

neutral molecule, but the reaction should be one of general occurrence.

In addition to this reaction the transformation of ND_3H^+ to ND_4^+ means that exchange between the protonated molecule ion, ND_4^+ , and the neutral molecule of another species, CH_4 , is very slow; that is, reaction 17 does not occur.



The ions at m/e 41 and 42 were doublets for which the lower components, C_3H_5^+ and $\text{C}_3\text{H}_6^+ + {}^{13}\text{C}^{12}\text{C}_2\text{H}_5^+$, passed through maxima in relative concentrations and then decreased with increasing pressure; the higher components, $\text{N}_2\text{D}_6\text{H}^+$ and N_2D_7^+ , became appreciable only at the highest pressures. Thus, the reaction of C_3H_5^+ and the existence of the higher ammoniated protons are both clearly established.

The relative concentration of C_3H_7^+ is much lower in this mixture than in pure methane: maximum abundance of 0.4% compared with 2–3%. Since, in addition, this small relative concentration of C_3H_7^+ passes

through a maximum with increasing pressure, proton transfer occurs for this ion as well.

There were two product ions of reasonable abundance which probably are C,N species: m/e 49, $\text{C}_2\text{H}_5\text{ND}_3^+$, and m/e 61, $\text{C}_3\text{H}_5\text{ND}_3^+$. Both ions are present to the extent of 3–4% of the total ionization at the highest pressures, but their structure and origin cannot be established conclusively.

Ammonia is, therefore, a very efficient proton-transfer agent and should have marked effects on ionic processes with little effect on radical processes. The present observation that small concentrations of ammonia have a major effect on the ionic distribution in methane at 2 torr is very good support for the suggestion³ that the very large inhibitory effect of traces of ammonia on the radiation-induced polymerization of cyclopentadiene in the liquid phase was the result of proton transfer from the hydrocarbon ions.

Acknowledgment. The authors are very grateful to Mr. W. C. Gieger for performing these experiments with his accustomed skill. This work was supported in part by Project SQUID under Contract Nonr. 3623 (S-18).

Equilibrium and Kinetic Studies of the Deprotonation of the Monoanion of Several Dicarboxylic Acids in Water and in Deuterium Oxide¹

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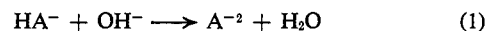
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received June 11, 1965

The rate constant for the rapid abstraction by hydroxide ion of a proton from the monoanion of three alkyl-substituted succinic acids varies inversely as the ratio of the acid dissociation constants K_{a1}/K_{a2} . These data confirm the generality of this result found previously for a series of 2,2-disubstituted malonic acids and for three cis-3,3-disubstituted cyclopropane-1,2-dicarboxylic acids. Acid dissociation constants and rate constants for the proton abstraction have also been determined in D_2O for the three cyclopropane acids as well as for the three succinic acids. These isotopic data as well as acid dissociation constants for the monomethyl esters of these acids are consistent with the interpretation that the breaking of an intramolecular hydrogen bond in the monoanion is rate determining although these data cannot conclusively establish the presence of such an intramolecular hydrogen bond.

(1) (a) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant AF-AFOSR-476-64, the National Institute of Arthritis and Metabolic Diseases Grant AM-06231, and the University of Utah Research Fund; (b) presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

Introduction

Recent temperature-jump kinetic studies^{2–5} have shown that the rate constant in aqueous solution for the reaction



where HA^- denotes the monoanion of three different cis-cyclopropane-1,2-dicarboxylic acids and also of a series of 2,2-dialkylmalonic acids, is inversely proportional to the ratio of the acid dissociation constants, K_{a1}/K_{a2} , for these acids. The dependence of the measured relaxation times on pH, sample acid concentration, and ionic strength have established beyond doubt the identity of the reaction being observed. However, these kinetic data do not permit a description of bonding of the acid hydrogen in the HA^- ion.

