

ture began to rise above 10°) the cycle could be repeated. In this way the values plotted in Figs. 1 and 2 were obtained.

In one experiment 0.556 g. of anisic acid in 50.0 ml. of 99.9% sulfuric acid (a typical freezing point solution) was poured onto ice after 90 minutes at approximately 10°. The precipitated anisic acid was filtered, washed with water and dried under vacuum. It weighed 0.349 g. (63% recovery).

Hydrolysis of Ethyl Anisate.—In a typical experiment, 0.761 g. (0.00458 mole) of II was added to 10.0 ml. of 100% sulfuric acid at 10°. The solution warmed rapidly on stirring, and was poured onto ice after 15 minutes at 25°. The precipitate was recrystallized from ether-petroleum ether, and identified as anisic acid, m.p. 181–183°. It weighed 0.070 g. (0.00046 mole, 10%).

Recovery of *p*-Methoxyacetophenone (III) from Sulfuric Acid.—A solution of 0.643 g. of III in 100% sulfuric acid was maintained at 25° for one hour and poured onto ice. The solid material, after recrystallization from ether-petroleum ether, had a m.p. and mixed m.p. with III of 37–38°. It weighed 0.423 g. (66% recovery). The same experiment carried out with *p*-dimethoxybenzene failed to yield any water-insoluble material.

Esterification of Benzoic Acid.—A solution of 2.23 g. (0.0183 mole) of benzoic acid in 10.0 ml. of 100% sulfuric acid was allowed to stand at room temperature for one hour and then poured into 50 cc. of cold (–5°) methanol. Water (100 cc.) was added and the mixture extracted with 100 cc. of ether, which was washed with dilute base and water, and evaporated to 1 cc. The remaining solvent was removed under vacuum, leaving 0.58 g. of methyl benzoate, n_D^{20} 1.5126. The yield was 0.0043 mole, or 23%. An authentic sample of methyl benzoate gave n_D^{20} 1.5129.

TABLE II
FREEZING POINT DATA

Time, 25°	Molality	F.p., °C.	$\Delta\theta$	i
Anisic acid (I)				
	None	9.904		
"	0.1031 (1.430 g.)	8.156	1.738	2.83
4 hr.		7.514	2.390	3.91
24 hr.		7.474	2.430	3.99
Ethyl anisate (II)				
	None	9.735		
"	0.0628 (0.950 g.)	8.734	1.001	2.69
1 hr.		8.565	1.170	3.15
3 hr.		8.263	1.472	3.96
24 hr.		8.092	1.643	4.43

^a Approximately 30 minutes at 10–15°.

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MD.

Fate of the Carboxyl Group in the Conversion of Furoic Acid to Mucobromic Acid

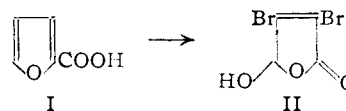
By WALTER J. GENSLER, ELLI SMAKULA AND AARON L. BLUHM

RECEIVED JANUARY 11, 1955

Bromine water oxidizes furoic acid (I) to mucobromic acid (II) and carbon dioxide.^{1,2} *A priori*, the carbon dioxide could come either from the carboxyl group or from the 5-position of the furoic acid. Wasserman and his co-workers,³ in their study of the conversion of 4-chlorofuroic acid to mucochlorobromic acid, showed that the carbon dioxide orig-

inates in the carboxyl group. We wish to report direct evidence corroborating this finding.

Furoic acid carrying C-14 in the carboxyl group⁴ was treated with bromine and water to form mucobromic acid. It was found that this mucobromic acid showed no activity, whereas the carbon dioxide



evolved (and collected as barium carbonate) did show activity. It follows, accordingly, that all four carbon atoms of mucobromic acid—and presumably of the other mucohalic acids—must come from the ring carbons of furoic acid, while the carbon dioxide comes from the carboxyl group.

Experimental

The preparation of mucobromic acid was based on published directions¹ modified, after considerable experimentation, to fit our needs. The procedure of Johnson⁵ offered but little advantage. Carboxyl-labeled furoic acid,⁴ m.p. 133° (cor.), assaying at 0.245 millicurie of C-14 per mole, was used as the starting material. The acid was prepared by carbonating furyllithium with radioactive carbon dioxide.⁴

