propiolic acid and their esters. Details will follow.

Summary

Hydrogen fluoride has been added to a number of acetylene homologs and has yielded generally 70 to 80% of the difluorides expected from Markownikow's rule. A technique is offered which uses a complex between hydrogen fluoride and an oxygenated compound able to form an oxonium addition product, as the agent of hydrofluorination. The physical properties of the fluorides are tabulated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Effect of Substituents on the Acid Strength of Benzoic Acid. VI. The Cyano Group

BY MARTIN KILPATRICK AND R. DEAN EANES

In order to test recent theoretical predictions on the effect of substituents on acid strength, the equilibrium constants for the reaction

$$p\text{-cyanobenzoic acid} + \text{benzoate} = \text{benzoic acid} + p\text{-cyanobenzoate} \quad (1)$$

and the corresponding reaction for *m*-cyanobenzoic acid have been determined in the solvents water, ethylene glycol, methyl alcohol, ethyl alcohol, and in the mixed solvent dioxane–water.

The experimental technique involving the measurement of the e. m. f. of concentration cells of the type

$$\mathrm{Au}\;\underset{\text{Quinhydrone}}{\left|\begin{array}{ll}\mathrm{HB} & 0.005\,M\\ \mathrm{LiB} & 0.005\,M\\ \mathrm{LiCl} & 0.045\,M\end{array}\right|}\;\begin{array}{c}\mathrm{LiCl}\\ 1.00\,M\\ \\ \end{array}\;\underset{\text{Quinhydrone}}{\left|\begin{array}{ll}\mathrm{HX} & 0.005\,M\\ \mathrm{LiX} & 0.005\,M\\ \mathrm{LiCl} & 0.045\,M\end{array}\right|}\;\mathrm{Au}$$

has been described in the earlier papers of this series.[1] These papers also describe the purification of the solvents and the preparation of the lithium chloride.

***p*-Cyanobenzoic Acid.**—The acid was dissolved in water, treated with norite, filtered and crystallized. This treatment was repeated several times, and after five recrystallizations from water the white product was dried in an Abderhalden pistol at room temperature. The product melted between 218.5 and 219° in agreement with the findings of Valby and Lucas.[2] A portion of the product was heated to 100° in the pistol, after which the melting point was found to be 214°, indicating decomposition as reported by Sandmeyer.[3] Titration with sodium hydroxide gave an equivalent weight of 147.3. The theoretical value is 147.1.

***m*-Cyanobenzoic Acid.**—This compound was prepared[4] from *m*-aminobenzoic acid by means of the Sandmeyer reaction, following closely the procedure described by Valby and Lucas[2] for the preparation of *p*-cyanobenzoic acid. The product was recrystallized four times from water (after treatment with decolorizing charcoal) and once from 50% ethanol. It formed fine, colorless needles melting at 220–221°. The reported melting point is 217°.[3] The equivalent weight by titration was 146.9.

Table I gives $K_{\mathrm{A_xB_0}}$, the equilibrium constant for the reaction of equation 1. This equilibrium constant is the ratio of the dissociation constant of *p*-cyanobenzoic acid to that of benzoic acid.

TABLE I

RATIO OF THE DISSOCIATION CONSTANT OF *p*-CYANOBENZOIC ACID TO THAT OF BENZOIC ACID AT 25°

Solvent	Dielectric constant	$K_{A_xB_0}$ (obs.)	$K_{A_xB_0}$ (calcd. by equation 2)
Water	78.5	4.48[a]	4.51
Ethylene glycol	37.7	6.59	6.68
Methyl alcohol	31.5	8.13	7.85
Ethyl alcohol	24.2	9.97	10.2
Dioxane–water	25	9.27	9.80

[a] Calculation from the data of Kirschner, Wingfield and Lucas, THIS JOURNAL, 52, 27 (1930), yields 4.64.

The results for the pure solvents may be expressed by the equation

$$\log K_{A_xB_0} = 0.496 + (12.4/D) \quad (2)$$

and the agreement between experiment and equation (2) is shown in Fig. 1 and the last

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[1] Elliott and Kilpatrick, *J. Phys. Chem.*, **45**, 454, 466, 472, 485 (1941).

[2] Valby and Lucas, THIS JOURNAL, **51**, 2718 (1929).

