[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Rates of Reaction of Isocyanates with Alcohols. I. Phenyl Isocyanate with 1- and 2-Butanol[1]

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In this Laboratory a program of investigating the factors influencing the reactivity of polymers both in solution and in solid form has been undertaken. In order to interpret the results it is desirable to secure information on lower molecular weight analogs of the polymers to be studied. Therefore, as a basis for understanding the reactivity of hydroxy-containing polymers with isocyanates, kinetic data have been secured on the interaction of normal and secondary butyl alcohols with phenyl isocyanate.

The first work on the kinetics of the action of alcohols with isocyanates was that of Davis and Farnum[5] who studied the relative reactivities of phenyl isocyanate with the lower aliphatic alcohols by allowing two alcohols to compete for a limited quantity of phenyl isocyanate and then determining the ratio of the two products from freezing points of the mixtures obtained. Tarbell, Mallatt and Wilson[6] showed the effect of certain acid and basic catalysts on the yields of urethans obtained from α-naphthyl isocyanate and phenols. A detailed investigation of the kinetics of the base-catalyzed reaction of various isocyanates with methanol was made by Baker and Holdsworth.[7] By the use of the Stagg[8] method of analysis for isocyanate groups, Baker and Holdsworth showed that the addition of the alcohol to the isocyanate follows second order kinetics in the presence of a constant concentration of a tertiary base. In subsequent papers Baker and Gaunt[9,10,11,12] have studied thoroughly both the base-catalyzed and "spontaneous" reactions of phenyl isocyanate with methyl, ethyl and isopropyl alcohols in di-*n*-butyl ether and in benzene solutions, and have secured kinetic evidence for the mechanism of these reactions.

In the present investigation a dilatometric method was developed for the determination of the reaction rates of *n*- and *s*-butyl alcohols with phenyl isocyanate. The correctness of the method was verified by chemical analyses.

Experimental

Equipment.—The dilatometer was of the coil type in order to provide adequate surface for heat transfer. The coil, made from forty inches of Pyrex tubing, 10 mm. o. d., was sealed to two lengths of capillary tubing, 1.5 mm. i. d. The open ends of the capillaries were attached to stopcocks carrying calcium chloride tubes. The dilatometer was calibrated by the thermal expansion of water in order to make certain that there were no irregularities in the capillaries.

For the kinetic studies at 15, 25 and 35° the dilatometer was immersed in a stirred seven-gallon water-bath, the temperature of which was controlled by an "H-B Red Top Thermoregulator." Readings taken once a minute for twenty minutes showed a regular cycle of sharp rise and slow decline with an outside variation of 0.03 to 0.04°. This variation could be taken care of when necessary by applying a slight experimental correction of 0.009 scale unit per 0.01°. The reactions at 0° were carried out in a one-gallon thermos jug in which a mixture of ice and water was kept stirred. The temperature variation was found to be negligible by checking with a Beckmann thermometer.

Materials.—Xylene was a satisfactory solvent for the dilatometric work. Solvents such as benzene and dioxane could not be used because of their volatility.

Care was taken to remove water from all solvents and reagents. Xylene was distilled over sodium and fractionated. Acetone was dried over calcium chloride and distilled. Piperidine was fractionated after standing over solid potassium hydroxide. Phenyl isocyanate was distilled under reduced pressure, b. p. 58.2–59.5° at 18–20 mm. Normal and secondary butyl alcohols were purified by treatment with sodium followed by fractionation. A convenient test for the absence of moisture was to let a mixture of the alcohol, isocyanate and solvent stand for two days; if water was present crystals of the very insoluble diphenyl urea separated. Tertiary butyl alcohol was purified by refluxing over barium oxide, followed by several distillations from sodium. Alpha terpineol[13] was a redistilled sample, m. p. 34.5–35.5°.

