

Reactivity of Isocyanates in Terms of the Hammett Equation

Meta- and Para-Substituted Phenyl Isocyanates

MELVIN KAPLAN

National Aniline Division, Allied Chemical Corp., Buffalo, N. Y.

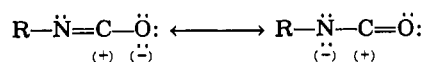
THE MAJOR FACTORS to be considered in the reactivity of molecules are steric and electronic effects. When a particular reaction is to be studied, it is desirable to observe one of these effects in order to minimize variables and to isolate activating or deactivating influences.

In a given series of meta- and para-substituted benzene derivatives, the effect of structure on rate of reaction is generally dependent upon a single basic factor: the polar or electronic effect of the substituent. Substituents that are held rigidly at large distances from the reaction center have an almost negligible steric effect.

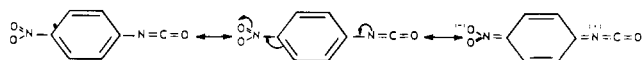
The polar effects in the reaction of substituted phenyl isocyanates and an alcohol (2-ethylhexanol) were studied. This reaction normally follows second-order kinetics; however, for convenience of comparison, it can be considered "pseudo-unimolecular" (6) following first-order kinetics by use of a substantial excess of 2-ethylhexanol.

Studies on the influence of substituents on the reaction of aryl isothiocyanates and ethyl alcohol (4) indicated that the effect of more than one substituent is approximately equal to the sum of the effects of the individual substituents acting alone, and that the meta-substituted compound is always more reactive than the corresponding ortho- or para-substituted derivative. The reactivity is dependent on the nature of the substituent group, and there is an anomalous behavior of the ortho-substituted compounds which in some cases exhibit the usual phenomenon of steric hindrance.

The mechanism of the reaction of isocyanates with a compound containing an active hydrogen can be explained by considering the electronic structure of the isocyanate group. The resonance hybrids are shown as follows:



A qualitative consideration on the basis of the molecular orbital theory (1) indicates that the electron or charge density is greatest on the oxygen, and least on the carbon. The reaction of isocyanates and an alcohol involves attack by the nucleophilic center of the alcohol on the electrophilic carbon of the isocyanate. It follows, therefore, that any R group attached to the NCO which is electron releasing, will decrease the positive charge on the carbon atom and retard isocyanate reactivity. Conversely, any R group which is electron withdrawing will enhance the rate of reaction—e.g.,



Baker and Holdsworth (3) found that the over-all effect of the substituent group on the relative reactivity of the isocyanate with methanol is:

p-nitrophenyl isocyanate: phenyl isocyanate:
p-methylphenyl isocyanate: *p*-methoxyphenyl isocyanate:
cyclohexyl isocyanate = 142,800: 1076: 586: 471: 1

Bailey, Kirss, and Spaunburgh (2) have studied the reaction kinetics of various mono- and diisocyanates with 2-ethylhexanol and have concluded that the relative effects of substituent groups on isocyanate reactivity are:

p-sulfone: *p*-nitro: *m*-chloro: *m*- or *p*-isocyanato:
(none): *m*- or *p*-methyl: *o*-methyl: *o*-methoxy =
> 50: > 35: 7: 6: 1: 0.5: 0.08: 0.04

Burkus and Eckert (5) in a similar study showed the effects of various substituents on the relative reactivity of isocyanates with 1-butanol as follows:

m-isocyanato: *p*-isocyanato: *m*-urethano:
p-urethano: (none): *p*-methyl: *o*-methyl =
6-7: 4: 2: 1: 1: 1/2: 1/4-1/6.

DISCUSSION

Although much of the available data on the effect of various substituents on the isocyanate molecule are extremely useful, general theories can be applied only on a qualitative basis. In view of current industrial interest in polyisocyanates and polyurethanes, it would be extremely valuable to predict, with a reasonable degree of accuracy, the effect of almost any substituent (or substituents) on the reactivity of an isocyanate molecule with an alcoholic hydroxyl group.

