TAUTOMERISM OF 5-NITRO-2-FURYLNITROMETHANE

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Received December 17th, 1980

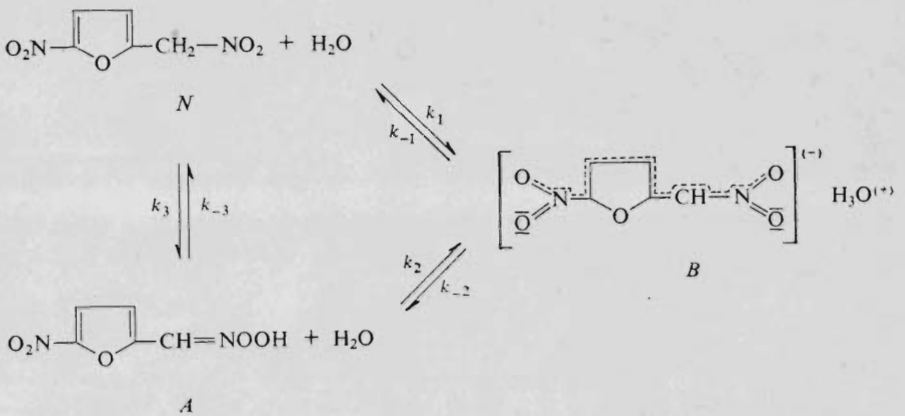
UV study of properties of 5-nitro-2-furylnitromethane (*I*) in various solvents has shown that this compound is a very strong acid (pK_a 3·98) forming an ion pair in protic solvents (water, alcohols) and existing exclusively as nitro-form in aprotic solvents (tetrachloromethane, chloroform, n-hexane, diethyl ether, dioxane). Kinetic study of tautomerism in water has given experimental values of combined rate constants of parallel reactions. Thermodynamic parameters of the tautomeric transformations have been calculated from temperature dependence of the rate constants.

Tautomerism kinetics of phenylnitromethane in aqueous solutions were studied in detail by soviet authors[1–4]. It was found that mutual conversion of the nitro- and aci-forms proceeds through a phase of their dissociation giving the same anion. Existence of the second form of anion presumed originally in ref.[1] was not proved kinetically. Furthermore it was found that dissociation and recombination of nitro-form are very much slower than those of the aci-form, the latter being several orders of magnitude faster than with usual nitro-forms. The mentioned transformations follow the rules of protolytic reactions of acids and bases. In previous papers[5,6] we described a synthesis of 4-nitro-2-furylnitromethane (*I*). In the present paper properties of the compound *I* are studied with respect to the tautomerism due to acidity of hydrogen atoms in methylene group.

The compound can exist in nitro- or aci-forms (*N* and *A*, respectively, Scheme 1) Its synthesis always gave the nitro-form. We tried to isolate the acinitro-form by acidification of the respective sodium salt. For this purpose we prepared sodium salt of the compound *I* or that of the acinitro-form. In ^{1}H-NMR spectrum of the sodium salt the H_A proton at double bond is split by long-range interaction with the protons of furan ring. The interaction through five bonds ($^5J_{4,A}$) is highly stereospecific, and from its magnitude it is possible to estimate conformation of the furan cycle. High value of this interaction constant (0·8 Hz) in the sodium salt of *I* indicates *s-cis* conformation[7]. Acidification of the sodium salt and immediate extraction

in chloroform produced only the nitro-form. Mass spectrum of the compound *I* does not exhibit the peak corresponding the molecular ion $M^{+\bullet}$ 172. The last peak of the spectrum corresponds to the fragment *m/e* 126 (rel. int. 70%) which is further split according to Scheme 2.

The measured UV spectra of the compound *I* in aprotic solvents (tetrachloromethane, n-hexane, diethyl ether, dioxane) exhibit a single band only corresponding to $\pi - \pi^*$ transitions of furan ring (in the region 290 to 304 nm, Table I). In protic



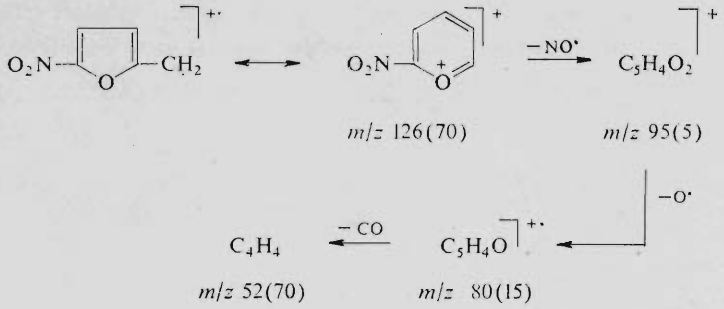
SCHEME 1

solvents (alcohols, water) this compound exhibits two bands: in UV region (300 to 306 nm) and in visible (430–442 nm), the latter being shifted as far as 476 nm (lower intensity) in propanol. The bands in visible region of spectrum correspond either to acinitro-form or to the resonance-stabilized anion. It can be presumed that in these solvents equilibrium is established between the nitro- (*N*), acinitro-