(2) M. Eigen and W. Kruse, *Z. Naturforsch.*, **18b**, 857 (1963).

(3) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, **2**, 285 (1964).

(4) J. L. Haslam, E. M. Eyring, W. W. Epstein, G. A. Christiansen, and M. H. Miles, *J. Am. Chem. Soc.*, **87**, 1 (1965).

(5) M. H. Miles, E. M. Eyring, W. W. Epstein, and R. E. Ostlund, *J. Phys. Chem.*, **69**, 467 (1965).

Table I. Thermodynamic Acid Dissociation Constants^a at 25° in Water and Deuterium Oxide

Acid	pK ₁ ^T			pK ₂ ^T		
	Water	D ₂ O	ΔpK ₁ ^T	Water	D ₂ O	ΔpK ₂ ^T
Spiro[cyclopropane-1,9'-fluorene]- <i>cis</i> -2,3-dicarboxylic	2.98 ^b	3.44 ± 0.05	0.46	6.78 ^b	7.14 ± 0.02	0.36
<i>cis</i> -Caronic	2.38 ^b	3.04 ± 0.03	0.66	8.25 ^b	8.57 ± 0.03	0.32
<i>cis</i> -3,3-Diphenylcyclopropane-1,2-dicarboxylic	2.30 ^b	2.58 ± 0.06	0.28	9.20 ^b	9.57 ± 0.02	0.37
Tetramethylsuccinic	3.56 ^c	4.20 ^c	0.64	7.41 ^c	7.75 ^c	0.34
Tetraethylsuccinic	3.39 ^c	4.29 ^c	0.90	8.06 ^c	8.50 ^c	0.44
<i>rac</i> -α,α'-Di- <i>t</i> -butylsuccinic	2.20 ^c	2.77 ^c	0.57	10.25 ^c	10.92 ^c	0.67
Monomethyl ester		pK _E ^H		pK _E ^D	ΔpK _E	K ₁ ^H /K ₂ ^H
Spiro[cyclopropane-1,9'-fluorene]- <i>cis</i> -2,3-dicarboxylic		3.78 ± 0.04		4.62 ± 0.03	0.84	6.32
<i>cis</i> -3,3-Diphenylcyclopropane-1,2-dicarboxylic		4.43 ± 0.04		5.17 ± 0.03	0.74	1.34 × 10 ²

^a K₁^T = [H⁺][HA⁻]/[H₂A]; K₂^T = [H⁺][A⁻²]/[HA⁻]. ^b Reference 4. ^c Reference 10.

Large values of K_{a1}/K_{a2} have been ascribed primarily to the presence of an intramolecular hydrogen bond in the monoanion of these substituted dicarboxylic acids.⁶ Temperature-dependence studies of the kinetics of reaction 1 and the reverse reaction have yielded values of E_a , ΔH^* , and ΔS^* which suggest that a melting of approximately two to four solvent molecules frozen about the dianion occurs in reaching the activated complex as the reaction proceeds from dianion back to monoanion.^{4,5} While these results are not inconsistent with the intramolecular hydrogen bond model of the monoanion, they clearly do not prove its validity. To better understand the behavior of these dicarboxylic acids, we have made a temperature-jump rate study of reaction 1 for three substituted succinic acids in water and have found, as will be shown below, that here again the rate constant is inversely proportional to K_{a1}/K_{a2} . We have also measured rate constants for reaction 1 for the succinic and cyclopropane acids in deuterium oxide solvent. The experimental kinetic isotope effect for all the acids is comparatively small with no pronounced trends.

Experimental Section

The preparation of *cis*-caronic acid (*cis*-3,3-dimethylcyclopropane-1,2-dicarboxylic acid), *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid, and spiro[cyclopropane-1,9'-fluorene]-*cis*-2,3-dicarboxylic acid have all been described previously.⁴

The monomethyl ester of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid was prepared by the method of Ebersson,^{7a} m.p. 129–130°, neut. equiv. 296 (found 290). The monomethyl ester of spiro[cyclopropane-1,9'-fluorene]-*cis*-2,3-dicarboxylic acid was prepared in a similar manner using acetic anhydride instead of acetyl chloride, m.p. 156–158°, neut. equiv. 294 (found 289).