The Hammett Equation (7) is an empirical relationship designed to correlate the structure of organic compounds and their chemical reactivity. This equation relates the nature of a substituent, R, and the reactivity of a functional group, Y



in the form of:

$$\log \frac{k}{k^0} = \sigma \rho$$

in which k and k^0 are the rate constants for reaction of the substituted and unsubstituted compounds, respectively; σ is the substituent constant which depends on the nature and position of R and is independent of the nature of the reaction. In general, σ is a quantitative measure of the electronic effect of a given meta or para substituent relative to a hydrogen atom. ρ is a reaction constant which is dependent on the reaction, the conditions under which it takes place, and the nature of Y. Since substituent groups with a positive σ value exhibit an electron-withdrawing effect, a reaction series in which rates of reaction are enhanced by electron withdrawal will have a positive ρ value. A negative ρ value indicates that the rate of reaction will be enhanced by electron-releasing substituents.

The reaction constant, ρ , was determined from the slope of the best straight line derived from a plot of the experimental values for $\log k$ (Table I) vs. the corresponding values of σ (Figure 1). Calculated by the method of least

Table I. First-Order Reaction Rate Constants for Substituted Phenyl Isocyanates + 2-Ethylhexanol at $28^\circ \pm 1^\circ$ C.

Monosubstituent	$k_1 \times 10^4$, Sec. ⁻¹	Disubstituents	$k_1 \times 10^4$, Sec. ⁻¹
<i>p</i> -Nitro	45.5	<i>m</i> -Chloro	15.2
<i>m</i> -Nitro	36.3	<i>p</i> -Chloro	
<i>m</i> -Trifluoromethyl	10.8	<i>m</i> -Isocyanato	12.2
<i>m</i> -Chloro	7.65 ^a	<i>p</i> -Chloro	
<i>m</i> -Bromo	7.63	<i>m</i> -Chloro	
<i>m</i> -Isocyanato	5.14	<i>p</i> -Methyl	3.99
<i>p</i> -Isocyanato	3.89	<i>m</i> -Isocyanato	2.00
<i>p</i> -Chloro	3.66	<i>p</i> -Methyl	
<i>p</i> -Urethano	1.56	<i>m</i> -Isocyanato	0.735
<i>p</i> -Phenyl	1.48	<i>p</i> -Methoxy	
<i>m</i> -Urethano	1.47	<i>m</i> -Methyl	0.700
<i>m</i> -Methoxy	1.39	<i>p</i> -Methoxy	
None	1.09 ^a	<i>m</i> -Methyl	0.700
<i>p</i> - <i>n</i> -Butyl	0.712	<i>p</i> -Methoxy	
<i>m</i> -Methyl	0.695	<i>m</i> -Methyl	0.370
<i>p</i> -Methyl	0.660 ^a	<i>p</i> -Methyl	
<i>p</i> -Methoxy	0.552		

^a Bailey, Kirss, and Spaunburgh (2).

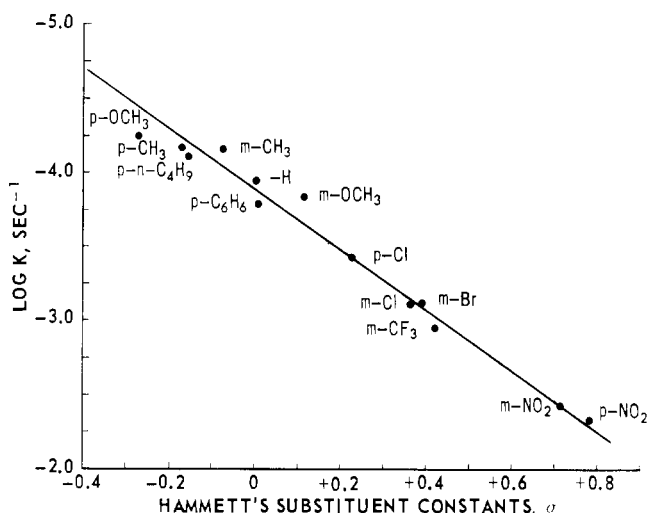


Figure 1. Determination of the reaction constant, ρ , for the reaction of meta- and para-substituted phenyl isocyanates with 2-ethylhexanol at 28° C.

