Nature of the active center in the cyclotrimerization of isocyanates catalyzed by the tertiary amine—α-oxide—protondonor system

2.* Composition and structure of the dimethylbenzylamine—phenylglycidyl ether—phenol complex

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The structure of the dimethylbenzylamine (DMBA)—phenylglycidyl ether (PGE)—phenol complex was studied by IR and ^{1}H NMR spectroscopy under various conditions of its formation. The active catalyst in the cyclotrimerization of isocyanates is a complex of composition DMBA : PGE : PhOH = 1 : 1 : 2, in which the oxygen atom of the zwitter-ion $PhCH_2N^+Me_2CH_2CH(O^-)CH_2OPh$ that forms after opening of the epoxide cycle is bound to two phenol molecules by a very strong hydrogen bonds. In this complex, the oxygen atom of both the zwitter-ion and the phenolate anion can be catalytic centers. Two schemes of the cyclotrimerization of isocyanate in the presence of the aforementioned catalytic system are suggested, depending on whether the catalytic complex has time to form or not.

Key words: cyclotrimerization of isocyanates, catalytic complex, hydrogen bonds, active center.

The nature of the active center in the cyclotrimerization of isocyanates in the presence of the tertiary amine—α-oxide—proton donor catalytic system is open to dispute.

In the previous work, for several phenols of different acidities,[1] we studied the effect of a proton donor on the rate of cyclotrimerization of phenyl isocyanate in the presence of the aforementioned catalytic systems and performed some studies of the structure of the complexes formed. The purpose of this work is to study in detail the composition and structure of the tertiary amine—α-oxide—proton donor complex using the dimethylbenzylamine—phenylglycidyl ether—phenol system under various conditions of formation of the complex and reactions occurring in the medium of isocyanate under the action of the given catalytic system.

Experimental

IR spectra were recorded on M-80 and Perkin-Elmer 457 spectrometers and on Bruker ISF-25 and Bruker ISF-113v IR Fourier spectrometers. Solutions were registered in a 0.054 mm KBr cell as KBr pellets.

^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer at a frequency of 200.13 MHz in methylene dichloride.

Initial substances were purified by distillation *in vacuo* or by recrystallization to obtain compounds corresponding to the published data.

Results and Discussion

It is known that phenol forms H-bonded complexes with tertiary amines. In the IR spectrum, the interaction between the amine and phenol molecules is manifested as a substantial change in both the vibrational frequencies and the intensities of the absorption bands of both molecules. When the H-complex decomposes under the action of additional reagents, the spectrum changes substantially.

The IR spectrum of the amine—phenol mixture ([DMBA] = [PhOH] = 0.5 mol L^{-1} in a solution of methylene dichloride) contains bands of the N...H—OPh associate (a very broad absorption in the 3600 to 1600 cm^{-1} region, bands of free OH groups of phenol at 3580 cm^{-1}, and bands of the phenol self-associate at 3400 cm^{-1}. The estimation performed using model solutions of phenol in methylene dichloride showed that the content of free and self-associated phenols in the initial solutions of the two-component and three-component mixtures is ~20 % of the total amount of phenol in the solution, while 80 % is bound to the amine by strong donor-acceptor interaction. When PGE is added to the binary mixture ([DMBA] = [PhOH] = [PGE] = 0.5 mol L^{-1}), at first the picture in the region of stretching vibrations of OH groups remains almost the same as in

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* For Part 1, see Ref. 1.

