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3d-ORBITAL RESONANCE IN DIVALENT SULPHIDES—IX

A STUDY ON THE MECHANISM OF THE BASE CATALYSED DECARBOXYLATION OF α-MERCAPTOCARBOXYLIC ACIDS*

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Abstract—The kinetics of the base-catalysed decarboxylation of a few α-mercaptoacetic acids and other related acids in DMSO using a large excess ot triethanolamine has been investigated. The apparent first order rate constant increases gradually as the reaction proceeds, presumably due to the change of the relative concentrations of the carboxylate ion and the undissociated acid, while the major species undergoing the decarboxylation is considered to be the carboxylate ion. There is a linear relation between the p*Ka*'s of these mercapto acids in 50% v/v ethanol–water and the apparent dissociation constants in DMSO in the presence of the amine base (pK_A). The mechanism of the decarboxylation of the mercapto acid is considered to involve the rate-determining decarboxylation from the carboxylate ion to form the corresponding carbanion.

ALTHOUGH decarboxylation of organic carboxylic acids is a very common reaction, few mechanistic works available.[1] The lack of significant contributions presumably is due to the complication of the kinetic study. It is well known that carboxylic acids with strong electron withdrawing groups attached to the α-carbon, undergo a facile base-catalysed decarboxylation in polar solvents, resulting presumably in the formation of the corresponding carbanions as the intermediates in the rate determining step.[1,2] Thus, α-nitroacetic acid and α-nitroisobutyric acid decarboxylate very rapidly with sodium methoxide in methanol but not in methanol or ether alone.[3] Similar facile base-catalysed decarboxylations are known for malonic, dibromomalonic[4] and trihaloacetic acids.[5] Ammonium α-cyano-α-phenyl-propionate decomposes much faster than α-cyano-α-benzyl-butyric acid in ethylene glycol.[6]

The accelerated decarboxylation in the presence of an electron withdrawing substituent at the α-C atom is undoubtedly due to the stabilization of the resulting carbanion intermediate by both inductive and resonance effects of the substituent. Therefore, by measuring the rates of the base-catalysed decarboxylations of α-substituted carboxylic acids, the stabilizing effects of various substituents on the incipient carbanions may be measured as in the base-catalysed hydrogen isotopic exchange of the related mercaptals and orthothioformate.[7] Thus, we have extended our study on the 3d orbital resonance in divalent sulphides to the base-catalysed decarboxylation of various α-mercapto- and aryloxyacetic acids in order to obtain quantitative data to confirm the importance of the 3d orbital resonance effect of the

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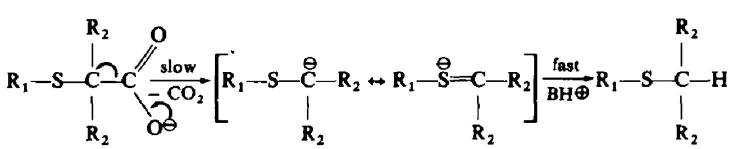
divalent sulphide group in the stabilization of the incipient carbanion formed in the rate-determining step of the reaction as shown below:



R_1; Ph, Et. R_2; Ph, Me, H, EtS, PhS, etc

A preliminary study has revealed that the α-mercapto acids are decarboxylated almost quantitatively to the corresponding sulphides with no marked side reaction.[8] Although, the decarboxylation appears to be simple and clearcut, unlike the base-catalysed isotopic exchange, the kinetics of the reaction is not straightforward. In addition, the decarboxylation of diphenoxyacetic acid is complicated by a side reaction yielding a small amount of phenol. Therefore, a thorough investigation of the kinetics was necessary before the effect of the substituent could be estimated. This paper describes the kinetic investigations of a few representative α-mercaptoacetic acids, dichloro- and diphenoxyacetic acids.