Approximately 1 g. of *rac*-α,α'-di-*t*-butylsuccinic anhydride was generously supplied by Dr. Lennart Ebersson. We have synthesized tetramethylsuccinic acid and tetraethylsuccinic acid using techniques reported by Ebersson.^{7b}

Heavy water (99.7%) was obtained from Columbia Organic Chemicals. The purity of this D₂O was checked using a quantitative n.m.r. technique.⁸ D₂O

(6) For a bibliography see L. Ebersson and I. Wadsö, *Acta Chem. Scand.*, **17**, 1552 (1963).

(7) (a) L. Ebersson, *ibid.*, **13**, 211 (1959); (b) *ibid.*, **13**, 40 (1959).

(8) "This is NMR at Work," Varian Associates, Palo Alto, Calif., No. 57 of the Varian series.

of less than 98% purity was rejected for these studies.

Our temperature-jump and potentiometric titration techniques were the same as previously described.^{4,5} The titrations in D₂O were carried out with 0.104 and 0.0103 *N* NaOD standardized both by potentiometric titration and titration to the phenol red end point using potassium hydrogen iodate.

Results and Discussion

Equilibrium Data. In Table I we have assembled thermodynamic acid dissociation constants K_a^T for the monoanion of all our sample acids in water and in D₂O. To convert some of these constants back to the mixed dissociation constants K_a^M that we reported previously for the *cis*-cyclopropane-1,2-dicarboxylic acids in water,⁴ one would use, for instance, the relation^{9,10}

$$pK_{a_2}^T = pK_{a_2}^M - 3 \log \gamma_{\pm} = \text{pH} + \log \frac{[\text{HA}^-]}{[\text{A}^{-2}]} - 3 \log \gamma_{\pm} \quad (2)$$

where γ_{\pm} is the activity coefficient of hydronium ion calculated from Debye-Hückel theory, [HA⁻] is the equilibrium concentration of monoanion, etc.

Let us denote pK_a^T of the monoanion of a dibasic acid in water by pK_2^H and similarly in D₂O by pK_2^D . It has been noted previously that the quantities $pK_2^D - pK_2^H \equiv \Delta pK_2$ and $pK_1^D - pK_1^H \equiv \Delta pK_1$ for "normal" acids such as oxalic, fumaric, and benzoic acids are roughly 1/2 and in a plot of ΔpK vs. pK^H lie near a straight line of slope 0.02.¹¹

Long and co-workers^{12,13} have found abnormally high values of ΔpK_1 and abnormally low values of ΔpK_2 for maleic acid, the monoanion of which is thought to be strongly intramolecularly hydrogen bonded on the basis of its ratio¹⁴ $K_{a1}/K_{a2} = 2 \times 10^4$. As is evident from Table I, all three of the *cis*-cyclopropanedicarboxylic acids have $\Delta pK_2 \approx 0.35$. Their values of pK_1 are more irregular. Since K_{a1}/K_{a2} for spiro[cyclopropane-1,9'-fluorene]-*cis*-2,3-dicarboxylic

(9) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 55 ff.

(10) P. K. Glasoe and L. Ebersson, *J. Phys. Chem.*, **68**, 1560 (1964).

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 189.

(12) G. Dahlgren, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **82**, 1303 (1960).

(13) A. O. McDougall and F. A. Long, *J. Phys. Chem.*, **66**, 429 (1962).

(14) W. L. German, G. H. Jeffery, and A. I. Vogel, *Phil. Mag.*, **22**, 790 (1936).