TABLE I
UV spectra of 5-nitro-2-furylnitromethane in various solvents

Solvent	λ_{max} (log ε)	Solvent	λ_{max} (log ε)
n-Hexane	290 (4·01)	Ethanol	306 (3·88); 442 (4·19)
Tetrachloromethane	304 (4·02)	1-Propanol	300 (4·00); 476 (2·90)
Chloroform	300 (4·01)	Water	304 (3·42); 430 (3·90)
Dioxane	306 (4·02)	0·1M-NaOH	306 (3·68); 438 (4·25)
Diethyl ether	302 (4·01)	0·1M-KOH	310 (3·76); 437 (3·21)

-forms (*A*) and the mesomeric anion (B) (Scheme 1). This presumption is confirmed by the fact that on acidification of the sodium salt of *I* the band in visible region rapidly decreases until it disappears (with simultaneous increase of the band at 306 nm). This



SCHEME 2

process was followed by stopped-flow technique. The rate of tautomeric transformation of acinitro- into nitro-form was followed at 20 to 40°C. In this temperature range the rate constant varied within the limits $4-20 \cdot 10^{-2}$ s^{-1}. The measurements are complicated by the presence of the mesomeric anion (*B*). So far only the combined rate constants $k_{obs}^{\rightarrow}$ and $k_{obs}^{\leftarrow}$ of the parallel reactions are accessible experimentally (Tables II and III), and, furthermore, they are complicated by the tautomeric equilibrium constant $K_T = k_3/k_{-3}$. The latter constant could be estimated by some relaxation method (T-jump). However, even then it is only possible to measure the sums $k_1 + k_2$ or $k_{-1} + k_{-2}$. From temperature dependences of the rate constants we calculated the frequency factors A and activation energies E^* of the Arrhenius

TABLE II

The $k_{obs}^{\rightarrow}$ values at various temperatures at λ 430 nm at pH 7·06

t, °C	$k_{obs}^{\rightarrow} \pm \sigma_k$
16·0	$3{\cdot}03 \cdot 10^{-2} \pm 5{\cdot}47 \cdot 10^{-4}$
20·5	$4{\cdot}78 \cdot 10^{-2} \pm 1{\cdot}76 \cdot 10^{-4}$
25·0	$7{\cdot}32 \cdot 10^{-2} \pm 1{\cdot}22 \cdot 10^{-4}$
30·2	$1{\cdot}05 \cdot 10^{-1} \pm 3{\cdot}47 \cdot 10^{-3}$
35·5	$1{\cdot}53 \cdot 10^{-1} \pm 3{\cdot}46 \cdot 10^{-3}$

relation and activation enthalpies (ΔH^*) and entropies (ΔS^*) of the Eyring relation (Table IV). To verify the presumption that the compound *I* is a strong acid, we measured its pK_a value by spectrophotometric method. The found value 3·98 ± 0·006 (at the ionic strength $I = 0{\cdot}01$) is comparable with those of some carboxylic acids and practically identical with pK_a of 2-nitromethylpyridine[8] (pK_a 3·92). Thus the compound *I* is almost by two orders of magnitude more acidic than its benzene analogue 4-nitrophenylnitromethane[9] (pK_a 5·89).

EXPERIMENTAL

The electronic absorption spectra were measured with a Specord UV VIS (Zeiss, Jena) within 200 to 800 nm using 1 cm cells and $5 \cdot 10^{-5}$ mol l^{-1} concentrations. The ^{1}H-NMR spectra were measured with a 80 MHz apparatus BS-487 C (Tesla, Brno) in deuteriochloroform or hexadeuteriodimethyl sulphoxide using tetramethylsilane as internal standard. The pH values of the buffers used were measured with a Präzisions-Labor-pH-Messgerät MV 85 (GDR). The mass spectra were measured with a MS 902 S spectrometer (AEI, Manchester). The kinetic measure-

TABLE III

The $k_{obs}^{\leftarrow}$ values at various temperatures at $\lambda = 430$ nm at pH 1·47

t, °C	$k_{obs}^{\leftarrow} \pm \sigma_k$
15·2	$7{\cdot}07 \cdot 10^{-2} \pm 1{\cdot}00 \cdot 10^{-3}$
20·5	$1{\cdot}18 \cdot 10^{-1} \pm 1{\cdot}80 \cdot 10^{-3}$
25·0	$1{\cdot}50 \cdot 10^{-1} \pm 4{\cdot}10 \cdot 10^{-3}$
29·8	$2{\cdot}96 \cdot 10^{-1} \pm 6{\cdot}80 \cdot 10^{-3}$
34·7	$4{\cdot}08 \cdot 10^{-1} \pm 1{\cdot}70 \cdot 10^{-2}$

TABLE IV

Values of thermodynamic parameters of nitro-acinitro tautomerism of 5-nitro-2-furylnitromethane

Parameter	$k_{obs}^{\rightarrow}$	$k_{obs}^{\leftarrow}$
A	0·887	0·607
*E**	+ 61·0 kJ mol^{-1} K^{-1}	+ 64·9 kJ mol^{-1} K^{-1}
ΔS^*	—66·8 ± 8·8 J mol^{-1} K^{-1}	—41·2 ± 16·9 J mol^{-1} K^{-1}
ΔH^*	59·8 ± 2·6 kJ mol^{-1}	65·1 ± 5·0 kJ mol^{-1}

ments were carried out by the stopped-flow technique using a Durrum D-100 apparatus at $\lambda =$ = 430 nm.

