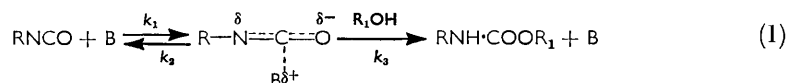


979. Reaction of Hexamethylene Di-isocyanate with Alcohols.

By J. N. GREENSHIELDS, R. H. PETERS, and R. F. T. STEPTO.

The reaction between hexamethylene di-isocyanate and alcohols has been studied in three solvents. The rate of reaction increases with the dielectric constant of the solvent, and with the nucleophilic character of the alcohol. Although only approximate rate equations were tested, the reaction appears to follow the mechanism of Baker *et al.*¹ In contrast to the kinetic order of the reactions of alk-1-enyl and aryl isocyanates, that of hexamethylene di-isocyanate cannot always be represented by Sato's equation.²

THE reaction of aryl isocyanates with alcohols was first studied systematically by Baker and his co-workers,¹ who found that the reaction was amenable to base catalysis. They suggested the reaction mechanism



where B could be catalyst, the alcohol R₁OH, or the urethane produced in the reaction. For the most part, Baker and his co-workers confined their attention to the earlier stages of the reaction where autocatalysis (by the urethane) could be neglected.

After assuming a stationary concentration of base-isocyanate complex, the above mechanism gave for the rate of reaction,

$$dx/dt = k_1 k_3 (a - x)(b - x)[\text{B}]/[k_2 + k_3(b - x)] \quad (2)$$

Here, x is the concentration of urethane at time t , and a and b are the initial concentrations of isocyanate and hydroxyl groups, respectively. Within the conditions of one experiment Baker and his co-workers found that second-order kinetics were obeyed:

$$dx/dt = k(a - x)(b - x) \quad (3)$$

The mechanism proposed by them appears to be essentially correct. First, the ease of formation of the complex should depend on the degree to which the carbon atom in the isocyanate group is positively charged and, in fact, after steric effects have been taken into account the rate of reaction increases with the electrophilic nature of the isocyanate

¹ Baker and Holdsworth, *J.*, 1947, 713; Baker and Gaunt, *J.*, 1949, 9,19; Baker, Davies, and Gaunt, *J.*, 1949, 24; Baker and Gaunt, *J.*, 1949, 27.

² Sato, *J. Amer. Chem. Soc.*, 1960, **82**, 3893.

group.¹⁻⁹ Secondly, the effectiveness of basic catalysts depends on their nucleophilic character rather than their basic strength since, for complex formation, a close approach to the isocyanate group is required.^{4,10-12} Moreover, in spontaneous reactions (*i.e.*, in the absence of added catalyst) the rate of reaction increases with the nucleophilic character of the alcohol.^{4,9,10,13-16} Thirdly, the second-order rate constants (k) which have been determined are increasing functions of the concentration of added catalyst or, in spontaneous reactions, of the initial hydroxyl concentration.^{1,10-12,15-18} This follows directly from comparison of equations (2) and (3), giving

$$k = k_1 k_3 [\text{B}] / [k_2 + k_3 (b - x)]$$

Finally, association between phenyl isocyanate and tertiary amine molecules in solution, as required by scheme (1), has been detected from infrared spectra.¹⁹

Catalysis of the isocyanate-alcohol reaction by acids has also been observed;^{10,20-23} the activation complex is formed through attack by the catalyst at the oxygen atom of either the isocyanate group^{10,21,23} or the hydroxyl group.^{10,23}

Most of the above kinetic work has been restricted to aromatic isocyanates. Except in those systems where di-isocyanates with isocyanate groups of unequal reactivity have been used, the deviations from second-order kinetics have been slight, and these were attributed to autocatalysis or to the solvent. The modification of the kinetic order of the reaction by change of solvent will be discussed later.

Sato^{2,18} has studied the reactions of ethyl and alk-1-enyl isocyanates with methanol in di-n-butyl ether at 25°; autocatalysis was appreciable. The rate of the spontaneous reaction was equal to the sum of two terms, each of the form of the R.H.S. of equation (2). One term resulted from the reaction of the isocyanate-alcohol complex ($[\text{B}] = b - x$), and the other from the reaction of the isocyanate-urethane complex ($[\text{B}] = x$). Sato assumed that the rates of formation and decomposition of these complexes were fast compared with their reactions with the alcohol to give urethane. This assumption led to equation (4).

$$dx/dt = \frac{k_1 k_3}{k_2} (a - x)(b - x)^2 + \frac{k_1' k_3'}{k_2'} (a - x)(b - x)x \quad (4)$$

The primed constants refer to the autocatalytic reaction. In addition, Sato^{2,18} found that for reactions with added base catalyst the deviations from second-order kinetics were slight; the catalysed reaction predominated leading to equation (5),

$$dx/dt \approx (k_1'' k_3'' / k_2'')(a - x)(b - x)[\text{B}] \quad (5)$$

More recently, Okada and Iwakura²⁴ have shown the spontaneous reaction between

³ Bailey, Kirss, and Spaunburgh, *Ind. Eng. Chem.*, 1956, **48**, 794.

