions of this type have recently been designated as σ^-.

Now the unimolecular decomposition of the sodium phenylpropiolates involves the formation of a carbanion in the rate-determining step:



The transition state for a reaction proceeding by this mechanism will resemble this carbanion intermediate to an extent depending upon the amount of carbon-carbon bond rupture in the transition state and, indeed, the accelerating influence of electron-withdrawing substituents on reaction rates is in accordance with this interpretation of the reaction pathway. It is of interest to enquire whether or not this carbanion intermediate, and hence the transition state leading to it, derives stabilization from canonical structures of the type II in which the reaction centre is conjugated with an electron-withdrawing para substituent.



I II

Certainly, if the contribution of structure II is important, the effect of such substituents will be large, and the ordinary σ values will be inadequate in correlating the reaction rates. In other words, one would expect serious deviations from the Hammett relationship. It may be, however, that the contribution of structure II will be small since the terminal carbon has but a sextet of electrons including the unshared pair and the structure might, therefore, be expected to correspond to a relatively high energy.

With the primary objective of shedding light on this interesting problem, a careful study of the effect of substituents on reaction rate has been undertaken.

HISTORICAL INTRODUCTION

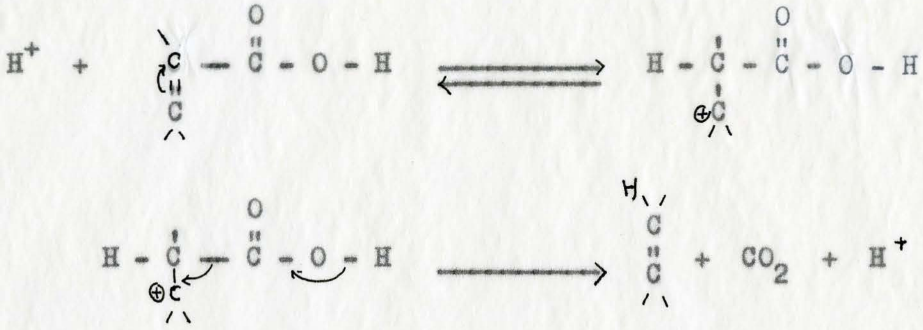
A - Mechanisms of Thermal Decarboxylation

Introduction

The kinetics of the decarboxylation of a wide variety of organic acids have been studied (1). The reaction, which is an electrophilic substitution involving replacement of a carboxyl group by a proton, has been found (2) to proceed by both unimolecular and bimolecular mechanisms. These have been designated (3) S_E1 and S_E2, respectively. A complete survey of decarboxylation reactions is not presented in this thesis as the literature on the reaction is very extensive and recent reviews are available (2, 4). Only a brief discussion of the various bimolecular mechanisms will be presented, and this will be followed by a general survey of unimolecular decarboxylations with particular attention being given to acetylenic acids since their decarboxylations is the subject of this thesis.

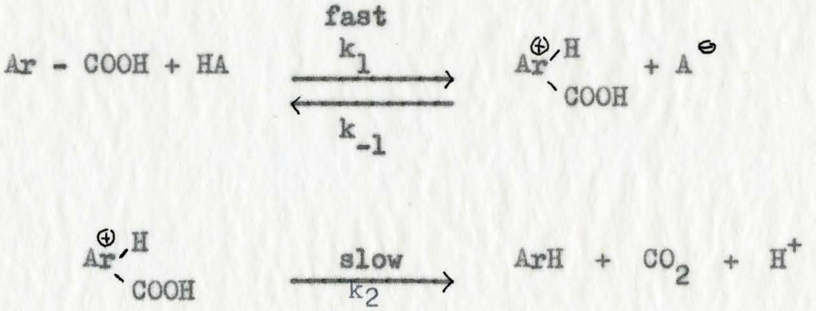
The Bimolecular Reactions

It has been found that reactions proceeding by the bimolecular mechanism usually take place in a strongly acidic medium. An initial attack of a proton on the α-carbon atom produces (1) a carbonium ion intermediate which, in a subsequent step, undergoes carbon-carbon bond fission.



Among the acids which are known to decarboxylate by this mechanism are substituted cinnamic acids (5, 6, 7), anthracene 9 - carboxylic acid (8), mesitoic acid (9), mono- and polyhydroxybenzoic acids (10, 11, 12, 13), and 2-hydroxynaphthoic acid (14), in all of which, it will be observed, the carboxyl group is attached to an unsaturated carbon atom.

Three distinct bimolecular mechanisms are possible. One, which involves the transfer of a proton in a pre-equilibrium followed by a first-order rate-determining step, is shown as follows:



$$\mathrm{Ar-COOH + HA} \underset{k_{-1}}{\overset{\text{fast}}{\underset{\longleftarrow}{\xrightarrow{k_1}}}} \mathrm{Ar}^{\oplus}\begin{smallmatrix}\mathrm{H} \\ \mathrm{COOH}\end{smallmatrix} + \mathrm{A}^{\ominus}$$

$$\mathrm{Ar}^{\oplus}\begin{smallmatrix}\mathrm{H} \\ \mathrm{COOH}\end{smallmatrix} \xrightarrow[k_2]{\text{slow}} \mathrm{ArH + CO_2 + H^+}$$

(where $\mathrm{Ar = C_6H_5,\ X-C_6H_4,\ C_6H_5-CH=CH,\ X-C_6H_4-CH=CH}$).

The rate law for this reaction is:

$$\text{rate} = k_2 \left(\overset{\oplus}{\mathrm{Ar}}{}^{\diagup \mathrm{H}}_{\diagdown \mathrm{COOH}} \right)$$

$$= \frac{k_2 k_1}{k\text{-}1} \; \frac{(\mathrm{HA})(\mathrm{ArCOOH})}{(\mathrm{A}^-)} \qquad \text{(i)}$$

A decarboxylation proceeding by this mechanism would be subject to specific acid catalysis. Also, it would be expected to show a carbon isotope effect because the rate-determining step involves rupture of the bond between the carboxyl group and the rest of the molecule. Long and Paul (15) have suggested that formic, benzoyl formic, citric and triphenylacetic acids may decarboxylate, in concentrated mineral acids, by this mechanism.

When the decomposition of the intermediate, $\overset{\oplus}{\mathrm{Ar}}{}^{\diagup \mathrm{H}}_{\diagdown \mathrm{COOH}}$, is fast relative to its return to reactants, that is, $k_2 \gg k_{-1} (\mathrm{A}^-)$, the rate-determining step is the transfer of a proton from an acid, HA, in the medium. If there are a number of acids (HA, HA^{1}, HA^{11}, etc.) present in the reaction mixture, each will transfer protons to the substrate Ar-COOH, and the following rate law will be observed:

$$\text{rate} = k_1 (\mathrm{ArCOOH})(\mathrm{HA}) + k_1^{1} (\mathrm{ArCOOH})(\mathrm{HA}^{1})$$

$$+ k_1^{11} (\mathrm{ArCOOH})(\mathrm{HA}^{11}) + \ldots\ldots\ldots \qquad \text{(ii)}$$

Hence this reaction is subject to general acid catalysis. A zero carbon isotope effect would be expected, as the bond between the carboxyl group and the rest of the molecule is essentially intact in the rate-determining step.

General acid catalysis has been observed in the decarboxylation of anthracene 9-carboxylic acid (8), mesitoic acid (9), 2:4:6-trihydroxybenzoic acid (10, 11, 12) and of 2-hydroxynaphthoic acid (14). Furthermore, Stevens (16) has obtained a zero isotope effect in the decarboxylation of anthranilic acid. Although, from these observations, it may be concluded that the acids listed decarboxylate via the second mechanism, the possibility of the reaction proceeding by a "concerted" process (displacement of the carboxyl group by a proton without formation of an intermediate) is not excluded.

$$\mathrm{Ar{-}COOH} + \mathrm{HA} \longrightarrow \mathrm{ArH} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{A^-}$$

Much evidence has recently accumulated in support of a two-step mechanism for aromatic electrophilic substitution reactions in general, including reactions such as hydrogen-isotope exchange (17, 18) and aromatic decarboxylation (19) in which a proton is the electrophile. It is therefore very likely that acid-catalysed decarboxylation reactions follow a similar pathway, although a single-step process is not out of the question particularly with less activated substrates. Recent work by Willi on the solvent isotope effect (k_{D_2O}/k_{H_2O}) has served to establish that proton transfer is rate-determining in the decarboxylation of 2:4-dihydroxybenzoic acid (20) and *p*-aminobenzoic acid (21). This finding, although important, does not distinguish between the two-step and concerted mechanisms.

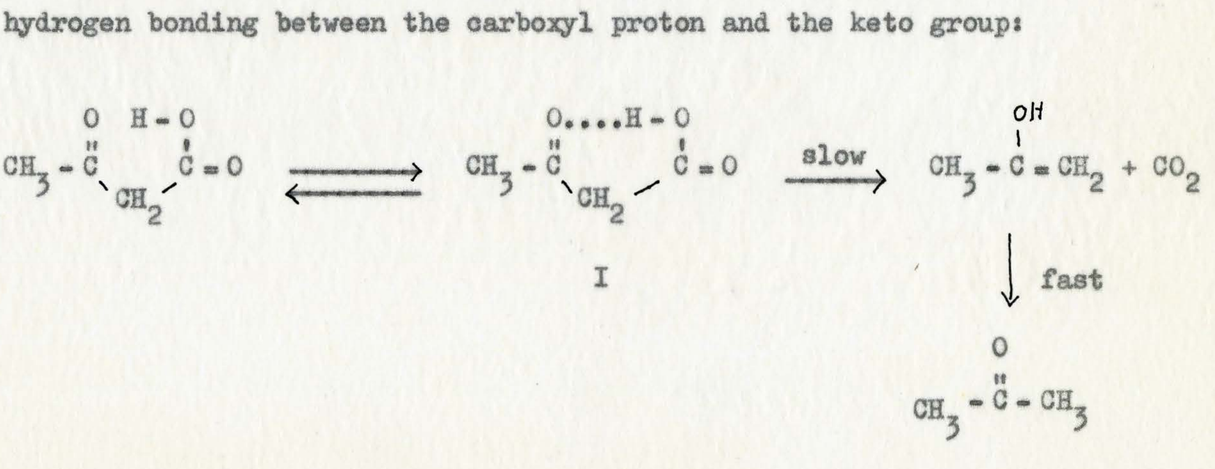
The Unimolecular Reactions

The decarboxylation of a majority of organic acids is known to proceed by a unimolecular mechanism (2, 4) involving the heterolytic fission of the bond between the carboxyl group and the rest of the molecule which departs as a carbanion. It has been shown, by investigation of the kinetics of the reactions, that organic acids in either their undissociated or dissociated forms may be decarboxylated unimolecularly.

One of the first decarboxylations studied, by Widmark (22) in 1920, was that of acetoacetic acid. This reaction, as well as that of αα-dimethylacetoacetic acid, was examined more thoroughly by Petersen (23, 24) and by Westheimer (25) who observed the following rate law:

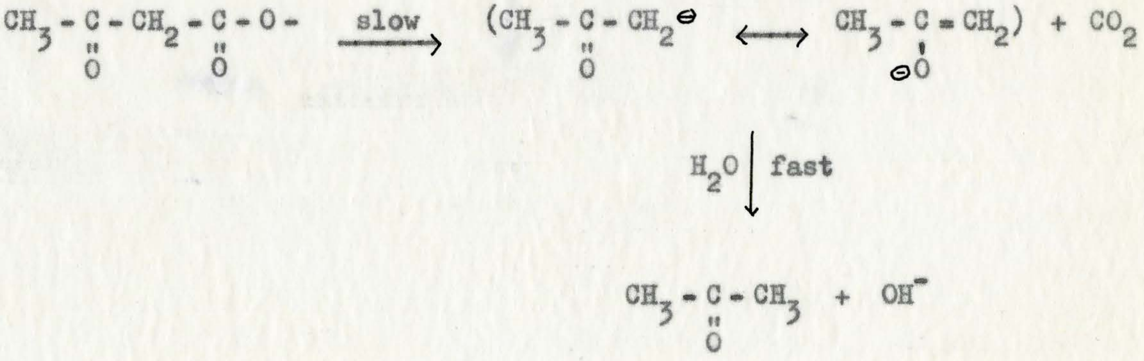
$$\text{rate} = k\,(\text{ketoacid}) + k^1\,(\text{ketoacid anion}) \qquad \text{(iii)}$$

That is, the acetoacetic acids decarboxylate in both free acid and anionic forms. Westheimer also found that k was, surprisingly, much greater than k^1, whereas one expects the proton on the carboxyl group to inhibit rather than to accelerate reaction. It was suggested that the decarboxylation of the free acid proceeds by the following mechanism involving a cyclic intermediate, I, in which there is intramolecular hydrogen bonding between the carboxyl proton and the keto group:



Recent investigations (26) of the effect of hydrogen ion concentration on the rate of decarboxylation of malonic acid in aqueous solution have shown that undissociated malonic acid, $HOOC-CH_2-COOH$, decarboxylates much faster than the monovalent ion, and that the bivalent ion under the same experimental condition does not decompose at all. The relative rates of decarboxylation of these species, and the negative entropy of activation of undissociated malonic acid in water and other solvents (24) suggest that the reaction of the free acid proceeds by a mechanism involving a cyclic intermediate similar to that proposed for undissociated β-ketoacids. β-Imino acids (28, 29, 30) and β, γ-unsaturated acids (31, 32) also are considered to decarboxylate by way of a cyclic intermediate.

The anions of most organic acids, for example, of β-ketoacid (23, 24, 25), trihalogenacetic acid (33, 34 35), α-nitroacetic and α-nitroisobutyric acids (36), dibromomalonic acid (37, 38), and 2:4:6-trinitrobenzoic acid (39) are thought to decarboxylate by the slow formation of a carbanion which then in a rapid subsequent step reacts with water to form product.



$$CH_3-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{\|}{O}}{C}-O^- \xrightarrow{\text{slow}} (CH_3-\underset{\overset{\|}{O}}{C}-CH_2^{\ominus} \longleftrightarrow CH_3-\underset{\underset{\ominus O}{|}}{C}=CH_2) + CO_2$$

$$H_2O \Big\downarrow \text{fast}$$

$$CH_3-\underset{\overset{\|}{O}}{C}-CH_3 + OH^-$$

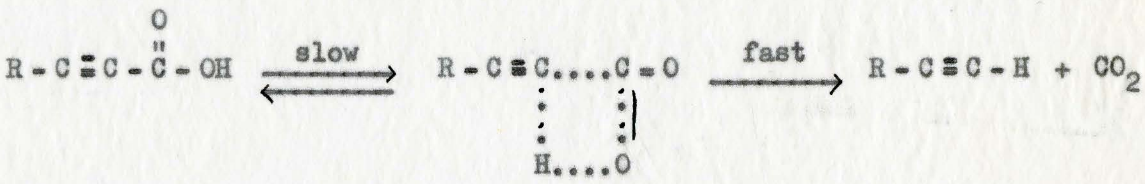
The decarboxylation of a zwitterion can be considered as a special case of that of an organic acid in its anionic form: the reaction centre of both is an anion, and the positive charge on the zwitterion does not change the unimolecular nature of its reaction. Typical examples of organic acids which decarboxylate as zwitterions are picolinic acid (30, 43), α-methyl-α-2-pyridylbutyric acid (40), 4-pyridylacetic acids (40), thiazo-2-carboxylic acid (41, 42) isoquinaldic and quinaldic acids (30).

One of the classes of carboxylic acid which is most prone to decarboxylation is that of the acetylenic acids ($R-C\equiv C-COOH$ where R can be a hydrogen, an alkyl, or an aryl group). The first rate study of decarboxylation of an acetylenic acid (phenylpropiolic acid) was made in 1938 by Fairclough (39) who observed first order kinetics, an energy of activation of 31.5 Kcal/mole and log PZ = 13.95 ($\Delta S^{\ddagger} = 5.66$ e.u.). It was also observed that the rates of decarboxylation decreased steadily with reaction time at 100°, and, that this phenomenon became even more significant at lower reaction temperatures. Fairclough tentatively attributed this decrease to a side reaction involving the addition of water to the acetylenic linkage to form benzoylacetic acid. Triple bond hydration is known to occur in both strong acid (44, 45) and strong base (46) and might be expected to compete more effectively at the lower reaction temperatures since its energy of activation would probably be less than the 31.5 Kcal/mole found for the decarboxylation process.

Recently, Halonen (27, 47) has investigated the kinetics of decarboxylation of aliphatic acetylenic acids ($R-C\equiv C-COOH$ where $R=H$,

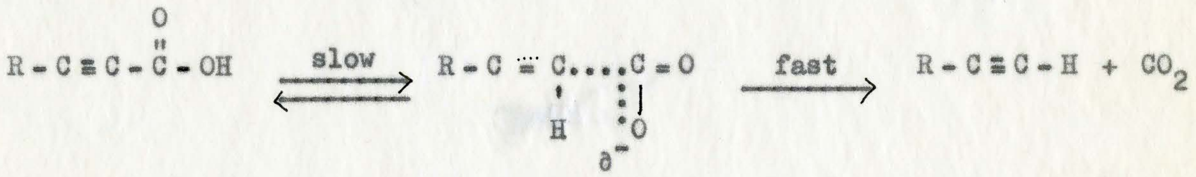
CH_3, $(CH_3)_3C$, COOH) and their sodium salts in water, dioxane-water, ethanol-water, and methanol-water. This study is presented in some detail in the following paragraphs.

The decarboxylation reactions of propiolic, tetrolic and t-butylpropiolic acids (R = H, CH_3, $(CH_3)_3C$) were found to be first order with respect to the concentrations of the carboxylic acid. Further, the rates of decarboxylation in all solvents employed were in the order: $H-C\equiv C-COOH > CH_3-C\equiv C-COOH > (CH_3)_3C-C\equiv C-COOH$. The addition of mineral acid caused an increase in reaction rate (10^6 k sec.$^{-1}$ for propiolic acid at 75°C: 1.08 in the absence of added acid, 1.43 at 0.1 M hydrochloric acid). This Halonen interpreted as being due to the conversion of carboxylate ion to the more reactive undissociated acid which then decarboxylates unimolecularly. It should be noted, however, that a similar dependence of rate on hydrogen ion concentration would be exhibited by a reaction involving bimolecular attack of a proton on the carboxylate ion, although Halonen did not appear to consider this a possibility. The entropies of activation for the decarboxylation of all three acids in water and other solvents were found to be negative, suggesting a comparatively ordered transition state for which Halonen postulated the cyclic structure, II, in the mechanism shown below:



II

Halonen also investigated the decarboxylation of acetylene dicarboxylic acid, HOOC - C ≡ C - COOH, which was found to proceed with a rate which was dependent on the first power of the concentration of the organic acid. The dependence on hydrogen ion concentration was not measured, but the reaction was considered to be unimolecular. Because the entropy of activation was positive for the decarboxylation in water, the non-ordered transition state, III, was postulated.



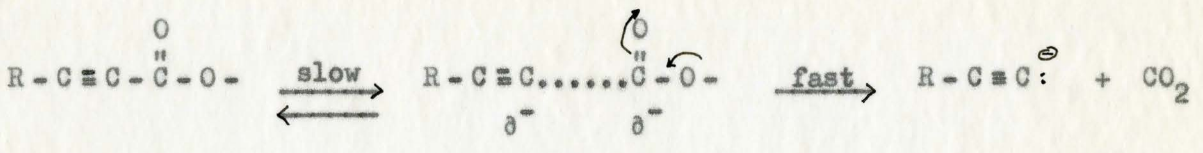
$$\mathrm{R-C\equiv C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightleftharpoons{\text{slow}} \mathrm{R-C\equiv \underset{\underset{\displaystyle H}{\vdots}}{C}\cdots\underset{\underset{\displaystyle O^{\delta-}}{\vdots}}{C}=O} \xrightarrow{\text{fast}} \mathrm{R-C\equiv C-H + CO_2}$$

III

As the polarity of the reaction medium was decreased, the entropy of activation became negative and reaction was considered, under these conditions, to proceed via a mechanism similar to that for propiolic acid (above).

