Reactivity of Aryl Isocyanates

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The rate constants reported in the literature for the reactions of several aryl isocyanates and diisocyanates with various alcohols under different experimental conditions have been correlated successfully by means of the Hammett linear free-energy relationship,[1] $\log k/k_0 = \rho\Sigma\sigma$. In this equation, ρ is the reaction series constant and $\Sigma\sigma$ is the sum of the substituent constants. Based on limited data, ρ is calculated to be 1.69.

In Table I are listed the reaction series and rate constants. Figures 1 to 3 are plots of $\log k/k_0$ vs. $\Sigma\sigma$, where the k values designated as k_1 in Table I, refer to the reaction of the first isocyanato group. In every series the rate constants for the phenyl isocyanate reactions are taken as k_0.

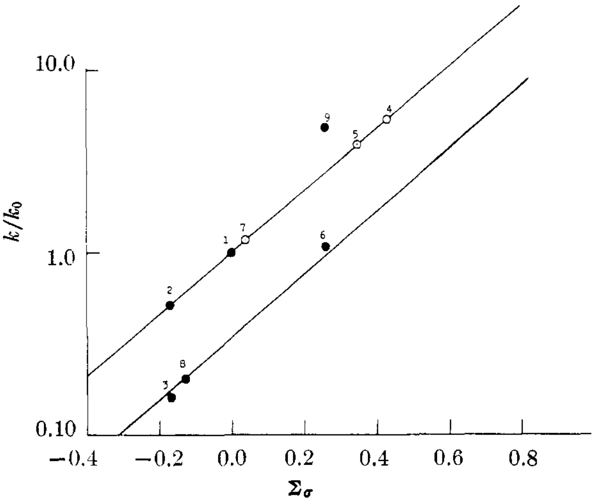

Fig. 1. Plot of $\log k/k_0$ vs. $\Sigma\sigma$; series I: ⊙, used to evaluate σ values. Numbers refer to compounds in Table I

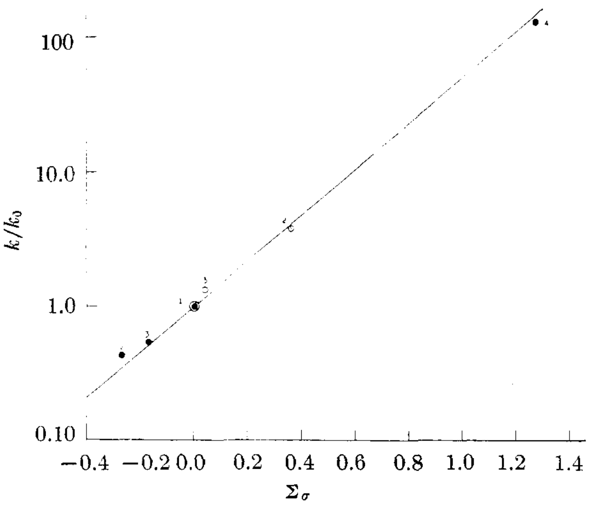

Fig. 2. Plot of $\log k/k_0$ vs. $\Sigma\sigma$; ○, series II; ●, series III. Numbers refer to compounds in Table I

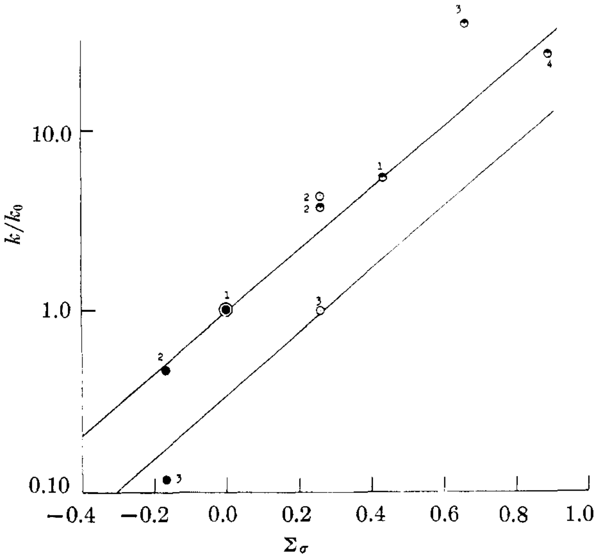

Fig. 3. Plot of $\log k/k_0$ vs. $\Sigma\sigma$; ●, series IV; ○, series V; ◓, series VI. Numbers refer to compounds in Table I

