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Kinetics and Mechanism of the Catalytic Cyclotrimerisation and Polycyclotrimerisation of Isocyanates

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The available literature data concerning the kinetics and mechanism of the cyclotrimerisation and polycyclotrimerisation of isocyanates in the presence of catalysts of various kinds are presented and analysed in this review. Attention has been concentrated on studies published during the last ten years. A number of features characterising the kinetics of the cyclotrimerisation of isocyanates have been deduced from the information about the process presented here. The mechanism of the reaction in the presence of basic catalysts is examined.
The bibliography includes 263 references.

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I. INTRODUCTION

Among the numerous reactions of isocyanates, their cyclotrimerisation (CT) and polycyclotrimerisation reactions have found extensive applications at the present time. This can be accounted for by a number of factors, namely the high thermal stability, fire resistance, and resistance to the action of organic solvents of corrosive media of isocyanurate-containing polymeric materials and the large assortment and availability of catalysts of the cyclotrimerisation of isocyanates, which permit the specific synthesis of the polymers under mild conditions.

The CT reaction of isocyanate groups is used in polymerisation processes in the preparation of coatings, films, varnishes, elastomers, adhesives, and various resins.[1-9] However, the greatest number of advances in this field concern the preparation of polyisocyanurate-containing foam plastics,[10-50] which have been finding increasing applications as thermostable, fire resistant, thermally insulating, electrically insulating, sound proofing, and constructional materials in applied fields such as building, refrigeration technology, instrument making, transport, shipbuilding aeroindustry, space technology, etc.[29,30,51-53]

Despite the fact that the cyclotrimerisation of isocyanates was achieved more than a century ago,[54-56] their study and practical utilisation were not resumed until the end of the 1960's and the beginning of the 1970's. Numerous communications devoted both to the study of the CT and cocyclotrimerisation reactions of isocyanates[57-117] and to the synthesis of various materials based on them[1-53] have now been published. The majority of the studies concerning the CT reactions were undertaken to investigate the efficiency of various kinds of catalysts in this process; many fewer studies have dealt with the reaction kinetics and mechanism. The data published in the above communications are frequently contradictory. At the same time the great interest in this process, associated with the practical possibilities for its utilisation in the formation of new materials, requires the analysis and survey of the data concerning it which have now accumulated. The existing reviews[8,41-43,58,62,63,118-129] do not contain sufficiently complete information about this question.

The cyclotrimerisation of isocyanates in the absence of a catalyst takes place slowly at 373 K. In order to carry it out under milder conditions and to ensure process selectivity, a large assortment of both acid and basic catalysts is used at the present time. The acids are fairly weak catalysts of the above process and are effective only at elevated temperatures.[41,130] The basic catalysts of the cyclotrimerisation of isocyanates known at the present time are tertiary amines,[5,12,15,32,50,59,84,95,100,115,131-138] phosphines and phosphites[5,96-98,139,140] metal alkoxides,[95,102,142,141-144] metal carboxylates[4,5,9,56,59,60,62,82,83,101,102,108,109,115,118,125,145,146] metal oxides,[77,110] quaternary ammonium bases as well as their alkoxides and carboxylates[8,95,147-150] hydrides,[111] cobalt, iron, and tin acetylacetonates,[79,80] organometallic compounds,[61,112,113,145,146,151-154] combined catalysts (amine/epoxide, amine/aldehyde, amine/imine, amine/alkylene carbonate, amine/alcohol, amine/epoxyalkane/proton donor, amine/carboxylic acid, amine/metal carboxylate, amine–organometallic compound, alkali metal carboxylate/oligoether, and amine/metal alkoxide),[6-8,21,25,29,31,34,45-50,74,88,91-95,104,116,118,120,128,150,155-160,161-171] and other catalysts (aminoimides, sulphonium zwitter-ions, alkali metal salts of aminoacids and glycine amide, as well as their combinations with other catalysts).[24,172-179] Among the entire enormous assortment of the catalysts quoted, alkali metal and alkaline earth metal carboxylates, quaternary ammonium carboxylates (and also alkoxides or phenoxides), certain tertiary amines, namely mono- di- and tri-substituted dialkylaminoalkylphenols and *NN'N''*-tri(dialkylaminoalkylene)-*sym*-hexahydrotriazines, as well as certain combined catalysts and catalytic systems are at present of greatest practical importance.[8,10-40,45,46,128,148-150,161-168,180-182]

II. CATALYSIS BY TERTIARY AMINES AND CATALYTIC SYSTEMS BASED ON THEM

The relative catalytic activities of various tertiary amines in the CT reaction of isocyanates have been estimated.[50,95,136] A number of investigators have noted in this connection that, in the presence of aliphatic or alicyclic tertiary amines, the formation of cyclic trimers from isocyanate is observed only

at elevated temperatures.[84,137] Even in the presence of an amine active in the urethane-formation process, such as triethylenediamine (TEDA), the formation of only the phenyl isocyanate (PIC) dimer has been observed.[94] In the presence of an alcohol or a urethane and an amine, an increase of the yield of the trimer has been noted, which led Kogan to propose a mechanism for the cyclotrimerisation of an isocyanate in a system of this kind via the formation of a dimer and allophanate:[84]

$$PhNCO + C_2H_5OH \begin{cases} \xrightarrow{\sim 293\ K} PhNHCOOC_2H_5; \\ \xrightarrow{398\ K} PhNHCON(Ph)COOC_2H_5 + (PhNCO)_2; \\ \xrightarrow[398\ K]{amine} (PhNCO)_3 + PhNHCOOC_2H_5. \end{cases}$$

Subsequent studies have established, however, that the formation reaction of the isocyanate dimer is independent of the CT process[62,79] and that the formation-dissociation reaction of the allophanate is coupled with the CT process.[50]

The most active tertiary amines in relation to the CT reaction of isocyanates proved to be mono-, di-, and tri-(dialkylaminoalkyl)phenols as well as symmetrical tri(dialkylaminoalkyl)hexahydrotriazines, which have found fairly extensive applications in real processes designed to synthesise polyisocyanurate-containing materials.[31-40] Early investigations[92,94,95] already established, however, that compounds such as olefin oxides, aldehydes, alkyleneimines, and 2-methylimidazole are effective cocatalysts of the CT reaction of isocyanates in the presence of tertiary amines. It has been shown[80] that ethylene carbonate and β-propiolactone can function as cocatalysts in analogous systems and alkylene sulphides have also been used for this purpose in other investigations.[72,73] Ketones (isobutyl methyl ketone and acetone), ethers (dioxan, tetrahydrofuran, and the dimethyl ether of diethylene glycol), esters (ethyl acetate), as well as acrylonitrile do not activate appreciably the CT reaction of isocyanates in the presence of tertiary amines,[94] although subsequently the acceleration of the CT reaction of 2,4-tolylene diisocyanate (2,4-TDI) in the presence of a number of ethers, including epoxides, was observed.[134,136] However one should note that in this case ethers behaved more like a second solvent (they were introduced in a large excess relative to 2,4-TDI), influencing the properties of the medium and the specific solvation of the reactants. The data in Table 1 as well as the efficiencies of various types of catalysts in the CT reaction of isocyanates, quoted by Behrendt and Joel,[50] show that, in the presence of an epoxide, the catalytic activities of all the amines investigated increase. The basicity of the amine is not then the only decisive factor; the process is also influenced by the structure of the substituents at the nitrogen atom.[136]

The relative efficiences of all the cocatalysts in the CT reaction of phenyl isocyanate in the presence of triethylenediamine have been estimated[94] and it has been established that low-molecular-weight olefin oxides and aldehydes are much more effective cocatalysts than their higher homogogues. The cocatalytic activity series of olefin oxides has been established: epoxyethane > epoxypropane > epoxybutane > epichlorohydrin > styrene oxide > 1,2-epoxyhexane > 1,2-epoxyoctane. It has also been demonstrated that *N*-methylethyleneimine is itself a catalyst of the CT reaction of isocyanates, but in combination with TEDA its activity increases. This also happens when it is combined with an epoxyalkane.[94] Having estimated the dependence of the rate of the CT reaction of 2,4-TDI on the catalyst, cocatalyst, and monomer concentrations, Beitchman[92] showed that, with increase of the concentration of each ingredient of the catalytic mixture, the rate of reaction increases too and in all cases the reaction obeys a formal first order kinetic equation. By analogy with the hypothetical structures of the zwitterions formed in the CT reactions of isocyanates in the presence of tertiary amines, proposed by Jones and Savill,[88] i.e.

$R_3\overset{\oplus}{N}-CH_2-\underset{R'}{CH}-O^{\ominus}$ for the amine/epoxyalkane combination,

$R_3\overset{\oplus}{N}-CH_2-CH_2-COO^{\ominus}$ for amine/propiolactone,

he suggested, in discussing the possible mechanism of the observed cocatalytic effect of various compounds in the above reactions, that the catalytic structures

$R_3\overset{\oplus}{N}CH_2CH_2-\overset{\ominus}{N}(R')$; $R_3N\cdots\overset{R'}{CH}\cdots O$

are active for the amine/imine and amine/aldehyde combinations. Bearing in mind the presence of an induction period in the CT reaction of an isocyanate in the presence of amine/cocatalyst systems and the absence of autocatalysis by the reaction product (the isocyanate dimer and trimer), Beitchman also suggested that the observed autocatalysis is associated with the formation of an intermediate transition compound at a constant concentration and that it may comprise a catalyst–isocyanate complex with one or two isocyanate molecules, in conformity with the following mechanism:

$$C + I \rightleftarrows CI,$$
$$CI + I \rightleftarrows CI_2,$$
$$CI_2 + I \rightleftarrows C + T,$$

where C = TEDA/cocatalyst, I = isocyanate, and T = trimer.

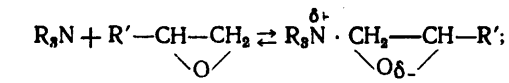
Table 1. The relative activities of tertiary amines in the cyclotrimerisation of isocyanates.[95,136]

In chlorobenzene (4 *N* PIC solution Ref.95)		2,4-TDI (0.35 mole), in bulk, in the presence of epoxypropane (0.03 mole) (Ref.136)			
catalyst	relative rate of CT	catalyst	amount of amine, mole	τ up to T_{max}, min	pK_a of amine
2,4,6-Tri(dimethylaminomethylene)phenol (I)	1.0	triethylenediamine	0.0022	6.0	8 6
(I) + diglycidyl ether of bisphenol (A) (1 : 1)	1.2	*NNN'N'*-tetramethylbutylenediamine	0.0035	30.8	10.6
NN'N''-Tri(dimethylaminopropylene)-*sym*-hexahydrotriazine (II)	2.4	pyridine	0.0025	75.0	5.29
(II) + diglycidyl ether of bisphenol (A)	7.7	*N*-methylmorpholine	0.0023	**	7.41
Triethylamine + epoxypropane	*	2-methylimidazole	0.012	**	—
2-Hydroxypyridine	*	—	—	—	—

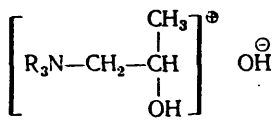
*The reaction was not observed for 30 min.
**The reaction was not observed for 120 min.

