A New Method for a Kinetic Study of Reactions between Di-isocyanates and Alcohols. Part 1. Symmetrical Di-isocyanates

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A new method of following the kinetics of the uncatalysed reaction between di-isocyanates and alcohols, which allows the determination of the concentration of all the species occurring during the reaction, by means of the high performance liquid chromatography (HPLC), is described. It has been found that the relationship between the unchanged fraction and the fraction that reacts, theoretically inferred for ideal systems (null catalytic effects), is validated over the whole reaction for real systems. This fact is a verification that the reduced time, τ, is a result of the total catalytic effects, and is a surprising simplification of the kinetics of this type of complex process. The following value ratios of the rate constants (*R*) for the first and the second NCO groups for various di-isocyanates were determined: 4,4'-BDI *R* = 1.36, 4,4'-BBDI *R* = 1.30, *p*-PDI *R* = 2.57, *m*-PDI *R* = 3.07.

The study of the uncatalysed reaction between isocyanates and monohydroxylic alcohols has clearly distinguished the existence of chemical effects *e.g.* the catalytic effect of the alcohol and of the formed urethane, and the effect of solvent *etc.*, which indicate that the kinetics of these processes arise largely from simple second-order reactions.[1,2]

Researchers who proposed kinetic equations in which they took these above-mentioned catalytic effects into account, were compelled to introduce into the respective equations, a great number of rate constants. Thus, Becker *et al.*[2] considering only the catalytic effect of the alcohol in accordance with the mechanism shown in equation (1) established the rate reaction [equation (2)].[2]

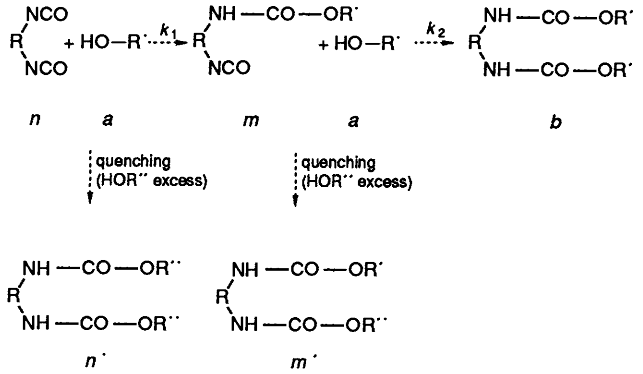
$$\mathrm{RNCO} + \mathrm{R'OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{bmatrix}\mathrm{RNCO}\\ \mathrm{R'OH}\end{bmatrix} + \mathrm{R'OH} \xrightarrow{k_3} \mathrm{RNHCO_2R} + \mathrm{R'OH} \quad (1)$$

$$\frac{\mathrm{d[RNCO]}}{\mathrm{d}t} = -\frac{k_1k_3\mathrm{[RNCO][R'OH]}^2}{k_2 + k_3\mathrm{[ROH]}} \quad (2)$$

In order to simplify the kinetic study some authors decided to work with an excess of alcohol, a situation which can indeed be represented by pseudo-first-order kinetics.[3,4] Certainly, this simplification led to significant loss of detail of the chemical phenomenon.

The kinetics associated with the di-isocyanate reaction render the kinetic equations extremely complex and very difficult to verify experimentally. However, by the use of HPLC it was possible to obtain a more complete data set, without which the study of such complex chemical reactions would not be possible.

In this study we examined the variation in the concentration of all species which appeared during the reaction *i.e.*, unchanged starting material and initial and final products. This is in contrast with classical procedures which yielded only the overall number of the unchanged NCO groups.[3-5] Aliquots from the reaction mixture were withdrawn at various time intervals and were added to a large excess of a different alcohol. Upon this treatment, the molecular species in which reactive NCO groups were present *i.e.*, *n* and *m* (Scheme) were transformed into equivalent quantities of stable urethane derivatives *n'* and *m'*.



Scheme.