Slope, $\rho = +1.979$; intercept, $\log k^0$ (calcd.) = -3.882

squares, $\rho = +1.979$. The values for the standard deviations, s , and correlation coefficient, γ , are 0.098 and 0.991, respectively, indicating that the precision of the fit of data to the Hammett equation is excellent (9).

From the value which was obtained for ρ , the rate constant can be determined for any other meta- or para-substituted phenyl isocyanate for which a value of σ is available. Hammett (8) and Jaffe (9) have tabulated σ values for over 100 substituents. The substituent constants, σ , used in this study are tabulated in Table II.

If it is desirable to determine a new substituent constant, the reaction rate constant, k , is experimentally determined and substituted into the following equation:

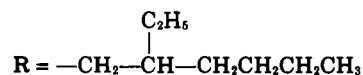
$$\sigma = \left(\frac{1}{\rho}\right) \log \left(\frac{k}{k^0}\right)$$

The substituent constants, σ , for the isocyanato ($-\text{NCO}$) group and the urethano ($-\text{NHCOOR}$) group were calculated from experimental k values obtained for the reaction of *m*-phenylene and *p*-phenylene diisocyanates with 2-ethylhexanol. The per cent reaction per unit time for these two isocyanates is shown in Figure 2.

Calculated values for the new substituent constants are:

Substituent	σ , Calcd.
<i>m</i> -NCO	+0.299
<i>p</i> -NCO	+0.238
<i>p</i> -NHCOOR	+0.038
<i>m</i> -NHCOOR	+0.025

where



Extension of the Hammett equation to multiple substitu-

Table II. Hammett Substituent Constants, σ , Used in Correlation

Substituent	σ^a	Substituent	σ^a
<i>p</i> -Nitro	+0.778	<i>m</i> -Methoxy	+0.115
<i>m</i> -Nitro	+0.710	<i>p</i> -Phenyl	+0.009
<i>m</i> -Trifluoromethyl	+0.415 ^b	none	0.000
<i>m</i> -Chloro	+0.373	<i>m</i> -Methyl	-0.069
<i>m</i> -Bromo	+0.391	<i>p</i> - <i>n</i> -Butyl	-0.161 ^b
<i>p</i> -Chloro	+0.227	<i>p</i> -Methyl	-0.170
		<i>p</i> -Methoxy	-0.268

^a From Hammett (8), except as noted. ^b Jaffe (9).

