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## BRIEF COMMUNICATIONS

# IR SPECTROSCOPY METHOD FOR DETERMINING THE REACTIVITY OF ISOCYANATE GROUPS IN ISOPHORONE DIISOCYANATE REACTIONS

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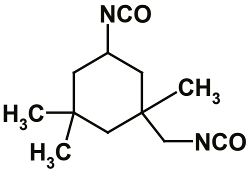
*We have developed a fast IR spectroscopy method for determining the concentrations of cycloaliphatic and aliphatic isocyanate groups in isophorone diisocyanate that react to form urethanes. It is based on the experimentally established fact that there is a difference between the frequencies of the stretching vibrations for the N–H bond in urethanes formed by cycloaliphatic and aliphatic isocyanate groups in isophorone diisocyanate, when the IR spectra are recorded for dilute solutions of the reaction mixture in carbon tetrachloride. The method can be used to determine the reactivity of isocyanate groups in different reactions involving isophorone diisocyanate.*

***Keywords:*** *isophorone diisocyanate, IR spectroscopy method, reactivity, urethane, aliphatic and cycloaliphatic isocyanate groups.*

**Introduction.** A major feature of isophorone diisocyanate (IPDI) is the presence in the molecule of aliphatic and cycloaliphatic NCO groups, located on primary and secondary carbon atoms:



The isocyanate groups of IPDI, depending on the synthesis conditions, may exhibit different reactivity, characterized by the ratio of the corresponding kinetic rate constants for reactions of the cycloaliphatic and aliphatic NCO groups.

A limited number of publications have been devoted to study of the reactivity of NCO groups in IPDI [1–3], using NMR ($^1$H and $^{13}$C) [1, 2] and gas chromatography [3]. The IR spectroscopy method, which is broadly applicable and very convenient for studying chemical reaction kinetics and identifying structures of synthesized compounds, has not been previously used to determine differences in reactivity of the NCO groups in IPDI. This is associated with the fact that the bands for asymmetric stretching vibrations of aliphatic and cycloaliphatic NCO groups overlap in the 2270 cm$^{-1}$ region and it is impossible to draw a conclusion concerning which of them is involved in the reaction. We should point out that the IR spectroscopy method does not require expensive solvents, is simple to use, and makes it possible to carry out fast analyses. Accordingly, in this paper we propose an IR spectroscopy method for determining the concentrations of cycloaliphatic and aliphatic NCO groups, allowing us to establish the differences between the reactivities in the course of reactions involving participation of IPDI.

**The Experiment.** We used the isocyanates IPDI and cyclohexyl isocyanate (CHI) (Aldrich), which were purified by distillation at 60°C ($2 \cdot 10^{-2}$ torr) and 50°C (20 torr). The NCO group content, determined by a chemical method [4], was 99.9% of the theoretical value. The alcohols were 1-propanol (PA), 2-propanol (IPA), and the solvents were purified before

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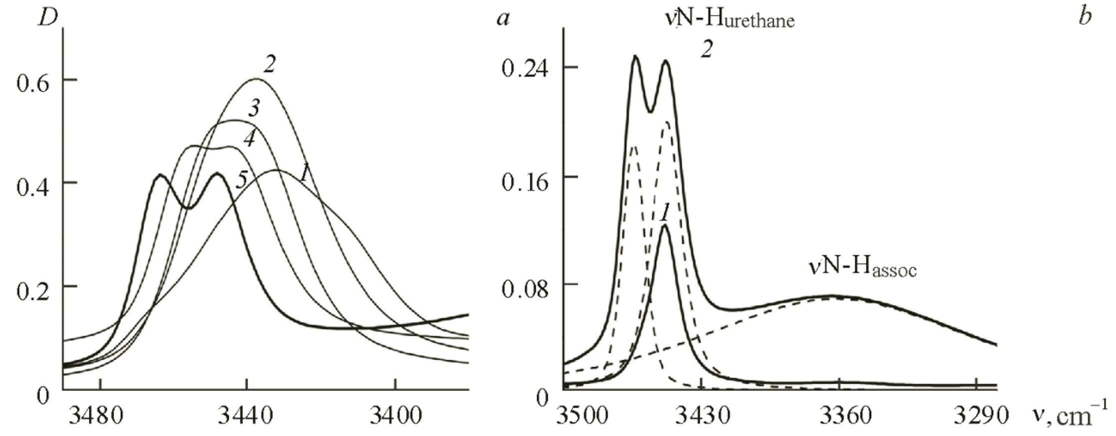

