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3d-ORBITAL RESONANCE IN DIVALENT SULPHIDE—X

THE EFFECTS OF α-ARYL AND α-ALKYLMERCAPTO GROUPS ON THE RATE OF DECARBOXYLATION OF α-SUBSTITUTED CARBOXYLIC ACIDS *

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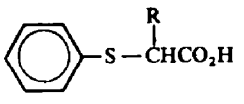
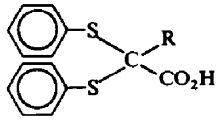
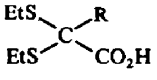
Abstract—Several α-mercaptoacetic and related acids were synthesized and the rates of the amine-catalysed decarboxylation were measured. In the carbanion-forming reaction, the α-mercapto group exhibits a dramatic rate-enhancement, due to the 3d-orbital resonance effect of the divalent sulphide group. For example, the rate of the decarboxylation of diphenylmercaptoacetic acid was $8{\cdot}8 \times 10^3$ fold greater than that of the oxygen analog, diphenoxyacetic acid; while the substitution of one phenylmercapto group at α-position of phenylmercaptoacetic acid was found to accelerate the rate by $1{\cdot}7 \times 10^3$. These results can be correlated with those of the base-catalysed H–D exchange reactions of various sulphides previously reported[1] and explained on the basis of 3d orbital resonance involving the S atom in divalent sulphides.

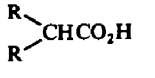
IN THE base-catalysed H–D exchange reaction of various mercaptals, the marked rate enhancement by the α-mercapto group, substantiates the importance of the 3d-orbital resonance effect of divalent sulphur in the transition state of the reaction.[1]

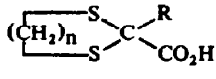
This investigation has been extended to include the base-catalyzed decarboxylation reaction of various α-mercapto substituted carboxylic acids (A, B, C, D and E, shown below) in order to obtain additional evidence for the 3d-orbital resonance of divalent sulphur groups.

A;  I: R = H; V: R = Ph

B;  II: R = H; III: R = Me; IV: R = Ph; XVI: R = PhS

C;  VI: R = H; VII: R = Me; VIII: R = EtS; IX: R = Ph

D;  II: R = PhS; X: R = PhO; XI: R = Cl; VI: R = EtS

E;  XII: R = H; n = 2; XIII: R = H 3; XIV: R = Me 3; XV: R = H 4

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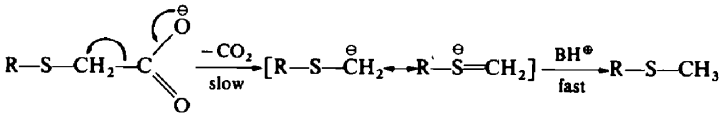
The kinetic investigation and the mechanism of decarboxylation of these acids has been described.[2] Undoubtedly, the formation of carbanion is involved in the rate-determining step of the reaction. Therefore, as in the base-catalysed hydrogen isotopic exchange reaction, the mercapto group stabilizes the carbanion by the 3d-orbital resonance involving the S atom as illustrated in Eq. (1) and which results in a marked rate increase.



(1)

Thus, the contribution of the 3d-orbital resonance of divalent sulphur in each mercapto-substituted compound can be estimated by measuring the decarboxylation rate of each acid. This paper describes the rate-enhancing effect of the α-mercapto group, the effect of other α-substituents and that of ring size and the conformational change in the decarboxylation of the α-mercapto-carboxylic acids.