⁴ Arnold, Nelson, and Verbanc, *Chem. Rev.*, 1957, **57**, 47.

⁵ Kogon, *J. Org. Chem.*, 1959, **24**, 438.

⁶ Brock, *J. Org. Chem.*, 1959, **24**, 1802.

⁷ Case, *J. Chem. Eng. Data*, 1960, **5**, 347.

⁸ Kaplan, *J. Chem. Eng. Data*, 1961, **6**, 272.

⁹ Lovering and Laidler, *Canad. J. Chem.*, 1962, **40**, 31.

¹⁰ Farkas and Mills, "Advances in Catalysis," Academic Press, London, 1962, Vol. 13, p. 393.

¹¹ Burkus, *J. Org. Chem.*, 1961, **26**, 779.

¹² Farkas and Flynn, *J. Amer. Chem. Soc.*, 1960, **82**, 642.

¹³ Cunningham and Mastin, *J. Org. Chem.*, 1959, **24**, 1585.

¹⁴ Davis and Farnum, *J. Amer. Chem. Soc.*, 1934, **56**, 883.

¹⁵ Dyer, Taylor, Mason, and Samson, *J. Amer. Chem. Soc.*, 1949, **71**, 4106.

¹⁶ Iwakura, Okada, and Yamashiro, *Makromol. Chem.*, 1962, **58**, 237.

¹⁷ Ephraim, Woodward, and Mesrobian, *J. Amer. Chem. Soc.*, 1958, **80**, 1326.

¹⁸ Sato, *J. Org. Chem.*, 1962, **27**, 819.

¹⁹ Pestemer and Lauerer, *Angew. Chem.*, 1960, **72**, 612.

²⁰ Tarbell, Mallatt, and Wilson, *J. Amer. Chem. Soc.*, 1942, **64**, 2229.

²¹ Britain and Gemeinhardt, *J. Appl. Polymer Sci.*, 1960, **4**, 207.

²² Weisfeld, *J. Appl. Polymer Sci.*, 1961, **5**, 424.

²³ Tazuma and Latourette, 130th A.C.S. Meeting, Atlantic City, Sept. 1956, Div. of P. P. and P.I. Chem., Paper No. 35.

²⁴ Okada and Iwakura, *Makromol. Chem.*, 1963, **66**, 91.

phenyl isocyanate and n-butanol also follows eqn. (4), and the catalysed reaction the combination of eqns. (4) and (5).

We studied the reaction of isocyanates with alcohols in the context of work connected with the cross-linking of polymers containing hydroxyl groups with alkyl di-isocyanates. The reactions of alkyl isocyanates have not previously been studied in great detail, and an examination of the kinetics is presented here.

The reactions of hexamethylene di-isocyanate with butan-2-ol, an "O-propylated trimethylolpropane," and a polyethylene glycol in toluene, *o*-dichlorobenzene, and nitrobenzene were studied. This di-isocyanate is suitable since Burkus and Eckert²⁵ showed its isocyanate groups to be equally reactive.

EXPERIMENTAL

Materials.—Hexamethylene di-isocyanate (*H.D.I.*). The sample, supplied by Imperial Chemical Industries Limited, was freed from traces of hydrochloric acid by stirring with calcium oxide at 100° for 2 hr., then distilled. The fraction of b. p. 135—136°/15 mm., was accepted (Equiv., by analysis, 84.1).

Alcohols. (a) Butan-2-ol was distilled. (b) Polyethylene glycol 200 (P.E.G. 200), supplied by Union Carbide Ltd., was dried by refluxing with toluene, and subsequent distillation of the toluene-water azeotrope. The excess of toluene was removed under reduced pressure (Equiv., by acetylation, 99.8 ±0.4). (c) "O-Propylated trimethylolpropane" (O.P.T.M.P.), supplied by Imperial Chemical Industries Limited, was dried as for P.E.G. 200 (Equiv. by acetylation 225 ±7).

The equivalent weights of the P.E.G. 200 and the O.P.T.M.P. means of four determinations. The uncertainties shown correspond to the maximum and minimum values found.

Solvents.—Toluene, *o*-dichlorobenzene, and nitrobenzene were dried and distilled.

Kinetic Procedure.—Solvent and alcohol were weighed into a two-necked flask. One neck was closed with a silica-gel guard tube, and the other fitted with a sealed stirrer. The flask was immersed in a constant-temperature oil-bath (±0.1°) and thermal equilibrium attained. The isocyanate, previously brought to temperature, was then added, either from a previously calibrated pipette, or from a weighing pipette.