Dilatometer Method.—Equal volumes of xylene solutions of alcohol and the isocyanate, of known concentration and previously brought to the bath temperature, were mixed quickly and introduced into the dilatometer by suction. Readings were made of time, accurate to ±1 second, and of the scale, accurate to ±0.01 unit, at periodic intervals until no further contraction occurred. In the initial work at least fifty readings were taken for each determination. For calculation of the velocity constants the customary second order expressions (1) and (3) were used in the form of equations (2) and (4) for equal and unequal reactant concentrations, respectively.[14]

$$(1) \quad k = \frac{1}{t}\frac{x}{a(a-x)}$$

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[1] From the Master's theses of Hugh A. Taylor, September, 1947, Shirley J. Mason, June, 1948, and Jan Samson, June, 1949, University of Delaware. Presented before the Organic Division at the Chicago meeting of the American Chemical Society, April, 1948.

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[5] Davis and Farnum, THIS JOURNAL, **56**, 883 (1934).

[6] Tarbell, Mallatt and Wilson, *ibid.*, **64**, 2229 (1942).

[7] Baker and Holdsworth, *J. Chem. Soc.*, 713 (1947).

[8] Stagg, *Analyst*, **71**, 557 (1946).

[9] Baker and Gaunt, *J. Chem. Soc.*, 9 (1949).

[10] Baker and Gaunt, *ibid.*, 19 (1949).

[11] Baker, Davies and Gaunt, *ibid.*, 24 (1949).

[12] Baker and Gaunt, *ibid.*, 27 (1949).

[13] This material was furnished in pure condition through the courtesy of the Hercules Powder Company.

[14] A derivation of equations (1) and (4) and a discussion of errors in their use is given in the thesis of J. Samson, University of Delaware, June, 1949.

$$(2)\quad k = \frac{1}{t}\,\frac{R_0 - R_t}{a(R_t - R_\infty)}$$

$$(3)\quad k = \frac{1}{t}\,\frac{2.303}{a - b}\log\frac{b(a - x)}{a(b - x)}$$

$$(4)\quad k = \frac{1}{t}\,\frac{2.303}{a - b}\log\frac{a(R_0 - R_\infty) - b(R_0 - R_t)}{a(R_t - R_\infty)}$$

Where R_0, R_t and R_∞ are dilatometer readings at the times indicated.

The R_0 was found for equation (2) by extrapolating the plot of $1/(R_t - R_\infty)$ against time and for equation (4) by extrapolating the plot of $\log (R_t - R_\infty)$ against time. The k values were determined graphically from data such as those shown in Figs. 1 and 2. At least fourteen points were plotted to obtain the slopes of the lines.

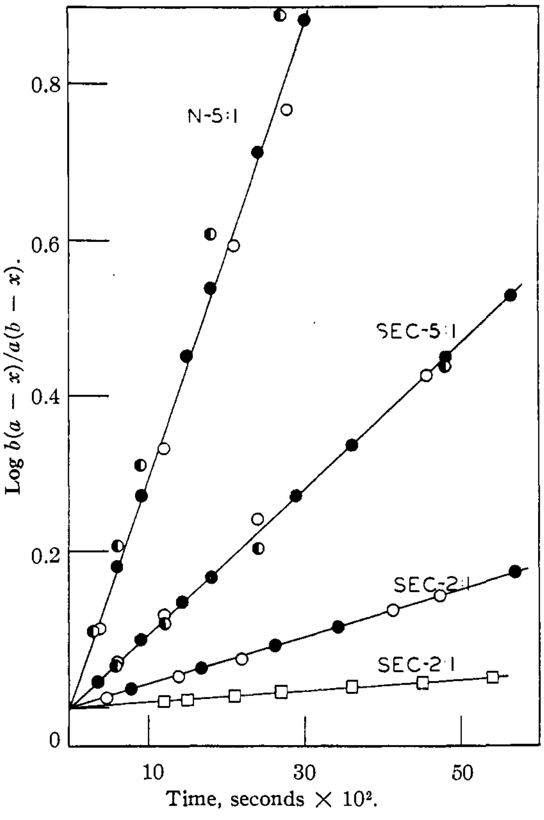


Fig. 1.—Second order curves for the reactions of *n*- and *s*-butyl alcohols with phenyl isocyanate in varying ratios of alcohol to isocyanate: ○ and ●, duplicate dilatometric analyses at 25°; ◐, chemical analysis at 25°; □, dilatometric analysis at 0°; *a* and *b*, initial concentrations of -OH and -NCO; *x*, -NCO reacted, moles/l.

