

KINETICS OF THE CYCLOTRIMERIZATION AND COCYCLOTRIMERIZATION OF ISOCYANATES CATALYZED WITH ALKALI METALS ALKOXIDES

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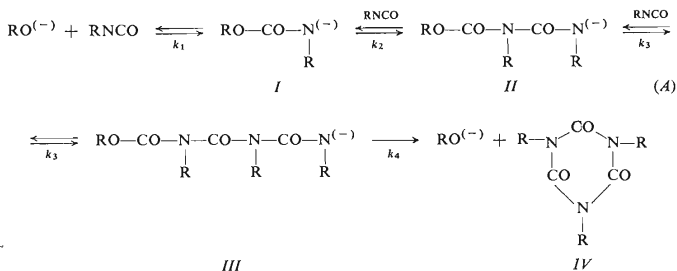
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For the rate of cyclotrimerization v_t of phenyl isocyanate (I) in tetrahydrofuran catalyzed with Li, Na or K tert-butoxides (A) at 30°C, the coefficients k , a , b of the empirical relation $v_t = k[I]^a[A]^b$ were determined. The same coefficients were also determined for the cyclotrimerization of ethyl isocyanate with lithium tert-butoxide as the catalyst. The composition of the products of cocyclo-trimerization of ethyl and butyl isocyanate corresponds to ratios of the rates of trimerization of the individual isocyanates. With respect to the fast decay of initiator in acetonitrile, data reported in the literature on the rate of cyclotrimerization in this solvent are not real.

Cyclotrimerization of organic isocyanates is achieved by means of a large number of catalysts^{1,2}. Strongly basic compounds, such as alkali metals alkoxides, rank among the most active ones³. The following mechanism has been suggested for the cyclotrimerization of isocyanates due to alkali metals alkoxides^{1,4}:



It has also been reported⁵ that linear trimer *III* can react with the monomer, giving rise to *I* and *IV* (with the rate constant k_5). An assumption has been forwarded⁵ that

the rate constants of the individual partial reactions obey the inequalities $k_1 \ll k_2$, and $k_4 \ll k_5$. This assumption is based among other things, also on the finding that cyclotrimerization initiated with alkoxide can be accelerated by an addition of urethane^{6,7}. It has been reported⁷ that in this case the overall rate is of second order with respect to isocyanate and of first order with respect to alkoxide. With another strong base, bis-(2-methoxyethoxy)sodiumaluminiumhydride used as catalyst it was found, however, that the reaction is first-order with respect to the monomer⁸. A view has also been expressed⁹ that with tertiary potassium butoxide used as catalyst, linear polymers are formed from phenyl isocyanate. Hence, a cyclic trimer could be formed not only from the linear trimer *III*, but also from higher oligomers.

With respect to the complexity of the reaction scheme, it may rather be expected that cyclotrimerization is not controlled by simple relations, and the kinetics of this reaction was therefore examined in greater detail, using alkali metals alkoxides as catalysts.

EXPERIMENTAL

Chemicals

Phenylisocyanate (Fluka), freshly redistilled, butyl isocyanate (Fluka) were purified as reported¹⁰; ethyl isocyanate and dodecyl isocyanate (Fluka), freshly redistilled. Lithium, sodium and potassium tert-butyl alkoxide¹¹ were dissolved in tetrahydrofuran dried with lithiumaluminium hydride. Potassium propoxide was prepared by dissolving potassium in dry propanol. Acetonitrile was repurified as reported¹². All operations took place in an inert atmosphere.

