A DISCUSSION OF THE CYCLOTRIMERIZATION MECHANISM OF ISOCYANATES

Ivan KRAKOVSKÝ and Milena ŠPÍRKOVÁ

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

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

A reaction scheme of cyclotrimerization of phenyl isocyanate in the presence of potassium 2-ethylhexanoate as a catalyst was proposed. From kinetic equations, the reaction orders and concentrations of intermediates were calculated using quasistationary approximation. Concentrations of biuret and urea (products of reaction intermediates with water) can provide information on the reaction mechanism.

Cyclotrimerizations are among the most important isocyanate reactions. They are catalyzed by compounds such as carboxylates, amines, metal oxides, etc.[1]. The kinetics of the reaction using various catalysts has been studied by several authors. The observed decrease in the isocyanate concentration was described as a reaction of the first[2 – 4], second[4 – 8] or third order with respect to isocyanate, depending on the catalyst used. It was also found that the reaction order can change with the conversion of isocyanate[10]. Moreover, the kinetics of the cyclotrimerization of isocyanates is not simple with respect to the initial catalyst concentration. Some investigators reported a first-order dependence[3 – 6], while others found more complex relations[2,8,9]. It follows from the results published so far that the kinetics of the cyclotrimerization of isocyanates is not simple. Also, the type and concentration of the catalyst are important factors controlling the overall kinetics.

Recently, the cyclotrimerization of phenyl isocyanate in 1,4-dioxane at 30 – 50 °C using DABCO K-15 catalyst (essentially potassium 2-ethylhexanoate) was studied[11] by HPLC. In addition to the main product of the reaction, isocyanurate, other compounds were found, such as urea and biuret (products of reaction intermediates with water). The most important conclusions resulting from these experiments are as follows:

– Traces of water lead to the formation of 1,3-diphenylurea and 1,3,5-triphenylbiuret, the biuret being formed sooner and in larger amount than the urea. The urea is predominant at the end of the reaction at higher temperatures and higher catalyst concentrations.

– Cyclic dimer or other oligomers of phenyl isocyanate were not detected.

– Cyclotrimerization of phenyl isocyanate can be described as a first-order reaction for short reaction times (i.e., lower isocyanate conversions) while a second-order kinetics with respect to isocyanate was found for longer times. The first-order rate constant is proportional to the catalyst concentration.

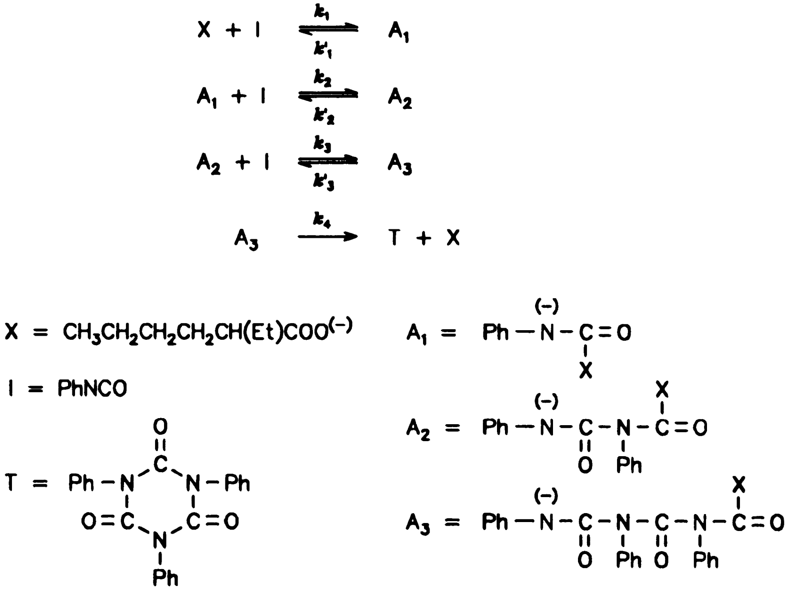
The objective of this paper is to discuss the kinetic results in view of the new information provided by side products. Experimental details can be found elsewhere[11].

