

MOLECULAR-IONIC TAUTOMERISM OF HYDROGEN BOND COMPLEXES
OF METHYLNITRAMINE WITH ALIPHATIC AMINES

Yu. V. Ulashkevich, N. S. Golubev,
A. G. Bazanov, G. S. Denisov,
and I. V. Tselinskii

UDC 541.127+539.196.3

During the spectroscopic investigation of complex formation between OH acids and amines in inert solvents, it was shown that a molecular-ionic tautomerism is possible in the complexes formed [1, 2]. The process of the tautomeric transformation consists in proton transfer inside a complex with a strong hydrogen bond, and takes place immeasurably fast in the time scale of the PMR method, even at a very low temperature (-170°C). With increase in the acid strength, the tautomeric equilibrium is shifted in the direction of ionic pairs [3].

The equilibrium between the molecular and ionic complexes was also found in systems with hydrogen bond of type $\text{CH}\dots\text{N}$ [4]. In this case, the proton transfer occurs in a very weak hydrogen bond, and its kinetics can be measured at normal temperatures [5]. We should note that the evolution of complex formation from the molecular to the ionic complex with gradual increase in complex strength though tautomeric equilibrium is not general in character. Thus in systems with hydrogen bond of type $\text{OH}\dots\text{O}$, with increase in the complex formation energy, a gradual change in the structure of the complex takes place, which acquires an increasingly ionic character, but up till now no tautomerism has been detected.

Lensovet Leningrad Technological Institute. A. A. Zhdanov Leningrad State University.
(Presented by Academician M. I. Kabachnik February 21, 1977.) Translated from Doklady
Akademii Nauk SSSR, Vol. 234, No. 4, pp. 872-875, June 1977. Original article submitted
February 14, 1977.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

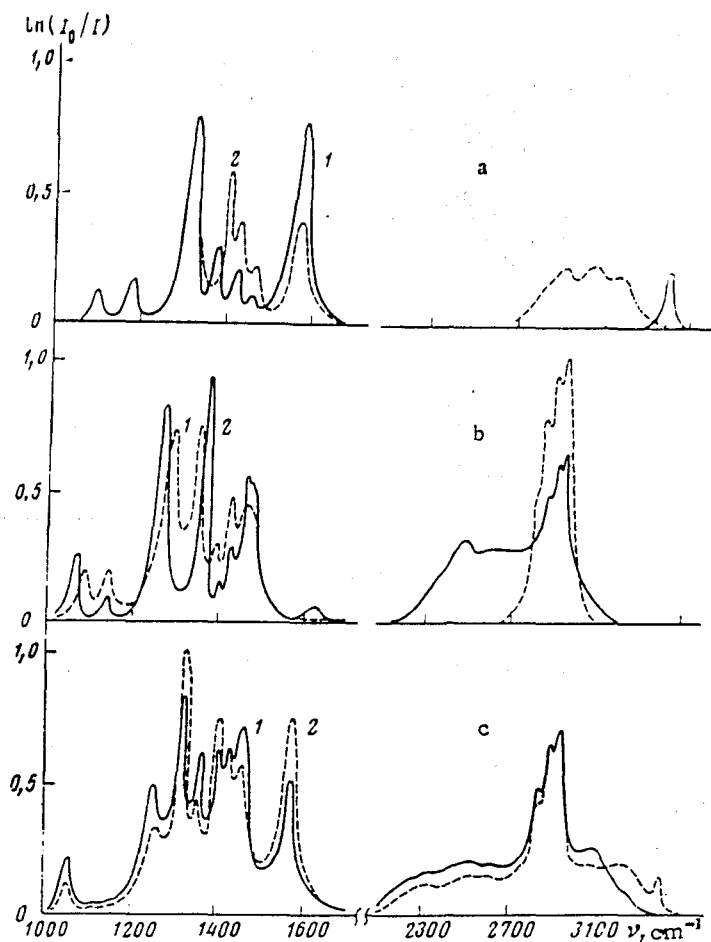


Fig. 1. IR spectra of solutions. a: 1) 0.01 M methylnitramine in CCl_4 and C_2Cl_4 , layer thickness $d = 1.0$ mm; 2) 0.04 M methylnitramine and 0.2 M dimethyl sulfoxide in CCl_4 , $d = 0.3$ mm. b: 1) 0.003 M methylnitramine tetrabutylammonium salt in CCl_4 , $d = 3.0$ mm; 2) 0.04 M methylnitramine and 0.1 M diisooamylamine in C_2Cl_4 , $d = 0.2$ mm. c: 0.1 M methylnitramine and 0.5 mole/liter of tributylamine in C_2Cl_4 , $d = 0.3$ mm: 1) 5° , 2) 50°C .

