

TABLE I

	Methyl	Ethyl	<i>n</i> -Propyl	<i>n</i> -Butyl
Sp. gr. at 25°	1.48	1.35	1.28	1.23
Ref. index 20°	1.414	1.416	1.422	1.427
B. p., °C.	48.1 at 29 mm.	42.3 at 10 mm.	53.2 at 10 mm.	69 at 10 mm.
% S, calcd.	24.53	22.18	20.18	18.65
% S, found	24.8 ± 0.2	22.0 ± 0.2	20.4 ± 0.2	18.3 ± 0.2
% Cl, calcd.	27.13	24.54	22.38	20.56
% Cl, found	27.0 ± 0.1	24.5 ± 0.1	22.2 ± 0.1	20.5 ± 0.1

They are colorless liquids, insoluble in water, but quite soluble in the common organic solvents.

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Nitrogen-Terminated Conjugated Systems and Maleic Anhydride

BY FELIX BERGMANN

The ability of 9-vinylphenanthrenes to condense with maleic anhydride¹ induced us to investigate whether conjugated systems consisting of a cyclic C-N double bond and an exocyclic ethylenic linkage would add maleic anhydride. 2-Styrylquinoline gave a well-defined reaction product, which, however, besides the components, contained one molecule of water, and therefore was styrylquinolinium maleate. This became obvious in its reaction with diazomethane, yielding dimethylpyrazoline-4,5-dicarboxylate.² Analogous observations have been made recently by La Parola³ in the case of antipyrine and pyrimidone. For comparison purposes, we studied the interaction between maleic anhydride and cinnamylidene-aniline, which contains the nitrogen-terminated conjugated system entirely in an open chain. Here, too, the reaction involves one molecule of water (from the air), but the maleate, presumably formed as above, is unstable and decomposes spontaneously into cinnamic aldehyde and maleanilic acid, HOOCCH=CHCONNH-C₆H₅.

Experimental

2-Styrylquinoline⁴ (1.2 g.) and maleic anhydride (0.5 g.) were heated on the water-bath or in xylene solution for some minutes. The mixture turned yellow at once and deposited on cooling yellow crystals, which were recrystallized from xylene or butyl acetate. 2-Styrylquinolinium maleate formed long, silky needles, m. p. 165-167°.

(1) E. Bergmann and F. Bergmann, *THIS JOURNAL*, **59**, 1443 (1937).

(2) Von Pechmann, *Ber.*, **27**, 1888 (1894); v. Pechmann and Burkard, *ibid.*, **33**, 3590 (1900).

(3) La Parola, *Gazz. chim. ital.*, **67**, 645 (1937).

(4) Skraup and Boehm, *Ber.*, **59**, 1013 (1927).

Anal. Calcd. for C₂₁H₁₇O₄N: C, 72.6; H, 4.9. Found: C, 72.8; H, 5.3. The salt was kept in contact with an excess of ethereal diazomethane solution; on evaporation a crystalline mass was obtained which was triturated with light petroleum (b. p. 80-100°) and recrystallized from the same solvent. Dimethyl pyrazoline-4,5-dicarboxylate was obtained in the form of leaflets, m. p. 103-105°. *Anal.* Calcd. for C₇H₁₀O₄N₂: C, 45.2; H, 5.4; N, 15.1. Found: C, 44.8; H, 5.5; N, 15.6.

Cinnamylidene-aniline⁵ (1 g.) and maleic anhydride (0.5 g.) were heated together on the water-bath; the mixture turned brown, then red and an intense odor of cinnamic aldehyde developed. After fifteen minutes, benzene was added, whereupon maleanilic acid crystallized, yield 300 mg.; from butyl acetate as rhombohedra, m. p. 210°. *Anal.* Calcd. for C₁₀H₉O₃N: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.5; H, 4.5; N, 7.7. Diazomethane gave as above the expected methyl ester-anilide of pyrazoline-4,5-dicarboxylic acid, from xylene or butyl acetate; crystals, m. p. 175° (dec.). *Anal.* Calcd. for C₁₂H₁₃O₃N₂: N, 17.0. Found: N, 17.4.

(5) Doebner and v. Miller, *ibid.*, **16**, 1665 (1883).

(6) The highest m. p. recorded before is 198° [Auwers and Schlicher, *Ann.*, **309**, 347 (1899)]. A preparation made according to Anschutz [*Ber.*, **20**, 3214 (1897)] showed m. p. 210°, after recrystallization from butyl acetate or butyl alcohol.