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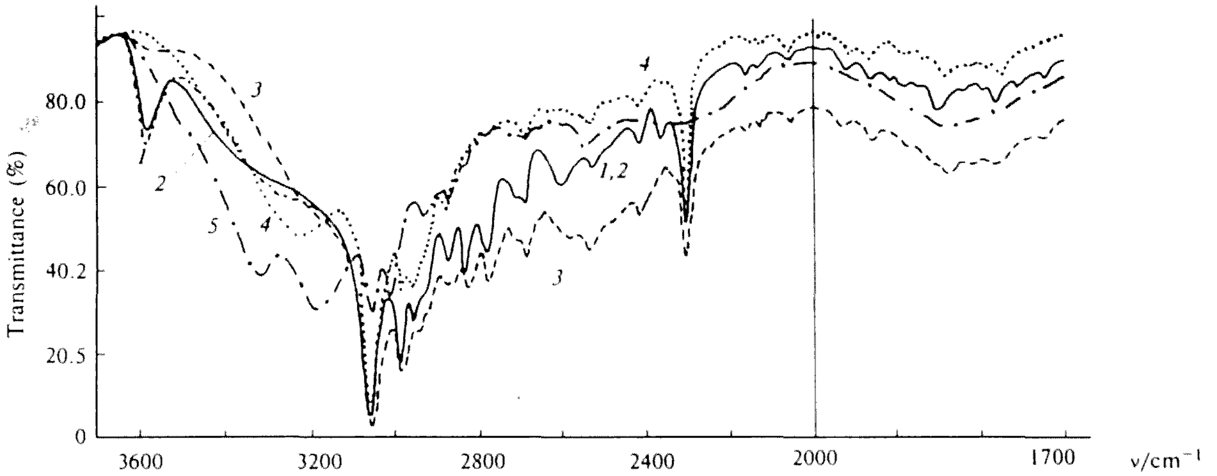


Fig. 1. IR spectra of CH_2Cl_2 solutions of a mixture containing [PhOH] = [DMBA] = 0.5 mol L^{-1} (*1*), of a freshly prepared mixture of [PhOH] = [DMBA] = [PGE] = 0.5 mol L^{-1} (*2*), the same mixture 24 h after preparation (*3*), after the addition of water to the solution exposed more than 24 h (*4*), and crystals of hydrate of the cation-anion complex PhOH : DMBA : PGE = 1 : 1 : 1 (mol. ratio) (*5*).

the two-component system, then the intensity of the band of the free OH group of phenol decreases somewhat, and a small absorption with a maximum at 3450 cm^{-1} appears, which is caused by the stretching vibrations of the OH groups bound to oxygen atoms of PGE by hydrogen bonds. The spectrum in the 3000 to 2700 cm^{-1} region simultaneously indicates an increase in the content of free amine, because a portion of the phenol is consumed to form the hydrogen complex with PGE.

Thus, the addition of PGE to the binary mixture at first slightly affects the H bonds typical of the binary system and caused by the strong donor-acceptor amine—phenol interaction. The situation gradually begins to change with time. As can be seen from the spectra in Fig. 1 (curves *1* and *2*) and Fig. 2, *a*, the bands corresponding to vibrations of free (3580 cm^{-1}) and self-associated (3400 cm^{-1}) OH groups of phenol begin to decrease. At the same time, the intensity of the broad band at 3000 to 1600 cm^{-1} caused by the formation of a strong hydrogen bond increases, and the intensities of the bands typical of the α-oxide ring (915 and 865 cm^{-1}) decrease. The strongest changes occur during the first 10 h, then the reaction rate decreases, and the reaction ceases after 1 day. In the IR spectrum, the bands of OH groups of free and self-associated phenol molecules almost disappear, and the intensity of the bands of epoxide