The reactions were studied for periods ranging from 1 to 12 hr. when conversions of up to 90% were achieved. During each of these periods 7—10 samples were taken. The reaction in a sample was stopped by its addition to 25 ml. of 0.2N-di-n-butylamine in dry toluene, in a tared stoppered flask. The weight of a sample was then found by difference. After 15 min., 100 ml. of propan-2-ol were added to the flask and the excess of di-n-butylamine titrated with 0.1N-aqueous hydrochloric acid, with bromocresol green as indicator. A blank titration was done using the above quantities of di-n-butylamine solution and propan-2-ol. The concentration of isocyanate in the sample was then given by (blank titre—test titre)/(weight of sample) × normality of HCl × 10⁻³ eq. g.⁻¹. This method of analysis was adapted from that given by the A.S.T.M., standard D1638—59T.

Analysis of Results.—Initially the results were considered in the light of eqn. (4). Sato² applied this equation in two ways. First, he neglected the second term on the R.H.S. in the initial stages of the reaction, giving,

$$dx/dt = K(a - x)(b - x)^2 \quad (6)$$

Here $K = k_1 k_3 / k_2$. He then evaluated the apparent second-order rate constant (k) using the integrated forms of eqn. (3), and by extrapolation determined k at $t = 0$. Comparison of eqns. (3) and (6) shows that this value of k equals Kb . K being known, a value of K' ($= k'_1 k'_3 / k'_2$) was chosen to give agreement with the experimental conversion-time curve (x versus t) using the integrated forms of eqn. (4):

$$t = \left(\frac{K' - K}{a^2 K'^2} \right) \ln \left(\frac{K'x + K(a - x)}{K(a - x)} \right) + \frac{x}{a^2 K'(a - x)} \quad (7)$$

²⁵ Burkus and Eckert, *J. Amer. Chem. Soc.*, 1958, **80**, 5948.

when $a = b$, and

$$t = \left(\frac{K' - K}{[aK' + K(b-a)]bK'} \right) \ln \left(\frac{K'x + K(b-x)}{bK} \right) + \frac{1}{(b-a)[bK + a(K' - k)]} \ln \frac{a}{a-x} - \frac{1}{(b-a)bK'} \ln \left(\frac{b}{b-x} \right) \text{ when } a \neq b$$

Secondly, Sato neglected the first term of the R.H.S. of eqn. (4) in the latter stages of the reaction, giving after integration,

$$K't = \frac{1}{a^2} \ln \frac{x}{a-x} + \frac{1}{a(a-x)} + \text{Const. when } a = b, \text{ and}$$

$$K't = \frac{1}{ab} \ln x + \frac{1}{a(a-b)} \ln(a-x) - \frac{1}{b(a-b)} \ln(b-x) + \text{Const.} \quad (8)$$

when $a \neq b$. Sato found that a plot of the R.H.S. of eqn. (8) against time tended to a straight line, of slope K' , as t increased. Using this value of K' , he found that value of K which gave the best agreement with the experimental conversion-time curve, again using eqn. (7).

Many of the present results were analysed by Sato's methods but the results were unsatisfactory. As an example, expt. 2 may be quoted. Figs. 1 and 2 give the data for the initial and final stages of this reaction, respectively. Fig. 1 shows that the value of the intercept at $t = 0$ is not accurately defined, and much depends upon the certainty of the first point. The best value for K appeared to be $14.4 \text{ sec.}^{-1} \text{ equiv.}^{-2} \text{ g.}^2$. Use of the second method did not yield a straight line at large times, although the first and last points shown in Fig. 2 refer to 75 and 87% reaction, respectively. The slope of the straight line through the last three points gave a value of $115 \text{ sec.}^{-1} \text{ equiv.}^{-2} \text{ g.}^2$ for K' . By use of this value, the best agreement with the experimental conversion-time curve was obtained with $K = 11.0_5$, a value in poor agreement with that from the first method.

For these reasons a different approach was adopted in which for given values of K and K' , the times corresponding to the experimental values of x were calculated from eqn. (7). As a measure of the agreement with experiment, the difference between these times ($t_{\text{calc.}}$) and those at which the experimental readings were taken ($t_{\text{expt.}}$) were expressed as percentage errors on " $t_{\text{expt.}}$ ". The moduli of these percentage errors were averaged over the number of readings (n), excluding the point $x = 0, t = 0$ as this must be satisfied irrespective of the values of K and K' , giving

$$|\text{mean \% error}| = \sum_n \left(\frac{100}{n} \left| \frac{t_{\text{calc.}} - t_{\text{expt.}}}{t_{\text{expt.}}} \right| \right)$$

The value of the $|\text{mean \% error}|$ for expt. 2, with $K' = 115 \text{ sec.}^{-1} \text{ eq.}^{-2} \text{ g.}^2$ and $K = 11.0_5 \text{ sec.}^{-1} \text{ eq.}^{-2} \text{ g.}^2$, was 7.6. It was found subsequently that in all cases better agreement with experiment could be obtained, and with less effort, by evaluating K and K' according to the criterion of least squares, using the differential equation (4). The above value of 7.6 for $|\text{mean \% error}|$ given by Sato's method may be compared with the value 1.54 obtained by use of the "least squares" method (Table 1).