The kinetic equations characterizing the simple idealized second order mechanism are given by equations (3)–(6) where *N* is the molar concentration of the di-isocyanate *n*, *M* is the molar concentration of the initial product *m*, *A* is the molar concentration of the alcohol *a*, and *B* is the molar concentration of the final product *b*. k_1 and k_2 are rate constants.

$$\mathrm{d}N/\mathrm{d}t = -2k_1NA \quad (3)$$

$$\mathrm{d}M/\mathrm{d}t = 2k_1NA - k_2MA \quad (4)$$

$$\mathrm{d}B/\mathrm{d}t = k_2MA \quad (5)$$

$$\mathrm{d}A/\mathrm{d}t = -2k_1NA - k_2MA \quad (6)$$

Taking the initial molar concentration of the di-isocyanate N_0, to be equal to the initial molar concentration of the alcohol A_0, the material balance gives rise to equations (7) and (8).

$$A_0 - A = N_0 - N + B = M + 2B \quad (7)$$

$$N_0 = N + M + B \quad (8)$$

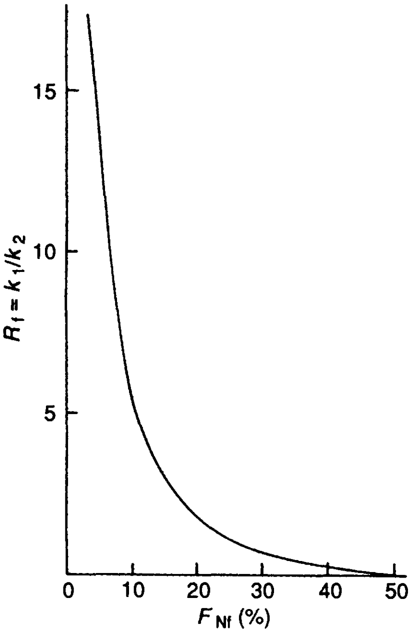


Figure 1. Dependence of R_f on F_{Nf}(%) in accordance with equation (23).

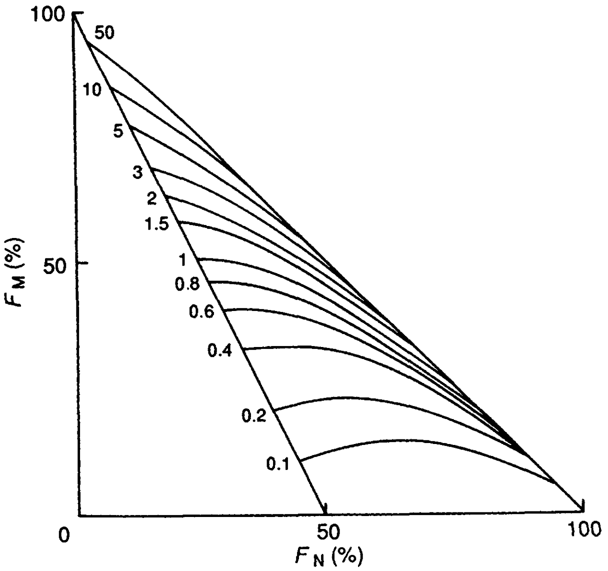


Figure 2. Dependence of F_M(%) on F_N(%) obtained from equation (21) for different values of R in the 0.1–50. The straight line represents the final composition.

In order to integrate equations (3)–(6), we introduced a new variable [equation (9)].

$$d\tau = A\,dt \text{ and so } \tau = \int_0^t A\,dt \qquad (9)$$

Equations (3)–(6) can now be expressed as equations (10)–(13).

$$dN/d\tau = -2k_1N \qquad (10)$$

$$dM/d\tau = 2k_1N - k_2M \qquad (11)$$

$$dB/d\tau = k_2M \qquad (12)$$

$$dA/d\tau = -2k_1N - k_2M \qquad (13)$$

Table 1.

	$R^1OCONHR^2NHCOOR^3$ (1)		
	R^1	R^2	R^3
1	Me	p-$C_6H_4CH_2C_6H_4$-p'	Me
2	Bu^n	p-$C_6H_4CH_2C_6H_4$-p'	Bu^n
3	Me	p-$C_6H_4(CH_2)_2C_6H_4$-p'	Me
4	Bu^n	p-$C_6H_4(CH_2)_2C_6H_4$-p'	Bu^n
5	Me	p-C_6H_4	Me
6	Bu^n	p-C_6H_4	Bu^n
7	Me	m-C_6H_4	Me
8	Bu^n	m-C_6H_4	Bu^n
9	Me	p-$C_6H_4CH_2C_6H_4$-p'	Bu^n
10	Me	p-$C_6H_4(CH_2)_2C_6H_4$-p'	Bu^n
11	Me	p-C_6H_4	Bu^n
12	Me	m-C_6H_4	Bu^n

The solution is expressed as equations (14)–(17).