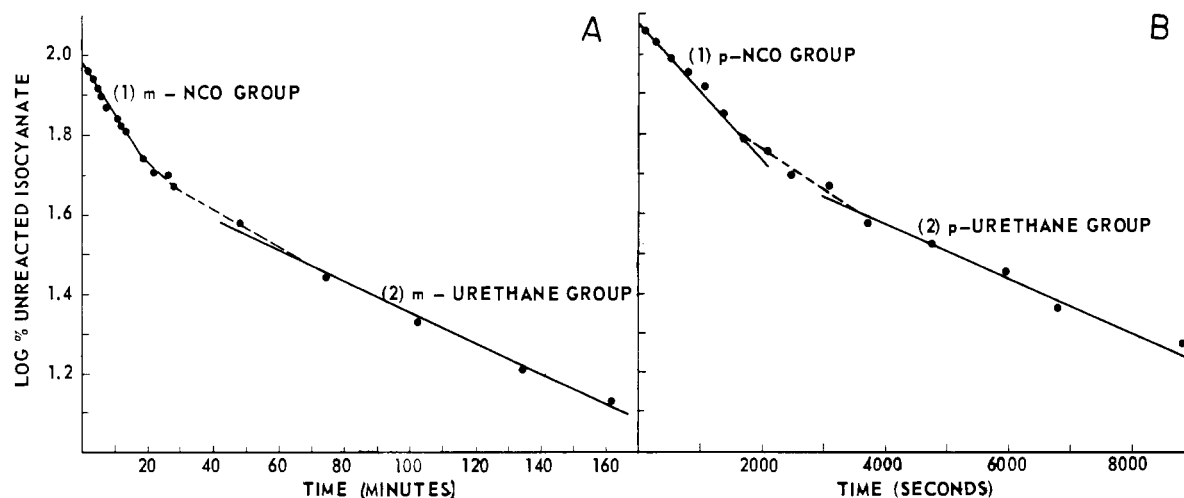


Figure 2. Per cent reaction vs. time plot for substituted phenylene diisocyanate + 2-ethylhexanol at 28° C.

A. Meta derivative

B. Para derivative

ents in the 3, 4, and 5 positions relative to the reactive side chain have indicated that polar effects are additive. The effect of multiple substituents can be expressed through the sum of their substituent constants (9, 10):

$$\log \left(\frac{k}{k^0} \right) = \rho \sum \sigma$$

where $\sum \sigma$ = sum of σ values of substituents present.

The following series of disubstituted phenyl isocyanates (Table III) reacted with 2-ethylhexanol in the same manner as described for monosubstituted phenyl isocyanates.

For a series of approximately 36 combinations of multiple substitution, Jaffe (10, 11) found a median deviation ($\Delta \sum \sigma$) of 0.052. Considering the variables and effects involved in a reaction study of this nature, the above values for $\Delta \sum \sigma$ are considered very satisfactory, with the exception of the *p*-methoxy-substituted compounds. At present, the reason for the large deviation is not clearly understood. Addition of anisole ($C_6H_5OCH_3$) to the reaction of phenyl isocyanate with 2-ethylhexanol did not affect the reaction rate constant, k .

EXPERIMENTAL DETAILS

Materials and Purification. The mono- and diisocyanates used for this study were prepared, by conventional laboratory procedures (11), by the reaction of the corresponding amines with phosgene in a suitable solvent—monochlorobenzene. The isocyanates were purified by distillation under reduced pressure. The purity of the isocyanates was checked by titration with dibutylamine and was in excess of 99.0%. Physical properties of the substituted phenyl isocyanates are shown in Table IV.

The alcohol, 2-ethylhexanol



(Union Carbide Corp.), was used without further purification.

The solvent, benzene, was purified by distillation.

Kinetic Method. The spectrophotometric method of Bailey, Kirss, and Spaunburgh (2) was used to determine the rate of reaction of the isocyanate with 2-ethylhexanol.

In a 1000-ml. volumetric flask, a solution of isocyanate in benzene was prepared which was 0.04*N* with respect to isocyanate (standard solution). In a second 1000-ml. flask, an identical amount of isocyanate was dissolved in approximately 900 ml. of benzene; 51.6 grams (0.4 mole) of 2-ethylhexanol was added and the volume was made up to the calibration mark with benzene (reaction mixture). Samples of both solutions were placed in 0.1-mm. sodium chloride cells and the infrared spectrum was scanned from 4 to 5 microns using a Baird Model B spectrophotometer at slow scan with 2 × slits. A matched sodium chloride

cell filled with benzene was used as the reference cell. At proper time intervals, the reaction mixture was scanned in the 4- to 5-micron region.

Since isocyanate concentration is directly proportional to absorbance (following Beer's law), the concentration of unreacted isocyanate can be determined at each given time interval by the standard spectrophotometric methods of calculation.