RESULTS AND DISCUSSION

Influence of inductive and resonance effects. The rate of decarboxylation is accelerated by electron-withdrawing groups attached to the α-carbon, while electron-donating groups attached to the α-carbon retard it. For example, α-nitroacetic acid[3] decomposes readily in a polar solvent in the presence of a base. α-Phenyl substituted carboxylic acids react much faster than the corresponding α-benzyl substituted acids[4] as the carbanion formed from the former compound is stabilized by resonance with a α-Ph group whereas no such resonance stabilization of the carbanion is expected in the second compound. A comparison of the effect of α-Me and α-Ph groups on the rate of the decarboxylation of the four α-mercaptocarboxylic acids (A, B, C, and E) shows that the α-Me group retards the reaction due to its electron-releasing inductive effect which destabilizes the resulting carbanion, whereas the α-Ph group increases the decarboxylation rate since the resulting carbanion is stabilized not only by resonance with the α-Ph group but also by its electron-withdrawing inductive effect.

As can be seen in Tables 1 and 3, all the Me-substituted compounds (III, VII and XIV) react slower than the corresponding unsubstituted compounds (II, VI and XIII). The rate of α,α′-diphenylmercaptopropionic acid (III) is 14 times slower than that of the unsubstituted acid (II), and a similar rate-retardation by the α-Me group was observed both in α,α′-diethylmercaptopropionic (VII) and the cyclic acids (XIV), where the rate reductions are about 2·5 and 1·9 respectively. On the other hand, the substitution of a Ph group accelerates the rate. Thus, α,α′-diphenylmercaptophenylacetic acid (IV) decarboxylates about $4{\cdot}9 \times 10^2$ times faster than the unsubstituted acid (II). In the case of α,α′-diethylmercaptophenylacetic acid (IX) and α-phenylmercaptophenylacetic acid (V), a α-Ph group increases the rate by $4{\cdot}7 \times 10^4$ and $3{\cdot}4 \times 10^3$ respectively. These results clearly indicate that the stability of the resulting carbanion intermediate is responsible for the rate of decarboxylation and the rate is affected by the nature of the α-substituent.

Effects of α-mercapto groups. Phenylmercaptoacetic acid (I) decarboxylates very slowly (only 30% of the starting compound decomposes in 8 hr at 170°) with the reaction rate of $1{\cdot}4 \times 10^{-5}$ (sec^{-1}) at 170° ± 0·15, but one additional phenylmercapto group at the α-carbon increases the rate considerably, the reaction being complete in 6 hr at 90° and the decarboxylation rate of α,α'-diphenylmercaptoacetic acid (II) is $1{\cdot}7 \times 10^3$ faster than that for acid I. A similar rate increase was found by the substitution of an additional phenylmercapto group. Thus, triphenylmercaptoacetic acid (XVI) decarboxylates $1{\cdot}3 \times 10^3$ times faster than acid II. The substitution of an ethylmercapto group at the α-position gives a similar rate increase. Thus triethyl-

TABLE 1. THE RELATIVE RATES OF THE BASE-CATALYSED DECARBOXYLATION OF α-MERCAPTO SUBSTITUTED CARBOXYLIC ACIDS

Compound		Temp (°C)	First-order rate constant $k_1 \times 10^5$ (sec^{-1})	Relative rate[b]	$\Delta H^{\ddagger}$ kcal/M	$\Delta S^{\ddagger}$ cal/deg
$PhS—CH_2CO_2H$	(I)	160	0·83	1·1	18·5	−32·6
$(PhS)_2CHCO_2H$	(II)	90	19·5	$1{\cdot}9 \times 10^3$	31·7	13·5
$(PhS)_2\overset{Me}{\overset{|}{C}}CO_2H$	(III)	90	1·45	$1{\cdot}4 \times 10^2$		
$(PhS)_2\overset{Ph}{\overset{|}{C}}CO_2H$[f]	(IV)	10	69·3	$9{\cdot}3 \times 10^5$	11·9	−29·0
$(PhS)_3CCO_2H$[f]		10	41·2	$2{\cdot}4 \times 10^6$	15·5	−17·0
$PhS\overset{Ph}{\overset{|}{C}}HCO_2H$	(V)	90	38·2	$3{\cdot}7 \times 10^3$	28·9	7·0
$(EtS)_2CHCO_2H$	(VI)	160	4·65	1·0	26·6	−15·6
$(EtS)_2\overset{Me}{\overset{|}{C}}CO_2H$	(VII)	160	2·42	0·52[c]		
$(EtS)_3CCO_2H$[g,h]	(VIII)	100	108	$3{\cdot}8 \times 10^3$[d]		
$(EtS)_2\overset{Ph}{\overset{|}{C}}CO_2H$[g]	(IX)	80	165	$4{\cdot}7 \times 10^4$[e]		