Subsequently several studies of the kinetics of the CT reactions of isocyanates in the presence of an amine/epoxide system, which were also designed to elucidate the role of the cocatalysts and the possible process mechanism, were carried out.[6-8,74,120,136,155-158,163,164,168,169,183] Various hypotheses

were put forward concerning the mechanism of the catalytic action of epoxides in this system. Together with the structure of the zwitter-ion proposed previously[94] and discussed in a later investigation,[145,184] the following features were considered: the complex of the epoxide with the amine formed as a result of the partial redistribution of charges without the opening of the epoxide ring:[74]

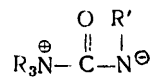


the complex of the epoxide with the isocyanate;[135,136] the product of the interaction of the tertiary amine, the epoxide, and water (traces of which are as a rule present in the catalytic systems):[6,8,94]



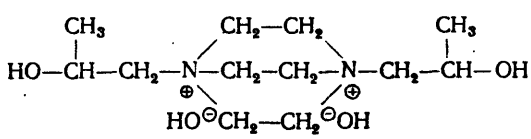
(III)

the complex of 3C* with the isocyanate trimer, where C* is a compound with an active centre initiating the CT reaction of the isocyanate, which can consist either of a zwitter-ion or a product of type (III).[120,155–158] Unfortunately, none of the proposed structures has been demonstrated experimentally. However, it has been confirmed quantitatively that, in the presence of an amine/epoxide system, the rate of cyclotrimerisation of isocyanates varies in proportion to the change in the concentrations of both ingredients,[74] although it has been shown[136] that the proportionality between the rate of the CT reactions of isocyanates and the epoxide concentration is not maintained in all solvents. On the basis of this factor and bearing in mind also the negative result of the Auerbach test for the presence of quaternary ammonium compounds and the constant content of the epoxy-groups in the course of the reaction, the authors explain the cocatalytic effect of epoxides (as well as that of several ethers) by the formation of a complex with the isocyanate. The proposed mechanism of the catalysis of the given reaction presupposes the direct interaction of the tertiary amine with the isocyanate to form a zwitter-ion having the following structure:[135,136]



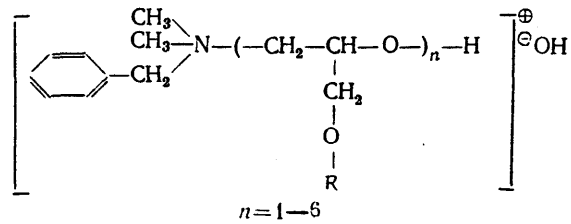
However, one should note that the constant concentration of epoxy-groups in the course of the CT reaction is not apparently an unambiguous indication that there is no possibility of interactions in the system involving the opening of the epoxide ring and the formation of active products, because the concentration of the latter may be extremely low compared with the initial concentration of the epoxide.

The hypothesis of the possible formation of a product of type (III) in the amine/epoxide catalytic system was put forward in an early study by Beitchman,[94] who showed that the product of the interaction of TEDA, epoxypropane, and water, for which he proposed the structure



is an effective catalyst of the cyclotrimerisation of TDI. In the case where TEDA and epoxypropane were thoroughly dried and the CT reaction was carried out in a tube *in vacuo*, the formation of a trimer was not observed over a period greater than 4.5 h. Taking this finding into account, the author presumes that the presence of traces of moisture in the amine/epoxide catalytic system is essential for the formation of an active catalytic complex. However, the CT reaction of the isocyanate in the presence of a product of type (I) retained an induction period,[94] which is evidence that the formation of this product is not a sufficient condition for the effective initiation of the process.

In later studies[6,8] it was also shown that under conditions excluding the access of moisture to the dimethylbenzylamine/glycidyl phenyl ether catalytic system, the CT reaction of 2,4-TDI is not observed. These workers also noted the disappearance of epoxy-groups in the interaction of equimolar amounts of benzyldimethylamine, glycidyl phenyl ether, and water. The appearance of the absorption band due to the hydroxy-group was then noted in the infrared (IR) spectrum. The authors proposed the following structure for the products isolated under these conditions:



$n = 1—6$

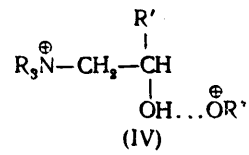
It was shown that their catalytic activity in the CT reaction of 2,4-TDI and poly(diene diisocyanates) is much greater than the catalytic activity of the amine/epoxide binary system. However, here too the reaction had an induction period. The comparatively high catalytic activity of quaternary ammonium hydroxides in the CT reaction of isocyanates had also been noted earlier.[95] In connection with the results described, catalysts of this kind at one time found practical application in the synthesis of polyisocyanurate materials.[148,149,181,185–187]

The dependence of the rate of the CT reaction of isocyanates on the preliminary contact time between the components of the amine/epoxide system has been reported.[188] In the same communication it is also noted that the presence of a third component—a proton donor—is essential for the formation of an active intermediate compound in the above system. Subsequently it was observed[182] that the interaction of tertiary amines (TEDA, etc), epoxyalkanes, and proton donors (PD) such as alcohols, phenols, or any other compounds with a mobile hydrogen atom (urethane, allophanate, urea, and biuret)[150,189] lead to products of the type of alkoxides (phenoxides) of quaternary ammonium bases, which are much more active catalysts of the cyclotrimerisation of isocyanates than the initial binary catalytic systems and are more active than adducts based on tertiary amines, epoxides, and water.

The dependence of the kinetics of the CT reaction of an isocyanate on the duration of the preliminary interaction of the components of the amine/epoxide and amine/epoxide/PD catalytic systems and also on the type of PD was first investigated in several studies.[163,164,168,190] In the investigation of the kinetics of the CT reaction of phenyl isocyanate

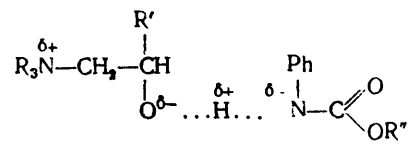
in chlorobenzene in the presence of the 2-methyltriethylenediamine/glycidyl phenyl ether (GPE) catalytic system, it was established that, with increase of the preliminary contact time between the components of the catalytic system and also with increase of its moisture content, the rate of the CT reaction of phenyl isocyanate increases while the induction period shortens.[163,168,190] It has also been observed that, after the preliminary interaction of the amine, the epoxide, and PD such as alcohols and phenol, the activity of the catalytic system investigated in the CT reaction of an isocyanate increases by more than two orders of magnitude, while the induction period is sharply reduced under these conditions. The interaction then terminates after 2–48 h depending on the reaction conditions, the reactant concentrations, and the type of PD, while the active adducts formed are stable during storage in the absence of moisture. It has been observed in addition that the products of the primary and secondary reactions of an isocyanate with alcohol or water (urethane, allophanate, urea, and biuret) can also play the role of active PD in the catalytic system investigated.[163,168] The character of the dependence of the rate of the main reaction and of the reciprocal of the induction period on the treatment time (and hence on the activity) of the amine/epoxide/PD catalytic system is identical in all cases, which indicates the decisive role of the initiation stage in the overall process kinetics. It has also been shown that the duration of the induction period and the rate of reaction depend on the concentration of each of the three components of the catalytic system, i.e. the involvement of all three components is obligatory for the formation of the active products. In the presence of carefully purified components of the amine/epoxide binary mixture the CT reaction of phenyl isocyanate was not observed for several hours.[168] Subsequently the authors studied in detail the role of the PD in the catalysis of the CT reaction of isocyanates by the amine/epoxide system.[150] It has been established by argentimetric titration[150,168] that the concentration of the epoxy-groups decreases with time in the 2-methyl-TEDA/epoxide/PD system; the rate of change of their concentration increases with increase of the amount of PD and when methanol is replaced by phenol. It has been established by dielectrometric and potentiometric titration methods[150,163] that the epoxy-rings are opened during the interaction in the 2-methyl-TEDA/epoxide/PD system and 1:1:1 molecular complexes are formed, their polarity being greater than that of the initial components and their basicity being at the level of that of quaternary ammonium bases. According to IR spectroscopic data,[164,169] the above interaction is accompanied by appreciable changes in the PD structure, particularly by an intense ionisation of the O–H and N–H bonds respectively. Thus it has been shown that the role of the PD in the catalytic system investigated consists in the fact that it is capable of opening the epoxide ring in the presence of a tertiary amine and forms part of the composition of the product—the active catalyst of the CT reaction of isocyanates.

Analysis of studies in the field of the polymerisation of epoxy-compounds in the presence of tertiary amines and alcohols[191–200] which are, in principle, not associated with the cyclotrimerisation of isocyanates but are devoted to the investigation of the interaction in ternary amine/epoxide/alcohol systems, has shown that products of the type of tertiary ammonium alkoxides (phenoxides), which are in fact the effective catalysts of the polymerisation of epoxides, are formed in such systems. Studies in this field[197–199] have shown that the interaction in the amine/epoxide/alcohol system entails the disappearance of epoxy-groups and the appearance of hydroxy-groups with an absorption band at 3280 cm^{-1}, which have been identified[195] as the OH groups in the catalytic complex having the following structure:



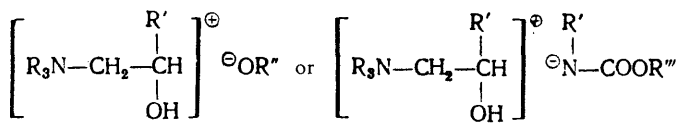
(IV)

The rate of interaction in the amine/epoxide/alcohol system does not depend directly on the basicity of the amine but is to a large extent determined by the steric structure of the latter.[136] It has been suggested[150,168] that analogous reactions take place in the catalytic systems for the cyclotrimerisation of isocyanates based on amines and olefin oxides in the presence of a proton donor. The structure of the products formed in the case of an alocohol as the proton donor is then assumed to be analogous to that of complex (IV) and in the case of a urethane as the proton donor the product is believed to be a complex having the following structure:



(V)

The study of the probability of the formation of donor–acceptor complexes in the amine/epoxide/PD system by the semiempirical quantum-chemical LCAO-MO SF method in terms of the CNDO/BW approximation has shown[201] that compounds of types (IV) and (V) should be formed as transition compounds in the formation of ionic tetraalkylammonium compounds:



(VI) (VII)

It has been established[150,183] that the concentration of adducts of types (VI) and (VII) is proportional to the rate of trimerisation of PIC (the partial order of the reaction with respect to the catalytic adduct is unity). In this case the adduct based on urea proved to be the most active. The adduct based on phenol also showed an enhanced activity. The increase of activity on passing from water and methanol to phenol can be accounted for by the increase of the polarity and basicity of the catalytic adduct formed.[150] The relatively high catalytic activity of the system based on urea can apparently be explained by the fact that water and the products of its interaction with isocyanate exert different influences on the processes investigated, depending on their concentration in the system. In small amounts, they can behave as effective PD cocatalysts, while an increase in their concentration can lead to an appreciable decrease of the rate of cyclotrimerisation of isocyanates.[8,144]

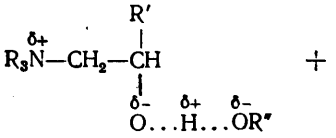
In a weakly polar solvent (for example in chlorobenzene) the form of the kinetic curves for the cyclotrimerisation of PIC in the presence of compounds of the type of quaternary

ammonium alkoxides corresponds to a quasi-unimolecular first-order reaction up to a conversion of ~90% with an induction period whose duration is determined by the concentration and structure of the catalysts. At the end of the induction period, the rate of reaction is close to the maximum value and the concentration order with respect to the monomer is then two.[150]

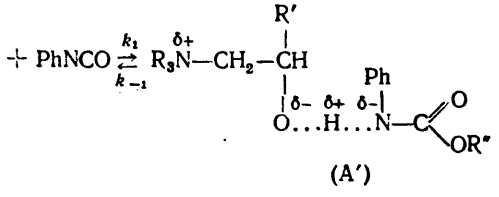
The kinetics of the cyclotrimerisation of isocyanates in the presence of basic catalysts are significantly influenced by acid inhibitors.[150] Presumably, the induction period in the reaction investigated is determined by two factors, namely by the action of the inhibitor and by the slow initiation.

According to the results obtained, the hypothetical process mechanism proposed by Zhitinkina et al.[168] is as follows (Scheme 1):

Scheme 1

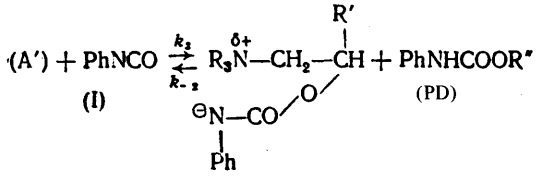


(A)



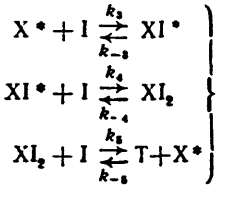
(1)

(A')



(2)

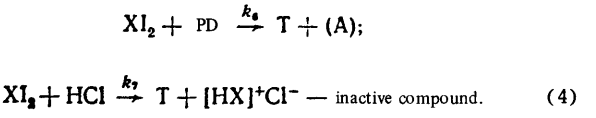
(X*)



(3)

where X* is the initiator.

