has a slope divided by intercept of 8.06. It is now seen that

$$k_4^\circ + k_2^1 + k_2^2 = 8.06\, k_3^\circ\, (1 + k_5^\circ P_2/k_3^\circ) = 41.6\, k_3^\circ \quad (14)$$

Since $k_4^\circ = 20.8k_3^\circ$ from the initial slope it follows that $k_2^1 + k_2^2 = k_4^\circ$ and the amount of quenching of the I_2° molecule is approximately equal to the amount of transfer to other energy levels. While from equation (13) the initial and high pressure slopes are equal, the figure for the initial slope cannot be obtained with high precision.

While it is not possible to draw quantitative conclusions concerning the life times and quenching of the intermediate states there is no reason to assume that they differ radically in these respects from the initially formed state. Probably their quenching would be slightly lower if anything.

The curve may be described in words as follows. At the beginning one excited state predominates and it either fluoresces or is quenched by a Stern–Volmer mechanism (equations (1–5)). During the horizontal portion of the curve the importance of intermediate state formation becomes greater and greater until the relative concentrations of all excited states attain approximately constant values, after which the high pressure straight line portion is reached.

In conclusion the authors wish to express their appreciation to Dr. R. M. Fuoss for evaluating the constants in equation (13).

Summary

1. The quenching of iodine fluorescence by benzene at pressures of the latter below 1 mm. has been studied.

2. The quenching is not of the simple type encountered in some systems and a complete explanation necessarily involves the assumption of several excited states which may be formed from the primarily excited state by collision. The use of two such states leads to a satisfactory equation, but a larger number probably take part in the phenomenon.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Constants of Acetylenic Compounds. VI. Acetylenic Acids

BY C. J. WILSON AND H. H. WENZKE

It has been shown by the authors[1] that the members of the fatty acids are not associated in dioxane and this is undoubtedly true for at least the majority of organic acids. In their work on acetylenic compounds the authors obtained a certain number of propiolic acids as intermediates in their preparations and it was felt that the moments of these compounds might be of some interest. While the carboxyl group is quite complex, it was thought that it might be possible to determine whether or not the triple bond has an effect on that moment. The article also reports data obtained on some substituted benzoic acids, benzoic acid and phenylacetic acid.

Preparation of Compounds

The substituted phenylpropiolic acids were made from the corresponding substituted toluenes. These substituted toluenes were oxidized to aldehydes with chromic acid, converted to the corresponding cinnamic acids by means of the Perkin synthesis and the acids changed to the ethyl esters. The ethyl esters were brominated and the dibromo esters treated with alcoholic potassium hydroxide. The phenylpropiolic acids were precipitated in a rather impure condition by the addition of water and hydrochloric acid. They were purified by dissolving them in a basic solution followed by fractional precipitation from an ice-cold solution by the addition of hydrochloric acid. The acids were further purified by crystallizing them from acetic acid until a constant melting point was obtained.

Propiolic acid was prepared by first brominating fumaric acid in a bomb at a temperature of 130°. The impure α,β-dibromosuccinic acid was purified by crystallization from water. The dried dibromosuccinic acid was treated with alcoholic potassium hydroxide, the solution filtered and the filtrate acidified with sulfuric acid. After refluxing for an hour the acid was extracted with ether, the ether distilled and the acid purified by fractional distillation under reduced pressure. The acid was further purified by crystallization from carbon bisulfide until a constant melting point was obtained.

In the preparation of tetrolic acid, acetoacetic ester was chlorinated to form β,β-dichloroethyl butyrate. The chloro compound was dehydrohalogenated by treating it with an aqueous solution of potassium hydroxide to which a few cc. of ethyl alcohol had been added. The alkaline solution was acidified with dilute hydrochloric acid and the tetrolic acid extracted with ether. The ethereal solution was dried over calcium chloride, the ether distilled and the acid fractionally distilled under reduced pressure. After

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(1) Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

distillation the acid was purified to constant melting point by repeated crystallization from a carbon bisulfide solution.