[a] Carboxylic acid ($0{\cdot}5 \times 10^{-3}$ moles) in 50 ml DMSO containing 5×10^{-3} moles triethanolamine.

[b] Relative rates were extrapolated to 90° by Arrehnius equation (see also Experimental).

[c] At 160°.

[d] At 100°.

[e] At 80°.

[f] Triethanolamine (25×10^{-3} moles) was used in order to prevent freezing the solution, in which case amine concentration did not affect the reaction rate (see Fig. 4 of previous paper[2]).

[g] A sample ($0{\cdot}6 \times 10^{-3}$ moles) was reacted in 29 ml DMSO with an equivalent amount of Et_3N.

[h] This compound is unstable and hence the concentration was determined just before kinetic measurement (see Experimental).

[i] At 90°.

mercaptoacetic acid (VIII) decomposes about $3{\cdot}8 \times 10^3$ times faster than diethylmercaptoacetic acid (VI). These marked rate increases are in keeping with similar rate increases in the base-catalysed H-D exchange reactions of corresponding sulphides, in which triethylmercaptomethane reacts about $3{\cdot}7 \times 10^2$ times faster than diethylmercaptomethane.[2] The effect of an α-ethylmercapto group in both the amine-catalysed decarboxylation of the α-substituted acetic acids and the base-catalysed isotopic exchange reactions of ethylmercaptals and ethyl orthothioformate suggests that the rate-enhancing effect is operating in a similar fashion, namely by stabilization of the resulting α-ethylmercapto-carbanion at the respective rate-determining step of each reaction. As the further rate-enhancement by the substitution of an additional mercapto group, especially in the compounds IV, XVI, IX and VIII may be considered due to the steric strain produced by two or three bulky mercapto, one phenyl and a carboxyl groups, the following noteworthy points are cited from the data.

(1) The rate enhancement induced by the substitution of one ethylmercapto group in both the H–D exchange reaction of triethylmercaptomethane and the decarboxylation of triethylmercaptoacetic acid is $3{\cdot}7 \times 10^2$ and $3{\cdot}8 \times 10^3$ respectively. If the steric effect is important, the decarboxylation should be accelerated much more by the substitution of an additional relatively bulky ethylmercapto group.

(2) The rate enhancement ($1{\cdot}7 \times 10^3$) by the substitution of a phenylmercapto group in the mono-substituted acid (I–II) is comparable with that ($1{\cdot}3 \times 10^3$) of the phenylmercapto group in α,α′-diphenylmercaptoacetic acid (II–XVI). Usually the effect of steric strain is not additive in nature but appears suddenly in one marked change, this was not found to be the case.

(3) A large rate reduction was observed by the substitution of a Me group at the α-position of both diphenylmercaptoacetic acid (II) and diethylmercaptoacetic acid (VII). If steric strain is responsible for the rate-enhancement in the decarboxylation of these compounds, then a Me group at the α-position would increase the rate of decarboxylation, and not reduce it.

Therefore, it can be concluded that steric factors do not play any significant role in these decarboxylation reactions and the rate enhancement is due to the stabilization of the transition state by the 3d-orbital resonance effect of divalent sulphur in the carbanion forming reaction as seen in Eq. (1).

