same and, in at least one instance (HCN, DCN),[14] this is borne out by the experimental results.

Since the same value of $\alpha\epsilon$ can be used for bonds where the degrees of hybridization of one of the bonding AO's are different (HCl, H—C≡CH it suggests that only the gross directional properties of the bonding AO's are important in defining $\alpha\epsilon$. This is reasonable if we remember that the overlap moment depends on electronegativity to a large extent[15] and we consider α as a correction factor for the overlap moment of the bond. The change of overlap moment with hybridization is then accounted for by the change of the electronegativity of the atom with hybridization,[9] giving correct BDM's though α remains constant.

Only a limited number of BDM's have been determined from infrared intensity data and some of these are collected together in Table III and compared with the calculated values from equation 1. On the basis of this comparison the dynamic BDM most closely approximating the static BDM can be selected. In the event that the dynamic BDM's have been obtained from different symmetry species this comparison indicates in which symmetry species the orbital following is a maximum and bond–bond interaction on bending a minimum, since it is just this symmetry species, on the simple theory used, which would have a dynamic BDM most closely approximating the static value.[16]

TABLE III

COMPARISON OF BDM'S FROM INFRARED INTENSITY DATA WITH THE CALCULATED VALUES

Bonding[a] AO's	Molecule	r_e	$\mu_{\text{calcd.}}$[b]	$\mu_{\text{obsd.}}$[c]
p, p	BF_3	1.30	1.36	1.7 (0.9, 2.16)[d]
	SF_6	1.58	0.76	0.65 (2.65)[e]
	S_1F_4	1.565	1.92	2.3 (3.3)[e]
	CF_4	1.326	0.76	1.12 (2.36)[e]
	CF_3CF_3	1.326	1.00	1.07 (1.49)[f]

[a] Gross directional property of the bonding AO's (see text). [b] Calculated with $\alpha\epsilon = 2.08$ (for p,p bonding AO's) and using group electronegativities.[9] [c] The value not within the brackets is considered to approximate the static bond dipole moment most closely. [d] D. C. McKean, *J. Chem. Phys.*, **24**, 1002 (1956). [e] P. N. Schatz and D. F. Hornig, *ibid.*, **21**, 1516 (1953). [f] D. G. Williams, W. B. Person and B. Crawford, Jr., *ibid.*, **23**, 179 (1955).

---

(14) G. E. Hyde and D. F. Hornig, *ibid.*, **20**, 647 (1952).

(15) H. O. Pritchard, *Disc. Faraday Soc.*, **19**, 276 (1955).

(16) D. McKean and P. Schatz, *J. Chem. Phys.*, **24**, 316 (1956).

THE DECARBOXYLATION OF OXALIC ACID IN 6-METHYLQUINOLINE AND IN 8-METHYLQUINOLINE

BY LOUIS W. CLARK

Contribution from the Department of Chemistry, Saint Joseph College, Emmitsburg, Maryland

Received December 26, 1957

The decomposition of oxalic acid has been studied previously in eight non-aqueous solvents.[1] If these solvents are arranged in the order of decreasing enthalpy of activation for the oxalic acid decomposition they fall in the same order as they do for the malonic acid decomposition, with the single exception of dimethyl sulfoxide.[2] These results strongly suggest that the mechanism for the decomposition of oxalic acid in these solvents (dimethyl sulfoxide excepted) is similar to that for malonic acid. They suggest further that the mechanism for the decomposition of oxalic acid in dimethyl sulfoxide must be different from that for the decomposition in the other solvents studied. Other unstable organic acids have been observed to undergo decomposition of the un-ionized acid in solvents of weak ionizing power, and to decompose by an anion mechanism in more strongly basic solvents.[3–5] Furthermore, Dinglinger and Schober have shown that, in aqueous solution, the acid oxalate ion decomposes more slowly than the diacid.[6] Since oxalic acid is a stronger acid than malonic acid, and since dimethyl sulfoxide is the most strongly ionizing of any of the eight solvents in which the oxalic acid decomposition has been studied, the possibility of the ionization of oxalic acid was indicated in this case. In order to test this suggestion experiments have been conducted in this Laboratory on the decomposition of oxalic acid in another solvent comparable in ionizing power to dimethyl sulfoxide, namely, 8-methylquinoline, and also in an isomer of this substance, namely, 6-methylquinoline.

