Chemistry

Ya. I. Tur' yan, Yu. M. Tyurin, and P. M. Zaitsev

1960

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Chemistry

Ya. I. Tur' yan, Yu. M. Tyurin, and P. M. Zaitsev

Polarographic Study of the Nitro-aci Tautomerism of Nitrocyclohexane

(Presented by Academician A. N. Frumkin, May 16, 1960)

The polarographic method developed by us (^{1}) for the analysis of nitrocyclohexane (NCH) has made it possible to study the kinetics and equilibrium of the nitro-aci tautomeric transformation of NCH. In contrast to analogous polarographic studies of other nitro compounds (^{2,3}), we have studied not only the nitro-aci transformation and the reverse reaction, but also the corresponding equilibrium*. The nitro form of NCH gives a distinct wave over a wide pH range; the aci form of NCH is not reduced at the dropping mercury electrode.

Fig. 1

The initial solutions of NCH ($\sim 0.01\ M$) were prepared in water or in alkali, depending on the direction in which the reaction was being studied. Citrate-phosphate and borax-alkali buffer mixtures, with KCl added to maintain a constant ionic strength $\mu = 1.0$–1.4, served as the background. The concentration of the nitro form of NCH was recorded with an electronic polarograph PE-312. The nitro-aci ($N \to A$) transformation was studied in the pH range 8–12, and the reverse reaction was studied at pH 3-9.5. The study was carried out at temperatures of 25, 32, 40, and 50°C.

Figure 1 shows the dependence of the ratio C_∞/C_0 on pH at 25°C, where C_0 is the initial concentration of NCH in the nitro or aci form, and C_∞ is the concentration of the nitro form of NCH after completion of the reaction.

As is seen from Fig. 1, at pH > 9.5 the nitro form of NCH is completely converted into the aci form, while at pH 4.5–7.0 the aci form can be completely converted into the nitro form. At pH 7.0–9.5 an equilibrium is observed, which can be reached from either side. The decrease in C_∞/C_0 at pH < 4.5 ($A \to N$) is apparently explained by the simultaneous conversion, at low pH, of the aci form into cyclohexanone according to the Nef reaction (^{5}).

The kinetic data obtained are well described by the following equations (Figs. 2, 3, 4; h is the wave height):

$$K_0 a_{\mathrm{OH}^-} = K_N = \frac{2.3}{t} \lg \frac{C_0}{C_N} \ (N \to A); \tag{1}$$

$$\frac{K_0' a_{\mathrm{H}^+}}{1 + \frac{a_{\mathrm{H}^+}}{K_1} + \frac{a^2_{\mathrm{H}^+}}{K_1 K_2}} = K_A = \frac{2.3}{t} \cdot \frac{C_\infty}{C_0} \lg \frac{C_\infty}{C_\infty - C_N} \ (A \to N), \tag{2}$$

* The possibility of a polarographic study of the aci-nitro transformation of nitromethane is indicated in (^{4}).

where C_N is the concentration of the nitro form at time t; K_N' is the experimental rate constant of the reaction $N \to A$ at pH = const; K_A' is the same for the reaction $A \to N$; K_0, K_0', K_1, K_2 are constants at the given ionic strength; a_{H^+} and a_{OH^-} are the activities of hydrogen and hydroxyl ions.

At pH = const, equation (1) corresponds to a first-order reaction and in this part agrees with the data (^{2,3}) on the nitro-aci transformation of other substances.

Equation (2) at pH = const and in the region of complete transformation $A \to N$ (pH 4.5-7.0) also corresponds to a first-order reaction, while at less than 100% yield of the nitro form (pH $<$ 4.5) it corresponds to two parallel first-order reactions.

Fig. 2. 1—pH 10.8, $h_0 = 7.6$ cm, $h_\infty = 0$; 2—pH 4.0, $h_0 = 7.5$ cm, $h_\infty = 5.7$; 3—pH 5.0, $h_0 = h_\infty = 7.8$; 4—pH 11.6, $h_0 = 7.6$ cm, $h_\infty = 0$. For 1, 4, $N \to A$,

$$x = \lg \frac{h}{t};$$

for 2, 3, $A \to N$,

$$x = \frac{h_\infty}{h_0} \lg \frac{h_\infty}{h_\infty - h_t}.$$

The values of K_N and K_A at 25° and different pH values are given in Table 1. The dependence $\lg K_N$—pH is linear (Fig. 3), while the dependence $\lg K_A$—pH passes through a maximum at pH $\simeq 5$ (Fig. 4).