Comparison of sulphur and oxygen compounds. Decarboxylation rates of diphenylmercaptoacetic acid (II) and the corresponding oxygen analogue (X) shows that the sulphur compound (Table 2) decarboxylates about $8{\cdot}8 \times 10^3$ times faster than the oxygen analogue. Meanwhile, the p*Ka* values of diphenylmercapto- and diphenoxyacetic acids measured in 50% v/v aqueous ethanol are 4·12 and 3·64 respectively[5] and the rates of alkaline hydrolysis of the ethyl esters of phenylmercaptoacetic acid and phenoxyacetic acid in 80% aqueous alcoholic solution at 10° are 2·28 and 7·89 $l\,mol^{-1}\,.\,min^{-1}$ respectively.[6]

If the electron-withdrawing inductive effect alone increases the rate of decarboxylation, then this should be faster in the oxygen compound than in the sulphur analogue. As this is not the case, the easy decarboxylation of diphenylmercaptoacetic acid must be associated with the stabilization of the incipient carbanion formed in the rate-determining step of the reaction by the 3d-orbital resonance of the S atoms. If the greater inductive effect of the oxygen group is not operative, the difference in the rates would be much greater.

TABLE 2. THE COMPARISON OF THE RATES OF DECARBOXYLATION OF A FEW REPRESENTATIVE α-SUBSTITUTED ACETIC ACIDS AND THEIR ACID DISSOCIATION IN 50% V/V AQ. ALCOHOLIC SOLUTION

Compound		Temp (°C)	First-order rate constants, $k_1 \times 10^5$ (sec^{-1})	Relative rate[a]	pKa (25°)
$(PhS)_2CHCO_2H$	(II)	90	19·5	$1·9 \times 10^{3b}$	4·12 × 0·04
$(PhO)_2CHCO_2H$	(X)	160	3·41	0·73[b,c]	3·64 ± 0·03
$(EtS)_2CHCO_2H$	(VI)	160	4·65	1·00	4·52 ± 0·05
Cl_2CHCO_2H[d]	(XI)	115	16·8	$1·2 \times 10^2$	2·51 ± 0·04

[a] Relative rate at 90°.
[b] The relative rate of II to X at 160 is $8·8 \times 10^3$.
[c] Relative rate of VI at 160.
[d] $\Delta H^{\ddagger} = 28·8$ kcal/mole, $\Delta S^{\ddagger} = 0·1$ cal/deg.

A comparison of the effect of various electron-withdrawing substituents on the decarboxylation of disubstituted carboxylic acids, was made for the following substituents, ethylmercapto, phenylmercapto, phenoxy, chloro and phenyl groups. The phenylmercapto group has a greater rate-enhancing effect than ethylmercapto group. Thus, diphenylmercaptoacetic acid decarboxylates about $1·9 \times 10^3$ times faster than the diethylmercaptoacetic acid. Probably conjugation with the phenyl ring makes the S atom of the phenylmercapto group more positive in character than the ethylmercapto group. This brings about an orbital contraction of 3d-orbitals on the divalent S atom, thus facilitating a more pronounced overlapping between 3d-orbitals of the S atom and a 2p-orbital of the α-C atom in the developing carbanion from the former compound at the transition state. Another explanation may be that in the phenylmercapto substituted compound, the lone electron pair on the α-carbon of the developing carbanion enters into conjugation with Ph ring through the S atom using its 3d orbitals, thus giving the extra stabilization of the transition state complex. A choice between the two mechanisms could be made if the effect of substituents on the decarboxylation of the ring substituted arylmercapto carboxylic acids were known and this study is now underway.