THEORETICAL AND CALCULATIONS

Reaction Scheme

All interpretations of the kinetics of cyclotrimerization of isocyanates published so far are based on hypothetical reaction schemes. The authors often derive their conclusions without analyzing in more detail the results following from the reaction scheme under consideration. Even rate constants of different dimensions are sometimes compared.

As mentioned above, potassium 2-ethylhexanoate is the active component of DABCO K-15 catalyst. Potassium cation is known to form complexes with oligoethers[12]. Therefore, nearly complete dissociation of potassium 2-ethylhexanoate and solvation of K^+ can be expected also in 1,4-dioxane and the anion is supposed to be the active species participating in the reaction.



SCHEME 1

The experimental data[11] have not provided any evidence of the presence of dimer, tetramer or higher oligomers of phenyl isocyanate. Hence, the formation of these compounds will not be considered. The proposed course of the reaction is described in Scheme 1.

In the first step reactive intermediate A_1 is formed from carboxylate anion X and isocyanate I. The intermediate A_1 can decompose in the reverse reaction or can be attacked by another molecule of isocyanate in the following step. In the latter case, another intermediate A_2 carrying the active centre is formed and prepared for a next attack. This step reaction can proceed further until it is terminated by the attack of the electrophilic group of the same (growing) molecule, under the formation of cyclic trimer T by ring closure, or by the addition of another reactive molecule (e.g. water) present in the reaction system. In both cases carboxylate anion is recovered and the whole process can start again. As small amounts of water are always present in the system, side products such as amine, urea and biuret are formed by the reaction of intermediates A_1, A_2 and A_3 with water. If they are detectable by analytical methods (e.g. HPLC, ref.[11]) they can be used for the estimation of relative concentrations of intermediates. The kinetic consequences of the mechanism outlined in Scheme 1 will be now discussed.

The reaction course (time dependences of concentrations) is described by the system of differential equations:

$$\frac{d[I]}{dt} = -(k_1[X][I] - k_1'[A_1]) - (k_2[A_1][I] - k_2'[A_2]) - (k_3[A_2][I] - k_3'[A_3])$$

$$\frac{d[X]}{dt} = -(k_1[X][I] - k_1'[A_1]) + k_4[A_3]$$

$$\frac{d[A_1]}{dt} = (k_1[X][I] - k_1'[A_1]) - (k_2[A_1][I] - k_2'[A_2])$$

$$\frac{d[A_2]}{dt} = (k_2[A_1][I] - k_2'[A_2]) - (k_3[A_2][I] - k_3'[A_3])$$

$$\frac{d[A_3]}{dt} = (k_3[A_2][I] - k_3'[A_3]) - k_4[A_3]$$

$$\frac{d[T]}{dt} = k_4[A_3] \quad , \qquad (1)$$

where k_1, k_2, k_3 are the rate constants of addition steps, k_1', k_2', k_3' are the rate constants of decomposition of the intermediates, k_4 is the rate constant of ring closure and [I], [X], [A_1], [A_2], [A_3] and [T] are the concentrations of isocyanate, carboxylate anion, intermediates and cyclic trimer, respectively. Initial concentrations (at $t = 0$) are $[I]_0$, $[X]_0 = c_{cat}$, $[A_1]_0 = [A_2]_0 = [A_3]_0 = [T]_0 = 0$ (complete dissociation of potassium 2-ethylhexanoate is supposed).

Two mass balance conditions are:

$$[I]_0 = [I] + [A_1] + 2[A_2] + 3[A_3] + 3[T]$$

$$c_{cat} = [X] + [A_1] + [A_2] + [A_3] \; . \qquad (2)$$

Thus, the reactions in Scheme 1 are completely described by Eqs (*1*) and (*2*).