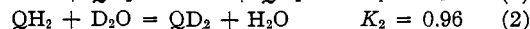
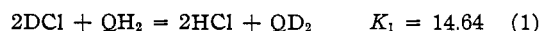
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RECEIVED JULY 12, 1938

The Calculation of the Dissociation Constant of Weak Acids in H₂O-D₂O Mixtures

BY FRANK BRESCIA

From the exchange equilibria



Korman and La Mer¹ have calculated the equilibrium constant for the process, D⁺ + H₂O = H⁺ + HDO, to be K₄ = 7.1. Their derived equation for the calculation of dissociation constants of weak acids in H₂O-D₂O mixtures

$$K_M = K_D \left[1 + 7.1 \frac{C_{\text{H}_2\text{O}}}{C_{\text{HDO}}} / 1 + 7.1 \left(\frac{K_D}{K_H} \right) \frac{C_{\text{H}_2\text{O}}}{C_{\text{HDO}}} \right] \quad (5)$$

contains, therefore, the factor 7.1. K_M is the dissociation constant of the acid in the mixtures of H₂O-D₂O, K_D is the dissociation constant of

(1) Korman and La Mer, *THIS JOURNAL*, **58**, 1396 (1936).

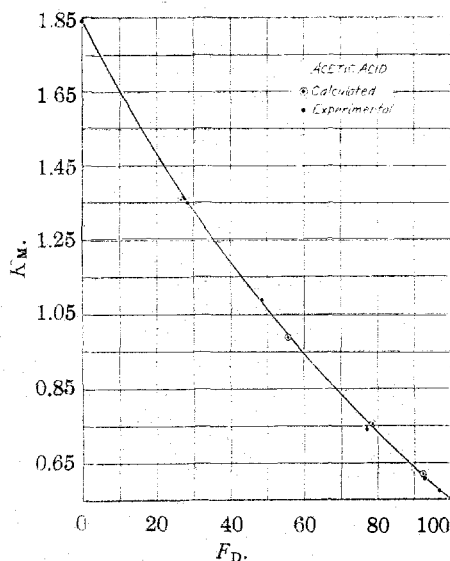


Fig. 1.—Acetic acid: ●, calculated; ●, experimental.

the heavy acid, and K_H is the dissociation constant of the light acid. This equation, tested by Chittum and La Mer,² does not give the same K_M constants as those calculated from the conductance data. The sag of the experimental curve for acetic acid is opposite from that predicted by equation (5).

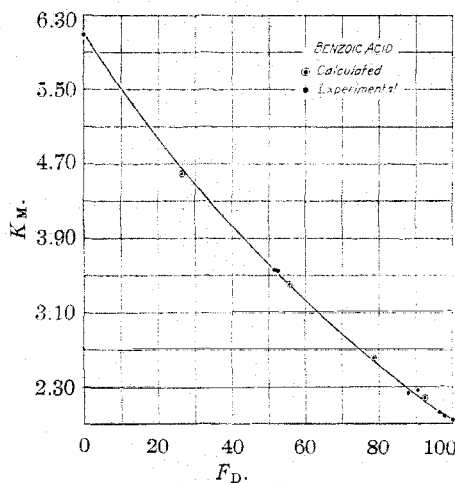


Fig. 2.—Benzoic acid: ●, calculated; ●, experimental.

The value of K_4 can now be arrived at by an independent method. K_4 (column 4, Table I) has been calculated from the customary $K_3 = 3.27^3$ and from the values of C_{H^+} and C_{D^+} (columns 2 and 3, Table I), obtained through kinetic measurements of a specific hydrogen-ion catalyzed reac-

(2) Chittum and La Mer, *THIS JOURNAL*, **59**, 2425 (1937).

(3) Topley and Eyring, *J. Chem. Phys.*, **2**, 217 (1934).

TABLE I

(1) F_D	(2) $C_{H^+} \times 10^7$	(3) $C_{D^+} \times 10^7$	(4) K_4
26.40	3.68	0.624	3.99
55.60	1.93	1.16	3.72
78.49	0.827	1.49	3.46
92.51 ⁴	0.303	1.65	3.86

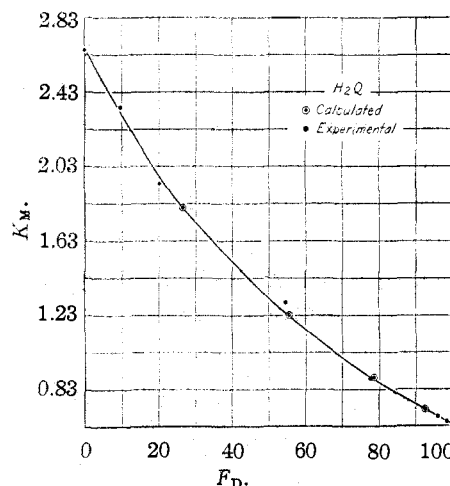


Fig. 3.— H_2Q : ●, calculated; ●, experimental.

tion: hydrolysis of ethyl orthoformate in mixtures of H_2O - D_2O .⁵ The average value thus obtained, 3.76, is much smaller than the previous value, 7.1. Equation (5) is, therefore, corrected to

$$K_M = K_D \left[1 + 3.76 \frac{C_{H_2O}}{C_{HD_2O}} / 1 + 3.76 \left(\frac{K_D}{K_H} \right) \frac{C_{H_2O}}{C_{HD_2O}} \right] \quad (6)$$

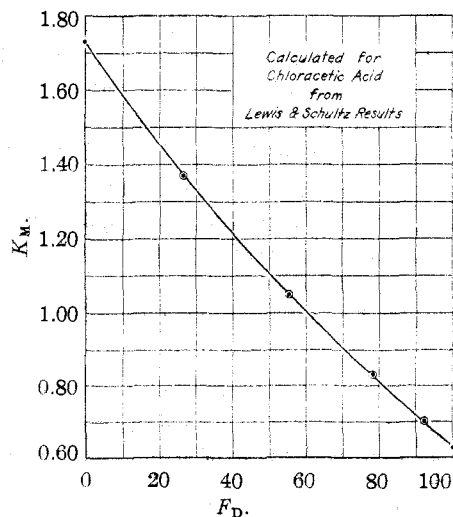


Fig. 4.—Calculated for chloroacetic acid from the results of Lewis and Schultz.