Investigation of the Kinetics of Trimerization

Preliminary experiments with the cyclotrimerization of phenyl isocyanate by sodium tert-butyl-alkoxide used as catalyst showed the reaction to proceed at such a rate that the usual titration method^{2,8,10,13} (determination of unreacted phenyl isocyanate) was very unreliable. Since cyclotrimerization is a strongly exothermal reaction¹⁶ ($-\Delta H = 65-85$ kJ/mol), the method of differential calorimetry could be employed¹⁴ (allowing us to observe the course of exothermal reactions whose halftimes lie in the range 0.5–10 min). Into each glass cell of a differential calorimeter (20 ml), 10 ml of solvent was introduced with syringes, and isocyanate and initiator were gradually added into the measuring cell. The temperature difference was measured with copper-constantan thermocouples (microvoltmeter Keithley, 150 B) and recorded with a Varian G-4000 recorder. Both thermal losses and delay of the measuring apparatus were borne in mind when the records were evaluated.

Cotrimerization

Stock solutions of two isocyanates were added into the reaction cell thermostated to 25°C and a solution of tert-BuONa used as initiator was added with stirring. After 4 h the base was neutralized by adding acetic acid. In the cotrimerization of ethyl- and butyl isocyanates the

TABLE I

Instantaneous rates (v_t) and k values from Eq. (1) at a 0.63 and b 1.22 in the cyclotrimerization of phenyl isocyanate catalyzed with lithium tert-butoxide at 30°C

$[I]_0$ mol/l	$[A]_0$ mmol/l	t s	$[I]$ mol/l	$v_t \cdot 10^4$ mol/l ³ s	k
0.207	1.56	31	0.180	7.94	0.38
		126	0.120	4.90	0.38
		311	0.060	1.97	0.36
0.165	1.56	77	0.120	5.10	0.37
		184	0.080	2.89	0.37
		272	0.060	2.07	0.37
0.075	1.56	70	0.060	1.92	0.36
		208	0.040	1.24	0.38
0.165	0.80	116	0.120	3.18	0.38
		420	0.040	0.85	0.38
	3.21	46	0.120	7.58	0.37
		114	0.080	4.68	0.38
	3.12	51	0.120	6.40 ^a	0.32 ^a
131	0.080	3.73 ^a	0.31 ^a		

^a $T = 20.2^\circ\text{C}$.

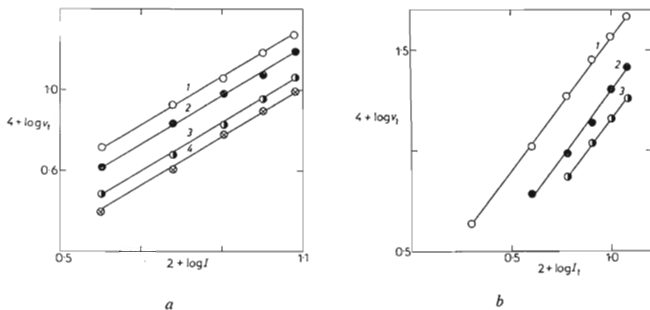


FIG. 1

Cyclotrimerization of phenyl isocyanate ($[I]_0 = 0.165$ mol/l) catalyzed with sodium (a) or potassium (b) tert-butoxide (A) at 30°C in tetrahydrofuran — instantaneous rates v_t at various instantaneous concentrations of isocyanate (I). a) $[A]_0$, mmol/l, 1, 1.674, 2, 1.107, 3, 0.837, 4, 0.567; b) $[A]_0$, mmol/l: 1, 1.037, 2, 0.543, 3, 0.296

products were analyzed with GLC (on a 1 m column with a 10% Versamide 60 on Chromosorb N), using benzophenone as the internal standard. In the case of cotrimerization of dodecyl- and phenyl isocyanate, the reaction mixture was analyzed by means of GPC.

RESULTS AND DISCUSSION

Reaction Medium

The choice of solvents suited for the investigation of the kinetics of cyclotrimerization of isocyanates is rather narrow. The solvent must be inert and must adequately dissolve the trimers formed. Kresta and coworkers² and Sergeev and coworkers⁸ used acetonitrile, which however is known to add alcohols¹⁵. The reaction is so fast that it appeared to be very disturbing in the catalysis with potassium propoxide, and somewhat less, though still rather markedly, disturbing with potassium tert-butylalkoxide used as catalyst. Dimethylformamide also is not a suitable medium for reactions of isocyanates because of the possibility of 1,2-cycloaddition¹. Of the tested solvents, tetrahydrofuran was found to be the best.