TREATMENT OF RATE DATA

The number of data available in every series is limited, and each series was run at a different temperature. Hence, the assumption was made that the ρ and σ values are independent of temperature. The experimental rate constants for the symmetrical diisocyanates were divided by 2 in order to evaluate the reactivity of one isocyanato group.

Series I.[2] Fig. 1 shows a plot of the data of series I using a ρ value of 1.69, the values of k/k_0 for compounds 4, 5, and 7 being plotted on this line. The σ values obtained for the substituents of these compounds are presented in Table II. Although these values were used for the appropriate compounds in this and in the other series and appear to be applicable in these particular reactions, they are considered to be preliminary, since no other confirmatory data are available. Also listed in Table II are other σ values derived from these reactions together with the literature values of those required in this paper. The points for the compounds that have an o-CH_3 group, namely 3, 6, and 8 define a line parallel to that of the sterically unhindered compounds, the σ values of the p-substituents of compounds 7 and 8 being considered equal to each other.

Series II[3] and III[4]: In Fig. 2 are presented the data for these series. All the σ values are known

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(1) L. P. Hammett, *Physical Organic Chemistry*, McGraw Hill Co., New York, 1940, p. 184; also, R. W. Taft, Jr., in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 570.

(2) J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958).

(3) L. L. Ferstandig and R. A. Scherrer, *Am. Chem. Soc. Div. Petrol. Chem. Symposium* 1 (Chemicals from Petroleum) Gen. Papers No. 2, 69 (1956).

(4) J. W. Baker, and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

TABLE I

SUMMARY OF RATE DATA

Series I: Reaction with 1-Butanol in Toluene, 0.0313*M* Triethylamine Catalyst, at 39.69°		
Monoisocyanates	k_1	k_2(1 mol.$^{-1}$ min.$^{-1}$)
1. Phenyl	0.406	...
2. *p*-Tolyl	0.210	...
3. *o*-Tolyl	0.0655	...
Diisocyanates		
4. *m*-Phenylene	4.34	0.517
5. *p*-Phenylene	3.15	0.343
6. 2,6-Tolylene	0.884	0.143
7. 4,4′-Diphenylmethane	0.960	0.33
8. 3,3′-Dimethyl-4,4′ diphenylmethane	0.165	0.070
9. 2,4-Tolylene	1.98	0.166

Series II: Reaction with Ethanol in Toluene, 30°		
	$k_1 \cdot 10^2$	$k_2 \cdot 10^2$ units unknown
1. Phenyl isocyanate	2.39	...
2. 3,5-Tolylene diisocyanate	9.20	0.362
3. 4,4′-Diphenylmethane	6.24	2.25

Series III: Reaction with Methanol in Di-*n*-butyl Ether, 0.0306*N* Triethylamine Catalyst, at 20°	
	$k_1 10^2$(1 mol.$^{-1}$ min.$^{-1}$)
1. Phenyl isocyanate	22.6
2. *p*-Methoxyphenyl isocyanate	9.06
3. *p*-Tolyl isocyanate	12.25
4. *p*-Nitrophenyl isocyanate	~3,000

Series IV: Reaction with Ethanol in Carbon Tetrachloride, 0.072*N* Triethylamine catalyst, at 28°	
	$k_1 10^4$(1 mol.$^{-1}$ sec.$^{-1}$)
1. Phenyl isocyanate	43.30
2. *p*-Tolyl isocyanate	18.42
3. *o*-Tolyl isocyanate	5.16