In the present work, we used IR and PMR spectroscopy to study systems with a $\text{NH}\dots\text{N}$ hydrogen bond to find the type of complex formation. As NH acid, we chose the simplest representative in the nitramine series, methylnitramine, and as proton acceptors we used tertiary and secondary amines. The IR absorption spectra in the $1000\text{--}3600\text{ cm}^{-1}$ region were run on Perkin-Elmer 457 apparatus; the PMR spectra were run on a JEOL C-60 apparatus. At temperatures of $5\text{--}70^\circ\text{C}$, we used tetrachloroethylene as the solvent, and at temperatures of 0 to -170°C , Freon-22 (CHF_2Cl). The technique of the operation in Freon solutions at low temperature has already been described [6]. To interpret the spectra, we used model systems (solutions containing methylnitramine and oxygenated proton acceptors as the models of molecular complexes, and a solution of methylnitramine tetrabutylammonium salt as the model of the ionic pair).

During the reaction between methylnitramine and oxygenated proton acceptors (dimethyl sulfoxide- D_6 , acetone- D_6), as expected, pronounced changes took place in the IR spectrum in the region of the ν_{NH} band (Fig. 1a). Instead of the 3420 cm^{-1} band, corresponding to free molecules, there appears a broad band with a complex form of the contour in the $2800\text{--}3300\text{ cm}^{-1}$ region, which is characteristic of complexes with a hydrogen bond of medium strength. Almost no changes took place in the $1000\text{--}1700\text{ cm}^{-1}$ region. Only a decrease in the integral intensity of the ν_{ANO_2} band at 1585 cm^{-1} is observed, as well as a shift in the δ_{NH} 1393 cm^{-1} band into the short wavelength region by a value of the order of magnitude of $10\text{--}20\text{ cm}^{-1}$.

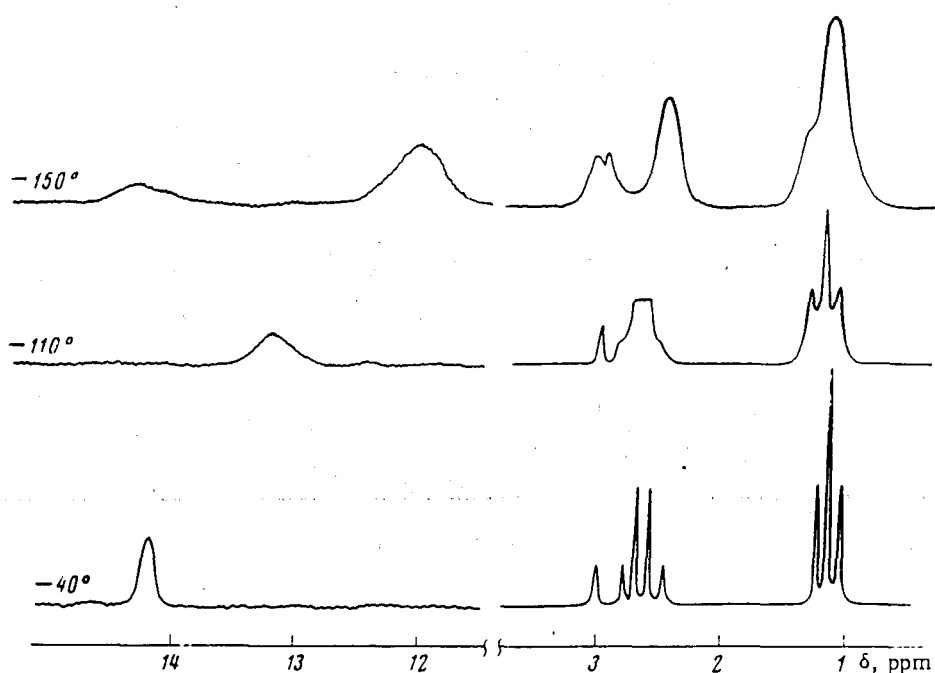
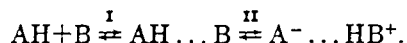


Fig. 2. PMR spectra of a solution containing 0.05 mole/liter of CH_3NHNO_2 and 0.2 mole/liter of $(\text{CH}_3\text{CH}_2)_3\text{N}$ in $\text{CHF}_2\text{-Cl}$ at different temperatures.

During the reaction between methylnitramine with secondary amines (diethyl- and diisopropylamine) at room temperature and in the presence of an excess of the amine, bands appeared in the spectrum similar to those of the anion in the ionic pair with a tetrabutylammonium cation (but not identical with it; this indicates the presence of a fairly strong interionic hydrogen bond in the ionic pair with the proton-containing cation (Fig. 1b)). Bands characteristic of the molecular complex are completely absent. Bands are observed corresponding to the vibrations of the NH_2^+ group in the hydrogen bond forming cation (the $\delta_{\text{NH}_2^+}$ band at 1630 cm^{-1} and broad stretching vibration bands in the $2400\text{-}3000\text{ cm}^{-1}$ region). We can conclude that the complexes of methylnitramine with secondary amines at room temperature are purely ionic in structure.

