

## Kinetics and Mechanism of *p*-Nitrochlorobenzene Nitration with Nitric Acid

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**Abstract**—Kinetics of homogeneous nitration of *p*-nitrochlorobenzene with 85–95% nitric acid was investigated. An introduction of a nitro group into a chlorobenzene molecule results in 1600 times deceleration of nitration. It was presumed from comparison of kinetic parameters and correlations of  $\log k_{\text{eff}}$  for the mono- and dinitration with the acidity functions of nitric acid that the limiting stage in *p*-nitrochlorobenzene nitration was the transformation of diffusion pairs into reaction products, whereas in chlorobenzene nitration the limiting stage consisted in diffusion pairs formation.

2,4-Dinitrochlorobenzene is widely used as an initial compound in the organic synthesis. The most common method of its production is a nitration of nitrochlorobenzene with mixtures of nitric and sulfuric acids [1]. The kinetics of homogeneous nitration of nitrochlorobenzene by nitric acid in sulfuric acid medium is sufficiently well studied. It was demonstrated that like the behavior of nitrobenzene, *p*-nitrotoluene, 2,4-dinitrotoluene and the other aromatic compounds the bimolecular rate constant of nitration of *o*- and *p*-nitrochlorobenzenes into 2,4-dinitrochlorobenzene went through a maximum at 25°C in 89–90% sulfuric acid, and its decrease at further increase in sulfuric acid concentration was apparently due to diminishing activity coefficient of the non-ionized aromatic substrate [2, 3].

No publications appeared on kinetics of homogeneous nitration of nitrochlorobenzene isomers with nitric acid only.

We studied [4] kinetics of chlorobenzene nitration with nitric acid under homogeneous conditions into a mononitrocompound. In order to compare the mechanism of the mono- and dinitration, of their limiting stages, it was necessary to measure the rate of dinitrochlorobenzene formation in this system.

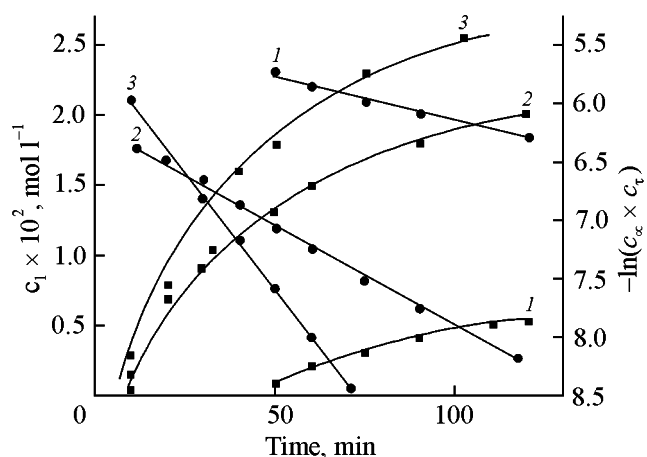
The nitration was carried out with *p*-nitrochlorobenzene that furnished a single reaction product, 2,4-dinitrochlorobenzene [3].

We established that due to the deactivating effect of a nitro group the nitration of the *p*-nitrochlorobenzene into 2,4-dinitrochlorobenzene occurred with a measurable rate only in nitric acid of concentration greater than 85%.

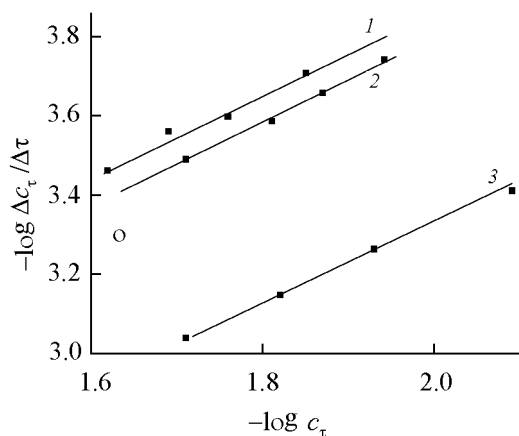
Typical curves of 2,4-dinitrochlorobenzene accumulation and their semilog plots are given on Fig. 1.

The dependence of nitration rate on the concentration of the arising dinitrochlorobenzene in all studied ranges of nitric acid concentrations and of temperature (Fig. 2) is linear in bilog coordinates, and the slope is close to unity ( $n$  0.98–1.08), and thus the assignment to the selected conditions of the pseudofirst order is valid [5].

