The nature of active centers in cyclotrimerization of isocyanates catalyzed by the tertiary amine—α-oxide—proton donor system

1. The role of the proton donor

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The rate of cyclotrimerization of phenyl isocyanate in chlorobenzene at 120 °C in the presence of the tertiary amine—α-oxide—proton donor (PD) ternary catalytic system has been studied using a dual calorimeter and a series of phenols with various acidities as the PD. In the presence of weakly acidic phenols, complexes of quaternary ammonium type bases are formed in the ternary catalytic systems. Acidic phenols afford salt complexes with the transfer of a proton from phenol to the tertiary amine in a quantitative yield, while the α-oxide present remains unaffected. The structures of the complexes were studied by IR and ^{1}H NMR spectroscopy.

Key words: catalytic systems; cyclotrimerization; isocyanates, hydrogen bonds; molecular complexes.

The effect of a proton donor (PD) on the catalytic activity of tertiary amine—α-oxide—PD systems and, correspondingly, on the rate of cyclotrimerization of isocyanates has been repeatedly discussed in the literature.[1,2] The nature of the active center of this system (whether it is an ion pair, a zwitterion, or a compound resembling a quaternary ammonium base) is still a debated problem, although the authors of some studies are inclined to believe that the latter is true.[2—4]

It has been found previously[3,4] that the interaction of the components of the tertiary amine—α-oxide—PD (water, alcohols, phenols, ureas, the products of their interaction with isocyanates, carboxylic acids) system yields quaternary ammonium base type products such as alkoxides or carboxylates, possessing high catalytic activity in the cyclotrimerization of isocyanates.

However, along with the search for highly efficient catalysts of polycyclotrimerization of diisocyanates, the opposite task, *viz.*, decreasing the activity of catalytic systems at room temperature, is no less urgent; this would ensure high shelf life of isocyanate—epoxide systems. These catalytic complexes should exhibit high activities at elevated temperatures, *i.e.*, the final purpose is to develop latent catalysts for cyclotrimerization of isocyanates. For this purpose, we prepared catalytic systems based on complexes of dimethylbenzylamine and phenylglycidyl ether with a number of phenols of various acidities and studied the effect of PD on the catalytic activities of these complexes in the cyclotrimerization of phenyl isocyanate.

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Experimental

IR spectra were recorded on M-80, Perkin-Elmer 427, Bruker IFS-113v, and Bruker IFS-25 spectrophotometers. The ^{1}H NMR spectra were obtained on a Bruker WP-200-SY spectrometer operating at 200.13 MHz for solutions in dichloromethane.

Phenyl isocyanate was synthesized by acylation of phenol with cyanogen bromide in the presence of triethylamine; b.p. 42 °C (1 Torr) (*cf.* Ref. 5).

The starting compounds were purified by vacuum distillation or by recrystallization; the physicochemical characteristics were in agreement with published data.

The rate of cyclotrimerization of phenyl isocyanate was measured in chlorobenzene at 120 °C based on heat evolution in time using a dual calorimeter. The four-component reaction system was placed into two glass tubes. The reaction tube contained phenyl isocyanate, dimethylbenzylamine (DMBA) in chlorobenzene and a sealed thin-walled tube with weighed portions of phenylglycidyl ether (PGE) and PD in chlorobenzene. At the instant of the beginning of an experiment, the thin-walled tube was broken, and the components were thoroughly mixed with a glass stick. It was found in preliminary experiments that heating phenyl isocyanate in the presence of DMBA for 2 h at 120 °C does not lead to its cyclotrimerization; PGE and PD also do not react with each other.

Results and Discussion

The rate of cyclotrimerization of phenyl isocyanate in a chlorobenzene solution was measured at 120 °C in the presence of the DMBA—PGE—PD ternary catalytic system. 3,4-Dimethylphenol (DMP; pK_a 10.3), phenol

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1382—1385, June, 1996.