According to this scheme, the interaction during the induction period between the catalyst and the isocyanate leads to the formation of the initiator X*, which is much more active than the initial catalyst. Stage (2) can then apparently include also more complex interactions between the initial catalytic complex and the isocyanate (or the products of their reactions). On the other hand, when the initial catalyst, obtained from a tertiary amine, an olefin oxide, and a urethane, is used as a proton donor, the process must be regarded as starting with stage (2). The chain termination in stage (3) can then occur as a result of the proton donor present in the system or other impurities (mainly acid ones), for example, HCl:

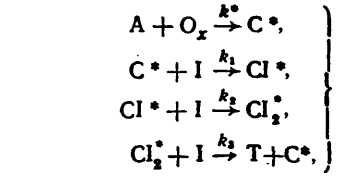


(4)

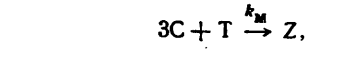
However, Korzyuk et al.[169] were not able to establish a correlation between the rate of cyclotrimerisation of the isocyanate and the concentration of the quaternary ammonium catalyst. In their study of the kinetics of the cyclotrimerisation of PIC in a mixed solvent (chlorobenzene/dimethyl sulphoxide) by IR spectroscopy, they observed that the reaction consists of two stages and begins under conditions without an induction period. The proportionality between the catalyst concentration and the rate of formation of the trimer is then observed only for the first stage of the process. According to the authors, the observed two-stage nature of the reaction is associated with the rearrangement of the catalyst during the reaction. However, presumably in the systems investigated the anomalous kinetics can be due to the possible interaction of the monomer with dimethyl sulphoxide.[145,146,154]

In the series of studies devoted to the kinetics of the cyclotrimerisation of isocyanates in the presence of an amine/epoxide catalytic system (CS), a special place is occupied by a number of investigations.[120,155–158] In their study of the kinetics of the cyclotrimerisation of *m*-chlorophenyl isocyanate (*m*-Cl-PIC) in dioxan in the presence of the epoxypropane/triethylenediamine catalytic system, the authors found that the trimer obtained in the presence of the TEDA/epoxypropane catalytic system accelerates the cyclotrimerisation of the isocyanate (in contrast to the trimer obtained in the presence of TEDA alone). When it is introduced into the reaction mixture simultaneously with the catalytic system, the trimer does not accelerate the reaction, while, after it has been kept together with the catalytic system beforehand, it does accelerate the cyclotrimerisation of *m*-Cl-PIC and shortens the induction period. From these findings and also taking into account the fact that they found the order of the reaction to be 1–3 with respect to the active centre C* and 2.6 with respect to the monomer, the authors proposed a template mechanism of the catalysis of the cyclotrimerisation of isocyanate. According to this mechanism, the trimer formed plays the role of a template on which three active centres are grouped. This structure of the template catalyst is believed to enable the simultaneous coordination of three isocyanate molecules on the catalyst. Thus the process proceeds via the mechanism (Scheme 2)

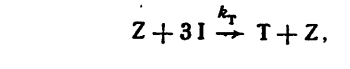
Scheme 2



(1)



(2)

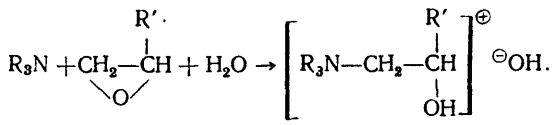


(3)

where A is the amine, O_x the epoxyalkane, and C* the active centre. The first stage is the formation of the trimer (seed) and the second stage involves the formation of the template catalyst Z, capable of rapidly coordinating three monomer molecules with formation of the final product.

The modelling of the proposed kinetic scheme on an analogue computer makes it possible to attain qualitative agreement between the principal calculated and experimental features of the reaction kinetics. The authors believe that the set of data which they obtained for the CT reaction of isocyanates definitely constitutes evidence in support of the view that a reactive product is formed on a catalyst of the template type consisting of the trimer molecule containing three active centres.[120,155-158]

However, one should not fail to note certain contradictions concerning the proposed mechanism. In the first place the accelerating role of the trimer in the cyclotrimerisation of isocyanates has not been confirmed in a number of studies.[94,136,137,147,150] One of the main features identifying the operation of the proposed mechanism is believed[158] to be a reaction order ranging from 1 to 3 with respect to C*. However, in order to calculate the concentration of C* at the instant of the reaction, the authors employ the effective rate constant k_{eff} for the formation of active centres from the amine and the epoxide, obtained by extrapolating the constants k_{eff} characterising the rate of the above reaction in aqueous dioxan to pure dioxan. In their study of the kinetics of the formation of active products from TEDA and epoxypropane (EP) in aqueous dioxan, the authors assume that the role of water in this process consists in altering the dielectric constant of the medium and in the possible solvation of the reactants (TEDA). On the other hand, the studies on the reactions occurring in the polymerisation of epoxides[191-200] and also other investigations[6,163,168,201] permits at the present time the unambiguous claim that the interaction in the amine/epoxide system with opening of the epoxide ring does not take place at all in the absence of at least traces of a PD. Water is an effective PD in systems of this kind and participates directly in the reaction, entering into the composition of the product (like alcohols and other PD):



When account is taken of this finding, one should apparently exercise cuation in using the k_{eff} obtained by means of the extrapolation described above, particularly in relation to a reaction system containing an isocyanate and possible active admixtures (for example, water and urea). The rate of accumulation of active centres in such a system is probably determined not only by the concentrations of the epoxide and the amine but also by the presence of a third coreactant, the participation of which is obligatory for the formation of active centres with the opening of the epoxide ring.[6,150,163,168]

It follows from the experimental data[158] that the preliminary maintenance of the trimer in contact with the TEDA/EP catalytic system leads merely to a decrease of the induction period in the CT reaction of *m*-Cl-PIC but not to its disappearance. At the same time, it appears evident that, on formation of a template catalyst under these conditions, the reaction should begin without an induction period.

On the other hand, it is known that, under certain conditions (temperature, catalyst), the stable isocyanurate ring can be cleaved on treatment with epoxides to form 2-oxazolidinones.[202] One cannot rule out the possibility that the observed effect of the trimer in the given process[120,155-15] is associated with reactions of this kind.

Naturally one of the confirmations of the template mechanism of the CT reaction of isocyanates may be the experimental detection of a complex catalyst of the template type.

Quantum-chemical calculations by the LCAO-MO SCF method in terms of the CNDO/BW approximation have shown that the structural characteristics of the components of the amine/epoxide catalytic system and of the trimer indicate a low probability of the formation of a template catalyst owing to steric hindrance.[201]

III. CATALYSIS BY TIN, ZINC, ANTIMONY, PHOSPHORUS, AND ARSENIC COMPOUNDS AND METAL NAPHTHENATES AND ACETYLACETONATES

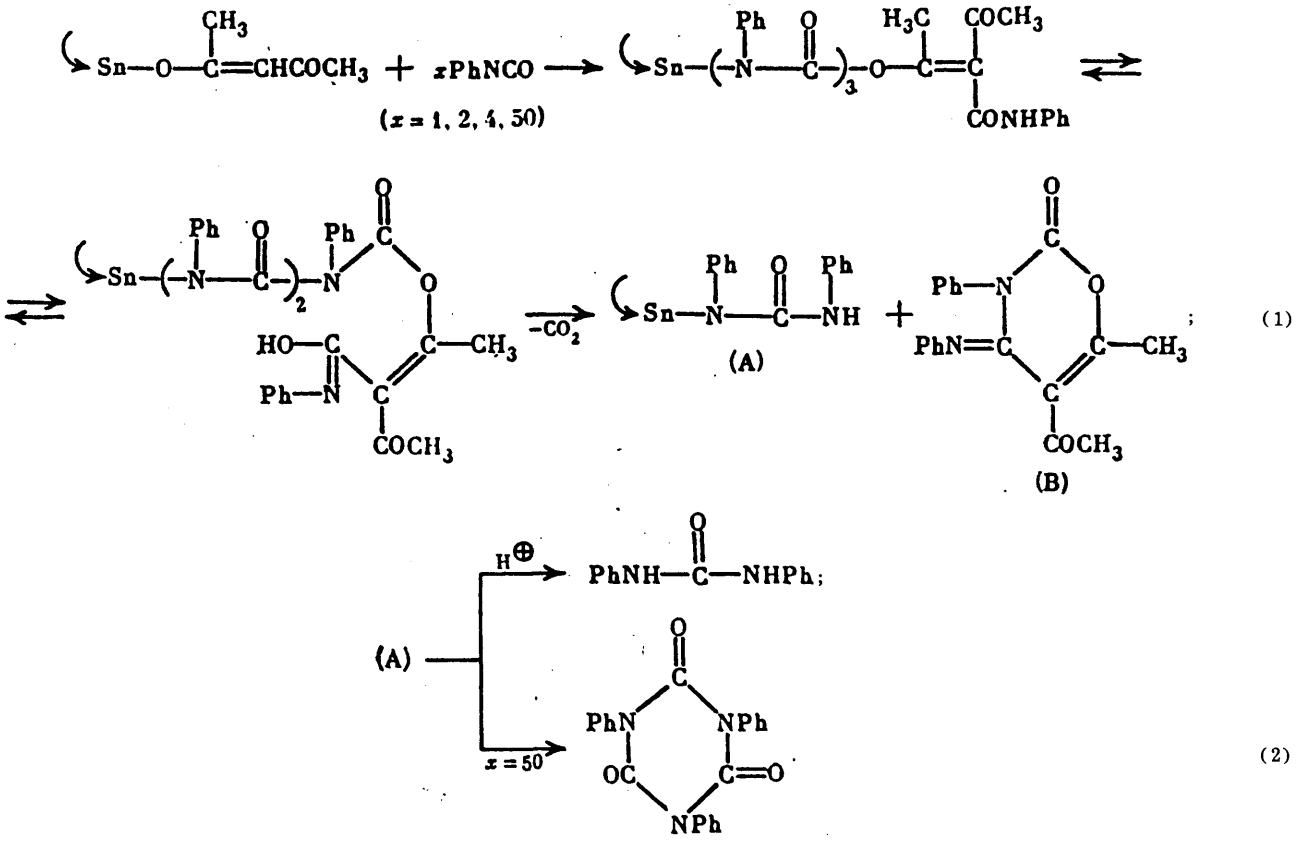
Virtually all the studies on the above types of catalysts[61,77-80,118,145,146,151-155] involved merely an estimate of the catalytic activity of compounds of this kind in relation to the cyclotrimerisation of isocyanates and certain ideas about the mechanism of this reaction under the conditions investigated. A distinctive feature of all the proposed mechanisms of the CT reaction of isocyanates in the presence of such catalysts is catalysis with the aid of "insertion" reactions.[61]

The catalytic activity of antimony and arsenic trialkoxides in the cyclotrimerisation of isocyanates has been reported.[77] In the presence of antimony tri-n-butoxide and arsenic triisobutoxide, the authors obtained high yields of the trimers of PIC, *o*-methoxyphenyl and ethyl isocyanates, hexamethylene diisocyanate, and *m*-nitro- and *m*-chloro-phenyl isocyanates. It was also observed that tri-n-butylantimony diethoxide and triisobutylantimony diacetate as well as the dioxides are active catalysts of the cyclotrimerisation of isocyanates. The more basic oxides of trialkylantimony and trialkylarsenic showed a higher catalytic activity in the cyclotrimerisation of isocyanates. The author suggested that catalysis by the test compound entails the initial formation of a stoichiometric complex of the isocyanate with the catalyst, which subsequently reacts with the excess isocyanate to form the trimer. The suggested complex has been isolated after the reaction of antimony tri-n-butoxide with a slight excess of PIC and has been characterised in terms of its elemental composition and by IR spectroscopy. The product exhibited a catalytic activity in the cyclotrimerisation of the isocyanate.