$$N = N_0\exp(-2k_1\tau) \qquad (14)$$

$$M = \frac{2k_1}{2k_1 - k_2}N_0[\exp(-k_2\tau) - \exp(-2k_1\tau)] \qquad (15)$$

$$B = N_0\left[1 + \frac{k_2}{2k_1 - k_2}\exp(-2k_1\tau) - \frac{2k_1}{2k_1 - k_2}\exp(-k_2\tau)\right] \qquad (16)$$

$$A_0 - A = N_0\left[2 - \frac{2(k_1 - k_2)}{2k_1 - k_2}\exp(-2k_1\tau) - \frac{2k_1}{2k_1 - k_2}\exp(-k_2\tau)\right] \qquad (17)$$

The mole ratios of these three species can be written $F_N = N/N_0$, $F_M = M/N_0$, and $F_B = B/N_0$, respectively. Equations (14)–(16) can then be expressed as equations (18)–(20).

$$F_N = \exp(-2k_1\tau) \qquad (18)$$

$$F_M = \frac{2k_1}{2k_1 - k_2}[\exp(-k_2\tau) - \exp(-2k_1\tau)] \qquad (19)$$

$$F_B = 1 - F_N - F_M \qquad (20)$$

Elimination of τ from equations (18) and (19) leads to equation (21).

$$F_M = \frac{1}{1 - 1/(2R)}(F_N{}^{1/(2R)} - F_N) \qquad (21)$$

At the end of the reaction, where $A = 0$, equations (7) and (8) lead to equation (22). Substitution of equation (21) into equation (22) gives rise to equation (23) the transcendental equation which makes it possible to calculate R_f, the subscript f indicating the mode by which it was determined.[6]

$$F_{Mf} = 1 - 2F_{Nf} \qquad (22)$$

$$1 - 2F_{Nf} = \frac{1}{1 - 1/(2R)}(F_{Nf}{}^{1/(2R)} - F_{Nf}) \qquad (23)$$

The R_f *versus* F_{Nf} plot is represented in Figure 1. In Figure 2 F_M is plotted *versus* F_N, representing the relation (21) for

Table 2. Models for HPLC.

	Recrystallisation				% Found (required)		
Model	Solvent	No.	M.p./°C	Formula	C	H	N
(*a*) Symmetrically disubstituted models							
(1)	MeOH	4	189–193[a]	$C_{17}H_{18}N_2O_4$	64.5 (64.94)	5.65 (5.73)	9.05 (8.92)
(2)	MeOH	2	119–122[b]	$C_{23}H_{30}N_2O_4$	69.4 (69.35)	7.55 (7.54)	7.1 (7.04)
	MeOH–H_2O (1:1)	2					
(3)	MeOH	3	206.5–210.5	$C_{18}H_{20}N_2O_4$	65.75 (65.85)	6.0 (6.10)	6.9 (8.54)
	Me_2CO	1					
(4)	DMF–H_2O (5:1)	2	165.5–166	$C_{24}H_{32}N_2O_4$	70.1 (69.90)	7.6 (7.77)	6.3 (6.80)
	MeOH	2					
(5)	MeOH	4	218–221[c]	$C_{10}H_{12}N_2O_4$	53.2 (53.57)	5.3 (5.39)	12.3 (12.49)
(6)	MeOH	4	161–163	$C_{16}H_{24}N_2O_4$	62.05 (62.32)	7.5 (7.84)	9.05 (9.08)
(7)	MeOH–H_2O (1:1)	4	162–166	$C_{10}H_{12}N_2O_4$	53.5 (53.57)	5.5 (5.39)	12.5 (12.50)
(8)	MeOH–H_2O (2:1)	4	78–82	$C_{16}H_{24}N_2O_4$	62.5 (62.32)	7.8 (7.84)	9.55 (9.09)
(*b*) Asymmetrically disubstituted models							
(9)			121–124	$C_{20}H_{24}N_2O_4$	67.75 (67.42)	6.7 (6.74)	7.75 (7.86)
(10)			165–167	$C_{21}H_{26}N_2O_4$	68.05 (68.09)	7.1 (7.07)	7.6 (7.56)
(11)			155–157	$C_{13}H_{18}N_2O_4$	58.35 (58.63)	6.55 (6.81)	10.5 (10.52)
(12)			72–74	$C_{13}H_{18}N_2O_4$	58.70 (58.63)	6.7 (6.81)	10.35 (10.52)

[a] lit.,[8] 183–183.6; 190. [b] lit.,[8] 121. [c] lit.,[8] 207; 209–210. DMF = *N,N*-Dimethylformamide.

different values of *R*. Both graphs show that, in order to obtain the value of *R* with the best possible precision, it is necessary that the experimental data of F_N and F_M in the average and final stages of the reaction be as accurate as possible, particularly as the values of *R* increase.

