

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Behavior of Organic Compounds in 100% Sulfuric Acid¹

BY MELVIN S. NEWMAN AND N. C. DENO

The behavior of organic compounds in 100% sulfuric acid has been studied by cryoscopic determination of the *i*-factors and by isolation experiments. A series of arylcarboxylic acids were studied to determine more closely the structural requirements for loss of hydroxyl anion to yield an oxocarbenium or cyclic carbonium ion. A series of arylcarboxanilides was studied in an unsuccessful search for a stable iminocarbenium ion. A series of diaryl ketones gave only proton addition or sulfonation.

This paper is a continuation of the work on cryoscopic determination of Vant Hoff *i*-factors of organic compounds in 100% sulfuric acid.² The classes of compounds studied were arylcarboxylic acids and anilides and arylketones.

i-Factors

The method of measurement was identical to that previously reported.^{2,3} An important part of the technique was to measure the *i*-factors as a function of time at specific temperatures. The results are summarized in Table I.

Preparation of Compounds.—Samples of the following compounds suitable for *i*-factor measurements were obtained by recrystallization of commercial samples: *o*-, *m*- and *p*-methoxybenzoic acids, 4,4'-dichlorobenzophenone, and 4,4'-bis-(dimethylamino)-benzophenone (Michler ketone).

The following compounds were prepared by previously described methods: pentamethylbenzoic acid⁴; 2,3,5,6-tetramethylbenzoic acid⁵; *o*-toluanilide⁶ and mesitanilide⁶; 2,6-dimethylterephthalic acid⁷; *p*-benzoylbenzoic acid⁸; *o*-mesitylbenzoic acid⁹; phthalaldehydic acid¹⁰; 1,8-naphthalaldehydic acid¹¹; 4,5-phenanthraldehydic acid¹²; 1,8-naphthalic anhydride¹³; dimesityl ketone¹⁴; triphenylmethyl 2-biphenyl ketone (a sample was kindly supplied by Dr. W. A. Mosher, Univ. of Delaware); 4,4'-dimethoxybenzophenone¹⁵; and tetraphenylcyclopentadienone.¹⁶

Pentamethylbenzoic acid.—A solution of the acid chloride (prepared from 4 g. of the acid and 10 cc. of thionyl chloride) in 50 cc. of benzene was added to a stirred solution of 10 cc. of aniline in 100 cc. of benzene. The benzene solution was washed with water and concentrated to 30 cc. The crystals were filtered and recrystallized from alcohol to give 2.75 g. (50%), m.p. 187.8–188.6°, of shiny flakes of the anilide.

*Anal.*¹⁷ Calcd. for C₁₈H₂₁ON: C, 80.9; H, 7.9; N, 5.2. Found: C, 81.1; H, 7.9; N, 5.2.

***m*-Benzoylbenzoic Acid.**—This acid was prepared in a manner identical to that used to prepare *p*-benzoylbenzoic acid.⁸ With both preparations, considerable quantities of crystalline neutral material were isolated from the chromic acid oxidation of the appropriate tolyl phenyl ketone. These materials were not further investigated. The yield

(1) This work was made possible through the support of the Office of Naval Research.

(2) M. S. Newman and N. C. Deno, *THIS JOURNAL*, **73**, 3644 (1951).

(3) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

(4) H. Clement, *Ann. chim.*, **13**, 243 (1940).

(5) R. C. Fuson and S. C. Kelton, *THIS JOURNAL*, **63**, 1500 (1941).

(6) Samples were kindly supplied by Dr. P. A. S. Smith, Univ. of Michigan.

(7) W. A. Noyes, *Am. Chem. J.*, **20**, 789 (1898).

(8) E. Wertheim, *THIS JOURNAL*, **55**, 2540 (1933).

(9) M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1540 (1941).

(10) R. L. Shriner and F. J. Wolf, *Org. Syntheses*, **23**, 74 (1943).

(11) C. Graebe and E. Gfeller, *Ann.*, **276**, 13 (1893).

(12) H. Vollmann, H. Becker, M. Corell and H. Streeck, *ibid.*, **531**, 65 (1937).

(13) Ref. 11, p. 6.