[3] Sandmeyer, *Ber.*, **18**, 1497 (1885).

[4] Preparation by H. J. Schneider under the direction of Dr. M. Carmack of this Laboratory.

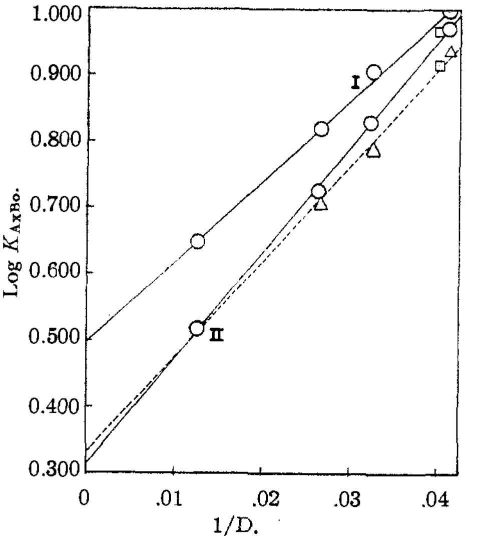

Fig. 1.—I, *p*-Cyanobenzoic acid *vs.* benzoic acid; II, *m*-cyanobenzoic acid *vs.* benzoic acid: ○, experimental values; △, calculated values; □, dioxane–water experimental values.

column of Table I. This relationship has been found to hold for the other substituted benzoic acids[5] and more recently for aliphatic acids.[6] The results for the dioxane–water mixture are also in conformity with our findings for other acids.

Table II and Fig. 1 give the corresponding results for *m*-cyanobenzoic acid.

TABLE II

RATIO OF THE DISSOCIATION CONSTANT OF *m*-CYANOBENZOIC ACID TO THAT OF BENZOIC ACID AT 25°

Solvent	Dielectric constant	$K_{A_xB_0}$ (obs.)	$K_{A_xB_0}$ (calcd. by equation 3)
Water	78.5	3.31	3.29
Ethylene glycol	37.7	5.31	5.48
Methyl alcohol	31.5	6.76	6.61
Ethyl alcohol	24.2	9.39	9.42
Dioxane–water	25	8.22	8.89

The dotted line in Fig. 2 represents the predicted value calculated on the basis of electrostatic theory.[7] The results for the pure solvents may be represented by the equation

$$\log K_{A_xB_0} = 0.314 + (16.0/D) \qquad (3)$$

for which the calculated values are given in column four of Table *II*. It should be noted that *p*-cyanobenzoic acid is a stronger acid than *m*-cyanobenzoic acid in all the solvents studied.

Summary

The relative acid strengths of *m*- and *p*-cyanobenzoic acids have been determined in the solvents water, ethylene glycol, methyl alcohol, ethyl alcohol and dioxane–water mixtures.

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[5] Kilpatrick, *Chem. Rev.*, **30**, 159 (1942).

[6] Kilpatrick and Eanes, THIS JOURNAL, **64**, 2065 (1942).

[7] From the dissertation of J. N. Sarmousakis presented to the Faculty of the Graduate School of the University of Pennsylvania, December 1, 1942.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY]

Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals[1]

BY ALEXANDER KOSSIAKOFF AND FRANCIS OWEN RICE

Introduction.—When a paraffin hydrocarbon such as propane is heated, the over-all decomposition, if limited to a small percentage, can be represented by the equations

$$C_3H_8 \longrightarrow H_2 + CH_2{=}CHCH_3 \qquad (1a)$$

$$C_3H_8 \longrightarrow CH_4 + CH_2{=}CH_2 \qquad (1b)$$

The actual mechanism of the decomposition has been the subject of much controversy and has been discussed in detail in a previous paper.[2] It was suggested that the most probable mechanism involves a rupture of the molecule into radicals, which initiate a series of changes resulting finally in the product molecules. A unimolecular rearrangement followed by a splitting of the molecule into the products seems unlikely on the basis of our present knowledge regarding interatomic forces.

One of the important predictions which can be made on the basis of the radical hypothesis concerns the nature and quantities of products expected from the thermal decomposition of a saturated hydrocarbon. The chain of reactions initiated and carried by the free radicals appears to consist of at least ten to twenty cycles[3] and may be several hundred links long. For this

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[1] Original manuscript received May 7, 1942.

[2] Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

[3] Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).