Experimental

Reagents.—(1) Oxalic acid, anhydrous, analytical reagent grade, assay 100.0%; (2) 6-methylquinoline, highest purity grade, b.p. 129–130° (15 mm.); (3) 8-methylquinoline, highest purity grade, b.p. 112–114° (8 mm.). Constant boiling fractions of each solvent were collected at atmospheric pressure directly in the reaction flask immediately before the beginning of each decarboxylation experiment.

Apparatus and Technique.—The kinetic experiments were conducted in a constant temperature oil-bath by measuring the volume of CO_2 evolved at constant pressure, as described in a previous paper.[7] The temperature of the oil-bath was measured by means of a thermometer calibrated by the U. S. Bureau of Standards. In each experiment a 0.1605-g. sample of oxalic acid (the amount required to produce 40.0 ml. of CO_2 at STP on complete reaction) was introduced in the usual manner into the reaction flask containing approximately 50 ml. of solvent which had been previously saturated with dry CO_2 gas.

Results and Discussion

The decarboxylation of oxalic acid was studied in each solvent at four different temperatures over a 20° temperature interval. When the corrected volumes of CO_2 were plotted against time and graphs made of log $(a - x)$ *vs.* t (where a is the maximum theoretical yield of CO_2 and x is the volume evolved in the time t) from representative points on the smoothed experimental plots, straight lines were obtained for the first 80% of the reaction. No change in rate was observed at the same temperature on changing the volume of the solvent from 40 to 60 ml. The decomposition of oxalic acid in these solvents is therefore *pseudo*-first order. Rate constants were determined from the slopes. These values are listed in Table I.

(1) L. W. Clark, THIS JOURNAL, **61**, 699 (1957).

(2) L. W. Clark, *ibid.*, **62**, 79 (1958).

(3) G. A. Hall, *J. Am. Chem. Soc.*, **71**, 2691 (1949).

(4) K. J. Pedersen, *ibid.*, **51**, 2098 (1929).

(5) G. Fraenkel, R. L. Belford and P. E. Yankwich, *ibid.*, **76**, 15 (1954).

(6) A. Dinglinger and E. Schöber, *Z. physik. Chem.*, **A179**, 401 (1937).

(7) L. W. Clark, THIS JOURNAL, **60**, 1150 (1956).

TABLE I

APPARENT FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION OF OXALIC ACID IN 6-METHYLQUINOLINE AND IN 8-METHYLQUINOLINE AT VARIOUS TEMPERATURES

Solvent	Temp., °C. cor.	$k \times 10^5$, sec.$^{-1}$
6-Methylquinoline	152.75	47.6
	160.57	81.5
	165.90	133
	173.00	240
8-Methylquinoline	154.20	42.2
	158.42	65.2
	164.50	124
	170.00	212

Arrhenius plots of the data in Table I yielded straight lines for both solvents, from which activation energies were calculated. For the decarboxylation of oxalic acid in 6-methylquinoline E^* is 33.14 kcal., and A is 5.89×10^{13}; in 8-methylquinoline E^* is 38.45 kcal., and A is 2.3×10^{16}.

According to the transition state theory, for the decarboxylation of oxalic acid in 6-methylquinoline $\Delta H^{\ddagger}$ is 32.26 kcal., and $\Delta S^{\ddagger}$ is +1.22 e.u.; in 8-methylquinoline $\Delta H^{\ddagger}$ is 37.65 kcal., and $\Delta S^{\ddagger}$ is +13.65 e.u.

Values of $\Delta H^{\ddagger}$ for the decarboxylation of oxalic acid in all the non-aqueous solvents reported to date in the literature as well as in the two solvents included in the present investigation are shown in Table II along with corresponding data for the decarboxylation of malonic acid. The data are arranged in the order of decreasing $\Delta H^{\ddagger}$ in the case of malonic acid.

TABLE II

ENTHALPIES OF ACTIVATION FOR THE DECARBOXYLATION OF OXALIC ACID AND MALONIC ACID IN VARIOUS SOLVENTS

Solvent	ΔH^{+} (kcal.) Malonic acid	ΔH^{+} (kcal.) Oxalic acid
Aniline	26.9[2]	40.71[1]
Quinoline	26.74[8]	39.0[1]
N-Methylaniline	26.6[9]	35.5[1]
N,N-Dimethylaniline	26.2[9]	32.6[1]
6-Methylquinoline	26.15[8]	32.26[a]
Triethyl phosphate	26.1[7]	28.85[1]
Dioxane		28.58[6]
Glycerol	24.6[10]	26.4[11]
8-Methylquinoline	24.44[8]	37.65[a]
Dimethylsulfoxide	22.3[10]	40.5[1]

[a] Data obtained in the present investigation.

