

THERMODYNAMICS OF *E-Z*-ISOMERATION OF β -ALKYL- β -NITROSTYRENES*

L. LEŠETICKÝ^a, M. FLIEGER^a and E. DRAHORÁDOVÁ^b

^a Department of Organic Chemistry, Charles University, 128 40 Prague 2, and

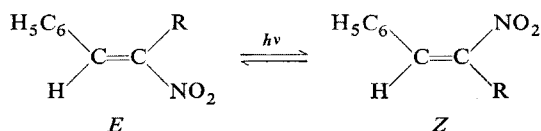
^b J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2

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The position of the equilibrium of the *E-Z*-isomeration was studied in the series 1-phenyl-2-nitroethylene (*I*), 1-phenyl-2-nitropene (*II*), and 1-phenyl-2-nitro-1-butene (*III*). The aim of this study was to estimate the thermodynamic stability of these isomers.

It is known from published data that in the 1-alkyl/or aryl-2-nitroethylenes prepared so far the prevailing configuration on the double bond is the *trans*-configuration¹⁻⁴. However, quantitative data are not available. The value of the equilibrium constant is known for 1-nitropropene^{1,2} and 1-nitro-1-butene³.

The procedures described earlier^{5,6} were employed to prepare *trans*-1-phenyl-2-nitroethylene (*I-E*), *E*-1-phenyl-2-nitropropene (*II-E*), and *E*-1-phenyl-2-nitro-1-butene (*III-E*). The structure of these compounds was confirmed by the ¹H-NMR spectra (Table I). When irradiating the *E*-isomers by ultraviolet light a mixture of the *E*- and *Z*-isomers and non-identified photolytic products is formed.



I, R = H; *II*, R = CH₃; *III*, R = C₂H₅.

Pure *Z*-isomers could not be separated in any of the above mentioned cases. Therefore, in the isomeration studies a mixture of both isomers was used separated by chromatography from the by-products of the photoisomeration. The identity of the *Z*-isomers in the mixture was confirmed by the ¹H-NMR spectra, their purity and composition by gas chromatography. The ¹H-NMR spectroscopic analysis of the mixture of the isomers showed that the composition of the samples did not change while the gas or column chromatography was carried out. Quantitative data from the gas chromato-

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graphy and the $^1\text{H-NMR}$ spectroscopy were in agreement within the accuracy limits of the NMR-spectroscopy.

Measurements of the equilibrium constants were carried out independently over the temperature range $150-225^\circ\text{C}$, starting either with the pure *E*-isomer or with the mixture of the *E*- and *Z*-isomers. The equilibrium constants measured in both ways agreed well. As a catalyst either boron fluoride etherate or iodine was used. Nitrobenzene was found to be the best solvent. The equilibrium constants were determined from the composition of the reaction mixture, if three subsequent analyses gave the same ratio of both isomers. The analyses of the reaction mixtures were

TABLE I
 $^1\text{H-NMR}$ Spectra of the Studied Substances

Substance	Chem. shift, δ^a	$J_{1,2}$, Hz
(3) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{H (1)} \\ \diagdown \\ \text{NO}_2 \end{array}$ $\begin{array}{c} \text{H (2)} \\ \diagdown \end{array}$	H (1) : 7.46 d H (2) : 7.90 d H (3) : 7.55–7.16	14
(3) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{NO}_2 \\ \diagdown \\ \text{H (1)} \end{array}$ $\begin{array}{c} \text{H (2)} \\ \diagdown \end{array}$	H (1) : 6.87 d H (2) : 6.64 d H (3) : 7.55–7.16	10
(3) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{CH}_3 \text{ (1)} \\ \diagdown \\ \text{NO}_2 \end{array}$ $\begin{array}{c} \text{H (2)} \\ \diagdown \end{array}$	H (1) : 2.39 H (2) : 7.95 H (3) : 7.39 sm	-1.2
(3) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{NO}_2 \\ \diagdown \\ \text{CH}_3 \text{ (1)} \end{array}$ $\begin{array}{c} \text{H (2)} \\ \diagdown \end{array}$	H (1) : 2.29 H (2) : 6.31 H (3) : 7.22 sm	-1.4
(4) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{CH}_2\text{-CH}_3 \text{ (1)} \\ \diagdown \\ \text{NO}_2 \end{array}$ $\begin{array}{c} \text{H (3)} \\ \diagdown \end{array}$	H (1) : 1.24 t H (2) : 2.81 q H (3) : 7.90 H (4) : 7.39 sm	7
(4) H_5C_6 $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ $\begin{array}{c} \text{NO}_2 \\ \diagdown \\ \text{CH}_2\text{-CH}_3 \text{ (1)} \end{array}$ $\begin{array}{c} \text{H (3)} \\ \diagdown \end{array}$	H (1) : 1.19 t H (2) : 2.65 q H (3) : 6.25 H (4) : 7.25 sm	7

^a sm Multiplet center; d doublet; t triplet; q quartet.

carried out by gas chromatography, the accuracy of the equilibrium constant determination was better than 3%. From the thermal dependence of the equilibrium constants the thermodynamic parameters of the reactions were determined using the least square method. The results are summarized in Table II and Table III.

