[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RESOURCES UTILIZATION, TOKYO INSTITUTE OF TECHNOLOGY, MEGURO-KU, TOKYO, JAPAN]

The Rates of Reaction of 1-Alkenyl Isocyanates with Methanol

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RECEIVED NOVEMBER 6, 1959

The kinetics of the spontaneous and triethylamine-catalyzed reactions of 1-alkenyl isocyanates with methanol were studied and the results were compared with those of ethyl isocyanate and phenyl isocyanate. The data were treated by the equation: $dx/dt = k_1(a - x)(b - x)^2 + k_2x(a - x)(b - x) + k_3$ (catalyst)$(a - x)(b - x)$, and k_1, k_2 and k_3 of ethyl, phenyl, vinyl, propenyl, isopropenyl, β-propylvinyl, α-*n*-hexylvinyl isocyanate and k_3 of α-*n*-butylvinyl, β-phenylvinyl isocyanate were determined. The k_1- and k_3-values of 1-alkenyl isocyanates were 10–300 times of those of ethyl isocyanate. The kinetics of the general reaction of isocyanates with alcohols were also discussed.

In previous communications[1] from this Laboratory, the preparation of 1-alkenyl isocyanates, the reaction of these isocyanates with amines, alcohols and mercaptans, and their copolymerization with other vinyl compounds have been reported. From studies[1,2] on the copolymerization of 1-alkenyl isocyanates, it was shown that the carbon–carbon double bond in vinyl isocyanate and in isopropenyl isocyanate is electron-rich; hence the NCO group becomes electron poorer than the NCO group in a saturated isocyanate. On the other hand, Baker, *et al.*,[3] showed that the experimental velocity in substituted phenyl isocyanates increased with increased conjugation of the unshared electron pair on the isocyanate group. As the electron density on the NCO group is changed with conjugation and the reactivity of the NCO group varies greatly, an investigation of the influence of the C=C double bond in 1-alkenyl isocyanates on the reactivity of the NCO group is of major interest.

The first work on the kinetics of the reaction of an isocyanate with an alcohol was carried out by Davis and Farnum[4] and a detailed investigation of the kinetics of the spontaneous and base-catalyzed reaction of various aromatic isocyanates with methanol was made by Baker, *et al.*[3] By the Stagg[5] method of analysis for isocyanate groups, they showed that the addition of an alcohol to an isocyanate follows second-order kinetics in the presence of a constant concentration of a tertiary base. In subsequent papers,[6–9] they have studied thoroughly both the base-catalyzed and "non-catalyzed" reactions of phenyl isocyanate with methanol and other alcohols in di-*n*-butyl ether and in benzene solutions, and have secured kinetic evidence for the mechanism of these reactions. Later studies on the reactions of isocyanates with alcohols were reported by Dyer,[10] Ephraim,[11] Burkus[12] and Kogon.[13]

In the present investigation, kinetic studies of uncatalyzed and triethylamine-catalyzed reactions of the various types of isocyanates, especially 1-alkenyl isocyanates, with methanol were made and the data were treated by the expression

$$dx/dt = k_1(a - x)(b - x)^2 + k_2x(a - x)(b - x) + k_3(\text{cat.})(a - x)(b - x)$$

where a and b represent the initial concentration of isocyanate and methanol, x represents the concentration of the product, and k_1, k_2 and k_3 represent the velocity coefficients for initial reaction, urethan-catalyzed reaction and base-catalyzed reaction, respectively.

Experimental

Materials.—Isocyanates were prepared by the reactions[1] of corresponding acid chlorides with sodium azide and were purified by fractional distillation and redistillation immediately before use. The specimens used had the following b.p.'s.: ethyl, 60.1° (760 mm.); phenyl, 63.5° (24.5 mm.); vinyl, 39° (760 mm.); propenyl, 81° (760 mm.); isopropenyl, 61.8° (760 mm.); β-propylvinyl, 133° (760 mm.); α-butylvinyl, 66° (60 mm.); α-*n*-hexylvinyl, 60° (8 mm.); β-phenylvinyl, 110° (18 mm.). Methyl N-ethylcarbamate, methyl N-vinylcarbamate and methyl N-phenylcarbamate were prepared by the action of an excess of pure methanol on the pure corresponding isocyanate. Methyl N-ethylcarbamate and methyl N-vinylcarbamate were purified by fractional distillation under reduced pressure and methyl N-phenylcarbamate by repeated crystallization from ligroin.