Quasi-Stationary Approximation

As the system of non-linear differential equations (*1*) cannot be solved analytically the numerical integration must be used. Consequently, the discussion of the results (calculated reaction courses) becomes less clear. Fortunately, after some time, the concentrations of intermediates A_1, A_2 and A_3 change very slowly in comparison to those of isocyanate. In such case a quasi-stationary approximation can be used:

$$\frac{d[A_1]}{dt} = \frac{d[A_2]}{dt} = \frac{d[A_3]}{dt} = 0 \, ,$$

from which a linear system of equations for the quasi-stationary concentrations of intermediates results. The solution has the form:

$$[A_1] = \frac{k_1 \, c_{cat} \, [I]}{a_0 + a_1 \, [I] + a_2 \, [I]^2 + a_3 \, [I]^3} \, [(k_2' + k_3 \, [I]) \, (k_3' + k_4) - k_3 k_3' \, [I] \,]$$

$$[A_2] = \frac{k_1 \, c_{cat} \, [I]}{a_0 + a_1 \, [I] + a_2 \, [I]^2 + a_3 \, [I]^3} \, k_2 \, (k_3' + k_4) \, [I]$$

$$[A_3] = \frac{k_1 \, c_{cat} \, [I]}{a_0 + a_1 \, [I] + a_2 \, [I]^2 + a_3 \, [I]^3} \, k_2 \, k_3 \, [I]^2 \quad , \qquad (3)$$

where $a_0 = k_1' k_2' (k_3' + k_4)$, $a_1 = k_1 k_2' (k_3' + k_4) + k_1' k_3 k_4$, $a_2 = k_3 k_4 (k_1 + k_2) + k_1 k_2 (k_3' + k_4)$, $a_3 = k_1 k_2 k_3$.

The concentrations of intermediates are proportional to the catalyst concentration, which leads to the following result:

$$[\mathrm{A}_1]:[\mathrm{A}_2]:[\mathrm{A}_3] = \left(\frac{k_4}{k_2[\mathrm{I}]} + \frac{k_2'}{k_2[\mathrm{I}]}\,\frac{k_3'+k_4}{k_3[\mathrm{I}]}\right) : \frac{k_3'+k_4}{k_3[\mathrm{I}]} : 1\,. \tag{4}$$

The rate of the isocyanate disappearance in quasi-stationary state is described by Eq. (*5*):

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = \frac{-3\,k_1\,k_2\,k_3\,k_4\,c_{\mathrm{cat}}\,[\mathrm{I}]^3}{a_0 + a_1\,[\mathrm{I}] + a_2\,[\mathrm{I}]^2 + a_3\,[\mathrm{I}]^3}\,. \tag{5}$$

From Eq. (*5*) it follows that the predicted reaction order can change from 0 to 3 in dependence on predominating term in the denominator. For the $a_i[\mathrm{I}]^i$ terms, Eq. (*6*) holds:

$$a_0 : a_1[\mathrm{I}] : a_2[\mathrm{I}]^2 : a_3[\mathrm{I}]^3 =$$

$$= \left(\frac{k_1'}{k_1[\mathrm{I}]}\,\frac{k_2'}{k_2[\mathrm{I}]}\,\frac{k_3'+k_4}{k_3[\mathrm{I}]}\right) : \left(\frac{k_2'}{k_2[\mathrm{I}]}\,\frac{k_3'+k_4}{k_3[\mathrm{I}]} + \frac{k_1'}{k_1[\mathrm{I}]}\,\frac{k_4}{k_2[\mathrm{I}]}\right) : \left(\frac{k_4}{k_1[\mathrm{I}]} + \frac{k_4}{k_2[\mathrm{I}]} + \frac{k_3'+k_4}{k_3[\mathrm{I}]}\right) : 1\,. \tag{6}$$

The fractions in Eq. (*6*) describe relative importance of forward and backward (or cyclization) reactions.

RESULTS AND DISCUSSION

A general analysis, i.e., which combinations of rate constants lead to a specific reaction order, is too complicated. The situation may become much simpler if any information about intermediates is available. A study of the side products arising by the reaction of intermediates with water can provide this information.