Into a 25-ml. round-bottomed flask was placed 61.8 mg. of the labeled furoic acid, and then 0.62 ml. of water followed by 0.13 ml. of bromine. The flask under a water-cooled condenser and containing a small boiling chip (carborundum) was placed in an oil-bath at 80°. The temperature was raised rapidly to 110° and held at this point until bubbles no longer formed on the boiling chip (*ca.* four minutes). The condenser was removed, a fresh chip was added to the reaction mixture, and the temperature of the bath was brought to 125°. Evaporation was allowed to continue for ten minutes at this temperature and for another ten minutes as the bath temperature dropped to 95°. Cooling and seeding at this point gave a mass of white crystals. After adding 0.6 ml. of water, the crystals were dissolved by warming the mixture on the steam-bath. The hot yellow solution was suction filtered through a preheated funnel (glass nail type), and the funnel and flask were rinsed with approximately 0.4 ml. of hot water. The combined filtrates were cooled to ice-bath temperature and the crystals collected by filtration. The white product was washed with 0.5 ml. of ice-water, sucked on the funnel for one-half hour, and finally dried *in vacuo* at 80° for two hours. White crystalline mucobromic acid (a small amount of discolored crystals was discarded), weighing 79.3 mg. (63%) and melting at 121.4–121.8°, was obtained.

A sample of mucobromic acid, m.p. 120.8–121.3°, prepared in an analogous manner from unlabeled furoic acid, was analyzed.

Anal. Calcd. for C₄H₃O₃Br₂: C, 18.6; H, 0.8; Br, 62.2. Found⁶: C, 18.7; H, 0.9; Br, 62.2.

Activity measurements were made with a Tracerlab flow counter. No increase in the background count was observed when a sample of the mucobromic acid from the radioactive furoic acid was bound on a small shallow dish with a minimal amount of lacquer and was placed in the counter. Further check was obtained by burning the compound in a standard combustion train. After removing water vapor in an absorption tube, the carbon dioxide was precipitated and collected as barium carbonate.⁷ The barium carbonate again gave no counts over background.

(4) Cf. W. J. Gensler and G. L. McLeod, Abstracts Am. Chem. Soc. Meeting, Sept., 1954, p. 88-0.

(5) J. R. Johnson, "Preparation of Nitro Compounds," Report to Division B, National Defense Research Committee of Office of Scientific Research and Development, Serial No. 98, September 15, 1941.

(6) Analysis by Carol K. Fitz, Ph.D., 115 Lexington Avenue, Needham Heights 94, Mass.

(7) The weights of water and barium carbonate from the mucobromic acid corresponded to a hydrogen content of 0.7% and a carbon content of 19.4%.

(1) Cf. O. R. Jackson and H. B. Hill, *Ber.*, **11**, 1671 (1878); *Am. Chem. J.*, **3**, 33 (1881).

(2) A complete summary of the literature is given in "The Furans," by A. P. Dunlop and F. N. Peters, Am. Chem. Soc. Monograph Series No. 119, Reinhold Publishing Corp., New York, N. Y., 1953.

(3) H. H. Wasserman, F. M. Precopio and Tien-Chuan Liu, *This Journal*, **75**, 2527 (1953).

In another experiment, carbon dioxide from the bromination mixture was collected in sodium hydroxide solution and precipitated as barium carbonate. This barium carbonate showed an activity of 118 counts per minute; the background count was 20.3 counts per minute.

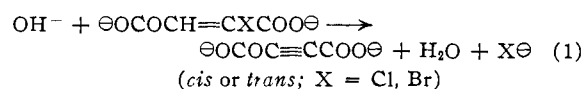
DEPARTMENT OF CHEMISTRY
BOSTON UNIVERSITY
BOSTON, MASSACHUSETTS

Mechanisms of Elimination Reactions. XIV. Solvent and Salt Effects in the Alkaline Dehydrohalogenation of Chloro- and Bromomaleate and -Fumarate^{1a}

BY ERNEST GRUNWALD^{1b} AND STANLEY J. CRISTOL

RECEIVED DECEMBER 17, 1954

In a recent kinetic study² of the elimination reactions it was noted that, at 0.1 *M* ionic strength, the



second-order rate constants were greater in 54.2% aqueous ethanol than in water. As the transition state in these reactions has a greater concentration of charge than the reactants, the results appeared to contradict the electrostatic theory of solvent effects.^{3,4}

We now wish to report an extrapolation of the available ionic strength-kinetic data^{2,5} for the reactions indicated in equation 1 to zero ionic strength. The resulting second-order rate constants at 70° are summarized in Table I, together with the respective quantities of activation. It may be seen that, at zero ionic strength, the specific rates in water are about three times those in 54.2% ethanol, in qualitative agreement with electrostatic theory.⁶ However, at ionic strengths even as low as 0.1 *M*, the solvent effect is masked by the large interionic effects, which are more important in the solvent of lower dielectric constant. The results show that estimates of solvent effects for ionic reactions may be in error, not only in magnitude, but even in direction, when working at moderate ionic strengths.