Kinetic Method.—An approximately 0.3722 M solution of the isocyanate in di-*n*-butyl ether was standardized by withdrawing a 10-ml. aliquot, adding to it a 20-ml. portion of di-*n*-butylamine–di-*n*-butyl ether solution which was about 0.25 M with respect to di-*n*-butylamine and then titrating the excess di-*n*-butylamine to a methyl red end-point with hydrochloric acid–ethanol solution which was about 0.25 M with respect to hydrochloric acid.

An exactly 0.3722 M solution of methanol (or methanol and the catalyst) in di-*n*-butyl ether was prepared. When the catalyst was used, the molarity with respect to the catalyst was 0.03722 M.

All experiments were carried out in the thermostat at 25° (±0.05°). A 100-ml. long necked flask with ground stopper containing 10 ml. of the isocyanate solution and the flask containing the methanol solution were placed in the thermostat and allowed to come to temperature equilibrium for 0.5 hour. Each kinetic run was initiated by adding 10 ml. of the methanol solution to the isocyanate solution. The reaction mixture was shaken thoroughly and the time when half of the methanol solution had been added was recorded as the start of the reaction. After a definite time the flask

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[2] R. Hart and A. Dormael, *Bull. soc. chim. Belg.*, **65**, 571 (1956).

[3] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

[4] T. L. Davis and J. McC. Farnum, THIS JOURNAL, **56**, 883 (1934).

[5] H. E. Stagg, *Analyst*, **71**, 557 (1946).

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

[7] J. W. Baker and J. Gaunt, *ibid.*, 19 (1949).

[8] J. W. Baker, M. M. Davis and J. Gaunt, *ibid.*, 24 (1949).

[9] J. W. Baker and J. Gaunt, *ibid.*, 27 (1949).

[10] E. Dyer, H. A. Taylor, S. J. Mason and J. Samson, THIS JOURNAL, **71**, 4106 (1949).

[11] S. Ephraim, A. E. Woodward and R. B. Mesrobian, *ibid.*, **80**, 1326 (1958).

[12] J. Burkus and C. F. Eckert, *ibid.*, **80**, 5948 (1958).

[13] I. C. Kogon, *J. Org. Chem.*, **24**, 438 (1959).

was cooled in a Dry Ice–acetone mixture, 20 ml. of standard di-*n*-butylamine solution was added and the excess di-*n*-butylamine was titrated with the standard hydrochloric acid–ethanol solution to a methyl red end-point. When the catalyst was used, the volume of standard hydrochloric acid–ethanol solution for zero reaction time had to be determined.

Discussion

The Kinetic Equation and Its Derivation.— It usually has been considered that the reaction of an isocyanate with an alcohol follows second-order kinetics, because in the reaction of phenyl isocyanate with alcohol the plots of the right side of the expression (1) against t give a straight line in any one of separate runs. That is

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^2;\ kt = x/\{a(a - x)\} \qquad (1a)$$

$$\mathrm{d}x/\mathrm{d}t = k(a - x)(b - x)$$
$$kt = \{2.303/(a - b)\}\log[b(a - x)/\{a(b - x)\}] \qquad (1b)$$

In comparing the reactivity of isocyanates, the k-value which was determined from the slope of the straight line of the reaction at a certain triethylamine concentration has been used. The k-values in non-catalytic reactions of phenyl isocyanate with methanol or other alcohols in di-*n*-butyl ether and benzene solutions described by Baker, *et al.*,[7,8] and Dyer[10] varied with the initial concentration of reactants. On the other hand, it is known that the alkyl phenylcarbamate produced in the reaction catalyzes this reaction. The reactions of various isocyanates with methanol were carried out by this author and among these experiments, the reaction of phenyl isocyanate with methanol apparently followed second-order kinetics with good agreement, but the reactions of ethyl and many 1-alkenyl isocyanates did not follow these kinetics (see Fig. 1). These results suggest that the rate equation of the reaction of an isocyanate with an alcohol should be corrected, *i.e.*, the kinetics are not of second order and the rate equation contains a urethan-catalyzed term. However, these facts have not been considered in the over-all course of the reaction up to the present time.