These equations describe the situation in which two real constants k_1 and k_2, determine theoretically the composition of the system, at any time. If this is the case, the plot of ln F_N *versus* τ is a straight line; the constant k_1 is given by the slope of this straight line.

In the situation we have studied, in which $N_0 = A_0$, it is assumed that the catalytic effects of the alcohol and the urethane influence the experimental data. As a result, equations (18)–(20) will be invalid; the plot of ln F_N *versus* τ would deviate from a straight line. A similar deviation from linearity of this plot would be expected if competitive reactions lead to additional consumption of the NCO groups. Such reactions involve traces of water, solvent, or the formation of allophanic acid derivatives.*

Our first aim was to determine experimentally, for real systems, the plots of ln F_N *versus* τ, and to evaluate how much the process deviates from the ideal case of simple bimolecular kinetics. Secondly, we wished to verify equation (13) and implicitly to determine the ratio *R*. Knowledge of this ratio is of practical importance since it provides information about the final composition of the reaction mixture, data which assists the structure determination of prepolymer intermediates for polyurethanes.

Symmetrical di-isocyanates are of two types; S_c and S_v were studied. The two NCO groups in S_c are located in different aromatic rings, isolated from each other by aliphatic segments. In S_v, both NCO groups are bound to the same aromatic ring, and their reciprocal interaction is quite strong. Isocyanates belonging to S_c are 4,4′-methylenebis(phenylisocyanate) (4,4′-MBI) and bibenzyl-4,4′-diyl di-isocyanate (4,4′-BBDI), and those belonging to S_v type are *p*-phenylenedi-isocyanate (*p*-PDI) and *m*-phenylenedi-isocyanate (*m*-PDI).

A series of twelve model compounds were prepared as standards for HPLC with the structures given in Table 1.

Experimental

Materials.—Di-isocyanates were purified by distillation at low pressure. The purity was determined by chemical means.[7] Benzene was dried on metallic sodium and distilled before use. Butan-1-ol *pa* was dried over calcium hydride and then distilled. Melting points were determined by means of a capillary tube. IR spectra (KBr) were recorded with a Perkin-Elmer 577 spectrometer. ^1H NMR measurements were performed with a 60 MHz JEOL spectrometer. HPLC was carried out with a Hewlett-Packard 1084 A UV variable-wavelength detector 1030B.

Model Synthesis.—The symmetrical disubstituted models [**(1)**–**(8)**] in Table 2(*a*) were obtained as follows. Freshly distilled and analysed di-isocyanates (5 g) were dissolved in anhydrous methanol or butanol (50 cm^3) and the mixture was refluxed for 4 h. The excess of alcohol was removed by distillation and the residue was purified by recrystallization four times to constant melting point. The yields in the crude products were quantitative. The appropriate solvents for purification, the melting points, and the elemental analysis are shown in Table 2(*a*).

Methylenebis(p-*carbanilic Acid*) *Methyl Butyl Ester* **(9)**.—The disubstituted asymmetrical model compounds were prepared by successive reaction, as follows. To a solution of freshly distilled 4,4′-MBI (2.57 g) in anhydrous benzene (25 cm^3), was added anhydrous butan-1-ol (0.76 g). The mixture was kept overnight at 60 °C. The next day the cooled solution was filtered and the liquid was concentrated by evaporation to a third of its volume, and filtered. It was then treated with three volumes of cyclohexane and filtered again. Concentration of the liquid layer left a monoisocyanate (2.36 g) which was treated with methanol (25 cm^3) at 60 °C and the solution was kept overnight. The solution was evaporated and the solid residue was purified by recrystallization from methanol. The solid obtained at room temperature was separated and the solution was cooled to 0 °C. The new solid product was filtered and purified by repeated recrystallizations from methanol–water (1:1). The compound obtained model **(9)** was characterized as shown in Table 2(*b*).

1,2-*Ethylenebis*(p-*carbanilic Acid*) *Methyl Butyl Ester* **(10)**.—

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* $H_2NCONHCO_2H$.