RESULTS AND DISCUSSION

Generally, the kinetic equation of decarboxylation can be expressed by Eq. (1),

$$d[CO_2]/dt = k_1[RCO_2^-] + k_2[RCO_2H] \qquad (1)$$

where, k_1 and k_2 are the first-order rate constants of the decarboxylation of the carboxylate ion and the undissociated carboxylic acid, respectively. The Eq. (1) can be transformed into Eq. (2),

$$d[CO_2]/dt = \{k_2 + \alpha(k_1 - k_2)\} \times [C_t] \qquad (2)$$

where, α is the degree of the dissociation of the acid and $[C_t]$ is the concentration of the acid at time t. The observed first-order rate constant (k_0) in Eq. (3)

$$k_0 = k_2 + (k_1 - k_2) \times \alpha \qquad (3)$$

is therefore the composite of k_1, k_2 and α, the separation of which is not easy except in a few cases. The following five cases are conceivable and three curves of different types have been drawn by plotting k_0 against χ, the portion of the reaction which has taken place.

(i) As the acidity of the acid is so strong that α is practically unity while k_2 is small, k_0 is equal to k_1 and independent of χ. This was found to be the case for the decarboxylation of dichloroacetic acid. If α is not large enough and the contribution of k_2 cannot be neglected, k_0 is dependent on the relative magnitude of k_1 and k_2. Here, the following four different cases (ii–v) are conceivable.

(ii) If k_1 is larger than k_2, k_0 usually increases as the reaction proceeds, giving an uprising curve. This was the case for α-phenylmercaptophenylacetic and α,α′-diphenylmercaptoacetic acids shown by the curves A and C in Fig. 1.

(iii) If, on the contrary, k_2 is larger than k_1, but not large enough and the contribution of k_1 cannot be neglected, k_0 appears as a constant at the beginning and tends to decrease at a later stage in the reaction as in curve B in Fig. 1.

(iv) If k_2 is so large that k_1 can be neglected, k_0 would decrease continuously till the end of the reaction—the reverse of case (ii). The decarboxylation of α-keto acids is apparently of this type, since the rate is known to be at maximum when it is undissociated.[1,9]

(v) If $k_1 = k_2$, the second term in Eq. (3) vanishes to give $k_0 = k_1$ or k_2. This cannot be distinguished kinetically from type (i). Types (i), (ii) and (iii) were actually observed in this investigation as shown in Fig. 1.

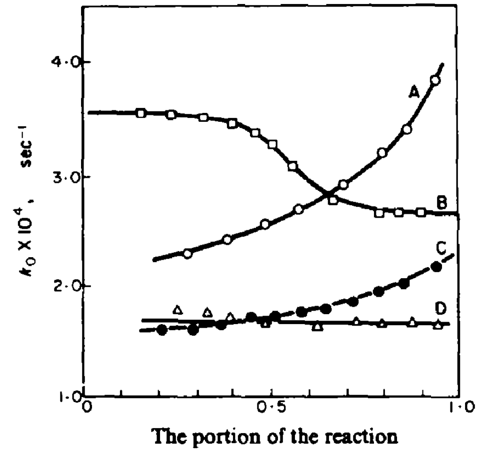


FIG. 1 Plot of the observed apparent rate constant (ko) against the fraction of carboxylic acid reacted (λ).

○ A, Phenylmercaptophenylacetic acid

□ B, Diphenoxyacetic acid (ordinal scale is ko × 10^{-5})

● C, Diphenylmercaptoacetic acid

△ D, Dichloroacetic acid

Since our primary concern was to determine the rate constant (k_1) of the decarboxylation of the carboxylate ion of α-mercaptoacetic acids, the kinetic analysis of this reaction is discussed in detail.

Triethanolamine was used as the base throughout the experiments, while DMSO was the choice solvent. The equilibrium between the carboxylic acid and the base is represented by Eq. (4),

$$K = \frac{[\mathrm{RCO_2^-}][\mathrm{BH^+}]}{[\mathrm{RCO_2H}][\mathrm{B}]} \qquad (4)$$

where [B] and [BH$^+$] are the concentrations of the free base and the conjugate acid respectively. Eq. (4) is further transformed into Eq. (5) by assuming that the concentration of the dissociated carboxylate ion is equal to that of the conjugate acid of the base in DMSO:

$$K = \frac{\alpha^2(1-\chi)}{(1-\alpha)\{\beta-(1-\chi)\alpha\}} \qquad (5)$$

here,

$$[RCO_2^-] = [BH^+] = \alpha[C_t]; \qquad [C_t] = [C_0] - [C_r]$$

$$[C_r] = \chi[C_0]; \qquad [B_0] = \beta \times [C_0];$$

where $[C_r]$ is the concentration of the acid reacted and $[C_0]$ and $[B_0]$ are the initial concentrations of the acid and the base, respectively; χ is the portion of the reaction which has taken place. Eq. (5) can be rearranged to Eq. (6), in which K is divided into three terms.

$$K = \frac{\alpha}{\beta - \alpha(1-\chi)} \times \frac{\alpha}{1-\alpha} \times (1-\chi) \tag{6}$$

In this case, the base is used in large excess over the acid and the kinetic measurement is limited only within the range of 20–70% of the reaction, the first term of the equation can be treated as constant, since β is much larger than $\alpha(1-\chi)$, while α is considered to remain constant within this range of concentration change of the acid. With this limitation, Eq. (6) can be rearranged to give an expression for α, i.e. Eq. (7),

$$\alpha = \frac{1}{1 + A(1-\chi)} \tag{7}$$

where,

$$A = \frac{1}{K} \times \frac{\alpha}{\beta - \alpha(1-\chi)} = \frac{1-\alpha}{\alpha} \times \frac{1}{1-\chi}$$

Since k_2 is considered to be much smaller than k_1, substitution of Eq. (7) for Eq. (3) and a subsequent rearrangement gives Eq. (8).

$$\frac{1}{k_0} = \frac{A+1}{k_1} - \frac{A}{k_1} \times \chi \tag{8}$$

Eq. (8) implies that a straight line should be obtained if the reciprocal of k_0 is plotted against the fraction of acid reacted, (χ). Therefore, the validity of the above approximation can be checked by examining the linearity of Eq. (8). Under normal kinetic conditions in which ten fold excess of the amine was used, most of the compounds obey the kinetic relationship of Eq. (8) within the range of 20–70% of the reaction, beyond which a slight deviation was observed as shown in Fig. (2). By such a manipulation, one can find experimentally from Eq. (8) not only the value of k_1, but also the value of A. This means that we can calculate apparent pK_A $(-\log \alpha_0^2/1 - \alpha_0)$ of a carboxylic acid in DMSO in the presence of a tertiary amine, since $A = 1 - \alpha_0/\alpha_0$ holds at the beginning of the reaction. The actual values of k_1, α_0 and pk_A, thus obtained for a few representative compounds, are tabulated together with their corresponding pK_A's in Table 2. Apparently there is a linear relation between this apparent pK_A and that found potentiometrically in an aqueous solvent (pKa).[11] Figure 3 shows such a correlation which indicates that highly dissociated carboxylic acids in 50% v/v ethanol–water also dissociate well in DMSO. Thus, α-phenylmercapto-phenylacetic acid (III) and diphenylmercaptoacetic acid (I) dissociate about 50% and 80% respectively at the beginning of the reaction at 90° in DMSO,

TABLE 1. A TYPICAL KINETIC RUN OF THE USUAL BASE-CATALYZED DECARBOXYLATION OF α-PHENYLMERCAPTOPHENYLACETIC ACID[a]

t (min)[b]	V_t (ml)[c]	$V_\infty/V_\infty - V_t$	$k_0 \times 10^4$ (sec^{-1})	$1/k_0 \times 10^{-3}$	χ (%)
10	3·42	1·149	2·31	4·33	27·0
20	6·78	1·345	2·47	4·05	37·0
30	9·82	1·590	2·58	3·88	47·3
40	12·73	1·928	2·74	3·65	56·5
55	16·47	2·650	2·85	3·39	68·4
70	19·57	3·840	3·21	3·12	78·2
85	21·81	5·700	3·41	2·93	85·3
105	24·14	11·45	3·87	2·58	92·7
295	26·45	—	—	—	100

[a] Carboxylic acid (5×10^{-4} mole) and triethanolamine (5×10^{-3} mole) in 50 ml DMSO at 90 ± 0·02°. See also curve A in Fig. 1 and B in Fig. 2.