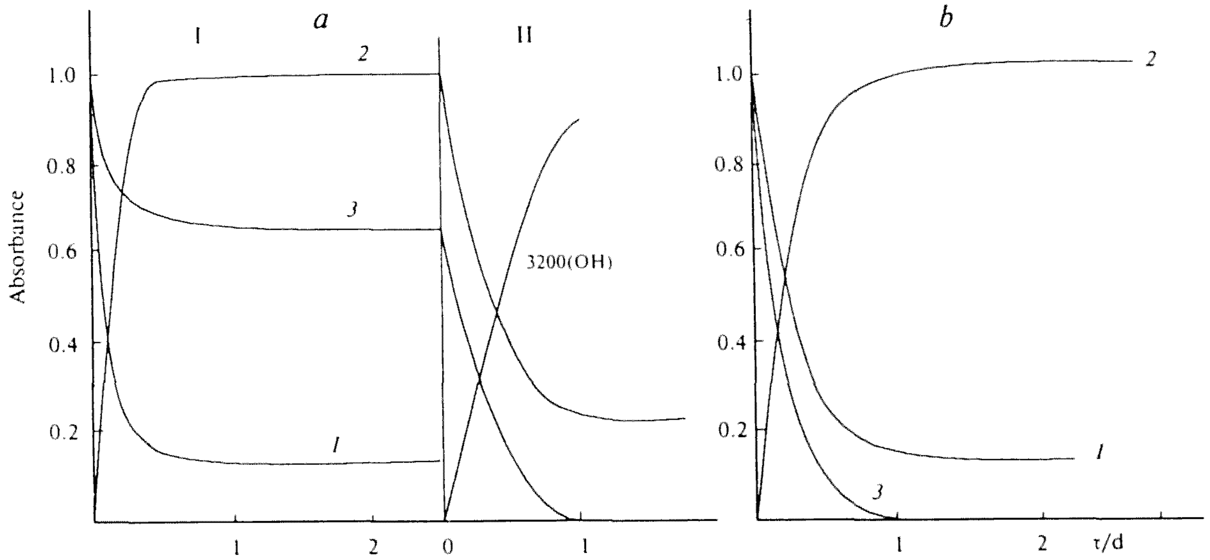


Fig. 2. Changes in the optical densities of bands of stretching vibrations of free OH groups of phenol (3580 cm^{-1}, curve *1*) and associated phenol (2600 cm^{-1}, curve *2*) and bands of epoxide groups (915 cm^{-1}, curve *3*) during the formation of the complex in a CH_2Cl_2 solution. Molar ratio PhOH : PGE : DMBA, 1 : 1 : 1 (*a*), 2 : 1 : 1 (*b*) before (I) and after addition of water (II). *a*, [PhOH] = [DMBA] = [PGE] = 0.5 mol L^{-1}; *b*, [PhOH] = 1.0 mol L^{-1}, [DMBA] = [PGE] = 0.5 mol L^{-1}.

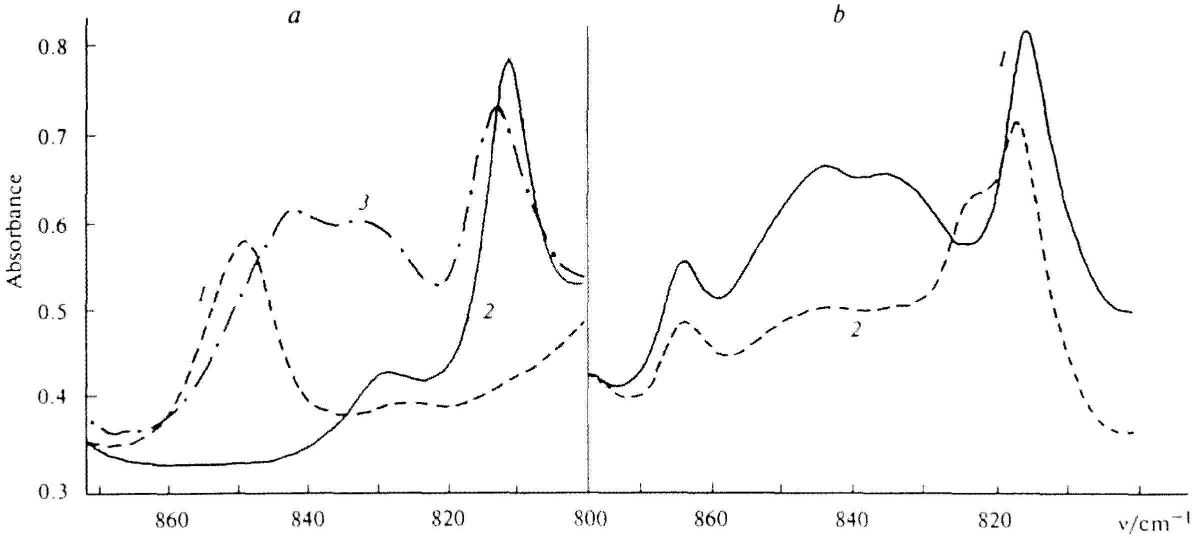


Fig. 3. IR spectra of solutions in CH_2Cl_2: *a*, DMBA (*1*), phenol (*2*), mixture [PhOH] = [DMBA] = 0.5 mol L^{-1} (*3*); *b*, freshly prepared mixture [PhOH] = [DMBA] = [PGE] = 0.5 mol L^{-1} (*1*), 7 h after preparation (*2*).