The chemically pure grades of phenylacetic, *p*-nitrobenzoic, benzoic, ortho-, meta- and para-hydroxybenzoic acids were obtained from the Eastman Kodak Co. These acids were purified by crystallization from aqueous solution until a constant melting point was obtained.

The dioxane used as a solvent in the determination of dielectric constant data was the technical grade from the Eastman Kodak Co. This substance was dehydrated by refluxing over metallic sodium for several days and then distilled. A fraction boiling over a temperature range of 0.2° was used.

TABLE I

MELTING POINTS OF ACIDS USED

Acid	Temp., °C.
Propiolic (b. p. 74–75° at 18 mm.)	9
Tetrolic	76
Phenylpropiolic	136
p-Chlorophenylpropiolic	147
o-Chlorophenylpropiolic	131
o-Nitrophenylpropiolic	155 (dec.)
p-Nitrophenylpropiolic	181
Phenylacetic	77
Benzoic	122
o-Hydroxybenzoic	159
m-Hydroxybenzoic	201
p-Hydroxybenzoic	215

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACIDS (SOLVENT DIOXANE, TEMP. 25°)

c_2	ϵ	d
	Propiolic acid	
0.091421	2.8003	1.02930
.066186	2.6425	1.02876
.035954	2.4576	1.02804
.000000	2.2375	1.02710
	Tetrolic acid	
0.067338	2.6757	1.03339
.048066	2.5544	1.03109
.027536	2.4182	1.02943
.000000	2.2375	1.02710
	Phenylpropiolic acid	
0.099051	3.0659	1.04652
.076852	2.8767	1.04229
.057555	2.7153	1.03831
.014871	2.3624	1.02943
.000000	2.2375	1.02710
	p-Chlorophenylpropiolic acid	
0.012084	2.3095	1.03980
.0077459	2.2844	1.03051
.0068613	2.2791	1.03013
.0000000	2.2375	1.02710
	p-Nitrophenylpropiolic acid	
0.013820	2.5467	1.03553
.0090854	2.4422	1.03267
.0060229	2.3693	1.03078
.0036079	2.3183	1.02924
.0000000	2.2375	1.02710
	o-Chlorophenylpropiolic acid	
0.025833	2.5140	1.03980
.016206	2.4090	1.03517
.0080823	2.3249	1.03103
.0000000	2.2375	1.02710
	o-Nitrophenylpropiolic acid	
0.010835	2.5075	1.03386
.0066505	2.4015	1.03036
.0038169	2.3314	1.02944
.0000000	2.2375	1.02710
	Benzoic acid	
0.041799	2.4297	1.03540
.029057	2.3661	1.03267
.021422	2.3345	1.03168
.000000	2.2375	1.02710
	Phenylacetic acid	
0.042506	2.4309	1.03451
.034760	2.3973	1.03328
.033812	2.3895	1.03324
.029088	2.3715	1.03211
.000000	2.2375	1.02710
	p-Nitrobenzoic acid	
0.011235	2.5114	1.03300
.006918	2.4061	1.03067
.0045499	2.3495	1.02949
.0000000	2.2375	1.02710
	o-Hydroxybenzoic acid	
0.015370	2.3953	1.03261
.010927	2.3500	1.03161
.0085199	2.3245	1.03016
.0000000	2.2375	1.02710
	m-Hydroxybenzoic acid	
0.029416	2.4342	1.03786
.019437	2.3492	1.03407
.016170	2.3213	1.03262
.000000	2.2375	1.02710
	p-Hydroxybenzoic acid	
0.019398	2.4527	1.03505
.011928	2.3703	1.03181
.008646	2.3336	1.03054
.000000	2.2375	1.02710