Series V: Reaction with Ethanol in Carbon Tetrachloride, at 28°	
	$k_1 10^4$(1 mol.$^{-1}$ sec.$^{-1}$)
1. Phenyl isocyanate	2.50
2. 2,4-Tolylene diisocyanate	10.70
3. 2,6-Tolylene diisocyanate	2.46

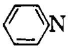
Series VI: Reaction with 1-Butanol in Toluene, at 25°		
	$k_1 10^3$	$k_2 10^3$(1 mol.$^{-1}$ sec.$^{-1}$)
1. *m*-Phenylene diisocyanate	1.7	0.17
2. 2,4-Tolylene diisocyanate	0.58	...
3. 4-Chloro-1,3-phenylene diisocyanate	5.8	0.75
4. 4,6-Dichloro-1,3-phenylene diisocyanate	8.4	0.92

for the compounds in series III, in which the rate constants vary by approximately 300 fold.

Series IV,[5] V[5] and VI.[6] Fig. 3 shows that the data of series IV and V are correlated within acceptable precision by the parallel lines obtained from series I. Since the rate constant for phenyl isocyanate was not determined in series VI, the relative rate constant values were determined by use of the rate constant for *m*-phenelene diisocyanate in series VI and its relative rate constant in series I. The rate constants for the isocyanates with two ortho groups have been omitted.

TABLE II

SUBSTITUENT CONSTANTS

Substituent	σ Value	Source
m-NCO	0.43	Cmpd. I-4
p-NCO	0.35	I-5
p–(CH$_2$NCO)	0.04	I-7
m-NHCOOnBu	0.06	I-4
	0.01	I-6
	0.04	I-9
	0.02	VI-1
	0.05	VI-4
*p*NHCOOnBu	−0.05	I-5
p–(CH$_2$NHCOOnBu)	−0.05	I-7
p–(CH$_2$NHCOOC$_2$H$_5$)	0.01	II-3
o,p-CH$_3$	−0.17	Ref. 1
m-CH$_3$	−0.07	Ref. 1
o,p-Cl	0.23	Ref. 1
p-OCH$_3$	−0.27	Ref. 1
p-NO$_2$	1.27	Ref. 1

DISCUSSION

The data of the sterically unhindered aryl isocyanates in every reaction series follow the Hammett linear free-energy relationship with acceptable precision. An *ortho*-methyl group causes a decrease in the rate constant by a factor of approximately 0.34.

The data for 2,4-tolylene diisocyanate deserve special comment. Most authors[5–7] have assumed that the reactivity of the *para*-isocyanato group is about 10 times that of the *ortho* group, whereas others[2] have considered them to be of equal reactivity. These assumptions simplified the mathematical analyses of the rate data. It will now be shown that in the light of this paper, the *para*-isoycanato group is computed to be 2.67 times as reactive as the *ortho* group.

Considering the *m*- and *p*-σ values to consist of contributions of inductive and resonance effects,[8] the resonance effects of a *meta*-isocyanato group is

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(5) J. C. Kogon, *J. Org. Chem.*, **24**, 438 (1959).

(6) J. J. Tazuma and H. K. Latourette, presented before the Division of Paints and Plastics at the 130th national meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

(7) M. Morton and M. A. Deisz, presented before the Division of Paints and Plastics at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

(8) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

very small. Furthermore, the steric inhibition of resonance of the *ortho*-isocyanato group by the methyl group is considered to be negligible. Hence, the m-σ value that is used in the evaluation of the reactivity of the *para*-isocyanato group by the *ortho*-isocyanato group is unaffected by the presence of the methyl group. Therefore, the calculated k/k_0 value for the *para* group is 2.75 using the determined value of ρ and the appropriate σ values from Table II. The k/k_0 value for the *ortho* group is 1.03, using the average of the experimental data of compounds I-6 and V-3 (or 0.93 using the data from the "ortho" line of Fig. 1). Thus, the expected initial k/k_0 value for 2,4-tolylene diisocyanate is 3.78. A comparison of the experimental log k/k_0 values to the calculated one is shown in Table III.

