NMR STUDY OF THE DYNAMIC STEREOCHEMISTRY OF NITROENAMINES AND OF NH EXCHANGE

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The presence of a mobile proton in the molecule of a nitroenamine containing the N-H bond introduces a specific feature into the mechanism of the Z, E isomerization of such compounds. Thus, in an investigation of the kinetics of rotation about the C = C bonds of α -nitro- β -aminoacrylate esters (Scheme 1) by the dynamic PMR method, thermal and associated mechanisms have been detected and also Z, E-isomerization taking place with ionization of the N-H bond [1, 2].

The question of the interrelationship of Z, E-isomerization and NH exchange in such molecules has remained unanswered.

 β -Arylamino-substituted derivatives of α -nitroacrylate esters (Scheme 2) are convenient model compounds for studying by the NMR method Z, E-isomerization (with COOMe as the indicator group) and NH exchange (with CH - as the indicator group, the signal from this being split on the NH proton with an SSCC J = 15 Hz).



In the present work, the kinetics of this process have been studied in $C_5D_5N-CH_2Cl_2$ (1:1 by volume). The rate of Z, E-isomerization of the nitroenamines (I)-(IV) was calculated from the temperature of the PMR spectra by a complete analysis of the shape of the lines of the signals from the protons of the COOMe groups. The error in the determination of the lifetimes of the isomers (7) $\leq 10\%$. As was found, the PMR spectrum of the COOMe groups of the Z- and E-isomers of the nitroenamine (I) at various temperatures is practically independent of the concentration, which was varied over the range of 0.18-0.9 M. The observed constancy of the rate of isomerization is evidence in favor of first-order kinetics of the reaction under investigation with respect to the dissolved substance, which is in harmony with the results of a study of rotation around the C = Cbond of compounds (I)-(IV) in pyridine $-CH_2Cl_2$ (7:3) [2]. Thus, it may be concluded that one molecule of a nitroenamine participates in the transition state of the kinetically controlled stage of Z, E-isomerization.

It follows from Table 1 that the rate of the Z, E-isomerization of (I)-(IV) depends on the electronic nature of the substituent X. A rise in the electron-accepting nature of the substituent X leads to an increase in the rate of the reaction and, correspondingly, to a decrease in the value of the energy barrier ΔG^{\neq} (Table 2). This is well illustrated by the correlation between the parameters $-\ln \tau_{\rm eff}$ and σ_p (Fig. 1). The results obtained correspond completely to an investigation of the kinetics of the Z, E-isomerization of compounds (I)-(IV) in $C_5H_5N-VH_2Cl_2$ (7:3) solution [2], where, on the basis of the isotope effect, it was concluded that the kinetically controlled stage of the isomerization of the nitroenamines (I)-(IV) is the ionization of the N-H bond.

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(1)

g° 40° 572 х ----40° 209 0,099 0,040 CH₃O 0,31 0,211 CH3 0,290,176 0.0810,0450,126 0,078 0,043 0,0173

0.0046

NO₂

0,38

0,038

TABLE 1. Dependence of the Lifetime $\tau_{eff} = (\tau_E \cdot \tau_Z)/(\tau_E + \tau_Z)$, sec, on the Substituent X in Compounds (I)-(IV)

TABLE 2. Dependence of the Energy Barrier to Rotation around the C = CBonds of the Nitroenamines (I)-(IV) on the Nature of the Substituent X*

X	$\Delta G_{E \to Z}^{298} \qquad \Delta G_{Z \to E}^{298}$		x	$\Delta G^{298}_{E \rightarrow Z}$	$\Delta G_{Z \to E}^{298}$
	kcal/mole			kcal/mole	
CH₃O CH₃	16,7 16,6	16,9 16,8	H NO2	16,2 14,4	$ \begin{array}{r} 16,3 \\ 14,5 \end{array} $

*The accuracy of the values of ΔG given is ± 0.2 kcal/mole.