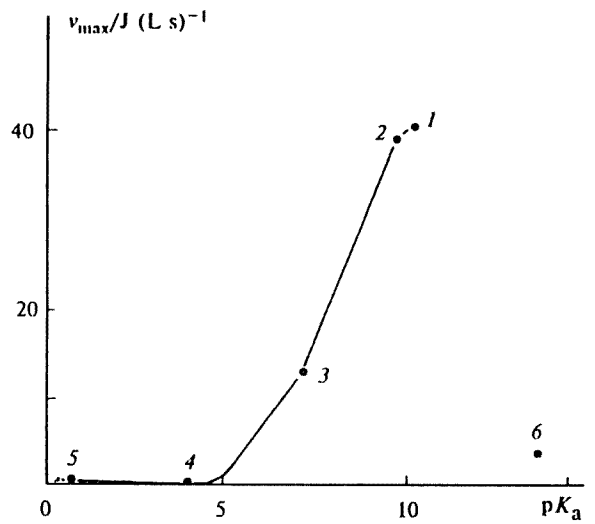


Fig. 1. Dependence of the maximum rate of cyclotrimerization of phenyl isocyanate in chlorobenzene at 120 °C in the presence of the DMBA—PGE—PD ternary catalytic system on the pK_a of the PD studied: 3,4-dimethylphenol (*1*); phenol (*2*); 4-nitrophenol (*3*); 2,4-dinitrophenol (*4*); 2,4,6-trinitrophenol (*5*); H_2O (*6*). [PIC] = 1.5 mol L^{-1}, [DMBA]=[PGE]=[PD] = 0.08 mol L^{-1}.

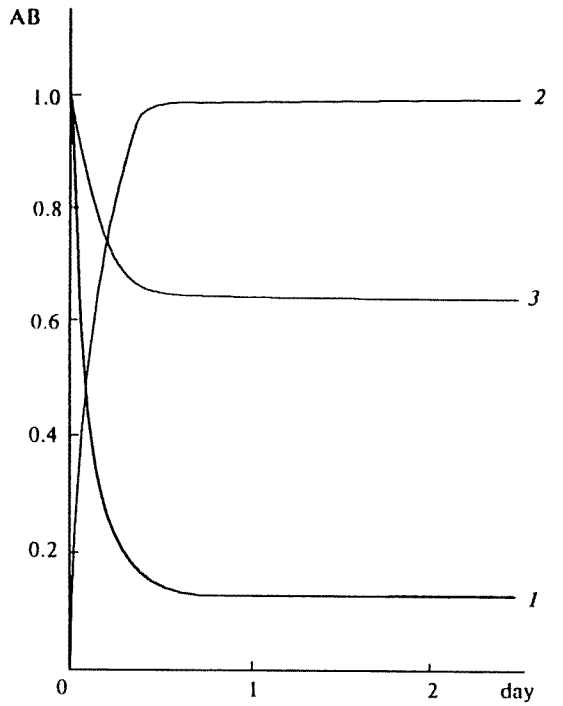
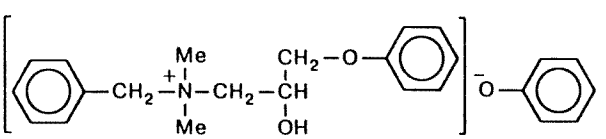


Fig. 2. Variation of the optical densities of the bands of stretching vibrations of the free OH groups in phenol at 3580 cm^{-1} (*1*), in associated phenol at 2600 cm^{-1} (*2*), and of the band due to the α-oxide ring at 915 cm^{-1} (*3*) during the formation of the complex in the mixture of the composition [P]=[DMBA]=[PGE] = 0.5 mol L^{-1} in CH_2Cl_2.

(P; pK_a 9.98), *p*-nitrophenol (*p*-NP; pK_a 7.15), 2,4-dinitrophenol (DNP; pK_a 4.07), and 2,4,6-trinitrophenol (TNP; pK_a 0.71) were used as PD's. It can be seen from Fig. 1 that the rate of cyclotrimerization of phenyl isocyanate decreases with a decrease in the pK_a in the series of phenols (points *1*, *2*, *3*) and that in the presence of acidic phenols such as DNP (point *4*) and TNP (point *5*) the reaction virtually does not occur under these conditions. For comparison, Fig. 1 presents the maximum reaction rate (point *6*) observed when the water impurity present in the solvent (the water content in the solvent, according to Fisher, was 0.15 %, which corresponded to [H_2O] = 0.075 mol L^{-1}) acts as the PD.