Least-squares Analysis.—The mechanism of Baker and his co-workers¹ [eqn. (1)] for the reaction in the absence of added catalyst leads to the rate equation,

$$\frac{dx}{dt} = \frac{k_1(a-x)(b-x)^2}{k_2/k_3 + (b+x)} + \frac{k_1'(a-x)(b-x)x}{k_2'/k_3' + (b-x)} \quad (9)$$

In order to obtain equations which could be solved analytically, eqn. (9) was simplified. Four approximations were considered.

(a) $k_2/k_3 \gg (b-x)$, and $k_2'/k_3' \gg (b-x)$, giving eqn. (4)

(b) $k_2/k_3 \gg (b-x)$, and $k_2'/k_3' \ll (b-x)$, giving

$$dx/dt = K(a-x)(b-x)^2 + k_1'(a-x)x \quad (10)$$

$$(c) \quad k_2/k_3 \ll (b-x), \text{ and } k_2'/k_3' \ll (b-x), \text{ giving} \\ dx/dt = k_1(a-x)(b-x) + k_1'(a-x)x \quad (11)$$

$$(d) \quad k_2/k_3 \ll (b-x), \text{ and } k_2'/k_3' \gg (b-x), \text{ giving} \\ dx/dt = k_1(a-x)(b-x) + K'(a-x)(b-x)x \quad (12)$$

Eqn. (12) was eliminated since it can be put in the form of eqn. (4). Eqn. (12) can be written

$$dx/dt = (a-x)(b-x)(k_1 + K'x)$$

and eqn. (4) gives

$$dx/dt = (a-x)(b-x)[Kb + (K' - K)x]$$

In addition, eqn. (12) will not explain all the deviations from second-order kinetics observed by Ephraim *et al.*¹⁷ for the reaction of phenyl isocyanate with methanol. These authors found that, in some solvents, the second-order rate constant decreased as x increased. Eqn. (12) predicts

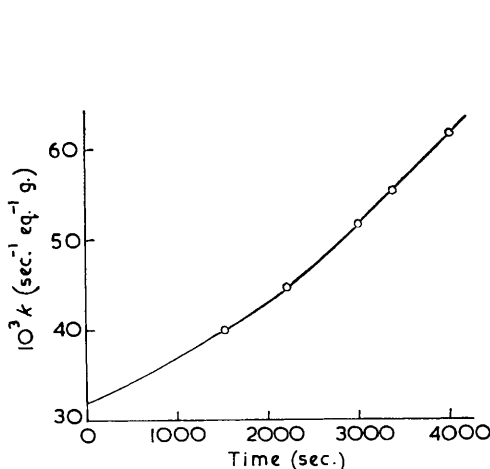


FIG. 1. Apparent second-order rate constants for the initial stages of the reaction in Expt. 2.

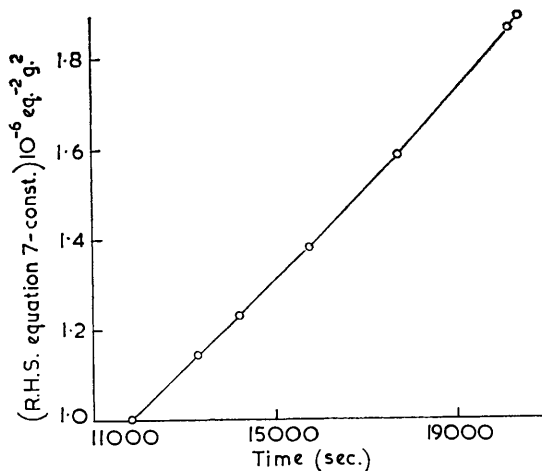


FIG. 2. R.H.S. of equation 7-Const *versus* time for the final stages of the reaction in Expt. 2.

an increase in second-order rate constant as the reaction proceeds, whereas eqn. (4) will explain both an increase and a decrease, depending on the relative magnitudes of K' and K .

Applying the criterion of least squares to eqns. (4), (10), and (11), respectively, we obtain the following equations.

$$(e) \quad K = \frac{(\Sigma YABX)(\Sigma A^2B^3X) - (\Sigma YAB^2)(\Sigma A^2B^2X^2)}{(\Sigma A^2B^3X)^2 - (\Sigma A^2B^4)(\Sigma A^2B^2X^2)} \quad (13)$$

$$K' = \frac{(\Sigma YAB^2) - K(\Sigma A^2B^4)}{(\Sigma A^2B^3X)}$$

$$(f) \quad K = \frac{(\Sigma YAX)(\Sigma A^2B^2X) - (\Sigma A^2X^2)(\Sigma YAB^2)}{(\Sigma A^2B^2X)^2 - (\Sigma A^2X^2)(\Sigma A^2B^4)} \quad (14)$$

$$k_1' = \frac{(\Sigma YAB^2) - K(\Sigma A^2B^4)}{(\Sigma A^2B^2X)}$$

$$(g) \quad k_1 = \frac{(\Sigma YAX)(\Sigma A^2BX) - (\Sigma A^2X^2)(\Sigma YAB)}{(\Sigma A^2BX)^2 - (\Sigma A^2X^2)(\Sigma A^2B^2)} \quad (15)$$

$$k_1' = \frac{(\Sigma YAB) - k_1(\Sigma A^2B^2)}{(\Sigma A^2BX)}$$

Here $Y = dx/dt$, $A = a - x$, $B = b - x$, $X = x$, and the summations are taken over the (x, t) points used.