Halonen's failure to trap a carbanion was considered by him to be evidence in support of the proposed mechanisms.

The rates of decarboxylation of salts of acetylenic acids were found to be first order with respect to the concentration of the anions, $R-COO^-$. Although the dependence of the reaction on the hydrogen ion concentration was not examined, Halonen assumed that the reaction was unimolecular and proceeded by the S_E1 mechanism



$$R-C\equiv C-\overset{O}{\overset{\|}{C}}-O^- \underset{\longleftarrow}{\xrightarrow{\text{slow}}} R-C\equiv \underset{\partial^-}{C}\cdots\cdots\underset{\partial^-}{\overset{O}{\overset{\|}{C}}}-O^- \xrightarrow{\text{fast}} R-C\equiv C:^{\ominus} + CO_2$$

IV

It was observed that the relative rates of decarboxylation were $H-C\equiv C-COONa > CH_3-C\equiv C-COONa > (CH_3)_3C-C\equiv C-COONa$. The effects of substituent on reaction rates thus support the S_E1 mechanism, as electron-releasing substituents decrease the rates of reactions which proceed by a mechanism involving the formation of a carbanion. The entropy of activation for the decarboxylation of sodium propiolate, sodium tetrolate and sodium t-butylpropiolate in water and in other solvents were found to be large and positive, and the postulation of the non-ordered transition state, IV, in which the carbon-carbon bond undergoing rupture is more extended than in the initial state, is supported.

Halonen assumed that the reaction was unimolecular: rates of decarboxylation with respect to the hydrogen ion concentration must be examined before the proposed mechanisms can be accepted.

B - The Hammett Equation

Introduction

One of the objectives of physical organic chemistry is to establish a quantitative correlation between structure and chemical reactivity. Although qualitative relationships have long been known, only in the last two decades have quantitative theories been developed. The oldest and the most successful of these is the Hammett equation which deals particularly with effects of substituents on reactions of *meta* and *para* substituted benzene derivatives.

In the early 1930's, Hammett found that a simple and quantitative relationship exists between the ionization constants of *meta* and *para* substituted benzoic acids and the rate constants for the hydrolyses of similarly substituted methyl benzoates (48). A straight line was obtained when the logarithms of the rate constants for the hydrolyses of the esters were plotted against those of the ionization constants of the acids, as shown in Figure I.

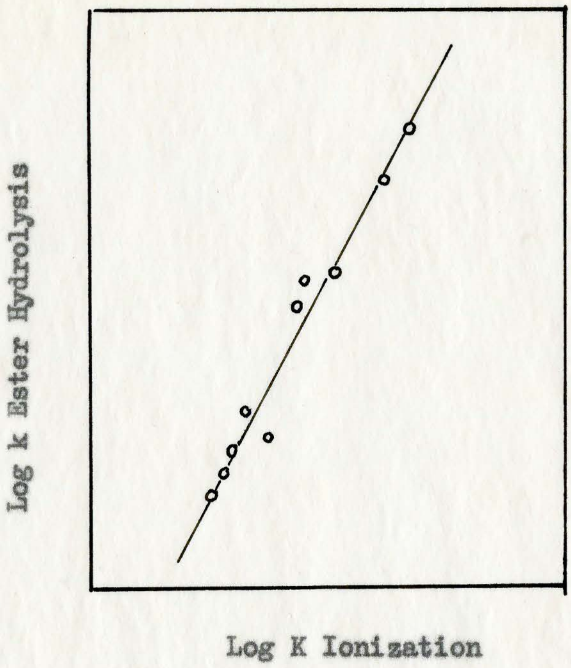


Figure I

Comparison of Hydrolysis Rates of Esters with Ionization Constants of Acids

The equation describing this relationship is:

$$\log k_h = \rho \log K_i + A \qquad \text{(i)}$$

where k_h is the rate constant for the hydrolysis, K_i the ionization constant, ρ the slope and A the intercept. By the mid-1930's, similar relationships had been demonstrated for rate and equilibrium constants of a number of other reactions of benzene derivatives (48). It was possible to relate the various series to one standard reference for which the ionization constants of substituted benzoic acids in water at 25°C was selected.

Equation (i) can be converted to the form

$$k = GK^{\rho} \quad (\text{where } \log G = A) \qquad \text{(ii)}$$

For unsubstituted compounds,

$$k_o = GK_o^{\rho} \qquad \text{(iii)}$$

By dividing equation (ii) by (iii), one obtains

$$k/k_o = GK^{\rho}/GK_o^{\rho} \qquad \text{(iv)}$$

$$\text{or } \log (k/k_o) = \rho \log (K/K_o)$$

where k is a rate or equilibrium constant of the substituted reactant, k_o the analogous constant for the unsubstituted reactant, and K and K_o are, respectively, the ionization constants for the substituted and unsubstituted benzoic acids. The term $\log (K/K_o)$ is designated σ, and is characteristic of a given substituent. Thus,

$$\log (k/k_o) = \rho\sigma \qquad \text{(v)}$$

The substituent constant, σ, is considered to be a measure of the ability of the substituent to change the electron density at the reaction centre and is independent of the reaction. A positive σ value indicates that the substituent is more strongly electron-withdrawing than is hydrogen. Substituents with negative σ values are more weakly electron-withdrawing than hydrogen.

The reaction constant ρ is a measure of the sensitivity of the equilibrium or rate process in question to a change in electron density at the reaction centre. A positive value of ρ implies assistance of reaction by electron-withdrawing substituents, a negative ρ assistance by electron-releasing substituents.

At the present time, constants for more than 110 different substituents have been calculated, and reaction constants for almost 400 different reaction series are known. Thus, about 44,000 rate and equilibrium constants are encompassed by equation (v) and the available σ and ρ values. Over 3,000 of these constants have been measured and found to agree with the values predicted by the Hammett equation (v) with a probable error of fifteen per cent (49). In addition, the Hammett equation has been found to correlate such diverse data as half-wave potentials from polarographic reductions, infrared absorption frequencies, and nuclear magnetic resonance absorption frequencies associated with the fluorine nuclei in substituted fluorobenzenes (50).

Theoretical Basis of the Hammett Equation

Equation (v) may be re-written as:

$$\log k - \log k_o = \rho \sigma \qquad \text{(vi)}$$

When k is an equilibrium constant, from thermodynamics

$$-\Delta F = 2.303\ RT \log k \qquad \text{(vii)}$$

(The ΔF values refer to standard free energy changes, but the superscript zero's have been omitted for simplicity.)

Substitution in equation (vi) gives,

$$-\Delta F - (-\Delta F_o) = 2.303\ RT\ \rho\sigma = -\Delta\Delta F \qquad \text{(viii)}$$

By definition,

$$\begin{aligned}\sigma &= \log\ (K/K_o)_{BI} \\ &= -\frac{(\Delta\Delta F)_{BI}}{2.303\ RT}\end{aligned} \qquad \text{(ix)}$$

where BI refers to the ionization of benzoic acids. By substituting equation (ix) into (viii), one obtains

$$\Delta\Delta F = \frac{2.303\ RT\ \rho\ (\Delta\Delta F)_{BI}}{2.303\ RT}$$

$$\text{or } \Delta\Delta F = \rho\ (\Delta\Delta F)_{BI} \qquad \text{(x)}$$

Hence, the Hammett equation is simply a relationship between the changes in the free energy of reaction which accompany substitution, for two different reaction series involving benzene derivatives.

The Scope of the Hammett Equation

The standard free energy change accompanying the conversion of reactant to product is comprised of potential and kinetic energy components (51). Thus, for an equilibrium

$$R_oY + Z \rightleftarrows P_o \qquad \text{(xi)}$$

where P_o may be a product or a transition state, Z a reagent and R_oY a reactant in which R_o is a substituent group and Y a functional group, the standard free energy change may be expressed as follows:

$$\Delta F_o = \Delta E_o - RT \ln \frac{q_{P_o}}{q_{R_oY}\, q_Z} \qquad \text{(xii)}$$

In this equation ΔE^o is the standard potential energy change, that is, it is the change in the electronic energy accompanying the reaction. The q's are partition functions.

An equation similar to (xii) may be written for the equilibrium

$$RY + Z \rightleftarrows P \qquad \text{(xiii)}$$

where R and P differ from R_o and P_o in the nature of a substituent. The difference between the standard free energy changes in the equilibria (xi) and (xiii) is then given by:

$$\Delta F - \Delta F_o = (\Delta\Delta F)_{RY} = (\Delta\Delta E)_{RY} - (RT \ln (\pi Q))_{RY} \qquad \text{(xiv)}$$

$$\text{where } \pi Q = \frac{q_P \,.\, q_{R_oY}}{q_{P_o} .\, q_{RY}} \qquad \text{(xv)}$$

If the reaction series represented by the above equilibria fit the Hammett equation, then from equation (x)

$$(\Delta\Delta F)_{RY} = \rho\, (\Delta\Delta F)_{BI}$$

$$\text{or } (\Delta\Delta E)_{RY} - (RT \ln (\pi Q))_{RY} = \rho\left[(\Delta\Delta E)_{BI} - (RT \ln (\pi Q))_{BI}\right] \qquad \text{(xvi)}$$

This relationship requires that the sum of the potential and kinetic energy effects in one series should quantitatively parallel the sum of the two effects in an entirely different series. Considering the wide variety of substituent sizes, entropy contents and solvating powers of the different reactants, this might seem rather unlikely. There are three circumstances, however, under which the Hammett relationship resolves itself into a simple proportionality between the potential energy terms of the two series:

(a) when both RT ln (πQ) terms are zero, a situation for which there is a considerable probability when the entropy of activation remains essentially constant within each series ($\Delta\Delta S = 0$),

(b) when a proportionality exists between the kinetic and potential energy terms in each series, i.e.,

$$\alpha(\Delta\Delta E)_{RY} = -(RT \ln(\pi Q))_{RY} \qquad \text{(xvii)}$$

$$\beta(\Delta\Delta E)_{BI} = -(RT \ln(\pi Q))_{BI} \qquad \text{(xviii)}$$

It can be seen that substitution of these equations into equation (xvi) gives

$$(\Delta\Delta E)_{RY} = \frac{\rho(1 + \beta)}{(1 + \alpha)} \cdot (\Delta\Delta E)_{BI} \qquad \text{(xix)}$$

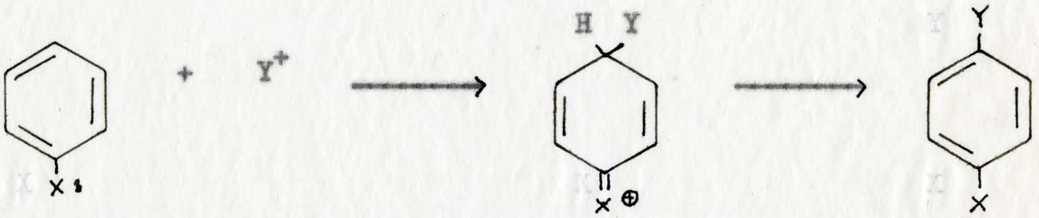
(c) when the RT ln (πQ) term of one series is zero and a proportionality exists between the potential and kinetic energy terms of the other series.

It follows that the Hammett equation will be obeyed under any of the above stated circumstances provided that at the same time there is a parallelism in the effects of the substituents on the change in the potential energy accompanying reaction in the two series. Conversely, if the Hammett relationship is quantitatively obeyed in any reaction series, one is justified in interpreting the effect of the substituents on equilibrium and rate constants in terms of their polar (electronic) effects, that is, in terms of their inductive, resonance and polar resonance effects.

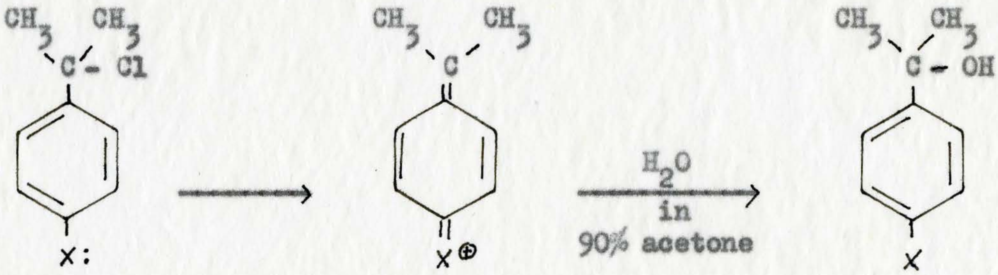
Modification of the Hammett Equation

The Hammett relationship holds reasonably well for the majority of *meta*-substituted compounds and for those *para*-compounds in which the substituent is no more than weakly conjugated with the reaction centre. If, however, strong conjugation does exist in either the reactant or product in an equilibrium process or in the reactant or transition state in a rate process, serious deviations are encountered. In fact, Hammett himself found it necessary to assign a special substituent constant for the *para*-nitro group in the ionization of phenol and anilinium salts. In these processes, the electron-withdrawing substituent is much more powerfully conjugated with the reaction centre in the product than in the reactant and causes an abnormally high enhancement of acidity. Similar special constants, higher than the normal σ values, are required in reactions of this type for other powerfully electron-withdrawing substituents, for example, *p*-cyano (52), *p*-methylsulphonyl (53, 54), *p*-carboxylic and *p*-carbonyl (55). Recently these constants have been designated as σ^- (56).

One may expect that a third type of substituent constant, σ^+, would be needed for reactions in which a strong electron-releasing substituent is conjugated with a reaction centre which is electron deficient. Several workers (57, 58, 59, 60, 61) have found, for example, that in aromatic electrophilic substitution where a substituent is in direct conjugation with the electron-withdrawing centre in the transition state, a poor fit of the reaction rates with the Hammett σ values is obtained.



Recently, Brown (57) has proposed a set of σ^+ values based on the effect of substituents on the solvolysis rates of the substituted phenyldimethylcarbinyl chlorides in 90% acetone.



The ρ for the reaction was obtained from a plot of the rates of solvolysis of meta substituted compounds versus the corresponding values. This value of ρ was then substituted into the equation

$$\log k_p/k_o = \rho \, \sigma_p^{+} \qquad \text{(xx)}$$

(where subscript p refers to para-substituted compound) to obtain the σ^+ values for the para substituents conjugated with the reaction centre. Brown was then able to demonstrate (62) an excellent correlation between these σ^+ values and the rates of a variety of aromatic electrophilic substitution reactions.

As stated above, the substituent constants σ^+ and σ^- are assumed to result from resonance interaction arising from conjugation between the reaction centre and a para substituent (56, 63, 64). Wepster has suggested (65) that if this is so, a continuous range of σ_p values would be expected to apply since the magnitude of the para interaction depends on the electron-releasing and -withdrawing effects of both the substituent and the reaction centre. In other words, a para-substituent conjugated with the reaction centre might be expected to have a different σ constant for each reaction considered. In support of this argument, Bordwell and his co-workers (66, 67), have shown that σ^- values for the p-nitro and p-methylsulphonyl groups obtained from the dissociation constants of substituted thiophenols ($\sigma^-_{p\text{-}NO_2} = 1.00$, $\sigma^-_{p\text{-}CH_3SO_2} = 0.83$) are considerably smaller than the corresponding values obtained from the dissociation constants of phenols ($\sigma^{-}_{\underline{p}\text{-}NO_2}$ = 1.22, $\sigma^{-}_{\underline{p}\text{-}CH_3SO_2}$ = 0.98) and these, in turn, are smaller than the values obtained from the dissociation constants of anilinium salts ($\sigma^{-}_{\underline{p}\text{-}NO_2}$ = 1.27, $\sigma^{-}_{\underline{p}\text{-}CH_3SO_2}$ = 1.13).

Wepster has recommended a procedure for measuring the magnitudes of resonance para interactions. Ten primary σ values which are considered as unambiguously normal (i.e., free from resonance para interaction) were selected, and from at least five of these, reliable ρ constants for reactions of all types were determined. These constants were then used to calculate the σ values for a variety of meta and para substituents by substitution in the equation (v).

$$\sigma = \frac{\log (K/Ko)}{\rho} \qquad \text{(v)}$$

The individual σ values so obtained, except those of para substituents which enter into resonance interaction with the reaction centre, were found to be in reasonably good agreement with the σ values based on ionization constants of substituted benzoic acids (56, 68).

For each para substituent, the mean of the σ values obtained by applying equation (v) to reactions in which resonance para interaction is negligible was calculated and designated as σ^{n}. At first sight, one expects that the degree of exaltation, $\sigma - \sigma^{n}$, may serve as a measure of resonance para interaction. Wepster (65) pointed out, however, that this is not so and that a true estimate of resonance para interaction should be measured in terms of a free energy difference $(\Delta\Delta F)_p$.

$$-\Delta\Delta F = 2.303\ RT\ \rho\sigma$$

$$= 2.303\ RT\ \rho\ [\sigma^n + (\sigma - \sigma^n)] \qquad \text{(viii)}$$

This free energy difference, $(\Delta\Delta F)$, can be considered to be made up of the free energy change, $(\Delta\Delta F)_n$, resulting from the inductive and polar-resonance* effects of substituents and the free energy change, $(\Delta\Delta F)_p$, resulting from the resonance-interaction or conjugation effect, that is

$$\Delta\Delta F = (\Delta\Delta F)_p + (\Delta\Delta F)_n \qquad \text{(xxi)}$$

It follows from equations (viii) and (xxi) that

$$-(\Delta\Delta F)_p - (\Delta\Delta F)_n = 2.303\ RT\ \rho\ \sigma^n + 2.303\ RT\ \rho\ (\sigma - \sigma^n) \qquad \text{(xxii)}$$

Also, from equation (viii)

$$-(\Delta\Delta F)_n = 2.303\ RT\ \rho\ \sigma^n$$

Therefore, $$-(\Delta\Delta F)_p = 2.303\ RT\ \rho\ (\sigma - \sigma^n) \qquad \text{(xxii)}$$

Thus, to estimate resonance para interactions, not only $(\sigma - \sigma^n)$, but also ρ and T should be taken into account.

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*The resonance effect of a substituent may influence the reaction centre at the para position in two ways. The effect which is transmitted to the para carbon atom of the benzene and then relayed to the reaction centre by induction is known as "polar-resonance" effect. The effect which is transmitted directly to the resonance centre is termed resonance-interaction or conjugative effect.

A parallel treatment for the evaluation of resonance effects on reactivity has been given by Taft (69). The procedure for the selection of primary σ values, determination of reliable ρ values and calculation of the exalted σ values is similar to that of Wepster. However, in the determination of σ^n values by Taft (who designated then σ^o), reactions of a series of para substituted compounds in which there is a methylene group between the benzene ring and the reaction centre were selected. The σ^o values are experimentally equivalent to the σ^n and both represent the inductive and polar-resonance effects and exclude the resonance-interaction effect.