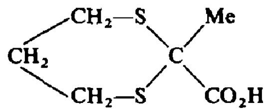
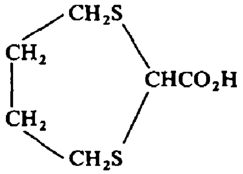
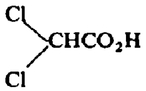
[b] The time measured from arbitrary initial time to start of counting.

[c] Volume of H_2SO_4 aq consumed during time t (min).

$A/k_1 = 2{\cdot}33 \times 10^3$ $\alpha_0 = 0{\cdot}53$

$(A + 1)/k_1 = 4{\cdot}95 \times 10^3$ $k_1 = 3{\cdot}82 \times 10^{-4}$ (sec^{-1})

TABLE 2. KINETIC DATA OF THE BASE-CATALYZED DECARBOXYLATION OF A FEW REPRESENTATIVE α-MERCAPTO CARBOXYLIC ACIDS AND OTHER RELATED ACIDS

	Compound	Temp. (°C)	First-order rate constants $k_1 \times 10^5$	α_0[a]	pK_A^{*}[b]	pKa[c]
I	$(PhS)_2CHCO_2H$	90	19·5	0·80	−0·50	4·12
II	$(PhS)_2C(CH_3)CO_2H$	90	1·45	0·64	−0·055	4·59
III	PhS—CH(Ph)CO_2H	90	38·2	0·53	0·22	4·70
IV	$(EtS)_2CHCO_2H$	160	4·65	0·68	−0·16	4·52
V		160	1·52	0·60	0·046	4·83
VI		160	7·94	0·78	−0·44	4·28
VII	 Cl_2CHCO_2H	115	16·8	—	—	—
VIII	$(PhO)_2CHCO_2H$[d]	160	3·41	—	—	—

[a] The initial degree of dissociation of carboxylic acid in reaction.

[b] $-\log(\alpha_0^2/1 - \alpha_0)$.

[c] Acid dissociation constant measured in 50% v/v aqueous ethanol-water at 25°.

[d] Average value without the usual manipulation through the range of 20–70% of the reaction.

while their p*Ka*'s are known to be 4·70 and 4·12 respectively in 50% v/v ethanol–water solution.

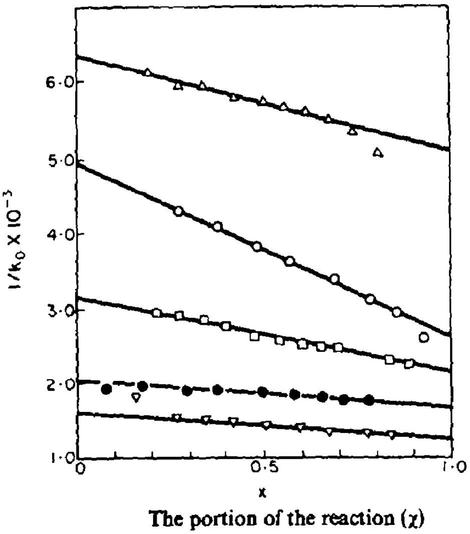


FIG. 2 Plot of 1/ko against the portion of carboxylic acid reacted (χ)

△ Diphenylmercaptoacetic acid
○ Phenylmercaptophenylacetic acid
□ Diethylmercaptoacetic acid
● α,α-diphenylmercaptopropionic acid
▽ Alyoxylic acid tetramethylene dimercaptal[a]
[a] ordinal scale is 1/ko × 10^{-4}

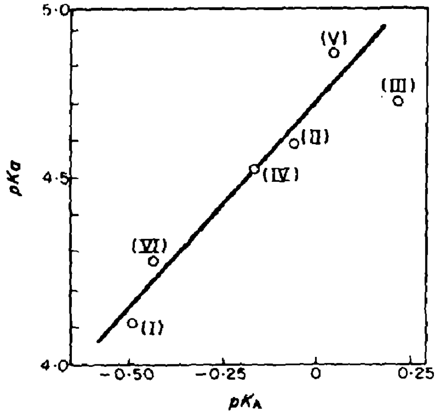


FIG. 3 Correlation of pK_A^a and pKa[b]