Chemical Method.—Solutions of the alcohol and isocyanate of known concentrations were made up by weighing into volumetric flasks and diluting at constant temperature with xylene. Ten-milliliter samples of the alcohol solutions were transferred by pipet to each of several test-tubes to which were added at appropriate intervals ten-milliliter portions of the isocyanate solutions, and the mixtures were allowed to stand in the constant temperature bath. At exactly the desired time each of the reactions was stopped by the addition of a known volume of a standard piperidine solution in xylene. After one-half hour the excess of piperidine was titrated with standard 0.1 *N* hydrochloric acid, using methyl red–methylene blue indicator. Blank determinations were always run on the piperidine and on the isocyanate. Thus the quantity of isocyanate which had reacted was determined by this modification of the Stagg method.[8] Analyses on known samples showed that the method had a precision of 3 parts per 1000 and an accuracy of 5 parts per 1000 or better. In work subsequent to that reported here the titration has been improved by the use of brom phenol blue as indicator and the addition of sufficient methanol-free acetone to give a one-phase system.

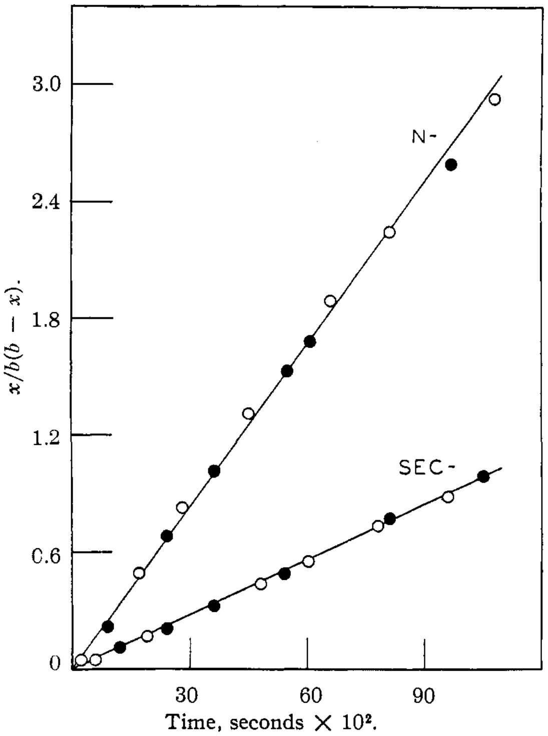


Fig. 2.—Second order curves for the reactions of *n*- and *s*-butyl alcohols with phenyl isocyanate in a 1:1 ratio at 25°: ○ and ●, duplicate dilatometric analyses; *b*, initial concn. of -NCO, moles/l.; *x*, -NCO reacted in time *t*.

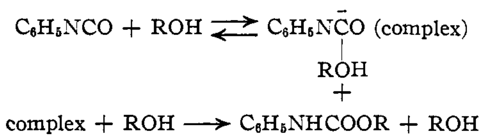
Determination of Volume Contraction.—The dilatometer was calibrated in terms of ml. per scale division by weighing water at constant temperature. From the calibration graph and the R_0 value for a given rate experiment the initial volume and hence the initial weight of isocyanate in the dilatometer was obtained. The total contraction, obtained from the value of $R_0 - R_\infty$, was used to find the contraction in ml. per mole of isocyanate reacted, shown in Table II.

Results and Discussion

A summary of the results obtained is given in Table I. All of the reactions studied were shown to follow the second order rate law to a high percentage of completion of reaction (see Figs. 1 and 2 and column 4 of Table I). The reactions at the lower reactant ratios are slow, but it was desirable to avoid the use of a catalyst so that in later work mixtures of polymers and reactants in films could be dried before appreciable reaction occurred.

The *k* values obtained by the chemical analysis were in the same general range as those from the dilatometric data, although in the 5:1 *n*-butyl alcohol–isocyanate reaction the points from the chemical plot are consistently slightly higher than those from the dilatometric one. In the other chemical run and in several not yet reported there is good agreement between dilatometric and titration data.