Table 3. Chromatography conditions.

		Mobile phase				Retention time		
		H_2O 80 °C	MeOH 40 °C					
No.	Di-isocyanate	%vol		Flow/ cm^3 min^{-1}	λ/nm	Species	Model	min
(1)	4,4′-MBI	25	75	1	248	*n′*	1	3.73
						m′	9	6.17
						b	2	12.27
(2)	4,4′-BBDI	20	80	1	244	*n′*	3	3.64
						m′	10	5.55
						b	4	9.79
(3)	*p*-PDI	38	62	2	256	*n′*	5	1.67
						m′	11	3.31
						b	6	8.17
(4)	*m*-PDI	35	65	2	240	*n′*	7	1.74
						m′	12	3.33
						b	8	9.30

Butan-1-ol (0.76 g, made free of water by being distilled from sodium) and a drop of pyridine were added to 4,4′-BBDI (2.71 g, freshly distilled) in anhydrous benzene (25 cm^3). The mixture was kept overnight at 60 °C, after which the product was cooled to room temperature and filtered. The solution was concentrated to a third of its volume, cooled to *ca.* 6 °C, and then filtered. The filtrate was diluted with three volumes of anhydrous cyclohexane, cooled to -15 °C and filtered. The solid (monoisocyanate) was treated with methanol (25 cm^3) and left overnight at 60 °C after which time the warm solution was filtered. Upon concentration, a diurethane residue (1.2 g) was left. This was purified by recrystallization from methanol–water (1:1). The melting point and elemental analyses are given in Table 2(*b*).

Butyl Methyl p-*Phenylenebis(carbamate)* (**11**).—To *p*-PDI (4 g) dissolved in a mixture of cyclohexane (10 cm^3) and anhydrous benzene (10 cm^3) were added methanol (0.8 g) and a drop of anhydrous pyridine. The mixture was stirred for 6 h at room temperature, after which the solid product (crude monoisocyanate) was washed with cyclohexane and dried *in vacuo.* To the crude monoisocyanate (3.65 g) dissolved in a mixture of benzene (30 cm^3) chloroform (20 cm^3), and anhydrous butanol (10 cm^3) was added anhydrous pyridine (0.25 cm^3) and the mixture was left overnight at 60 °C. The next day, the product was cooled, filtered, and dried. The model compound was purified by recrystallization three times from methanol–water (3:1) and then from a 1:2 mixture. The solid model compound (1.5 g) was obtained and characterized as shown in Table 2(*b*).

Butyl Methyl m-*Phenylenebis(carbamate)* (**12**).—To *m*-PDI (4 g) dissolved in anhydrous benzene (10 cm^3), were added anhydrous methanol (0.8 g), and a drop of anhydrous pyridine. The mixture was stirred for 6 h whereupon anhydrous cyclohexane (10 cm^3) was added. After filtration, the liquid was cooled and kept at 5–6 °C overnight. The crystalline solid, separated by filtration, was the crude monoisocyanate. The monoisocyanate was dissolved in a mixture of benzene (20 cm^3), chloroform (20 cm^3), anhydrous butan-1-ol (5 cm^3), and anhydrous pyridine (0.25 cm^3) and kept at 60 °C overnight. Concentration left a solid that became crystalline upon being rubbed. The crude model compound (3.88 g) was purified by recrystallization once from methanol–water (3:1), twice from cyclohexane–dichloroethane (3:1), and finally from water. The pure model compound (3.7 g) was characterized as shown in Table 2(*b*).

The model compound characterizations (**9**)–(**12**) are shown in Table 2(*b*). The structures were confirmed by IR and ^1H NMR spectroscopy and the purity was determined by HPLC.

Kinetics.—To a stirred solution of di-isocyanate (0.35 mol dm^{-3}; 5 cm^3) in anhydrous benzene at 60 ± 0.1 °C was added butan-1-ol in anhydrous benzene (0.35 mol dm^{-3}; 5 cm^3) at 60 ± 0.1 °C. From time to time samples of 0.1 cm^3 were taken out and the reaction was quenched by adding them to anhydrous methanol *pa* (25 ml). After a minimum reaction time of 24 h, the solution was analysed by HPLC. Alternatively, the solvent (benzene) was removed by evaporation and the initial concentration restored with fresh methanol.