Table II. Comparison of Rate Constants for the Reaction $\text{HA} + \text{OH}^- \xrightarrow{k_{23'}} \text{A}^- + \text{H}_2\text{O}$ in water ($\mu = 0.1 M$) at 25°

HA \equiv monoanion of	$k_{23'}$ (uncor.), ^a $M^{-1} \text{ sec.}^{-1}$	$k_{23'}$ (α cor.), ^a $M^{-1} \text{ sec.}^{-1}$	$k_{23'}$ (eq. 7), $M^{-1} \text{ sec.}^{-1}$
<i>cis</i> -3,3-Diphenylcyclopropane-1,2-dicarboxylic acid	$(3.61 \pm 0.57)10^6$	$(4.30 \pm 0.55)10^6$	$(4.29 \pm 0.32)10^6$
<i>cis</i> -Caronic acid	$(4.76 \pm 0.84)10^7$	$(5.49 \pm 0.66)10^7$	$(5.36 \pm 0.66)10^7$

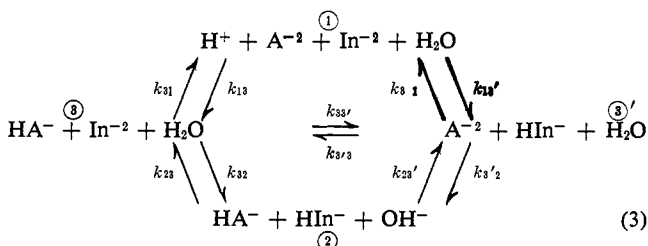
^a Calculated from eq. 5 and 6 of the text, respectively, and earlier experimental data. Reported previously in Table II of ref. 4.

acid is comparatively small, its failure to conform to the pattern of maleic acid is not surprising. The conformity of *cis*-caronic acid but not *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid to the "abnormal" pattern of maleic acid is made more interesting by some other recently observed examples. A "normal" deuterium effect has been observed for diethylmalonic, ethylisopropylmalonic, and *rac*- α, α' -di-*t*-butylsuccinic acids in spite of large values of K_{a1}/K_{a2} for each acid.^{10,15} The complexity of these results suggests that several factors contribute to the observed ΔpK values.

The thermodynamic acid pK_E^T values of the mono-methyl esters of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid and spiro[cyclopropane-1,9'-fluorene]-*cis*-2,3-dicarboxylic acid at 25° in water and in D_2O are also reported in Table I. Following Westheimer and Benfey¹⁶ we have used the dissociation constants of the acids and their monoesters to calculate the percentage of the monoanion present in the intramolecularly hydrogen-bonded form. In water at 25° the monoanion of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid is 98.5% intramolecularly hydrogen bonded according to this point of view. This result is consistent with the approximation made in our earlier kinetic calculations⁴ that the monoanion of this acid is entirely intramolecularly hydrogen bonded in aqueous solution.

A similar calculation for the spiro acid using the data of Table I indicates that the monoanion of this acid is 68% intramolecularly hydrogen bonded. Earlier⁴ we assumed that these spiro acid monoanions were 100% intramolecularly hydrogen bonded, but the bonds were uniformly very weak. A 68% value implies that our rate constants for reaction 1 reported previously⁴ for this acid are too low, but by a factor of not more than two. This uncertainty in the rate constants for the spiro acid precludes the inclusion of this acid in our kinetic deuterium isotope effect calculations below.

Kinetic Data. The complete reaction scheme for our temperature-jump sample solution is¹⁷



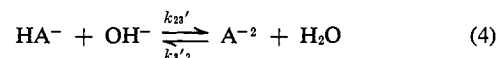
where in the case of *rac*- α, α' -di-*t*-butylsuccinic acid, for instance, HA^- denotes the monoanion of this acid

(15) P. K. Glasoe and J. R. Hutchison, *J. Phys. Chem.*, **68**, 1562 (1964).

(16) F. H. Westheimer and O. T. Benfey, *J. Am. Chem. Soc.*, **78**, 5309 (1956).