(14) E. P. Kohler and Baltzly, *THIS JOURNAL*, **54**, 4015 (1932).

(15) E. Bergmann and J. Hervey, *Ber.*, **62**, 916 (1929).

(16) W. Dilthey and F. Quint, *J. prakt. Chem.*, **123**, 139 (1930).

(17) Clark Microanalytical Lab., Urbana, Ill.

TABLE I

<i>i</i> -FACTORS IN 100% SULFURIC ACID			
Sample	Time, hr.	Temp., °C. ^b	<i>i</i>
2,3,5,6-Tetramethylbenzoic acid			
1	1/2	10	3.72
1	3	25	4.07
2	2/3	10	3.84
2	20	25	4.00
3	1/2	10	3.68
3 + 4	2	25	3.96
	Best final value		4.01
Pentamethylbenzoic acid ^a			
			4.02
Pentamethylbenzanilide			
1	2/3	10	2.37
1	4/3	10	2.90
1	2	25	5.47
1	4	25	5.76
1	26	25	5.84
	Best final value		5.8
2,6-Dimethylterephthalic acid ^a			
			2.14
<i>o</i> -Methoxybenzoic acid			
1	2/3	10	3.02
1	2	25	3.91
1	4	25	3.92
1	20	25	3.98
2	2/3	10	2.30
2	3/2	25	3.51
2	5	25	4.00
2	20	25	4.06
	Best final value		4.02
<i>m</i> -Methoxybenzoic acid			
1	2/3	10	2.42
1	2	25	3.98
1	4	25	4.01
2	1	25	3.97
2	30	25	3.97
3	2	25	4.03
	Best final value		4.00
Triphenylmethyl-2-biphenyl ketone			
1	1	10	5.30
1	5/3	10	5.74
1	7/3	10	6.69
	Extrap. to zero time		4.6
<i>p</i> -Methoxybenzoic acid			
1	2/3	10	2.45
1	4/3	10	2.84
1	2	25	3.68
1	20	25	3.76
2	2	25	3.85
2	4	25	3.85
	Best final value		3.80
<i>m</i> -Benzoylbenzoic acid ^a			
			2.52
<i>p</i> -Benzoylbenzoic acid ^a			
			2.49
<i>o</i> -Mesitylbenzoic acid ^a			
			3.68
Phthalaldehydic acid ^c			
			2.20
1,8-Naphthalaldehydic acid ^c			
			3.94
4,5-Phenanthraldehydic acid ^c			
			3.66
1,8-Naphthalic anhydride ^c			
			1.84
Dimesityl ketone			
1	2/3	10	1.93
1	2	25	2.47
2	1/2	10	2.16
2	6	25	4.47
4,4'-Dichlorobenzophenone ^a			
			1.99
4,4'-Bis-(dimethylamino)-benzophenone ^a			
			3.50
4,4'-Dimethoxybenzophenone			
1	1/2	10	2.60
1	2	25	4.20
1	4	25	4.47
1	6	25	4.61
1	28	25	5.25
Tetraphenylcyclopentadienone			
1	1/2	10	2.43
1	4/3	10	3.20
1	2	10	3.90
1	3	10	4.87
	Extrap. to zero time		2.0

^a The *i*-factors measured after 1/2 hr. did not change on continued standing at 10 or 25°. ^b A temperature listed as 10° means that the temperature throughout the processes of solution and freezing point measurement remained between 7 and 11°. A temperature listed as 25° means that the solution was allowed to stand at approximately 25° for the specified time and then cooled and the freezing point determined. ^c The *i*-factor measured after 1/2 hr. did not change on continued standing at 10°.

of *m*-benzoylbenzoic acid, m.p. 160–162°,¹⁸ from *m*-tolylphenyl ketone was 64%.

Isolation of Reaction Products.—The isolation experiments were conducted by holding a 2–5% solution of the compound in 100% sulfuric acid at 25° (except where noted) for the time specified, followed by pouring the solution onto

(18) M. E. Smith, *THIS JOURNAL*, **43**, 1921 (1921).

ice with stirring. The non-sulfonated organic products were isolated from ethereal extracts of these mixtures.