Fig. 1. IR spectra of urethanes: a) IPDI–IPA in toluene (1), dichloroethane (2), methylene chloride (3), chloroform (4), and $CCl_4$ (5); b) CHI–IPA (1) and IPDI–IPA (2) in the $\nu_{N-H}$ absorption region, with decomposition into component bands (dashed lines).

use and dried by standard methods [5]. 1,3-Diazidopropan-2-ol (DAPOL) was synthesized by the procedure in [6]; according to IR spectroscopy and $^1$H NMR data, the purity was ≥ 98.0%.

All the IR spectra were recorded on an ALPHA (Bruker) Fourier transform IR spectrometer in the 4000–1000 $cm^{-1}$ range, number of scans equal to 16, resolution 4 $cm^{-1}$, $T = 23°C$. For quantitative measurements, we recorded the IR spectra of solutions of the compounds in special $CaF_2$ cuvets of thickness 0.01, 0.0583, and 0.1 cm.

The overlapping bands in the IR spectra were separated using the program OPUS 6.5. As the input parameters for decomposition of the IR spectra, we used the frequencies of the maxima and the half-widths of the corresponding bands, determined experimentally. The residual root mean-square deviations of the envelopes (obtained by summing the separate bands) from the experimental values was no greater than $3 \cdot 10^{-3}$.

**Results and Discussion.** The method was developed in connection with the need to determine the differences in reactivity of aliphatic and cycloaliphatic NCO groups in IPDI. Considering that one of the urethane groups formed is located on a primary carbon atom while the other is located on a secondary carbon atom, we might expect this structural difference to show up as a doublet in the absorption region of the stretching vibrations of the NH groups. Accordingly, we carried out IR spectral analysis of solutions of previously synthesized urethanes, based on IPDI and the studied alcohols (PA, IPA, DAPOL), in different solvents: toluene, dichloroethane, methylene chloride, chloroform, and carbon tetrachloride ($CCl_4$) (Fig. 1a). As a result of analysis of the IR spectra, we established that the absorption bands corresponding to stretching vibrations of the NH groups ($\nu_{N-H}$) of the cycloaliphatic and aliphatic urethane groups for IPDI have different frequencies (a distinct doublet, $\Delta\nu = 16$ $cm^{-1}$) only for solutions in $CCl_4$ (curve *5*). Consequently, using $CCl_4$ as the solvent for analysis of the reaction mixture allows us to determine the concentration of NH groups of the urethanes derived from IPDI, formed with participation of cycloaliphatic and aliphatic NCO groups.

Figure 1b shows the separation of the overlapping bands in the $\nu_{N-H}$ absorption region of urethane obtained in reaction of IPDI with IPA. In order to assign the vibrations characteristic for $\nu_{N-H}$ of cycloaliphatic and aliphatic urethane derived from IPDI, we used the IR spectra of solutions in $CCl_4$ of model urethanes based on CHI reacted with PA and IPA, in connection with the fact that in the molecule of the monoisocyanate CHI, there is only one cycloaliphatic NCO group analogous to that group in IPDI. The stretching vibrations of the NH groups of urethanes obtained with participation of CHI, characterized by a frequency of ~3446 $cm^{-1}$, correspond to a cycloaliphatic urethane group. From this it follows that in the spectra of urethanes derived from IPDI, the band at 3446 $cm^{-1}$ is assigned to cycloaliphatic urethane, while the band at 3462 $cm^{-1}$ is assigned to aliphatic urethane (Fig. 1b).

Therefore, based on the data obtained on assignment of the absorption bands characteristic for cycloaliphatic and aliphatic urethane groups, we can calculate the concentrations of the different NCO groups in IPDI and their ratio according to the following procedure.