(17) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

and In^{-2} denotes the colored dianion of the acid-base indicator phenolphthalein. For pH greater than approximately 8.3 and a total indicator concentration $c_0' = 10^{-5} M$, we may calculate the rate constants $k_{23'}$ and $k_{3'2}$ of the equilibrium



from the experimentally determined relaxation time τ and one of the following eq. 5, 6, and 7

$$k_{23'}(\text{uncor.}) = \tau^{-1} \left([\text{HA}^-] + [\text{OH}^-] + \frac{K_W}{\gamma_{\text{H}^+} K_{a_2} M} \right)^{-1} \quad (5)$$

$$k_{23'}(\alpha \text{ cor.}) = \tau^{-1} \left(\frac{[\text{HA}^-]}{[\text{H}^+] + \alpha} + [\text{OH}^-] + \frac{K_W}{\gamma_{\text{H}^+} K_{a_2} M} \right)^{-1} \quad (6)$$

where

$$\alpha = \frac{[\text{HIn}^-]}{[\text{OH}^-] \left(1 + \frac{[\text{HIn}^-]}{[\text{In}^{-2}]} \right)}$$

or

$$k_{23'} = \frac{\frac{1}{\tau_2} - \frac{1}{\tau} A + B}{\frac{1}{\tau} C + D} \quad (7)$$

where

$$A = k_{33'}([\text{HA}^-] + [\text{In}^-]) + k_{3'3}([\text{A}^{-2}] + [\text{HIn}^-]) + k_{32} + k_{23}([\text{OH}^-] + [\text{HIn}^-])$$

$$B = k_{23}[\text{HIn}^-] \{ k_{33'}([\text{HA}^-] + [\text{In}^-]) + k_{3'3}([\text{A}^{-2}] + [\text{HIn}^-]) \} + (k_{32} + k_{23}[\text{OH}^-]) (k_{33'}[\text{In}^{-2}] + k_{3'3}[\text{HIn}^-])$$

$$C = [\text{HA}^-] + [\text{OH}^-] + K_W/\gamma_{\text{H}^+} K_{a_2} M$$

$$D = (C - [\text{HA}^-]) (k_{33'}[\text{In}^{-2}] + k_{3'3}[\text{HIn}^-]) - k_{23}[\text{HIn}^-] - C(A - k_{23}[\text{HIn}^-])$$

Equation 5 is obtained from eq. 3 by considering only the step (2 \rightarrow 3'). Under the conditions of some of our experiments, viz. pH near 7 or high indicator concentration, such an approximation is not justified. The α -corrected expression, eq. 6, attempts to take account of the proton exchange, but the approximations made early in the derivation of this equation are apparently such that when α becomes significant the rate constants are "over corrected." Equation 7 represents a rigorous treatment of the system 3. Table II compares rate constants calculated from the same set of a dozen experiments from each of the three equations for two of our acids. Since data for which α was large were excluded, the rate constants are the same within experimental error.

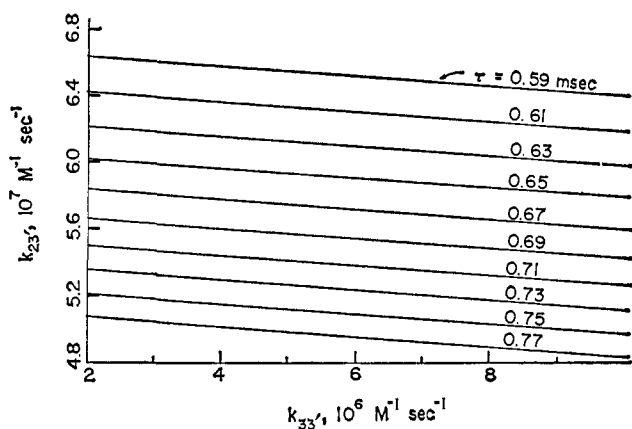


Figure 1. Rate constant k_{23}' at 25° in 0.1 M ionic strength D_2O solution of *cis*-caronic acid, $c_0 = 5 \times 10^{-4} M$, for abstraction of a proton from monoanion by hydroxide ion plotted vs. k_{33}' , the *cis*-caronic acid monoanion-phenolphthalein dianion proton exchange rate constant, as a function of relaxation time τ : k_{23}' calculated on IBM 7040 computer from eq. 7, pH 9.79, $c_0' = 1 \times 10^{-5} M$.