The cyclotrimerisation of 2,4-TDI in the presence of iron acetylacetonate as the catalyst has been observed.[79,80] The author showed that the dimerisation of the isocyanate is in this case an independent process. It was found that the initial rate of dimerisation decreases from the maximum value almost to zero at the equilibrium concentration of the dimer and the trimerisation process under these conditions does not correspond to equilibrium, the activation energy amounting to 44.2 kJ mol^{-1}.

In their study of the reaction of PIC in the presence of β-dicarbonyl complexes of tin, Wakechima et al.[151] proposed a mechanism of the catalysis involving "insertion" reactions, i.e. with insertion of the isocyanate in the Sn–O bond (Scheme 3). The products formed under these conditions in the first stage can undergo various transformations depending on the $PhNCO/Sn(acac)_2$ ratio:

Scheme 3



(1)

(2)

The occurrence of "insertion" reactions in the cyclotrimerisation of isocyanates in the presence of catalysts containing the Sn–S and Sn–O bonds (oxides and alkoxides) has been indicated in several studies.[61,155,203] In their investigation of the cyclotrimerisation of PIC and ethyl isocyanate in the presence of catalysts having the structure

$Sn(OR)_2$, where $R=C_2H_4N(CH_3)_2$ (A); $C_2H_4OCH_3$ (B); C_2H_5(C); $C(CH_3)=CH-COCH_3$ (D); $C(CH_3)=CHCO_2C_2H_5$ (E); 1,2-$C_6H_4(CO_2C_2H_5)$ (F)

Wakechima and Kijima[152] found that these compounds are active catalysts of the cyclotrimerisation of isocyanates. The highest activity was noted for compound (A) and the lowest for compound (F). Hence it was concluded that the nucleophilic properties of the oxygen atom are important in the catalysis of the cyclotrimerisation of isocyanates by bivalent tin compounds. The above workers also showed that compounds of quadrivalent tin such as $Sn(OC_4H_9)_4$ and $n\text{-}C_4H_9Sn(OS_4H_9)_3$ hardly catalyse the cyclotrimerisation of PIC under the same conditions. In their investigation of the interaction of isocyanates with quadrivalent tin oxides and alkoxides, Tiger et al.[155] found that in their presence the isocyanate is slowly converted into the trimer. Various isocyanates can then give rise to mixed isocyanurates. Hence the authors concluded that the cyclotrimerisation in the presence of R_3SnX proceeds via the consecutive insertion of the isocyanate between Sn(IV) and the counterion (X), affording initially a carbonate and then 1:2 (allophanate) and 1:3 adducts (Scheme 4):

Scheme 4

$$(C_4H_9)_3SnX + RNCO \rightleftarrows \underset{\text{(VIII)}}{(C_4H_9)_3Sn\cdot NRCOX}; \quad (1)$$

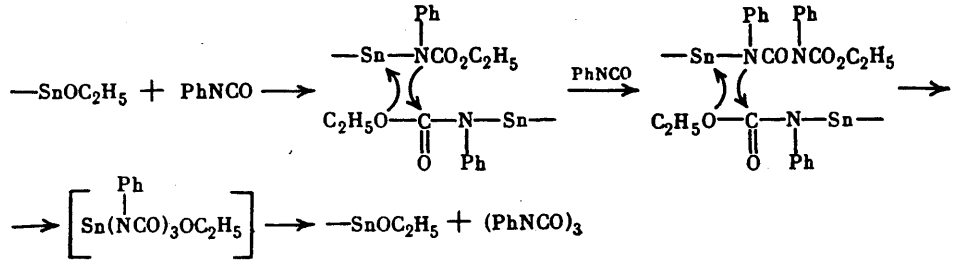
$$\text{(VIII)} + R'NCO \rightleftarrows \underset{\text{(IX)}}{[(C_4H_9)_3Sn\cdot NR'CONRCOX]}; \quad (2)$$

$$\text{(IX)} + R'NCO \rightleftarrows \underset{\text{(X)}}{[(C_4H_9)_3SnNR'CONR'CONRCOX]};$$

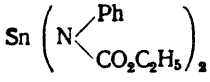
$$\text{(X)} \rightarrow (C_4H_9)_3SnX + T. \quad (3)$$

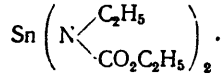
However, instances of the direct formation of a product of type (IX) could not be observed. In all cases the hydrolysis of the products yielded only the carbamate and the trimer, whence it was suggested that the allophanate reacts very rapidly with subsequent conversion into the carbamate.

In contrast to this, the mechanism of the catalysis of the cyclotrimerisation of isocyanates by bivalent tin compounds, involving the four-centre intermolecular interaction



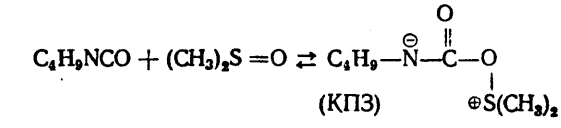
has been proposed[152] on the basis of the change in the yield of the hydrolysis products. The authors believe that the proposed reaction pathway is confirmed by the weakening of the nucleophilic attack by the nitrogen atom in



compared with .

Two groups of catalysts in the cyclotrimerisation of aromatic and aliphatic isocyanates have been investigated:[145,146,154] the first group $[(C_4H_9)_3Sn]_2O$, $Ti(C_4H_9)_4$, and $Zr(OC_4H_9)_4$, while the second includes lead, zirconium, and cobalt naphthenates. It was shown that the catalysts of the first group are effective in the cyclotrimerisation of aromatic isocyanates and are almost ineffective in that of aliphatic isocyanates. The addition of polar solvents [dimethylformamide(DMF) and dimethyl sulphoxide(DMSO)] to the isocyanate in proportions of 1 : 1 leads to a sharp acceleration of the cyclotrimerisation of PIC in the presence of catalysts of the first group, while in the presence of those in the second group the cyclotrimerisation of PIC is accelerated even after the addition of a small amount of DMF or DMSO. In the case of C_4H_9NCO the addition of polar solvents hardly accelerates the cyclotrimerisation in the presence of catalysts of the first group. On the other hand, the addition of small amounts of, for example, DMSO leads to an appreciable acceleration of the cyclotrimerisation of C_4H_9NCO by catalysts of the second group, although the overall process remains slower than in the case of PIC. Under these conditions, there is an optimum in the rate of cyclotrimerisation of C_4H_9NCO (in the presence of catalysts of the second group) as a function of the content of DMSO in the system at the concentration of the latter 5–10 times greater than that of the catalyst.

An explanation of the observed facts follows from the consideration of complex formation in isocyanate–solvent and isocyanate–catalyst systems. It was shown[145,146,154] that, compared with PIC, C_4H_9NCO interacts only weakly with DMSO and that the concentration of the charge–transfer complex (CTC) (which is more active than the initial monomer) formed under these conditions is very low.



(КПЗ)

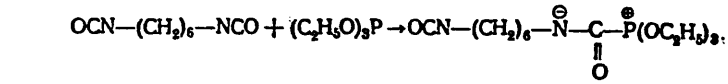
This in fact accounts for the absence of an increase in the rate of cyclotrimerisation of aliphatic isocyanates in the presence of polar solvents.

On the basis of the appreciable increase of the rate of cyclotrimerisation of isocyanates (both aromatic and aliphatic) in the presence of small amounts of DMSO in catalysis by compounds of the second group, the authors suggested that very low concentrations of the charge-transfer complex are effective in complex formation with the metal, which results in the formation of a catalytic complex of the isocyanate with the metal of the catalyst. In their study of complex formation in the isocyanate–cobalt naphthenate system by the spectrophotometric method, they found[146] that both PIC and C_4H_9NCO form a complex with the catalyst having the composition [NCO]/[Co] = 3. They demonstrated at the same time that, in the complex formation reaction with the metal, the NCO group in the aliphatic isocyanate is a much weaker ligand than that of PIC. As a result of this, in the reaction of the aliphatic isocyanate the DMF or DMSO present at high concentrations can compete with the isocyanate in the complex formation reaction with the catalyst metal, causing thereby an increase in the induction period of the CT reaction. On the other hand, in the case of PIC, which forms complexes with the catalysts of the second group much faster and with a much higher equilibrium constant, the observed rate of cyclotrimerisation is much higher under the same conditions.

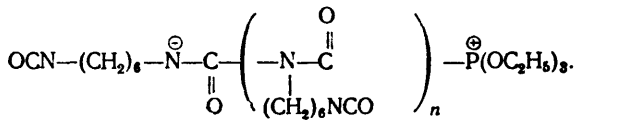
The cyclotrimerisation of organic isocyanates in the presence of organozinc compounds ($RZnNR'_2$ or $RZnOR'$) has been described.[113] Davydov et al.[106] and Cherednikova[118] investigated the cocyclotrimerisation of chlorohexyl isocyanate (CHIC) and PIC in the presence of zinc octanoate in toluene at 353–383 K and showed that CHIC is more reactive than PIC. The kinetic cyclotrimerisation curves were S-shaped: the rate of reaction increased to a maximum at the end of the induction period and then began to decrease slowly (for 30–50% conversion of the monomer). The results were interpreted by the authors from the standpoint of the template mechanism of catalysis, although the accelerating role of the PIC trimer had been demonstrated only after it had been kept in contact with the catalyst at 353 K. The formation of a stable complex of the catalyst with the PIC trimer under the conditions indicated is unlikely.

The catalytic action of certain phosphorus compounds on the cyclotrimerisation of isocyanates has been reported in a number of communications.[97,98,105,140] The active catalysts of this reaction are tertiary phosphines.[105] Trialkyl phosphites (TAP) are also vigorous nucleophiles which catalyse the formation of cyclic isocyanate dimers and trimers.[97,140] According to the authors, the polymerisation of diisocyanates initiated by TAP involves the nucleophilic attack by the phosphorus atom of the phosphite on the carbon atom of the

isocyanate group—the most electrophilic centre of the molecule:



This results in the formation of a dipolar ion; the addition of subsequent isocyanate molecules is to the anion:



The autocyclisation of the macroanion in the trimer stage can be achieved spontaneously with the regeneration of trialkyl phosphite.