TABLE III

VALUES OF RELATIVE RATE CONSTANTS FOR 2,4-TOLYLENE DIISOCYANATE

log k/k_0	Source
0.577	Calculated
0.688	Cmpd. I-9
0.631	Cmpd. V-2
0.562	Cmpd. VI-2

The agreement between the calculated and experimental values, which were derived under various conditions, is rather striking and within 0.1 log units which is the accepted limit of accuracy for this type of correlation. Thus, it is concluded that the ratio of reactivity of the *para* to the *ortho* group is about 2.67 to 1. The difference in reactivity of one order of magnitude that has been previously assumed does not apply to these groups, but is the ratio of the sum of the reactivities of both isocyanato groups compared to that of the *ortho*-isocyanato group when the *para*-substituent is a carbamide and not an isocyanato group.

Further corroboration for this approach lies in the similar explanation of the value for the rate constant of 4-chloro-1,3-diphenylene diisocyanate (compound VI-3). The difference between the experimental and calculated log k/k_0 values of 4,6-dichloro-1,3 phenylene diisocyanate (compound VI-4) is taken as the steric effect due to an *ortho*-chloro group. Hence, the expected k/k_0 values for the *para*- and *ortho*-isocyanato groups of compound VI-3 are 13.0 and 10.8, respectively, resulting in an initial relative rate constant of 23.8 (1.377 log units) *vs.* the experimental value of 36.5 (1.562 log units). Considering the scarcity of applicable data in this series, the agreement is quite good and again emphasizes the fact that the two isocyanato groups have reactivities of the same order of magnitude.

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Bisacylation of 4-Pyrones

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In a recent paper[1] a method describing the acylation of 4-pyrones under the catalytic influence of trifluoroacetic acid has been described. This contribution represents an elaboration of that method in which bisacylation is accomplished. The procedure, although relatively simple, produces the diketones in high yield and remarkably free of polymerized contaminants.

Bisacylation of 4-pyrones in the presence of trifluoroacetic acid appears to be nonspecific in the orientation and the acyl groups are apparently put on any position available on the pyrone nucleus.

The bisacylated compounds, I-A–G, are given in Table I. Several derivatives of compound I-A, a relatively simple substance and illustrative of the nature of this type of compound, are given in confirmation of its generalized structure as compounds III and IV.

Included in this communication are several instances in which either acid anhydrides or *p*-bromo phenacyl bromide have been induced to react with pyrones. These compounds are listed in Table II as the II-A–C Series.

Attempted reduction of compounds I-B, -D, -E, and -F under the conditions of the Meerwein-Pondorf-Verley reaction failed in every case. The analytical results indicated that the pyrone had been fragmented and the pyrone structure destroyed.

Reduction of compounds I-A, -D and -E and II-A and -B with potassium borohydride in absolute ethanol was fairly successful in that compounds I-D and II-B were reduced as expected. The three other compounds gave analytical results which could not be justified. Infrared data are given for most of the new compounds listed in Tables I and II in Table III.

EXPERIMENTAL[2]

Preparation of compounds I-A–G *series.* A mixture consisting of 0.2 mol. of the acyl halide, except in the case of I-E in which 0.3 mol. of benzoyl chloride was used, 0.1 mol. of the pyrone and 35 ml. trifluoroacetic acid was refluxed for 30 min. or sufficiently longer so that hydrogen chloride was no longer evolved. The mixture was then diluted with 150 ml. of water, cooled, and filtered. The sample was dried in air and the analytical sample obtained by recrystallizing the compound once from boiling heptane.

The isolation of compound I-G was handled somewhat differently in that after the reaction mixture was diluted with water the solution was neutralized with sodium bicarbonate and extracted with benzene. The substance was

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[1] L. L. Woods and P. A. Dix, *J. Org. Chem.* **24**, 1126 (1959).

[2] All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns melting point assembly.