Equation 7 was obtained from Eigen's¹⁷ eq. 16 by taking the negative root of the square term. This choice is dictated by the nature of (3) above wherein (2 \rightarrow 3) is very fast compared to the other steps, and hence the measured relaxation time corresponds to the slower rates. In applying eq. 7, one is required to know both k_{23} and k_{33}' . The value of k_{23} can be measured directly,³ but in many cases, *viz.* for those acids with $pK_{a_2}^M$ greater than about 8.7, the value of k_{33}' is not readily obtainable. From the behavior of those acids for which k_{33}' can be measured (see Table III and also

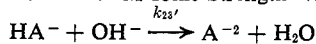
Table III. Average Experimental Rate Constants k_{33}' and k_{23} in 0.1 M Ionic Strength Solution at 25°

Acid	Rate constants, $M^{-1} \text{sec}^{-1}$	
	H_2O	D_2O
Tetramethylsuccinic, k_{33}'	2.4×10^7	1.2×10^7
Tetraethylsuccinic, k_{33}'	9.8×10^6	6.5×10^6
<i>o</i> -Cresol red, k_{23}	6.0×10^9	3.0×10^9

ref. 17), one would predict values about one order of magnitude smaller than k_{23}' . To investigate the error introduced by such an approximation, a parametric analysis of eq. 7 was carried out on an IBM 7040 computer. As is shown in Figure 1 the value of k_{23}' is relatively insensitive to the choice of k_{33}' under the conditions of our experiments. The range of τ taken for the analysis amounts to at least twice our experimental error and shows that the accuracy claimed for k_{23}' is conservative. Similar analysis of pH errors led to the same conclusions. For reactions in D_2O we substitute D for H in eq. 3 through 7. In Tables IV and V we have assembled the rate data taken in water and D_2O for the *rac*- α,α' -di-*t*-butylsuccinic acid. Similar data for the other acids led to the average values of the rate constants shown in Table VI. Rate constants in water for *cis*-caronic acid and *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid are based in part on data not reported previously.⁴ In calculating concentration of indicator species in D_2O a "normal" $\Delta pK_2 = 0.50$ was assumed for phenolphthalein, *i.e.*,

$pK_a^M = 9.55 + 0.50$. The pK_a^M of *o*-cresol red in D_2O was taken to be $8.30 + 0.50$. The pK_w in D_2O was taken to be 14.81.¹⁸

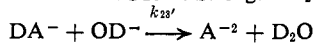
Table IV. Relaxation Spectra^a of *rac*- α,α' -Di-*t*-butylsuccinic Acid in 0.1 M Ionic Strength^b Water Solution for the Reaction



$c_0,^c$ $10^{-4} M$	$c_0',^d$ $10^{-6} M$	pH ^e	$\tau,^f$ msec.	$k_{23}',^g$ 10^6 $M^{-1} \text{sec}^{-1}$
5.0	1.0	9.49	0.610	3.09
5.0	1.0	10.02	0.745	2.69
5.0	1.0	10.30	0.900	2.07
10.0	1.0	8.95	0.330	3.15
10.0	1.0	9.45	0.620	1.75
10.0	1.0	9.85	0.800	1.55
10.0	1.0	10.11	0.590	2.34
10.0	1.0	10.39	0.840	1.66
				2.29 ± 0.53

^a All for 25° with phenolphthalein indicator. ^b Adjusted with KNO_3 . ^c Total sample acid concentration. ^d Total indicator concentration. ^e Sample solution pH at 25°. ^f Experimental relaxation time. ^g Rate constant calculated with eq. 7.