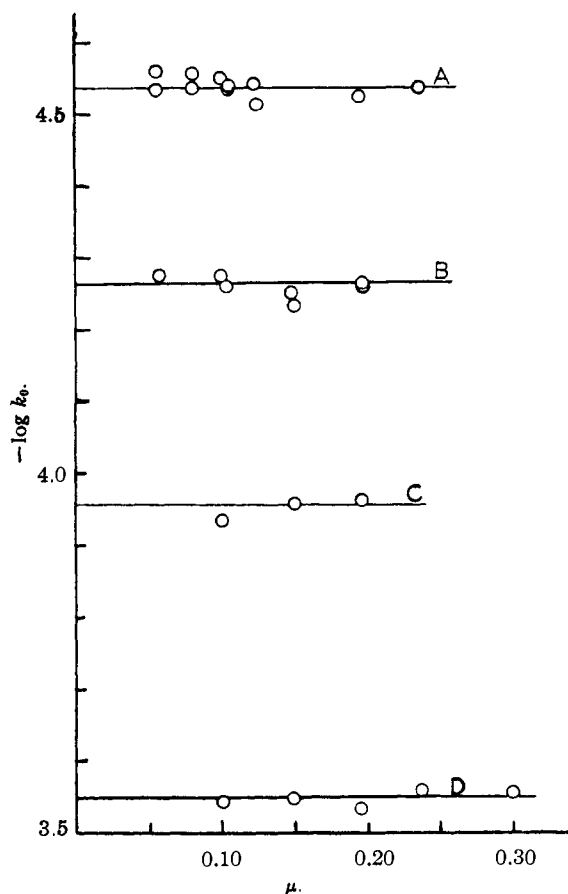


Fig. 1.—Plots of extrapolated rate constants, $\log k_0$ vs. ionic strength, μ , for the alkaline dehydrohalogenation of: bromomaleate in water, 45.12° (A); in 54.2% ethanol, 61.40° (B); chlorofumarate in 54.2% ethanol, 72.95° (C); in water, 71.02° (D).

The rate constants were extrapolated to zero ionic strength by means of the equation

$$\log k = \log k_0 + 4S\sqrt{\mu}/(1 + Aa\sqrt{\mu}) \quad (2)$$

where μ is the ionic strength; S is the Debye-

TABLE I
SPECIFIC REACTION RATE CONSTANTS AND QUANTITIES OF ACTIVATION FOR REACTIONS 1 AT 70.0°, EXTRAPOLATED TO ZERO IONIC STRENGTH

Compound	$10^4 k_0$, l./mole./sec.		$10^4 k$ at $\mu = 0.1 M$, l./mole./sec.		E_{act} , kcal./mole.		ΔS^\ddagger , cal./deg.	
	H ₂ O	54.2% EtOH	H ₂ O	54.2% EtOH	H ₂ O	54.2% EtOH	H ₂ O	54.2% EtOH
Chlorofumarate	2.54	0.845	8.15	9.96	21.0	23.1	-16	-12
Chloromaleate	0.279	0.088	0.809	0.832	24.9	24.0	-9	-14
Bromofumarate	43.3	19.2	139 ^a	204	17.9	19.7	-19	-16
Bromomaleate	3.84	1.30	11.3	12.3	22.6	22.5	-11	-13

^a The activation energy, extrapolated rate constant at 70°, and entropy of activation reported previously² should be corrected to 18.5 kcal./mole, 139×10^{-4} l./mole./sec., and -15 e.u., respectively, for bromofumarate in water.

(1) (a) Previous paper in series: S. J. Cristol, W. Barasch and C. H. Tieman, *THIS JOURNAL*, **77**, 583 (1955). (b) Florida State University.

(2) S. J. Cristol and A. Begoon, *THIS JOURNAL*, **74**, 5025 (1952).

(3) M. Born, *Z. Physik*, **1**, 45 (1920).

(4) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(5) A. Begoon, Ph.D. thesis, University of Colorado, 1950.

(6) This correction now removes the requirement for any unusual solvation effects with these compounds.⁷

(7) E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

Hückel limiting slope and is equal to $1.825 \times 10^6 / (DT)^{3/2}$; $A = 50.30 \times 10^8 / (DT)^{3/2}$ cm.⁻¹; and a is an average of the ion-size parameters for reactants and transition state.⁸ The values chosen for a were 5.0 Å. for the halomaleates in both solvents, and 4.0 Å. for the halofumarates in both solvents. Values of $\log k_0$ computed in this way were satisfac-

(8) See, for example, G. Scatchard, *THIS JOURNAL*, **52**, 52 (1930); V. K. La Mer, *J. Franklin Inst.*, **225**, 709 (1938).