

theless this aspect of the correlation is weakened for short-chain acids by this example.

As has been mentioned already, the spectral features of the isopropyl configuration have been observed for isobutyric, isovaleric and isocaproic acids.

From these observations it appears that the correlation as developed here may be to some extent applicable to fatty acids of low molecular weight.

However further work needs to be done on pure materials to establish its limitations.

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BERKELEY 4, CALIF.

[PHILLIPS PETROLEUM COMPANY, RESEARCH DIVISION]

Relationship Between Rates of Halogenation and Basicities of Methylbenzenes

BY FRANCIS E. CONDON

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The relative basicities of a series of methylbenzenes have been determined, and a relationship developed between basicity and the rate of halogenation of the compounds.

Figure 1 illustrates a relationship between calculated relative rates of halogenation¹ and measured relative basicities² (essentially, relative equilibrium constants for reaction with $\text{HF}\cdot\text{BF}_3$) of all the methylbenzenes except hexamethylbenzene. The straight line, drawn in accordance with the least squares principle, fits the equation

$$\log(\text{relative rate}) = 1.27 \log(\text{relative basicity}) + \text{a constant}$$

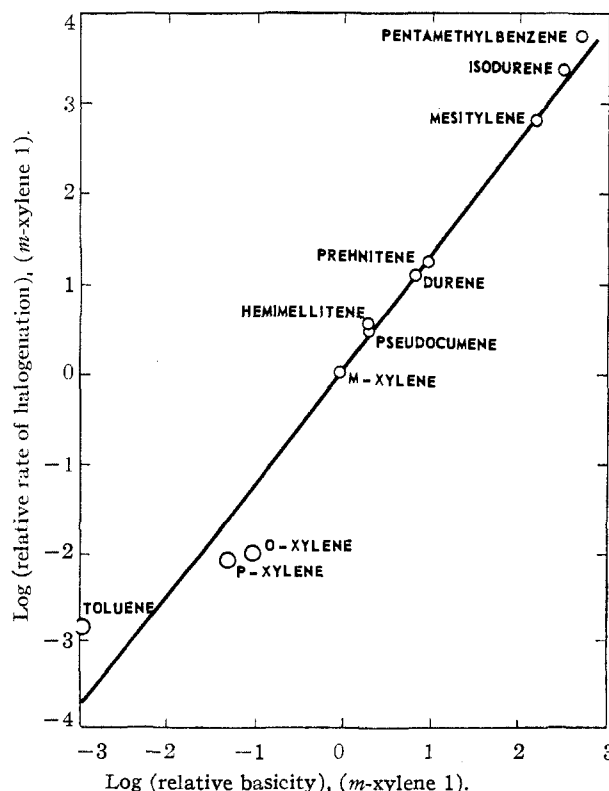


Fig. 1.—Relationship between rates of halogenation and basicities of methylbenzenes.

(1) F. E. Condon, *THIS JOURNAL*, **70**, 1963 (1948).

(2) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

The relative rate of halogenation of each polymethylbenzene was calculated as a sum of partial relative rates for each unsubstituted ring carbon. The relative rate at each unsubstituted ring carbon was in turn calculated as a product of two or more partial relative rates, each corresponding to a methyl and its position. The partial relative rates corresponding to an ortho, a meta and a para methyl were 600, 5 and 870, respectively. Calculated relative rates agreed with available experimental values within a factor of 2.¹

The relative basicities of the methylbenzenes can be similarly correlated, if it be ignored that hexamethylbenzene is the most basic of all the methylbenzenes. "Partial relative basicities" corresponding to an ortho, a meta and a para methyl were calculated by solution of suitable simultaneous equations for the measured² relative basicities of durene, isodurene, prehnitene, and pentamethylbenzene.³ The calculated "partial relative basicities" corresponding to an ortho, a meta and a para methyl were 103, 3.1 and 145, respectively. By use of these values and a value of 1 for each carbon in benzene, relative basicities of benzene and all the methylbenzenes, except hexamethylbenzene, were calculated. Calculated relative basicities are compared with experimental values in Table I.

The "partial relative basicities" corresponding to an ortho, a meta and a para methyl are empirically related to the corresponding partial relative rates of halogenation as

$$\log 600 / \log 103 = \log 5 / \log 3.1 = \log 870 / \log 145 = 1.39 \pm 0.03$$

Presumably, the value of the ratios of the logarithms should equal the slope of the line in Fig. 1. The slope is lowered by the position of the point for toluene, whose relative basicity is least accurately known. If toluene were excluded from the

(3) For durene, $2o^2m^2 = 6.7X$; for isodurene, $2o^2mp = 311X$; for prehnitene, $2om^2p = 9.4X$; and for pentamethylbenzene, $o^2m^2p = 484X$; where o , m and p are, respectively, the "partial relative basicities" corresponding to an ortho, a meta and a para methyl; and X is the basicity of m -xylene relative to that for each carbon of benzene. Division of the equation for pentamethylbenzene by each of the others in turn gives numerical values for o , m , and p .