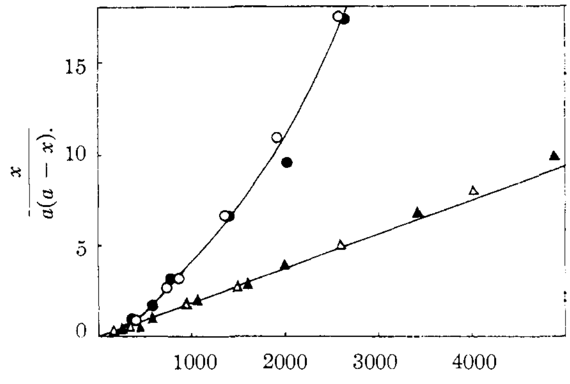

Fig. 1.—Relation between the right-hand side of eq. 1 and reaction time for uncatalyzed reaction; concn. of isocyanate and methanol: $a = b = 0.186$ *M;* solvent, di-*n*-butyl ether; reaction temp., 25 ± 0.05°: ○●, propenyl isocyanate; △▲, phenyl isocyanate.

Baker and co-workers assumed that an intermediate compound is formed between isocyanate and alcohol, one reactant and urethan or one reactant and catalyst, and that this compound reacts with another reactant to produce the urethan.

$$\mathrm{A} + \mathrm{X} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{Y} \qquad (2a)$$

$$\mathrm{Y} + \mathrm{C} \xrightarrow{k_3'} \mathrm{AC} + \mathrm{X} \qquad (2b)$$

When both urethan and catalyst are absent, X is C. If the stationary state condition is applied to equations 2a and 2b, these expressions result

$$k_{\mathrm{bi}} = k_1'k_3'[\mathrm{X}]/(k_2' + k_3'[\mathrm{C}]) \qquad (3a)$$

$$\mathrm{d}x/\mathrm{d}t = k_1'k_3'[\mathrm{X}][\mathrm{A}][\mathrm{C}]/(k_2' + k_3'[\mathrm{C}]) \qquad (3b)$$

In contrast to the assumption by Baker, *et al.*, that k_{bi} varies with k_3'[ROH] in the reaction of phenyl isocyanate with alcohol, it is supposed by this author that the first step in eq. 2 proceeds very fast to equilibrium due to ionic reaction, that k_2' is much greater than k_3', and that k_3'[C] can be neglected by comparison with k_2'. Therefore eq. 3b takes the form

$$\mathrm{d}x/\mathrm{d}t = k_1'k_3'/k_2'[\mathrm{X}][\mathrm{A}][\mathrm{C}] = k_1[\mathrm{A}][\mathrm{C}]^2$$

where $k_1 = k_1'k_3'/k_2'$. The urethan which is formed from the reaction of an isocyanate with an alcohol is able to produce the intermediate with an isocyanate and then this intermediate reacts with an alcohol to produce the urethan. Also in this case, equations 2 and 3 and the assumption that $k_2'' >> k_3''$ should hold and then the velocity of the urethan-catalyzed reaction is expressed in the form

$$\mathrm{d}x/\mathrm{d}t = k_1''k_3''/k_2''[\mathrm{X}][\mathrm{A}][\mathrm{C}] = k_2x[\mathrm{A}][\mathrm{C}]$$

where $k_2 = k_1''k_3''/k_2''$. When catalyst is used, the equations and the assumption mentioned above can also be applied and the velocity of the catalyst-catalyzed reaction represented as

$$\mathrm{d}x/\mathrm{d}t = k_1'''k_3'''/k_2'''[\mathrm{X}][\mathrm{A}][\mathrm{C}] = k_3(\mathrm{cat.})\,[\mathrm{A}][\mathrm{C}]$$

where $k_3 = k_1'''k_3'''/k_2'''$. In both of the spontaneous (non-catalyzed) and the catalyzed reaction of any isocyanate with an alcohol, the reaction will follow third-order kinetics and it is assumed that the over-all rate equation is given in the general expression