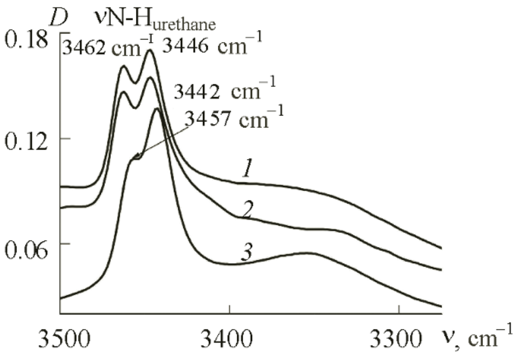

Fig. 2. Comparison of the IR spectra of the reaction mixture for the non-catalytic reaction of IPDI with different alcohols: 1) PA, 2) IPA, 3) DAPOL; conversion ~30%.

1. Before the experiment, use the spectra of solutions in $CCl_4$ of urethanes with 100% conversion of the NCO groups to determine the parameters of the $\nu_{N–H}$ bands (cycloaliphatic and aliphatic) for urethanes derived from IPDI: molar extinction coefficient, absolute integrated intensities of these bands, and their ratio.

2. Dissolve a reaction test sample (with experimentally determined total conversion of the isocyanate groups) in $CCl_4$, where the concentration of the substance should be ≤0.05 g-eq/L, calculated on the basis of the initial concentration of NCO groups.

3. In a cuvet of thickness > 0.6 mm, record the IR spectrum in the range 4000–2500 $cm^{-1}$.

4. Using the program for separating overlapping bands, decompose the IR spectrum into individual bands corresponding to the $\nu_{N–H}$ of urethanes based on cycloaliphatic and aliphatic NCO groups.

5. Based on the intensities and molar extinction coefficients of the absorption bands for the corresponding $\nu_{N–H}$ of the urethanes, calculate the ratios of the concentrations of the cycloaliphatic and aliphatic urethane groups.

6. Determine the concentrations of the cycloaliphatic and aliphatic NCO groups of isophorone diisocyanate that participated in the urethane formation reaction, from the ratio of the concentrations determined above, the total conversion, and the balance equations.

We must note that for a ratio of the intensities of the overlapping bands in the IR spectrum <4, according to the reproducibility of the results the uncertainty in the concentration ratios found is ≤5%. As this ratio increases, the uncertainty increases and can be as high as 10%–20%.

This procedure can be used in studying the characteristics of not only urethane formation but also other reactions involving NCO groups of IPDI (urea formation, trimerization, dimerization, etc.). To do this, we need to first determine the total conversion of the isocyanate groups at a certain instant of time, then we need to treat a small amount of the reaction mixture with excess alcohol and use the proposed method to find the amount of aliphatic and cycloaliphatic NCO groups of IPDI entering into the urethane formation reaction. Then using the balance equation, we calculate the concentrations of the NCO groups reacted over the course of the studied reaction.

The data obtained allow us to calculate the reaction rate constants separately for the cycloaliphatic and aliphatic NCO groups, and consequently to calculate the differences in reactivity for the isocyanate groups of IPDI. We must note that we can approximately (at a qualitative level) estimate the differences in the reactivities of the NCO groups in IPDI in urethane formation reactions even from the appearance of the IR spectrum of a solution of reaction test samples in $CCl_4$ in the $\nu_{N–H}$ absorption region. As shown by the calculation results, if there is a doublet with distinct separation of bands for conversion 30–50%, then the differences in the observed reaction rate constants for the cycloaliphatic and aliphatic NCO groups in IPDI are <2 (Fig. 2).

**Conclusions.** Our fast IR spectroscopy method for determining the concentrations of cycloaliphatic and aliphatic isocyanate groups of isophorone diisocyanate which have entered into the urethane formation reaction allows us to establish the differences in reactivity of the NCO groups in IPDI in reactions of this isocyanate.

## REFERENCES

1. N. Bialas and H. Hocker, *Macromol. Chem.*, **191**, No. 5, 1843–1852 (1990).
2. K. Hatada, K. Ute, R.-I. Oka, and S. P. Pappas, *J. Polym. Sci. A*: *Polym. Chem.*, **28**, No. 11, 3019–3027 (1990).
3. R. Lomolder, F. Plogmann, and P. Speier, *J. Coat. Technol.*, **69**, No. 868, 51–58 (1997).
4. H. E. Stagg, *Analyst*, **71**, No. 849, 557–559 (1946).
5. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, *Organic Solvents* [Russian translation], Inostr. Lit., Moscow (1958).
6. C. A. V. Werf, R. V. Heisler, and W. E. McEwen, *J. Am. Chem. Soc.*, **76**, No. 5, 1231–1235 (1954).