(a) apparent pK_A ($-\log \alpha_0^2/r\alpha_0$) of carboxylic acid in dimethylsulphoxide in the presence of 10 fold of triethanolamine, see Table (II).
(b) pKa measured in 50% v/v ethanol–water, see succeeding paper of this series (XI).

In the decarboxylation of α-phenylmercapto-phenylacetic acid, a number of kinetic runs were conducted in order to find an optimum condition under which these acids decompose with first order to the carboxylic acid and zero order to the amine. Then the concentration of the amine was changed while keeping the concentration of the carboxylic acid at 0·01M, the rate increase was found at low concentration of the amine as if the rate were dependent in the first order on the amine concentration. As the concentration of the amine increased (more than ten fold over that of the acid), the rate reached a plateau of a constant value and was no longer dependent on the concentration of the amine as seen in Fig. 4. These results clearly indicate that in a low concentration of the carboxylic acid with a sufficient amount of the amine base, A in Eq. (8) can be treated as a constant and one can calculate the value of k_1, the rate constant for the decarboxylation of the carboxylate ion to form the carbanion as the rate determining step.

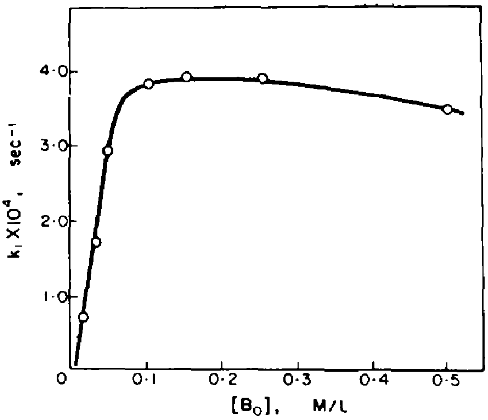
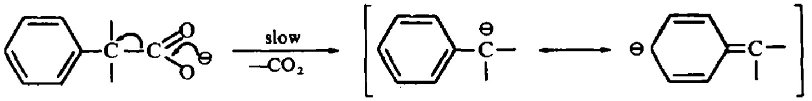


FIG. 4 Effect of Amine concentration in the Decarboxylation of Phenylmercaptophenylacetic acid at 90°C.[a]

(a) concentration of carboxylic acid was kept at 0·01 M.
[B$_0$] : total amine concentration.

The formation of the carbanion intermediate is supported by a number of observations published[9] and in the succeeding paper.[10] The substituent effect at the α-C seems to support the rate-determining formation of the carbanion intermediate. Namely, the substitution of a Me group at the α-C retarded the rate, whereas, a Ph groups was found to accelerate the rate (about 10^3 times faster than unsubstituted acids), indicating that the incipient carbanion is resonance-stabilized due to the Ph ring, thus lowering the activation energy of the deccrboxylation (Eq. 9).



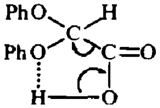
(9)

Detailed discussion on the effects of these substituents will be described in the succeeding paper.[10]

The kinetic behaviour of diphenoxy- and dichloro-acetic acids was compared with the mercaptosubstituted carboxylic acids. Dichloroacetic acid has a relatively high acidity; i.e. pKa in 50% v/v ethanol–water was found to be 2·51. Therefore, α would also be large in DMSO and hence, k_0 is expected to be practically the same as k_1, giving a straight line characteristic of type (i) reaction as seen in Fig. 1 (line D). Diphenoxyacetic acid shows a typical kinetic behaviour for type (iii) reaction, as shown by the curve B in Fig. 1. Therefore, the rate of the decarboxylation of the undissociated acid, k_2, is considered to be greater than that of the decarboxylation of the dissociated carboxylate ion (k_1). Although the values are approximate, the order of magnitude of k_1 and k_2 can be estimated in the following way. Substitution of Eq. (7) in Eq. (3) and a rearrangement gives Eq. (10) as the expression for k_2.