Fig. 1. Dependence of the logarithm of the rate of Z, E-isomerization $(-\ln \tau_{eff})$ of the nitroenamines XC_6H_4 -NHCH=C(NO₂)COOMe in C_5D_5N -CH₂Cl₂ (1:1) solution at 20°C on the σ_p parameter of the substituent X.

After having determined the mechanism of rotation around the C = C bond of the nitroenamines (I)-(IV) in $C_5D_5N-CH_2Cl_2$ (1:1), let us consider the temperature dependence of the NMR spectrum in the region of the signals of the olefinic protons which, as mentioned above, are represented in the form of two doublets. Figure 2 gives the experimental spectrum of the CH protons of the nitroenamine (I) in $C_5D_5N-CH_2Cl_2$ (1:1) at 9°C. This figure also shows the theoretical shape of the line (dashed) which was calculated on the basis of the value of τ_{eff} characterizing the rate of Z, E-isomerization at the same temperature found from the spectrum of the COOMe group. As follows from the results obtained, no correspondence is observed between the theoretical and experimental lines. It must be mentioned that the calculation of the spectrum of the CH groups of Z, E- isomers of (I) was carried out within the framework of a four center exchange, the form of which under the conditions of rapid transitions is given in Fig. 2. However, if the form of the line is considered with the disturbance of spin-spin coupling in the = CH-NH fragment taken into account, the theoretical spectrum obtained (points in Fig. 2) does coincide satisfactorily with the experimentally observed line shape. It must be mentioned that this is in complete harmony with the fact that the kinetically controlled stage of the Z, E- isomerization of the nitroenamines (I)-(IV) is the ionization of the N-H bond. Thus, on the basis of the facts



Fig. 2. PMR spectra of the CH- protons of (I) at 9°C: 1) experimental spectrum; 2) theoretical spectrum calculated without taking the disturbance of spin-spin coupling in the NHCH= fragment into account; the points are the theoretical line found when the disturbance of spin-spin coupling is taken into account.



Fig. 3. PMR spectra of the $CH = \text{protons of (I) in } C_5D_5N - CH_2Cl_2$ (1:1) at concentrations of (I) at 0.9 M (a) and 0.18 M (b).

given it may be concluded that it is possible to judge the existence and rate of the NH-exchange reaction between the molecules (I)-(IV) from the line shape of the signals of the CH = groups.

As follows from Fig. 3, the form of the spectrum of the CH = groups and, consequently, also the rate of NH exchange under the conditions studied does not depend on the concentration of the nitroenamine (I), which was varied in the range of 0.18-0.9 M. The constancy of the rate indicates first-order kinetics of the reaction and enables us to consider the participation of one molecule of the nitroenamine in its transition state. Thus, the rate of NH exchange between molecules of the type of (I)-(IV) is controlled by the cleavage of the N-H bond. In accordance with this, as can be seen from the line shape of the spectrum of the CH = groups shown in Fig. 4, the rate of NH exchange increases with a rise in the electron-accepting nature of the substituent X of the aromatic ring MeO < Me < H.

Unfortunately, because of its low solubility we were unable to investigate the p-nitro derivative (IV). On considering the group of experimental results obtained in the present work, it may be concluded that the transition state of the kinetically controlled stages of NH exchange and Z, E-isomerization of nitroenamines containing aromatic N-substituents is the common state



TABLE 3. Concentration and Temperature Dependence of the Chemical Shift of the NH Protons of the Z- and E-Isomers of the Nitroenamine (I) in $C_5D_5N-CH_2Cl_2$ (1:1) (δ , ppm from HMDS)*

С, М	40°		-	20°	0°	
	Z	E	Z	E	Z	E
0,3 0,6 0,8	11,86 11,82 11,75	11,02 11,00 11,00	11,72 11,68 11,60	10,98 10,94 10,95	11,58 11,55 11,49	10,91 10,89 10,90

*Accuracy of the determination 0.01 ppm.