Table V. Relaxation Spectra^a of *rac*- α,α' -Di-*t*-butylsuccinic Acid in 0.1 M Ionic Strength^b D_2O Solution for the Reaction



$c_0,^c$ $10^{-4} M$	$c_0',^d$ $10^{-6} M$	pD ^h	$\tau,^f$ msec.	$k_{23}',^g$ 10^6 $M^{-1} \text{sec}^{-1}$
5.0	1.0	10.05	1.38	1.53
5.0	1.0	10.31	1.20	1.84
5.0	1.0	10.66	1.94	1.24
5.0	1.0	10.76	1.82	1.34
5.0	1.0	10.91	1.98	1.21
10.0	1.0	9.46	0.955	1.21
10.0	1.0	9.96	0.940	1.24
10.0	1.0	10.25	1.01	1.23
10.0	1.0	10.45	1.13	1.20
10.0	1.0	10.97	1.10	1.56
				1.36 ± 0.17

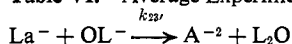
^{a-g} See Table IV. ^h pH measured at glass electrode vs. s.c.e. + 0.40.

It is obvious from Tables I and VI that the succinic acid monoanions react with hydroxide ion at rates inversely proportional to K_{a1}/K_{a2} . It is also true that the specific rate k_{23}' for *rac*- α,α' -di-*t*-butylsuccinic acid monoanion is as low as that for *cis*-cyclopropane-1,2,3-tricarboxylic acid dianion,⁴ the slowest such reaction we had previously observed. In neither case can steric or ionic charge effects begin to account for these rate constants which are $\sim 10^{-4}$ times the size of diffusion-controlled reaction rate constants.¹⁹

The experimental error in the rate constants of Table VI is such that the ratio $k_{23}',^H/k_{23}',^D$ is significantly larger than unity only for *rac*- α,α' -di-*t*-butylsuccinic acid. So small an experimental kinetic deuterium isotope effect for all five acids is at first surprising since, with or without the postulated intramolecular hydrogen bond, reaction 1 involves the breaking of a covalent oxygen-hydrogen bond which conceivably

(18) P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Am. Chem. Soc.*, **86**, 1 (1964).

(19) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 18.

Table VI. Average Experimental Rate Constants in 0.1 M Ionic Strength Water and D₂O Solutions at 25° for the Reaction

Acid	$k_{23}^{\text{H}}, M^{-1} \text{ sec.}^{-1} \text{ }^a$	$k_{23}^{\text{D}}, M^{-1} \text{ sec.}^{-1} \text{ }^b$	$k^{\text{H}}/k^{\text{D}}$
<i>cis</i> -Caronic	$(6.33 \pm 0.77)10^7$	$(5.85 \pm 0.72)10^7$	1.1
<i>cis</i> -3,3-Diphenylcyclopropane-1,2-dicarboxylic	$(4.43 \pm 1.17)10^8$	$(2.79 \pm 0.70)10^8$	1.6
Tetramethylsuccinic	$(2.54 \pm 0.25)10^8$	$(2.40 \pm 0.21)10^8$	1.1
Tetraethylsuccinic	$(5.31 \pm 0.85)10^7$	$(4.43 \pm 0.97)10^7$	1.2
<i>rac</i> - α, α' -Di- <i>t</i> -butylsuccinic	$(2.29 \pm 0.53)10^8$	$(1.36 \pm 0.17)10^8$	1.7

^a Average rate constant calculated from eq. 7 for data in water. ^b Average rate constant calculated from eq. 7 for data in D₂O.