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x)(b - x)^2 + k_2x(a - x)(b - x) + k_3(\mathrm{cat.})(a - x)(b - x) \qquad (4)$$

In fact, the results of Baker, *et al.*, showed that the third-order velocity coefficient keeps a better constancy than the second-order one. Also the preliminary experiments carried out by this author showed that the third-order velocity coefficient is valid for the reaction of phenyl isocyanate with methanol, each at concentrations in the range of 0.25 to 0.75 *M*.

For the non-catalyzed reaction, eq. 4 may be written in the forms 5a and 5b if the reactants are at equal concentration, or in the forms 5c and 5d if not

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x)^3 + k_2x(a - x)^2 \qquad (5a)$$

$$t = \frac{2.303(k_2 - k_1)}{\{ak_1 + a(k_2 - k_1)\}^2}\log\frac{ak_1 + (k_2 - k_1)x}{k_1(a - x)} + \frac{x}{a\{ak_1 + a(k_2 - k_1)\}(a - x)} \qquad (5b)$$

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x)(b - x)^2 + k_2x(a - x)(b - x) \quad (5c)$$

$$= \frac{2.303(k_2 - k_1)}{\{bk_1 + a(k_2 - k_1)\}\{bk_1 + b(k_2 - k_1)\}} \log \frac{bk_1 + (k_2 - k_1)x}{bk_1} + \frac{2.303}{(b - a)\{bk_1 + a(k_2 - k_1)\}} \log \frac{a}{(a - x)} - \frac{2.303}{(b - a)\{bk_1 + b(k_2 - k_1)\}} \log \frac{b}{(b - x)} \quad (5d)$$

It is usually difficult to determine k_1 and k_2 simultaneously by inserting t and x values into eq. 5. In such a case, k_1 is determined by extrapolating k_{calcd}(eq. 1) to zero of t or x, because at $t = 0$, k_{calcd} of eq. 1 is equal to bk_1 of eq. 5a or 5c, and then k_2 is obtained by using the k_1 value and the conversion–time curve at suitable conversion and correcting from the conversion–time curve by trial and error (method B in Table II). If $k_2 \gg k_1$, the reaction follows the second term in eq. 5 after a definite time. Integrating the second term of eq. 5a and 5c, the equations are obtained

$$k_2t = \frac{2.303}{a^2} \log \frac{x}{(a - x)} + \frac{1}{a(a - x)} + K \quad (6a)$$

$$k_2t = \frac{2.303}{ab} \log x + \frac{2.303}{a(a - b)} \log (a - x) - \frac{2.303}{b(a - b)} \log (b - x) + K \quad (6b)$$

If the plot of the right side of eq. 6a or 6b against t gives a straight line, the k_2 value is determined from that slope. The reactions of ethyl isocyanate and 1-alkenyl isocyanates with methanol are examples of such cases (Fig. 2). The k_1 value is determined by using the k_2 value and the conversion–time curve in consideration of the k_1 obtained from extrapolating the k value of eq. 1 to zero conversion or zero reaction time (method A in Table II). In both methods A and B, k_1 and k_2 values were checked from eq. 5 and the conversion–time curve (Fig. 3). Method A is applicable in all cases except phenyl isocyanate. The k_1 value of phenyl isocyanate was determined by method B and k_2 was obtained from the reaction which was carried out with methyl N-phenylcarbamate as catalyst.

