Cyclotrimerization of Isocyanate Groups.
I. Catalyzed Reactions of Phenyl Isocyanate

MILENA ŠPÍRKOVÁ,* MIROSLAV KUBÍN, PAVEL ŠPAČEK, IVAN KRAKOVSKÝ, and KAREL DUŠEK

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic

SYNOPSIS

Cyclotrimerization of phenyl isocyanate in the presence of various catalysts was studied. All reactions were carried out in 1,4-dioxane at 30–50°C. Reaction products were determined by reverse-phase liquid chromatography. 1,3,5-Triphenyl isocyanurate was formed and also traces of 1,3-diphenylurea and 1,3,5-triphenylbiuret were found. The catalytic activity decreased in the following series: quaternary ammonium salt > organic acid salt ≫ tertiary amine. Apparent rate constants of cyclotrimerization were calculated and the overall reaction order is discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The reactivity of isocyanates is high, especially in the presence of catalysts. The most important isocyanate reactions are shown in Scheme 1.

The type of catalyst, the initial molar ratio of functional groups, temperature, and reaction time are the main factors influencing the formation of various types of reaction products. The cyclotrimerization of isocyanate groups is catalyzed by a considerable number of compounds: amines; phosphines; alkoxides; metal oxides; N, P, As, Sb bases; carboxylates; organometallics; metal chelates; hydrides; or organic and Lewis acids and also by combination of catalysts (amines + epoxides, amines + alkylene carbonates, amines + alkylene imides, etc.).[1,2]

The cyclotrimerization of isocyanate groups can be considered as a system of consecutive reactions. In the first step, the catalyst reacts with the isocyanate to form a complex. The last step is the cyclization of another complex (after the addition of the third isocyanate group). The trimerization can be described by a system of equations:

$$I + C \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X_1 \qquad (1)$$

$$X_1 + I \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} X_2 \qquad (2)$$

$$X_2 + I \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} X_3 \qquad (3)$$

$$X_2 + I \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} T + C \qquad (4)$$

$$X_3 + I \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} T + X_1 \qquad (5)$$

$$X_3 \underset{k_6'}{\overset{k_6}{\rightleftharpoons}} T + C \qquad (6)$$

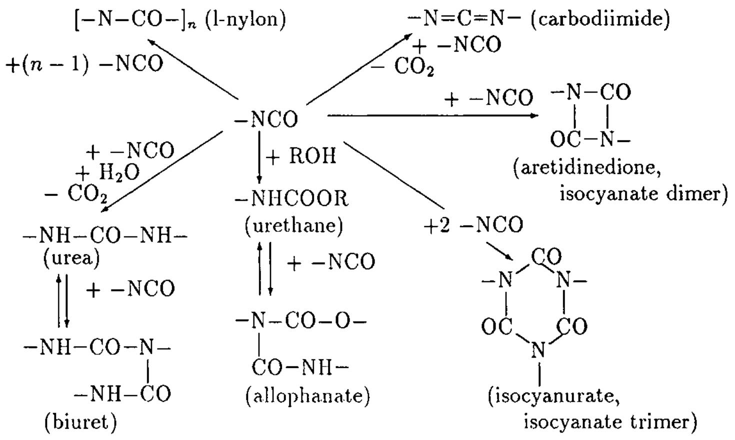
where I is the isocyanate; C, the catalyst (simple or in the form of a complex); X_1, X_2, and X_3, complexes of the isocyanate with a catalyst; and T, the cyclic trimer (isocyanurate, i.e., hexahydro-1,3,5-triazine-2,4,6-trione).

Bechara[3,4] described the decrease in the concentration of isocyanate as a reaction of the first order with respect to isocyanate (assuming that $k_1' = k_2' = k_3' = k_4' = k_5' = k_6' = k_4 = k_5 = 0$). This case was observed when the following catalysts were used: DABCO* TMR (N-hydroxyalkyl quaternary ammonium carboxylates) at low conversions and low catalyst concentrations[3] and DABCO* T (trimethylhydroxyethyl ethylenediamine).[4] The same reaction order was found by Kresta et al.[5] for 2,4,6-tris(dimethylaminomethyl)phenol.

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 52, 895–904 (1994)
CCC 0021-8995/94/070895-10



Scheme 1 Reactions of isocyanate groups.