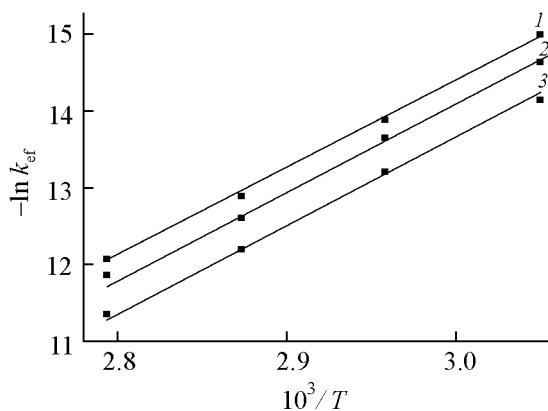
Effective rate constant of the pseudofirst order  $k'_{\text{eff}}$  corresponding to accumulation of dinitrochlorobenzene under experimental conditions does not change in the course of the process.



**Fig. 1.** Kinetic curves of 2,4-dinitrochlorobenzene accumulation during nitration of 4-nitrochlorobenzene with 90.5% nitric acid, and their semilog plots. (1) 65, (2) 75, (3) 85°C.



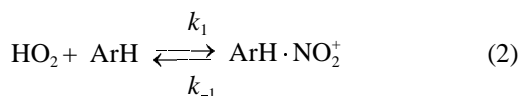
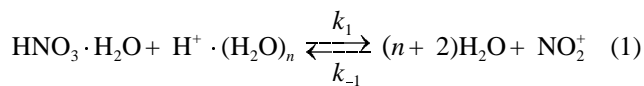
**Fig. 2.** Dependence of nitration velocity of 4-nitrochlorobenzene with nitric acid ( $V = \Delta c_t / \Delta \tau$ ) on concentration ( $c_t$ ) of arising 2,4-dinitrochlorobenzene at 85°C.  $[\text{HNO}_3]$ , %: (1) 85.0 ( $n$  1.01), (2) 90.50 ( $n$  0.98), (3) 95.10 ( $n$  1.08).



**Fig. 3.** Arrhenius plot for chlorobenzene nitration at various concentrations of nitric acid  $[\text{HNO}_3]$ , %: (1) 85.0, (2) 90.5, (3) 95.1.

The dependence of nitration velocity on the temperature fits to Arrhenius equation (Fig. 3). The obtained values of pseudofirst order rate constant  $k'_{\text{eff}}$  are presented in Table 1.

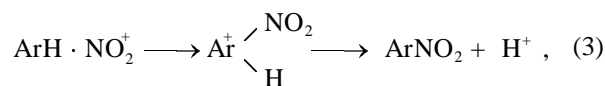
Taking into account the significant difference in nitration rates of chlorobenzene and its nitro derivative that will be demonstrated further, and also the participation of two water molecules in the reversible reaction of the nitronium cation formation in the aqueous nitric acid [6, 7], we suggest the following scheme for the nitration of nitrochlorobenzene:



**Table 1.** Dependence of pseudofirst order rate constant of 4-nitrochlorobenzene nitration<sup>a</sup> on nitric acid concentration and reaction temperature

$[\text{HNO}_3]$ , %	$k'_{\text{eff}} \times 10^4$ , 1/s				$E$ , kJ/mol
	55°C	65°C	75°C	85°C	
85.0	0.31	0.90	2.6	5.5	93±2
90.5	0.43	1.20	3.4	7.1	90±2
95.1	0.74	1.95	5.2	11.7	88±2

<sup>a</sup> In all experiments the concentration of 4-nitrochlorobenzene was 1.06 mol l<sup>-1</sup>.



where  $\text{ArH} \cdot \text{NO}_2^+$  is a diffusion pair [8].