Owing to their length, a digital computer was employed for the calculations now described. For one experiment the conversion-time curve was represented by polynomials of the form,

$$t = a_0 + a_1x + \dots + a_nx^n$$

with n between 3 and 10. The polynomials were evaluated using the criterion of least squares. The initial stage of the calculation yielded values of the coefficients, a_0, a_1, \dots, a_n . The agreement of the polynomials with the experimental conversion-time curve was then tested by calculating the values of t both at the experimental values of x , and at values of x midway between each consecutive pair of experimental values. dx/dt was also evaluated at these points. In general, it was found that the lowest-order polynomial ($n = 3$) did not agree at the experimental points to within experimental error. Polynomials of higher orders showed excellent agreement at the experimental points but, as n increased, erratic behaviour was found between these points. This was detected from the values of dx/dt and t at the points interposed midway between the experimental values. Polynomials showing smooth changes in dx/dt with x , and agreement at the experimental points were accepted.

The values of dx/dt and x , yielded by each polynomial, were used in eqns. (13)–(15) calculate "least squares" values of the rate constants of equations (4), (10), and (11), respectively. These rate constants together with the experimental values of x were then employed in the integrated forms of eqns. (4), (10), and (11), to calculate values of t , thus allowing evaluation of the |mean % error|.

The integrated form of eqn. (4) is eqn. (7), and integration of equations (10), and (11) between (0, 0) and (x, t) , yields eqns. (16) and (17), respectively.

$$t = A + \left\{ \frac{k_1' + 2K(a - b)}{[K(b - a)^2 + k_1'a][4Kk_1'b - k_1'^2]^{\frac{1}{2}}} \right\} \left\{ \tan^{-1} \left(\frac{k_1' - 2K(b - x)}{(4Kk_1'b - k_1'^2)^{\frac{1}{2}}} \right) - \tan^{-1} \left(\frac{k_1' - 2Kb}{(4Kk_1'b - k_1'^2)^{\frac{1}{2}}} \right) \right\}$$

when $4Kb - k' > 0$,

$$t = A + \frac{2[k_1' + 2K(a - b)]}{[K(a - b)^2 + k_1'a]} \left(\frac{1}{k_1'} - \frac{1}{k_1' + 4Kx} \right) \text{ when } 4Kb - k_1' = 0 \quad (16)$$

$$t = A - \left\{ \frac{k_1' + 2K(a - b)}{[K(b - a)^2 + k_1'a][k_1'^2 - 4Kk_1'b]^{\frac{1}{2}}} \right\} \left\{ \tanh^{-1} \left(\frac{k_1' - 2K(b - x)}{(k_1'^2 - 4Kk_1'b)^{\frac{1}{2}}} \right) - \tanh^{-1} \left(\frac{k_1' - 2Kb}{(k_1'^2 - 4Kk_1'b)^{\frac{1}{2}}} \right) \right\}$$

when $4Kb - k' < 0$.

$$\text{Here, } A = \left(\frac{1}{K(b - a)^2 + k_1'a} \right) \ln \left(\frac{a}{a - x} \right) + \left(\frac{1}{2[K(b - a)^2 + k_1'a]} \right) \ln \left(\frac{K(b - x)^2 + k_1'x}{Kb^2} \right)$$

$$t = \left(\frac{1}{k_1'(b - a) + k_1'a} \right) \ln \left(\frac{a[k_1'(b - x) + k_1'x]}{k_1'b(a - x)} \right) \quad (17)$$

RESULTS

The experimental results have not been given in detail, but the initial concentrations of the reactants in the various experiments are in Table 2.

Table 1 shows the agreement of eqns. (7), (16), and (17) with experiment, the |mean % error| having been calculated as described above. The relative agreement with experiment of eqns. (7) and (17) is given by the last column, being the values in the first column divided by those in the third column. Table 2 gives the "least squares" values of the rate constants pertaining to eqns. (4) and (11).

Figs. 3 and 4 are examples of conversion-time curves calculated using these rate constants. The plots given in Figs. 3 and 4 have been chosen on the basis that they represent the systems showing the best and worst agreement with eqn. (7) (Table 1).

FIG. 3. Experimental and calculated conversion-time curves, Expt. 2.

A, experimental.
B, eqn. (7).
C, eqn. (16).
D, eqn. (17).