IV. CATALYSIS BY ALKALI METAL AND QUATERNARY AMMONIUM CARBOXYLATES

Although alkali metal and quaternary ammonium carboxylates are nowadays used perhaps most extensively in practical systems for the preparation of isocyanurate-containing polymers and various materials based on them,[10,21,25,44-47,204] there have been comparatively few studies on the kinetics of this process and on its mechanism in the presence of catalysts of this kind.[9,62,101,102,125,128,147,161,166-168,205,206] Until recently it was believed that alkali metal carboxylates are weak catalysts of the cyclotrimerisation of isocyanates and are effective only at elevated temperatures.[136] They were therefore used most often in combination with other catalysts of the cyclotrimerisation of isocyanates.[21,25]

The characteristics of the cyclotrimerisation of aromatic isocyanates have been investigated in relation to PIC in solution in DMF in the presence of lithium acetate.[9,62,108,109,125] The conversion of PIC into a trimer took place over a period of ~3 h at 333 K. It was established that the reaction is of second order with respect to the isocyanate and of first order with respect to the catalyst. In the initial stages of the reaction, the authors observed, together with the formation of the trimer, the formation of the PIC dimer (as an independent parallel process), which at the end of the reaction was fully converted into the trimer. It has also been shown that the PIC dimer in solution in DMF at 333 K reacts rapidly to form the trimer when the reaction is catalysed by lithium acetate. The authors suggest that the interaction of the PIC dimer with lithium acetate entails the formation of catalytically active compounds capable of converting the dimer into the monomer and the trimer.[62,125] On the grounds of general considerations, the authors suggest that the active centre in the CT process is in this case the product of the addition of PIC to lithium acetate, i.e. the lithium salt of a substituted urethane.[62]

Tne cocatalytic effect of linear oligoethers in the cyclotrimerisation of isocyanates in the presence of alkali metal acetates (alkoxides, phenoxides) has been observed,[45] and it has been suggested that it be used in the synthesis of isocyanurate-containing foam plastics. Subsequently the same workers carried out a series of studies on the kinetics of the CT reaction of isocyanates in the presence of alkali metal acetates in various oligoethers and also of their low-molecular-rate analogues (glymes) as cocatalysts[44,128,161,162,165,190,206] and of the complex formation reaction in alkali metal acetate/oligoether (or glyme) systems.[44,167,168] They also carried out investigations designed to elucidate the role of oligoethers in the catalysis of the CT reaction of isocyanates by alkali metal acetates.[128,161,165,168]

The cocatalytic effect of compounds containing the ether linkage (diethylene glycol, triethylene glycol, and polyoxypropylenetriol with a molecular weight of ~3000) in the CT reaction of isocyanates (2,4-TDI) in the presence of potassium acetate as the catalyst was characterised quantitatively for the first time by Medved' and co-workers.[161,162] It has been shown that the activity of the AcOK/cocatalyst catalytic systems depends on the concentrations of both the catalyst and the cocatalyst and also on the equivalent ratio [−O−]/[AcOK]. With increase of this ratio, the rate of the CT reaction increases, while the induction period diminishes. Taking into account the data obtained for the heat of reaction of AcOK with the polyoxypropylenetriol (~21 kJ mol^{-1}; AcOK), the authors put forward the hypothesis that the observed cocatalytic effect of linear oligoethers in the process investigated is due to the specific solvation of the potassium ion by the polyether (analogously to the reaction of glymes and cyclic polyethers, namely crown-ethers, in solutions of alkali metal salts),[207-214] as a result of which the catalyst can pass from the state of contact ion pairs to one of solvate-separated ion pairs, whose activity is much higher, for example in relation to the anionic polymerisation of various monomers.[215-226]

In subsequent investigations[44,128,165,166,168,227-229] more detailed studies were made of the influence of various oligoethers on the kinetics of the CT reaction of 2,4-TDI[44,165,166,168] and of the nature and structure of the complexes formed in the AcOM/oligoether systems (where M = alkali metal).[128,227-229] It was established that AcOK in the form of solutions in methanol or ethylene glycol behaves as a very weak catalyst of the cyclotrimerisation of 2,4-DTI under the conditions investigated (298 K, in bulk) (the reaction was not observed in the course of at least 2 h).[168] The addition of even small amounts of polyethers based on epoxyethane (EE) or epoxypropane leads to a sharp increase of the rate of reaction (the process takes place over a period of several minutes). The study of the kinetics of the cyclotrimerisation of 2,4-TDI in the presence of the AcOK/polyether catalytic system established that the dependence of the rate of reaction on the equivalent ratio [−O−]/[AcOK] is represented by curves with saturation [a plateau] for a specific value of [−O−]/[AcOK], which depends on the structure and molecular weight of the polyether. It was established that oligoethers based on EE are much more effective cocatalysts in the process investigated than oligoethers based on EP; the effectiveness of the catalyst is also influenced by the molecular weight and functionality [the number and nature of functional groups (Translator)].[128,166,168] Dimethyl ethers of glycols (glymes) also accelerate the cyclotrimerisation of isocyanate in the presence of AcOK, but their activity is lower than that of their analogues having higher molecular weights—linear oligoethers based on EE (Table 2).[128,168]

According to Gerard et al.[213] and Davydova et al.,[230] the relative capacities of various compounds containing ether linkages for complex formation with alkali metal salts (NaCl, KI, CsCl) decrease in the sequence dibenzo-18-crown-6 > poly(ethylene oxide) (MW ≅ 18 000) > glyme 8 > glyme 7 > glyme 6 > glyme 5. On formation of complexes of the ligands considered with metal cations, appreciable heat changes are observed;[230] the entropies are then in most cases negative and reflect the restriction of the mobility of the ligand molecules. An important feature of the complex formation reaction of polyethers with metal salts is the decrease of the electrostatic interaction between the counterions, as a result

of which the ions are separated.[128] Since the majority of ionic catalysts are present in the polymerisation mixture in the form of ionic associated species and contact ion pairs, coordination to polyethers converts them into solvate-separated ion pairs or free ions. At the same time it is known that the catalytic activity of separated ion pairs in ionic polymerisation is higher by 2–5 orders of magnitude than that of contact ion pairs[215] and is close to the activity of free ions. Instances of the employment of glymes and cyclic polyethers as activators in the polymerisation of styrene,[216] α-methylstyrene,[217] propylene sulphide,[218] olefin oxides,[219] lactones,[220] butadiene,[215] and certain other monomers are known.

The study of the complex formation reaction between AcOK (in solution in methanol) and various linear oligoethers and glymes by calorimetric and conductimetric methods established[128,167,168] that, at a concentration in excess of 0.1 M, AcOK is present in methanol in the state of contact ion pairs and their aggregates. The addition of oligoethers to dilute AcOK solutions (10^{-3}–10^{-4} M) decreases their limiting equivalent conductance, which is a consequence of the increase of the bulk of the potassium ion and the decrease of its mobility as a result of its coordination to the polyether (the Stokes radius increases from 2.9 Å to 8.45 Å). The addition of oligoethers to a concentrated AcOK solution in methanol (0.5 M) entails partial separation of the ions and the disruption of the ionic aggregates, as a result of which the electrical conductivity of the solution increases somewhat. It has also been established[227–229] that linear polyethers based on EE and EP in solutions in methanol form partly dissociated coordination-saturated complexes via the donor–acceptor interaction of the oxygen in the ether linkage of the polyether with the potassium cation. The interaction of AcOK with polyethers is accompanied by a heat change, whose magnitude depends on the characteristics of the polyether: polyoxyethylenediols > polyoxypropylenediols (with the same degree of polymerisation) > polyoxypropylenetriols (with the same equivalent weight). The composition of the complexes depends on the molecular weight of the polyethers, i.e. on its content of electron-donating groups, namely ether linkages. Polyethers with a sufficiently high molecular weight (for example, MW ≥ 1000 for polyoxypropylenediols) can interact with two and more cations.[227–229] The interaction of polyethers with AcOK is characterised by comparatively low equilibrium constants:[229] for oligoethers based on EE, these values are greater by a factor of 2–3 (~250 litres per mole of AcOK) than for oligoethers based on EP (~100 litre $mole^{-1}$) with the same degree of polymerisation, which agrees with the data of other workers on the complex formation reactions of potassium thiocyanate with linear polyethers.[230]

It has been established[227] that the presence of ether linkages is a necessary but not a sufficient condition for the effective complex formation between the potassium ion and electron-donating ligands and for the corresponding cocatalytic effect of the latter in the cyclotrimerisation of isocyanates. Thus polyfurit, dioxan, and dibutyl ether do not solvate K^+ and do not accelerate the cyclotrimerisation of 2,4-TDI in the presence of potassium acetate. Evidently the solvating capacity of ligands of this kind is determined not only by their chemical structure but also by the conformation of their molecules. According to Gluck et al.,[231] the conformation of poly(ethylene oxide) is a helix with a repeat period of 19.3×10^{-10} m; in structured complexes poly(ethylene oxide) consists of a non-planar zig-zag with a repeat period of 11.75×10^{-10} m;[232] the conformation of polyfurit is a planar zig-zag, while dioxan has the chair conformation.[233] Only the first conformation ensures the possibility of the simultaneous involvement of two and more neighbouring electron-donating groups in the interaction with the metal cation by virtue of the high flexibility of the chain in poly(ethylene oxide) and poly(propylene oxide) and their polydentate structure.

The $\Delta H - \Delta S$ relation for the complex formation reactions of AcOK with polyoxyethylene and polyoxypropylene oligoethers is linear and is described by the equation[229]

$$-\Delta H = -0.36\,\Delta S + 1.85,$$

This relation is a common feature of donor–acceptor interactions.[234] The relation $-\Delta H = f\{[-O-]/[AcOK]\}$ has the form of curves with saturation for all the AcOK/oligoether systems investigated,[227,228] analogously to the situation demonstrated for the dependence of the rate of cyclotrimerisation on the same ratio [–O–]/[AcOK],[44,128,168,232] which indicates a direct relation between the complex formation reaction in the catalytic systems investigated and the catalytic activity of the latter in the cyclotrimerisation of isocyanates. This is also indicated by a number of other features common both to the complex formation reaction and to the cyclotrimerisation kinetics in the presence of the AcOK linear oligoether catalytic system: the high heats of reaction and the high equilibrium constants characterising the complex formation in the catalytic systems based on AcOK and oligooxyethylenes, compared with the catalytic systems based on AcOK and oligooxypropylenes, and the correspondingly higher catalytic activity of the former systems in the cyclotrimerisation of 2,4-TDI (Table 2), as well as the absence of interaction (and hence of the cocatalytic effect in the CT reaction) of polyfurite, dioxan, and dibutyl ether with AcOK, etc.

Table 2. Parameters of the complex formation reactions [$-\Delta H$(kJ/mol AcOK) and K_p (litre^n mol^{-n})] of various electron donors (ED) with AcOK and their cocatalytic activities in the cyclotrimerisation of 2,4-TDI.[168]

ED	MW	[–O–]/[AcOK] at V^1_{max} and ΔH_{max}	$-\Delta H$, kJ/mol AcOK	K_p, litre^n mol^{-n} [2]	Relative V_{max} for CT
Diglyme	134	—	15	42	1.0
Tetraglyme	222	20	33	66	1.4
POED-400	420	10	35	240	6.4
PEO[3]	520	10	41	260	6.7
POPD-500[4]	540	25	31	98	2.5
POPD-1000	1050	25	22	30	1.2
POPT-500	510	30	21	130	0.8
POPT-1000	1030	30	20	65	0.8

[1] V_{max} and ΔH_{max} are the maximum rates of cyclotrimerisation of 2,4-TDI and the enthalpy of complex formation respectively.
[2] n is the number of moles of the electron donor in the complex.
[3] PEO does not contain OH groups.
[4] POPD-500 was synthesised from diethyleneglycol and contains ~12% of hydroxyethyl groups.

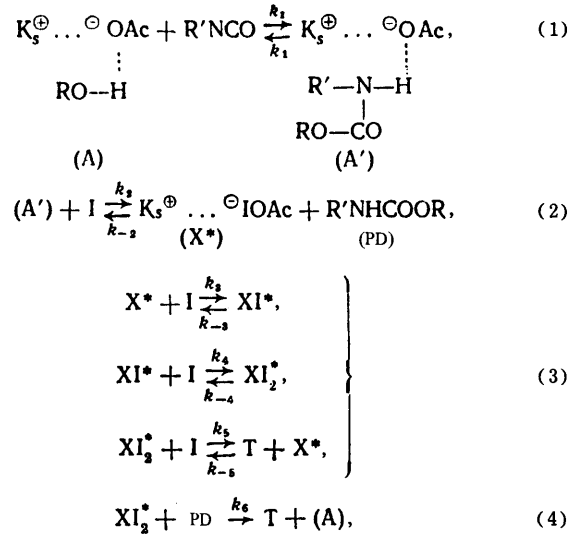
A study[235] using the potassium salts of aminoacids as catalysts of the cyclotrimerisation of isocyanates in the synthesis of isocyanurate-urethane foam plastics dealt with the principal rules governing the influence of linear oligoethers on the catalytic activity of systems, observed by

Denisov et al.[44] and Zhitinkina et al.[168] Thus, for the same content of the oligoether by weight in the composition, the replacement of oligooxyethylenediol-200 by oligooxypropylenediol-200 leads to an increase of the foaming time of the composition by a factor of 2 (from 35 to 68 s). An increase of the equivalent ratio $[-O-]/[K^+]$ diminishes the above parameter.