could yield a primary kinetic isotope effect as large as 6 or 8.²⁰ Since the experimental effect is a product of primary and secondary solvent kinetic isotope effects, it is interesting to estimate the secondary solvent kinetic isotope effect from stretching frequencies suggested by Bunton and Shiner²¹ and Bigeleisen's equation

$$(k^{\text{H}}/k^{\text{D}})_{\text{sec}} = \text{antilog} \frac{\sum \nu^{\text{H}} - \sum \nu^{\text{H}*}}{12.53T} \quad (8)$$

derived from absolute rate theory. Postulating a monoanion that lacks an intramolecular hydrogen bond but has six hydrogen bonds to solvent and an activated complex having a variety of possible structures, we calculate values of a secondary $k^{\text{H}}/k^{\text{D}}$ in the

(20) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, **87**, 1553 (1965).

(21) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42, 3207, 3214 (1961).

range 0.2 to 0.6.²² Even the introduction of an intramolecular hydrogen bond in the monoanion, explicitly omitted from the work of Bunton and Shiner, does not yield a calculated secondary solvent kinetic isotope effect greater than about 0.6. The tentative conclusion to be drawn from such calculations is that the primary kinetic isotope effect = (experimental effect) \times (calculated secondary effect)⁻¹ is significantly larger than unity and conceivably is as large as 6, depending upon which acid is under consideration. So large a primary kinetic isotope effect would indicate a symmetric transition state with approximately equal OH bond strengths in the initial and final states.^{20,21} It is clear in any case that the experimental kinetic isotope data do not permit a decisive choice between a monoanion structure containing an intramolecular hydrogen bond and one that does not.

(22) E. M. Eyring, in preparation.

Solid-State Reactions of Bromine with Aromatic Hydrocarbons

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Following a survey of the reactions of several solid aromatic hydrocarbons with bromine, a quantitative study was performed of the decomposition of a perylene-bromine charge-transfer complex in the solid state. The complex can be viewed as an intimate, stoichiometric mixture of reactants ordered at the molecular level. The reaction is first order to high conversion; at the lower temperatures, pure 3,9-dibromoperylene with no trace of monobromo or other dibromo derivatives is the product, but at -9°, some 3,10-dibromoperylene is obtained. The rates between 0 and -24° were measured; the half-life for the decomposition is 13 min. at 0°, and the activation energy is 10 kcal./mole. It is suggested that the solid state may serve as a useful matrix to exercise control of the rate, isomer distribution, and stereochemistry of many organic reactions.

Introduction

The operation of topochemical and topotactic forces in the reactions of organic solids has been established for certain photochemical reactions and polymerization systems.¹ Topochemical reactions are those in which

the process is dependent on the geometric arrangement of reactive groups within the lattice, and some notable examples are the photochemical dimerizations of substituted *trans*-cinnamic acids,² the photochromy of the anils,² and the solid-state polymerization of trioxane, diketene, and β -propiolactone.³ The term topotactic refers to solid-state reactions in which the product crystal orientation is related to that of the reagent. Some examples of topotactic reactions are the solid-state polymerizations of single crystals of trioxane³ and ϵ -aminocaproic acid,⁴ and the formation of oriented crystallites of N-phenylphthalimide from a single

(1) (a) For reviews of thermal reactions in the organic solid state, see H. Morawetz, "Physics and Chemistry of the Organic Solid State," D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y.: Vol. I, 1963, p. 287; Vol. II, 1965, p. 853. (b) For photochemical reactions, see H. S. A. Gilmour, *ibid.*, Vol. I, 1963, p. 329.

(2) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964).

(3) K. Hayashi and S. Okamura, *Makromol. Chem.*, **47**, 230 (1961); K. Hayashi, Y. Kitamishi, M. Nishii, and S. Okamura, *ibid.*, **47**, 237 (1961); S. Okamura, K. Hayashi, and Y. Kitamishi, *J. Polymer Sci.*, **58**, 925 (1962).

(4) N. Morosoff, D. Lin, and H. Morawetz, *J. Am. Chem. Soc.*, **86**, 3167 (1964).