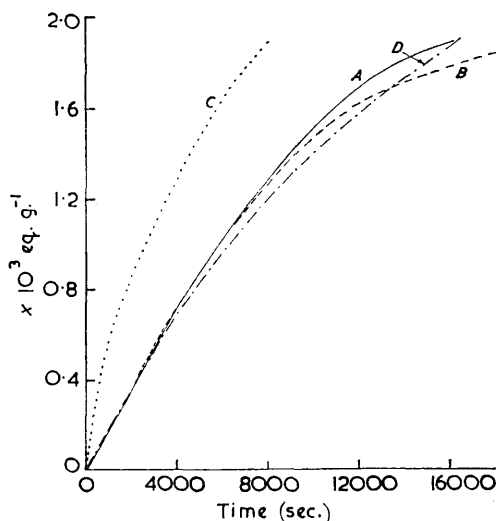
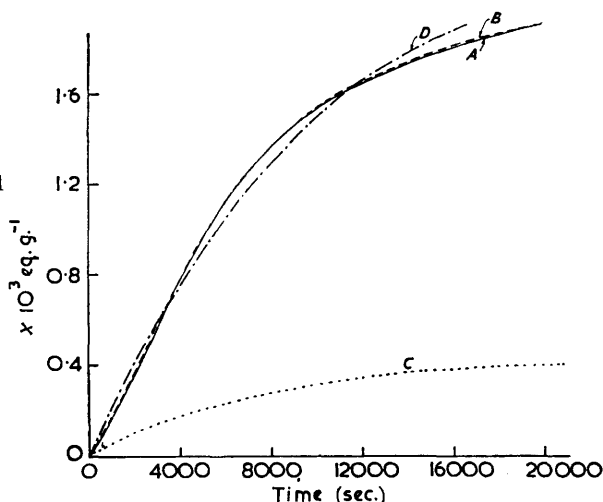


FIG. 4. Experimental and calculated conversion-time curves, Expt. 9.

A, experimental.
B, eqn. (7).
C, eqn. (16).
D, eqn. (17).

DISCUSSION

Table I shows that, for any one system containing solvent, the agreement between the equations tested and experiment differs from experiment to experiment. Most of this variation in | mean % error | arises from the loss in accuracy incurred when values of the rate, dx/dt , were evaluated from the derived polynomials. Errors in dx/dt ($=Y$) will affect, to approximately the same degree, the rate constants derived from equations (13), (14), and (15) as for one experiment the same values of Y were used. Therefore comparison across Table I (resulting in the last column), eliminates much of the effect of the errors in Y .

Reactions of Hexamethylene Di-isocyanate.—Equation (10) need not be further considered as Table I shows its integrated form (eqn. 16) to be in poor agreement with experiment.

The results in Table I (last column) indicate that, apart from the experiments in toluene, it is impossible to choose between equations (4), and (11), and that both these approximate equations do not give complete agreement with experiment. Hence emphasis should not be placed upon the actual values of the rate constants obtained, but rather on the trends in their values, apparent from Table 2.

Confining attention to the results from equation 11, we note that the constants

TABLE I.
Values of the | mean % error | for equations (7), (16), and (17).*

Expt.	System	Eqn. (7)	Eqn. (16)	Eqn. (17)	Eqn. (7)
					Eqn. (17)
1	H.D.I. + butan-2-ol + toluene at 90°	5.26—4.93	29.1—25.6	17.1—17.0	0.31—0.29
2		1.54	568	8.20	0.19
3		2.31—2.20	314—310	7.51—7.47	0.31—0.19
4	H.D.I. + butan-2-ol + <i>o</i> -dichloro-	14.0	662	9.04	1.5
5	benzene at 90°	5.51	801	7.68	0.72
6		6.92	871	9.43	0.73
7		9.87—8.56	1003—930	6.05—5.78	1.7—1.4
8	H.D.I. + P.E.G. 200 + <i>o</i> -dichloro-	7.79—7.51	35.0—34.2	11.3—10.7	0.73—0.66
9	benzene at 90°	18.0—17.6	63.9—68.4	17.8	1.0
10		6.57—5.26	47.6—45.3	3.68—1.80	3.7—1.4
11	H.D.I. + O.P.T.M.P. + <i>o</i> -dichloro-	5.21—4.24	406—286	2.34—2.06	2.5—1.8
12	benzene at 105°	4.16—3.15	201—160	4.14	1.00—0.76
13		4.07—3.86	196—140	4.36—4.01	1.01—0.89
14		9.56—4.93	468—184	5.66—3.63	2.63—0.87
15	H.D.I. + O.P.T.M.P. + nitrobenzene at	3.20—2.60	32.8—31.1	3.64—3.53	0.91—0.71
16	90°	6.36—5.90	31.8—29.2	3.24—3.11	2.1—1.8
17		8.38—4.96	63.7—58.6	5.18—4.92	1.70—0.96
18		13.8—13.4	75.0—71.0	12.4	1.1
19	H.D.I. + butan-2-ol at 90°	21.6—12.6	859—250	24.6—20.2	1.07—0.51
20	H.D.I. + P.E.G. 200 at 90°	6.84—5.74	40.1—39.6	13.2	0.52—0.43
21		7.17—6.98	—	3.34	2.1
22	H.D.I. + O.P.T.M.P. at 90°	2.35—1.97	52.6—36.4	4.99—4.93	0.48—0.39
23	H.D.I. + O.P.T.M.P. at 105°	2.71—2.34	655—523	3.49—3.28	0.83—0.67
24†	Phenyl isocyanate + methanol +	16.1	43.3	—	—
25†	toluene at 20°	8.95—3.50	33.5—9.67	—	—
26†		6.21—2.20	—	—	—

* For a given experiment, the ranges of values given in this Table arise mainly from differences between the polynomials used. Omitted figures signify that negative rate constants were obtained.