HPLC Analysis.—A Hewlett-Packard 1084 A chromatograph fitted with an UV variable wavelength detector 1030 B was used. The reversed-phase method was used: Lichrosorb RP-18, 10 μm Brownie Labs. USA column, 250 mm long, 4.6 mm internal diameter, 2 μm frit pore; column temperature 40 °C; injection volume 3 mm^3. The working conditions of the chromatograph are presented in Table 3.

The individual components were fully resolved; liquid chromatography can thus be used for the quantitative determination of reaction products. Under our conditions we found that the secondary reactions did not exceed 1–2% of the main reaction.

With a view to minimizing the effect of experimental error, the determinations were repeated a minimum of three times. It was established that the average of the values obtained was to within 2% of the absolute value.

Results and Discussion

The determination of the molar concentration of alcohol necessary for the calculation of τ by means of the equation $\tau = \int_0^t A dt$ has been performed indirectly $A = N - B$ (because $A_0 = N_0$). The integration was carried out *via* two numerical methods with variable steps: a spline-function method[9] and a method based on double quadratic interpolation.[10] Both methods give consistent results.

The plot ln $F_{N_{exp}}$ *versus* τ are presented in Figure 3, for all four of the di-isocyanates studied. As can be seen, the curve deviates somewhat from the linearity predicted for an ideal system (**4**); an observation noted by other authors.[1]

Table 4. The values of τ, k_1, and $F_{\mathrm{Ncalc}}\%$ for the reaction of 4,4′-MBI with butan-1-ol. $c_{\mathrm{NCO}} = c_{\mathrm{OH}} = 0.175$ mol dm^{-3} (benzene), 60 °C.

No.	t/min	F_{Nexp} (%)	τ/min mol dm^{-3}	k_1/dm^3 mol^{-1} min^{-1}	F_{Ncalc} (%)
(1)	0.0	100.00	0.000		100.00
(2)	7.5	95.84	1.282	0.0166	94.75
(3)	21.2	89.32	3.507	0.0161	86.28
(4)	35.6	82.00	5.645	0.0176	78.86
(5)	50.4	76.00	7.667	0.0179	72.43
(6)	65.8	70.16	9.571	0.0185	66.85
(7)	86.3	62.90	11.840	0.0196	60.77
(8)	105.2	56.78	13.658	0.0207	56.29
(9)	146.1	46.67	16.825	0.0226	49.27
(10)	190.4	40.20	19.401	0.0235	44.21
(11)	245.6	34.14	21.834	0.0246	39.91
(12)	300.5	30.86	23.596	0.0249	37.05
(13)	360.1	27.60	24.862	0.0259	35.13
$k_{1\mathrm{med}} = 0.0210$					

Table 5. $R = k_1/k_2$ values for the di-isocyanates studied. $c_{\mathrm{NCO}} = c_{\mathrm{OH}} = 0.175$ mol dm^{-3} (benzene), 60 °C.

	S_c		S_v	
Type	4,4′-MBI	4,4′-BBDI	*m*-PDI	*p*-PDI
R_{opt}	1.36	1.30	3.07	2.57
R_f	1.39	1.40	2.76	3.06

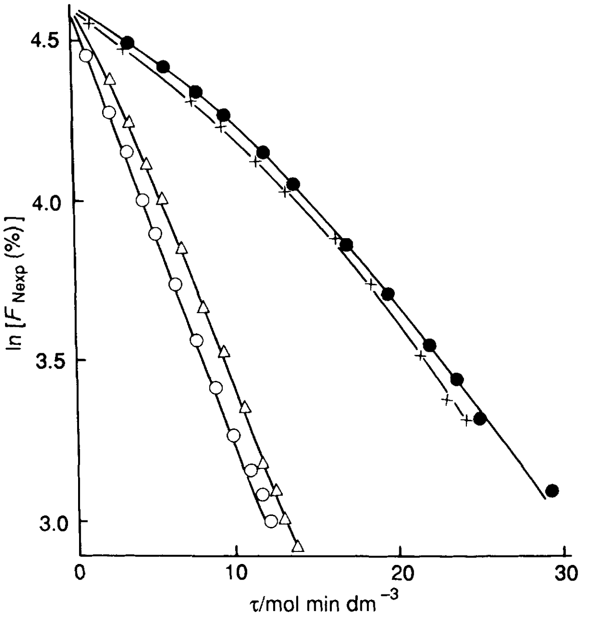

Figure 3. Dependence of ln $F_{\mathrm{Nexp}}(\%)$ function on τ: +, 4,4′-MBI; ●, 4,4′-BBDI; △, *p*-PDI; ○, *m*-PDI.