However, the same authors[5-9] assumed that the overall kinetics of trimerization seems to be like that of the reaction of the second order with respect to the isocyanate[6] when $k_4 = k'_2 = k'_3 = k'_4 = k'_5 = k'_6 = 0$ and $k_1 > k'_1$; $k_2 \gg k_1$; and $k_2 = k_3 = k_5$ and $k_5 \gg k_6$. This order was obtained for the reaction of 2-methyl-4-tetrahydrothiopheniumphenoxide dihydrate and potassium propoxide,[5] sodium ethoxide,[6,7] substituted ammonium carboxylate catalysts,[8] and DABCO* TMR in a wide range of catalyst concentrations and to a high degree of isocyanate conversion.[9]

The total order of reaction can also be higher than two, e.g., when using a combination of catalysts (tertiary amine + alkylene oxide).[10] The kinetics of the cyclotrimerization is sometimes considered to be of the first order with respect to the initial catalyst concentration[4-7]; sometimes, the relation between rate constant and catalyst concentration is more complicated.[3,9,10]

It follows from the results published so far that the kinetics of cyclotrimerization of isocyanate groups is not simple and the type and concentration of the catalyst are the main factors controlling the overall kinetics. Moreover, cross-linking by cyclotrimerization is complicated by other side reactions in which the isocyanate groups take part.

The main aim of our studies was the investigation of network buildup in polyurethane systems by various reaction mechanisms. Previously, we showed that gelation, increase in the gel fraction, and the buildup of the mechanical properties of diol–diisocyanate systems can be well described using the theory of branching processes.[11,12] The network was formed by urethane, allophanate, urea, and biuret linkages. The concentration of these linkages in the system as a function of time and conversion of isocyanate groups served as input information. The information on the relative rates of formation of these linkages was obtained from model experiments with monofunctional components (cf., e.g., Ref. 13).

The objective of this study was an investigation of cyclotrimerization and other side reactions of isocyanate groups in model systems that could serve as input information for the study of the network buildup catalyzed by conventional catalysts. This consists of two parts: (1) cyclotrimerization of phenyl isocyanate in the presence of a catalyst; and (2) cyclotrimerization of phenyl isocyanate in the presence of an alcohol (or urethane) and a catalyst. Attention was centered on the determination of products arising by side reactions and the kinetics of the overall cyclotrimerization reaction.

EXPERIMENTAL

Preparation, Purification, and Characterization of Materials

Phenyl isocyanate (PhI) was distilled under reduced pressure (47°C/1350 Pa); GC purity was over 99.9%. 1,4-Dioxane was dried with Na, and after redistillation, it was recirculated over Na and $LiAlH_4$ under nitrogen; the water content was 0.0035% by weight (coulometrically); GC purity was over 99.4%. Dibutylamine (DBA) was redistilled at reduced pressure (51°C/2000 Pa); its purity was over 99.5% (potentiometrically).

The catalysts (Air Products) were used as received. Their trademarks, codes, and compositions are summarized in Table I.

The preparation of 1,3-diphenylurea (DPU) and 1,3,5-triphenylbiuret (TPB) was described in a pre-

Table I Basic Information About Catalysts Used

Trademark and Type of the Catalyst	Code	Chemical Composition	Reference
DABCO* TMR catalyst (QAS)	TMR	Quaternary ammonium salt in ethylene glycol Quaternary ammonium carboxylate	14 15
DABCO TMR*-4 catalyst (QAS)	TMR4	Proprietary tertiary amine/glycol blend Quaternary ammonium carboxylate	14 15
DABCO* K-15 catalyst (OAS)	K15	Potassium 2-ethylhexanoate in diethylene glycol	14
POLYCAT* 41 catalyst (TA)	P41	Tertiary amine 1,3,5-Tris(3-dimethylaminopropyl)hexahydro-*s*-triazine	14 15
DABCO* catalyst (TA)	DABCO	1,4-Diazabicyclo[2.2.2]octane	14

QAS = quaternary ammonium salt; OAS = organic acid salt; TA = tertiary amine.

vious article.[13] 1,3,5-Triphenyl isocyanurate (TPIC) was obtained by purification[16] of a crude product (Spolana Neratovice, Czech Republic). 1,1-Dibutyl-3-phenylurea (DBPU) was prepared by the reaction of equimolar amounts of PhI and dibutylamine; the reaction product was purified by multiple recrystallization. The purity of all standard compounds was checked by melting points, elemental analysis, and HPLC.

Reaction Conditions and Techniques

Reactions were carried out at 30–50°C and PhI concentration 0.2–0.5 mol/L. The effectiveness of individual catalysts was tested in the system PhI (ca. 0.45 mol/L)-catalyst (ca. 8×10^{-4} g/mL) at 50°C. In the case of K15 (Table I), the content of potassium 2-ethylhexanoate in the catalyst was determined by using ion-exchange separation combined with potentiometric titration.

The composition of the reaction products was determined by HPLC; the unreacted PhI (after reaction with DBA) in the form of DBPU. The conditions for HPLC analysis are described in our previous article.[13] Retention times of individual standard compounds are about 3.5 min (TPIC), 6 min (DPU), 12 min (DBPU), and 13 min (TPB).

Stabilities of reaction products (TPIC, DPU, DBPU, and TPB) in 1,4-dioxane in the presence or absence of a catalyst were also tested.