Regarding the nitronium concentration as stationary we obtain the following expression for the reaction rate:

$$\frac{-d[\text{ArH}]}{d\tau} = \frac{k_1 k_2 k_3 [\text{ArH}] \cdot a_{\text{HNO}_3} \cdot a_{\text{H}^+} \cdot a_{\text{H}_2\text{O}}^n}{k_{-1} \cdot a_{\text{H}_2\text{O}}^2 \cdot a_{\text{H}_2\text{O}}^n (k_2 + k_3) + k_2 k_3 [\text{ArH}]} \quad (4)$$

At low concentrations of the aromatic compound in excess nitric acid

$$k_{-1} \cdot a_{\text{H}_2\text{O}}^2 \cdot a_{\text{H}_2\text{O}}^n (1 + k_2/k_3) \gg k_2 [\text{ArH}] \quad (5)$$

and expression (4) can be written as follows:

$$\frac{-d[\text{ArH}]}{d\tau} = \frac{k_1 k_2 \cdot a_{\text{HNO}_3} \cdot a_{\text{H}^+} [\text{ArH}]}{k_{-1} \cdot a_{\text{H}_2\text{O}}^2 (1 + k_2/k_3)} \quad (6)$$

At nitration of aromatic hydrocarbons of high reactivity  $k_3 \gg k_{-2}$ , and the pseudofirst order constant is

$$k_{\text{eff}} = \frac{K_{\text{p1}} k_2 \cdot a_{\text{HNO}_3} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{O}}^2} \quad (7)$$

where  $K_{\text{eq1}}$  is the equilibrium constant of reaction (1).

At nitration of aromatic hydrocarbons of low reactivity  $k_3 \ll k_{-2}$ , and the stage (3) of transformation of diffusion pair into reaction products becomes the rate limiting one. In this case the pseudofirst order constant is

$$k_{\text{eff}} = \frac{K_{p1} K_{p2} k_3 \cdot a_{\text{HNO}_3} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{O}}^2} \quad (8)$$

where  $K_{\text{eq}2}$  is the equilibrium constant of reaction (2).

To elucidate the nitration mechanism of nitrochlorobenzene we studied the dependence of the reaction rate on the acidity of the medium. Since for temperature higher than 25°C are no data on activity of the aqueous nitric acid in the calculation of the bimolecular rate constant along the equation  $k_{\text{eff}} = k'_{\text{eff}}/a_{\text{HNO}_3}$  were used  $k'_{\text{eff}}$  values extrapolated to 25°C. The values of  $k_{\text{eff}}$  obtained are given in Table 2.

The transformation of equation (8) gives the following expression for the bimolecular rate constant:

$$k_{\text{eff}} = \frac{K_{p1} K_{p2} k_3 \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{O}}^2} \quad (9)$$

and consequently

$$\log k_{\text{eff}} = \log K_{p1} K_{p2} k_3 - (H_{\text{R}} + \log a_{\text{H}_2\text{O}}). \quad (10)$$

The dependence of  $\log k_{\text{eff}}$  on acidity functions  $H_0$ ,  $H_{\text{R}}$  and  $(H_{\text{R}} + \log a_{\text{H}_2\text{O}})$  is described by equations (11–13) respectively.

$$\log k_{\text{eff}} = -(9.77 \pm 0.12) \times 10^{-2} - H_0 - (7.90 \pm 0.02) \quad (11)$$

$r$  0.99,  $s$  0.014.

$$\log k_{\text{eff}} = -(4.74 \pm 0.19) \times 10^{-2} - H_{\text{R}} - (7.74 \pm 0.01) \quad (12)$$

$r$  0.99,  $s$  0.075.

$$\log k_{\text{eff}} = -(3.06 \pm 0.16) \times 10^{-2} - (H_{\text{R}} + \log a_{\text{H}_2\text{O}}) - (7.68 \pm 0.02) \quad (13)$$

$r$  0.98,  $s$  0.098.

It is seen from these equations that the slopes of all these linear dependencies are very small, i.e., the nitration rate is weakly affected by the change in acidity of the aqueous nitric acid expressed by these functions.

These results are unlike those obtained in the study on kinetic and mechanism of the chlorobenzene mononitration. We showed in [4] that in the chlorobenzene nitration with aqueous nitric acid the  $\log k_{\text{eff}}$  depended linearly on the acidity functions  $H_0$ ,  $H_{\text{R}}$  and  $(H_{\text{R}} + \log a_{\text{H}_2\text{O}})$ , and the slope of the plot was close to unity. The comparison of kinetic parameters and dependencies thereof on the acidity of medium in nitration of chlorobenzene and nitrochlorobenzene suggests that in the chlorobenzene nitration with the aqueous nitric acid the process rate is determined by the stage of diffusion pairs formation (2). Apparently under conditions where the rate of diffusion pairs transformation into reaction products is considerably higher than the rate of their dispersion the nitration kinetics is described by equation (7), and the bimolecular rate constant  $k_{\text{eff}}$  characterizes the equilibrium process of nitronium cation formation along reaction (1) that is affected by the medium acidity. This reasoning is supported by the fact that for a linear correlation  $\log k_{\text{eff}} = f(H_{\text{R}} + \log a_{\text{H}_2\text{O}})$  which we have calculated from the data of [8] on nitration of mesitylene and *p*-xylene with aqueous nitric acid the slope was equal to 1.1. The rate of nitration for these compounds was limited by the stage of diffusion pairs formation [8].