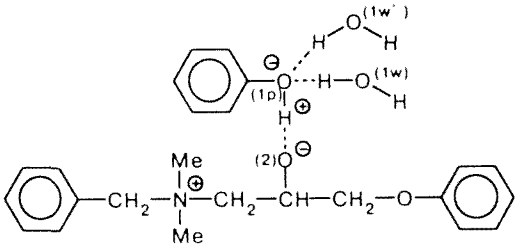
groups decrease by 50 % (Fig. 2, *a*). In addition, the band at 840 cm^{-1}, which characterizes the existence of the amine—phenol complex, disappears completely after 1 day. As can be seen from Fig. 3, *a*, this band does not occur in the individual spectra of amine and phenol and appears in the spectrum of their H-associate. It is also present in the freshly prepared trinary system (Fig. 3, *b*), but dramatically decreases with exposure time. Therefore, the intense increase in absorption in the region from 3000 to 1600 cm^{-1} is caused by the strong H bond in a complex different from the amine—phenol complex.

The study of hydrogen bonding of phenol with various bases shows that in strong H-complexes (ΔH > 6 kcal mol^{-1}) the absorption band of the stretching vibrations of the OH group has a complex structure caused by the Fermi-resonance perturbation of νOH by vibrations inherent in phenol.[2—5] The complex contour has several maxima, with four broad bands with maxima at 2800—2900 cm^{-1} (band A), 2500—2600 cm^{-1} (band B), 1850—1900 cm^{-1} (band C), and 1100 cm^{-1} (band D).[6,7] The frequencies of the A, B, C, and D bands depend slightly on the bond in the complex and the nature of the base, while their intensities, by contrast, change substantially as the strength of the H bond changes, increasing in the order A→B→C→D as the strength increases. In our case, as can be seen from Fig. 1 (curves *1* and *2*), the intensities of the longer-wave components of the B and C bands (OH) increase more noticeably, which also confirms the formation of a different and stronger H bond. The change in intensity of the band of the stretching vibrations of the OH groups bound in a strong H-complex is shown in Fig. 2 (the intensity was measured at the maximum of the B band at 2600 cm^{-1}).

These data agree with the data of the ^1H NMR spectra, according to which after 1 day in a reaction mixture of composition [DMBA] = [PhOH] = [PGE] = 0.5 mol L^{-1} in a methylene dichloride solution at room temperature ~50 % of the initial amine and PGE remains and ~50 % is bound in a triple complex similar to a quaternary ammonium base. This is confirmed by the appearance of two singlet signals of methyl groups at 2.70 and 2.78 ppm in the ^1H NMR spectrum caused by the formation of a diastereotopic center on the nitrogen atom.

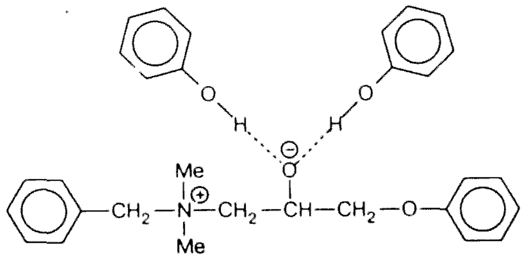
Based on the quantitative evaluation of the IR and ^1H NMR spectra of the reagents consumed to form the complex, it can be assumed that two phenol molecules, one DMBA molecule, and one PGE molecule are in the composition of the complex. To confirm this supposition, PGE was added to a mixture of phenol and DMBA in methylene dichloride in such a way that the concentrations were the following: [PhOH] = 1 mol L^{-1}, [DMBA] = [PGE] = 0.5 mol L^{-1}. The regularities observed in this case were the same as in the case of the mixture [PhOH] = [DMBA] = [PGE] = 0.5 mol L^{-1}. However, all components react quantitatively (Fig. 2, *b*), which confirms the composition of the complex PhOH : DMBA : PGE = 2 : 1 : 1 (mol, in a solution of methylene dichloride).