It will be seen in Table II that the order of decreasing $\Delta H^{\ddagger}$ for oxalic acid is the same as that for malonic acid down to and including glycerol, that is, for the first eight solvents listed. For the decomposition of oxalic acid in 8-methylquinoline and in dimethyl sulfoxide the $\Delta H^{\ddagger}$ values are out of line with those for the decomposition of malonic acid in these solvents. In the solvents listed in Table II the un-ionized diacid appears to be involved in the case of malonic acid. In the case of oxalic acid, the un-ionized diacid appears to be involved in all the solvents down to and including glycerol. Since 8-methylquinoline and dimethyl sulfoxide are the most efficient ionizing solvents included in Table II and, furthermore, since in these two solvents the $\Delta H^{\ddagger}$ values are out of line with the rest, it is not improbable that ionization of oxalic acid is involved in these two solvents.

A comparison of the entropy values for the reactions of the two acids in the different solvents is of interest in this connection. For the decomposition of oxalic acid in 6-methylquinoline $\Delta S^{\ddagger}$ is +1.22 e.u.; in 8-methylquinoline $\Delta S^{\ddagger}$ is +13.65 e.u. The steric effect of the methyl group in the 8-position is much greater than that of the methyl group in the 6-position, and it would therefore be expected that $\Delta S^{\ddagger}$ for 8-methylquinoline would be smaller than for 6-methylquinoline if the undissociated diacid mechanism is involved. (For malonic acid $\Delta S^{\ddagger}$ in 6-methylquinoline is −3.02 e.u. and in 8-methylquinoline it is −10.47 e.u.[8]). The fact that the reverse is true for oxalic acid suggests that coördination between oxalic acid and solvent no longer obtains in 8-methylquinoline. If ionization and not coördination is involved there would be no steric interference with the formation of the activated state by the methyl group in the 8-position. In the decomposition of malonic acid $\Delta S^{\ddagger}$ decreases from −3.55 e.u. in 6-methylquinoline to −15.0 e.u. in dimethyl sulfoxide, whereas in the case of oxalic acid $\Delta S^{\ddagger}$ *increases* from +1.22 e.u. in 6-methylquinoline to +20.23 e.u. in dimethyl sulfoxide.[6] It would appear therefore that in dimethyl sulfoxide also the decomposition of oxalic acid is not affected sterically in the manner which would be predicted on the basis of the undissociated diacid mechanism.

Further confirmation of the view that 8-methylquinoline promotes the ionization of oxalic acid was afforded by the observation of an anomaly in the experiments with this solvent. During the first minute or two after adding the capsule to the reaction flask there was a rather rapid evolution of CO_2 which quickly slowed down and continued at a smooth rate until the stoichiometric volume of gas was evolved. Zero time was extrapolated from the first 10% of the reaction. It would thus appear that when the oxalic acid first dissolved in the solvent it was in a completely un-ionized form, and a brief period of time was required for ionization to become complete. No such phenomenon was observed in the experiments in 6-methylquinoline.

Acknowledgments.—The support of this research by the National Science Foundation, Washington, D. C., is gratefully acknowledged. Miss Dolores Sicilia assisted in purification of the reagents and running the kinetics experiments.

A LAW FOR THERMAL EXPANSION OF NORMAL LIQUIDS

BY J. F. DUGGAR, JR.

Contribution from Georgia State Chemical Laboratory, Atlanta, Georgia

Received December 2, 1957

A law for thermal expansion of normal liquids has been derived by solving the modified Eötvös equation with the van der Waals equation. It was

---

(8) L. W. Clark, *ibid.*, **62**, 500 (1958).

(9) L. W. Clark, *ibid.*, **61**, 1575 (1957).

(10) L. W. Clark, *ibid.*, **60**, 825 (1956).

(11) L. W. Clark, *J. Am. Chem. Soc.*, **77**, 6191 (1955).