A comparison of the rates observed in compounds (II and V) and (IV and XVI) shows that the carbanion-stabilizing ability of the phenylmercapto group almost equals that of the Ph group. Diphenoxyacetic acid and diethylmercaptoacetic acid decarboxylate at almost the same rate. Although O atom has no readily available d-orbital for resonance, the O atom attached to the Ph ring is more electronegative due to the stronger resonance with the Ph ring than the oxygen attached to an aliphatic group and, hence, the increased electron-withdrawing inductive character enhances the rate of the decarboxylation in diphenoxyacetic acid. The rate of the decarboxylation of dichloroacetic acid is midway between those of diphenylmercapto and diethylmercaptoacetic acids. The Cl atom is more electronegative than S and hence its electron-withdrawing inductive effect should be greater than that of the ethyl-

mercapto group. In fact, p*Ka* values of these compounds are 2·51 for dichloroacetic acid and 4·52 for diethylmercaptoacetic acid measured in 50% v/v aqueous ethanol. Moreover Cl atom has empty 3d-orbitals available for 3d-orbital resonance with an adjacent carbanion. If the strong electron-withdrawing inductive effect is not in operation, the rate-enhancing 3d-orbital resonance effect of the Cl atom would be about equal to that of ethylmercapto group in the carbanion-forming reaction.

The additivity of polar-resonance effect of an α-substituent. Usually the polar effect is additive in character, but "saturation" of the polar effect has frequently been observed when an α-carbon is substituted with an increasing number of polar substituents. For example, the difference in p*Ka* values of di- and trisubstituted chloroacetic acids is smaller than the difference between mono- and disubstituted chloroacetic acids.[7]

Here, the main factor responsible is the decreasing solvation around the dissociated carboxylate ion together with an increase in the steric hindrance by the substitution of Cl atoms at the α-carbon. A similar saturation effect has been observed in the acidity of trisubstituted methanes, bearing nitro, carbonyl[8] and phenyl groups.[9] In these cases the electron-withdrawing conjugative effect of nitro, carbonyl and phenyl groups is considered to be responsible for the higher acidity of these compounds. Substitution at the α-C atom by these groups reduces the resonance effect because the resulting carbanion is unable to assume coplanarity owing to steric inhibition by the increased number of substituents on the α-carbon. Incidentally, the cyano group, being of linear shape and small, does not show any "saturation" and should be additive in character.[8] As shown in Fig. 1, additivity is observed in the

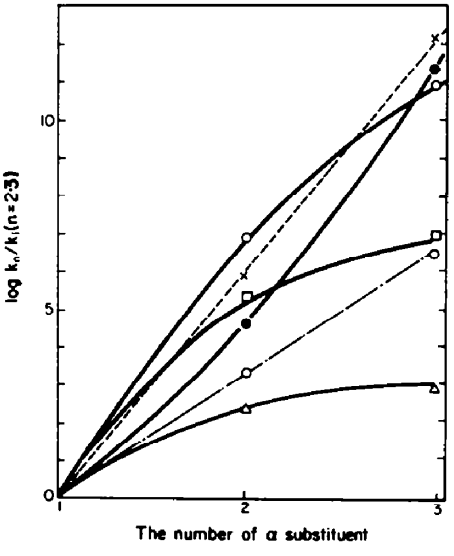


FIG. 1 The additivity of the carbanion stabilization effect of α-substituent in the base-catalysed decarboxylation, H–D exchange and the carbon acidity[9, 10]

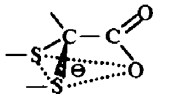
⊙ $(PhS)_nCH_{3-n}CO_2H$, decarboxylation of phenylmercaptoacetic acids at 90°

× —C≡N, ⊡ —$COCH_3$, ○ —NO_2 and ● —SO_2CH_3 for carbon acidity of α-substituted methane derivatives $XnCH_{4-n}$[9]

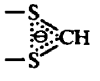
△ $LiNHC_6H_{11}$ catalyzed H–D exchange reaction of Ph-substituted methane,[10] $(Ph)_nCH_{4-n}$.