To explain the results obtained, we studied the initial components of the DMBA—PGE—PD catalytic systems and also the binary and ternary mixtures based on them by IR and ^{1}H NMR spectroscopy. We found that the IR spectra of the initial mixture with [DMBA]=[PGE]=[P] = 0.5 mol L^{-1} in dichloromethane or chlorobenzene exhibit bands due to free phenol hydroxyl (3580 cm^{-1}), phenol hydroxyl bound to another one through a hydrogen bond (3400 cm^{-1}), and phenol hydroxyl bound to tertiary amine (3200—1600 cm^{-1}). Over a period of 24 h, the intensities of the bands corresponding to free and self-associated phenol hydroxyls decrease, whereas absorption of phenol hydroxyl bound through a strong hydrogen bond to an electron donor (3200—1600 cm^{-1}) increases (Fig. 2). The intensities of bands corresponding to epoxy groups (865, 917, 3020, and 3100 cm^{-1}) decrease over this period of time by 50 %.

These data are consistent with the results of ^{1}H NMR spectroscopy, which indicate that, in the case where phenol is used as the PD, after 24 h at room temperature, the reaction mixture of the composition [DMBA]=[PGE]=[P] = 0.5 mol L^{-1} in dichloromethane contains ~50 % of the initial amine and phenylglycidyl ether, while the other 50 % are bound into ternary complex **1**, which is a type of quaternary ammonim base.



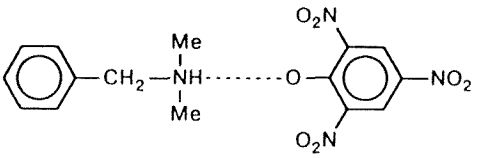
1

In addition to the singlets with δ = 2.12 and δ = 3.32 due to the H_3CN and CH_2N groups, respectively, of the initial amine, the ^{1}H NMR spectrum of the mixture exhibits new signals with δ = 2.70 and 2.78 corresponding to H_3CN and with δ = 4.41 and 4.47 corresponding to CH_2N. This is caused by the formation of a diastereotopic center at the nitrogen atom. The structure

of the complex formed will be discussed in detail in a subsequent paper.

In the case of more acidic *p*-NP, the same process occurs but its rate is lower. When TNF is used as the proton donor, the situation observed under the same conditions is quite different. The spectra of the initial ternary mixture of the composition [DMBA]=[PGE]=[TNP] = 0.5 mol L^{-1} in chlorobenzene and dichloromethane exhibit no bands due to free or self-associated phenol hydroxyls. These bands are also missing from the IR spectra of solutions of TNP in chlorobenzene or dichloromethane. This may be due to the formation of an intramolecular hydrogen bond. However, the spectrum of the ternary mixture incorporating TNP, unlike that of the mixture with phenol, exhibits a very intense band at 3200—1600 cm^{-1} with a maximum at 2700 cm^{-1}. Apparently, this indicates that the TNP proton has passed to the tertiary amine, giving a salt.

The data obtained are in full agreement with the results of ^1H NMR spectroscopy, according to which salt complex **2** of TNP with a tertiary amine is formed in a quantitative yield in a mixture of the composition [DMBA]=[PGE]=[TNP] = 0.5 mol L^{-1} in dichloromethane over a period of 24 h at room temperature (instead of the singlets with δ 2.12 and δ 3.32 corresponding to the $H_3C—N$ and $CH_2—N$ groups of the initial amine, respectively, new signals of $H_3C—N$ with δ 2.76 and 2.78 and of $CH_2—N$ with δ 4.17 and 4.19 and a broad signal with δ 10.74, corresponding to the proton at the nitrogen atom, appear in the spectrum). The ^1H NMR signals associated with the initial DMBA molecule completely disappear, whereas those due to PGE remain unchanged.



2

Previously it has been shown by X-ray diffraction analysis[6] that in the complex of 2,4,6-TNP with DMBA, complete charge separation occurs, accompanied by migration of the proton to the nitrogen atom of the tertiary amine and by the formation of a V-shaped hydrogen bond between the ammonium group and the picrate anion (Fig. 3).