TABLE II

RECOVERY OF COMPOUNDS FROM SOLUTION IN 100% SULFURIC ACID

Compound	Color of H ₂ SO ₄ soln.	Time, hr.	Yield of recovered starting compound, %
Pentamethylbenzoic acid	Colorless	3/2	100
2,3,5,6-Tetramethylbenzoic acid	Colorless	1/6	83
<i>p</i> -Benzoylbenzoic acid	Yellow ^a	3	100 ^b
<i>m</i> -Benzoylbenzoic acid	Yellow ^a	3	100 ^b
Phthalaldehydic acid	Colorless	2 ^c	75
1,8-Naphthalaldehydic acid	Yellow ^{a,d}	2 ^c	100
1,8-Naphthalic anhydride	Brown-red ^{a,e}	1	98

^a The color disappeared completely on dilution with water. ^b These two acids were also quantitatively recovered when the sulfuric acid solution was poured into methanol with cooling. ^c The solution was held at 10° instead of 25°. ^d The solution had a light green fluorescence. ^e The solution had a deep blue fluorescence.

TABLE III

PRODUCTS FROM R-CO-NH-C₆H₅ AND 100% SULFURIC ACID AT 25°

R	Time, min.	Isolated products, % ^a		
		RCOOH	R-CO-NH-C ₆ H ₅	Sulfonated anilide (by difference)
Pentamethylphenyl	30	68	32	0
Pentamethylphenyl	90	100	0	0
Mesityl	30	50	34	16
<i>o</i> -Tolyl	30	2	13	85

^a The products were isolated by separating the ethereal extract into neutral and acidic fractions. Both the acid and the anilide were pure as judged by the m.p.

With the following compounds, dilution with water gave only water-soluble products; the time of contact and color of the sulfuric acid solution are noted in parentheses: *o*-, *m*- and *p*-methoxybenzoic acids (six hr., colorless) and 4,4'-dimethoxybenzophenone (one hr., yellow becoming colorless on dilution).

Isolation experiments have been previously reported on tetraphenylcyclopentadienone¹⁹ (purple solution, after three hr. at 10° the color of the solution had changed to an extremely deep green). Isolation experiments were not performed on dimesityl ketone, 4,4'-dichlorobenzophenone and 4,4'-bis-(dimethylamino)-benzophenone. The colors of the sulfuric acid solutions were yellow, pale yellow, and nearly colorless, respectively, becoming colorless on dilution. Attempts to reisolate 4,5-phenanthraldehydic acid (orange-red solution) from solutions in 100% sulfuric acid gave impure material that was not characterized.

Discussion

Arylcarboxylic Acids.—Three types of ionization have been observed with arylcarboxylic acids. Addition of a proton (Eq. 1) has been observed with a large number of aromatic acids.¹⁹⁻²⁷

(19) A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908).

(20) A. Hantzsch, *ibid.*, **65**, 41 (1909).

(21) G. Oddo and A. Casalino, *Gazz. chim. ital.*, **47**, II, 200 (1917).

(22) H. P. Treffers and L. P. Hammett, *THIS JOURNAL*, **59**, 1708 (1937).

(23) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

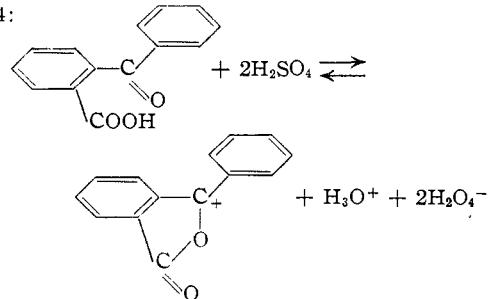
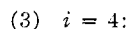
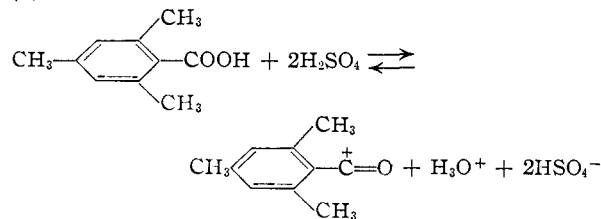
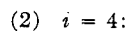
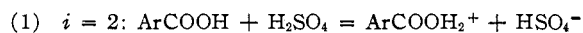
(24) M. S. Newman, R. A. Craig and A. B. Garrett, *ibid.*, **71**, 869 (1949).