Fig. 4. Dependence of the line shape of the signals in the PMR spectrum of the CH = groups of the nitroenamines $XC_{6}H_{4}$ -NHCH = C(NO₂)COOMe on the nature of the substituent X; a) MeO; b) Me; c) H.

Consequently, the characteristics, namely the isotope effect, the influence of substituents in the aromatic ring, and the first-order kinetics with respect to pyridine found for the Z, E-isomerization of the nitroenamines (I)-(IV) [2, 3] are also valid for NH exchange between these molecules. In other words, NH exchange is initiated by the solvent, and the rate of cleavage of the N-H bond in the complexes (A) determines the rate of the reaction.



Each proton-transferring act is accompanied by at least one rotation about the C=C bond of one of the nitro-amines (I)-(IV).

As follows from the NMR spectra, the isomeric equilibrium of the nitroenamine (I) in $C_5D_5N-CH_2Cl_2$ (1:1) is shifted somewhat in the direction of the Z- isomer ($K_{E=Z} = 1.2$ at 20°C). Taking into account the facts given above it may be assumed that this is due to the greater kinetic acidity of the NH proton of the isomer in which the NH₂ and NO₂ groups are present in the trans position. In fact, it can be seen from the PMR spectrum given in Fig. 2 that the spectrum of the CH = proton of the E- isomer of (I) is broader than that of the Z- isomer. In connection with this, it is interesting to compare the concentration and temperature dependences of the chemical shifts of the NH protons of the Z- and E- isomers of the nitroenamine (I). It follows from Table 3 that a decrease in the concentration of the sample and a lowering of the temperature causes a downfield shift of the resonance signal of the NH proton of the Z- isomer of (I). In our opinion, this observation can be interpreted by an interaction of (I) with pyridine and a shift of the equilibrium in the direction of formation of complexes with a H bond of type (A). However, in the case of the E- isomer the dependence of δ_{HN} is less pronounced. In view of the fact that the concentration of pyridine exceeds the concentration of nitroenamine by roughly an order of magnitude, this can be explained by the predominant formation of complexes (A). This conclusion is in harmony with the results given above, since it is known that the rate of transfer of a proton along a H bond is higher the stronger the bond [4].

In contrast to the facts given above, in the case of nitroenamines related to (I) but having N-alkyl substituents Z, E-isomerization and NH exchange takes place through different transition states. Thus, on the basis of a study of the kinetics of NH exchange in the compound MeNHCH = $C(NO_2)COOMe$ in pyridine [1] it was concluded that the reaction had an associative mechanism the transition state of which can be represented by the cyclic formula (B), as has usually been suggested for NH exchange [5-7].



Apparently, the pseudomonomolecular NH exchange of the nitroenamines (I)-(IV) in an aprotic solvent is due to the broad delocalization over the whole molecule of the electron pair of the N, decreasing its basicity, and therefore for proton transfer another, stronger, base is necessary, the role of which is filled by the pyridine. In fact, in nitrobenzene NH exchange is not recorded in the time scale of PMR. In contrast to the catalytic action of a base, the addition of CF_3COOH to a solution of the nitroenamine (I) in MeCN causes an inhibition of NH exchange; the spin-spin coupling constant in the = CHNH fragment is also retained in a solution of (I) in CF_3COOH .

EXPERIMENTAL

The PMR spectra were measured on an RYa-2309 (90 MHz) spectrometer with an accuracy of thermostating of $\pm 1^{\circ}$ C. The solvents were purified by standard methods [8]. The spectra were calculated by means of a program drawn up in Arnold's formalism [9].

SUMMARY

1. The kinetically controlled stages of NH exchange and of Z, E-isomerization of the nitroenamines studied have a common transition state that includes a molecule of the reactant and a pyridine molecule.

2. For the enamines studied, a pseudomonomolecular mechanism of NH exchange in an aprotic solvent has been observed.

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