However, if the equimolar ternary mixture is preliminarily heated for 5 min at 120 °C without a solvent and is then dissolved in dichloromethane in the concentrations [DMBA]=[PGE]=[TNP] = 0.5 mol L^{-1}, the picture changes. According to ^1H NMR spectra, the mixture contains small amounts of unreacted PGE and small amounts of the DMBA—TNP binary complex. The main bulk of the components are incorporated into a ternary complex similar to the above-described complex **1**, which is formed in the case of phenol. The [DMBA—PGE—TNP] : [DMBA—TNP] ratio between the ternary and binary complexes in the reaction mix-

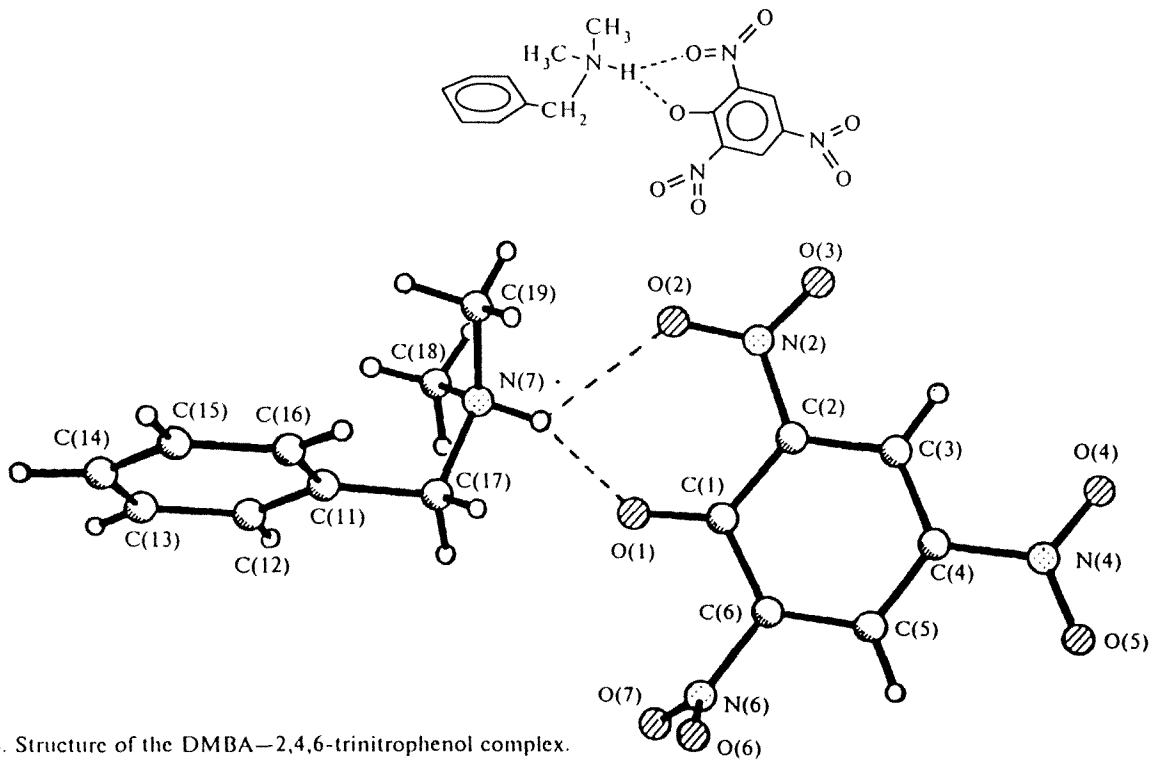


Fig. 3. Structure of the DMBA—2,4,6-trinitrophenol complex.

ture is 2 : 1. Unlike complex **1**, the ternary complex based on TNP does not efficiently promote cyclotrimerization of isocyanate even on prolonged heating (12 h at 140 °C). It can be suggested that the presence of strong electron-withdrawing substituents in the benzene ring substantially decreases the reactivity of the phenoxide anion due to polarization of the bonds and distribution of the charge among several atoms, thus transforming it from a "point" charge into a "delocalized" charge. As a consequence, the catalytic activity of the complex substantially decreases.

Thus, in the present work we studied the effect of proton donors (a series of phenols of various acidities) on the catalytic activity of DMBA—PGE—PD complexes and on the rate of cyclotrimerization of phenyl isocyanate, and also studied the structure of these complexes by IR and ^{1}H NMR spectroscopy. We showed that the presence of strong electron-withdrawing substituents in the phenolic ring of the PD considerably decreases the rate of cyclotrimerization of phenyl isocyanate in the presence of the catalytic complexes.

The authors are grateful to V. I. Bakhmutov for recording and interpretating the ^{1}H NMR spectra.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Projects No 95-03-09160 and 93-03-18044).

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Received December 29, 1995