The formation of the side products (amine, urea and biuret) is sketched in Scheme 2. It seems to be reasonable to postulate an equal reactivity of intermediates A_1, A_2 and A_3 with water. Then, Eq. (*4*) describes relative rates of the formation of amine, urea and biuret at the beginning of the reaction*. The water content must be small enough (in

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* The term "the beginning of the reaction" means the time sufficiently short in comparison with the overall reaction time but long enough to attain the quasi-stationary state. Amine, urea and biuret can naturally react further and then the information about intermediates is lost.

comparison to the isocyanate concentration) in order not to influence significantly the main cyclomerization reaction.

$$A_1 + H_2O \longrightarrow PhNH_2 + CO_2 + X$$
$$A_2 + H_2O \longrightarrow PhNHCONHPh + CO_2 + X$$
$$A_3 + H_2O \longrightarrow PhNHCONPhCONHPh + CO_2 + X$$

SCHEME 2

The assumption of equal reactivity of intermediates in the reactions with isocyanate ($k_2 = k_3$) and their equal proneness to decomposition ($k_1' = k_2' = k_3'$) seems to be reasonable, too. Experimental results[11] have shown that at the beginning of the reaction biuret was formed soon and in a much higher concentration than urea and amine. These facts result in the following conditions (see Eq. (*4*)):

$$\frac{k_2'}{k_2[\mathrm{I}]_0} \leq 1 , \qquad \frac{k_3' + k_4}{k_3[\mathrm{I}]_0} << 1 .$$

To obtain a first-order kinetics the $a_2[\mathrm{I}]^2$ term in denominator of Eq. (5) must predominate. So, the following condition must be fulfilled in a given range of the isocyanate concentration:

$$\frac{k_4}{k_1[\mathrm{I}]} >> 1 .$$

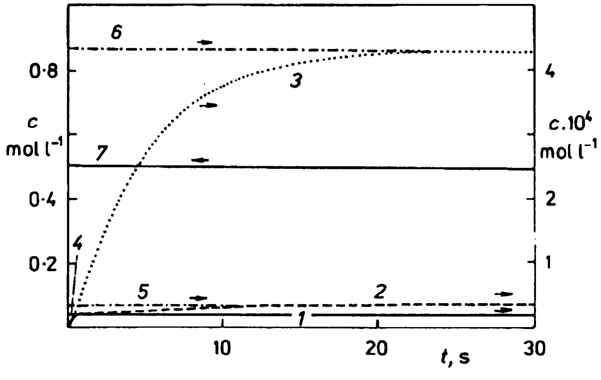

FIG. 1

The time dependences of the concentrations of phenyl isocyanate and reactive intermediates calculated by numerical integration (*1* A_1, *2* A_2, *3* A_3, *4* I) or using quasi-stationary approximation (*5* A_1, *6* A_2, *7* A_3). The values used: $k_1 = 0.04$ l mol^{-1} s^{-1}, $k_2 = k_3 = 10$ l mol s^{-1}, $k_1' = k_2' = k_3' = k_4 = 0.2$ s^{-1}, $[\mathrm{I}]_0 = 0.5$ mol l^{-1}, $c_{\mathrm{cat}} = 5$ mmol l^{-1}

The decrease in isocyanate concentration is then described by the equation

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = -k\,[I]\,,$$

where the first-order rate constant k is given by:

$$k = 3\,k_1\,c_{\mathrm{cat}}\,. \tag{7}$$

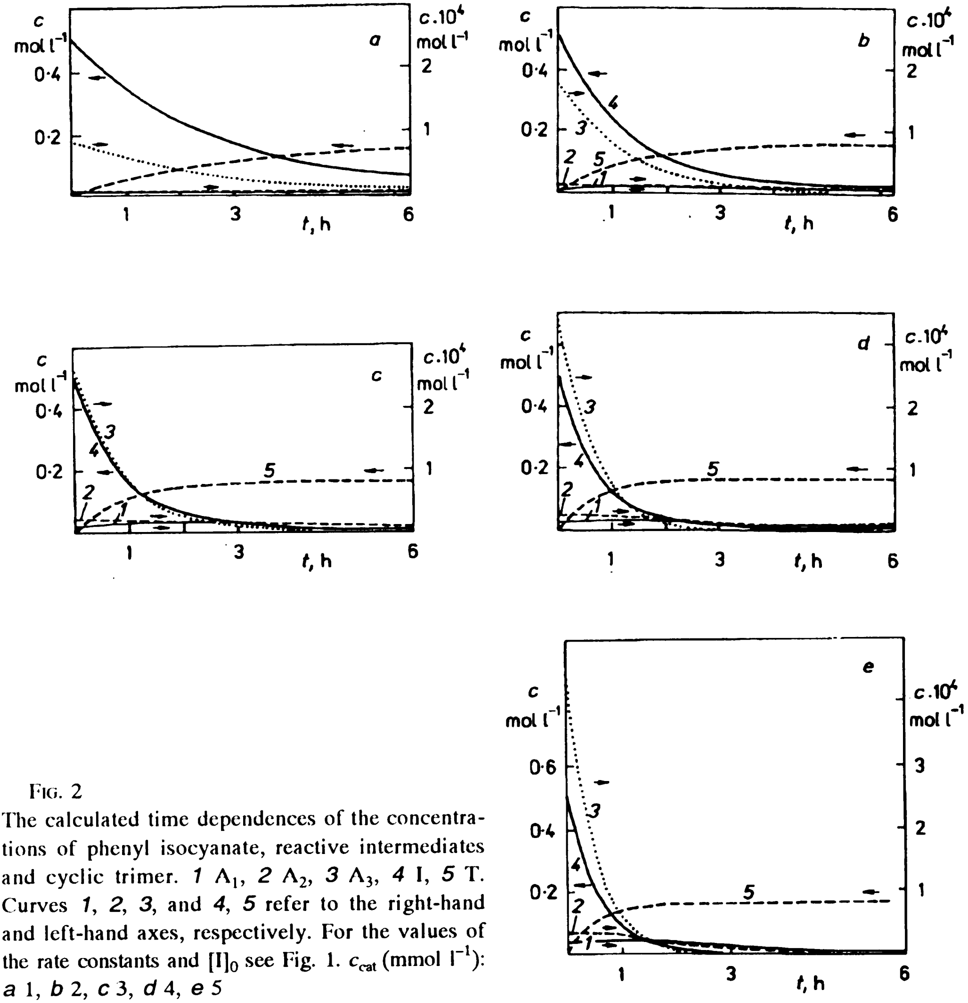

FIG. 2

The calculated time dependences of the concentrations of phenyl isocyanate, reactive intermediates and cyclic trimer. *1* A_1, *2* A_2, *3* A_3, *4* I, *5* T. Curves *1*, *2*, *3*, and *4*, *5* refer to the right-hand and left-hand axes, respectively. For the values of the rate constants and $[\mathrm{I}]_0$ see Fig. 1. c_{cat} (mmol l^{-1}): *a* 1, *b* 2, *c* 3, *d* 4, *e* 5

With decreasing isocyanate concentration the a_0 and $a_1[I]$ terms fall more slowly than $a_2[I]^2$ term and hence this term is not dominant any more. As a consequence, a deviation to higher reaction orders appears. From Eq. (*7*) it follows that the rate-determining step is the first addition step (formation of A_1).

To prove the above-mentioned conclusions the reaction courses of cyclotrimerization of phenyl isocyanate were calculated using the quasi-stationary approximation. The initial isocyanate and catalyst concentrations were chosen to be close to their experimental values ($[I]_0 \approx 0.5$ mol l^{-1}, $c_{cat} \approx 0.001 - 0.005$ mol l^{-1}; cf. ref.[11]).