In an extention of his treatment, Taft (69) has separated contributions to log (k/k_o) into inductive effects, I, and total resonance effects, R, which are the sum of polar-resonance and resonance-interaction effects. The following three general assumptions were made:

$$\log (k^p/k_o) = I + R^p \qquad \text{(xxiv)}$$

$$\log (k^m/k_o) = I + R^m \qquad \text{(xxv)}$$

$$R^m = \alpha R^p \qquad \text{(xxvi)}$$

where R^p and R^m are total resonance effects of para and meta substituents respectively, and α is a proportionality factor evaluated by the method of Roberts and Jaffe (70) or approximated as 1/3 for normal reactions and 1/10 for reactions in which there is strong resonance interaction (69).

Values of I were calculated from equation (xxvii) which is obtained (69) by substituting equation (xxvi) in (xxv), subtracting the result from (xxiv), and solving for I.

$$I = \frac{1}{1-\alpha} \left[\log (k^m/k_o) - \alpha \log (k^p/k_o) \right] \qquad \text{(xxvii)}$$

It was found that values of I so obtained obey the equation (xxvii),

$$I = \rho \sigma_I \qquad \text{(xxviii)}$$

where σ_I values are the inductive sigma constants evaluated previously by Taft (71) from the rates of base- and acid-catalyzed hydrolyses of aliphatic esters using equation (xxix)

$$\sigma_I = \frac{1}{6.23} \left[\log (k/k_o)_{OH^-} - \log (k/k_o)_{H^+} \right] \qquad \text{(xxix)}$$

The constants k_{OH^-} and k_{H^+} in this equation are, respectively, rate constants for base- and acid-catalyzed hydrolyses of aliphatic esters.

Using values of I and σ_I obtained from equations (xxvii) and (xxix), respectively, ρ was accurately estimated for a given reaction from equation (xxviii) using the method of "least squares" to obtain the best fit of the data. This value of ρ was then used to calculate, by means of equation (xxviii), a more accurate value of I for each substituent. This rather involved procedure was used because of a considerable uncertainty with respect to the appropriate value for α (1/3 or 1/10) appearing in equation (xxvii).

The quantities R^m and R^p were evaluated using equations (xxiv) and (xxv). These can then be used to calculate σ_R^{meta} and σ_R^{para}, the specific or resonance sigma values, since by definition

$$\sigma_R^{meta} = R^m/\rho \qquad \text{(xxx)}$$

$$\text{and} \quad \sigma_R^{para} = R^p/\rho \qquad \text{(xxxi)}$$

Alternatively, the σ_R values may be obtained from the following equations:

$$\sigma_R^{meta} = \frac{1}{\rho}\left[\log (k^m/k_o) - \rho\,\sigma_I\right] \qquad \text{(xxxii)}$$

$$\sigma_R^{para} = \frac{1}{\rho}\left[\log (k^p/k_o) - \rho\,\sigma_I\right] \qquad \text{(xxxiii)}$$

which are derived, respectively, by substituting equations (xxx) and (xxviii) into (xxv) and equations (xxxi) and (xxviii) into (xxiv). These σ_R values are a measure of the sum of polar-resonance and conjugative effects.

While σ_I values are independent of reaction type and substituent position (meta or para), σ_R are dependent on both unless they are derived from selected reactions in which a methylene group prevents any resonance interaction between substituents and reaction centres. In this latter case the resonance substituent constants, called by Taft σ_R^o, are a measure of the polar-resonance effects only and are independent of reaction type but dependent on substituent position.

Comparison of the Treatment by Taft and by Wepster

It is reasonable to expect from the foregoing discussion that although Taft and Wepster have used somewhat different arguments in their modifications of the Hammett equation, their conclusions should be comparable. That this is so can be seen from the following considerations.

For a given para substituent, by definition,

$$\sigma = \sigma_I + \sigma_R^{para} \qquad \text{(xxxiv)}$$

$$\sigma^o = \sigma_I + \sigma_R^{o} \qquad \text{(xxxv)}$$

By subtracting equation (xxxv) from (xxxiv), one obtains,

$$\sigma - \sigma^o = \sigma_R^{para} - \sigma_R^{o} \qquad \text{(xxxvi)}$$

By definition (65, 69) $\sigma^o = \sigma^n$ and therefore

$$\sigma - \sigma^o = \sigma - \sigma^n = \sigma_R^{para} - \sigma_R^{o} \qquad \text{(xxxvii)}$$

The difference ($\sigma_R^{para} - \sigma_R^{o}$) is attributed by Taft (69) to the direct resonance (conjugative) interaction between the para substituent and the reaction centre. The magnitude of this interaction is measured in terms of a resonance energy, ΔE_{ψ},

$$\Delta E_{\psi} = -2.303\ RT\rho\ (\sigma_R^{\ para} - \sigma_R^{\ o}) \qquad \text{(xxxviii)}$$

Wepster (65) terms the identical difference ($\sigma - \sigma^n$) the para interaction and expresses its magnitude in terms of the free energy change, $(\Delta\Delta F)_p$ (see equation (xxii)),

$$(\Delta\Delta F)_p = -2.303\ RT\rho\ (\sigma - \sigma^n)$$

Clearly, ΔE_{ψ} and $(\Delta\Delta F)_p$ are identical.

Application of the Treatment by Taft

It should be clear from the foregoing discussion that a study of the deviations from the Hammett relationship can provide precise information concerning differences in the extent of resonance interaction between the substituent and reaction centre in the initial and transition states of a reaction. Such investigations, therefore, provide a means of obtaining information concerning the properties of the transition state in reaction mechanism studies. Taft (69) has recommended the following procedure in studies of this kind.

A reliable value of ρ is obtained from a plot of logarithms of experimentally determined values of k/k_o versus σ for selected meta substituents (a minimum of hydrogen and four substituents covering the maximum possible range in σ values which are considered unambiguously normal, i.e., free from resonance interaction, is required (69)).

Using this value of ρ and the experimentally measured values of log k/k_o, σ values for the other substituents are calculated. Those σ values so obtained which do not agree with Hammett σ values within 0.07 unit are analyzed as follows. The resonance parameters R and σ_R are calculated from equations,

$$R = \log (k/k_o) - \sigma_I \rho \qquad \text{(xxxix)}$$

$$\sigma_R = R/\rho \qquad \text{(xxxx)}$$

Correlation of these resonance parameters with the corresponding values for potentially similar reaction processes may then be attempted in order to obtain an insight into the kind of resonance effects involved and the nature of the transition state.

EXPERIMENTAL AND RESULTS

This section of the thesis is presented under the following headings.

(a) The synthesis of a series of substituted phenylpropiolic acids.

(b) The method for the measurement of rates of decarboxylation of these acids.

(c) The determination of the pH dependence of the reaction.

(d) The analysis of products from the complete reactions.

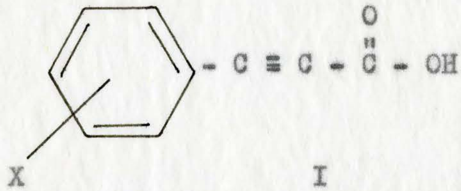
(e) Calculations of the rate constants and thermodynamic quantities.

(f) The results of the kinetic experiments.

The Synthesis of a Series of Substituted Phenylpropiolic Acids

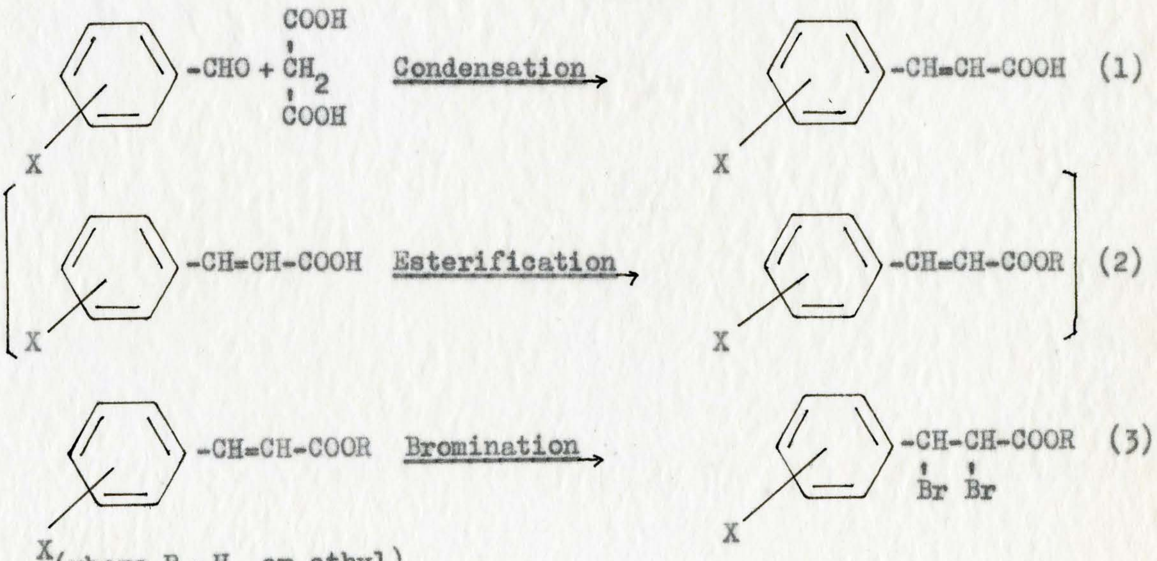
General Discussion

The compounds employed in this study were substituted phenylpropiolic acids (I),

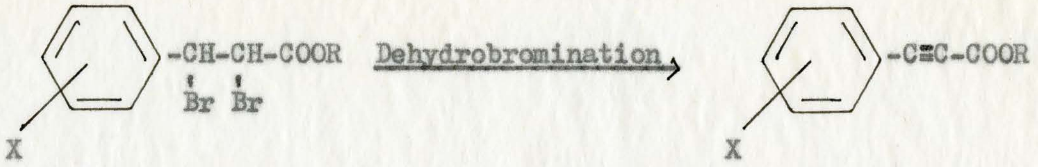


I

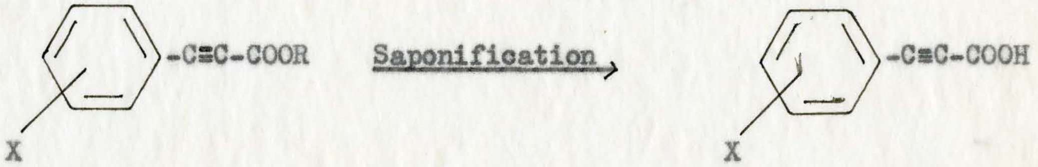
(where X is H, m-Cl, p-Cl, m-NO_2, p-NO_2, m-CH_3, and m-CF_3.) They were prepared by condensation of a suitable substituted benzaldehyde with malonic acid (72), bromination of the resultant cinnamic acid either as the free acid (73) or its ethyl ester (74), and dehydrobromination of the dibromo compound so formed. This reaction sequence is outlined below:


-CHO + CH2 (COOH)2
Condensation
-CH=CH-COOH (1)
-CH=CH-COOH
Esterification
-CH=CH-COOR (2)
-CH=CH-COOR
Bromination
-CH-CH-COOR (3)
Br Br
X

(where R = H, or ethyl)



(4)



(5)

It was only in the dehydrobromination that side reactions, substitution and elimination reactions (74, 75), were troublesome. Newman, who recently reported (74) the preparation of the ethyl esters of phenylpropiolic, and p-chloro-, m-chloro-, p-nitro-, and m-nitrophenylpropiolic acids, used a variety of dehydrobromination reagents in attempts to decrease the extent of formation of side products and his procedures were followed in the present study for the syntheses of these particular compounds.

For the preparation of m-chlorophenylpropiolic acid , the dehydrobromination reagent was alcoholic potassium hydroxide, while for the synthesis of the p-nitro compound sodium ethoxide in ethanol was used. In the latter case, it was necessary to avoid an excess of sodium ethoxide which, being a strong nucleophile, promoted substitution (74, 75).

The dehydrobrominating agent used in the syntheses of phenylpropiolic and p-chlorophenylpropiolic acids was a suspension of sodium hydride in benzene to which a minimum quantity of ethanol was added. This reagent was developed by Newman (74) to minimize the formation of ethyl β-ethoxycinnamate, the side-reaction product from substitution of the dibromide by ethoxide in the presence of excess alcohol.

Newman reported that the ethyl m-nitrophenylpropiolate could not be prepared by dehydrobromination of the corresponding ester dibromide in one step. He observed that with sodium hydroxide only one molecule of hydrogen bromide is eliminated forming cis-α-bromo-m-nitrocinnamic acid (the carboxyl group and the phenyl group are cis), which cannot be made to undergo further elimination until it has been isomerized to the trans configuration (74, 76). As a result he adopted the following three-step reaction route which also was employed in the present study:

(1) elimination and saponification to cis-α-bromocinnamic acid,

(2) isomerization to the trans-α-bromo acid,

(3) elimination to m-nitrophenylpropiolic acid.

The remaining compounds required for this study (m-methyl-, and m-trifluoromethylphenylpropiolic acids) were synthesized by dehydrobromination of the corresponding cinnamic acid dibromides with alcoholic potassium hydroxide using a procedure developed by Reimer (73).

Phenylpropiolic Acid

Ethyl Cinnamate Dibromide. - Bromine (64 ml.) was added slowly through a dropping funnel to a solution of ethyl cinnamate (220 g., 1.24 moles) in methylene chloride (500 ml.) and the solution was allowed to stand for twenty-four hours at 15° until the bromine color had almost disappeared. The solvent was distilled off under reduced pressure leaving, as a white solid, the crude ethyl cinnamate dibromide.

Ethyl Phenylpropiolate. - Ethyl phenylpropiolate was prepared by the dehydrobromination of the ethyl cinnamate dibromide using sodium hydride and ethanol (Newman (74)). The apparatus consisted of a 2-l. three-necked flask fitted with a dropping funnel, a mechanical stirrer and a condenser protected with a drying tube. To a solution of the crude ester dibromide in dry benzene (575 ml.) was added pulverized "50%" sodium hydride (124 g.). The resulting suspension was heated to near boiling, then the heating was discontinued and 2 ml. of absolute ethanol was added with stirring. After a short time there was vigorous evolution of hydrogen and the reaction temperature was controlled so that the maximum rate of reflux was maintained. Additional 2 ml. portions of absolute ethanol (8 ml. in all) were added from time to time, the reaction being continued for four hours. After cooling, wet ether (400 ml.) was added slowly to the reaction mixture to decompose the excess sodium hydride. The mixture so obtained was acidified with dilute hydrochloric acid, and water was added to dissolve the sodium bromide produced. The organic layer was separated, washed with 5% potassium carbonate (which was kept for recovery of phenylpropiolic acid) and then dried over sodium sulphate. The solvent was removed by distillation and the residue fractionated, at reduced pressure in a nitrogen atmosphere, through a column (18-in.) packed with glass helices. Eight portions (of approximately 4 ml. each) of the distillate were collected successively and tested for both bromine (77), and, by examination of the infrared spectra, for the acetylenic bond(78). On the basis of these tests it was concluded that portions beyond the fourth were mainly ethyl α-bromocinnamate, which indicated that only one molecule of hydrogen bromide had been eliminated. Furthermore, a considerable quantity of crystalline material, presumably unreacted dibromide, remained as residue. (The failure to obtain complete dehydrobromination was attributed to the use of aged and hence partially decomposed sodium hydride.) The solid residue and the fractions containing the monobromide were combined and the dehydrobromination described above repeated. The product of this second dehydrobromination was fractionated. The distillate, collected at 76 - 95°/0.4 - 0.6 mm. (Newman (74), b.p. 108 - 120°/1 mm.), was combined with the first four fractions from the previous dehydrobromination to give ethyl phenylpropiolate (79.5 g., 37.3% from ethyl cinnamate).

Phenylpropiolic Acid. - Ethyl phenylpropiolate (79.5 g., 0.41 mole) was added to a solution of sodium hydroxide (22 g.) in ethanol (30 ml.) and water (250 ml.). The mixture was warmed, shaken until homogeneous and then allowed to stand at 60° for two hours. The solution was extracted with ether and then acidified. The crude acid thus produced was combined with the acid recovered previously from the potassium carbonate washings (see above) and crystallized four times from carbon tetrachloride to yield phenylpropiolic acid (29.1 g., 16% from ethyl cinnamate), m.p. 136.8 - 137.0° (Newman (74), 136.9 - 137.5°). Neutralization Equivalent: found, 147.0; theoretical, 146.2.

m-Nitrophenylpropiolic Acid

m-Nitrocinnamic Acid. - m-Nitrobenzaldehyde (151 g., 1 mole) was condensed by the method of Wiley and Smith (72) with malonic acid (115 g., 1.1 moles) to yield m-nitrocinnamic acid (142.5 g., 74%), m.p. 199 - 200° (Wiley and Smith (72), 200 - 201°).

Ethyl m-Nitrocinnamate Dibromide. - Ethyl m-nitrocinnamate (138 g., 0.62 mole) obtained from esterification of the cinnamic acid was brominated for forty-eight hours by the method used in the synthesis of ethyl cinnamate dibromide described above. Ethyl m-nitrocinnamate dibromide (228.6 g., 94%), m.p. 82 - 84°, was obtained. Recrystallization from ethanol yielded a product, m.p. 86.5 - 87.5°.

m-Nitrophenylpropiolic Acid. - The ethyl m-nitrocinnamate dibromide (57.0 g., 0.15 mole) was stirred in a solution of sodium hydroxide (38 g., 0.94 mole), dioxane (50 ml.) and water (340 ml.) at 50°. The mixture was diluted with an equal volume of water, acidified and extracted with chloroform. The extract was dried over sodium sulphate and evaporated to about 150 ml. To this chloroform solution (which contained cis-α-bromo-m-nitrocinnamic acid) an excess of bromine was added. The reaction mixture was maintained at room temperature over a period of three days during which time cis-α-bromo-m-nitrocinnamic acid slowly isomerized to the trans isomer which was collected from time to time as it crystallized out. The crude acid (19 g.) so obtained was dissolved in hot 15% aqueous sodium hydroxide (60 ml.). On standing, sodium m-nitrophenylpropiolate precipitated and was crystallized from 10% sodium hydroxide. The salt was dissolved in water and the solution acidified and extracted with a benzene-ether mixture. The extract was dried over sodium sulphate and evaporated until crystallization occurred. The product so obtained was recrystallized from benzene-petroleum ether (b.p. 60 - 80°) to yield m-nitrophenylpropiolic acid (9.0 g., 31% from the ester dibromide), m.p. 144.7 - 145.2° (Becker (79), 143°; Roberts (80), 143 - 143.5°), was obtained. Neutralization Equivalent: found, 192.7; theoretical, 191.2.

p-Nitrophenylpropiolic Acid

Ethyl p-Nitrocinnamate Dibromide. - Ethyl cinnamate was nitrated, and the para isomer separated from the ortho by the method of Davey and Gwilf (81). Crystallization of crude ethyl p-nitrocinnamate from ethanol yielded a light yellow product (35.2%), m.p. 137.5 - 138.5° (Newman (74), 138.0 - 138.4°).

Ethyl p-nitrocinnamate (112 g., 0.50 mole) was brominated over a period of three days by the method described in the immediately proceeding synthesis. The dibromide (173 g., 90%) so obtained was crystallized from ethanol to yield a product with m.p. 113 - 114° (Newman (74), 113.8 - 114.4°).