acidity of the cyano derivatives. Similarly, in the sulphur compounds, additivity is found in the carbanion-stabilizing effect of the mercapto groups because the steric requirement of coplanarity for the d-orbital resonance is lacking.[10] Even in the case of a bulky sulphonyl group, additivity in the polar effect of alkylsulphonyl group is observed due to the increasing acidity of the polymethylsulphonyl substituted methanes with an increasing number of substituents.[8] Therefore, in the decarboxylation of phenylmercapto substituted carboxylic acids, further substitution by the phenylmercapto group increases the rate of decarboxylation. In fact, α,α′-diphenylmercaptoacetic acid (II) reacts about $1{\cdot}7 \times 10^3$ times faster than phenylmercaptoacetic acid (I), while triphenylmercaptoacetic acid (XVI) decarboxylates $1{\cdot}3 \times 10^3$ times faster than the disubstituted compound (II). This result, illustrated in Fig. 1, clearly shows the additivity of the polar-resonance effect of the phenylmercapto group.

Effects of ring size and conformation. As can be seen in Table 3, there is no appreciable rate difference between acyclic and cyclic compounds. Although small, a regular increase in the rates of decarboxylation was found in the 5- (XII), 6- (XIII) and 7-membered (XV) cyclic acids, while the rate of the open chain compound (VI) is in between that of the 6- and 7-membered acids. This is unexpected in view of the marked difference in the rates of the base-catalysed hydrogen isotopic exchange reaction of cyclic mercaptals.[1] Here the 5-membered compound is substantially more reactive than the 6- and 7-membered compounds which in turn are more reactive than the open chain compound. A special acidifying effect involving 3p–3d orbital sulphur-sulphur non-bonding interaction like "B" probably accounts for the difference, and in this connection a few interesting points are worthy of consideration. If the acidity of the carboxylic acid is a direct measure of the effect of the polar substituents, then the 6- and the 7-membered compounds should decarboxylate more readily than the 5-membered and the open chain carboxylic acids, since the p*Ka* values of the open chain compound (VI), the 5- (XII), 6- (XIII) and 7-membered (XV) acids are 4·52, 4·46, 4·27 and 4·27 respectively in 50% v/v aqueous ethanol solution. The results, however, are complicated. As it has been suggested that the dissociated carboxylate ion is the main species to decarboxylate,[2] then a non-bonding 2p–3d interaction between the carboxylate oxygen and the two S atoms in a dipolar and aprotic solvent such as DMSO, as shown by the structure (A), would retard the rate of decarboxyla-



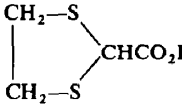
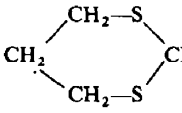
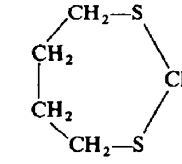
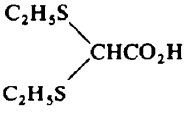
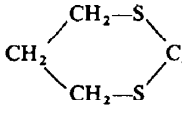
(A)



(B)

tion, since the non-bonding interaction would stabilize the carboxylate ion in the ground state. Perhaps, this interaction is most effective in the 5-membered compound, followed by 6-, 7-membered and the open chain compounds. The stabilization of the ground state of the 5-membered compound could easily cancel out the special stabilization effect of the incipiently developing carbanion by the favourable 3p–3d orbital resonance (B).[1] These two opposing effects may operate jointly in the decarboxylation of these cyclic dimercapto-carboxylic acids to give only small differences in the rates of the decarboxylation. A careful study of the UV spectra of these compounds in both acidic and alkaline media suggests such a non-bonding interaction for the carboxylate ion.[11]

TABLE 3. THE EFFECT OF RING SIZE ON DECARBOXYLATION

Compound	Temp (°C)	First-order rate constants $k_1 \times 10^5$ (sec^{-1})	Relative rate	pKa^a (25°)
 (XII)	160	2·18	0·47	4·64 ± 0·04
 (XIII)	160	3·75	0·81	4·27 ± 0·05
 (XV)	160	7·94	1·7	4·27 ± 0·04
 (VI)	160	4·65	1·00	4·52 ± 0·05
 (XIV)	160	1·52	0·33	4·83 ± 0·04

[a] In 50% v/v aqueous ethanol.