† Data from Ephraim *et al.*¹⁷

$K (=k_1k_3/k_2)$ and $K' (=k_1'k_3'/k_2')$ increase with dilution in the solvents of lower dielectric constant (*o*-dichlorobenzene and toluene). In these solvents the hydroxyl groups are self-associated and, since the reaction is assumed to go *via* free hydroxyl groups, the rate constants k_1 , k_3 , k_3' apparently increase with dilution.

In nitrobenzene, association of the hydroxyl groups with solvent will occur. At the higher initial concentrations the rate constants decrease on dilution but in the least concentrated system an increase is apparent. This is interpreted in the following terms. The decrease arises from a reduction in the relative number of free hydroxyl groups on dilution, but in more dilute systems the reaction rate is determined by the dielectric constant of the system. It is likely that the dielectric constant will change markedly in this system on dilution, since the reactants and products probably have low dielectric constants compared with that of nitrobenzene.

At present no datum is available for the molecules under consideration at 90 and 105°. However, the following dielectric constants may be quoted:²⁶ phenyl isocyanate $\epsilon_{20^\circ} = 8.8$, ethyl carbamate $\epsilon_{90^\circ} = 12$, butan-2-ol $\epsilon_{25^\circ} = 16$. For the solvents the dielectric constants are *o*-dichlorobenzene $\epsilon_{105^\circ} = 7.0$, toluene $\epsilon_{90^\circ} = 2.3$, nitrobenzene $\epsilon_{90^\circ} = 25$.

An increase in dielectric constant will first enable a larger polarisation of the reactants to be achieved (affecting the rates of the forward reactions), and secondly it will stabilise the activation complexes, as charge separation occurs on their formation. Both effects result in increases in K and K' .

Furthermore, comparison between systems shows that butan-2-ol reacts faster in *o*-dichlorobenzene than in toluene, and O.P.T.M.P. reacts faster in nitrobenzene than in

²⁶ Table of Dielectric Constants of Pure Liquids, National Bureau of Standards, Circular 514, Aug. 10th, 1951.

TABLE 2.

Least-squares values of the rate constants in equations (4) and (11).

Expt.	System	[NCO] ₀ [OH] ₀		Eqn. (4)		Eqn. (11)	
		(10 ³ eq. g. ⁻¹)	(10 ² eq. g. ⁻¹)	<i>K</i> (sec. ⁻¹ eq. ⁻² g. ²)	<i>K'</i> (sec. ⁻¹ eq. ⁻² g. ²)	<i>k</i> ₁ (sec. ⁻¹ eq. ⁻¹ g.)	<i>k</i> ₁ ' (sec. ⁻¹ eq. ⁻¹ g.)
1	H.D.I. + Bu ^o OH +	3.700	3.700	6.73—6.49	74.9—73.4	0.0327—0.0322	0.101—0.099
2	PhMe at 90°	2.216	2.216	14.1	94.7	0.0449	0.0606
3		1.582	1.582	19.1	116	0.0371	0.0603
4	H.D.I. + Bu ^o OH + <i>o</i> -	2.171	2.171	37.7	108	0.0876	0.0732
5	C ₆ H ₄ Cl ₂ at 90°	1.285	1.309	49.4	206	0.0716	0.0855
6		1.306	1.306	52.8	229	0.0799	0.0860
7		1.075	1.093	60.8—58.5	250—243	0.0755—0.0738	0.0880—0.0854
8	H.D.I. + P.E.G. 200 +	3.011	3.345	8.77—8.53	32.6—31.2	0.0348—0.0340	0.0403—0.0381
9	<i>o</i> -C ₆ H ₄ Cl ₂ at 90°	3.022	1.978	13.0—12.8	51.9—50.7	0.0311—0.0307	0.0270—0.0267
10		1.888	1.611	18.3—16.4	65.6—58.2	0.0336—0.0316	0.0382—0.0343
11	H.D.I. + O.P.T.M.P. +	2.576	2.576	13.7—12.1	67.0—58.9	0.0397—0.0369	0.0674—0.0642
12	<i>o</i> -C ₆ H ₄ Cl ₂ at 105°	2.130	2.162	14.1—12.9	93.8—83.3	0.0367—0.0348	0.0706—0.0687
13		1.600	1.635	19.4—16.9	118—104	0.0359—0.0329	0.0682—0.0662
14		0.929	0.947	40.8—33.2	209—173	0.0415—0.0361	0.0761—0.0679
15	H.D.I. + O.P.T.M.P. +	2.386	2.479	47.8—42.9	202—178	0.134—0.126	0.187—0.178
16	PhNO ₂ at 90°	1.494	1.723	40.7—36.1	111—96.1	0.0721—0.0675	0.0790—0.0726
17		1.677	1.144	42.7—36.4	175—147	0.0548—0.0498	0.0546—0.0496
18		0.5330	0.3852	207—187	251—215	0.0780—0.0741	0.0252—0.0213
19	H.D.I. + Bu ^o OH at 90°	6.320	6.320	8.43—6.10	58.2—52.5	0.0717—0.0590	0.110—0.094
20	H.D.I. + P.E.G. 200 at	5.768	4.876	5.16—5.09	32.3—31.4	0.0346—0.0343	0.0437—0.0434
21	90°	9.016	2.289	8.90—8.75	26.4—25.7	0.0240—0.0237	0.0163—0.0161
22	H.D.I. + O.P.T.M.P. at	3.174	3.174	4.52—4.06	32.4—28.8	0.0172—0.0161	0.0402—0.0390
23	90°						
23	H.D.I. + O.P.T.M.P. at	3.220	3.220	12.9—11.4	62.4—54.3	0.0466—0.0433	0.0688—0.0654
	105°						
24†	PhNCO + MeOH +	0.250	0.250	682	144	—	—
25†	PhMe at 20°	0.125	0.250	763—603	1160—229	—	—
26†		0.250	0.125	533—501	476—365	—	—