Ethyl p-Nitrophenylpropiolate. - Ethyl p-nitrocinnamate dibromide (120 g., 0.31 mole) was dissolved in dry benzene (200 ml.) in a 2-l. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a condenser protected with a drying tube. To this solution, maintained at near boiling temperature, was added dropwise and with vigorous stirring, a solution of sodium ethoxide (sodium metal (16 g., 0.64 mole) in absolute ethanol (300 ml.)). Addition of an excess of the base, which caused darkening* of the solution, was avoided. After complete addition of the ethoxide, the reaction mixture was cooled, acidified and diluted to 1.5 l. with water. This mixture was then extracted with ether (150 ml.) and the extract washed with dilute sodium carbonate and with water and then dried over sodium sulphate. Removal of the solvent furnished a solid which was crystallized twice from ethanol to yield ethyl p-nitrophenylpropiolate (41 g., 58%), m.p. 122.5 - 123.5° (Newman (74), 123.0 - 123.8°).

p-Nitrophenylpropiolic Acid. - Ethyl p-nitrophenylpropiolate (37 g., 0.17 mole) was dissolved in a hot solution of dioxane (80 ml.) and 10% sodium hydroxide (77 ml., 0.20 mole). The solution was evaporated to dryness and the residue dissolved in water and acidified. The crude p-nitrophenylpropiolic acid thus obtained (30.5 g., 93.4%) was crystallized from benzene to yield light-yellow crystals, m.p. 203.0 - 204.0° dec. (Baddar (82), 202° dec.). Neutralization Equivalent: found, 192.3; theoretical, 191.2.

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*During a trial experiment, a slight excess of the ethoxide accumulated and the solution turned dark. The addition of the base and heating were immediately interrupted and the ester was isolated as described above. An oil, which solidified at 0°, was obtained. Infrared spectra showed no carbon-carbon triple bond absorption at 2100 - 2250 cm^{-1} indicating the ester was not ethyl p-nitrophenylpropiolate. The compound was not examined further.

m-Chlorophenylpropiolic Acid

Ethyl m-Chlorocinnamate. - m-Chlorocinnamic acid was prepared in a yield of 48.6% by condensing malonic acid with m-chlorobenzaldehyde (72), which was synthesized from m-nitrobenzaldehyde in 70% yield by the method of Buck and Ide (83). The cinnamic acid was esterified to give ethyl m-chlorocinnamate, b.p. 174.0 - 177°/22 mm. (Kindler (84), b.p. 158°/10 mm.).

m-Chlorophenylpropiolic Acid. - Ethyl m-chlorocinnamate was brominated over a period of forty-eight hours by the method described in the immediately preceeding synthesis. The ethyl m-chlorocinnamate dibromide, obtained in 95% yield, was dissolved in alcoholic potassium hydroxide (39.9 g. in 300 ml. ethanol) and the solution refluxed for five hours. The hot solution was decanted from the potassium bromide which was washed with a 50 ml. portion of boiling ethanol. The potassium salt of m-chlorophenylpropiolic acid separated from the combined alcohol solutions on cooling. The salt was recrystallized from ethanol, then dissolved in water and acidified. The organic acid so produced was extracted with ether and the extract was then dried over sodium sulphate. Removal of solvent yielded crude m-chlorophenylpropiolic acid (21.5 g., 78.9%), m.p. 145.0 - 146.5°. Recrystallization from benzene gave a product, m.p. 146.6 - 147.1°, (Newman (74), 144.3 - 145.1°; Becker (79), 140 - 143°). Neutralization Equivalent: found, 181.0; theoretical, 180.6.

p-Chlorophenylpropiolic Acid

Ethyl p-Chlorophenylpropiolate. - Ethyl p-chlorocinnamate was prepared in the manner described for the synthesis of ethyl m-nitrocinnamate (see above), and was brominated over a period of thirty-six hours using methylene chloride as a solvent. A yield of 97.7% of ethyl p-chlorocinnamate dibromide was obtained. The resultant ester dibromide was dehydrobrominated by the method of Newman (74) using sodium hydride and ethanol. The crude ethyl p-chlorophenylpropiolate so obtained was not further purified as it has been reported (74) that the ester contained impurities even after fractional distillation.

p-Chlorophenylpropiolic Acid. - The crude ethyl p-chlorophenylpropiolate (70.0 g., 0.39 mole) was saponified by stirring at 50°C for ten hours in a solution of sodium hydroxide (18.8 g., 0.47 mole), ethanol (25 ml.) and water (200 ml.). The solution was filtered on cooling and the filtrate acidified to yield crude p-chlorophenylpropiolic acid (30 g., 50%). Crystallization three times from an ether-benzene mixture gave a product, m.p. 191 - 192° dec. (Newman (74), 192 - 193° dec., soften at 185°). Neutralization Equivalent: found, 181.5; theoretical, 180.6.

m-Methylphenylpropiolic Acid

m-Methylcinnamic Acid Dibromide. - m-Methylcinnamic acid was obtained in 41% yield by condensation of m-tolualdehyde with malonic acid (72). The required aldehyde was prepared in 79% yield by the reaction of m-xylyl bromide with a solution of sodium in 2-nitropropane and absolute alcohol (85), a method which had been applied previously to the preparation of p-tolualdehyde (86) and o-tolualdehyde (87). The m-methylcinnamic acid was converted to m-methylcinnamic acid dibromide, m.p. 172 - 175°, in 84% yield by the procedure developed by Reimer (73).

m-Methylphenylpropiolic Acid. - m-Methylcinnamic acid dibromide (19.5 g., 0.06 mole) was placed in an evaporating dish, a 25% solution (75 ml.) of potassium hydroxide in methanol added, and the mixture stirred over a steam bath until all the alcohol had evaporated. To the thick pasty residue methanol (50 ml.) was added and again evaporated. This procedure (addition of methanol and evaporation) was repeated three times to ensure complete reaction. The yellow product was subjected to strong suction to rid it of any trace of solvent, pulverized and dissolved in ice-water (400 ml.). The solution was acidified with 10% hydrochloric acid and m-methylphenylpropiolic acid, which first separated as are oil, crystallized on cooling and seeding (7.8 g., 80%), m.p. 127 - 130°. Recrystallization of the acid from n-hexane give colorless needles, m.p. 135 - 136° (Becker (79), 135 - 136°). Neutralization Equivalent: found, 160.5; theoretical, 160.2.

m-Trifluoromethylphenylpropiolic Acid

m-Trifluoromethylbenzaldehyde. - The benzaldehyde was prepared by the reaction between m-trifluoromethylphenylmagnesium bromide and formanilide (89, 90) in a yield of 58%, b.p. 63 - 65°/9 mm. (Hadlicky (89), b.p. 59 - 62°/10 mm.).

m-Trifluoromethylcinnamic Acid. - m-Trifluoromethylbenzaldehyde (45.1 g., 0.258 mole) was added to a solution containing ethanol (65 ml.), pyridine (6.5 ml.) and malonic acid (29.8 g., 0.286 mole). The mixture, after being refluxed for six to eight hours, was extracted with 10% sodium hydroxide and ether. The resultant basic solution (containing sodium salt of the cinnamic acid) was treated with ether. The ether extract, after being dried over sodium sulphate, was evaporated to yield m-trifluoromethylcinnamic acid (46.9 g., 76%), m.p. 120 - 123°. Recrystallization of the acid from ethanol-water (1:10) furnished colorless needles, m.p. 133.5 - 134.5°. Neutralization Equivalent: found, 215.7; theoretical, 216.2. Analysis: Calc. for $C_{10}H_7O_2F_3$: C, 55.56%; H, 3.27%. Found: C, 55.34%; H, 3.51%.

m-Trifluoromethylcinnamic Acid Dibromide. - m-Trifluoromethylcinnamic acid was brominated for four days by the method of Reimer (73, 88). Removal of solvent yielded crude m-trifluoromethylcinnamic acid dibromide. Crystallization from petroleum ether (b.p. 60 - 110°) gave a product, m.p. 123.5 - 124.0°, soften at 122°, in 87.5% yield.

m-Trifluoromethylphenylpropiolic Acid. - Dehydrobromination of m-trifluoromethylcinnamic acid dibromide by the procedure of Reimer (73) gave impure m-trifluoromethylphenylpropiolic acid in a very low yield. A slight improvement in the purity of the product was obtained by making the reaction condition milder. This is accomplished by stirring the reaction mixture over a water bath at about 60° instead of over a steam bath and not repeating the procedure (addition of methanol and evaporation). The crude propiolic acid so obtained was purified by dissolving it in dilute sodium bicarbonate and washing the solution with ether. After acidification, the organic acid produced was extracted with benzene and the extract was then dried over sodium sulphate. Removal of the solvent yielded an oil which solidified on standing at room temperature. Crystallization three times from n-hexane gave m-trifluoromethylphenylpropiolic acid, m.p. 86.5 - 87.5°, in 19% yield. Neutralization Equivalent: found, 218.5; theoretical, 214.2. Analysis; Calc. for $C_{10}H_5O_2F_3$: C, 56.08%; H, 2.35%. Found, C, 56.19%; H, 2.56%.

Method for Measurement of Decarboxylation Reaction Rates

General Discussion

Three methods have been used in previous studies to follow the reaction rates of decarboxylation processes.

(a) Spectroscopic determination of the concentration of either a reactant or a product (Cohen and Jones (7)).

(b) Volumetric measurement of evolved carbon dioxide (Fairclough (39)).

(c) Titrimetric determination of unreacted carboxylic acid (Halonen (27)).

The spectroscopic method was found unsuitable for the work reported here as the ultraviolet spectra of the reactant (a phenylpropiolic acid) and the product (a phenylacetylene) overlap (91, 92). In the only reported study of the kinetics of decarboxylation of sodium phenylpropiolate, Fairclough (39) obtained satisfactory results using the volumetric method. Halonen (29), in his recent investigation of the kinetics of decarboxylation of aliphatic acetylenic acids, has shown that the titrimetric method is convenient, reliable and accurate, and it was this method which was adopted in the present investigation.

Sodium phenylpropiolate decarboxylates to give the anion of phenylacetylene and carbon dioxide.

$$C_6H_5 - C \equiv C - COONa \longrightarrow C_6H_5 - C \equiv C:^{\ominus} + CO_2 + Na^+$$

During the course of the decarboxylation, the reaction mixture becomes alkaline,

$$C_6H_5 - C \equiv C:^{\ominus} + H_2O \longrightarrow C_6H_5 - C \equiv C - H + OH^-$$

and carbon dioxide is retained in solution. Addition of sulphuric acid to the reaction medium in an amount precisely equivalent to the initial weight of the organic acid liberates the carbon dioxide, and sets free from its salt the unreacted phenylpropiolic acid. Following degasification of the solution, the unreacted organic acid can then be estimated by titration with standard base. Use of small reaction samples to reduce the period required for temperature equilibration and of a mixed indicator system (cresol red - thymol blue) for the titration of the free propiolic acids with base were found to improve the reproducibility of the results.

The temperature of the electrically regulated oil thermostat used in the present study remained constant to ±0.03°. Temperature measurements were made with thermometers which had been standardized against a platinum resistance thermometer (calibrated by U.S. Bureau of Standards).

Procedure

A known weight of a propiolic acid was precisely neutralized with standard base (0.1 N sodium hydroxide, carbonate free). One millilitre samples of the solution were pipetted into thin-walled ampules (Pyrex) which then were sealed and placed in the thermostat. After suitable intervals of time the ampules were taken from the thermostat, rapidly cooled in an ice bath, washed with acetone and then with distilled water, dried and placed in flask A (Figure 2), containing 10 ml. of 0.01 N sulphuric acid (equivalent to the initial amount of the organic acid investigated). The ampules were crushed and the carbon dioxide formed during the reaction was removed in the apparatus shown in Figure 2. The flask A was attached to a splash head B and suction was applied slowly *via* trap T (cooled to -78°). The reaction vessel A was then shaken gently for three minutes. By opening stopcork S to the soda lime tube C, carbon dioxide free air was admitted to flask A which was detached and the propiolic acid immediately titrated into 0.01 N sodium hydroxide.

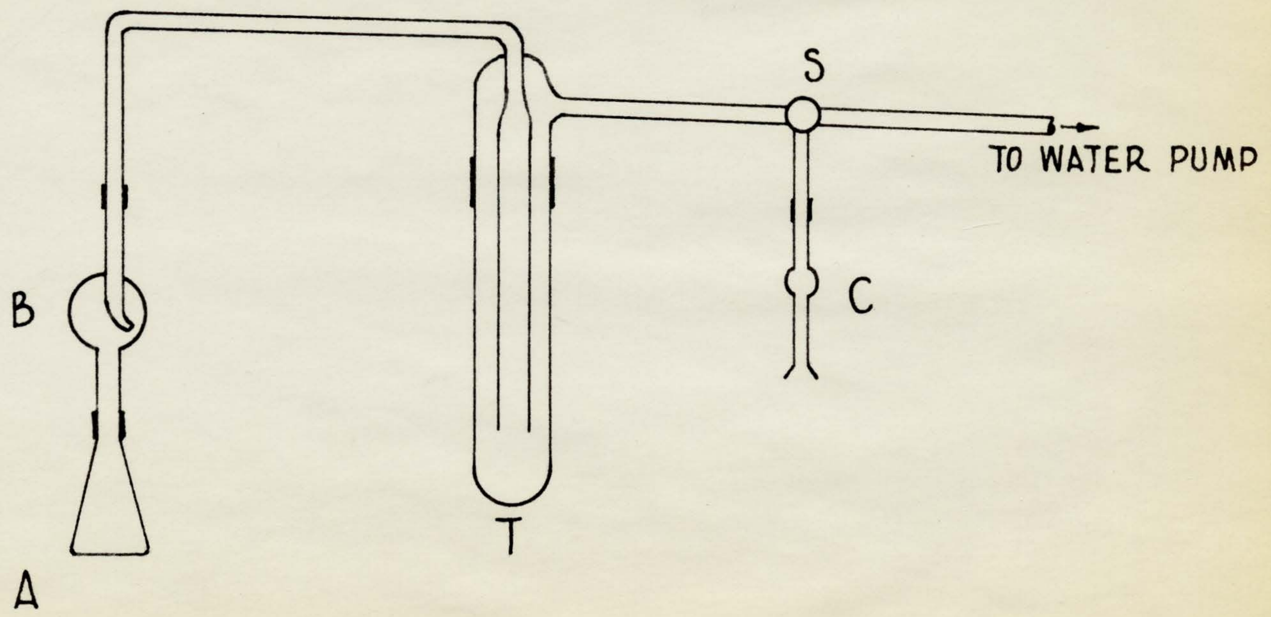

S
TO WATER PUMP
B
C
A
T

FIG. 2: APPARATUS FOR REMOVAL OF CARBON DIOXIDE.

The Method for Determining the pH Dependence of the Reaction

General Discussion

In seeking to establish the unimolecular nature of the decarboxylation, the effect of hydrogen ion concentration on the rate of the reaction was examined (see General Introduction). This was accomplished by studying the rates of decarboxylation of sodium phenylpropiolate at hydrogen ion concentration between 5 and 11 pH units. As the reaction proceeds, carbonate ion accumulates and acts as a buffer (at pH 8). Therefore, it was desirable to carry the decarboxylation only to five to ten per cent of completion, thus ensuring that no appreciable buffering of the reaction occurred.

Procedure

An accurately-weighed amount of phenylpropiolic acid was added to such a volume of 0.1 N sodium hydroxide that the pH of the solution was 5 pH units (Beckman pH meter calibrated with Beckman's Buffer Standards of pH 5, 8 and 11). The solution was divided into three equal aliquots. With the standard base, one aliquot was adjusted to pH 8 and one to pH 11. The ionic strengths of the three solutions were then made approximately equal ($u = 0.1$) by addition of 0.1 M sodium chloride.

Samples of the above solutions were prepared for kinetic measurements as described previously. The concentrations of phenylpropiolic acid in the three solutions were estimated at zero time of reaction and at the approximately five per cent reaction period. From these concentrations the rate constants were calculated. The pH of each of the reaction solutions was again measured at the end of the five per cent reaction period. The results obtained are shown in Table I.

TABLE I

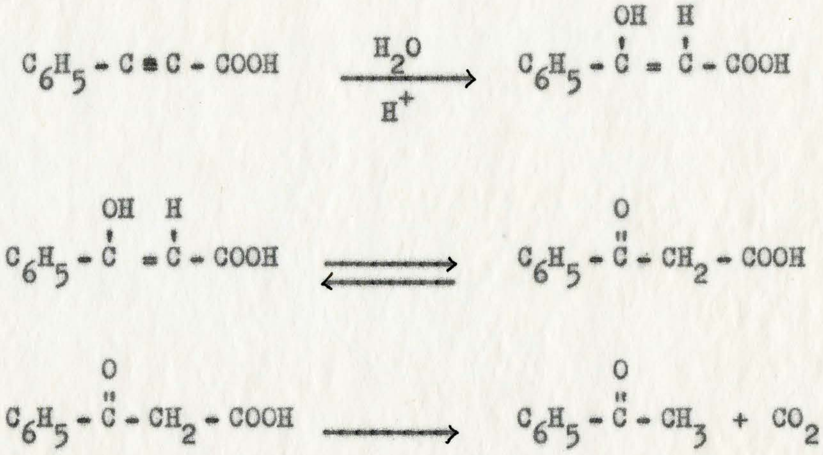
Decarboxylation Rates at Different Hydrogen Ion Concentration

Initial pH of the Solution	pH of Solution at the End of the 5% Reaction Period	pH Range	$k \times 10^4$ sec.
11.00	9.75	-1.25	1.03
8.80	7.95	-0.85	1.04
5.50	7.45	+1.95	1.07

The Procedure for the Analysis of Products from the Complete Reactions

General Discussion

In a study of the kinetics of decarboxylation of sodium phenylpropiolate, Fairclough (39) tentatively attributed the decrease in reaction rate at temperatures below 100° to an accumulation of the β-ketoacid.



$$C_6H_5-C\equiv C-COOH \xrightarrow[H^+]{H_2O} C_6H_5-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-COOH$$

$$C_6H_5-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-COOH \rightleftharpoons C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-COOH$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-COOH \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$$

It was necessary, therefore, to establish whether, under the reaction conditions of the present study, any significant portion of the decarboxylation proceeded by this route. This was accomplished by analysis of the products, as direct decarboxylation yields a phenylacetylene and hydration/decarboxylation produces an acetophenone.

Procedure

A weighed amount of phenylpropiolic acid was precisely neutralized with 0.1 N sodium hydroxide. A volume of 25 ml. of the solution was sealed in a 75 ml. glass tube (Pyrex) and immersed in the thermostat (normally at 100°) for a period corresponding to ten decarboxylation "half-lives". The tube was then cooled, opened, and the solution extracted with carbon tetrachloride (spectral grade). The extract was washed with water, dried over sodium sulphate, and this solution was concentrated to about 5 ml. by removing the solvent in a distillation column.

The infrared spectra of this solution and of standard solutions of acetophenone and phenylacetylene were compared by examination of the relative peak heights of the acetylenic hydrogen absorption band at 3300 $cm.^{-1}$ and of the carboxyl band at 1690 $cm.^{-1}$. By means of this comparison, the approximate yield of phenylacetylene and acetophenone in the reaction was determined.

The results of the product analysis study, which was performed for three of the phenylpropiolic acids, are shown in Table II.