The thermodynamic stability of the isomers is influenced on the one hand by the *cis*-interaction of the nitrogroup with the benzene ring in the *Z*-isomer, on the other hand by the conjugation in the system phenyl–double bond–nitro group. It is justifiable to assume a planar conjugated system by the *E*-isomers (if $R = \text{CH}_3$ and C_2H_5 , this conjugation is somewhat perturbed by the interactions phenyl $\cdots R$ and $R \cdots \text{NO}_2$). In the *Z*-isomers the conjugated system will be appreciably perturbed;

TABLE II
Equilibrium Constants and Conditions for *E*–*Z* Isomeration of Substances *I*–*III*

Temperature	Procedure	K^a	ΔG , kcal mol ⁻¹
<i>I</i> – <i>E</i> \rightleftharpoons <i>I</i> – <i>Z</i>			
170	B	0.012 \pm 0.001	3.89
199	B	0.034 \pm 0.003	3.17
209	B	0.048 \pm 0.002	2.91
230	B	0.084 \pm 0.004	2.47
241	B	0.100 \pm 0.003	2.35
<i>II</i> – <i>E</i> \rightleftharpoons <i>II</i> – <i>Z</i>			
168	B	0.024 \pm 0.002	3.267
186	B	0.027 \pm 0.001	3.293
198	B	0.030 \pm 0.001	3.211
220	B	0.041 \pm 0.001	3.128
225	A	0.042 \pm 0.001	3.135
245	A	0.047 \pm 0.001	3.147
<i>III</i> – <i>E</i> \rightleftharpoons <i>III</i> – <i>Z</i>			
150	A	0.062 \pm 0.008	2.336
192	B	0.094 \pm 0.001	2.184
210	B	0.098 \pm 0.003	2.228
220	A	0.104 \pm 0.005	2.216
230	B	0.110 \pm 0.008	2.220
240	A	0.126 \pm 0.005	2.110

^a Listed errors of the equilibrium constant values represent the maximum scatter about the arithmetic mean value of 2–4 measurements.

analysis of the particular model shows that *cis*-1-phenyl-2-nitroethylene cannot take up the planar configuration; the nitro-group and the benzene ring planes are distorted from a coplanar position with the double bond plane. As a result, a severe change of the lower vibrational (and internal rotational) states occurs which in turn leads to a very high value of the entropy term. Introducing an alkyl into the β -position results in two effects: 1) relative differences between the energies of isomers are reduced due to an unfavourable *cis*-interaction phenyl... alkyl; 2) the rotational-vibrational freedom of the nitro group decreases (the rotational energy barrier increases) and this may explain the observed steep decrease of the entropy of the reaction (eight times for CH_3 , sixteen-times for C_2H_5). Steric requirements of the ethyl are not so high — in comparison with the methyl — so that the observed change is not as pronounced.

EXPERIMENTAL

Synthesis

1-Phenyl-2-nitroethylene (*I-E*) was prepared using the published procedure⁵; its melting point was 58°C. Similarly, *E*-1-phenyl-2-nitropropene (*II-E*), m.p. 64°C, and *E*-1-phenyl-2-nitro-1-butene (*III-E*), b.p. 118–120°C/4 Torr, m.p. 12°C, were prepared as described in the literature⁶.

Photoisomeration

The *E*-isomers were dissolved in benzene (thiophene-free, 1 g/100 ml) and irradiated in a quartz flask by a low-pressure mercury lamp for 3–6 days. Benzene was evaporated at a reduced pressure and the product was subjected to a chromatographic separation (silica gel column L 160/120, with dichloromethane as the eluent). The mixture of the *E*- and *Z*-isomers migrated with the front zone. Attempts to find conditions for a separation of the *Z*-isomers were not successful.

TABLE III
Thermodynamic Functions of *E-Z*-Isomeration

Reaction	ΔH , kcal mol ⁻¹	ΔS , cal mol ⁻¹ deg ⁻¹
<i>I-E</i> \rightleftharpoons <i>I-Z</i>	13.8	22.4
<i>II-E</i> \rightleftharpoons <i>II-Z</i>	4.5	2.8
<i>III-E</i> \rightleftharpoons <i>III-Z</i>	2.9	1.4

Equilibrium Constant Measurements

A. 10 ml of 0.1M solution of the studied substance was introduced into a 50 ml ampule and 10 mol % iodine (a solution in benzene) was added. The ampule was thermostated⁷ to $\pm 1^\circ\text{C}$. After the cooling, iodine was removed by sodium thiosulphate and the sample was subjected to a gas-chromatographic analysis.

B. A mixture of 1M solution of nitroolefin in nitrobenzene and 20 mol % of boron trifluoride etherate was thermostated in a fused ampule for a sufficient time and after the cooling it was analyzed. Control samples showed that during the gas-chromatographic analysis no change of the reaction mixture composition occurred.

Gas Chromatography Methods

Checking of the purity and the analyses of the reaction mixtures were carried out on a Chrom 2 instrument with a flame-ionization detector; the glass column was 240 cm long and its internal diameter was 0.4 cm. The stationary phase was the silicon elastomer SE-52, 3% on Chromosorb W, 60–80 mesh. The instrument Chrom 32 was also equipped with a flame-ionization detector, the metal column was 240 cm long and its internal diameter was 0.6 cm; it was filled with SE-52 (7% anchored on the porous base 0.2–0.3 mm).

The $^1\text{H-NMR}$ spectra were measured using a Tesla BS 487 instrument with the proton stabilization, performing at the frequency 80 MHz. As internal standards 0.5M solutions in tetrachloromethane with hexamethyldisiloxane were used. The measurements were carried out at 25°C .

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