TABLE II

Cyclotrimerization of ethyl isocyanate ($[I]_0 = 0.122$ mol/l) catalyzed with lithium (or sodium) tert-butoxide at 30°C: Instantaneous rates (v_t) and k values from Eq. (1) for a 1 and b 1.22

$[A]_0 \cdot 10^3$ mol/l	t s	$[I]$ mol/l	$v_t \cdot 10^3$ mol/l s	k
Cation : Li				
2.318	16	0.08	1.795	16.9
	28	0.06	1.346	18.0
	45	0.04	0.782	17.1
1.558	24	0.08	1.246	18.1
	40	0.06	0.854	17.0
	68	0.04	0.544	17.7
0.798	55	0.08	0.625	17.1
	95	0.06	0.432	16.8
	149	0.04	0.266	16.9
Cation : Na				
1.722	55.2	0.06	6.25	112
	8.5	0.04	3.70	109
	15.6	0.02	1.61	110

Effect of the Cation

The rate of cyclotrimerization of isocyanates (I) in tetrahydrofuran catalyzed with alkali metals tert-butylalkoxides (A) can be expressed, in the conversion range 10 to 90%, through an empirical relation (Fig. 1, Table I)

$$v_t = k[I]^a [A]_0^b \quad (I)$$

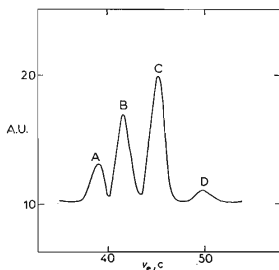
The catalytic effect of O- and N-anions in the first approximation in the range of conditions under investigation can be regarded as equivalent to the effect of alkoxides, so that the concentration of a catalytically active base is constant throughout the reaction ($[A] = [A]_0 = \text{const.}$). Using the dependence of the rate of cyclotrimerization of phenylisocyanate on the concentrations of alkoxides and isocyanate, the following coefficients of Eq. (I) were determined for 30°C:

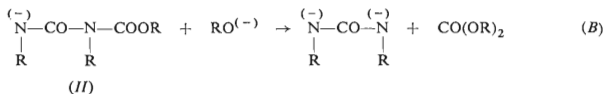
Alkoxide	Li	Na	K
k	0.38	2.16	10.7
a	1.22	1.22	1.22
b	0.63	0.63	0.76

The noninteger reaction order can be explained by the fact that the cyclotrimerization proceeds gradually through several stages and that the alkoxides are not completely dissociated. Moreover, the alkoxide anion reacts with carbonyl groups of products of the individual reaction stages with formation of neutral dialkyl carbonate and N-anions, *e.g.* diphenyl urea. For intermediate II , this can be expressed by the scheme:

FIG. 2

Gel chromatogram of the products of cotrimerization of phenyl isocyanate ($[P]_0 = 0.2$ mol/l) with dodecyl isocyanate ($[D]_0 = 0.2$ mol/l) catalyzed with sodium tert-butoxide. Mole fractions of trimers in the product: A DDD 0.133, B DDP 0.325, C DPP 0.504 and D PPP 0.035





In the cyclotrimerization of phenyl isocyanate, diphenylurea has a strongly inhibitive effect; thus, *e.g.* in the reaction of phenyl isocyanate (0.154 mol/l) catalyzed with alkoxide (0.00174 mol/l), 96% isocyanate reacted at 25°C within 4 min, while only 37% reacted in the presence of 8.8% mol diphenylurea. Thus, the originally suggested mechanism^{1,4,5} of cyclotrimerization of isocyanates must obviously be supplemented.

Table I shows that in the investigated temperature range 20–30°C the rate of cyclotrimerization of phenyl isocyanate increases with increasing temperature less than in the case of usual reactions ($E_a \approx 15$ kJ/mol).

