KINETICS OF THE REACTION BETWEEN HEXAMETHYLENEDIISOCYANATE AND 1-PENTANOL

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

The reaction between hexamethylenediisocyanate and 1-pentanol in toluene was studied by means of reversed-phase liquid chromatography. By employing this method, it was possible to determine all components of the reaction mixture including both products, *i.e.* N-(6-isocyanate hexyl)pentylcarbamate and N,N'-bis(pentyloxycarbonyl)hexamethylenediamine. Relations for the calculation of kinetic constants were derived assuming a competitive consecutive second-order reaction. It was demonstrated that the reaction involved in this case is indeed a second-order reaction, and the rate constants of the first and second consecutive reactions were determined.

The study of the reaction between diisocyanate and hydroxy compounds is still topical and does not lose in importance, in particular because this type of reaction is the basis of the synthesis of polyurethane which becomes increasingly important in the polymer chemistry. The reaction has been investigated by many authors[1-8]; up to now, however, with respect to the consecutive character of the reaction, they have met with difficulties in the evaluation of kinetic constants in the first and second stages of the reaction. The lack of suitable analytical methods which would allow to determine changes in the concentrations of the initial compounds and in the content of forming products in the first and second stage necessitated several mathematical procedures, mainly based on the loss of isocyanate groups as a whole[1,4,7], or — more conveniently — on an additional determination of carbamate groups[7,8,10]. In some cases, such reaction conditions were chosen which enabled the reaction to be evaluated as pseudomonomolecular[7-9].

It has been the objective of this study to determine kinetic constants of the reaction between hexamethylenediisocyanate and 1-pentanol, using an analysis of the reaction mixture by means of reversed-phase liquid chromatography.

EXPERIMENTAL

Chemicals

Toluene, 1-pentanol, methanol and ethylbenzene were reagent grade (Lachema), redistilled prior to use and dried by storing over a molecular sieve. After distillation in vacuo, hexamethylenediisocyanate (Desmodur H, Bayer) contained 99·05% of the substance (b.p. 127°C/2·4 kPa). Acetonitrile (Avondale Labs., England) was used in liquid chromatography as supplied.

N,N′-bis(pentyloxycarbonyl)hexamethylenediamine was synthesized as an analytical standard in an apparatus for reaction kinetics investigation (*cf.* below). A mixture of hexamethylenediisocyanate and 1-pentanol (molar ratio 1 : 10) was kept in toluene with stirring under nitrogen at 70 °C for 8 h; after that, the solution was cooled and left to stand at 4°C for 48 h. The crystals thus obtained were filtered with suction, washed with cool toluene and dried *in vacuo* at room temperature. For $C_{18}H_{36}N_2O_4$ (344·5), calculated: 62·76% C, 10·56% H, 8·13% N; found: 62·98% C, 10·68% H, 8·12% N.

Addition of Diisocyanate and Alcohol

The reaction vessel used in the kinetic studies was a glass flask 100 ml in volume, provided with a stirrer, supply of dry nitrogen and a $CaCl_2$ closure. The flask was placed in a thermostat the temperature of which was maintained at 50 ± 0·1°C. The individual components of the reaction mixture were dosed using a Pipetman–Gilson pipette. The total volume of the reaction mixture was 50 ml. A corresponding amount of toluene together with hexamethylenediisocyanate was thermostated in the reaction vessel after flushing with dry nitrogen. After 30 min, 1-pentanol was added on preliminary thermostating to the reaction temperature in the same ultrathermostat. The time was measured starting from the moment of its addition; 0·5 ml of the reaction mixture was then taken each time with a micropipette in certain intervals, transferred into 5 ml of dry methanol containing ethylbenzene (2% by vol.; internal standard for liquid chromatography).

Analysis

The individual samples were analyzed by high-performance liquid chromatography on reversed phase. Silicagel, mean particle size 5 μm, with chemically modified surface by means of octadecyltrichlorosilane was used as the stationary phase; isocratic mixture acetonitrile–water (6 : 4 v/v), volume flow rate 0·5 ml/min, was the mobile phase. A "cartridge" type column, *i.e.* a glass column (3·4 mm i.d., 150 mm long) with chemically treated surface[11] (resistance up to 80 MPa) provided with a duralumin jacket was used in the measurements. The signal was recorded with a differential refractometer (Waters Ass., type R 401).