RESULTS AND DISCUSSION

The activity of various catalysts for cyclotrimerization at 50°C was tested in Series 1–5 (Table II). The kinetics of overall reaction and its dependence on temperature, isocyanate, and catalyst concentrations was studied in Series 3 and 6–15 (Table III). Time dependencies of the concentrations of the reaction products of Series 1–5 are given in Figures 1–5. It follows from Figures 1–4 that isocyanurate, the cyclic trimer of isocyanate, is the main reaction product. Moreover, traces of water led to the formation of urea and biuret. (The cyclic dimer of PhI, 1,3-diphenyl-1,3-diazetidine-2,4-dione,[16] was not found, although it is very well detectable at the retention time of about 9 min. On the other hand,

Table II Apparent First- (k_I) and Second-Order (k_{II}) Rate Constants for Cyclotrimerization of Phenyl Isocyanate (PhI) at 50°C in the Presence of Various Catalysts

Series No.	$(c_{PhI})_0$ (mol/L)	Catalyst (cat)	$c_{cat} \times 10^4$ g/mL	$k_I \times 10^4$ (1/s)	$k_{II} \times 10^3$ (L/[mol s])
1	0.447	TMR	8.37	—	151
2	0.422	TMR4	8.88	—	17.5
3	0.442	K15	8.16	7.4	10.8
4	0.436	P41	8.15	0.2	0.014
5	0.434	DABCO	8.42	Uncalculated	

Table III Apparent First- (k_I) and Second-Order (k_{II}) Rate Constants of Cyclotrimerization of Phenyl Isocyanate (PhI) in the Presence of K15 Catalyst

Series No.	$(c_{PhI})_0$ (mol/L)	$c_{K15} \times 10^3$ (mol/L)	Temperature (°C)	$k_I \times 10^4$ (1/s)	$k_{II} \times 10^3$ (L/[mol s])
3	0.442	2.91	50	7.4	10.8
6	0.444	1.43	30	1.9	1.8
7	0.433	2.96	30	2.7	3.5
8	0.230	0.74	40	1.7	1.1
9	0.239	1.49	40	3.4	4.7
10	0.441	0.30	40	0.8	0.2
11	0.447	0.44	40	1.0	0.7
12	0.424	0.73	40	2.2	2.2
13	0.455	1.47	40	3.7	2.7
14	0.444	2.86	40	5.7	11.7
15	0.457	1.42	50	5.3	5.8

traces of aniline were detected with the retention time of about 1.5 min, but this amount was not sufficient for quantitative determination.)

As urea and biuret are formed only in very small amounts, the influence of their formation on the main (cyclotrimerization) reaction can be neglected in the first approximation. The time dependencies of the isocyanate decrease (Fig. 6) were taken as a measure of the catalytic activity for isocyanate cyclotrimerization. The activity decreased in the following order: TMR > TMR4 > K15 ≫ P41 > DABCO, i.e., quaternary ammonium salt > organic acid salt ≫ tertiary amine.

The reaction products were compared for two systems: with catalysts in the form of pure substances (e.g., DABCO) and with blended catalysts (e.g., TMR, TMR4, K15). The same products were found.

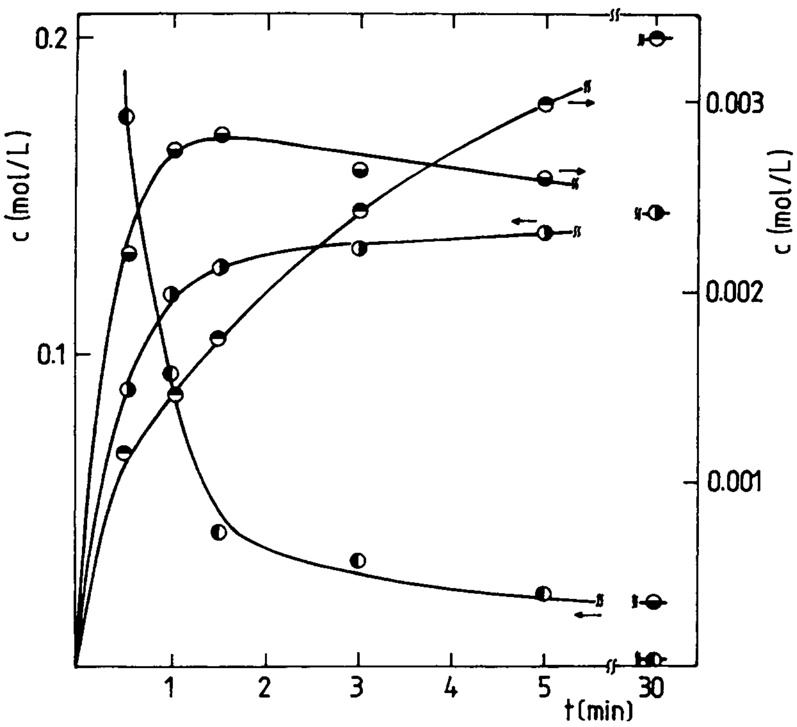


Figure 1 Time dependence of the reaction of PhI in the presence of DABCO* TMR catalyst. $(c_{PhI})_0 = 0.447$ mol/L; $(c_{TMR})_0 = 8.37 \times 10^{-4}$ g/mL (Series 1). Reaction products denoted as (◑) TPIC, (◓) DPU, (◐) DBPU, and (◒) TPB.