(25) R. A. Craig, A. B. Garrett and M. S. Newman, *ibid.*, **72**, 163 (1950).

(26) L. P. Kuhn and A. H. Corwin, *ibid.*, **70**, 3370 (1948).

(27) L. P. Kuhn, *ibid.*, **71**, 1575 (1949).

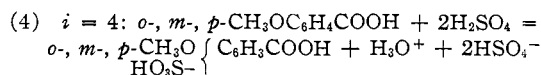
Loss of the hydroxyl ion to give an oxocarbenium (Eq. 2) has been observed with mesitoic acid.^{22,23,25} Loss of the hydroxyl ion to give a cyclic carbonium ion (Eq. 3) has been observed with *O*-benzoylbenzoic acid.²³



The six acids and one anhydride listed in Table II were studied to determine more closely the structural requirements for ionization according to equation 2 (see Table I). Pentamethylbenzoic and 2,3,4,6-tetramethylbenzoic acids were found to have *i*-factors of 4 indicating ionization to the oxocarbenium ion (Eq. 2). Since absorption spectra of an oxocarbenium ion in sulfuric acid has not been reported, the spectra of pentamethylbenzoic, 2,3,5,6-tetramethylbenzoic and benzoic acids were measured in 100% sulfuric acid (Fig. 1).

2,6-Dimethylterephthalic acid has been reported to give an *i*-factor of 2.4, indicating partial ionization to the corresponding oxocarbenium ion.²⁸ When the sample was thoroughly dried at 140° *in vacuo*, we found the *i*-factor was 2.14, which indicates that the amount of oxocarbenium ion was about 5%. This compound is of particular interest because evidence from chemical reactions indicated the presence of oxocarbenium ion.²⁸

The *i*-factor measurements with *p*-methoxybenzoic acid emphasize the importance of recording these measurements as a function of time. An *i*-factor of 3.38 had been previously reported and interpreted as due to the partial formation of oxocarbenium ions.²⁶ We found that the *i*-factor increased from a value of 2.45 after 40 minutes at 10° to a final equilibrium value of 3.8. After the *i*-factor had reached its equilibrium value, it was no longer possible to obtain ether extractable material on dilution. We believe that the *p*-methoxybenzoic acid slowly sulfonated (equation 4) and the change in *i*-factor with time was the result of sulfonation.



(28) M. S. Newman and H. L. Gildenhorn, *THIS JOURNAL*, **70**, 317 (1948).

o- and *m*-methoxybenzoic acids exhibited similar behavior which is more easily understood on the basis of sulfonation than on the basis of partial formation of oxocarbenium ions.

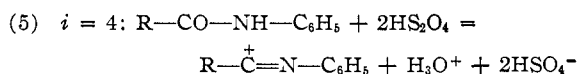
Naphthalic anhydride gave an *i*-factor of 1.84, evidently due to proton addition.

The remaining six acids were studied to determine the structural requirements for ionization according to equation 3. The only acid previously reported to undergo this ionization was *o*-benzoylbenzoic acid.²³ Arguments based on studies of pseudo and normal ester formation have been advanced to show that the *i*-factor of 4 was due to ionization according to Eq. 3 instead of the alternative possibility of Eq. 2. With Eq. 3 it would be expected that the *m*- and *p*-benzoylbenzoic acids would give different behavior from the *ortho* isomer. These expectations have been confirmed. Both acids gave yellow solutions (colorless on dilution) with *i*-factors of 2.5 in contrast to the orange-red solution with *i*-factors of 4 obtained with *o*-benzoylbenzoic acid. Both acids were recovered quantitatively by pouring the sulfuric acid solution into either methanol or water. This shows that the *i*-factor of 2.5 was due to addition of an average value of 1.5 protons and not to partial oxocarbenium formation.