As mentioned above, when the ratio of the reagents is 1 : 1 : 1, the formation of the PhOH—DMBA—PGE complex is completed in 1 day. Then the situation remains unchanged for a long time if the reaction system contains no moisture. When moisture is introduced to the system (Fig. 1, curve *1* and Fig. 2, *a*), the intensities of the bands at 915 and 865 cm^{-1}, caused by vibrations of the α-oxide cycles, decrease until they completely disappear. The intensity of the band of the strong hydrogen bond at 3000 to 1600 cm^{-1} decreases, and a new band of the H-bonded OH groups at 3200 cm^{-1} appears and increases (Fig. 1, curve *3* and Fig. 2, *a*). When the amount of absorbed water is sufficiently large, crystals begin to precipitate from the solution. The IR spectrum of these crystals has been obtained (Fig. 1, curve *4*) and they have been studied by X-ray diffraction analysis.[8] The crystals are the monohydrate of the cation-anion associate PhOH : DMBA : PGE = 1 : 1 : 1 (**1**). The cation of the associate forms a comparatively strong and almost symmetric hydrogen bond with the phenoxide counterion due to the hydroxyl group. In the IR spectrum, this bond is manifested as a complex band at 3700 to 1600 cm^{-1} (Fig. 1, curve *4*). The distances are the following: O(2)...O(1p), 2.514(8) Å; O(2)...H(2), 1.35(3) Å; and O(1p)...H(2), 1.21(3) Å; the O...H...O angle is 159(5)°.[8] A somewhat weaker and less symmetric hydrogen bond is formed between the phenoxide anion and the solvate water molecule: O(1p)...O(1w), 2.698(9) Å; O(1p)...H, 1.50(3) Å; and O(1w)...H, 1.27(3) Å; the O...H...O angle is 155(5)°.[8] In the IR spectrum, this hydrogen bond manifests itself as a band at 3160 cm^{-1}. The strong monohydrate complexes are united in centrisymmetric dimers due to the weaker O(1p)...HO(1w') hydrogen bonds, where O(1p)...O(1w') is 2.843(9) Å, O(1p)...H is 2.03(3) Å, and the O—H...O angle is 163(5)°.[8] In the IR spectrum, this hydrogen bond is manifested as a band at 3300 cm^{-1} (Fig. 1, curve *4*). Thus, in a crystal the phenolate O(1p) atom acts as a strong acceptor of three hydrogen bonds. This may be one of the main reasons why the complex crystallizes only in the presence of traces of water: only in this case is there a sufficiently complete saturation of the coordination sphere of the phenolate group.



1

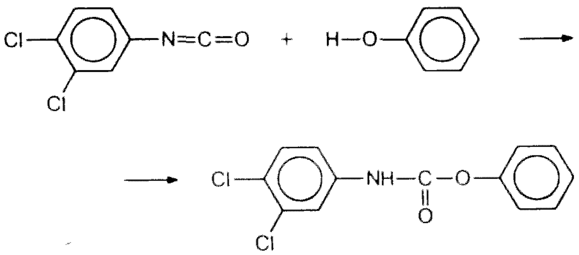
A complex of composition PhOH : DMBA : PGE = 2 : 1 : 1 (mol. ratio) is formed in a solution of methylene dichloride or chlorobenzene in the absence of water. Two phenol molecules form hydrogen bonds with the zwitter-ion, which, judging from their manifestation in the IR spectrum, are identical in nature and strength. This can be hypothetically presented by structure **2**.



2

It is likely that this complex of composition PhOH : DMBA : PGE = 2 : 1 : 1 (mol. ratio) possesses catalytic properties. It is also formed with an equimolar ratio of initial components in methylene dichloride, but, as has been shown above, ~50 % of the initial DMBA and PGE remain unreacted. Complex **1** of composition 1 : 1 : 1, with a water molecule in the coordination sphere of phenol, exhibits weak catalytic activity, which is likely related to loss of solubility and blocking of the phenolate anion with water. In soluble complex **2**, which has two phenol molecules, both the oxygen atom of the zwitter-ion and the O atom of the phenolate anion can be active centers.