Sodium Salt of 5-Nitro-2-furylnitromethane (*I*)

Dioxane solution of 0·01 mol *I* was treated with 0·01 mol sodium ethoxide with stirring at room temperature. The formed red precipitate was collected by suction, washed with ethanol, and dried. Yield 92%. IR spectra (KBr, cm^{-1}): ν(COC) 1 020, $\nu_s(NO_2)$ 1 360, $\nu_{as}(NO_2)$ 1 525, 1 570, ν(C=N) 1 645. UV spectrum (50% ethanol, λ_{max} (log ε)): 308 nm (3·64), 438 nm (4·22). ^{1}H-NMR spectrum (δ(ppm), J (Hz)): 6·87 dd, H_A; 6·93 dd, H_3; 7·61 dd, H_4; $J_{3,4} = 4{\cdot}2$; $^5J_{4,A} = 0{\cdot}8$; $^5J_{3,A} = 0{\cdot}5$. For $C_5H_3N_2NaO_4$ (178·1) calculated: 33·76% C; 1·68% H; 15·74% N; found: 34·00% C; 1·76% H; 16·04% N.

Determination of pK_a Value

The extinction E_1 of the non-ionized form *I* was measured in 0·1M-HCl at 20°C at λ = 312 nm in 1 cm cells ($c = 5 \cdot 10^{-5}$ mol l^{-1}); the extinction E_2 of the respective ionized form was measured in 0·1M-NaOH at λ 438 nm. The extinction E_x of mixtures of the both forms was measured in buffers (pH 3·59 to 4·41) prepared according to Perrin[10] from 0·1M succinic acid and 0·05 M-KOH. For the calculations the following relation was used

$$pK_a = pH - \log((E_x - E_1)/(E_2 - E_x))$$

Kinetic Measurements

Stock solution of the compound *I* ($c = 1 \cdot 10^{-2}$ mol l^{-1})was prepared in dioxane. Reaction solutions ($c = 2 \cdot 10^{-4}$ mol l^{-1}) were prepared by diluting the stock solution with the corresponding amount of redistilled water. (*i*) The solution was mixed with buffer (pH 7·06, $I = 0{\cdot}01$) in the Durrum D-110 apparatus within 3 ms. The absorbance increase was followed at λ = 430 nm, and the combined rate constants $k_{obs}^{\rightarrow}$ were measured at various temperatures (Table II). (*ii*) The solution was mixed (in the same way as sub (*i*)) with solution of hydrochloric acid ($c = 0{\cdot}03372$ mol l^{-1}, pH 1·47, $I = 0{\cdot}03$), the absorbance decrease was followed at $\lambda = 430$ nm, and the combined rate constants $k_{obs}^{\leftarrow}$ were measured at various temperatures (Table III). From temperature dependence of the rate constants we calculated the frequency factors A and activation energies E^* of the Arrhenius relation and activation enthalpies and entropies (ΔH^*, ΔS^*) of the Eyring equation.

REFERENCES

1. Mairanovski S. G., Belikov V. M., Korchemnaya C. B., Klimova V. A., Novikov S. S.: Izv. Akad. Nauk SSSR, (1960), *1787*.
2. Belikov B. M.: Izv. Akad. Nauk SSSR, (1960), *1675*.
3. Belikov V. M., Mairanovski S. G., Korchemnaya C. B., Novikov S. S.: Izv. Akad. Nauk SSSR, (1961), *1108*.
4. Belikov V. M., Mairanovski S. G., Korchemnaya C. B., Novikov S. S.: Izv. Akad. Nauk SSSR, (1962), *605*.
5. Sroková I., Jurášek A., Dandárová M., Kováč J.: This Journal *43*, 463 (1978).
6. Sroková I., Rajniaková O., Jurášek A.: Chem. Zvesti, in press.

7. Haslinger E., Wolschann P.: Org. Magn. Resonance *9*, 1 (1977).
8. Fischer A., King M. J., Robinson F. P.: Can. J. Chem. *56*, 3059 (1978).
9. Bordwell G. F., Boyle W. J.: J. Amer. Chem. Soc. *94*, 390 (1972).
10. Perrin D. D.: Aust. J. Chem. *16*, 572 (1963).

Translated by J. Panchartek.