In the case of the reaction with triethylamine as catalyst, the exact eq. 4 should be used; eq. 4 can be transformed into the form

$$\mathrm{d}x/\mathrm{d}t = \{bk_1 + k_3(\text{cat.}) + (k_2 - k_1)x\}\,(a - x)(b - x)$$

From extrapolating the plot of the k value (eq. 1) against zero reaction time or zero conversion, the $[bk_1 + k_3\text{ (cat.)}]$ value was determined (method A in Table III). If $\{bk_1 + k_3\text{ (cat.)}\} >> (k_2 - k_1)x$, the $bk_1 + k_3$(cat.) value was determined from the usual method in second-order kinetics (method B in Table III). In the present experiments in which both concentrations of an isocyanate and methanol were 0.1861 M and that of triethylamine was 0.01861 M, the bk_1 value was neglected against the k_3(cat.) value, because the error introduced was within experimental.

Results.—The use of second-order kinetics for the reactions of various isocyanates with alcohols could not be adequate, because the product catalyzed the reaction and the velocity coefficient for the product catalysis varied greatly with the type of compound. Methyl N-ethylcarbamate, methyl N-vinylcarbamate and methyl N-phenylcarbamate affected the reaction rate of phenyl isocyanate with methanol to a different extent (Table I).

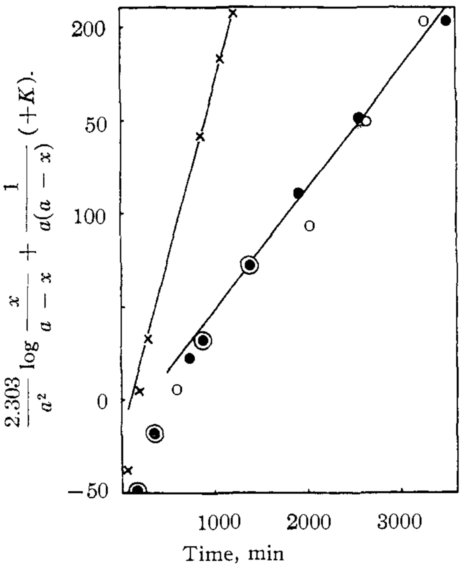

Fig. 2a.—Relation between right-hand side of eq. 6a and reaction time for uncatalyzed reaction; solvent, di-n-butyl ether; reaction temp., 25 ± 0.05°; concn. of isocyanate and methanol, $a = b = 0.186$ M: ×, vinyl isocyanate; ○●, propenyl isocyanate.

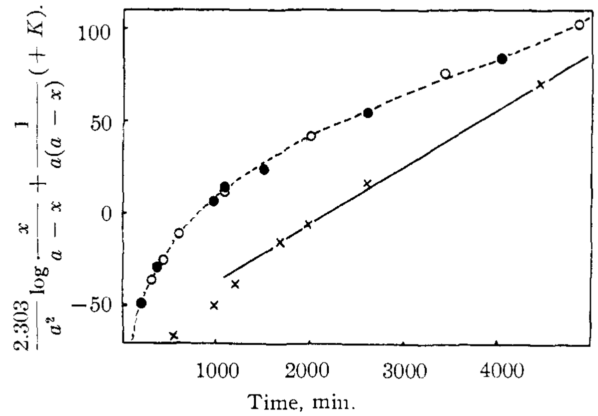

Fig. 2b.—Relation between right-hand side of eq. 6a and reaction time for uncatalyzed reaction; solvent, di-n-butyl ether; reaction temp., 25 ± 0.05°; concn. of isocyanate and methanol, $a = b = 0.186$ M: ×, 1-n-hexylvinyl isocyanate; ○●, phenyl isocyanate.

Table I

k_3 Values for the Reaction of Phenyl Isocyanate (0.25 M) with Methanol (0.25 M) in the Presence of Carbamates (0.25 M) as Catalyst at 25° in Di-n-butyl Ether

Carbamate	k_3, mole^{-2} l.^{2} min.$^{-1}$	$k_3/k_{3\text{ (phenyl)}}$
Methyl N-ethyl-	11×10^{-2}	20
Methyl N-vinyl-	1.6×10^{-2}	3
Methyl N-phenyl-	0.55×10^{-2}	1

Therefore, the second term for the product should be necessary in the kinetic equation over the course of any one individual run. From these facts, eq. 4 was used in the general reaction of various isocyanates with the alcohol.