We attempted to follow the changes in the reaction medium in the reaction of isocyanate with the studied catalytic system. 3,4-Dichlorophenyl isocyanate (IC) was chosen as a model. When a freshly prepared solution of a mixture of the components of the catalytic system (catalytic complex **2** has not yet been formed) is added to a solution of IC ([DMBA] = [PGE] = [PhOH] = [IC] = 0.5 mol L^{-1} in methylene dichloride), the IR spectrum has bands belonging to vibrations of the urethane fragment, in particular, stretching vibrations of carbonyl at 1752 cm^{-1} (Fig. 4, *a*, curve *1*), *i.e*, the known reaction of addition of PhOH to IC occurs in the reaction mixture, and the conversion of IC is quantitative.



The situation remains unchanged for 1 h, and no trimerization is observed (Fig. 4, *b* and *c*, curves *1*). Neither is the cyclic trimer (1420 and 1720 cm^{-1}) formed after 1 day.

The formation of urethane is also observed when a solution of PhOH is added to a solution of IC ([PhOH] = [IC] = 0.5 mol L^{-1}). In two min (time of pouring the initial solutions together, filling a cell, and the spectrum is recorded on a Bruker IFS-25 spectrometer) ~50 % of the initial PhOH and IC remain, and 50 % of them are bound in urethane. In the presence of tertiary amine, PhOH completely reacts with IC in the same amount of time to form urethane ([DMBA] = [PhOH] = [IC] = 0.5 mol L^{-1} in methylene dichloride). When the triple catalytic system is stored for 10 min after preparation ([DMBA] = [PGE] = [PhOH] = [IC] = 0.5 mol L^{-1} in methylene dichloride) and then added to IC, almost only urethane is formed; however, the trimer is also formed, but does not make up more than 5 % of the yield. When the triple catalytic system is stored for 3.5 h