The second order *k* values for both the *n*- and *s*-butyl alcohols decreased with decreasing concentration of the alcohols. This is in accord with the behavior of methyl, ethyl and isopropyl alcohols with phenyl isocyanate as observed by Baker and Gaunt.[10] The explanation given by these investigators was that the alcohol acted as a catalyst through the formation of an intermediate complex with the isocyanate



$$C_6H_5NCO + ROH \rightleftharpoons C_6H_5N\overset{-}{C}O \text{ (complex)} \quad \text{with } \overset{+}{ROH} \text{ attached to C}$$

$$\text{complex} + ROH \longrightarrow C_6H_5NHCOOR + ROH$$

The validity of this mechanism was established by the derivation of the following kinetic equation which could be tested graphically.

$$(ROH)/k_0 = k_2/k_1k_3 + (ROH)k_1$$

A similar test of the data from this investigation

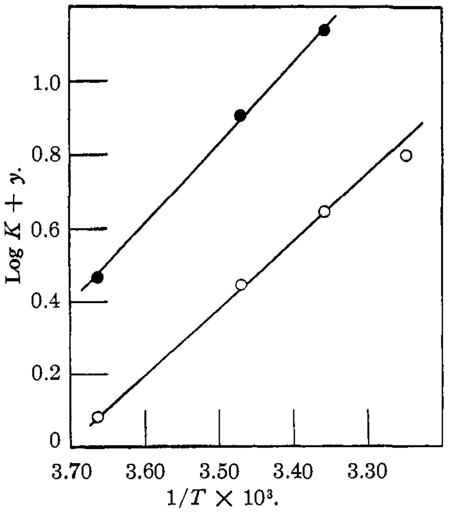


Fig. 3.—The temperature dependence of the rate constants for reactions of *n*- and *s*-butyl alcohol with C_6H_5NCO (2:1 ratio): ○, *n*-; ●, sec-. The constant *y* was used for convenience in plotting; *y* = 4 for the *n*-, 5 for the *s*.

TABLE I

KINETICS OF THE INTERACTION OF *n*- AND *s*-BUTYL ALCOHOLS WITH PHENYL ISOCYANATE IN XYLENE SOLUTION

Ratio of concn. of OH:NCO	NCO concn., moles/l.	Temp., °C.	$k^a \times 10^4$ l. mole^{-1} sec.$^{-1}$	P,[b] %
	n-Butyl Alcohol with Phenyl Isocyanate			
2:1	0.4948	35	6.27	68
2:1	.5386		6.34	
5:1	.3464	25	4.63	89
5:1	.3629		4.66	
5:1	.5004		4.53	
5:1	.4992		4.39	
5:1[c]	.3761		4.88	
2:1	.5004		4.38	71
2:1	.4978		4.46	
1:1	.3710		2.41	86
1:1	.3713		2.43	
2:1	.4985	15	2.78	51
2:1	.4960		2.80	
2:1	.4945	0	1.19	53
2:1	.4926		1.23	
	s-Butyl Alcohol with Phenyl Isocyanate			
5:1	0.3699	25	1.60	87
5:1	.3696		1.54	
5:1	.4975		1.55	
5:1	.4978		1.48	
5:1[c]	.3815		1.39	
2:1	.5052		1.35	66
2:1	.5057		1.37	
1:1	.3715		1.01	59
1:1	.3667		0.95	
2:1	.5044	15	0.83	53
2:1	.5062		0.78	
2:1	.4967	0	0.295	31

[a] Second order rate constants. [b] *P* is the minimum per cent. completion of the reaction which follows the straight line slopes of the graphs, such as those in Figs. 1 and 2. [c] Chemical method; the others are dilatometric.