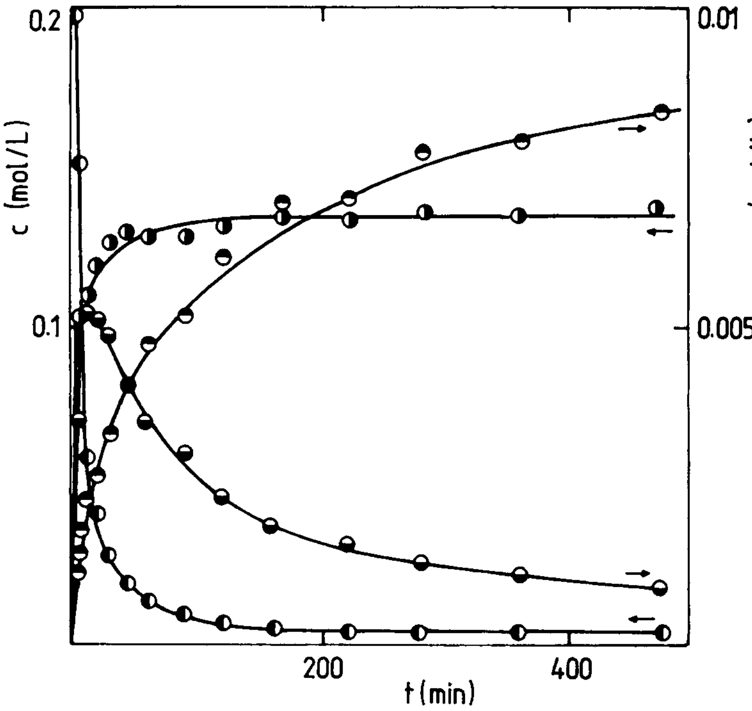


Figure 2 Time dependence of the reaction of PhI in the presence of DABCO* TMR-4 catalyst. $(c_{\text{PhI}})_0 = 0.422$ mol/L; $(c_{\text{TMR4}})_0 = 8.88 \times 10^{-4}$ g/mL (Series 2). Symbols as in Figure 1.

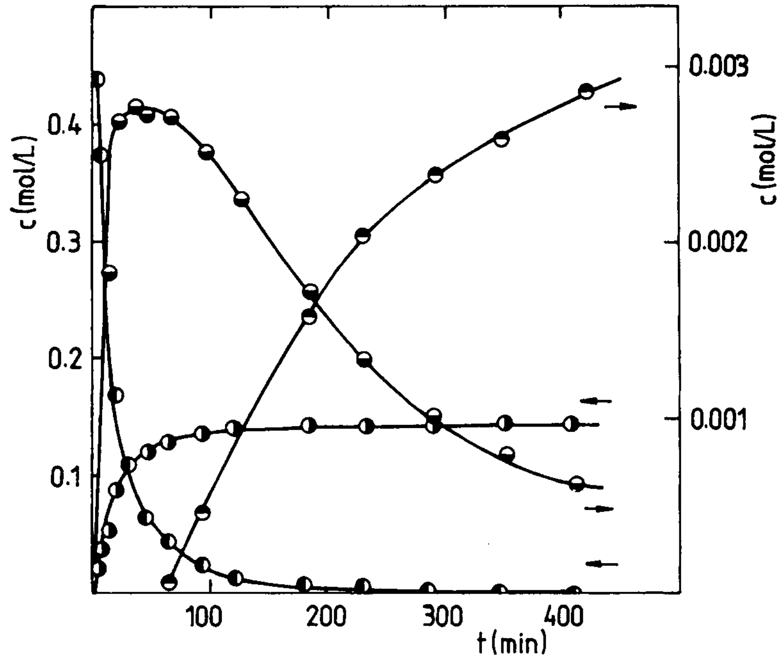


Figure 3 Time dependence of the reaction of PhI in the presence of DABCO* K-15 catalyst. $(c_{\text{PhI}})_0 = 0.442$ mol/L; $(c_{\text{K15}})_0 = 8.16 \times 10^{-4}$ g/mL (Series 3). Symbols as in Figure 1.