Phthalaldehydic and 1,8-naphthaldehydic acids gave strikingly different behavior. Phthalaldehydic acid gave absolutely colorless solutions in 100% sulfuric acid with an *i*-factor of 2.2 (due to addition of an average value of 1.2 protons); naphthaldehydic acid gave deep yellow solutions with an *i*-factor of 3.9 (due to ionization according to Eq. 3). Both were recovered unchanged on dilution. 4,5-Phenanthraldehydic acid gave an orange-red solution with an *i*-factor of 3.7. It probably ionized according to Eq. 3, but the interpretation is in doubt because of the failure to reisolate the acid in satisfactory amounts on dilution.

o-Mesitylbenzoic acid was studied because it does not yield a pseudo-methyl ester when the acid chloride is treated with methanol in pyridine.⁹ Its solution in sulfuric acid was deep red and the *i*-factor was 3.7, which probably indicates a cyclic carbonium ion of the same type as that given by *o*-benzoylbenzoic acid (Eq. 3).

Arylcarboxanilides.—It was thought that certain arylcarboxanilides might lose a hydroxide ion in 100% sulfuric acid to yield iminocarbenium ions according to equation 5.



No conclusive evidence for this type of ionization was found although an interesting gradation in behavior toward sulfuric acid was observed with the anilides of pentamethylbenzoic, mesitoic and *o*-toluic acids (Table III). The *i*-factor actually measured for pentamethylbenzanilide can be ex-

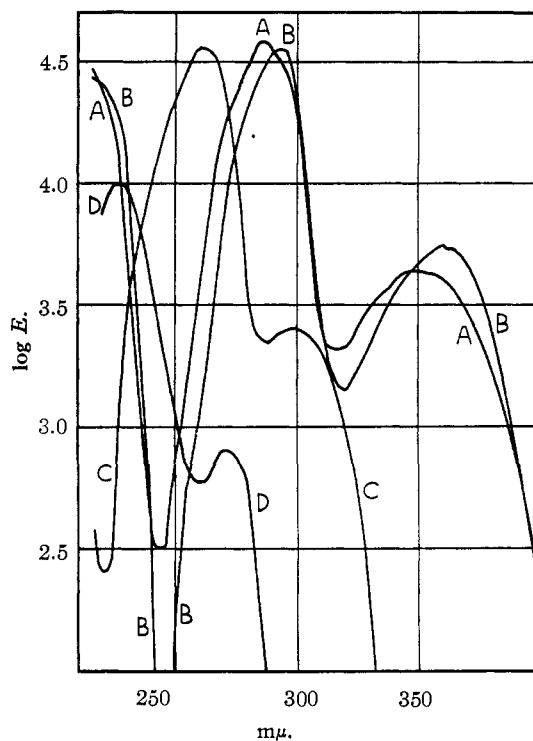
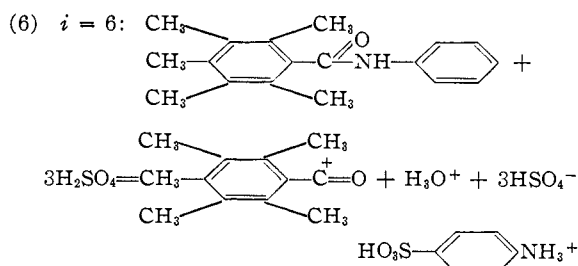


Fig. 1.—Absorption spectra in 100% sulfuric acid: (A) pentamethylbenzoic acid, (B) mesitoic acid and (C) benzoic acid, absorption spectra in water (D) benzoic acid. The spectra were recorded by Mr. Arlene Brooks on a Beckman ultraviolet spectrophotometer. All three solutions were colorless to the eye.

plained by cleavage in the early stages. The final equilibrium value of 5.85 approximates that expected from equation 6.



Aryl Ketones.—Five aryl ketones were studied. Dimesityl ketone and 4,4'-dichlorobenzophenone added a single proton. 4,4'-Bis-(dimethylamino)-benzophenone added an average value of 2.5 protons. 4,4'-Dimethoxybenzophenone sulfonated so rapidly that the *i*-factor could not be easily interpreted. Tetraphenylcyclopentadienone showed initial addition of a single proton followed by decomposition.