Direct calibration made possible determination of the dependence of molar concentrations of hexamethylenediisocyanate (I), 1-pentanol (A) and N,N′-bis(pentyloxycarbonyl)hexamethylenediamine (further called briefly diurethane, D) on the ratio of their peak height (a) to the peak of the internal standard (b): $[I] = 0{\cdot}248a_I/b - 0{\cdot}033$, $[A] = 1{\cdot}384a_A/b$, $[D] = 1{\cdot}017a_D/b$. A similar relation for N-(6-isocyanatohexyl) pentylcarbamate (further on, only monourethane, M) could be obtained from the mass balance,

$$[A]_o - [A] = [M] + 2[D]\,, \qquad (1a)$$

$$[I]_o - [I] = [M] + [D]\,, \qquad (1b)$$

and thus

$$[M] = 2([I]_0 - [I]) - ([A]_0 - [A]) ; \qquad (1c)$$

linear regression of these values gave the relation for monourethane $[M] = 0{\cdot}357 a_M / b$.

A typical chromatogram of the reaction mixture is shown in Fig. 1.

RESULTS AND DISCUSSION

Reactions between hexamethylenediisocyanate (I) and 1-pentanol (A) at the starting molar ratios of the compounds 1 : 1, 1 : 2 and 1 : 3 were investigated for 480 min. Mathematical evaluation of the measured concentration changes (Figs 2*a*–*c*) was based on the assumption that the formation of the monoadduct (M) and diadduct (D) proceeds *via* a competitive consecutive second-order reaction

$$\underset{A}{C_5H_{11}OH} + \underset{I}{OCN(CH_2)_6NCO} \xrightarrow{k_1} \underset{M}{C_5H_{11}OCONH(CH_2)_6NCO} \qquad (A)$$

$$C_5H_{11}OH + OCN(CH_2)_6NHCOOC_5H_{11} \xrightarrow{k_2}$$

$$\longrightarrow C_5H_{11}OCONH(CH_2)_6NHCOOC_5H_{11} \qquad (B)$$

Since the analytical method used allows also the instantaneous concentrations of the transitional reaction product to be determined, the following procedure was em-

FIG. 1

Liquid chromatography record: 1 hexamethylenediisocyanate, 2 1-pentanol, 3 monourethane, 4 toluene, 5 ethylbenzene (internal standard), 6 diurethane ployed in the determination of the ratio between the two kinetic constants k_1, k_2:

$$\mathrm{d}[\mathrm{I}]/\mathrm{d}t = -k_1[\mathrm{A}]\,[\mathrm{I}]\,, \tag{2a}$$

$$\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_1[\mathrm{A}]\,[\mathrm{I}] - k_2[\mathrm{M}]\,[\mathrm{A}]\,, \tag{2b}$$

here, the concentrations of all components of the reaction mixture are expressed in molar concentrations. By dividing Eq. (*2b*) by (*2a*) and substituting $\varkappa$ for k_2/k_1, we