In addition to the kinetics of cyclotrimerization of phenyl isocyanate, the kinetics of cyclotrimerization of ethyl isocyanate catalyzed with lithium and sodium tertbutylalkoxide was also studied (Table II), and the following parameters of Eq. (1) were determined: $a = 1.22$, $b = 1$, k (for Li) = 65, k (for Na) = 110. As documented by Tables I and II, the rate of cyclotrimerization of aliphatic isocyanates is higher than that of aromatic ones, at variance with the reported results⁵.

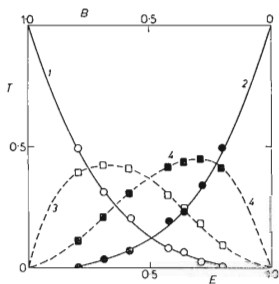


FIG. 3

Effect of the initial composition of the reaction mixture on the molar content of cyclic trimers, c_T , in the cotrimerization of ethyl isocyanate (E) with butyl isocyanate (B); $[E + B]_0 = 0.213$ mol/l, $[t\text{-BuONa}]_0 = 2.8$ mmol/l, 25°C, 4 h. c_T : 1 EEE, 2 BBB, 3 cotrimer EEB, 4 cotrimer EBB

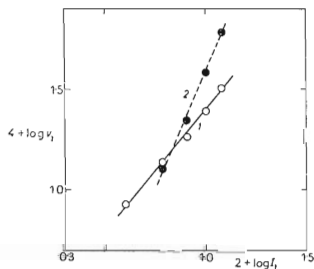


FIG. 4

Cyclotrimerization of phenyl isocyanate with lithium tert-butoxide ($[A]_0 = 0.80$ mol/l) at 25°C in tetrahydrofuran 1 and acetonitrile 2 — instantaneous rates v_t at various isocyanate concentrations

In the nucleophilic addition of an anion to isocyanate, not only electrophilicity of the isocyanate group, but also nucleophilicity of the added anion is of importance. The observed higher rate of cyclotrimerization of alkyl isocyanates compared with aryl isocyanates can be explained by the fact that N-anions of the individual intermediates of cyclotrimerization (*I-III*) possess a higher nucleophilicity in the case of aliphatic derivatives than in the case of aryl derivatives. Hence, the effect of nucleophilicity of these anions is more pronounced than the polar effect of substituents of the isocyanate group. This is why in the cocyclotrimerization of equimolar amounts of phenyl isocyanate with dodecyl isocyanate, much less phenyl isocyanate homotrimer than dodecyl isocyanate homotrimer was formed (Fig. 2). On the contrary, in the cocyclotrimerization of equimolar amounts of ethyl- and butyl isocyanate for which approximately the same reactivity of isocyanate groups and the same nucleophilicity of N-anions of intermediates can be assumed, the individual reaction products were represented in amounts approaching the theoretical ones (Fig. 3).

Effect of the Medium

According to earlier data, the rate of cyclotrimerization of isocyanates is affected by the type of the solvent and increases with the increasing dielectric constant of the solvent³. In acetonitrile the cyclotrimerization of phenyl isocyanate proceeds more quickly than in tetrahydrofuran only up to a conversion of 40% (Fig. 4), while in later stages it is slower. This slow-down (or the apparently higher reaction rate to isocyanate) should however be assigned to the decay of the catalyst by the known addition of alkoxide to nitrile¹⁵. The decay of the catalyst was marked if potassium propylalkoxide was used, where the catalytic activity disappeared already before the isocyanate had been consumed. This fact is obviously the main cause of the low rates of cyclotrimerization of phenyl isocyanate reported in the literature¹². In the case of tert-butylalkoxide one can expect that, because of the bulky tert-butyl group, the competitive addition to nitrile will be suppressed; for this reason, the rate of cyclotrimerization in acetonitrile is less disturbed by the decay of the catalyst than in the catalysis with propoxide.

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