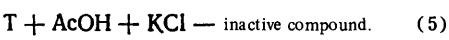
The cocatalytic effect of linear oligoethers based on EP and EE has been used[236] to establish highly effective catalytic systems suitable for the synthesis of isocyanurate-urethane foam plastics with effective physicomechanical parameters, thermal stability, and fire resistance.[45-47]

Analysis of data[44,128,166,168] on the kinetics of the cyclotrimerisation of isocyanates in the presence of the AcOK/oligoether catalytic systems has shown, however, that the complexes formed are not apparently the "true" initiators of this reaction, since the induction period persists (at sufficiently low catalyst concentrations). At the end of the induction period, the reaction begins at a rate close to the maximum and obeys a formal kinetic first-order equation. The order of the reaction with respect to the catalyst is unity.[168] On the basis of the factors indicated, a hypothetical mechanism of the cyclotrimerisation of isocyanates in the presence of catalytic systems of this kind has been put forward[166,168] in the following way (for systems containing ROH, Scheme 5):

Scheme 5



or

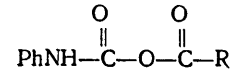


The chain termination in stage (3) of this system can apparently be due to cyclisation in the presence of a proton donor with regeneration of the initial catalyst. It is also possible that stage (2) involves more complex interactions.

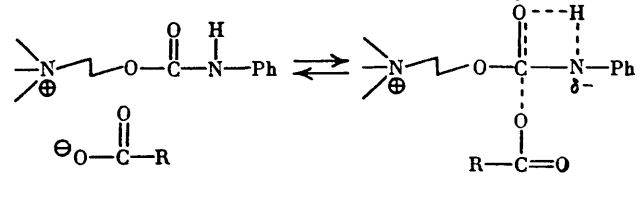
The kinetics of the cyclotrimerisation of PIC in the presence of various catalysts, including quaternary ammonium carboxylates, have been described recently.[147,205] The authors reported[205] that, in the presence of a quaternary ammonium carboxylate, the reaction is of first order with respect to the isocyanate at low degrees of conversion: at high degrees of conversion, the reaction deviates from the first order. However, in the next study[147] by the same workers involving the cyclotrimerisation of PIC in diglyme, it was stated that the reaction is of second order with respect to the monomer in the presence of a catalyst of the same type. In addition they established that the rate of reaction in the presence of a quaternary ammonium carboxylate (the DABCO TMR product) varies non-linearly under these conditions with the concentration of the catalyst and the order of the reaction with respect to the catalyst is close to two. For other types of catalysts, the order of the reaction is unity.[147] Thus fairly contradictory data have been obtained. Unfortunately, the information quoted in these communications concerning the kinetics of the cyclotrimerisation of PIC was obtained using commerical catalysts (DABCO TMR; APCI). There are no data concerning their exact structure and purity, which precludes the analysis of the results from the standpoint of the influence of various factors.

It has been established[147] that the PIC trimer does not have an accelerating effect on the cyclotrimerisation in the presence of the catalysts investigated (in the presence of the trimer, the rate of cyclotrimerisation is actually somewhat lower). The author showed that, in the presence of a quaternary ammonium carboxylate (DABCO TMR), the rate of cyclotrimerisation of PIC diminishes with increase of temperature. Since the catalyst itself does not lose its activity after being thermostatted at 323 K, they suggest that this effect is associated with the depolymerisation of the growing chain in the stages preceding cyclotrimerisation. In a study of the influence of the catalyst structure on the rate of cyclotrimerisation of PIC, Bechera[147] established that, among compounds of the given type, the catalysts with primary OH groups are more effective than catalysts with secondary OH groups while the latter are more effective than catalysts with tertiary OH groups. On the other hand, an increase of the number of OH groups in the catalyst leads to a decrease of the rate of cyclotrimerisation of PIC. It has also been established that, with increase of the basicity of the carboxylate anion, the activity of the catalyst rises, while the addition of a carboxylic acid to the catalyst reduces the rate of cyclotrimerisation of PIC. The authors do not attempt to interpret the latter fact in any way.

At a low concentration or at a low activity of the catalyst the induction period persists. In the case of substituted quaternary ammonium benzoates, its duration is inversely proportional to the basicity of the carboxylate anion. It is believed[147] that the induction period is due to the slow formation of an activated catalyst as a result of the addition of an isocyanate molecule to the OH group and that this product exhibits a somewhat higher catalytic activity than the initial catalyst in the cyclotrimerisation of PIC. In their study of the structure of the product of the addition of PIC to hydroxyethyltrimethylammonium nitrobenzoate (in equivalent proportions) by IR and NMR spectroscopy, the authors observed the presence of the absorption band of the urethane carbonyl group and the absence of free NCO groups and of the mixed anhydride of carbamic acid:

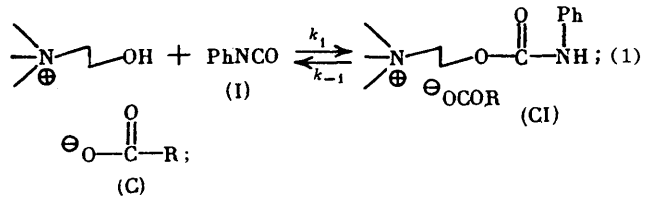


On the other hand, the presence of a very "acid" proton was revealed by the NMR spectra. On the basis of the results obtained, they represented the structure of the isocyanate-activated catalyst in the following way:



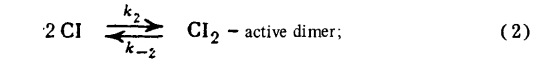
However, in an attempt to explain the observed second order of the reaction with respect to the catalyst, the authors assumed further that this product forms a very active dimer in the initiation stage and put forward the following mechanism for the cyclotrimerisation of isocyanate in the presence of ROH (Scheme 6):

Scheme 6

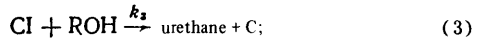


(1)

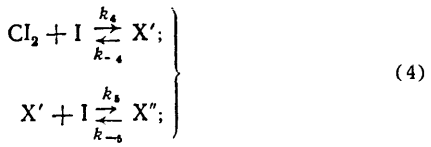
(C)



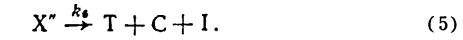
(2)



(3)



(4)

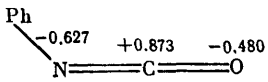


(5)

It is fairly difficult to imagine the nature of such a dimer, which was in fact stated by the authors themselves.

V. SOME FEATURES OF THE KINETICS OF THE CYCLOTRIMERISATION OF ISOCYANATES AND THE PROPOSED PROCESS MECHANISM

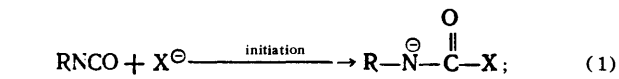
Isocyanates belong to the class of unsaturated compounds with cumulated double bonds,[237-240] which determines their reactivity in relation to various compounds, including their reactivity in relation to one another. The electron density in the NCO group is distributed in such a way that the nitrogen and oxygen have electron-donating properties, while carbon has electron-accepting properties. Quantum-chemical calculations of the distribution of electron density in isocyanates, carried out by the CNDO/BW method with optimised geometry, which agree qualitatively with non-empirical calculations,[241] have shown that the nitrogen atom carries a larger negative charge than the oxygen atom:



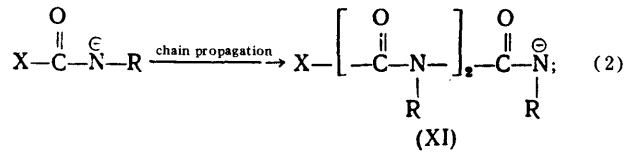
From the C=O (635 kJ mol^{-1}) and C=N (375 kJ mol^{-1}) bond energies quoted by Fedotova et al.,[242] one can assume that the addition to the N=C bonds is easier. The results of studies on the EPR spectra of the radicals formed on γ-irradiation of isocyanates and ρn their interaction with active hydrogen atoms confirm this.[243] All subsequent studies devoted to the synthesis of linear homopolymers of isocyanates,[244-247] their copolymers,[64-71] and cyclic trimers indicate the preferential cleavage of the N=C bond.
A number of studies have been devoted to the elucidation of the causes of the anionic polymerisation of isocyanates preferentially via the N=C bond,[241,248] in which it was shown, from quantum-chemical calculations, that at the instant of interaction with nucleophiles the N=C bond undergoes an intense polarisation (compared with the C=O bond), which explains its high reactivity in such processes.

The CT reaction of isocyanates was first considered as a special case of anionic homopolymerisation in two studies.[249,250] In the presence of typical catalysts of anionic polymerisation (sodium cyanide and others) at 173–253 K a linear polymer with a polyamide structure was obtained in a high yield (MW = 10^4–10^5) and the trimer was isolated as a side product. The authors proposed a general stepwise mechanism for the polymerisation of isocyanates under the influence of anions, in which the cyclotrimerisation reaction is a special case (Scheme 7):

Scheme 7

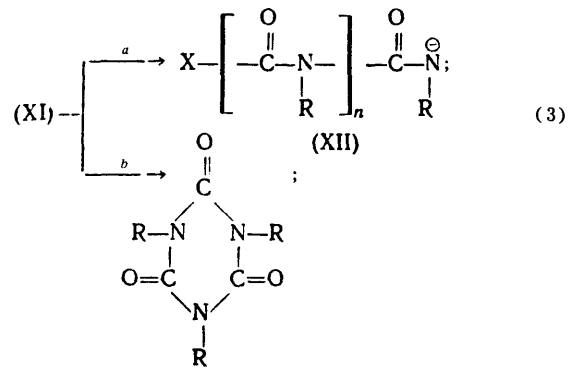


(1)



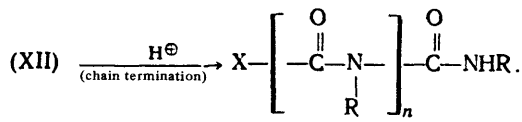
(2)

(XI)



(3)

(XII)



Pathway *a* responds to a low temperature and a low catalyst concentration and pathway *b* to a high temperature and a high catalyst concentration.

There is at present no doubt about the ionic character of the polymerisation of isocyanates.[60] Even under the influence of γ-radiation (^{60}Co) the process proceeds via a radical mechanism.[251] Cyclic trimers of aliphatic and aromatic isocyanates have been obtained by the anionic electroinitiated polymerisation.[252-254] The typical features of the cyclotrimerisation of isocyanates via the anionic mechanism are as follows. The activity of the isocyanates in cyclotrimerisation depends on the donor–acceptor properties of the substituents adjoining the NCO groups: isocyanates with electron-accepting substituents (aromatic) are more reactive than isocyanates with electron-donating substituents (aliphatic).[58,60,145] In a series of substituted phenyl isocyanates, those containing electron-accepting substituents in the *para*-position cyclotrimerise faster than the unsubstituted

PIC, while isocyanates with electron-donating substituents in the *para*-position cyclotrimerise more slowly.[60,95]

The high positive Hammett constant ρ for substituted isocyanates[59,95] shows that electron-accepting substituents increase k_{cat}, i.e. the activation process involves the electrophilic carbon centre of the isocyanate group. The initiation of the cyclotrimerisation of isocyanates as a result of the influence of nucleophilic groups on the electrophilic carbon atom of the isocyanate is also indicated by the increase of k_{cat} in the CT reaction with increase of the nucleophilicity of the catalytic centre, which has been recently demonstrated.[60,147,205]

It has been frequently noted in studies on the kinetics of the cyclotrimerisation of isocyanates in the presence of various kinds of catalysts at fairly low catalyst concentrations that the reactions investigated in many cases have an induction period, whose duration depends on the concentrations of the catalyst, the cocatalyst, the isocyanate, and the nature and polarity of the solvent. Inadequate attention has apparently been devoted to the study of the causes of the induction period in the cyclotrimerisation of isocyanates and of the relation between this factor and the overall process mechanism. Analysis of the data examined suggests that the appearance of the induction period in the cyclotrimerisation of isocyanates is due to the slow initiation, on the one hand, and the possibility of the action of an inhibitor, on the other.