EXPERIMENTAL

The preparation of triethyl- and triphenyl-mercaptoacetic acids. Into a soln of 3·2 g ethyl diethylmercaptoacetate in 15 ml n-hexane, 2·3 g SO_2Cl_2 dissolved in 15 ml n-hexane was added portionwise during 10 min, and the final mixture refluxed for 30 min. Removal of the solvent *in vacuo* gave a pale yellow residue, which was dissolved in 10 ml abs ether, into which 1·4 g ethylmercaptan dissolved in 5 ml abs ether was added at once and the mixture refluxed for 1 hr. The reaction mixture was washed with dil Na_2CO_3 aq and then with water, dried over Na_2SO_4, concentrated and finally vacuum-distilled to give a colourless oil, 3·5 g b.p. 135/1 mm Hg. The NMR spectra of this ester showed three quartet peaks at 4·20, 2·68 and 1·30 ppm (TMS external standard) corresponding to 2, 6 and 12 protons respectively. (Found: C, 45·15; H, 7·49. Calc. for $C_{10}H_{20}O_2S_3$: C, 44·74; H, 7·51%). The above ester (3·4 g) was hydrolysed in 20 ml anhyd ether mixed with 1·5 g KOH. The usual work up and vacuum distillation gave a pale yellow oil, b.p. 65–67/0·05 mm Hg. This acid is rather unstable and therefore, kept in N_2 atmosphere at 0°.

The synthesis of XVI was carried out by carbonating the anion of the corresponding triphenyl-orthothioformate in DMSO.[12] The crude crystals were recrystallized 3 times from $CHCl_3$ n-hexane as slightly brown coloured crystals yielding of a compound 40%. This compound is stable at room temp and decarboxylates at 108–109°. (Found: C, 62·77; H, 4·33. Calc. for $C_{20}H_{16}O_2S_3$: C, 62·47; H, 4·19%), m.p. 108–109° (dec).

The syntheses and the properties of carboxylic acids other than VIII and XVI have been described.[5, 12]

Kinetics. The concentrations of carboxylic acids and triethanolamine used in each kinetic run are 0·01M and 0·1M respectively. The kinetic procedures and the treatment of the data have been described for all the acids except IV, VIII and XVI.[2] These three compounds required some modification for kinetics

due to the rapidity of the reaction. In the case of compounds IV and XVI, kinetic measurement was done as follows: DMSO soln 50 ml containing 25×10^{-3} moles triethanolamine was kept in a reaction flask under N_2 at kinetic temp for 1 hr. Then, the sample crystals, $0{\cdot}5 \times 10^{-3}$ moles, were put directly into the reaction flask to start the reaction.

The subsequent assay of CO_2 evolved was carried out by the method using the apparatus described in the previous paper.[2] Triethylmercaptoacetic acid could only be purified through its ester, and the free acid was found to decompose during distillation, the decomposition taking place even during storage at 0°. Hence the amount of acid used was determined by titration with standard NaOH soln just before the kinetic run. The subsequent procedure was similar to that used for other compounds.

The relative rates shown in Table 1, 2 and 3 were calculated by extrapolating the observed rate constants to 90° with each activation energy. The observed rate constants are as follows.

$k_1 \times 10^4$ (sec^{-1})

0·475, 0·672, 0·950 (at 160, 165, 170) for VI
0·083, 0·14, 0·22 (at 160, 170, 180) for I
1·17, 1·95, 3·85 (at 85, 90, 95) for II
1·24, 3·82, 11·6 (at 80, 90, 100) for V
4·12, 7·38, 10·9 (at 10, 15, 20) for XVI
6·93, 10·4, 14·7 (at 10, 15, 20) for IV
1·05, 1·68, 2·85 (at 110, 115, 120) for XI

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