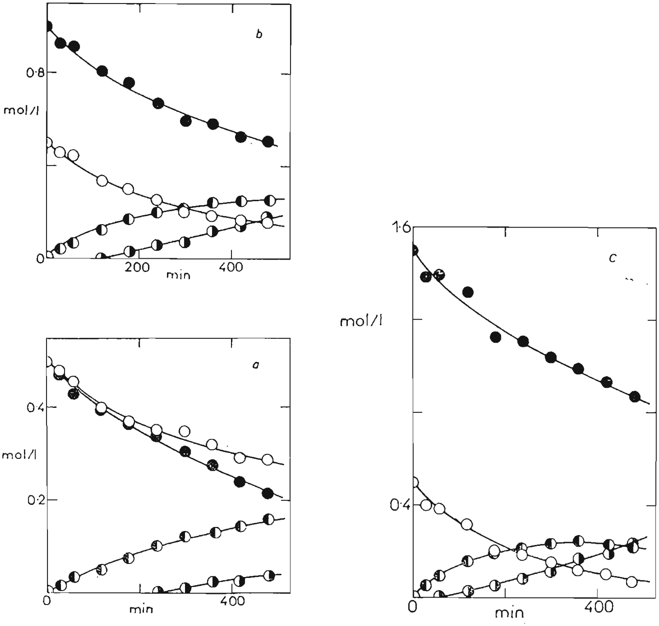

FIG. 2

Time dependence of the reaction between hexamethylenediisocyanate ($[\mathrm{I}]_0 = 0{\cdot}500\ \mathrm{mol\ l^{-1}}$) and 1-pentanol (A), ○ I, ● A, ◐ monourethane, ◑ diurethane; $[\mathrm{A}]_0/[\mathrm{I}]_0$: *a*) 1 : 1, *b*) 2 : 1, *c*) 3 : 1

obtain

$$\frac{d[M]}{d[I]} = -1 + \varkappa \frac{[M]}{[I]} . \qquad (3)$$

Solution to this differential equation in the respective limits after the substitution $[M]/[I] = v$ is

$$\frac{1}{1-\varkappa} \ln \left[1 + (1 - \varkappa) v\right] = \ln \frac{[I]_0}{[I]} . \qquad (4a)$$

A simple rearrangement gives

$$\frac{[M]}{[I]} = \frac{1}{1-\varkappa} \left(\frac{[I]_0}{[I]}\right)^{1-\varkappa} - \frac{1}{1-\varkappa} . \qquad (4b)$$

Relation (*4b*) allows us to determine the ratio of the rate constants, $\varkappa$. Fig. 3 shows experimentally obtained values of all molar ratios, along with the theoretical dependences of $[M]/[I]$ on $[I]_0/[I]$. It can be said that they correspond to the theoretical

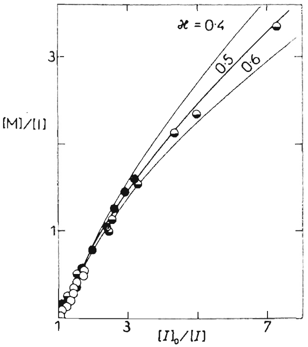

FIG. 3

Determination of kinetic constants ($k_2/k_1 = \varkappa$) using relation (*4b*). $[A]_0/[I]_0$: ○ 1 : 1, ● 2 : 1, ◒ 3 : 1

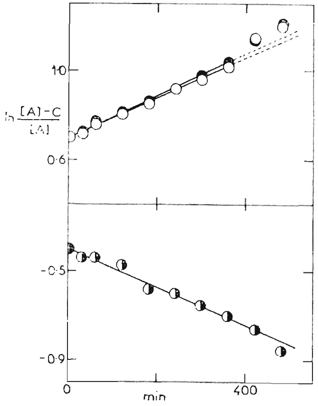

FIG. 4

Determination of the rate constant k_2 using relation (*5d*). $[A]_0/[I]$: 1 : 1 ○ ($[A]_0 = 0{\cdot}498$), ● ($[A]_0 = 0{\cdot}500$); 3 : 1 ◑

dependence for $\varkappa = 0{\cdot}5$. Thus, the ratio of rate constants, k_1/k_2, is two, which means that the reactivity of isocyanate groups in diisocyanate (with two reactive groups) and in monourethane (with one reactive group) is the same and can be characterized by the constant k_2.

For the amount of alcohol consumed by addition reactions we have

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1[\mathrm{A}]\,[\mathrm{I}] + k_2[\mathrm{A}]\,[\mathrm{M}]\,. \tag{5a}$$

By substituting $2k_2$ for k_1 and from Eq. (*1c*) for [I], we obtain

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_2[\mathrm{A}]([\mathrm{A}] - [\mathrm{A}]_0 + 2[\mathrm{I}]_0)\,, \tag{5b}$$

where $[\mathrm{A}]_0 - 2[\mathrm{I}]_0$ is a constant, so that

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_2[\mathrm{A}]([\mathrm{A}] - C) \tag{5c}$$

and after integration

$$\ln\frac{[\mathrm{A}] - C}{[\mathrm{A}]} = \ln\frac{[\mathrm{A}]_0 - C}{[\mathrm{A}]_0} - k_2Ct\,. \tag{5d}$$