The value of the constant $k_1 = 0.04$ l mol^{-1} s^{-1} was chosen so that the resulting values of the first-order rate constant k (see Eq. (*7*)) were of the same order as values obtained experimentally[11]. The values of the rest constants were chosen to fulfil the conditions established above ($k_2 = k_3 = 10$ l mol s^{-1}, $k_1' = k_2' = k_3' = k_4 = 0.2$ s^{-1}).

In Fig. 1 the reaction course for very short times is shown. The quasi-stationary state is achieved very quickly (the higher the value of k_4 the faster). With the exception of very short reaction times the results of quasi-stationary approximation and those of the numerical integration of differential equations system (*1*) (by the Runge–Kutta method) are practically identical. The calculated reaction courses, in dependence on the catalyst concentrations, are shown in Figs 2*a* – 2*e*.

The calculated concentration of intermediate A_3 at the beginning of the reaction is approximately ten times higher than that of A_1 or A_2 and it decreases with time and the catalyst concentration. The initial rates of formation of biuret, urea and amine should be proportional to the concentration of catalyst (see Eq. (*4*)).

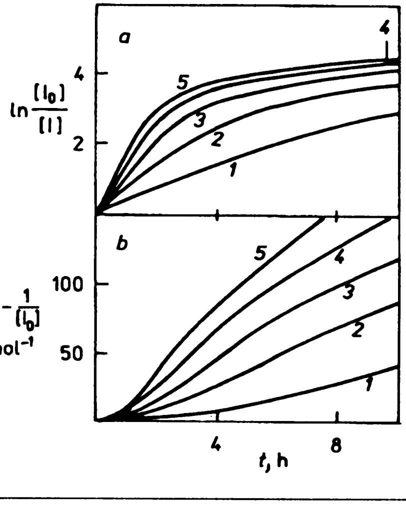

FIG. 3

First- (*a*) and second-order (*b*) plots of the calculated concentration–time dependences from Figs 2*a* – 2*e*. c_{cat} (mmol l^{-1}): *1* 1, *2* 2, *3* 3, *4* 4, *5* 5

The first- and second-order kinetics plots were constructed from the calculated courses of the reaction. For short reaction times, the reaction follows a first-order kinetics (see Fig. 3*a*). The slower the reaction, the longer is the first-order kinetics region. For longer times, a nearly linear dependence in the second-order plot is obtained (Fig. 3*b*). A small deviation from linearity may not have been found out experimentally due to large experimental errors in this region. The rate constant *k* is proportional to the concentration of catalyst (Fig. 4).

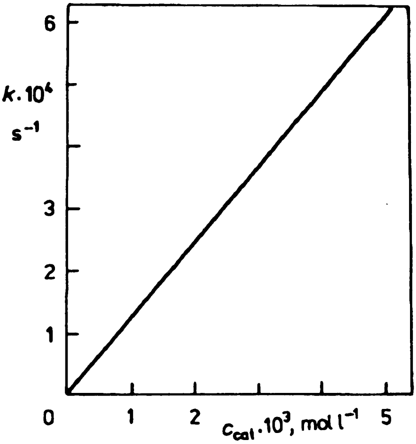

FIG. 4
The calculated dependence of the first-order constant *k* on the initial catalyst concentration c_{cat}

CONCLUSIONS

It has been shown that basic features of the cyclotrimerization of phenyl isocyanate catalyzed by an organic acid salt can be described by a general scheme. From some experimental facts[11] (reaction order and concentrations of the products of the reaction of intermediates with water), relative rates of individual reaction steps were derived. It was found that the formation of the reactive intermediate from phenyl isocyanate is the slowest and hence rate-determining step of the reaction. Thus, the products of the reaction of intermediates of cyclotrimerization with water (urea and biuret) can provide an important information about the reaction mechanism.

The obtained results have general validity and can be used for the description of catalyzed cyclotrimerization of isocyanates or related compounds such as cyanates with similar reaction mechanisms.

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