TABLE III

POLARIZATIONS OF ACIDS

Acid	P_∞	MR_D	P_{A+M}
Propiolic	107.09	16.99	90.10
Tetrolic	113.52	20.40	93.12
Phenylpropiolic	154.27	45.40	108.87
p-Chlorophenylpropiolic	126.79	48.34	78.45
o-Chlorophenylpropiolic	191.63	48.34	143.29
p-Nitrophenylpropiolic	348.33	52.20	296.13
o-Nitrophenylpropiolic	386.54	52.20	334.34
Phenylacetic	100.12	36.98	63.14
Benzoic	94.50	34.10	60.40
p-Nitrobenzoic	377.22	40.90	336.32
o-Hydroxybenzoic	178.10	34.30	143.80
m-Hydroxybenzoic	151.26	34.30	116.96
p-Hydroxybenzoic	189.62	34.30	155.32

The polarizations at infinite dilution were determined from the slopes of the dielectric constant and density curves at zero concentration.

TABLE IV

ELECTRIC MOMENTS OF ACIDS

Acid	$10^{18}\ \mu$
Propiolic	2.08
Tetrolic	2.12
Phenylpropiolic	2.29
p-Chlorophenylpropiolic	1.95
o-Chlorophenylpropiolic	2.63
p-Nitrophenylpropiolic	3.78
o-Nitrophenylpropiolic	4.02
Benzoic	1.71
Phenylacetic	1.75
p-Nitrobenzoic	4.02
o-Hydroxybenzoic	2.63
m-Hydroxybenzoic	2.37
p-Hydroxybenzoic	2.73

TABLE V

ELECTRIC MOMENTS AND IONIZATION CONSTANTS OF SOME ACIDS

Acid	$10^{18}\ \mu$	*K*
Acetic	1.73	1.8×10^{-5}
Propionic	1.75	1.4×10^{-5}
Phenylacetic	1.75	5.6×10^{-5}
Benzoic	1.71	7.3×10^{-5}
Propiolic	2.08	14.0×10^{-3}
Tetrolic	2.12	2.5×10^{-3}
Phenylpropiolic	2.29	5.9×10^{-3}

Discussion of Results

Although the moment of the carboxyl group is the resultant of several individual moments and hence difficult to interpret, an inspection of the data of Table V will note some interesting relationships. The moments of acetic, propionic, phenylacetic and benzoic acids are very nearly the same and there is little difference in their ionization constants. A somewhat similar statement applies to the three propiolic acids listed. The proximity of the triple bond has a marked effect on both the electric moment and the ionization constant. The moments of propiolic, tetrolic and phenylpropiolic acids are 2.08, 2.12 and 2.29 *D*, respectively, while the moments of acetic, propionic, phenylacetic and benzoic acids are 1.73, 1.75, 1.75 and 1.71 *D*, respectively. The ionization constants of acetic, propionic, phenylacetic and benzoic acids are 1.8×10^{-5}, 1.4×10^{-5}, 5.6×10^{-5} and 7.3×10^{-5}, respectively, while the ionization constants for propiolic, tetrolic and phenylpropiolic acids are 14.0×10^{-3}, 2.5×10^{-3} and 5.9×10^{-3}, respectively. The presence of the triple bond undoubtedly causes the hydrogen of the carboxyl group to become more positive in character, the increased polarity of the hydrogen to oxygen linkage being manifested in an increased resultant moment for the carboxyl group and an increased ionization constant for the acetylenic acids. The resultant moments for the molecules of the substituted phenylpropiolic acids are due to such complex structures that little can be done with them at present. A similar statement applies to the substituted benzoic acids.

Summary

1. The presence of the triple bond has a pronounced effect on the moments of the carboxyl group in the propiolic acids and on the ionization constants of these acids. The data indicate that the hydrogen of the carboxyl group is more positive in the acetylenic acids than such acids as acetic.

2. Electric moments have been determined for propiolic, tetrolic, phenylpropiolic, *p*-chlorophenylpropiolic, *o*-chlorophenylpropiolic, *p*-nitrophenylpropiolic, *o*-nitrophenylpropiolic, phenylacetic, benzoic, *p*-nitrobenzoic, *o*-hydroxybenzoic, *m*-hydroxybenzoic and *p*-hydroxybenzoic acids.

NOTRE DAME, INDIANA

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