On the basis of ideas about acid-base catalysis of the nitro-aci tautomeric transformation (^{6}), we shall adopt the following mechanism for the reactions studied:

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

$$\begin{gathered}
\text{Nef reaction} \quad \underset{K_0''}{\longleftarrow} \; [C_6H_{10} : NO_2H]H^+ \underset{K_2}{\overset{H^+}{\rightleftarrows}} C_6H_{10} : NO_2H \underset{K_1}{\overset{H^+}{\rightleftarrows}} \\
H^+ \underset{K_1}{\rightleftarrows} C_6H_{10} : NO_2^- \xrightarrow[\text{slow stage}]{H^+,\, K_0'} C_6H_{11}NO_2, \\
C_6H_{10} : NO_2^- \xleftarrow[\text{slow stage}]{OH,\, K_0} C_6H_{11}NO_2,
\end{gathered} \tag{3}$$

where K_0, K_0', K_0'' are the corresponding rate constants,

$$K_1 = \frac{[C_6H_{10} : NO_2^-][H^+]}{[C_6H_{10} : NO_2H]},$$

K_2 is the same for the protonated complex: $[C_6H_{10} : NO_2H]H^+$.

The adopted reaction mechanism makes it possible to obtain kinetic equations coinciding with the experimental equations (1) and (2) for the following values of the constants (25°): $K_0 = 50\ (\text{mol/l})^{-1} \cdot \text{min}^{-1}$, $K_0' = 2.8 \cdot 10^5\ (\text{mol/l})^{-1} \cdot \text{min}^{-1}$, $K_0'' = 0.11\ \text{min}^{-1}$, $K_1 = 4.3 \cdot 10^{-7}$, and $K_2 = 2.3 \cdot 10^{-4}$.

In Fig. 4 the points are experimental data, and the curves are calculated. In the calculations, the corresponding activities were used instead of C_{H^+} and C_{OH^-}.

It follows from the mechanism considered that in the limiting stage of the Nef reaction (at pH < 4.5) the protonated complex $[C_6H_{10} : NO_2H]H^+$ participates. Such an assumption agrees with the indication of acid participation in analogous reactions (^{7}).

Since at pH $\geqslant 9.7$ the isomerization reaction of NCG is catalyzed by hydroxyl ions, and at pH $\leqslant 7$ by hydrogen ions, the equilibrium constant cannot be calculated from the ratio K_0/K_0'. The results of a direct determination of the equilibrium constant (in studying the equilibrium $N \rightleftarrows A$ in the pH range 7.0-9.5) are presented in Table 2 (25°). The equilibrium constant was calculated from the equation:

Fig. 3

Fig. 4

$$K_p = \frac{[C_6H_{10} : NO_2^-]\, a_{H^+}}{[C_6H_{11} : NO_2]}.$$

To determine $[C_6H_{10} : NO_2^-]$, the values K_1 and K_2 were used.

Table 1

pH	K_N, min^{-1}	pH	K_A, min^{-1}
9.7	$3.4 \cdot 10^{-3}$	3.1	$3.0 \cdot 10^{-2}$
10.0	$6.4 \cdot 10^{-3}$	3.8	$5.6 \cdot 10^{-2}$
10.2	$7.8 \cdot 10^{-3}$	4.0	$7.5 \cdot 10^{-2}$
10.8	$4.8 \cdot 10^{-2}$	4.6	0.10
11.2	0.12	5.0	0.11
11.6	0.29	5.2	$9.5 \cdot 10^{-2}$
11.8	0.38	5.6	$9.8 \cdot 10^{-2}$
		5.9	$8.1 \cdot 10^{-2}$
		6.3	$6.1 \cdot 10^{-2}$
		7.0	$2.3 \cdot 10^{-2}$

Table 2

pH	Initial form of NCG	C_∞/C_0	$K_p \cdot 10^9$
7.9	aci	0.67	6.1
7.9	aci	0.65	6.8
7.9	nitro	0.70	5.3
7.9	nitro	0.65	6.8
8.2	aci	0.51	6.0
9.4	aci	0.10	3.5
9.4	nitro	0.11	3.1
			5.0 ± 1.0

From Table 2 one sees good agreement of the data for K_p when approaching equilibrium from both sides. From the linear plots $\lg K_0 - 1/T$ and $\lg K_0' - 1/T$, the activation energies of the processes were found: $N \to A$, 18.4 kcal/mol, and $A \to N$, 16.0 kcal/mol.

Lysychansk Branch
of the State Institute of the Nitrogen Industry
and Products of Organic Synthesis

Received
12 III 1960

CITED LITERATURE

1. Ya. I. Tur' yan, Yu. M. Tyurin et al., *Zav. lab.*, No. 6 (1960).
2. E. W. Millet, A. P. Arnold, M. J. Astle, *J. Am. Chem. Soc.*, **70**, 3971 (1948).
3. G. W. Goward, C. E. Bricker, W. C. Wildman, *J. Organ. Chem.*, **20**, 378 (1955).
4. S. G. Mairanovskii, Abstracts of reports, All-Union Conference on the Polarographic Method of Analysis, Kishinev, 1959.
5. J. Nef, *Ann.*, **280**, 263 (1894).
6. R. Bell, *Catalysis, Study of Homogeneous Processes*, IL, 1957.
7. A. V. Topchiev, *Nitration of Hydrocarbons and Other Organic Compounds*, USSR Academy of Sciences Press, 1949.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.