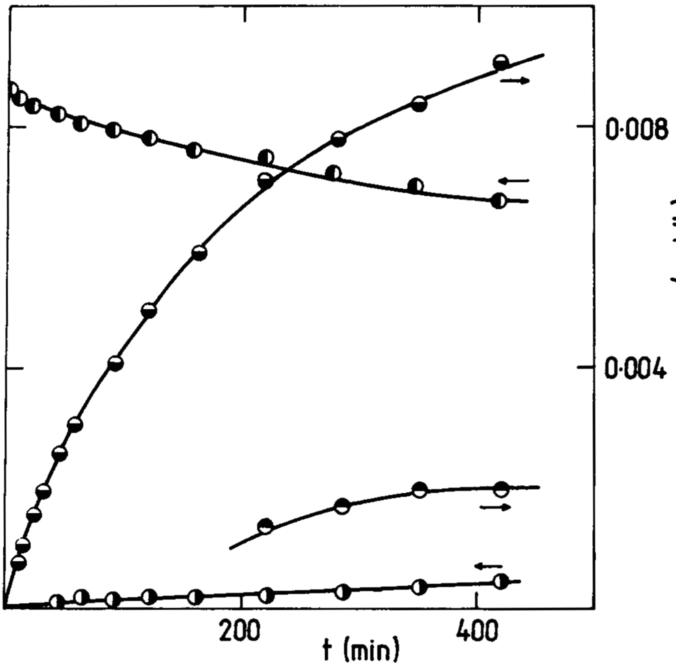


Figure 4 Time dependence of the reaction of PhI in the presence of POLYCAT* 41 catalyst. $(c_{PhI})_0$ = 0.436 mol/L; (c_{P41}) = 8.15 × 10^{-4} g/mL (Series 4). Symbols as in Figure 1.

The effect of the fact that commercial catalysts contain some other substances (glycols) in addition to the catalytically active component was analyzed in more detail with the catalyst K15. It was found that the amount of diethylene glycol in the catalyst has no detectable influence on the consumption of

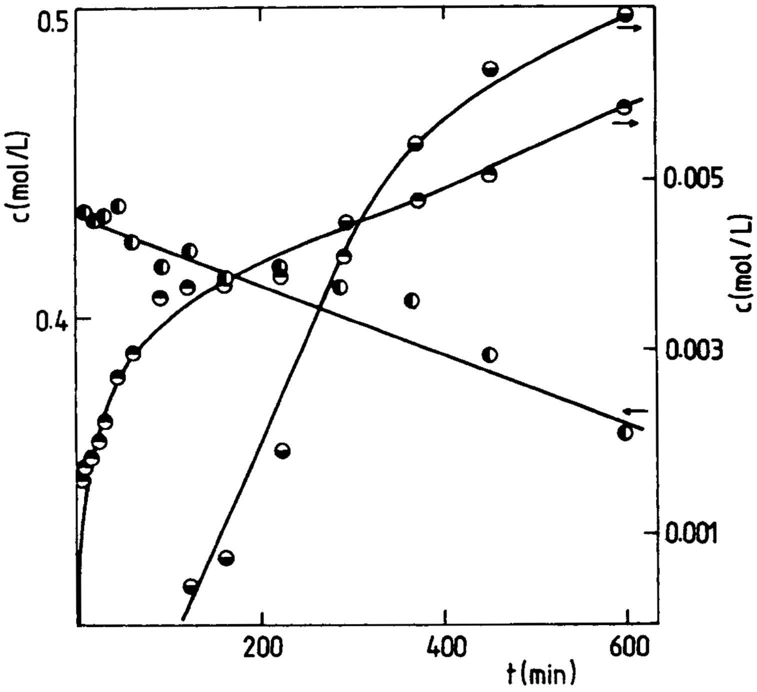


Figure 5 Time dependence of reaction of PhI in the presence of DABCO* catalyst. $(c_{PhI})_0$ = 0.434 mol/L; $(c_{DABCO})_0$ = 8.42 × 10^{-4} g/mL (Series 5). Symbols as in Figure 1.

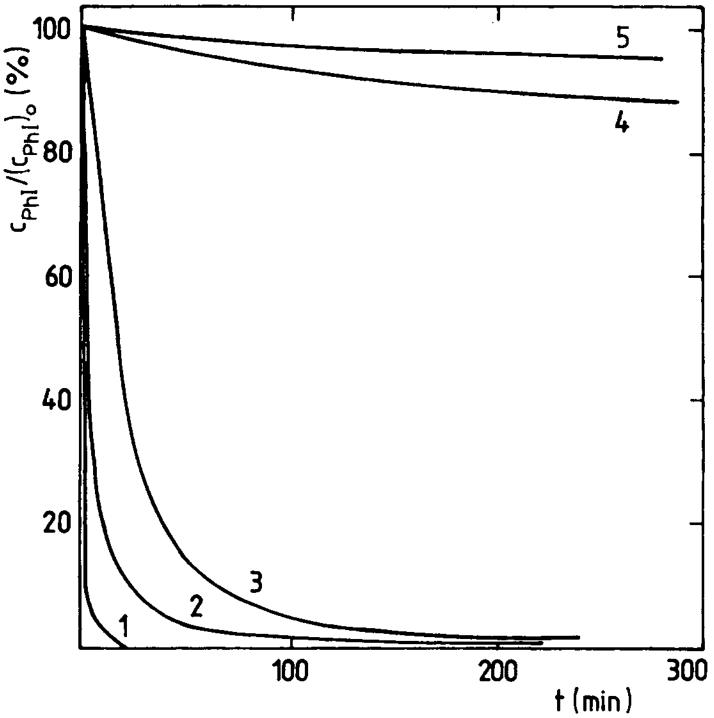


Figure 6 Time dependences of unreacted PhI concentration (in %) in the presence of various catalysts. Series 1 (TMR); 2 (TMR4); 3 (K15); 4 (P41); 5 (DABCO).