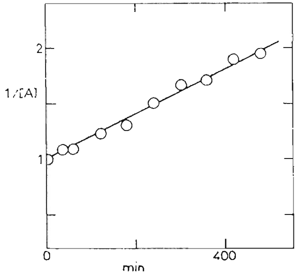

FIG. 5

Determination of the rate constant k_2 using relation (*6a*) at $[\mathrm{A}]_0/[\mathrm{I}])$ 2 : 1

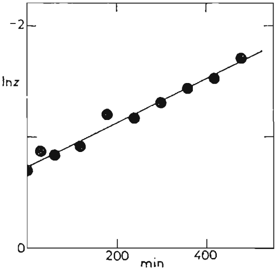

FIG. 6

Time function $z(t)$ expressed as $\ln z = \ln z_0 - bt$ for calculation of the rate constant k_1 using relation (*7b*) at $[\mathrm{A}]_0/[\mathrm{I}]_0$ 3 : 1

By plotting the left-hand side of Eq. (*5d*) *vs* t, a linear dependence was obtained (Fig. 4); after dividing by the constant C, its slope gives the kinetic constant k_2. The values thus obtained are given in Table I.

In a special case where $[A]_0 = 2[I]_0$, C in Eq. (*5c*) is zero, so that

$$-d[A]/dt = k_2[A]^2 , \tag{6}$$

and

$$k_2 t = 1/[A] - 1[A]_0 . \tag{6a}$$

It may be inferred from Fig. 5 that in this case it does hold that $k_1 = 2k_2$; at the same time, k_2 can be determined (the slope of the straight line). The respective value determined by linear regression is also given in Table I.

If the instantaneous concentration of the intermediate product (monourethane) is known, the problem can be approached in another way. If Eq. (*5a*) is written as

$$-d[A]/dt = k_1[A]([I] + k_2/k_1[M]) , \tag{7}$$

then, by substituting $\varkappa$ for k_2/k_1 and rearrangement, we obtain

$$d \ln [A] = -k_1([I] + \varkappa[M])\, dt \tag{7a}$$

and after integration

$$k_1 = \frac{\ln([A]_0/[A])}{\int_0^t z(t)\, dt} , \tag{7b}$$

TABLE I

Kinetic constants k_1 and k_2 ($l\ mol^{-1}\ min^{-1}$) for the reaction between hexamethylenediisocyanate (I) and 1-pentanol (A)

$[A]_0$ $mol\ l^{-1}$	$\frac{[A]_0}{[I]_0}$	according to Eqs (*5d, 6a*)		according to Eq. (*7c*)	
		$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$
0·498	1 : 1	4·10	2·05	4·23	2·12
0·500	1 : 1	4·14	2·07	3·74	1·87
0·997	2 : 1	4·16	2·08	3·97	1·98
1·500	3 : 1	3·48	1·74	3·58	1·79

where $z(t) = [I] + \varkappa[M]$. We found, by using a plot in the coordinates $\ln z$ *vs* t, that in our case the function $z(t)$ can be expressed by an empirical equation $\ln z = \ln z_0 - bt$, where $z_0 = [I]_0$, so that the integral in Eq. (*7b*) is equal to $z_0(1 - e^{-bt})/b$. The function $z(t)$ is shown in Fig. 6. Eq. (*7b*) then becomes

$$k_1 = b \ln ([A]_0/[A])/[I]_0(1 - e^{-bt}) . \qquad (7c)$$

Calculation gave the values of the constant k_1 whose average values for all three molar ratios are given in Table I.

Thus, it can be said that in this case the reaction is indeed a competitive consecutive second-order one. The absolute values of the rate constants have been confirmed by mutually independent procedures, taking into account concentration changes of the two starting compounds and the instantaneous concentrations of the monoderivative. The values of these constants are independent of the alcohol concentration and do not vary with conversion. The rate constants of the reaction between the isocyanate group and pentanol are the same for diisocyanate and monourethane.

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