In the following we present the treatment of the experimental data in the case of 4,4′-MBI, where the catalytic effects are visible (Figure 3). Table 4 shows the experimental values F_{Nexp}, the τ function calculated using equation (9), and the apparent values of k_1, calculated from equation (24).

$$k_1 = -0.5 \ln (F_{\mathrm{Nexp}})/\tau \qquad (24)$$

The k_1 values were checked by comparison of the value of F_{Nexp} with the value F_{Ncalc} obtained from equation (25) where

$$F_{\mathrm{Ncalc}}\% = 100 \exp(-2k_{1\mathrm{med}}\tau) \qquad (25)$$

$k_{1\mathrm{med}}$ represents the arithmetic mean of the k_1 values, as presented in Table 4.

The experimental verification of the equations (18)–(20) was carried out in two ways.

Using equation (21) and the experimentally determined R_f value, we calculated for each experimental F_N, the F_M values at different stages of the reaction. We then compared them with the value determined experimentally, F_{Mexp}. For 4,4′-MBI and 4,4′-BBDI, very good agreement exists between F_{Mcalc} and F_{Mexp} throughout the reaction. Optimized agreement was also obtained *via* a second procedure using a numerical search method.[11] This method aims to find the best ratio F_{opt} which ensures the optimum agreement between the calculated and the experimental data, by using the least-squares technique. Table 5 displays the experimental data for R, obtained with both methods, for the four di-isocyanates. Since the second method takes into account a larger data set, these values are probably more precise.

In Table 6 are given the F_{Mexp} and F_{Mcalc} values, calculated according to equation (21), using F_{Nexp} and R_{opt} values, taken from Table 5.

The small differences between the experimental and the calculated values verifies both the precision of the experimental determinations and the validity of equation (23).

Taking into account the non-averaged values of F_{Nexp} the variation interval of the R values amounts to a maximum of 7%.

If we identify the R value thus determined from the ratio k_1/k_2 and take into account the previously determined apparent $k_{1\mathrm{exp}}$ value, we can ascertain the apparent $k_{2\mathrm{exp}}$ value. The apparent k_1 and k_2 values are presented in Table 7.

As can be seen, for S_c-type isocyanates, the ratio R is close to unity. This shows that the change in reactivity of the NCO group after the reaction of the first group, is small, whereas for S_v type isocyanates the change is larger. The agreement between F_{Mexp} and F_{Mcalc} is fairly good in both cases, *i.e.* for symmetrical di-isocyanates of constant reactivity (type S_c) and for those of variable reactivity, of the S_v type. These observations lead to the conclusion that it is possible to determine a single R value, valid for the whole pattern of the reaction.

Conclusions

By studying the kinetics of symmetrical di-isocyanates reaction with alcohols using the HPLC technique, it could be shown that relation (21) obtained primarily for the ideal second-order mechanism is also valid in the case of real systems throughout the whole of the reaction. This implies that the perturbation processes which cause the reaction to deviate

Table 6. Comparison of F_{Mexp} and F_{Mcalc} values in %. $c_{\mathrm{NCO}} = c_{\mathrm{OH}} = 0.175$ mol dm^{-3} (benzene) 60 °C.