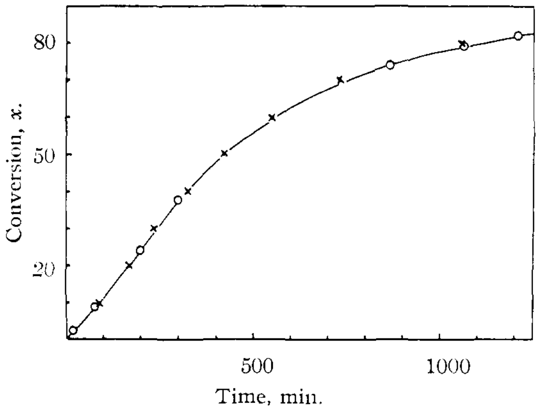

Fig. 3.—Conversion–time curve for uncatalyzed reaction of vinyl isocyanate with methanol: O, the values obtained, a = 0.1839 M, b = 0.1861 M, in di-n-butyl ether at 25 ± 0.05°; ×, the values calculated from eq. 5b, k_1 = 0.0283, b = 0.191, $a = b$ = 0.186 M.

(A) **Spontaneous Reaction.**—Table II shows the results when the catalyst was not used. If k_1 is equal to k_2 or k_1 is nearly equal to k_2, the reaction follows in appearance second-order kinetics. In the case of using $k_1 = 0.80 \times 10^{-2}$ and $k_2 = 0.50 \times 10^{-2}$ in the reaction of phenyl isocyanate with methanol, the plots of the right side of eq. 1 against t calculated from eq. 5 give straight lines (Fig. 4). The reactions of phenyl isocyanate with alcohols (methanol or other alcohols) are the same case.

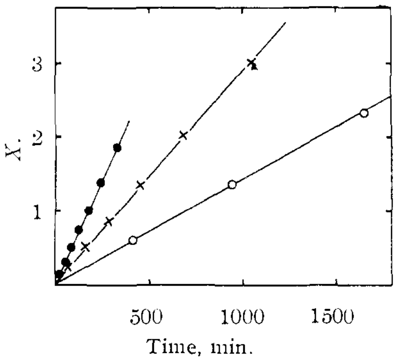

Fig. 4.—Right side of eq. 1 against t calculated from eq. 5 with phenyl isocyanate, $k_1 = 0.80 \times 10^{-2}$, $k_2 = 0.50 \times 10^{-2}$: ●, a = 0.25, b = 0.75; ×, $a = b$ = 0.50; O, $a = b$ = 0.25 mole/l.; X = right side eq. 1 = $x/\{a(a-x)\}$ or $\{2.303/(b-a)\} \log [\{a(b-x\}/\{b(a-x)\}]$

But all of the isocyanates examined except phenyl isocyanate did not follow the second-order kinetics and the k value from eq. 1 increased with increased reaction time (see Fig. 1 in propenyl isocyanate). This fact shows that the reaction product catalyzes strongly the reaction. In such a case, k_1 and k_2 values can be determined by the two methods described above. By method B, the K_2 values were determined initially from the equation, $dx/dt = K_1(a-x)(b-x) + K_2x(a-x)(b-x)$ and these K_2 values are given in parentheses in column 6 of Table II. These values are smaller than the k_2 values by method A, but the k_2 values calculated from the assumptions that K_1 is bk_1 and K_2 is $k_2 - k_1$ in the above general eq. 4 do not vary from the k_2 values by method A. This fact seems also to indicate that the third-order kinetics is correct for the reaction of isocyanate with alcohol.