Analysis of Experimental Data. The reaction of an isocyanate and an alcohol is normally a second-order reaction; however, in the present study, since a 10-fold excess of alcohol was used, the reaction can be considered pseudo-unimolecular—that is, the reaction follows first-order kinetics.

The specific reaction rate or velocity constant, k , was obtained by a graphical method:

$$t = 2.303/k \log a - 2.303/k (\log a - x)$$

where

- a = initial concentration of isocyanate
- t = time
- x = concentration of isocyanate after time, t
- $(a - x)$ = concentration of unreacted isocyanate

A graphical plot of time, t , vs. log of concentration of

Table IV. Physical Properties of Substituted Phenyl Isocyanates

Substituent	Boiling Range, ° C./Pressure, Mm. Hg	
	Exptl.	Lit. (11)
Monosubstituted		
<i>p</i> -Nitro	145/14	137-8/11
<i>m</i> -Nitro	136-7/12	130-1/11
<i>m</i> -Trifluoromethyl	104/83	...
<i>m</i> -Chloro	111-2/45	83.6/10.5
<i>m</i> -Bromo	127/44	...
<i>m</i> -Isocyanato	108/15	104-6/12
<i>p</i> -Isocyanato	108/10	110-2/12
<i>p</i> -Chloro	93-5/10	80.6-.9/9.5
<i>p</i> -Phenyl	137-40/2-3	...
<i>m</i> -Methoxy	95-6/10	94.6-.8/10
None	60-3/18	55-7/16
<i>p</i> - <i>n</i> -Butyl	121/17	...
<i>m</i> -Methyl	96/44	65.7-6.3/9.5
<i>p</i> -Methyl	68-9/10.5	67.6-.8/10
<i>p</i> -Methoxy	109-10/17	97.6-.8/9.5
Disubstituted		
<i>m</i> -Chloro, <i>p</i> -chloro	131.8-3.2/25	111-2/11
<i>m</i> -Isocyanato, <i>p</i> -chloro	128-9/10	122-4/11
<i>m</i> -Chloro, <i>p</i> -methyl	121-2.5/26	...
<i>m</i> -Isocyanato, <i>p</i> -methyl	120/10	124-6/18
<i>m</i> -Isocyanato, <i>p</i> -methoxy	149/12	...
<i>m</i> -Methyl, <i>p</i> -methyl	112.8-3.0/25	...
<i>m</i> -Methyl, <i>p</i> -methoxy	119.5/17	...

Table III. Substituent Constants for Multiple Substituents

Position of Substituents		Hammett Substituent Constant, σ^a		$\sum \sigma$	$\sum \sigma_{\text{Exptl.}}^b$	$\Delta \sum \sigma$
Meta	Para	Meta	Para			
Cl	CH ₃	+0.373	-0.170	+0.203	+0.286	+0.083
CH ₃	CH ₃	-0.069	-0.170	-0.239	-0.237	+0.002
Cl	Cl	+0.373	+0.227	+0.600	+0.578	-0.022
NCO	OCH ₃	+0.299 ^c	-0.268	+0.031	-0.137	-0.168
NCO	CH ₃	+0.299 ^c	-0.170	+0.129	+0.133	+0.004
NCO	Cl	+0.299 ^c	+0.277	+0.526	+0.530	+0.004
CH ₃	OCH ₃	-0.069	-0.268	-0.337	-0.148	+0.189

^a From Hammett (8), except as noted. ^b Calculated from rate constant, k , and $\rho = 1.979$. ^c Calculated σ value.

unreacted isocyanate, $\log(a - x)$, is linear. The slope of the resultant straight line is equal to $-2.303/k$.

The plot of the reaction rate of phenyl isocyanate with 2-ethylhexanol is shown in Figure 3.