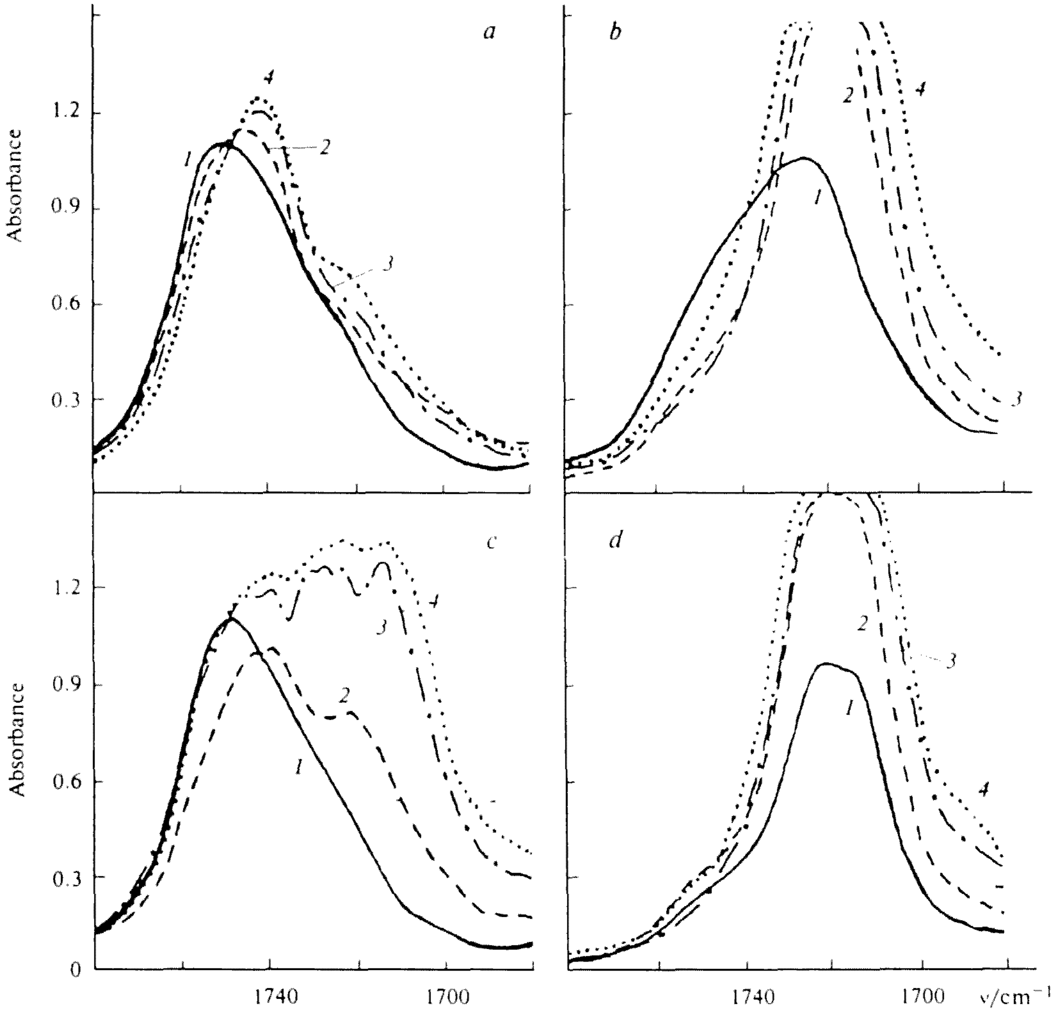


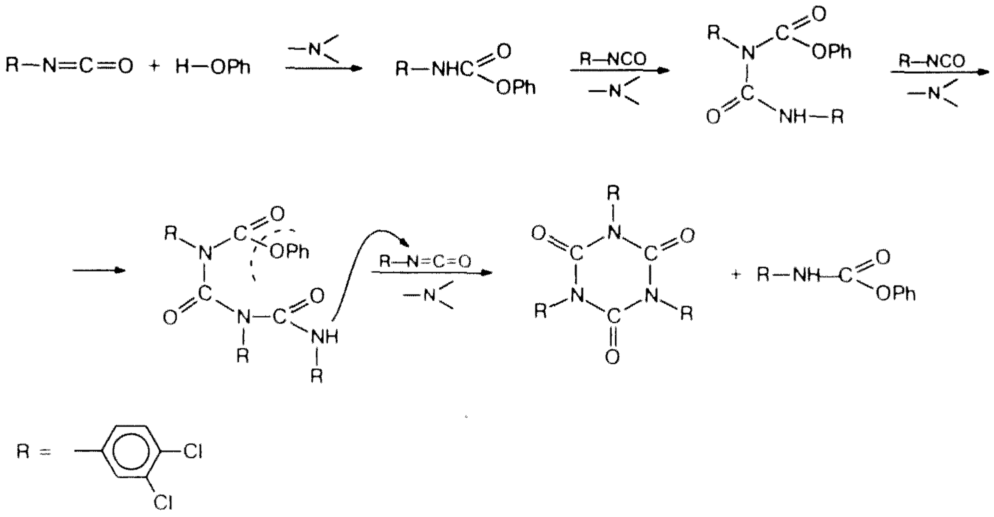
Fig. 4. IR spectra in the region of the frequencies of stretching vibrations of C=O of the mixture [PhOH] = [DMBA] = [PGE] = 0.5 mol L^{-1} in a CH$_2$Cl$_2$ solution. [IC], mol L^{-1}: 0.5 (*1*), 1.0 (*2*), 1.5 (*3*), and 2.0 (*4*). *a*, 2 min after preparation of the four-component mixture; *b*, 15 min after preparation of the four-component mixture; *c*, 4 h after preparation of the four-component mixture; *d*, after preliminary storage of a solution of the triple catalytic system PhOH : DMBA : PGE = 1 : 1 : 1 (mol. ratio) for 1 day before addition of IC.

and then added to IC, the formation of urethane and trimer is observed. The amount of urethane formed (~30 %) corresponds to the amount of phenol that did not form a stable associate with DMBA and PGE in this time. When the triple equimolar mixture is stored for 1 day, *i.e.*, when all of the phenol is bound in stable associate **2** and then added to IC, almost only trimer is formed immediately, based on the appearance of intense bands in the 1720 and 1420 cm^{-1} region (Fig. 4, *d*), and the amount of urethane is <5 %.