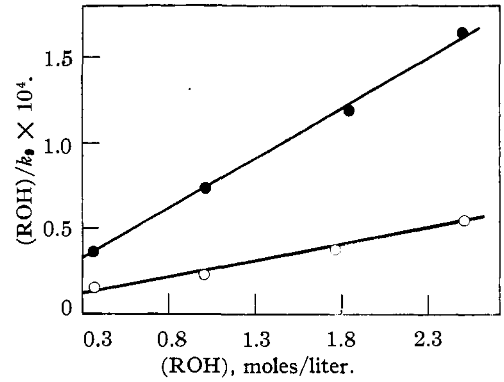


Fig. 4.—Effect of alcohol concentration on velocity constants: ○, *n*-butyl alcohol; ●, *s*-butyl alcohol, both with PhNCO in xylene solution at 25°. Each k_0 value is the average of those of approximately the same concentration from Table I.

is given in Fig. 4. The linearity of the plot of (ROH)/k_0 against (ROH) shows that the action of *n*- and *s*-butyl alcohols may be explained by the Baker and Gaunt mechanism.

It is of interest to compare the constants obtained in this work for the *n*- and *s*-butyl alcohols with the relative values reported by Davis and Farnum.[5] Their value for k_n/k_s is 3.03. In this investigation the value of k_n/k_s is 2.95 for the 5:1 ratio of reactants, and 3.24 for the 2:1 ratio of reactants, using in both cases the average of the dilatometric figures at 25°.

The rate of reaction of *t*-butyl alcohol with phenyl isocyanate to give a carbamate could not be determined because of the rapid formation of diphenyl urea. The reaction of α-terpineol with phenyl isocyanate in a 1:1 ratio at a concentration of 0.36 *M* for each reactant was followed by chemical analysis for a period of eight weeks. The data obtained were in accord with a second order reaction rate for the first five weeks; the velocity constant was 9×10^{-7} mole^{-1} l. sec.$^{-1}$. This may not be a correct value, however, because in this case also diphenyl urea was formed, although more slowly. It is not known whether the dehydration preceded or followed the interaction of the hydroxyl and isocyanate groups. Even with the *s*-butyl alcohol there was evidence of the same dehydration in the presence of phenyl isocyanate; at 35° an appreciable quantity of diphenyl urea was formed, although all reactants were anhydrous. At 25° or lower the *s*-butyl alcohol and phenyl isocyanate yielded traces of diphenyl urea, formed when 80% or more of the reaction had been completed. In the calculation of the velocity constants on the *s*-butyl alcohol experiments a possible source of error is the assumption that the R_∞ reading was not appreciably affected by the presence of traces of diphenyl urea crystals.

The effect of temperature on the rate constants for the action of *n*- and *s*-butyl alcohols with phenyl isocyanate at 2:1 reactant ratios is shown in Fig. 3. The slopes of the straight line graphs of log k against $1/T$ were determined by the method of least squares. The energy of activation, calculated by the Arrhenius equation, was 8100 cal./mole for the *n*- and 9900 cal./mole for the *s*-butyl alcohol.

The volume changes during the reactions, calculated as described in the experimental section, are given in Table II. It is apparent that the shrinkage per mole of isocyanate used is practically the same for various concentrations of the two different alcohols.

TABLE II

VOLUME CONTRACTION DURING REACTIONS AT 25°

Reactant ratios	Contraction, ml. of solution per mole C_6H_5NCO n-BuOH	s-BuOH
5:1	18.7	19.8
2:1	21.1	20.0
1:1	19.9	20.2
Average	19.9	20.2

Work is in progress on the reactivity of difunctional isocyanates with simple alcohols, and also with polymeric alcohols in the film state.

Acknowledgment.—The authors are indebted to Dr. H. M. Spurlin of the Hercules Powder Company for suggesting this problem and giving valuable advice during the course of the work, to Dr. C. C. Lynch of the University of Delaware for helpful discussions, and to Mr. G. W. Creighton for making some of the measurements.

Summary

A dilatometric method has been developed for the measurement of the reaction rates of isocyanates with alcohols in solution. The velocity constants for the action of phenyl isocyanate with *n*- and *s*-butyl alcohols, respectively, in xylene at various temperatures are reported. It has been shown that these reactions follow closely second order kinetics, regardless of whether the ratio of alcohol to isocyanate is 5:1, 2:1 or 1:1. The value of the constant is somewhat higher, however, in the presence of an excess of the alcohol. The values for energy of activation are 8100 and 9900 cal./mole for the *n*- and *s*-butyl alcohols, respectively. The volume contraction during the reactions at 25° is approximately 20 ml. of solution per mole of isocyanate used.

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