It is known[150,255] that strong acids (for example, HCl) are effective inhibitors of the cyclotrimerisation of isocyanates at moderate temperatures. At the same time, the possibility of the presence of traces of HCl in isocyanates (which is almost always the case) is as a rule disregarded in kinetic studies. This may be the reason why a non-proportional dependence of the rate of cyclotrimerisation of the isocyanate on the catalyst concentration is sometimes observed at inhibitor concentrations comparable to those of the catalysts.[132] However, one should note that in the vast majority of experiments the reaction is of first order with respect to the catalyst.[60,62,74,94,118,125,128,136,137,144,150,168,172]

When the CT reaction of isocyanates is carried out in highly polar media (DMF, DMSO), an induction period is as a rule not observed, which indicates an increase of the rate of initiation in solvents of this kind. The study of the dependence of the rate of cyclotrimerisation of isocyanates on the dielectric constant of the medium[60] has demonstrated agreement with the Kirkwood equation.[256] This shows that the charge separation in the polymerisation active centre formed as a result of initiation is greater than in the initial reactants. On the other hand, it has been demonstrated that the rate of cyclotrimerisation of isocyanates cannot be unambiguously determined by properties of the solvents such as the dielectric constant and the dipole moment.[60,136] The electron-donating capacity of the solvent and the specific solvation of the reactants by the solvent also have a considerable influence under these conditions.[60,128,168]

The orders of the reaction of isocyanates observed in various experiments with respect to the main monomer ranged from zero[137] to two[60,147,150] and above,[155–158] depending on the type of catalyst used, the solvent, etc. In most cases the kinetic curves for the reaction obey a formal first-order kinetic equation.[62,74,94,136,150,168,172]

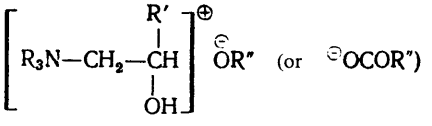
In non-polar and virtually non-solvating solvents (benzene, chlorobenzene), with the initiation as the slow stage limiting the rate of the main reaction, it has been noted that the order of the CT reaction of isocyanates with respect to the monomer is preferentially unity in terms of time and 2 in terms of concentration.[150,163,168] The above relations and also the finding that at the end of the induction period the reaction begins close to the maximum rate show apparently that initiation, involving the interaction of the catalyst with the isocyanate, leads to the formation of an initiator which is much more active than the highly polar initial catalyst.

In principle, when one considers the most effective catalysts of the cyclotrimerisation of isocyanates or the catalytic systems recommended at present for practical use, it is easy to see that they are all ion pairs with separated charges, in which the cation is to a considerable degree localised:

1. The alkali metal carboxylate (alkoxide)/oligoether systems consisting of solvate-separated ion pairs:[44,168]

$$M_s^{\oplus} \ldots {}^{\ominus}OCOR$$

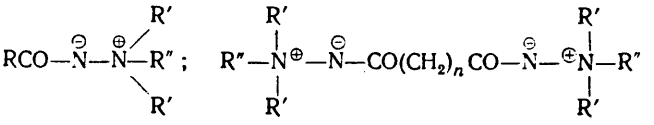
2. Quaternary ammonium derivatives obtained from tertiary amines, epoxyalkanes, and PD (water, alcohols, phenols, and carboxylic acids):[147,150,163,168,205]



(XIV)

Analysis of the structures of compounds of type (XIV) by means of quantum-chemical calculations[201,257] has shown that the anion in such compounds has a considerable capacity for free migration.

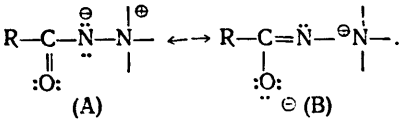
3. Aminoimides:[173–175]



(XV)

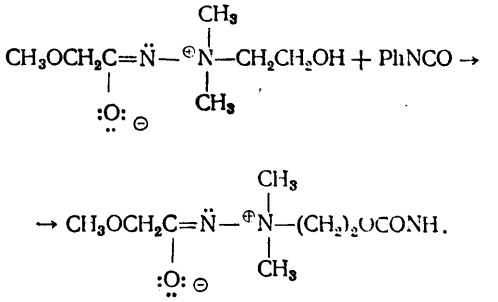
R, R′ = Alk; R″ = CH_2—CH(OH)—CH_3 or CH_2CH_2OH

The most active are the derivatives with primary OH groups. Acylamine imides are zwitter-ions having the following resonance structure:[173]

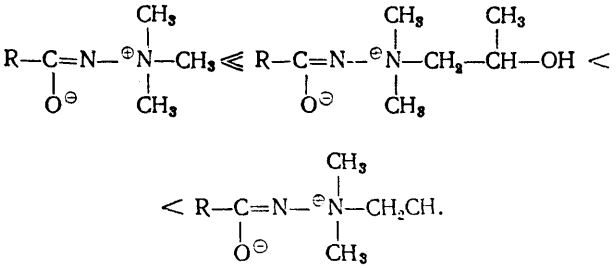


(A) (B)

From IR spectroscopic data, preference is given to structure (B). The authors have shown that the interaction of dimethyl-2-hydroxyethylaminomethoxyacetimide with PIC in acetonitrile leads to the formation of a carbamate:

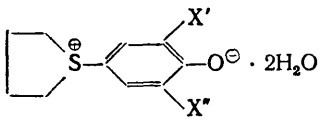


The authors believe that the carbamate promotes the induced polarisation of the isocyanate via the formation of a hydrogen bond and explain by its formation the higher catalytic activity of hydroxyl-containing acylaminoimides compared with the alkyl-substituted derivatives:



Unfortunately experimental kinetic data are not quoted in the relevant study,[173] which makes it impossible to infer the principal kinetic characteristics of the CT reaction of isocyanates in the presence of catalysts of this kind.

4. Sulphonium zwitter-ions:[159,160]



X', X'' = H, R

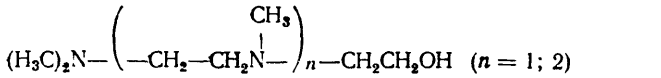
According to the data of Kresta et al.,[160] the CT reaction of PIC in acetonitrile in the presence of a catalyst of this kind is of first order with respect to the catalyst and of second order with respect to the monomer. At 298 K in the presence of this catalyst, a cyclic trimer is obtained in a quantitative yield; 93% of the trimer and 7% of a linear polymer are formed at 248 K and 64% of the trimer and 36% of the linear polymer are formed at 233 K. An important factor which determines the activity of the catalyst in the cyclotrimerisation of isocyanates is the nucleophilicity of the anion. With increase of the electron density of the oxygen atom in cyclic sulphonium zwitter-ions, the catalytic rate constant for cyclotrimerisation increases. Analogous results have been obtained by other workers[147] in the cyclotrimerisation of PIC in the presence of quaternary ammonium carboxylates as catalysts. At the same time, it has been shown[60] that the presence of bulky substituents in the anion of catalysts of the type of MOR does not exert a significant influence on the rate of cyclotrimerisation of PIC.

The characteristics noted above and others observed in the study of the kinetics of the cyclotrimerisation of isocyanates are the reason why there are at present no clear-cut ideas about the mechanism of this process despite the fairly large amount of experimental data. Generally speaking, all the hypotheses put forward concerning this question reduce to the consideration of two main process mechanisms: the insertion mechanism (or the mechanism of "insertion reactions) involving the M–X bond, where X = O, N, S,[61,155,203] or N–H,[84,87] and the mechanism involving addition to the anion.[41,86,94,136,168,258]

The template polymerisation mechanism has also been proposed for the cyclotrimerisation of isocyanates.[155–158]

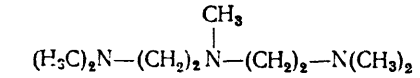
When ionic catalysts, which as a rule consist of ion pairs dissociated to different extents[128,147,168,205] or zwitter-ions,[159,160,173] are used for the cyclotrimerisation of isocyanates (which normally takes place at moderate or elevated temperatures), one should apparently consider polymerisation in the presence of separated ion pairs. In order to achieve the process involving free anions, the latter must be stabilised under these conditions.[41,215] The charge separation in the initial catalysts of the cyclotrimerisation of isocyanates of the type (XIII)–(XVI) is apparently a necessary but not a sufficient condition for effective catalysis via attack on the carbonyl component of the NCO group. Additional activation of the reactants is necessary, for example, the polarisation of the monomer and the catalyst by employing highly polar solvents or powerful solvating agents, which promotes the interaction of the catalyst with the isocyanate in the initiation stage.

In the study of the cyclotrimerisation of PIC in DMF in the presence of sodium ethoxide ($NaOC_2H_5$), it has been establisned[141–143] that in the presence of carbamates the rate of reaction increases in proportion to their concentration. The authors explained the cocatalytic effect of urethane by the polarisation of the NCO groups (as for hydroxyl-containing acylimides). The authors showed that, in the presence of carbamates the quantity ρ for the cyclotrimerisation of isocyanate diminishes under the conditions investigated. The authors suggest that the polarisation of the NCO groups then proceeds to an extent such that the inductive effect of the substituents in the aromatic ring of the isocyanate is less pronounced. However, the coordination interaction between the isocyanate and the urethane has not been observed.[259] The variation of the catalytic activity of hydroxyl-containing quaternary ammonium carboxylates in the catalysis of the cyclotrimerisation of isocyanates had also been attributed to the cocatalytic effect of the carbamate groups.[147,205] The recently observed catalytic activity of a series of tertiary amines having the structure



(XVII)

in the cyclotrimerisation of isocyanates has been explained by the same effect[172] on the basis of the fact that amines of the type

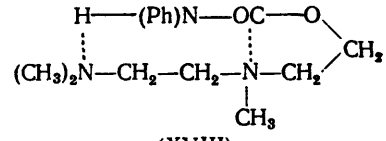


are ineffective under these conditions. However, it has been shown that dimethylethanolamine is also ineffective, like amines of the type

$$(CH_3)_2N—CH_2—CH(OH)CH_2—N(CH_3)_2.$$

It has likewise been established that the cyclotrimerisation of isocyanates in the presence of catalysts of this kind in toluene is of first order with respect to the catalyst and the monomer and is characterised by the presence of an induction period, whose duration is inversely proportional to the catalyst concentration. Catalysts with primary OH groups are much more active than those with secondary hydroxyls; an increase of the number of substituents with OH groups at the same nitrogen atom returns the cyclotrimerisation of the isocyanate (analogously to the situation which obtains for quaternary ammonium carboxylates).[117] In the presence of an alcohol, the formation of a urethane in the presence of the catalysts indicated above always precedes the cyclotrimerisation and, under conditions where there is a slight excess of isocyanates (2 : 1), this is followed by the formation of the allophanate and cyclotrimerisation is observed only on further increase of the excess of isocyanate. The product of the addition of trimethylaminoethylethanolamine to PIC has been isolated and characterised[172] with the aid of infrared spectra and the following structure has been

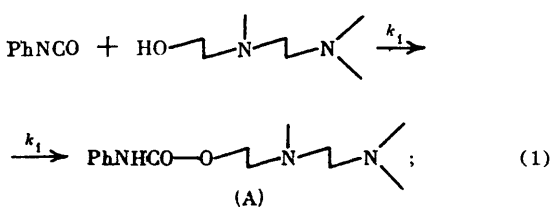
attributed to it:



(XVIII)

Since the urethane-formation reaction in the presence of catalysts of type (XVII) is of first order with respect to the alcohol and is almost independent of the isocyanate concentration, the authors believe that the complex (XVIII), formed rapidly in the presence of ROH, interacts with the alcohol, which entails the formation of a urethane and the regeneration of the catalyst. However, it is fairly difficult to imagine such interaction. It appears more probable that under these conditions the alcohol competes with the urethane in the complex formation reaction with the amine, forming the catalytic complex $R_3N.R'OH$ (in conformity with the general mechanism of the catalysis of the urethane-formation reaction by tertiary amines[260]), which then interacts comparatively rapidly with the isocyanate, forming the urethane. The trimerisation reaction is regarded as the consecutive addition of the isocyanate to the N–H bond in the complex (XVIII) (Scheme 8):

Scheme 8



(A)

$$(A) + PhNCO \xrightarrow{k_2} (B); \quad (2)$$

$$(B) + PhNCO \xrightarrow{k_3} (C); \quad (3)$$

$$(C) + PhNCO \xrightarrow{k_4} T + (A). \quad (4)$$

Bearing in mind that the product (A) is formed very rapidly, this scheme cannot, however, account for the induction period in the CT reaction with a subsequent high rate of the latter. In this connection, the authors, noting that the nature of the induction period is unknown, expressed the view, which conflicts with Scheme 8, that the induction period may be caused by the slow formation of a "synergistic intermediate complex". The possibility of the inhibition of the CT reaction by slowly reacting impurities is also allowed.