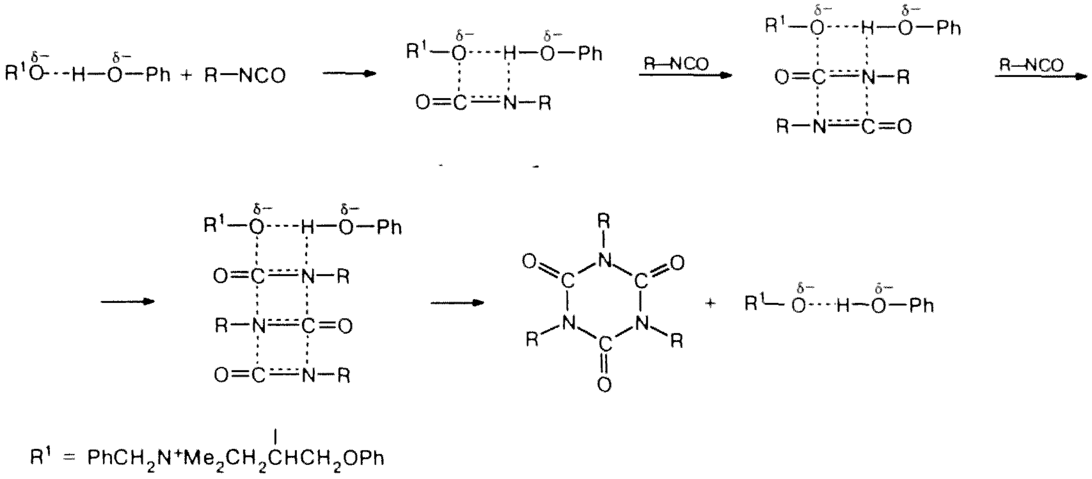
Thus, the reaction of isocyanate with phenol resulting in the formation of urethane is accelerated in the presence of tertiary amine; cyclotrimerization of IC occurs when complex **2** (PhOH : DMBA : PGE = 2 : 1 : 1, mol. ratio) is formed in the reaction mixture. The cyclotrimerization of isocyanate occurs immediately when complex **2** is added to excess (two-, three-, and fourfold) isocyanate. The IR spectrum contains absorption bands only of the isocyanurate cycle, and no formation of intermediate products is observed (Fig. 4, *d*).

When the freshly prepared equimolar triple mixture in methylene dichloride is added to the same excess IC, the formation of urethane (1752 cm^{-1}, Fig. 4, *a*) is observed within 2 min, and some amount of isocyanate (a band at 2268 cm^{-1}) remains unreacted. The isocyanate is completely consumed in 15 min, and new bands of the stretching vibrations of C=O appear in the IR spectrum in the 1700 to 1750 cm^{-1} frequency range. The greater the excess of isocyanate, the more bands are observed, and the yield of the trimer is low (Fig. 4, *b*). A longer time (~4 h, Fig. 4, *c*) is necessary for the formation of the trimer. Thus, when excess IC is used, the trimer is also formed in the presence of the freshly prepared catalytic system, but the reaction occurs considerably more slowly than in the case of complex **2**. The scheme of the reactions for the IC

Scheme 1



Scheme 2



catalysis in the first case can be presented as follows (Scheme 1).

The reaction of IC with PhOH catalyzed by tertiary amine occurs at the first stage to form urethane. Then the second molecule of IC is added to form allophanate, then the third and fourth molecules are added followed by the isolation of the cyclotrimer and the initial urethane.

The reactions of the cyclotrimerization of IC catalyzed by formed complex **2** can be presented by Scheme 2. As has been established above, a very strong H bond, which prevents the reaction of phenol with IC, is formed between the zwitter-ion and phenol. This H bond is very polar; therefore, catalytic complex **2** exerts an intense polarizing effect on the adjacent IC molecules. The polarization results in the redistribution of the charge on IC molecules and the fast formation of dipole-dipole associates with one, two, and three IC molecules. Rearrangement accompanied by the formation of a more energetically favorable cyclic trimer is possible at this stage.

Thus, in the presence of the freshly prepared DMBA—PGE—PhOH mixture, the trimerization of IC occurs *via* the formation of urethane catalyzed by tertiary amine followed by the addition of the other IC molecules to form the cyclic trimer. The DMBA : PGE : PhOH = 1 : 1 : 2 complex that forms a very strong and polar H bond induces the formation of dipole-dipole associates of IC molecules, which favors very fast trimerization resulting in the formation of the isocyanurate cycle.

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