TABLE II

Products of the Complete Decarboxylation Of Some Phenylpropiolic Acids

Compound	Temp. (°C)	Yield of Phenylacetylene in Per Cent	Yield of Acetophenone in Per Cent
Phenylpropiolic Acid	100.00	95 ± 5	~ 1
	115.83	90 ± 5	< 0.5
	125.83	90 ± 5	< 0.5
m-Nitrophenylpropiolic Acid	100.00	90 ± 5	< 0.5
p-Chlorophenylpropiolic Acid	115.83	95 ± 5	< 0.5

Calculation of the Rate Constants and Thermodynamic Quantities

The rate constants were obtained by calculating the "least squares" line of a plot of log $\frac{a}{a-x}$ *versus* t (where a is the initial concentration of the reactant and (a-x) is the concentration of the reactant at time t). The slope (b) and the standard deviation (S_b) of the slope of the regression line were obtained by use of the following equations (93):

$$b = \frac{\Sigma(x - \bar{x})\,Y}{\Sigma(x - \bar{x})^2} \qquad \text{(i)}$$

$$S_b = \sqrt{\frac{\dfrac{\Sigma Y^2 - \dfrac{(\Sigma Y)^2}{n} - b\,(x - \bar{x})\,Y}{(n - 2)}}{\Sigma(x - \bar{x})^2}} \qquad \text{(ii)}$$

where x is equivalent to t, Y equivalent to log $\frac{a}{a-x}$, $\bar{x}$ the average of x, and n the number of samples in a kinetic experiment.

The rate constant k was obtained by multiplying the slope (b) of the regression line by 2.303, and the standard deviation (S_b) of the slope by 2.303. Samples in which the reaction was quenched before decarboxylation had proceeded to approximately thirty per cent of completion were not used in the estimation of rate constants because the temperature equilibration of the samples introduced errors in the measurements of t. Those in which decarboxylation had proceeded beyond seventy per cent of completion were also rejected because of errors in titration of the small amounts of residual organic acid.

The energy of activation E_a and its standard deviation were calculated from the Arrhenius plot of log k *versus* 1/T using the method of "least squares" described above. The intercept of this plot is the log PZ factor.

The heat of activation $\Delta H^{\ddagger}$, the entropy of activation $\Delta S^{\ddagger}$, and the free energy of activation $\Delta F^{\ddagger}$ were calculated from the following equations (94, 95).

$$\Delta H^{\ddagger} = E_a - RT \tag{iii}$$

$$\Delta S^{\ddagger} = 2.303\,R\,(\log PZ - \log \frac{k^{1}T}{h}) - R \tag{iv}$$

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{v}$$

where k is the experimental rate constant, k^1 the Boltzmann's constant and h the Planck's constant.

The Results of the Kinetic Experiments

The rate constants for the decarboxylation of a series of substituted sodium phenylpropiolates at three or more temperatures are shown in Table III. From these results energies of activation and other thermodynamic quantities have been evaluated and are presented in Table IV.

The kinetic data of a typical kinetic experiment at 115.83° for each of the seven salts studied and the log $\frac{a}{a-x}$ *versus* t plots based on this data are given in the appendix. Also in the appendix are found the log k *versus* 1/T plots used to evaluate the Arrhenius parameters.

TABLE III

Rate Constants for Thermal Decarboxylation Of Substituted Sodium Phenylpropiolates

Substituents	Temp. (°C)	$k \times 10^4$ sec.$^{-1}$	
$\underline{m}$-CH_3	115.83	1.04 ± 0.01	
		1.04 ± 0.02	
			Avg. 1.04 ± 0.02
	122.83	2.26 ± 0.03	
	129.83	4.79 ± 0.02	
H	115.83	1.22 ± 0.01	
		1.22 ± 0.01	
			Avg. 1.22 ± 0.01
	125.81	3.61 ± 0.02	
		3.65 ± 0.02	
			Avg. 3.63 ± 0.02
	132.92	7.29 ± 0.08	
		7.39 ± 0.04	
			Avg. 7.34 ± 0.08
$\underline{p}$-Cl	115.83	1.59 ± 0.02	
		1.58 ± 0.02	
			Avg. 1.59 ± 0.02
	122.83	3.30 ± 0.04	
		3.31 ± 0.04	
			Avg. 3.31 ± 0.04
	129.83	6.71 ± 0.06	
		6.82 ± 0.09	
			Avg. 6.77 ± 0.09

TABLE III (Continued)

Rate Constants for Thermal Decarboxylation
Of Substituted Sodium Phenylpropiolates

Substituents	Temp. (°C)	x 10^4 k sec.	
m-Cl	100.00	0.433 ± 0.004	
		0.437 ± 0.03	
			Avg. 0.435 ± 0.004
	108.83	1.22 ± 0.01	
		1.22 ± 0.01	
			Avg. 1.22 ± 0.01
	115.83	2.64 ± 0.01	
		2.67 ± 0.01	
			Avg. 2.66 ± 0.01
	122.83	5.76 ± 0.08	
		5.68 ± 0.06	
			Avg. 5.72 ± 0.08
m-CF_3	108.83	1.33 ± 0.01	
	115.83	2.82 ± 0.02	
		2.83 ± 0.02	
			Avg. 2.83 ± 0.02
	122.83	6.12 ± 0.08	

TABLE III (Continued)

Rate Constants for Thermal Decarboxylation Of Substituted Sodium Phenylpropiolates

Substituents	Temp. (°C)	k x 10^4 sec.^{1}	
m-NO_2	108.83	2.31 ± 0.02	
		2.28 ± 0.01	
			Avg. 2.30 ± 0.02
	115.83	5.02 ± 0.07	
		5.05 ± 0.03	
			Avg. 5.04 ± 0.07
	122.83	10.5 ± 0.2	
		10.6 ± 0.1	
			Avg. 10.6 ± 0.2
p-NO_2	100.00	1.24 ± 0.01	
		1.21 ± 0.01	
			Avg. 1.23 ± 0.01
	108.83	3.33 ± 0.02	
		3.28 ± 0.01	
			Avg. 3.31 ± 0.02
	115.83	6.80 ± 0.05	
		6.69 ± 0.07	
			Avg. 6.75 ± 0.07

TABLE IV

Energies of Activation and Other Thermodynamic Quantities for Thermal Decarboxylation Of Substituted Sodium Phenylpropiolates

Substituent	E (K cal. mole^{-1})	Log PZ	$\Delta H^{\ddagger}$ (K cal. mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger}$ (K cal. mole^{-1})
m-CH_3	34.3	15.3	33.5	8.8	30.1
H	33.0	14.6	32.2	5.9	29.9
p-Cl	32.3	14.4	31.6	4.7	29.8
m-Cl	33.1	15.0	31.4	7.7	29.4
m-CF_3	32.9	14.9	32.1	7.2	29.3
m-NO_2	32.8	15.1	32.0	8.0	28.9
p-NO_2	31.2	14.4	30.4	4.1	28.6

DISCUSSION

A - Mechanism of Decarboxylation of a Series Of Substituted Sodium Phenylpropiolates

Hydration/Decarboxylation Mechanism *versus* Direct Decarboxylation Mechanism

The hydration/decarboxylation mechanism involves addition of a molecule of water to the triple bond of a phenylpropiolic acid to form a benzoylacetic acid (44, 45) which, like other β-ketoacids, readily undergoes decarboxylation to produce an acetophenone (see equations on Page 58). On the other hand, direct decarboxylation yields a phenylacetylene (see equations on Page 53).

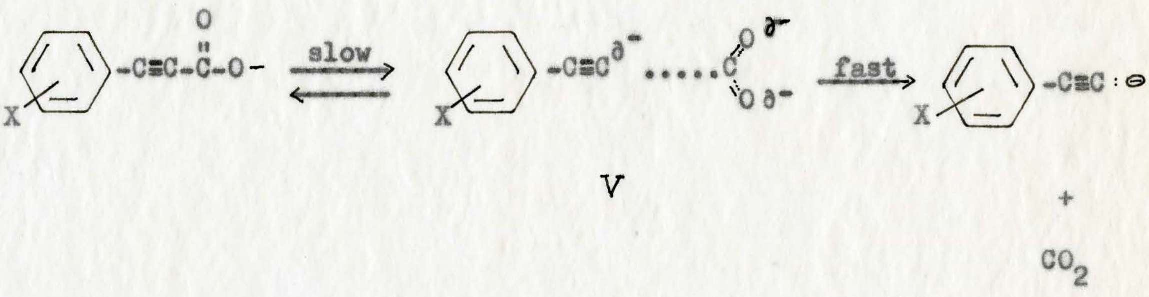
Analysis of the products from complete decarboxylation of phenylpropiolic, *m*-nitrophenylpropiolic and *p*-chlorophenylpropiolic acids at three different temperatures (Table II, Page 60) showed that only from the reaction of the first acid at 100° was there obtained more than 0.5% yield of acetophenone (1% was produced). Also, not less than 90% of the expected phenylacetylene was obtained from each of the three acids examined. It is thus clear that no significant portion of the reaction proceeded by way of the hydration/decarboxylation process.

The Molecularity of the Decarboxylation Reaction

The effect of hydrogen ion concentration on the rate of decarboxylation of phenylpropiolic acid was examined by measuring the rate of reaction in solutions at pH between 5 and 11 units, under which conditions the fraction of substrate in its anionic form was not less than 0.999. If the hydrogen ion concentration played any role in the decarboxylation, it was expected that the experimentally determined rate constants would vary with variations in the concentration of this species. It was found (Table I, Page 57) that the values of the first order rate constants obtained were constant within experimental limits, and thus it may be concluded that the decarboxylation is not catalysed by hydrogen ions, and proceeds by a unimolecular mechanism.

Effects of Substituents on Reaction Rates

Reactions proceeding by the bimolecular mechanism will be favoured by electron-releasing substituents which will provide stabilization of the transition state leading to the carbonium ion. The opposite effect is expected for the unimolecular (S_E1) mechanism, as electron-withdrawing groups will facilitate fission of the bond between the carboxylic group and the α-acetylenic carbon atom.



The results of the study of the effects of substituents on the rates of decarboxylation are presented in Table III, Page 64 where it will be observed that the relative rates are p-NO_2 > m-NO_2 > m-CF_3 > p-Cl > H > m-CH_3. That is, electron-withdrawing groups increase the rates of decarboxylation. This result provides further support for the postulation of a S_E1 mechanism.

Effect of Entropy of Activation

The S_E1 mechanism for the decarboxylation of the sodium salts of phenylpropiolic acids requires that the transition state has a non-ordered structure, V (see above), the formation of which would result in a positive entropy of activation. Furthermore, the delocalization of the negative change in the transition state, which in the initial state is concentrated on the carboxylate group, will result in disorientation of solvent molecules around the solute species, and hence in an increased entropy of the system. In the S_E2 mechanism, however, the transition state leading to the carbonium ion intermediate is more rigidly orientated and a negative entropy of activation is expected to be associated with this process.

In Table IV (Page 67), entropies of activation for the thermal decarboxylation of substituted sodium phenylpropiolates are shown to be large and positive and the postulation of transition state, V, of the S_E1 mechanism is thus supported.

B - The Application of Hammett's Free Energy Relationship

The Significance of the Value of Rho

A reliable value of ρ for the decarboxylation reaction was obtained by Taft's recommended procedure (69) using the meta substituents H, m-CH_3, m-Cl, m-CF_3, m-NO_2 (see Figure 3). The value of ρ, obtained by the method of "least squares", was +0.886, the correlation coefficient r (49), 0.9996 and standard deviation S_ρ, 0.013. This value of ρ may be compared with those obtained from the ionization constants of substituted phenylpropiolic acids in 35% aqueous dioxane, and in 50% aqueous ethanol at 25° (+0.70 and +0.65 respectively, see Table II, reference 69). It may be noted that the ρ value is less than unity, that is, the effects of substituents on the decarboxylation rates are less than those on the ionization constants of substituted benzoic acids.

The positive ρ value means, of course, that the decarboxylation rates are increased by electron-withdrawing substituents as expected in a S_E1 mechanism involving the formation of a carbanion in the rate-determining step.

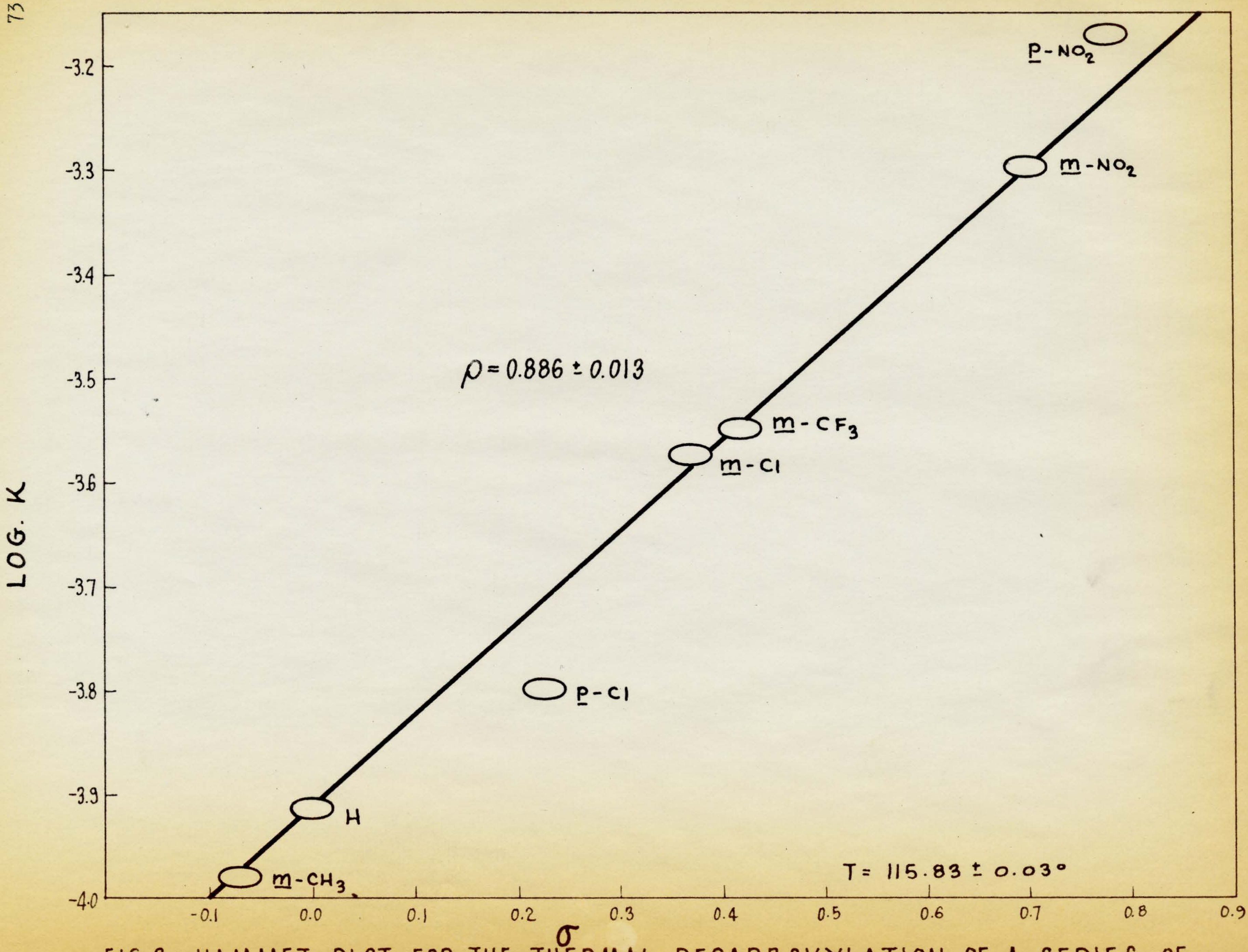


FIG. 3: HAMMET PLOT FOR THE THERMAL DECARBOXYLATION OF A SERIES OF SUBSTITUTED SODIUM PHENYLPROPIOLATES.

Deviation from Hammetts' Free Energy Relationship

Values of σ required to give a precise fit to the line of Figure 3 were calculated from the equation

$$\sigma = \frac{\log k/k_o}{\rho}$$

where ρ is the reaction constant obtained by the best plot of the data for sodium phenylpropiolate and the m-substituted sodium phenylpropiolates. For a given substituent the difference between the σ values so calculated and the Hammett σ values, that is $\sigma - \sigma_{\text{Hammett}}$, is a measure of the difference between the electron-releasing or electron-withdrawing effect of the substituent in the decarboxylation reaction and in the ionization of benzoic acid.

TABLE V

Substituent Constants $\sigma_{\text{estimated}}$ Obtained

by Taft's Recommended Procedure

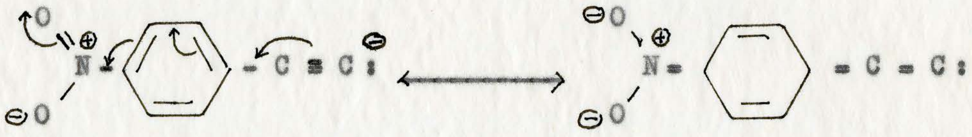
Substituent	$\sigma_{\text{est.}}$	σ_{Hammett}[a]	$\sigma - \sigma_{\text{Hammett}}$
m-CH_3	-0.08	-0.07	-0.01
H	0.00	0.00	0.00
p-Cl	0.13	0.23[b]	-0.10
m-Cl	0.38	0.37	+0.01
m-CF_3	0.41	0.42	-0.01
m-NO_2	0.69	0.70	-0.01
p-NO_2	0.84	0.78[b]	+0.06

[a] Taken from Table V and Table VI, reference 69

[b] Taken from Table VII, reference 68

It can be seen from Table V that the calculated σ values for all meta substituents agree with the Hammett σ values to within 0.01 unit, which is well within the 0.07 unit permitted in the Taft's procedure (69). The values for the para substituents, as expected, deviate more although that found for the p-NO_2 group is still within the allowable limit. The higher value of 0.06 for this group means that the rate of decarboxylation of sodium p-nitrophenylpropiolate is somewhat faster than expected on the basis of the effect of the p-NO_2 group on the ionization of benzoic acid, while the lower value of 0.10 unit for the p-Cl substituent means that sodium p-chlorophenylpropiolate reacts more slowly than might have been expected.

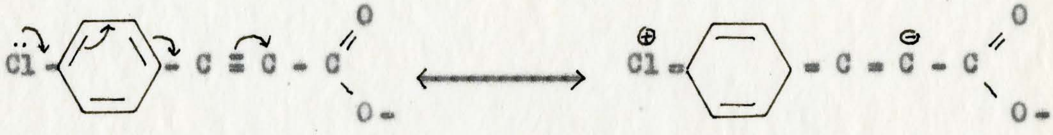
The faster rate of decarboxylation of the p-NO_2 compound can be accounted for if the carbanion intermediate, and hence the transition state leading to it, derives some stabilization from a contribution of the canonical structure II



II

If such a structure were to make an important contribution, the σ value required to obtain a fit in the Hammett plot would be expected to have a value approaching that of σ^-. In fact, the σ^- value of 1.27 for the p-NO_2 deviates very much more from the experimental value $\left(\frac{\log k/k_o}{\rho}\right)$ of 0.84 than does the Hammett σ of 0.78. The extent of conjugation in the transition state, and presumably also in the carbanion intermediate, between the *p*-NO_2 group and the developing negative reaction centre must be very small. This conclusion is probably not unreasonable since the terminal carbon atom in structure II with its sextet of electrons would be expected to correspond to a rather high energy state.

The deviation of the experimental σ value for the *p*-Cl group is larger than might have been expected but has a logical explanation. The initial state will derive stabilization from the conjugation of the substituent with the triple bond (structure III)



III

Since no such conjugation is possible in the carbanion formed in the rate-determining step there will be a loss in resonance energy in going from the initial state to the transition state. This will partly compensate for the electron-withdrawing inductive effect which acts to increase the reaction rate. A similar explanation was used by Halonen (96) in accounting for the lower decarboxylation rate of sodium methylpropiolate compared to sodium propiolate. The electron-releasing methyl group in the former was considered to enter into hyperconjugation with the triple bond in the initial state.