PhI at catalyst concentrations used and that potassium 2-ethylhexanoate is the only active component for cyclotrimerization in K15. The temperature and starting concentrations of PhI and the catalyst K15 are given in Table III. (The concentration c_{K15} in mol/L is taken as the concentration of potassium 2-ethylhexanoate in the system.)

As the courses of individual reaction products differ substantially when various catalysts are used, it is useful to compare them (cf. Figs. 1–6). PhI disappeared very quickly for TMR ($t > 30$ min), but this case was not characteristic of the other catalysts (traces of PhI were identified for TMR4 and K15 even after 8 h). Most of isocyanate remained unreacted after 10 h when P41 and DABCO were used.

DPU and TPB formation proceeded immediately and in comparable amounts when TMR and TMR4 were used. In the case of K15, biuret was formed first and then, after its concentration reached a maximum, urea appeared in the reaction system. When P41 was used, biuret was also formed and it was followed by urea. On the other hand, by using DABCO, urea was formed very quickly, whereas biuret was found considerably later. There exists a maximum biuret concentration (the more effective catalyst, the shorter time of reaching the maximum). Urea and biuret formation must be catalyzed reactions—in the uncatalyzed system, urea was formed considerably later and biuret was not found at all.

The formation of TPIC analyzed by HPLC corresponded to the overall mass balance of PhI (within experimental errors) in all cases. In the uncatalyzed system, cyclotrimerization did not occur under reaction conditions used.

The stability of reaction products was tested. All products were stable in 1,4-dioxane in the presence or in absence of the catalyst, with the exception of TPB in the presence of the catalyst. The experimental results obtained for reactions of PhI in the presence of K15 at 30–50°C (i.e., Series 3 and 6–15) were analyzed from the point of view of kinetics.

Time dependencies of the concentration of isocyanate were analyzed using an empirical equation:

$$dc_{PhI}/dt = -k_n(c_{PhI})^n \qquad (7)$$

where n is the order of the reaction, and k_n, the respective rate constant of cyclotrimerization (i.e., $3I \rightarrow T$; traces of urea and biuret were not taken into account). It is assumed that the concentration c_{PhI} is equal to the concentration determined by HPLC, i.e., it includes the unstable complexes of the catalyst containing isocyanate, X_i.