It is evident that the C=C double bond in 1-alkenyl isocyanates affects strongly the reactivity of the isocyanate group, since these isocyanates have greater k_1 values than the saturated alkyl isocyanate, ethyl isocyanate. Among these isocyanates, the k_1 values vary greatly, vinyl isocyanate being the greatest and β-propylvinyl isocyanate, propenyl isocyanate and isopropenyl isocyanate following in decreasing order; the 1-alkenyl isocyanates with a large group in the α-position, *e.g.*, α-butylvinyl isocyanate and 1-n-hexylvinyl isocyanate, have smaller k_1 values than the former. Phenyl isocyanate has the same value as isopropenyl isocyanate.

The ratio of k_2/k_1 (in column 8 of Table II) varied greatly; that of ethyl isocyanate is the highest and those of the 1-alkenyl isocyanates rank next. Among these compounds, α-n-hexylvinyl isocyanate has the largest value and the others have values approximately equal to one another. In the 1-alkenyl isocyanates, it seems to be that the isocyanate of which the reactivity of the NCO group is only slightly affected by the C=C double bond has a large k_2/k_1 value. Phenyl isocyanate has the lowest value. It is very interesting that the three types of isocyanates have different values of k_1, k_2 and k_2/k_1.

(B) **Catalyzed Reaction.**—The reaction of isocyanates with methanol using triethylamine as catalyst follows in appearance second-order kinetics and the plots of the right side of eq. 1 against t give straight lines. The results obtained by the usual method (method B) are given in column 3 of Table III. But the plot of k_3 calculated from eq. 1 against t or x gives a line with a certain inclination and the k_3 value was obtained by extrapolating it to zero of reaction time or conversion. The results obtained by this method (method A) are given in column 3 of Table III. There are small differences between the two methods. With ethyl isocyanate, having the smallest k_3/k_2 value, the difference is comparatively large and the velocity coefficient obtained from eq. 1 increased with increasing reaction time. With phenyl isocyanate, which has the largest k_3/k_2 value, the k_2 term can be neglected by comparison with the k_3 term and the velocity coefficient obtained from eq. 1 will be maintained constant, but this value decreases with increasing reaction time. This fact seems to be due to the formation of a catalyst–reactant complex, because when the concentration of the reactant was corrected by subtracting the concentration of the catalyst from the initial concentration of one reactant, the value was constant until 70% conversion. The ratio k_3/k_2 varied greatly with the type of isocyanate. Phenyl isocyanate has the largest k_3/k_2 value. 1-Alkenyl isocyanates have values of several tens and ethyl isocyanate has the lowest value. The k_3 values of the various isocyanates examined are in order: β-phenylvinyl > vinyl, phenyl > propenyl, β-propylvinyl, isopropenyl > α-butylvinyl > ethyl.

TABLE II

NON-CATALYZED REACTION AT 25 ± 0.05°[c]

Isocyanate	Isocyanate, mole/l.	k_1 Method A	k_1 Method B	k_2 Method A	k_2 Method B	$k_1/k_{1(\text{ethyl})}$[a]	k_2/k_1[a]
Ethyl	0.1840	0.00017	0.00016	0.0066	0.0066 (.0064)	1	39
Phenyl	.1859		.0080		.0055[b]	47	0.7
Vinyl	.1838	.028	.033	.19	.16 (.13)	160	6.8
Propenyl	.1843	.014	.014	.068	.061 (.047)	82	4.9
β-Propylvinyl	.1848	.017	.016	.075	.073 (.057)	100	4.4
Isopropenyl	.1891	.0074	.0074	.034	.033 (.026)	44	4.6
α-Hexylvinyl	.1798	.0017	.0016	.030	.029 (.027)	10	18

[a] Calculated from the value of method A. [b] Determined from the reaction with methyl *N*-phenylcarbamate as catalyst; unit of all rate constants = mole^{-2} l.^{2} min.$^{-1}$. [c] Initial methanol concn. = 0.1861 *M;* solvent, di-*n*-butyl ether.