If the foregoing explanation for the deviation in the σ value for the p-Cl group is the correct one, a very much larger deviation should be found for more powerful electron-releasing conjugation substituents. Future work, therefore, includes the study of the rate of decarboxylation of sodium p-methoxyphenylpropiolate.

APPENDIX

TABLE VI

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium m-Methylphenylpropiolate

(T = 115.83 ± 0.02°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k $\times 10^4$ sec.
0	9.90[a]		
3600	6.80	0.1631	1.04
4500	6.17	0.2053	1.05
5400	5.65	0.2436	1.04
6300	5.07	0.2906	1.06
7500	4.55	0.3376	1.04
8700	3.96	0.3979	1.05
10500	3.31	0.4758	1.04
12300	2.75	0.5563	1.06
			Avg. 1.05

$k = 1.04 \pm 0.02$[b]

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE VII

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium Phenylpropiolate

(T = 115.83 ± 0.02°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k x 10^4 sec.
0	9.98^a		
2580	7.24	0.1394	1.25
3360	6.60	0.1796	1.23
4200	5.98	0.2224	1.22
5100	5.34	0.2716	1.23
6000	4.76	0.3215	1.24
6900	4.28	0.3677	1.26
8100	3.70	0.4309	1.23
9600	3.10	0.5068	1.22
			Avg. 1.24

k = 1.22 ± 0.01^b

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE VIII

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium *p*-Chlorophenylpropiolate

(T = 115.83 ± 0.03°)

Time of Heating in sec.	$a-x$ Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	$k \times 10^4$ sec.
0	9.90[a]		
2100	7.00	0.1505	1.65
2700	6.37	0.1915	1.63
3300	5.75	0.2359	1.65
4200	5.05	0.2923	1.60
5100	4.36	0.3561	1.61
6000	3.86	0.4090	1.57
7200	3.21	0.4891	1.57
			Avg. 1.60

$k = 1.58 \pm 0.02$[b]

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE IX

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium m-Chlorophenylpropiolate

(T = 115.83 ± 0.02°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k x 10^4 sec.
0	9.78[a]		
1380	6.80	0.1578	2.63
1800	6.10	0.2050	2.62
2220	5.45	0.2539	2.63
2700	4.75	0.3136	2.68
3180	4.18	0.3691	2.67
3720	3.66	0.4268	2.64
4320	3.09	0.5004	2.67
			Avg. 2.65

k = 2.67 ± 0.01[b]

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE X

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium m-Trifluoromethylphenylpropiolate

(T = 115.83 ± 0.02°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k x 10^4 sec.
0	9.43[a]		
1200	6.76	0.1446	2.78
1500	6.22	0.1807	2.78
1800	5.74	0.2156	2.76
2100	5.30	0.2502	2.75
2520	4.67	0.3052	2.78
3000	4.05	0.3670	2.82
3480	3.56	0.4231	2.80
3960	3.10	0.4831	2.81
		Avg.	2.79

k = 2.82 ± 0.02[b]

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE XI

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium m-Nitrophenylpropiolate

(T = 115.83 ± 0.03°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k x 10^4 sec.
0	9.83[a]		
780	6.64	0.1704	5.03
1080	5.76	0.2322	4.95
1380	4.91	0.3015	5.03
1740	4.08	0.3819	5.05
2100	3.43	0.4573	5.02
2520	2.84	0.5393	4.93
			Avg. 5.00

k = 5.04 ± 0.03[b]

---

a = Initial concentration

b = Standard deviation of rate constant

TABLE XII

Results of a Typical Kinetic Experiment On the Thermal Decarboxylation of Sodium p-Nitrophenylpropiolate

(T = 115.83 ± 0.03°)

Time of Heating in sec.	a-x Volume of 0.01 N NaOH in ml.	Log $\frac{a}{a-x}$	k x 10^4 sec.
0	9.87[a]		
480	7.10	0.1428	6.84
660	6.30	0.1948	6.80
840	5.58	0.2475	6.79
1020	4.93	0.3013	6.80
1200	4.36	0.3546	6.80
1440	3.82	0.4120	6.59
1680	3.17	0.4930	6.76
			Avg. 6.77

k = 6.70 ± 0.07[b]

a = Initial concentration

b = Standard deviation of rate constant

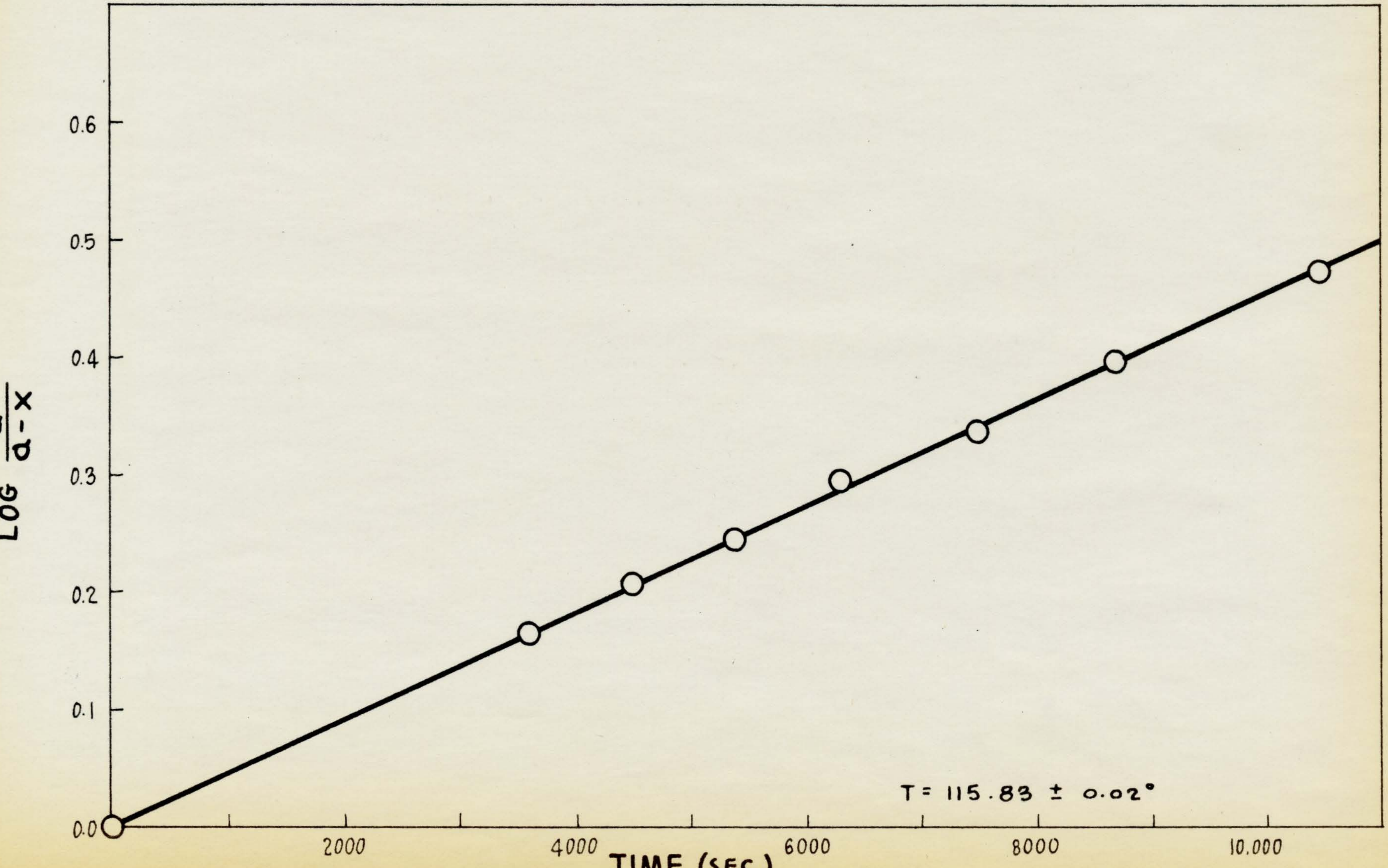


FIG. 4 : PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM m-METHYLPHENYLPROPIOLATE.

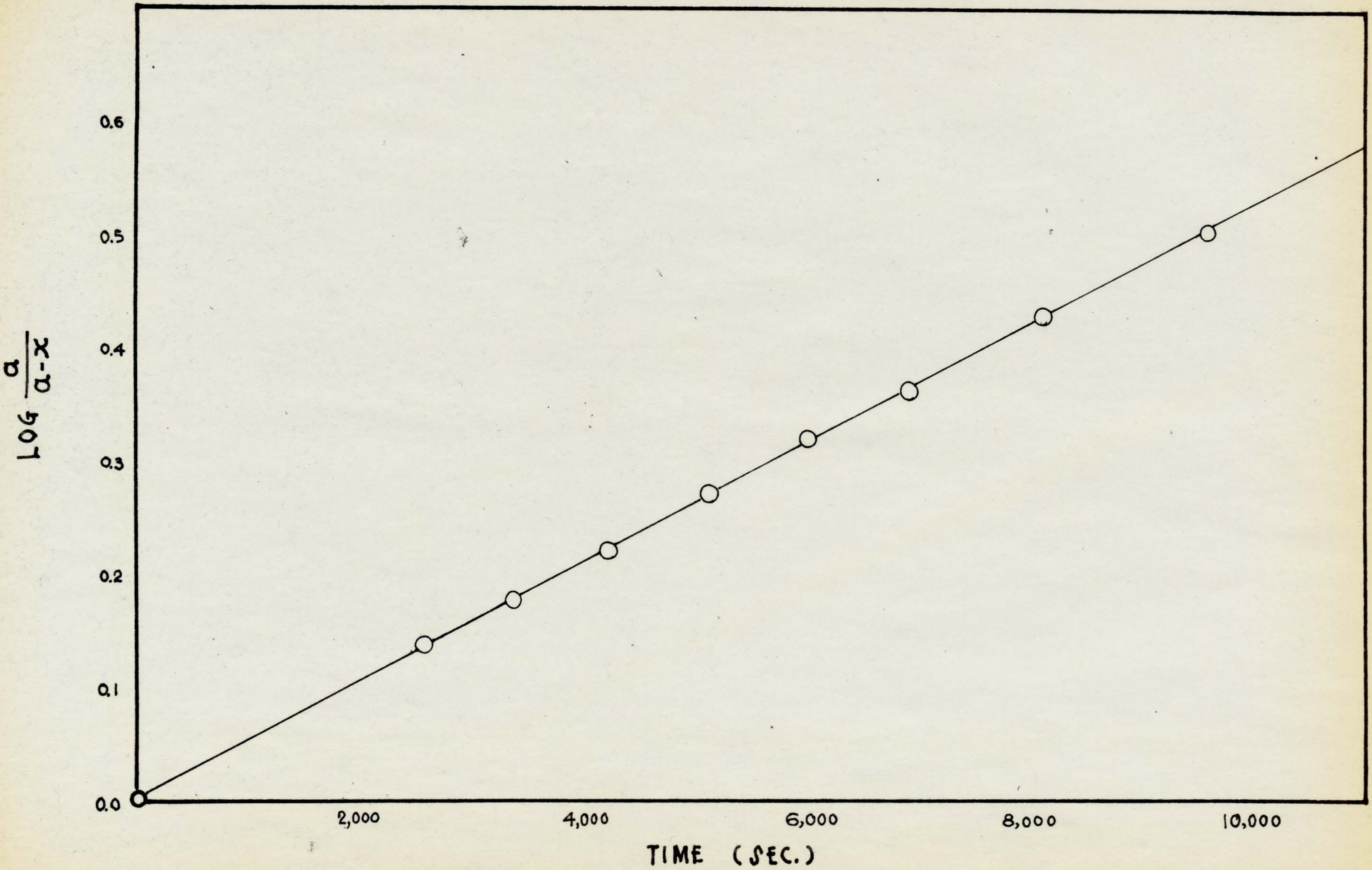


FIGURE 5: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM PHENYLPROPIOLATE

(T = 115.83 ± 0.02°)

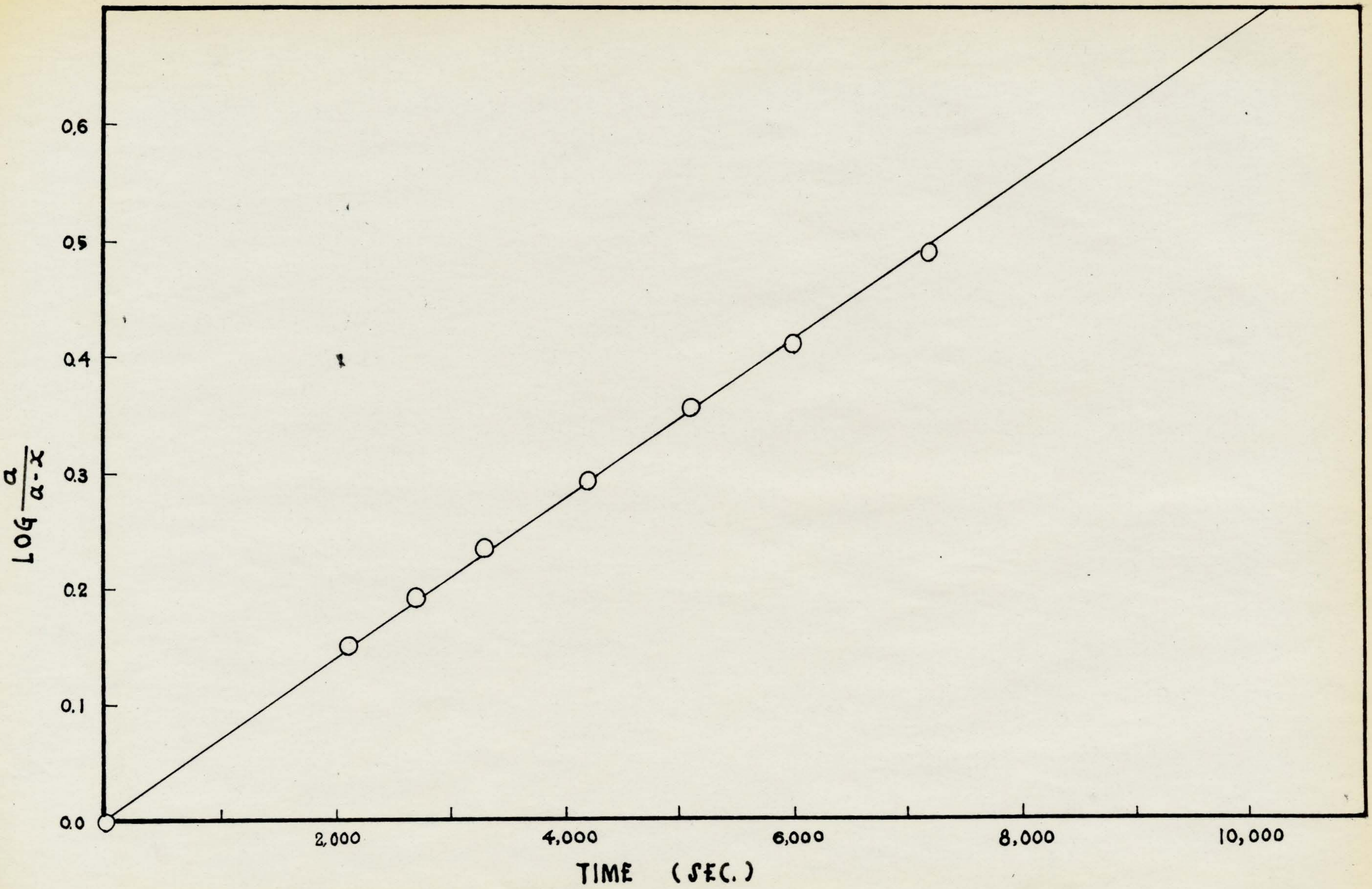


FIGURE 6: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM p-CHLOROPHENYLPROPIOLATE

(T= 115.83 ± 0.03°)

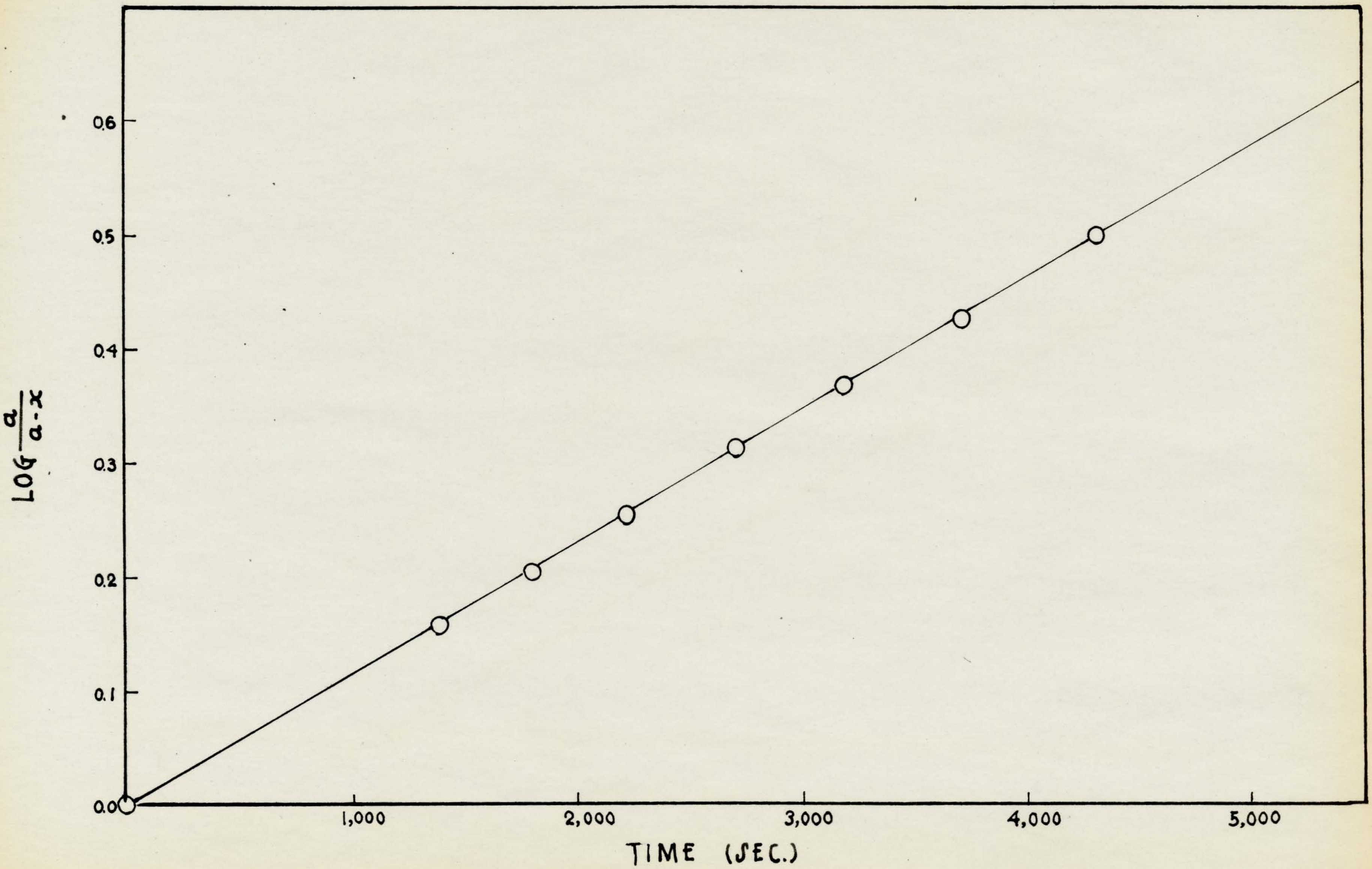


FIGURE. 7: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM M-CHLOROPHENYLPROPIOLATE (T = 115.83 ± 0.02°)