The weak dependence of the nitration rate of the nitrochlorobenzene on the medium acidity may show that due to the low reactivity of the substrate the dispersion rate of diffusion pairs is higher than the rate of their transformation into the reaction products. Therefore the stage (3) becomes limiting, and its rate constant is not directly dependent on the medium acidity and is determined solely by reactivity of the substrate.

It is seen from the data of Table 2, that  $k_{\text{eff}}$  grows only insignificantly with increasing concentration of the nitric acid. It is presumable that as an additional factor reducing the influence of the medium acidity on the reaction rate operates the decrease in activity coefficient of the substrate in the more concentrated

**Table 2.** Values of nitration rate constant for 4-nitrochlorobenzene nitration with nitric acid, and the acidity functions of the latter, 25°C

[HNO <sub>3</sub> ], %	$k'_{\text{eff}} \times 10^6$ , 1 s <sup>-1</sup>	$k_{\text{eff}} \times 10^8$ , 1 mol <sup>-1</sup> s <sup>-1</sup>	$-\log k_{\text{eff}}$	$\log a_{\text{HNO}_3}$	$-H_0$	$-\log a_{\text{H}_2\text{O}}$	$-H_{\text{R}}$	$-(H_{\text{R}} + \log a_{\text{H}_2\text{O}})$
85.0	1.06	3.80	7.42	1.45	4.96	1.61	6.57	8.18
90.5	1.59	3.89	7.40	1.65	5.00	2.05	7.05	9.10
95.1	2.93	4.57	7.34	1.81	5.75	2.58	8.33	10.91

nitric acid as was observed for nitration of nitrobenzene isomers in sulfuric acid medium [4].

The data in Table 1 indicate that in nitrochlorobenzene nitration the experimental value of activation energy  $E$  only slightly decreases with growing concentration of nitric acid; apparently the activation energy is weakly affected by  $\Delta H$  of the process of nitronium cation formation along reaction (1).

The comparison of  $k_{\text{eff}}$  values for mono- and dinitration of chlorobenzene shows that introduction of a nitro group in the para-position with respect to chlorine results in 1600 times reaction rate decrease, whereas in homogeneous nitration in sulfuric acid medium the ratio  $k_{\text{eff}}^{\text{mono}}/k_{\text{eff}}^{\text{di}}$  equals 135 [9]. Presumably this difference is due to lower activity and consequently higher selectivity of the nitrating agent in the aqueous nitric acid [3].

### EXPERIMENTAL

The procedure for preparation of nitric acid water solutions was described in [4].

We used *p*-nitrochlorobenzene of mp 83.5°C, 2,4-dinitrochlorobenzene of mp 51.0°C from ethanol).

The nitration kinetics was studied by means of GLC on a gas chromatograph Tsvet-500M by measuring 2,4-dinitrochlorobenzene accumulation under conditions of pseudofirst order at 20-fold molar excess of nitric acid. The stationary phase used was XE-60 (5%) on Chromaton-N-AW-DMC with particle size 0.325–0.400 nm. Carrier gas helium, detector katharometer, detector temperature 360°C, oven temperature programmed from 90 to 360°C.

The reaction was carried out in a flask kept at constant temperature and equipped by stirrer, thermometer, and sampling device. A weighed portion of *p*-nitrochlorobenzene was charged to the flask at stirring into the nitric acid of a given concentration. The reaction progress was monitored by sampling. Temperature in the course of reaction was controlled within  $\pm 0.1^\circ\text{C}$ . The samples of the reaction mixture were diluted with excess 2-propanol and analyzed for

content of mono- and dinitrochlorobenzene isomers. The effective constants of pseudofirst order were calculated by the formula:

$$k' = \tau^{-1} \ln \frac{(c_\infty - c_0)}{(c_\infty - c_\tau)},$$

where  $c_0$ ,  $c_\tau$ ,  $c$  is dichlorobenzene concentration, mol l<sup>-1</sup> at the start of reaction, at the moment of measurement, and at the end of the experiment respectively.

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