In the IR spectra of solutions containing nitramine and a tertiary amine (tributyl-, triethylamine) bands of both the ionic and molecular complexes are observed simultaneously (Fig. 1c). Thus, the spectrum includes the ν_{NH^+} and ν_{NH} bands and the stretching vibration bands of the NO_2 group of the ionized and nonionized forms of nitramine. With increase in temperature, bands of the free nitramine appear at 3425 cm^{-1} and 1393 cm^{-1} . With decrease in temperature, bands of the ionic form increase somewhat in intensity, while the band intensities of the molecular complexes decrease. Thus, molecular-ionic tautomerism exists in complexes of methylnitramine with tertiary amines:



The two equilibria are shifted to the right with decrease in temperature. It should be noted that in the $\text{OH} \cdots \text{N}$ systems, the tautomerism begins to be apparent at very high strength of the complex (the shift of the $\nu_{\text{O-H}}$ band has an order of magnitude of 1000 cm^{-1}), while in the $\text{NH} \cdots \text{N}$ system studied, proton transfer takes place in a hydrogen bond of a medium strength (a shift of ν_{NH} band of about 300 cm^{-1}). This again indicates that the acidity and the proton-donating capacity in the hydrogen bond are determined by different factors.

Figure 2 illustrates the PMR spectra of a solution containing methylnitramine and triethylamine in Freon. The temperature changes in the spectrum are similar to those in the carboxylic acid-amine systems [6]. The quadruplet corresponding to α -methylene protons of the triethylamine molecule shifts into the weaker field with decrease in temperature. In the -120° to -130°C region, this signal splits into two. The high-field signal corresponds to molecules of the free amine ($\delta = 2.5$), and the low-field to molecules included in the composition of the complex (both molecular and ionic). The splitting is the result of retardation

of the molecular exchange between the complexes (process I). The temperature at which it is observed depends on the strength of the complex. For example, in carboxylic acid-amine systems, the molecular exchange proceeds slowly even at -70°C . With further decrease in temperature, the triethylamine signal continues to be shifted with shift in equilibrium II to the right. The signal of the mobile proton (of the NH and NH^+ groups in the complex) is shifted to the stronger field, since the magnetic screening of this proton is stronger in the ionic pair than in the molecular complex (as in the $\text{OH}\dots\text{N}=\text{NH}^+\dots\text{O}^-$ systems also). In the temperature range of -140° to -155°C , this signal splits into two. This cannot be explained by the presence of complexes of different composition in the solution, since the relative intensity of the individual signals is independent of the ratio between the concentrations of the acid and the base, as well as the absolute concentrations. In the case of tributylamine, when the equilibrium at temperatures lower than -90°C is completely shifted in the direction of the ionic form, the low-field signal is always absent. We can thus attribute the low-field signal to the NH proton of the molecular complex, and the high-field signal to the NH^+ proton of the ionic pair. Hence, the proton transfer in the $\text{NH}\dots\text{N}$ hydrogen bond can take place quite slowly at low temperatures.

The evaluation of the mean lifetime of the molecular complex of methylnitramine with triethylamine at coalescence point of the signals (-145°C) gives the value $\tau = 8 \cdot 10^{-4}$ sec. No splitting of the signal of α -methylene protons of triethylamine bound into a complex was observed in the accessible range of temperatures because of the small difference between the chemical shifts of the molecular and the ionic forms, but only a broadening, compared with the signal of the free amine, is noted. At -160°C , equilibrium II is completely shifted in the direction of the ionic pair, while the low-field signal of the NH proton disappears.

Thus, complexes with $\text{NH}\dots\text{N}$ hydrogen bond can undergo a molecular-ionic tautomerism, which can be observed by IR and PMR spectroscopy. The rate of proton transfer in the $\text{NH}\dots\text{N}$ system is intermediate between the rates in the $\text{OH}\dots\text{N}$ and $\text{CH}\dots\text{N}$ systems. The decrease in the strength of the complex occurs in the same sequence. It is possible that these facts are interrelated.

LITERATURE CITED

1. G. M. Barrow, J. Am. Chem. Soc., 78, 22, 5802 (1956).
2. G. S. Denisov and N. S. Golubev, Proceedings of the 3rd International Symposium on Specific Interactions between Molecules and Ions, Wroclaw (1976), p. 114.
3. G. S. Denisov, N. S. Golubev, and V. M. Schreiber, Stud. Biophys., 57, 25 (1976).
4. P. M. Borodin, N. S. Golubev, et al., in: Nuclear Magnetic Resonance [in Russian], No. 5, Izd-vo Leningr. Gos. Univ., Leningrad (1974), p. 83.
5. P. M. Borodin, N. S. Golubev, et al., Org. Magn. Reson., 7, No. 4, 185 (1975).
6. N. S. Golubev, G. S. Denisov, and A. I. Kol'tsov, Dokl. Akad. Nauk SSSR, 230, No. 4 (1976).