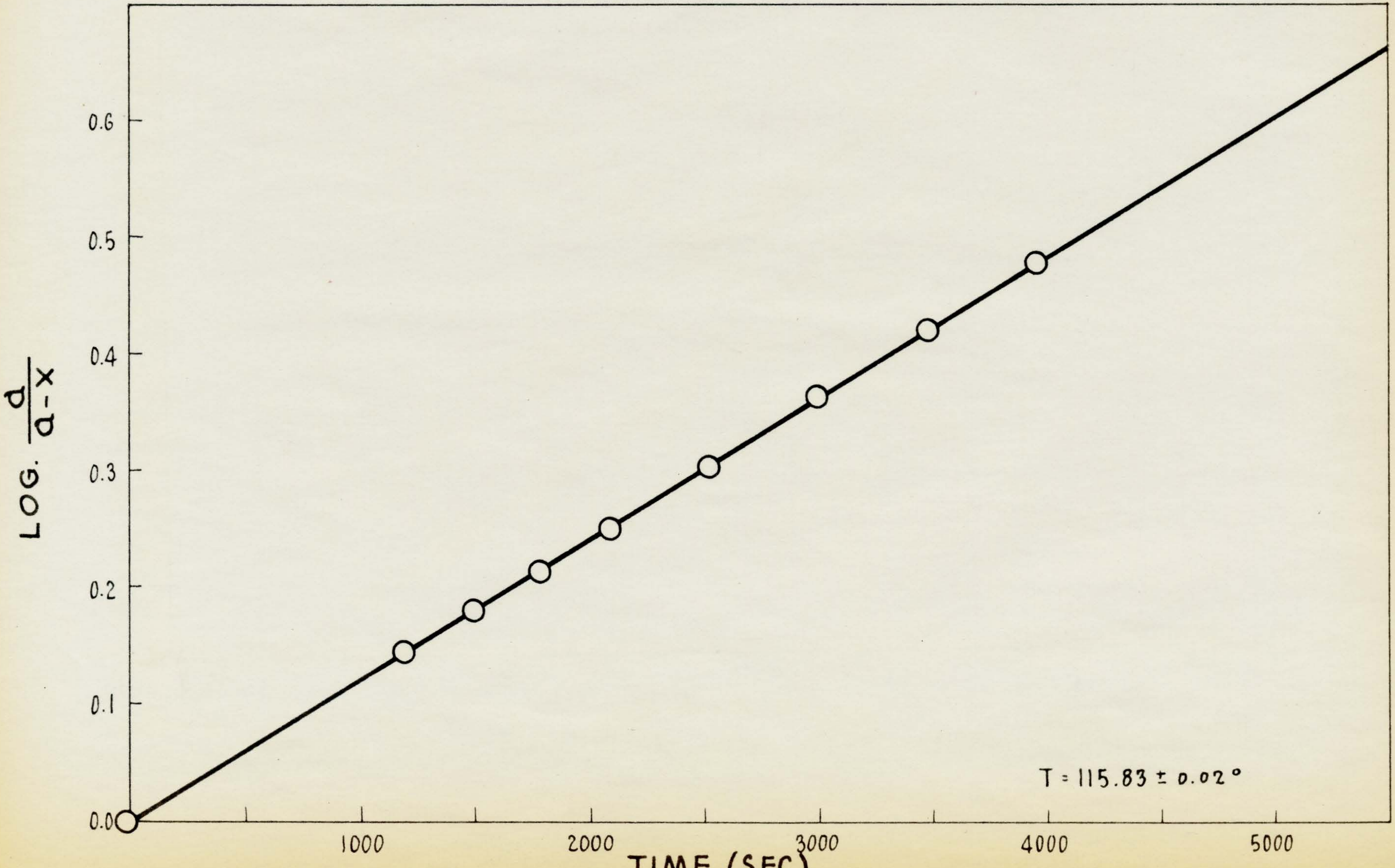


FIG. 8: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM m-TRIFLUOROMETHYLPHENYLPROPIOLATE.

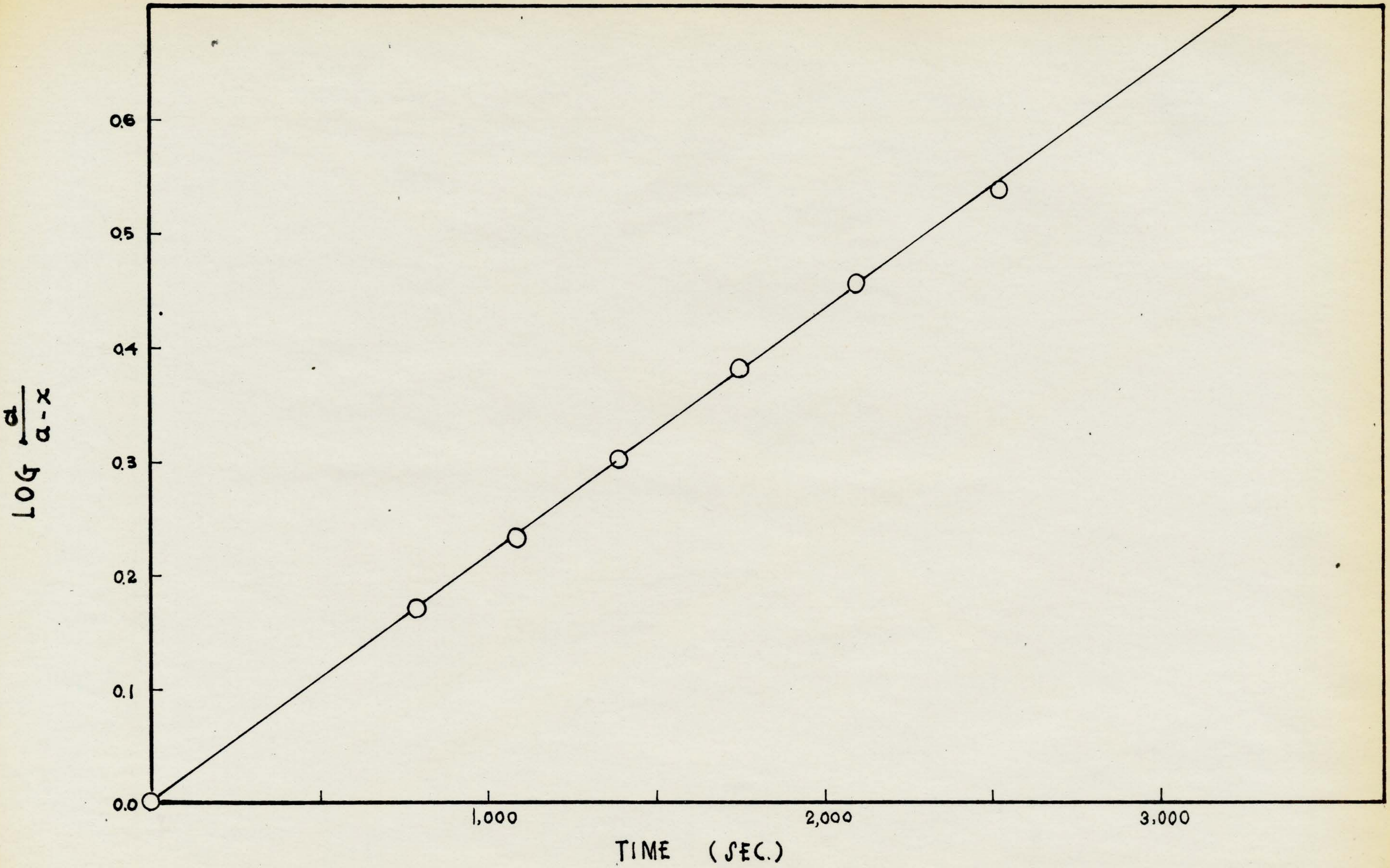


FIGURE 9: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM m-NITROPHENYLPROPIOLATE

(T = 115.83 ± 0.03°)

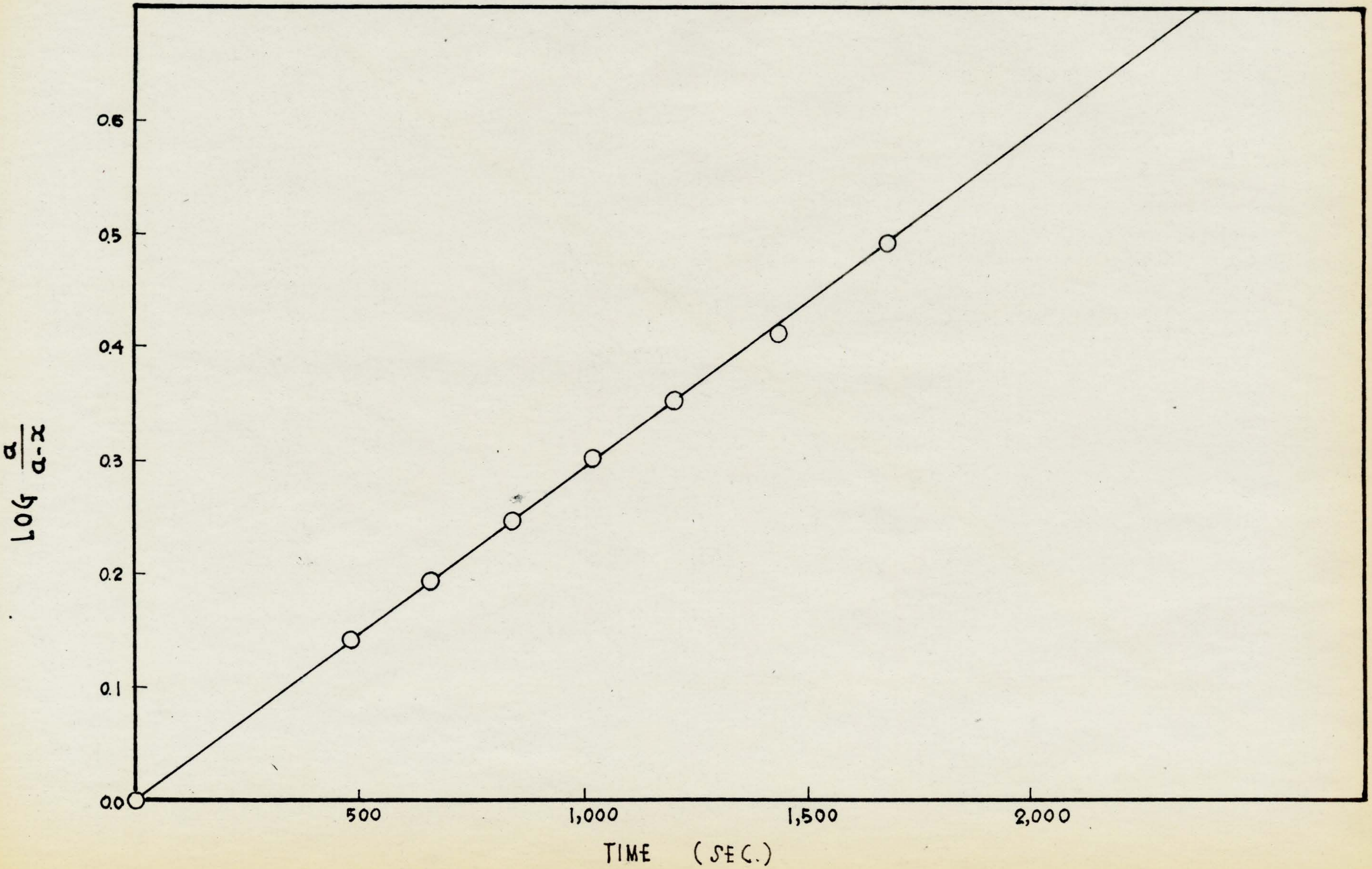


FIGURE 10: PLOT OF RESULTS OF A TYPICAL KINETIC EXPERIMENT ON THE THERMAL DECARBOXYLATION OF SODIUM p-NITROPHENYLPROPIOLATE

(T = 115.83 ± 0.02°)

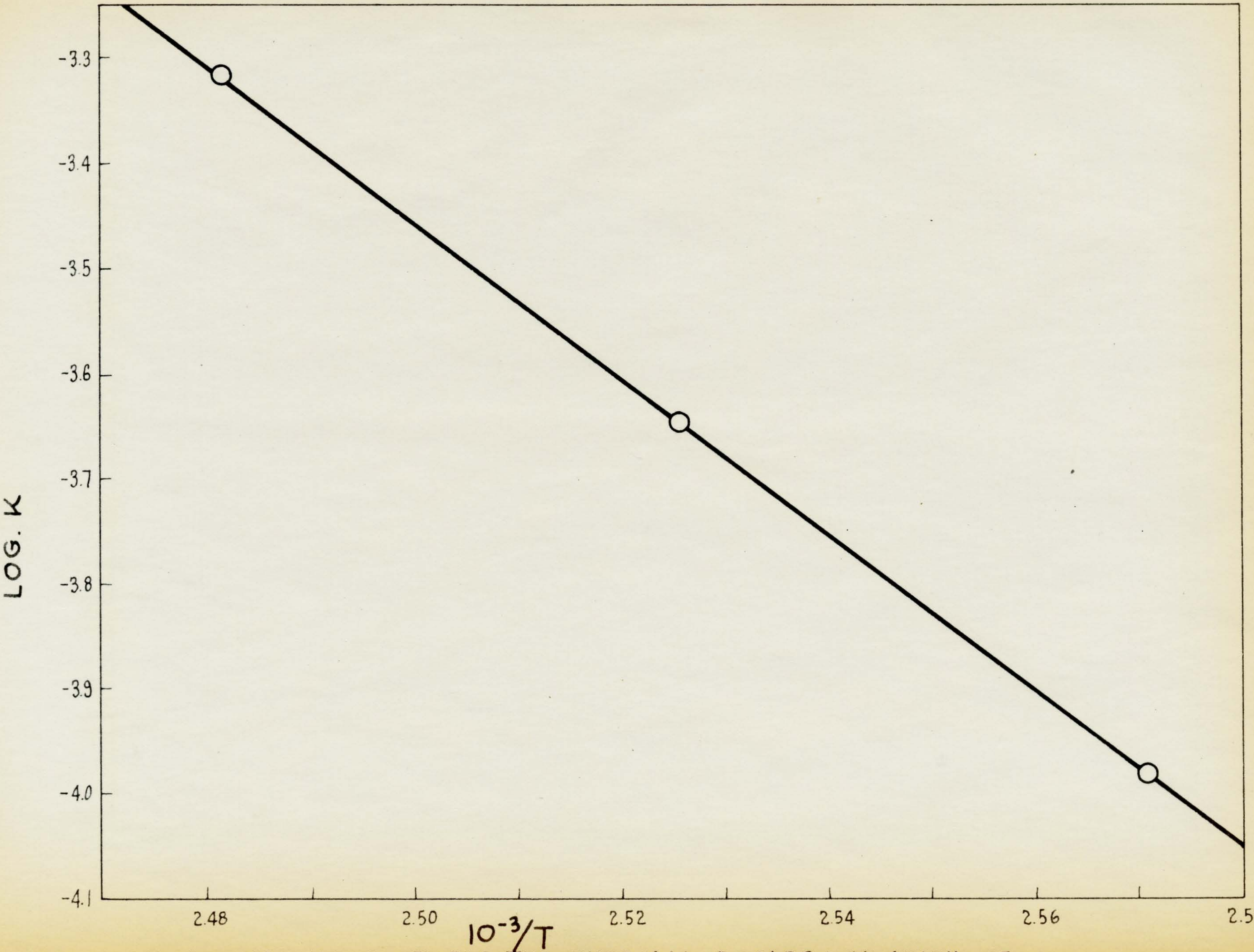


FIG.11: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM m-METHYLPHENYLPROPIOLATE

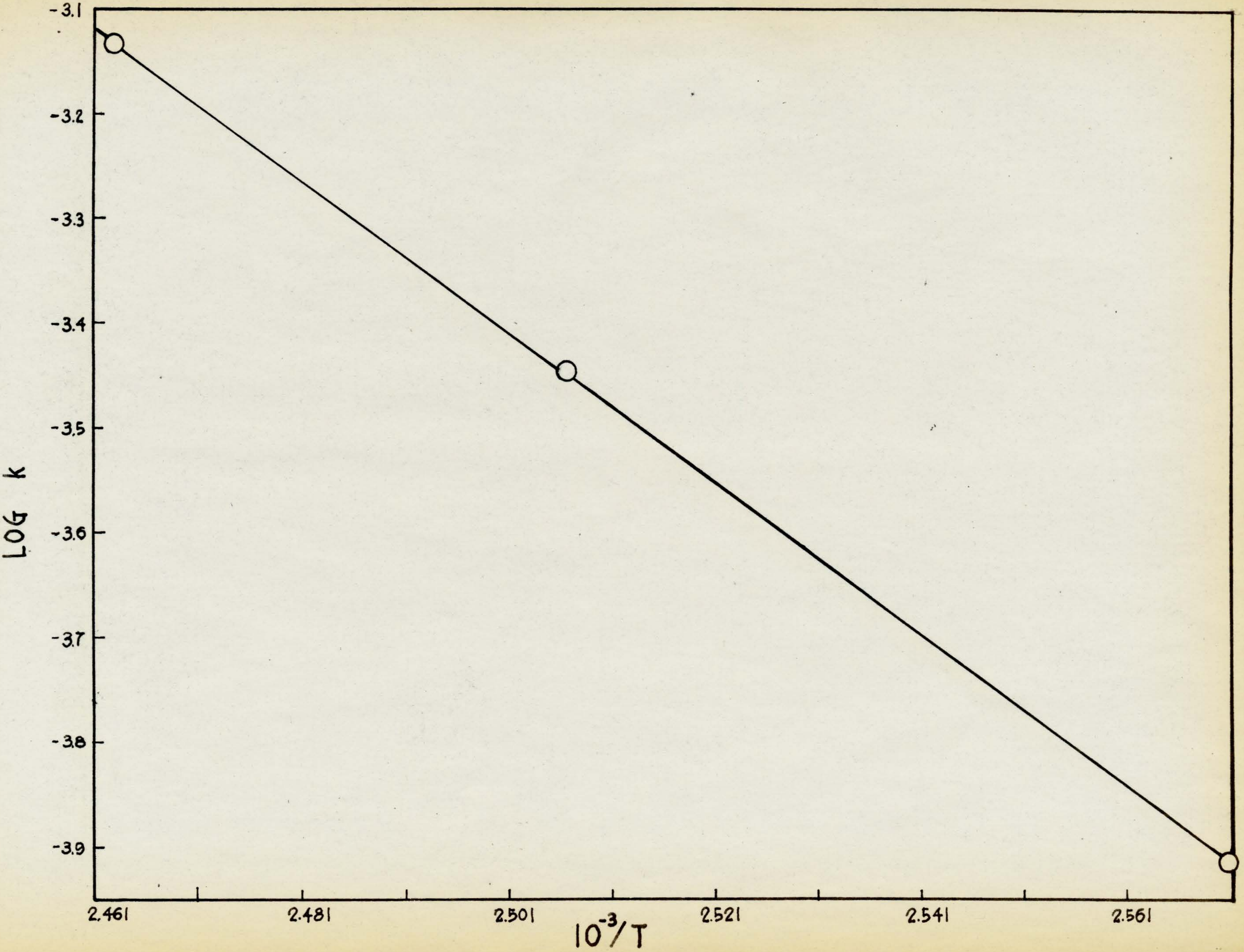


FIGURE 12: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM PHENYLPROPIOLATE