From the standpoint of a more complete explanation of the majority of the characteristics of the kinetics of the cyclotrimerisation of isocyanates in the presence of basic catalysts which have been observed and described here, the scheme proposed in a number of studies[60,163,168] is apparently more favourable. It can be represented in the following general form (taking into account the possible inhibition) (Scheme 9):

Scheme 9

$$A + I \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^* \text{ — initiation;} \quad (1)$$

$$\left.\begin{aligned} A + I &\xrightarrow{k_2} N, \\ X^* + I &\xrightarrow{k_2'} N', \end{aligned}\right\} \text{ inhibition;} \quad (2)$$

$$\left.\begin{aligned} X^* + I &\underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} XI^*, \\ XI^* + I &\underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} XI_2^*, \end{aligned}\right\} \text{ chain propagation;} \quad (3)$$

$$XI_3^* + I \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} T + X^* \text{ — chain transfer;} \quad (4)$$

$$\left.\begin{aligned} XI_2^* &\xrightarrow{k_6} T + A, \\ XI_2^* + PD &\xrightarrow{k_7} T + A', \\ XI_2^* + Inh &\xrightarrow{k_8} T + N, \end{aligned}\right\} \text{ chain termination;} \quad (5)$$

Inh = inhibitor; N, N′ = inactive compounds.

Without taking into account the effect of the inhibitor and for conditions in a quasi-stationary process, where

$$k_1 > k_{-1};\ k_{-3} \ll k_3 \simeq k_4 \gg k_1;\ k_5 \gg k_6 \simeq k_7,$$
$$[A_0] = [A] + [X^*] + [XI^*] + [XI_2^*],$$

the above scheme can be described by the equations

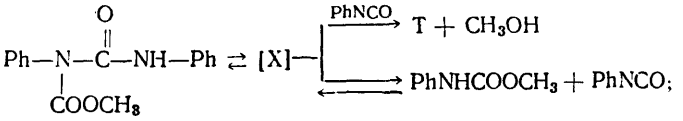
$$-\frac{d[I]}{d\tau} = k_{cat}\,\frac{[A_0][I]^2}{1 + B[I]};\quad B = \text{const};$$

$$\frac{[I_0] - [I]}{[I]\,[I_0]} + B \ln \frac{[I_0]}{[I]} = k_{cat}\,[A_0]\cdot\tau = k_{exp}\tau.$$

According to the results of Kresta and Hsieh,[60] the experimental results agree well with the latter equation. Scheme 9 includes, in principle, two kinetic chains: with regeneration of the initiator (X*) and with regeneration of the initial catalyst (A). Presumably the preferential realisation of one of them (depending on the reaction conditions and the type of catalyst) and the associated changes in the relative values of the constants for the individual stages of the process do in fact lead to differences between the observed characteristics of the CT reactions of isocyanates (different reaction orders with respect to the monomer, the presence or absence of the induction period, etc). When the rate of termination can increase during the reaction (for example, as a result of an increase in the concentration of active impurities and an increase of temperature), the reaction should be retarded according to the above scheme and there should be a corresponding increase of the reaction order with respect to the monomer (from first to second). Certain kinetic data indicate such features of the cyclotrimerisation of isocyanates.[147] However, the question of the structure of the initiator and of the interactions leading to its formation remains obscure.

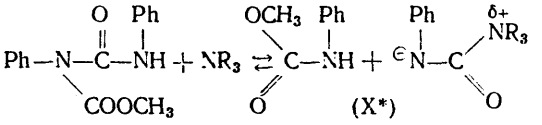
Examination of the kinetic data for the cyclotrimerisation of isocyanates reveals the striking fact that in many cases the reaction is accelerated in the presence of proton-donating compounds (alcohols, urethanes, and hydroxyl-containing catalysts),[84,141–143,147,172,173,205] even when highly basic catalysts are employed. In the presence of tertiary amines (TEDA) at moderate temperatures the cyclotrimerisation of isocyanates takes place only in the presence of an alcohol, urethane, or allophanate in the system.[137,171] Another feature which has been observed by some investigators consists of facts indicating that the reaction preceding cyclotrimerisation[84,172] or coupled with it[137,171] involves the formation-dissociation of the allophanate.

In the presence of 2-methyltriethylenediamine the cyclotrimerisation of PIC in chlorobenzene was not observed at 353 K for 2–3 h;[137,171] when methyl αγ-diphenylallophanate (MDA) was introduced into this system, PIC trimerised at a high rate. It has also been shown that in the presence of 2-methyltriethylenediamine and MDA the cyclotrimerisation of PIC begins with an induction period, the duration of which is inversely proportional to the MDA concentration and depends only slightly on the isocyanate concentration. The rate of the main reaction under these conditions is proportional to the concentrations of the catalyst and MDA and is independent of the concentration of the monomer. It was established that two coupled reactions take place in the system: the dissociation of the allophanate and cyclotrimerisation with a common induction period, whose nature the authors explain by the influence of the inhibitor on the intermediate (X) formed from the allophanate:



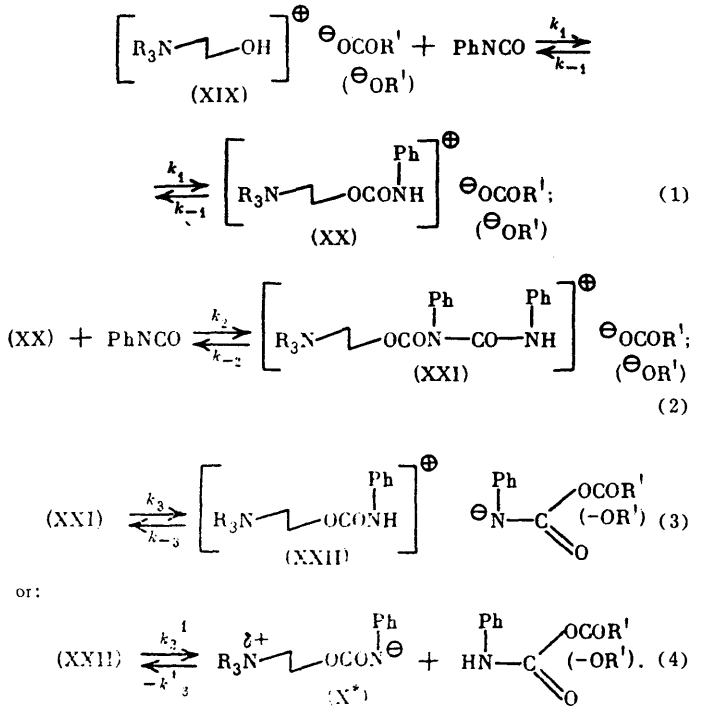
The action of the inhibitor precisely on the product (X) is caused, in their view, by the fact that the induction period persists even in the presence of a high content of MDA, which is known to exceed the possible content of the inhibitor.

On the other hand, one can assume that the formation of active polymerisation centres (X*) in systems of this kind is coupled with the allophanate dissociation step via the interaction of the catalyst with its active (possibly tautomeric) form:



Since this stage is apparently extremely slow (bearing in mind the reversibility of the process) and limits the rate of cyclotrimerisation of the isocyanate, the latter is almost independent of the isocyanate concentration but should be proportional to the MDA and catalyst concentrations. On the other hand, the possibility that the inhibitor acts on the active centres just as much as the initial catalyst cannot be ruled out in this case either. The appearance of active polymerisation centres of the type (X*) can lead to the cyclotrimerisation of isocyanates at a higher rate than that observed at the end of the induction period of the reaction. From the standpoint of the possible involvement of the allophanate in the initiation step of the cyclotrimerisation of isocyanates (via the interaction of its active form with the catalyst), it is apparently possible to explain also other instances of the influence of hydroxyl-containing agents (or urethanes) on the kinetics of this reaction; presumably in the presence of hydroxyl-containing quaternary ammonium carboxylates (alkoxides) the following interactions take place in the initiation process (Scheme 10):

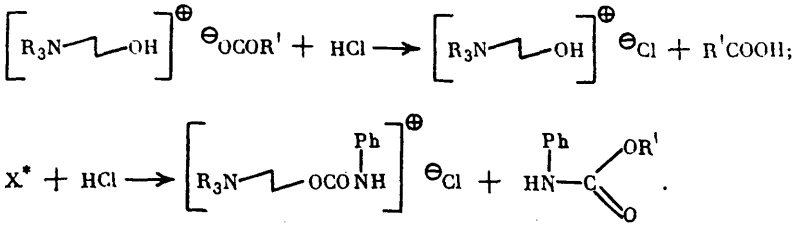
Scheme 10



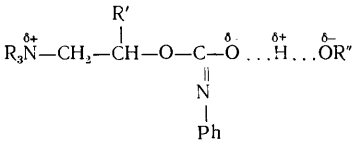
Stages (2) and (3) can then involve additional interactions.

The separated ion pair (XXII), which is more polar than the initial catalyst, or the dipolar anion (X*) initiates the CT process at a high rate in conformity with stages (3) and (4) (Scheme 9). Chain termination may be caused under these conditions by the regeneration of products of the type (XIX) or (XX) in the cyclisation stage and also by the inhibition of the active centres by impurities. With increase of temperature, the probability of such termination also increases, which may lower the rate of cyclotrimerisation of isocyanates.[132] The shift of equilibrium in stages (2) and (3) (Scheme 10) to the left should also diminish the rate of the main process.

In terms of Scheme 10, it is possible to explain also the decrease of the activity of catalysts of this kind when the primary hydroxy-groups are replaced by secondary hydroxy-groups and following an increase of the number of OH-containing substituents. The addition of carboxylic acids to such systems should entail the formation of associated species with the anion[261] and hence a decrease of the activity of the catalyst. Strong acids (HCl) can apparently convert into an inactive form both the initial catalyst and products of type (X*), inhibiting thereby the cyclotrimerisation of the isocyanate:



Analogously, it is possible to account for the catalytic activity in the cyclotrimerisation of isocyanates of a number of hydroxyl-containing amines[172] and acylaminoimides,[173] as well as the activity of carbamates as cocatalysts in the cyclotrimerisation of isocyanates in the presence of C_2H_5ONa.[141-143] The possibility of the dissociation of a urethane in the presence of products of type (III), which has been established recently,[8] also constitutes a precondition for the formation of initiators of type (X*) in systems containing a urethane (allophanate) and a strong base. One cannot rule out the possibility that products of this kind are formed also in reactions involving the possible interaction of the isocyanate trimer with an epoxide in the presence of catalysts (strong bases) or with the product of the addition of the epoxide to the catalyst of type (III)–(V), and ultimately lead to the formation of oxazolidinones[202] or products having the tentative structure[262]



The study of the above characteristics of the kinetics and the proposed mechanism of the CT reaction of isocyanates from the standpoint of conformational ideas[263] is undoubtedly of great interest.

The data presented in this review indicate the great variety of catalysts and catalytic systems used in the cyclotrimerisation of isocyanates and also the existence of different points of view on the mechanism of this reaction. Analysis of the data available on this question established that the most effective catalysts of the cyclotrimerisation of isocyanates are ion pairs with separated charges in which the active centre is the anion, the counterion being fairly well localised.

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Vladimir