TABLE III

TRIETHYLAMINE-CATALYZED REACTION AT 25 ± 0.05°[c]

Isocyanate	Method	k_3, mole^{-2} l.^{2} min.$^{-1}$	k_3/k_2[a]	$k_3/k_{3(\text{ethyl})}$	Cat. eff.[a]
Ethyl	A	0.038	5.8	1	1
	B	0.043			
Phenyl	A	13	2.4×10^3	3.4×10^2	7.2
	B	10			
Vinyl	A	13	68	3.4×10^2	2.1
	B	15			
Propenyl	A	2.9	43	7.6×10	0.93
	B	2.8			
β-Propylvinyl	A	2.8	37	7.4×10	0.74
	B	2.8			
β-Phenylvinyl	A	60	..	1.6×10^3	..
	B	58			
Isopropenyl	A	1.9	56	5.0×10	1.1
	B	2.0			
α-Butylvinyl	A	0.9	..	2.4×10	1.3[b]
	B	0.9			

[a] Using the value from method A of Table II. [b] $k_1 = 3.3 \times 10^{-3}$, $k_1/k_{1(\text{ethyl})} = 19$. [c] Isocyanate concn. = 0.186 to 0.180 *M;* methanol concn. = 0.1861 *M;* triethylamine concn. = 0.01861 *M;* solvent, di-*n*-butyl ether; cat. eff. = $(k_3/k_1)/(k_3/k_1)_{\text{ethyl}}$.

The efficiency of the catalyst, $(k_3/k_1)/(k_3/k_1)_{\text{ethyl}}$, is calculated (column 6 of Table III). The value for phenyl isocyanate is comparatively greater than for the others which resemble each other. However, small differences between the reactivities in non-catalyzed and catalyzed systems are present, and should be taken into account in comparison of the reactivity of various types of isocyanates.

Conclusions

The non-catalyzed and catalyzed reactions of isocyanates with methanol show that: (1) The second-order kinetics which have been used by other authors cannot be applied to the spontaneous reactions of isocyanates with alcohols and the second term in eq. 4 must be added. With alkyl isocyanates and 1-alkenyl isocyanates, the second term becomes important and after the reaction proceeds to some extent the reaction rate follows almost exclusively that term.[14]

(2) There is a great difference between the three types of isocyanates. Both 1-alkenyl isocyanates with the C=C double bond conjugated to the NCO group and phenyl isocyanate with the aromatic double bonds in conjugation with the NCO group have greater reactivity than ethyl isocyanate without such conjugations. This is probably because the decreasing electron density on the NCO group accelerates the approach of a nucleophilic reagent to the NCO group and the reactivity increases.

Among 1-alkenyl isocyanates, β-phenylvinyl isocyanate which has many resonance structures shows the largest reactivity and vinyl isocyanate without substitution in the α- and β-position to the NCO group has the second. β-Alkyl-substituted vinyl isocyanates with inductive effects and without large steric effects on the NCO group, β-propylvinyl isocyanate and propenyl isocyanate, rank next. In α-substituted 1-alkenyl isocyanates, the reactivity decreases owing to the steric effect, but in isopropenyl isocyanate the reactivity is not very much smaller than that of propenyl isocyanate and therefore it is evident that the steric effect of the methyl group is not large. But the reactivity decreases with increasing steric effect and α-*n*-butylvinyl isocyanate and α-*n*-hexylvinyl isocyanate have smaller values than isopropenyl isocyanate. From these results, it is probable that the substitution in α-position has an influence on the reactivity of the NCO group.

The assumption, proposed at first in this paper, is confirmed to be correct and this fact agrees with the results of copolymerization studies.

Acknowledgment.—The author wishes to express his deep appreciation to Prof. Y. Iwakura of this Laboratory for his active interest and encouragement during the investigation. The author also expresses his gratitude to Prof. T. Shiba for many suggestions and valuable advice during the course of the work and to Mr. K. Tanaka for making some of the measurements.

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(14) If the catalytic power or the concentration of catalyst is small, in catalyzed reactions the product-catalyzed term should be also considered for the isocyanate having the low k_3/k_2.