F_{Nexp}	F_{Mexp}	F_{Mcalc}	Δ	F_{Nexp}	F_{Mexp}	F_{Mcalc}	Δ
4,4′-MBI[a]				4,4′-BBDI[a]			
100.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00
95.15	4.85	4.81	0.04	96.08	3.92	3.89	0.03
87.63	12.37	12.07	0.30	88.57	11.43	11.16	0.27
73.96	23.26	24.58	−1.32	74.70	22.78	23.87	−1.09
68.37	27.78	29.39	−1.61	69.22	27.92	28.59	−0.67
60.97	34.33	35.42	−1.09	62.32	33.57	34.22	−0.65
55.52	38.86	39.58	−0.72	56.78	37.72	38.46	−0.74
48.28	43.77	44.65	−0.88	46.67	44.60	45.41	−0.81
41.97	48.64	48.56	0.08	40.20	48.83	49.17	−0.34
33.18	53.09	52.95	0.14	34.14	53.26	52.05	1.21
29.03	54.45	54.46	−0.01	30.86	53.59	53.29	0.30
27.44	54.89	54.91	−0.02	27.60	53.84	54.25	−0.41
				23.21	54.80	55.01	−0.21
				21.84	56.50	55.10	1.40
p-FDI[b]				*m*-FDI[b]			
100.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00
89.92	10.07	9.97	0.10	86.19	13.80	13.64	0.16
79.26	20.73	20.26	0.47	71.75	28.25	27.46	0.79
69.79	28.11	29.12	−0.01	63.17	34.78	35.39	−0.61
60.22	37.14	37.73	−0.59	54.96	42.41	42.71	−0.30
54.08	42.02	43.02	−1.00	49.50	47.00	47.41	−0.41
46.81	47.41	49.00	−1.59	42.16	53.51	53.43	0.08
38.78	55.04	55.12	−0.08	35.21	58.74	58.74	0.00
33.89	58.12	58.52	−0.40	30.56	62.26	62.00	0.26
28.57	61.94	61.84	0.10	26.50	64.60	64.59	0.01
24.19	64.69	64.18	0.51	23.60	66.36	66.26	0.10
22.13	65.43	65.12	0.31	21.70	66.40	67.25	−0.85
20.21	65.75	65.89	−0.14	20.05	66.59	68.03	−1.44
18.64	66.42	66.42	0.00	15.95	58.09	68.32	−0.23

$\Delta = F_{\mathrm{Mexp}} - F_{\mathrm{Mcalc}}$. [a] S_c-type di-isocyanate. [b] S_v-type di-isocyanate.

Table 7. Values of k_1 and k_2. $c_{\mathrm{NCO}} = c_{\mathrm{OH}} = 0.175$ mol dm^{-3} (benzene), 60 °C.

			k_1/dm^3 mol^{-1} min^{-1}			($k_2 = k_1/R_{\mathrm{opt}}$)/dm^3 mol^{-1} min^{-1}	
No.	Type	Di-isocyanate	Initial	Average	$R_{\mathrm{opt}}{}^a = k_1/k_2$	Initial	Average
(1)	S_c	4,4′-MBI	0.0200	0.0214	1.36	0.0147	0.0157
(2)		4,4′-BBDI	0.0181	0.0210	1.30	0.0139	0.0162
(3)	S_v	*p*-PDI	0.0560	0.0575	2.57	0.0218	0.0224
(4)		*m*-PDI	0.0717	0.0699	3.07	0.0234	0.0228

[a] k_1/k_2 was determined by use of the search method.

from the 'ideal' bimolecular simple mechanism, are reflected only by the structure of function τ.

Undoubtedly, verification of the equation (21) for other systems, to establish whether the regularity found by us is of general applicability, is necessary. We have observed the same regularity for other systems where the curvature of the plot F_N on τ is even more accentuated than in the present work.[12]

References

1 J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 1947, 713.
2 J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 1949, 19.
3 M. E. Bailey, V. Kirss, and R. S. Spaunburgh, *Ind. Eng. Chem.*, 1956, **48**, 794.
4 A. Barbalata, A. A. Caraculacu, and V. Iurea, *Eur. Polym. J.*, 1972, **14**, 427.
5 G. Anzuino, A. Pirro, O. Rossi, and L. Polofriz, *J. Polym. Sci., Part A-1, Polym. Chem.*, 1975, **13**, 1657.
6 A. A. Caraculacu, I. Agherghinei, and M. Gaspar, *Marcromol. Chem., Rapid Commun.*, 1986, 761.
7 S. Siggia and J. G. Hanna, *Anal. Chem.*, 1948, **20**, 1084.
8 D. J. David and H. B. Staley, 'Analytical Chemistry of the Polyurethanes,' vol. XVI, part III, Wiley–Interscience, New York, 1969, pp. 564, 574.
9 Gh. Micula, 'Spline Functions and Applications,' Technique Publishing House, Bucharest, 1978, p. 149 (in Romanian).
10 I. Todoran, 'Mathematical Treatment of Experimental Data,' RSR Academy, Bucharest, 1976, p. 193 (in Romanian).
11 E. R. Robinson, 'Time Dependent Chemical Processes,' Applied Science Publishers Ltd., London, 1975, p. 224.
12 I. Agherghinei, C. Prisecariu, and A. Caraculacu, in preparation.

Paper 9/03315G
Received 26*th January* 1990
Accepted 15*th March* 1990