To determine the order of reaction, $\ln[(c_{PhI})_0/$

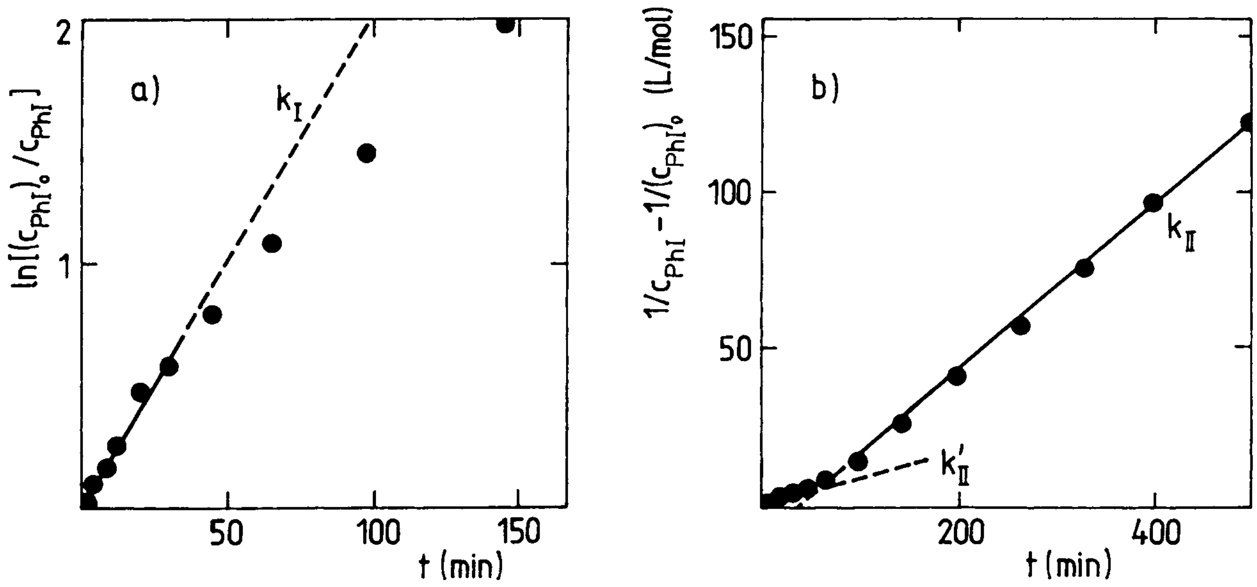


Figure 7 Typical (a) $\ln[(c_{PhI})_0/c_{PhI}]$ and (b) $1/c_{PhI} - 1/(c_{PhI})_0$ vs. time plots taken from (●) experimental results and (——) dependencies fitted by linear regression (Series 9). c_{PhI} and c_{PhI0} are isocyanate concentration in time t and starting concentration, respectively.

c_{PhI}] and $1/c_{PhI} - 1/(c_{PhI})_0$ were plotted vs. time. $(c_{PhI})_0$ is the starting isocyanate concentration and c_{PhI} is the isocyanate concentration at time t. The data of Series 9 are shown as a representative example of these dependencies (Fig. 7).

For shorter times (lower conversions of isocyanate), experimental results give linear dependencies in both plots. The corresponding calculated constants, i.e., k_I for the first-order plot and k'_{II} for the second-order one, are not independent. The following relation [resulting from the Taylor expansion of the solutions of eq. (7) for $n = 1$ and 2] holds:

$$k_I = k'_{II}(c_{PhI})_0 \tag{8}$$

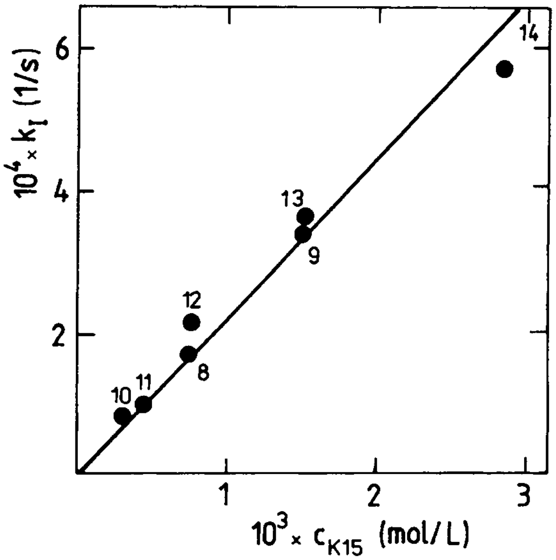


Figure 8 Dependence of first-order rate constant k_I on the concentration of K15 at 40°C.

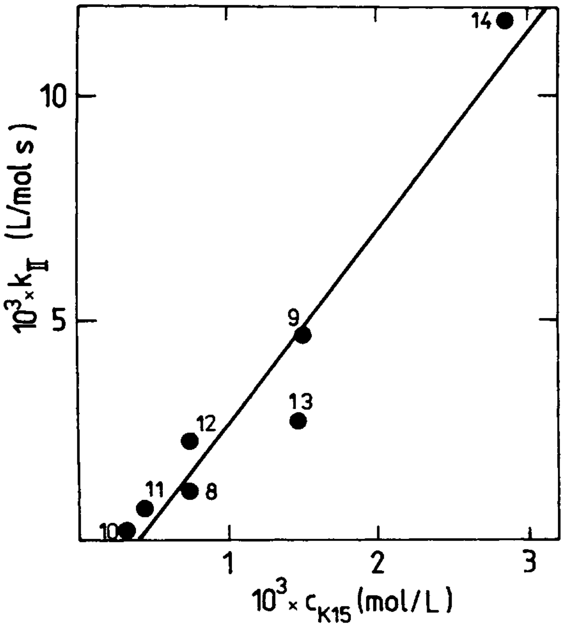


Figure 9 Dependence of second-order rate constant k_{II} on the concentration of K15 at 40°C.

The dependence of k_I on the concentration of catalyst is approximately linear (Fig. 8). Therefore, in the low-conversion region, the reaction can be described by first-order kinetics.

For longer times, the first-order plot departs from linear dependence. The second-order plot is linear but the slope in this region is steeper for majority of runs. The dependence of calculated apparent second-order rate constant (k_{II}) on the concentration of catalyst is linear but a threshold value of the c_{K15} was obtained. Therefore, in the long-time region, the reaction seems to be closer to the second-order kinetics (Fig. 9). The larger scatter of k_{II} values is caused by larger errors in determination of $1/c_{PhI}$ values for low PhI concentrations.

The calculated rate constants of cyclotrimerization corresponding to the first- and the second-order kinetics for Series 3 and 6–15 are given in Table III. It was found that dependencies of reaction rate on temperature and isocyanate (catalyst) concentration are weak.