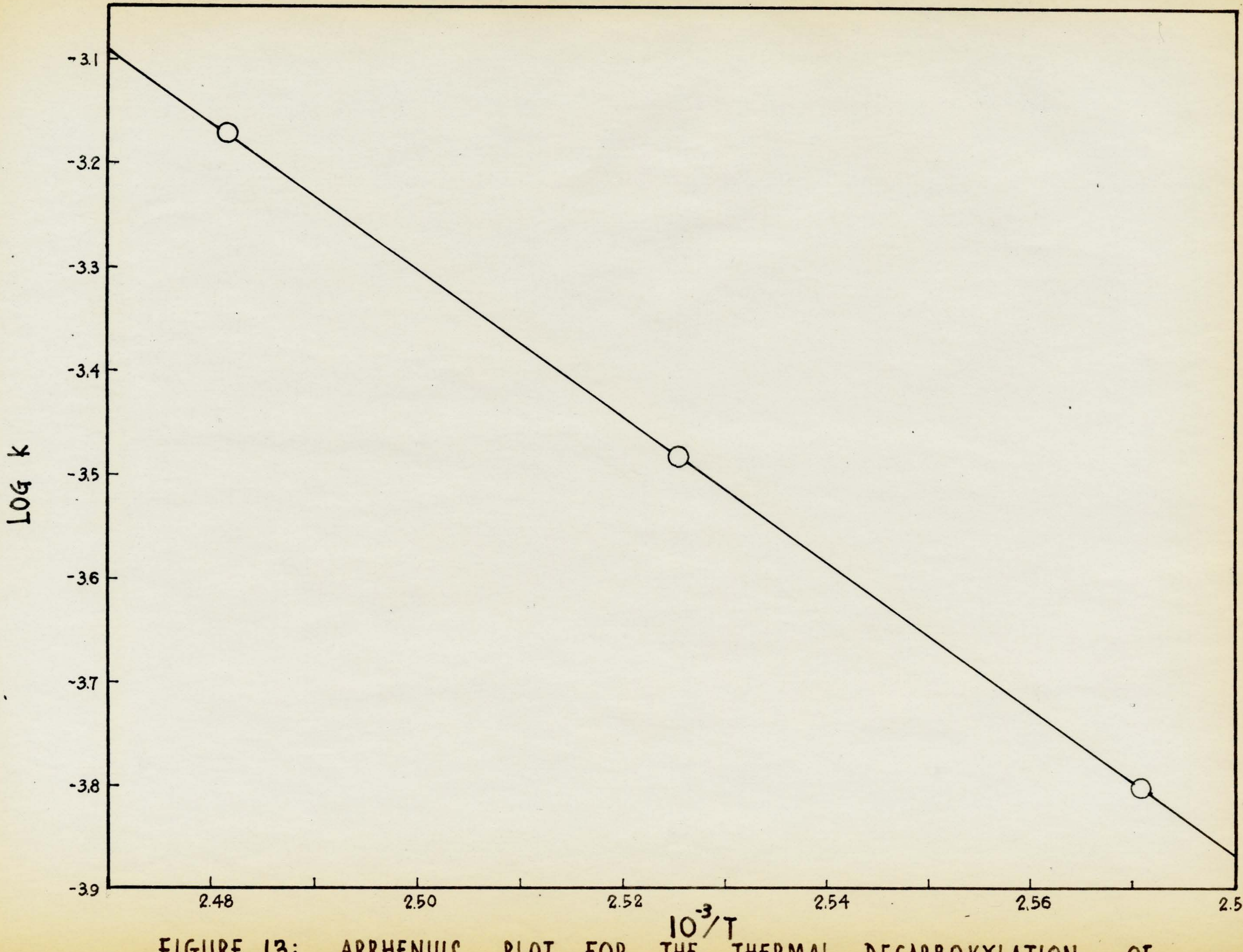


FIGURE 13: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM p-CHLOROPHENYLPROPIOLATE

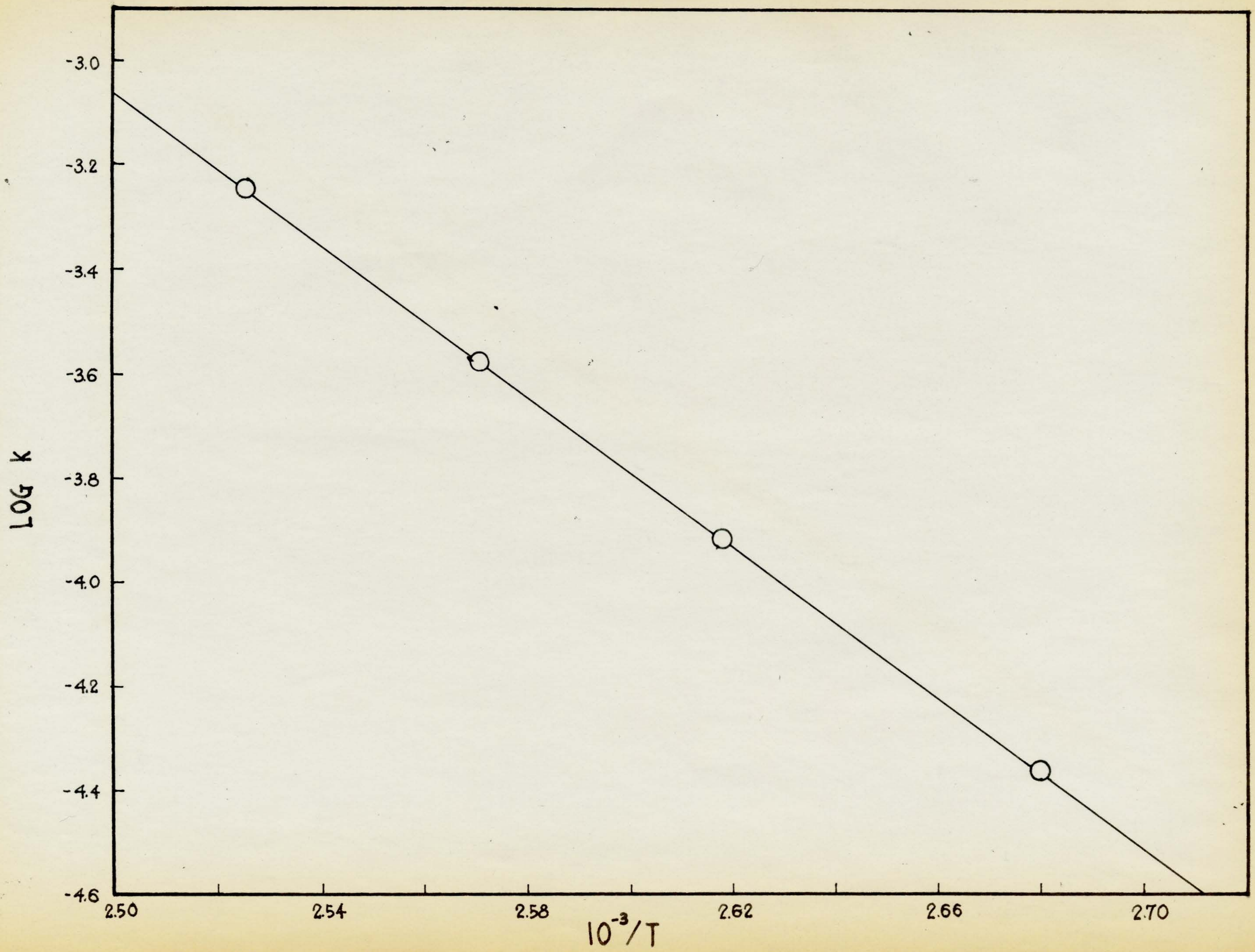


FIGURE 14: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM *m*-CHLOROPHENYLPROPIOLATE

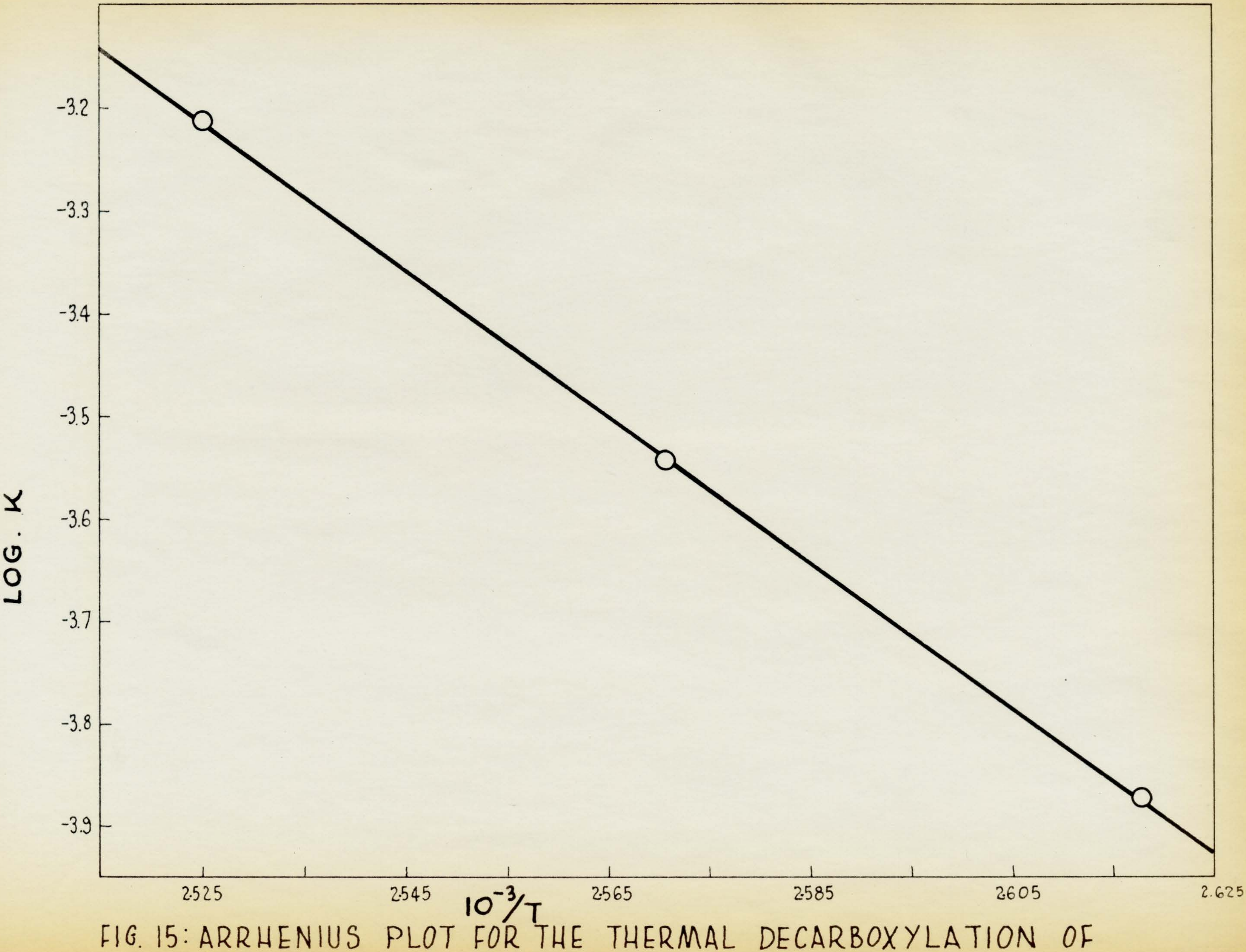


FIG. 15: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM m-TRIFLUOROMETHYLPHENYLPROPIOLATE.

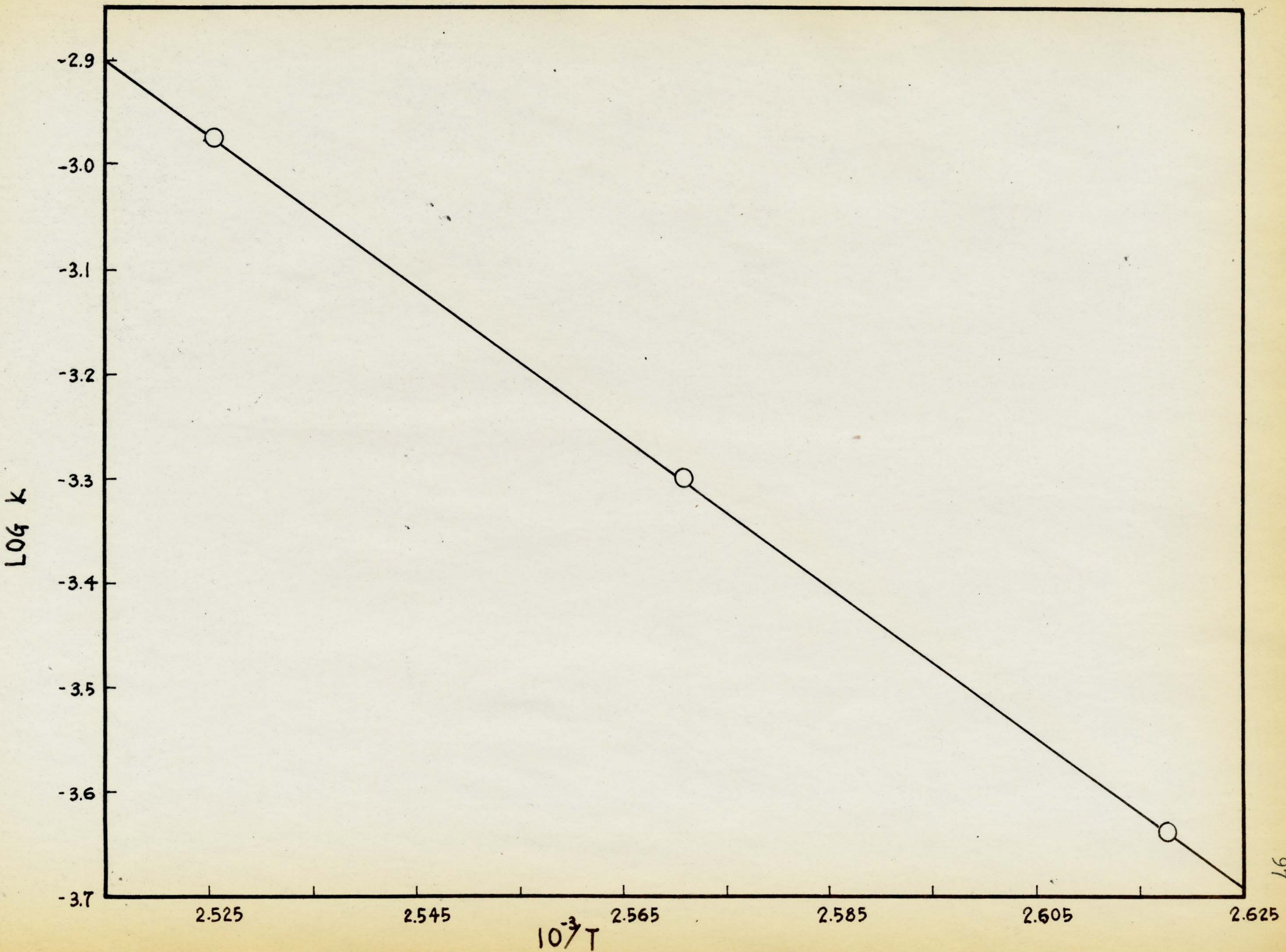


FIGURE 16: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM m-NITROPHENYLPROPIOLATE.

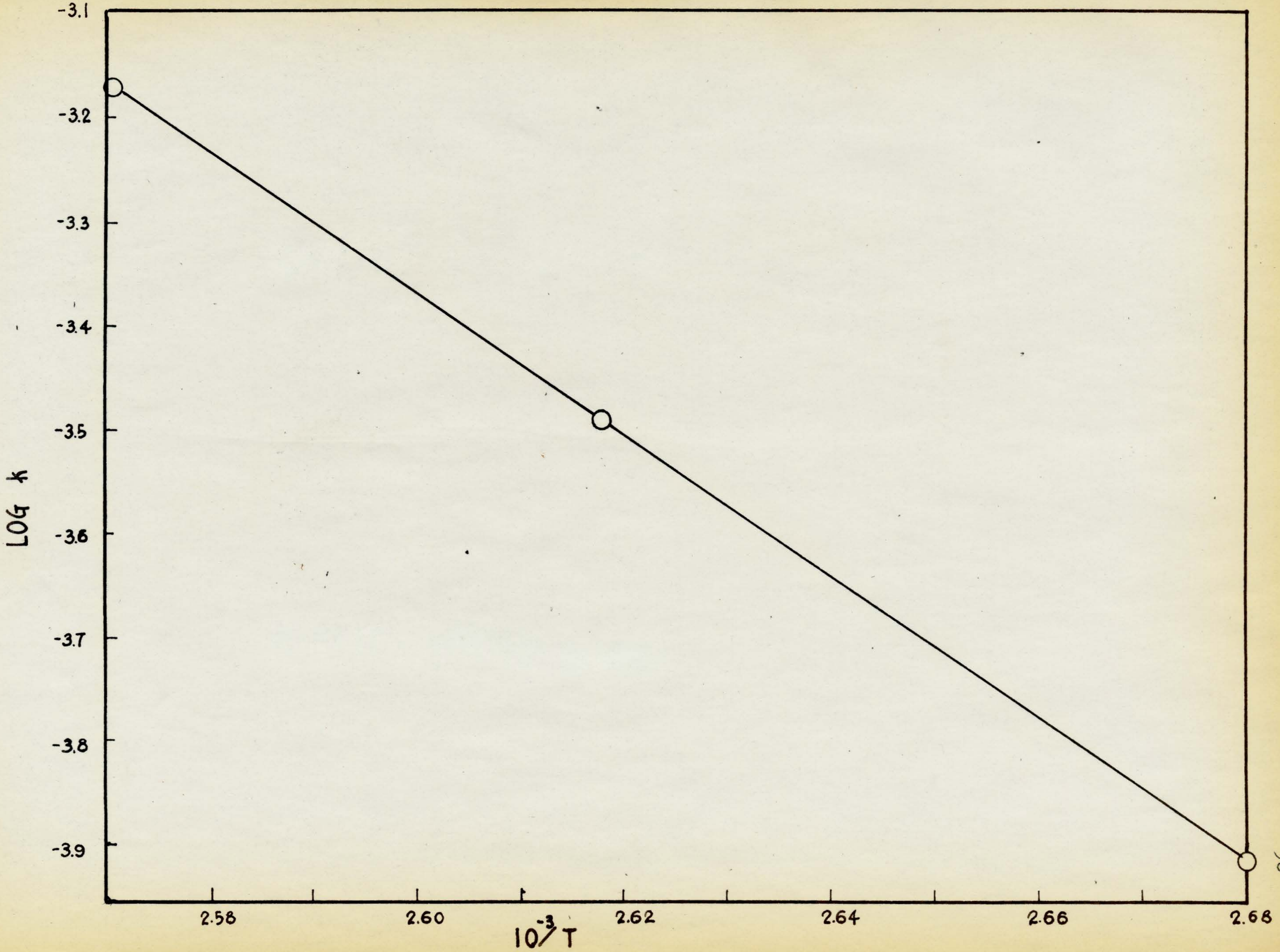


FIGURE 17: ARRHENIUS PLOT FOR THE THERMAL DECARBOXYLATION OF SODIUM p-NITROPHENYLPROPIOLATE

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