(4) The rate constant used to calculate this value of C_{H^+} and C_{D^+} was taken from the experimental curve in preference to the slightly lower determined value since the calculation in this region of F_D is very sensitive to small changes in the rate constant. $F_D = \Delta S(100)/0.1079$ = fraction of deuterium in the solvent.

(5) Brescia and La Mer, *THIS JOURNAL*, **60**, 1962 (1938).

TABLE II
 SUMMARY OF CALCULATED VALUES USING EQUATION (6) AND OF EXPERIMENTAL DATA

F_D	$K_M \times 10^4$ HAc		$K_M \times 10^5$ HB		$K_M \times 10^{11}$ H:O		$K_M \times 10^4$ ClHAc	
	Exptl. ⁶	Calcd.	Exptl. ⁷	Calcd.	Exptl. ⁷	Calcd.	Exptl. ⁸	Calcd.
0.0	1.84	(1.84)	6.09	(6.09)	2.66	(2.66)	1.73	(1.73)
9.61					2.35			
25.18					1.94			
26.40		1.36		4.60		1.81		1.37
28.4	1.352							
48.4	1.088							
51.45			3.56					
52.42			3.55					
54.69					1.30			
55.60		0.988		3.41		1.23		1.05
77.1	0.741							
77.49					0.889			
78.49		.756		2.61		0.895		0.827
87.99			2.23					
92.51		.622		2.18		.722		.700
93.0	.608							
96.00					(.684)			
96.51			2.03					
97.0	.575							
97.87			1.99					
98.67					.657			
100	(.555)	(.555)	(1.95)	(1.95)	(.639)	(.639)	(0.631)	(.631)

The K_M values, calculated from the revised equation (6), are now in very good agreement with the experimental results. These are summarized in Table II and plotted in Figs. 1, 2, and 3. The predicted slope for chloroacetic acid is given in Fig. 4; no experimental data for comparison are available. The value of K_D for salicylic acid is extrapolated with equation (6) from the average value $K_M = 0.24 \times 10^{-3}$, a. d. 12%, at $F_D = 91.7$, and from the average $K_H = 0.98 \times 10^{-3}$, a. d. 2%, determined by Korman and La Mer.¹ The K_D thus calculated is 0.21×10^{-3} which also has not yet been determined experimentally.

It is apparent that true values of hydrogen and deuterium ion concentrations are obtainable from kinetic data when tested by means of acid dissociation constants.

(6) (Acetic acid) Chittum and La Mer, *THIS JOURNAL*, **59**, 2524 (1937).

(7) (Benzoic acid and hydroquinone) Rude and La Mer, *ibid.*, **60**, 1974 (1938).

(8) (Chloroacetic acid) Lewis and Schultz, *ibid.*, **56**, 1913 (1934).

DEPARTMENT OF CHEMISTRY
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THE COLLEGE OF THE CITY OF NEW YORK
NEW YORK, N. Y. RECEIVED AUGUST 25, 1938

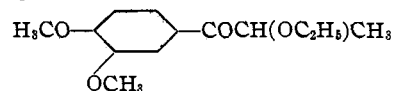
The Structure of Lignin

BY A. B. CRAMER, M. J. HUNTER AND HAROLD HIBBERT

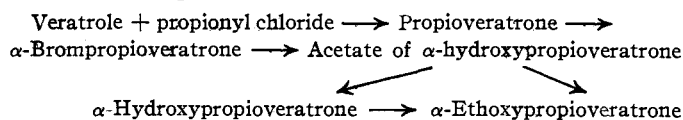
In a recent note¹ the isolation of a new aromatic

(1) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **60**, 2274 (1938).

ketone ($C_{13}H_{18}O_4$) was described. This has now been identified (by direct synthesis and mixed melting point determination) as α -ethoxypropioveratrone



The synthesis (after numerous unsuccessful attempts, and using a variety of methods) was accomplished as follows:



The synthetic compound melted at 81–82°; a mixed melting point with natural compound gave no depression. The melting point of the 2,4-dinitrophenylhydrazone of the natural compound is 134–136°; synthetic compound, 134–136°; the mixed melting point also showed no depression.

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The Classification of Chelating Groups

BY HELMUT M. HAENDLER AND BRADFORD P. GEYER

In the course of preliminary work on organic analytical reagents which form inner complex