The apparent change of the reaction order could be explained by a complex reaction mechanism. It includes concentration-dependent steps (additions) and steps independent of the concentration of isocyanate (decomposition of intermediates and ring formation). The reaction order is determined by the steps dominating in the given concentration region. A more detailed analysis will be published later.[17]

The activation energies of the reaction at 40°C were determined from the Arrhenius plot of the temperature dependence of rate constants. For the first- and second-order rate constants, the activation energies are approximately the same: about 42–50 kJ/mol (i.e., 10–12 kcal/mol). It is a little more than the activation energy for the uncatalyzed reaction of PhI with 1-butanol in dioxane (9.3 kcal/mol).[18]

Time dependencies of cyclotrimerization of PhI in the presence of other (blended) catalysts (Series 1, 2, and 4) were also studied kinetically; still, the results have only an orientational value, because the commercial catalysts used are not pure substances. As it was mentioned above, in the case of K15, the kinetics can be described as first order for shorter times (i.e., lower isocyanate conversions) and second-order for longer times. Systems with the P41 exhibit the same features. However, the most powerful catalysts (TMR and TMR4) exhibit second-order kinetics. The apparent rate constants of PhI cyclotrimerization vary in the ratio $k_{TMR} : k_{TMR4} : k_{K15} : k_{P41} = 10800 : 1250 : 770 : 1$ (second-order kinetics) and $k_{K15} : k_{P41} = 37 : 1$ (first-order kinetics) (cf. Table II).

CONCLUSIONS

The activity of catalysts for cyclotrimerization of isocyanate groups decreases in the following series: quaternary ammonium salt (DABCO* TMR, DABCO* TMR-4), organic acid salt (DABCO* K-15), tertiary amine (POLYCAT*41, DABCO*).

Traces of water led to the formation of 1,3-diphenylurea (DPU) and 1,3,5-triphenylbiuret (TPB); biuret is formed sooner and in higher amounts than is urea (valid for all tested catalysts with the exception of DABCO). There exists a maximum of biuret concentration (the more effective catalyst, the shorter time of reaching the maximum).

The cyclic dimer or higher oligomers of phenyl isocyanate (PhI) were not detected. The kinetics of cyclotrimerization of phenyl isocyanate seems to be first order at lower isocyanate conversions and of the second order at higher conversions for the less active catalysts (DABCO* K-15 and POLYCAT* P41). In the case of the most active catalysts (DABCO* TMR and DABCO* TMR-4), the overall kinetics can be considered to be of the second order.

Activation energies of cyclotrimerization of PhI at 40°C in the presence of DABCO* K-15 are about 40–50 kJ/mol for both the first- and second-order rate constants.

REFERENCES

1. T. Nawata, J. E. Kresta, and K. C. Frisch, *J. Cell. Plast.*, **11**, 267 (1975).
2. A. K. Zhitinkina, N. A. Shibanova, and O. G. Tarakanov, *Usp. Khim.*, **54**, 1866 (1985).
3. I. S. Bechara, *J. Cell. Plast.*, **15**, 102 (1979).
4. I. S. Bechara and F. P. Carroll, *J. Cell. Plast.*, **16**, 89 (1980).
5. J. E. Kresta, C. S. Schen, and K. C. Frisch, *Makromol. Chem.*, **178**, 2495 (1977).
6. J. E. Kresta and K. H. Hsieh, *Makromol. Chem.*, **179**, 2779 (1978).
7. J. E. Kresta and K. H. Hsieh, *Makromol. Chem.*, **180**, 793 (1979).
8. J. E. Kresta, I. S. Lin, K. H. Hsieh, and K. C. Frisch, *Org. Coat. Plast. Chem.*, **40**, 910 (1979).
9. I. S. Bechara and R. L. Mascioli, *J. Cell. Plast.*, **15**, 321 (1979).
10. R. P. Tiger, I. G. Babajeva, S. P. Bondarenko, and S. G. Entelis, *Vysokomol. Soedin.*, **A19**, 419 (1977).
11. K. Dušek, M. Špírková, and I. Havlíček, *Macromolecules*, **23**, 1774 (1990).
12. K. Dušek, M. Špírková, and M. Ilavský, *Makromol. Chem. Macromol. Symp.*, **45**, 87 (1991).

13. M. Špírková, M. Kubín, and K. Dušek, *J. Macromol. Sci.-Chem.*, **A24,** 1151 (1987).
14. Air Products, Material Safety Data Sheets.
15. K. C. Frisch and S. W. Wong, *Cell. Polym.*, **8,** 433 (1989).
16. Z. Bukač, F. Puffr, and J. Šebenda, *Chem. Prum.*, **34,** 374 (1984).
17. I. Krakovský and M. Špírková, *Collect. Czech. Chem. Commun.* **58,** 2663 (1993).
18. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology, I.*, Wiley-Interscience, London, 1962, p. 145.

Received June 11, 1993
Accepted August 15, 1993