$$k_2 = k_0 + \frac{1}{A(1 - \chi)} \times (k_0 - k_1) \tag{10}$$

Extrapolation of the curve B in Fig. (1) gives k_0 ($\chi = 0$) = $3{\cdot}5 \times 10^{-5}$ sec^{-1} and k_0 ($\chi = 1$) = $2{\cdot}7 \times 10^{-5}$ sec^{-1} respectively. Since k_0 ($\chi = 1$) = k_1, Eq. (10) can be written as, $k_2 = (3{\cdot}5 + 0{\cdot}8/A) \times 10^{-5}$ sec^{-1} at the beginning of the reaction ($\chi = 0$). Since the value of A was found to be 0·89 for α-phenylmercapto-phenylacetic acid which is a weaker acid than diphenoxyacetic acid (p*Ka* values in 50% v/v ethanol-water are 4·70 for the former and 3·64 for the latter compound), the value of A must be smaller than 0·89 for diphenoxyacetic acid. Thus, even a minimum value of k_2 is estimated to be $4{\cdot}3 \times 10^{-5}$ sec^{-1} (160°), which is somewhat larger than k_1 ($2{\cdot}7 \times 10^{-5}$ sec^{-1}). A faster decomposition of the undissociated diphenoxyacetic acid is further supported by the solvent effect. This carboxylic acid was found to decarboxylate at almost the same rate ($2{\cdot}39 \times 10^{-5}$ sec^{-1} at 173°) in 50% v/v DMSO–decalin mixture without any amine base as in DMSO with an excess of amine. Thus in this case the presence of amine has a very small catalytic effect. Meanwhile, the addition of amine to the solvent enhances the reactivity about one hundred fold in the case of the sulphur analog as is depicted in Table 3. The lack of the catalytic effect may be due to the hydrogen-bonding of the carboxylic group to one of the phenoxy groups as shown below and this enhances the rate of the decarboxylation of the undissociated acid.



Such hydrogen-bonding is expected to be weak for the sulphur compounds. One way to test this hypothesis is to examine the kinetic isotope effect k_H/k_D, of the decarboxylation of diphenoxyacetic acid which has a deuterated OH group and (2) the effect of various substituents on the Ph ring on the rate of decarboxylation.

Solvent effect

The decarboxylation of diphenylmercaptoacetic acid (I) was examined in various solvents. (Table 3). The very fast rate observed in DMSO, may be due to the fact that DMSO is a polar and aprotic solvent capable of stabilizing the resulting carbanion by strong solvation. A large rate reduction was observed in ethylene glycol in spite of its polar character. In this solvent the reactive carboxylate ion would be strongly hydrogen-bonded, hence stabilizing the ground state. A similar, but less pronounced phenomenon was observed in t-butanol. In decalin, which is non-polar and has poor solubility for these carboxylic acids, the reaction proceeds very slowly during 6 hr heating at 90°. This is quite reasonable since in decalin the carboxylic acids would be less dissociated to form the reactive carboxylate ions. These solvent effects suggest that in the decarboxylation of the mercapto-substituted carboxylic acids, the carboxylate ions are the reactive species which undergo decarboxylation to form the carbanion intermediates.

TABLE 3. SOLVENT EFFECT IN DECARBOXYLATION OF α,α-DIPHENYLMERCAPTOACETIC ACID[a]

Solvent	Base	First-order rate constant (sec^{-1})	Apparent relative rate constant[d]
Dimethyl sulphoxide	TEA[e]	$1\cdot95 \times 10^{-4}$ (90°)	1
	no base	$1\cdot80 \times 10^{-6}$ (100°)[b,c]	$2\cdot7 \times 10^{-2}$
Ethylene glycol	TEA	$9\cdot2 \times 10^{-7}$ (120°)[c]	$1\cdot5 \times 10^{-4}$
t-Butanol	TEA	$6\cdot0 \times 10^{-7}$ (80°)[c]	$1\cdot0 \times 10^{-2}$
Decalin	TEA	no reaction for 6 hr (90°)	

[a] 1×10^{-2}M acid, 1×10^{-1}M triethanolamine in 50 ml solvent.