TABLE I
 RELATIVE BASICITIES OF METHYLBENZENES

	Calcd.	Exptl. ³
Benzene	0.0002
Methylbenzene (toluene)	.012	(ca. 0.001)
1,4-Dimethylbenzene (<i>p</i> -xylene)	.042	.05
1,2-Dimethylbenzene (<i>o</i> -xylene)	.050	.10
1,3-Dimethylbenzene (<i>m</i> -xylene)	1.3	1
1,2,4-Trimethylbenzene (pseudo-cumene)	2.6	2
1,2,3-Trimethylbenzene (hemi-mellitene)	3.1	2
1,2,4,5-Tetramethylbenzene (durene)	6.6	6.7
1,2,3,4-Tetramethylbenzene (prehnitene)	9.4	9.4
1,3,5-Trimethylbenzene (mesitylene)	151	156
1,2,3,5-Tetramethylbenzene (isodurene)	312	311
Pentamethylbenzene	484	484
Hexamethylbenzene (mellitene)	4950

figure, a line with a slope of 1.45 could be drawn through the remaining points in accordance with the least squares principle.

The relationship noted here between two reactions involving aromatic ring carbons is similar to previously observed relationships between reactions involving aromatic side chains⁴ for which

$$\log k/k_0 = \rho\sigma$$

where k and k_0 are rate or equilibrium constants for a substituted and an unsubstituted compound, respectively, and ρ and σ are constants characteristic of the reaction and the substituent, respectively. Since σ for meta methyl is -0.069 and σ for para methyl is -0.170 , it can be calculated that ρ for halogenation is $-\log 5/0.069 = -10.1$ or $-\log 870/0.170 = -17.3$ and that ρ for reaction with $\text{HF}\cdot\text{BF}_3$ is $-\log 3.1/0.069 = -7.1$ or $-\log 145/0.170 = -12.7$. The large differences between the ρ 's calculated from the σ for meta methyl and the ρ 's calculated from the σ for para methyl suggests that a set of σ -values different from those used to correlate reactions of aromatic side chains may be useful for correlating reactions of aromatic ring carbons.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

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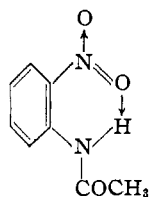
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Polarographic Reduction and Indicated Tautomeric States of the Nitroacetanilides in Ethanol¹

By M. E. RUNNER² AND E. C. WAGNER

Study of the polarographic behaviors of *o*-, *m*- and *p*-nitroacetanilides and of the isomeric *N*-nitrophenyl-*N'*-phenylacetamidines in absolute ethanol buffers revealed (1) analogy between the two types considered as aquo-ammono and ammonoacids, (2) a tentative correlation between the pK characteristics of the buffers and induced tautomeric or ionic states of the nitro compounds, (3) the effects of the acetamino and acetimino groups in facilitating polarographic reduction of the nitro group, (4) a similar effect, in the ortho-nitro isomerides only, attributable to chelation, presence of which is suggested also by their relatively greater volatilities, and (5) four-electron polarographic reduction, with indecisive indication of six-electron reduction in acid media.

This paper reports the results of polarographic reductions of *o*-, *m*- and *p*-nitroacetanilides in absolute ethanol. Interpretation with respect to tautomeric states is similar to that applied in the similar study of the isomeric *N*-nitrophenyl-*N'*-phenylacetamidines³ (of which the nitroacetanilides are the half-oxygen system analogs), and justifies the inference that the structure of *o*-nitroacetanilide permits chelation



Such involvement of the nitro group would be expected to increase its reducibility. Other inferen-

tial evidence for chelation in this compound is available in the finding⁴ that in naphthalene it is less associated than its isomerides, and that its wet melting point depression is less than that of *p*-nitroaniline.^{4,5}

The structures of the nitroacetanilides may undergo alterations induced by the pK of the environment, to test which of the polarographic examinations were made at intervals through the range pK 1 to 17. The use of absolute ethanol as solvent necessitated elaboration of a suitable system of buffers.⁶

Since the polarographic reductions of the *N*-ni-

(4) H. O. Chaplin and L. Hunter, *J. Chem. Soc.*, 875 (1938).

(5) W. Baker, *ibid.*, 1687 (1934).

(6) The buffers used, and the pK value calculated for each, are as follows: perchloric acid, 1; *o*-bromoaniline hydrochloride, 3; β -naphthylamine hydrochloride, 5; chloroacetic acid, 6; *m*-bromobenzoic acid, 8; benzoic acid, 9; *o*-chlorobenzylamine hydrochloride, 10; diethylbarbituric acid, 12; guanidine hydrochloride, 13; lithium ethoxide, 17. Lithium chloride was added in amounts such that in each case the total concentration of the supporting electrolyte was at an ionic strength 0.05. This system of buffers, used here recently in the polarographic examination of the isomeric nitrobenzimidazoles,⁷ was developed for the present study by the junior author.

(7) J. L. Rabinowitz and E. C. Wagner, *THIS JOURNAL*, 78, 3080 (1951).

(1) This paper represents the first part of the Ph.D. Dissertation of Mervin E. Runner, University of Pennsylvania, 1950.

(2) Chemistry Dept., The Illinois Institute of Technology, Chicago 16, Illinois.

(3) M. E. Runner, M. L. Kilpatrick and E. C. Wagner, *THIS JOURNAL*, 69, 1406 (1947).