The first-order reaction rate constants of the isocyanates

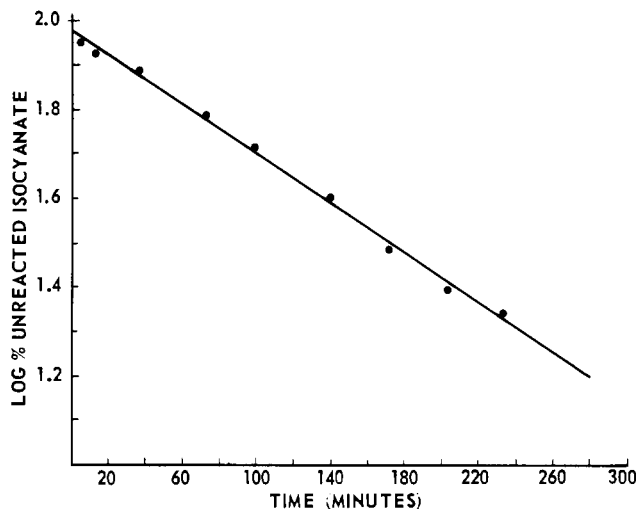


Figure 3. First-order plot of phenyl isocyanate and 2-ethylhexanol at 28° C.

described herein were determined in this manner (Table I).

When the substituent group was a meta- or para-isocyanato group—e.g., *m*- or *p*-phenylene diisocyanates—the specific reaction rate, k , was determined from the data shown in Figure 2.

ACKNOWLEDGMENT

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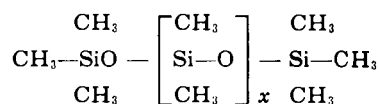
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Flow Characteristics of Linear, End-Blocked Dimethylpolysiloxane Fluids

GORDON C. JOHNSON, Silicones Division, Union Carbide Corp., Tonawanda, N. Y.

HIGH VISCOSITY silicone fluids offer important advantages over organic fluids for many mechanical applications. The shear stability, inertness, and flow characteristics of dimethyl silicone fluids make them ideally suited for use in fluid couplings, torsional vibrational dampers, dash pot dampers, shock absorbers, and power boosters. Proper design of these devices requires knowledge of the flow characteristics of the silicone fluids under the varying conditions of shear and temperature. The flow properties of silicone fluids from room temperature to 200° C. and at shear rates to 750,000 reciprocal seconds are presented in this article. Currie and Smith (4) studied the apparent viscosity-shear relationship of dimethyl silicone fluids at shear rates to 10,000 reciprocal seconds.

The structural formula and general physical properties of dimethylpolysiloxanes have been discussed (7, 11). To review, an end-blocked dimethylpolysiloxane has the following formula:



where the average value of x can vary from 0 to over 2000. The viscosity of the dimethylpolysiloxanes used in this investigation ranged from 1000 to 100,000 centistokes (x varying from 250 to 2000) as determined using Ostwald and Ubbelohde viscometers. The viscosities were measured

at shear rates of less than 1 reciprocal second, which is in the range of Newtonian behavior for these fluids. The viscosities so measured are referred to as the Newtonian viscosity. Typical properties are given in Table I.

EXPERIMENTAL

The experimental work was conducted using a capillary rheometer developed by the Research Department, Union Carbide Chemicals Co., for accurate examination of the melt flow behavior of high polymers. This equipment provides for measuring pressure and temperature immediately ahead of the orifice with accuracies within $\pm 0.5\%$, preselecting any piston speed, and maintaining the speed constant within $\pm 0.25\%$ irrespective of load.

The fluids were first extruded through the small-diameter capillaries, then reloaded into the chamber and extruded through the larger capillaries. New samples were used at each temperature. This procedure of using the small capillary first, with the resulting higher shear rates, was used to detect possible polymer degradation which would cause a decrease in viscosity. As a further check on possible degradation of the polymer, the Newtonian viscosities of the 60,000- and 100,000-cs. fluids were measured after the fluids were sheared at 400° F. using the smaller capillaries. A comparison of the original Newtonian viscosity and the Newtonian viscosity after the fluids had been sheared at 400° F. showed no significant change in viscosity.