[b] In DMSO without amine base; $1\cdot5 \times 10^{-3}$M acid in 15 ml DMSO.

[c] Reaction rates were too small to follow the reaction completely and hence these are apparent rate constants and roughly estimated.

[d] These relative rates were estimated using $E_A = 30\cdot4$ Kcal/mole for rough comparison at 90°.

[e] Triethanolamine.

EXPERIMENTAL

Preparations of carboxylic acids. The synthetic methods and the properties of the carboxylic acid have been described.[8,10] *Purification of solvent and amine.* Commercial grade DMSO was treated with BaO first and then distilled at 70° at reduced press under N_2. Freshly distilled DMSO was kept on Molecular sieve 4A (pretreated at 300° for 3 hr before use) in a ratio of 15 g/100 ml DMSO for half a day, under N_2 at room temp and then redistilled at 70° at reduced press under N_2.[11] Commercial grade triethanolamine was distilled under reduced press., and then treated with molecular sieve 4A as mentioned above, and then redistilled at reduced press. under N_2.

Kinetics and calculations

Apparatus. The apparatus for the complete absorption of CO_2 evolved during the reaction is shown in Fig. 5.[12]

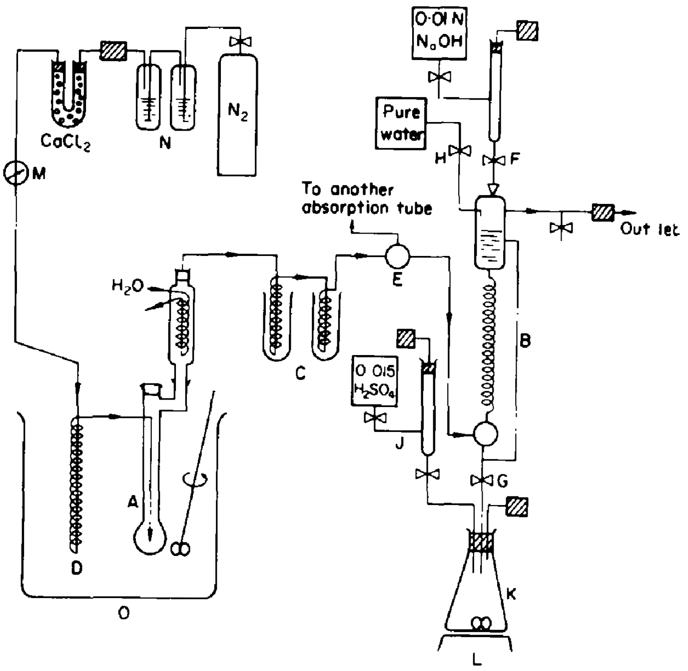
CO_2 evolved from the reaction flask (A) was carried to the helical coil absorption tube (B) containing aqueous alkaline soln with a constant stream (55 ml/min) of N_2 which was freed from O_2 and moisture. A trap was cooled in a dry ice–acetone bath (C) set between the reaction flask (A) and the absorption tube (B) in order to condense any volatile material coming from the reaction flask. All the terminals of this apparatus were connected with drying tubes containing soda-lime.

Actual run. Before charging the reaction mixture, the air in the apparatus was completely replaced with N_2 during 5 hr. The reaction mixture was placed in the flask and after passing N_2 for an additional $\frac{1}{2}$ hr, a blank titration was taken. Then the flask was placed in a thermostated paraffin bath kept at 90° $\pm$ 0·02° to start the reaction.

After 25 min, the first point was taken, then two absorption tubes were switched back and forth from time to time for each titration by turning the 3-way cock (E). The reaction was followed until CO_2 evolution ceased.