† Data from Ephraim *et al.*¹⁷; units: concn., 10³eq. ml.⁻¹; *K, K'* sec.⁻¹ eq.⁻² ml.².
[]₀ denotes initial concentration.

o-dichlorobenzene. In addition, only for the reactions in toluene is equation (4) in markedly better agreement with experiment than eqn. (11) (see Table 1). Thus, owing to the low dielectric constant of toluene, Sato's assumptions that $k_2 \gg k_3(b-x)$ and $k_2' \gg k_3'(b-x)$ are valid in this solvent.

The observed rate constants for the reactions in *o*-dichlorobenzene are of further interest in that they show differences in the alcohols used. Steric hindrance is least in butan-2-ol and this reacts the fastest of the three alcohols examined.

Experiments 22 and 23 allow approximate corrections to be made to the rate constants from experiments 11—14 to values pertaining to 90°. These show that at similar initial hydroxyl concentrations P.E.G. 200 reacts faster than O.P.T.M.P. The former molecule contains primary hydroxyl groups, whereas those of the latter molecule are secondary.

The rate constants from eqn. (11) show less variation with initial concentration than those deduced from eqn. (4). In the latter equation the hydroxyl concentration occurs to higher powers than in eqn. (11). The values of k_1 for the reactions in nitrobenzene show the same trends as *K* and *K'* with dilution. However, k_1' decreases with dilution. This probably results from hydrogen bonding of the urethane with the solvent, as the alcohol concentration does not appear in the reaction described by k_1' .

Little can be said regarding the data for the bulk systems (experiments 19—23) except that again butan-2-ol has the fastest reaction and the constants obtained are similar in magnitude to those obtained in the solvents of lower dielectric constant.

Comparison of Alkyl, Alk-1-enyl and Aryl Isocyanates.—In Table 2 the rate constants

for the reaction between phenyl isocyanate and methanol are given. The relative values of K and K' are an indication of the autocatalysis of the reaction by the urethane.²

In contrast to *N*-alkylurethanes, there is no inductive effect in *N*-arylurethanes to enhance the electron density at the nitrogen atom, and hence the ability to complex with the isocyanate. The autocatalytic effect is, therefore, less with *N*-arylurethanes than with *N*-alkylurethanes. Conjugation between the urethane groups and the aryl groups in the former urethanes will emphasise this difference. These observations are in agreement with Sato's results,² which showed that autocatalysis decreased in the substituent order alkyl > alk-1-enyl > aryl. It can be seen from Table 2 that the effects of induction and conjugation on the actual rates of reaction are the converse of the above. Sato's results also indicated that in part conjugative and inductive effects determined the rates of reaction, and in addition that the size of the substituent group had to be considered. In general, the rates of reaction decreased in the order aryl ~ alk-1-enyl > alkyl. Sato's results further showed that the effectiveness of triethylamine as a catalyst was determined by the polarisation it induced in a particular isocyanate.

From the calculations on the results of Ephraim *et al.*,¹⁷ it appears that eqn. (11) is not applicable to the reactions of phenyl isocyanate. In contrast to the reactions of H.D.I., the formation and decomposition of the activation complexes in the reactions of phenyl isocyanate are fast compared to the rates of their subsequent reactions with alcohols. For the spontaneous reactions of alk-1-enyl and aryl isocyanates Sato's eqn. (4) appears to be valid,^{2,24} whereas with alkyl isocyanates eqn. (9) should ideally be used.

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