TAUTOMERISM OF NITRO COMPOUNDS

COMUNICATION 2. POLAROGRAPHIC INVESTIGATION OF THE KINETICS OF THE TAUTOMERIC TRANSFORMATIONS OF α-NITROTOLUENE

S. G. Mairanovskii, V. M. Belikov, Ts. B. Korchemnaya,
V. A. Klimova, and S. S. Novikov
Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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In the preceding communication [1] it was stated that the kinetics of the transformations in the system α-nitrotoluene → its anions → its aci form had been investigated polarographically. We now describe the procedure used in this work and give the results of the experiments.

Experimental

An investigation was made of the polarographic behavior of the aci and nitro forms of α-nitrotoluene; it was found that these forms differed in behavior*. This fact made it possible for us to study the kinetics of transformations in the system

\[
N + B \xrightarrow{k_{ND}} N^- + BH^+ \xrightarrow{k_4} A^- + BH^+ \xrightarrow{k_{AR}} A + B
\]

(1)

In this equation the constants have the same significance as in the preceding communication; N and A denote the nitro and aci forms of α-nitrotoluene; B and BH+ denote the base and its conjugate acid. The kinetics of the transformation of aci-α-nitrotoluene into the nitro form were studied in the pH range 1-4, of the nitro form into the anion in the pH range 7-10, and of the anion into the nitro form in the pH range 4-6. Also, the dissociation constants of the aci and nitro forms were determined polarographically and potentiometrically.

The kinetics of the reactions were studied in buffer solutions, so that the measured reaction rate was the over-all rate of reaction with all the bases present in the buffer mixture. To find the rate constants for reaction with each of the bases we measured reaction rates at different concentrations of the given base, keeping the pH of the solution, the concentrations of the other bases, and the ionic strength constant. Thus, we determined the rate of reaction of α-nitrotoluene with OH-, HPO₄²⁻, and H₂BO₃⁻ and the rate of reaction of aci-α-nitrotoluene with H₂O, CH₃COO⁻, ClCH₂COO⁻ and the nitrate ion. As will be shown below, the rate of reaction of α-nitrotoluene with water is very low; its value (< 5 \times 10⁻⁵ sec⁻¹) lies within the limits of experimental error and so cannot be determined experimentally. As Maron and La Mer [2] showed, the reaction under consideration obeys the Bronsted equation. To find, and to determine with greater accuracy, the constants of the Bronsted equation, we determined also the rate of reaction of α-nitrotoluene with NH₄⁺ and with acetate and diethylbarbiturate ions.

*The anions of the substances are polarographically inactive.
The work was carried out with a manual polarograph. Current measurement was carried out with an M-91 microammeter. The potential of the dropping electrode with respect to the anode (a saturated calomel electrode) was determined in the kinetic measurements with an LM-1 voltmeter accurately within 0.01 v. In the taking of polarograms the potential of the dropping electrode was determined potentiometrically with respect to a subsidiary saturated calomel electrode with a P-4 potentiometer with an extended measurement range [3]. The experiments were carried out in a thermostated cell [4] at 25 + 0.1°. The cathode was a dropping mercury electrode fitted with a blade for forced drop removal [5]. Most of the work was carried out with a capillary having the following characteristics: \( m = 1.81 \text{ mg/sec; } t = 0.29 \text{ sec; } m^{2/3}t^{1/6} = 1.209 \text{ mg}^{2/3} \text{ sec}^{-1/2} \). Before the measurements were carried out, oxygen was removed from the solution by passage of nitrogen saturated with solvent vapor [4].

The measurements were carried out in the following buffer solutions: HCl + KCl; CH₃CO₂Na + HCl; K₂HPO₄ + Na₂B₄O₇; NazB₄O₇ + NaOH. The measurement of the pH values of the solutions and the direct determination of the dissociation constant of the aci form were carried out with the aid of a glass electrode and an LP-5 or LP-59 potentiometer. The reagents used had the following characteristics: 1) \( \alpha \)-Nitrotoluene; b.p. 88° (2 mm); m² 1.5320; 2) Potassium salt of \( \alpha \)-nitrotoluene. Found: K 22.43; 22.11%. C₇H₆NO₂K. Calculated: K 22.32% The salts for the preparation of buffer mixtures were of "Chemically Pure" or "Pure for Analysis" qualities.

Polarographic Investigation of Aci and Nitro Forms of \( \alpha \)-Nitrotoluene. The determination of the polarograms of the nitro form of \( \alpha \)-nitrotoluene presented no difficulties. On the other hand, because of the instability of the aci form it was not possible to determine their polarograms in the usual way; they were determined as follows. Buffer solution of pH 1.15 (9.5 ml) was poured into the cell and left to attain 25° while nitrogen was passed to removed dissolved oxygen. The dropping electrode was polarized at the given potential and the residual current was measured. After this, 0.5 ml of an aqueous-alcoholic (8% of alcohol by volume) solution of the potassium salt of \( \alpha \)-nitrotoluene was poured rapidly into the cell and vigorously agitated with nitrogen for 5-7 sec; then, after every 15 sec, the limiting current was read off; it diminished continuously because of the conversion of the aci form into the nitro form. In these experiments the potential of the dropping electrode was varied from -0.1 to -1.2 v in 0.1-v intervals (and in 0.05- and 0.025-v intervals in the region of the rise in the curve). The value of the current corresponding to the aci form at a given potential was found by extrapolation of the values found to zero time. The concentration of the substance investigated in the cell was 4.8 \( \times \) 10^{-4} mole/liter; the alcohol concentration was 0.4%.

Figure 1 gives the polarograms of the aci form (Curves 1 and 1a) and nitro form of \( \alpha \)-nitrotoluene (Curve 2). Curve 1a was obtained in presence of a little methyl red, added for the suppression of the polarographic maximum. The polarogram of the nitro form was determined in the same buffer solution and with the same concentration of the substance under investigation. The half-wave potentials \( E_{1/2} \) of the two forms in solution at pH 1.15 were found to be -0.52 v for the nitro form and -0.66 for the aci form.

The height of the wave of the aci form was about 1.5 times that of the nitro form. This difference is probably to be explained by the fact that reduction of the aci form occurs with the participation of six electrons, whereas the reduction of the nitro form under the same conditions only four electrons participate.

Kinetics of the Dissociation of \( \alpha \)-Nitrotoluene. An examination of the polarograms of \( \alpha \)-nitrotoluene determined at various pH values showed that at pH < 5.5 \( \alpha \)-nitrotoluene gives a clearly marked reduction wave in which the limiting current is independent of pH and is proportional to the \( \alpha \)-nitrotoluene concentration in the solution. With rise in the pH of the solution to above 6 at a given \( \alpha \)-nitrotoluene concentration, as a result of its dissociation, the wave height begins to fall with time and tends to a certain limit. The magnitude of this limit appears to correspond to the undissociated part of the \( \alpha \)-nitrotoluene which is in equilibrium with its anion. With rise in pH the value of the current established diminishes and approaches to zero at pH 9.0. The equilibrium character of this limit is indicated by the fact that for a given pH of the solution the same value of the limiting current is obtained when a salt of \( \alpha \)-nitrotoluene is taken instead of \( \alpha \)-nitrotoluene itself. Hence, the equilibrium state can be attained both by