Titration and blank test. The blank titration was carried out by adding 30 ml 0·01N alkaline aqueous soln containing 0·1% (by wt) n-butanol as the surface active agent and 2% Na_2SO_4 to suppress the dissociation of $NaHCO_3$, into the absorption tube (B) from burette (F), and after bubbling N_2 for 10 min., this alkaline soln was then poured into a 300 ml Elenmayer flask through cock (G). The absorption tube was washed 3 times each with 35–40 ml pure water which was poured into the tube from the pure water tank (H) and the combined aqueous alkaline soln (about 150 ml) was titrated with 0·015N H_2SO_4 using phenolphthalain as indicator. The blank tests were repeated 3 times before each reaction and then again a few times after 2 hr. From these blank tests, the average volume (V_0 ml) of H_2SO_4 aq required to neutralize 30 ml of 0·01N aqueous alkaline soln without absorbing CO_2 was determined. In an actual run, the CO_2 which was evolved during the reaction and carried with N_2 was absorbed in this alkaline soln and the titration of the resulting partially neutralized alkaline soln was conducted in exactly the same way as in the blank titration.

Apparatus for CO_2 absorption



(A) Reaction flask (100 ml)
(B) Absorption tube
(C) Acetone-dryice trap
(D) Preheating coil of N_2 carrier gas
(E) Three-way cock
(F) Aq. alkaline burret (50 ml)
(H) Pure water tank
(J) Aq. H_2SO_4 burret (20 ml)
(K) 300 ml Elenmayer flask
(L) Magnetic Stirrer
(M) Flow Meter
(N) Oxygen absorption tube
(O) 10 l thermostatic paraffin bath
▨ Soda lime tube

FIG. 5

The actual running condition of the kinetic experiments. The time required for the complete absorption of CO_2 evolved was examined, under conditions similar to the actual kinetic run by generating CO_2 from a Na_2CO_3 aq added to conc H_2SO_4. It was found that 25 min was necessary for the absorption of the total CO_2 formed. The flow rate of N_2 carrier gas and the amount of CO_2 evolved did not affect the results, provided the conditions were similar to those used in the actual kinetic runs. Therefore, 25 min was the time lag between the moment of CO_2 evolution in the reaction flask and the absorption of the gas in the tube. Hence the initial time was corrected by subtracting 25 min from the actual reaction time. In order to determine the possible consumption of alkali, a mixture without carboxylic acid (50 ml DMSO containing 5×10^{-3} mole triethanolamine) was treated under similar conditions at 160° for 6 hr. This blank test showed that a small definite amount of alkali was consumed, hence, 0·6% correction was made to V_0 for each run of the kinetic experiment. The amount of CO_2 produced during the reaction time (t) was calculated using Eq. (11),

$$M = C \times \{(1 - 0{\cdot}006)\,V_0 - V\} \times 10^{-3}\,(\text{mole}) \tag{11}$$

in which C and V represent the concentration and the volume of H_2SO_4 aq required to back-titrate the alkaline soln. Table 1 shows the kinetic data of a typical run of α-phenylmercaptophenylacetic acid at 90°. The first-order rate constant (k_1) and the initial degree of dissociation (α_0) of carboxylic acid were calculated from the intercept and the slope of the straight line obtained by the plot of $1/k_0$ against the portion of reaction (χ) using Eq. (8). Application of the least square method gave $1/k_0 = 4{\cdot}95 \times 10^3 - 2{\cdot}33 \times 10^3 \times \chi$ from which k_1 and α_0 were calculated to be $3{\cdot}82 \times 10^{-4}$ (sec^{-1}) and 0·53, respectively. The temp dependency of the reaction rate of α-phenylmercaptophenylacetic acid was also examined at 80°, 90° and 100° to give the rates of $1{\cdot}20 \times 10^{-4}$, $3{\cdot}82 \times 10^{-4}$, and $12{\cdot}3 \times 10^{-4}$ (sec^{-1}), respectively. The usual Arrhenius plot of log k_1 against $1/T$ gave a straight line, from which the apparent activation energy was calculated. $E_A = 30{\cdot}4$ Kcal/mole $\Delta S^{\ddagger} = 1{\cdot}23$ e.u.

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