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Kinetics and Mechanism of the Nitration of Chlorobenzene with Nitric Acid

E. A. Veretennikov, B. A. Lebedev, and I. V. Tselinskii

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 198013 Russia
fax: (812) 112 7791

Abstract—The rate of homogeneous nitration of chlorobenzene with 70–90% nitric acid is proportional to the chlorobenzene concentration and activity of nitric acid. The existence of linear correlations between the rate constants $k_{2\,ap}$ and the acidity function $-H$ and between $\log k_{2\,ap}^{*}$ values (calculated using NO_2^{+} concentration) and the acidity function $-(H_R + \log a_{H_2O})$ indicates that the nitrating species is nitronium ion generated by reaction of H_3O^{+} with nitric acid monohydrate. Increase in the energy of activation with rise in water concentration is explained by increase of ΔH for equilibrium formation of nitronium ion.

The main preparative procedure for synthesis of chloronitrobenzene is based on the nitration of chlorobenzene with a mixture of nitric and sulfuric acids [1]. Chlorobenzene is poorly soluble in the acid mixture; therefore, the reaction mixture is heterogeneous (it consists of organic and inorganic phases). The reaction was found to occur at a high rate in the acid phase; the overall reaction rate is determined by the slowest stage, diffusion of the reactants into the reaction zone [2, 3]. Unlike mixtures of sulfuric and nitric acids, chlorobenzene is readily soluble in nitric acid at elevated temperature; therefore, the use of nitric acid alone as nitrating agent should eliminate decelerating effect of diffusion on the overall rate of the process. However, the kinetics of nitration of chlorobenzene was studied only for aqueous solutions of nitric acids with a concentration of 65–70% at 25°C [4].

In the present work we examined the nitration of chlorobenzene with 70–90% nitric acid under conditions of pseudofirst-order reaction over a wide temperature range. Figure 1 shows typical kinetic curves for accumulation of chloronitrobenzene in the nitration of chlorobenzene with 75.33% nitric acid and the corresponding semilog plots. The slope of the linear logarithmic plots of the nitration rate versus chloronitrobenzene concentration is close to unity ($n = 0.97$ to 1.05) throughout the examined ranges of nitric acid concentrations and temperature (Fig. 2). This indicates the first order of the reaction in chlorobenzene under the given conditions [5].

The kinetic parameters of the nitration of chlorobenzene are given in Table 1. Figure 3 shows that the temperature dependences of the pseudofirst-order rate constants are well described by the Arrhenius equation.

In order to determine the mechanism of nitration we examined the dependence of the reaction rate on the acidity of the medium. According to the data of spectrophotometric measurements, in 70–90% aqueous solutions nitric acid exists as the hydrate $HNO_3 \cdot H_2O$ and its dissociation into nitrate ion and hydroxonium ion is minimal [6]. On raising the nitric acid concentration, the degree of hydration decreases, and the contribution of self-ionization to formation of nitronium ion increases.
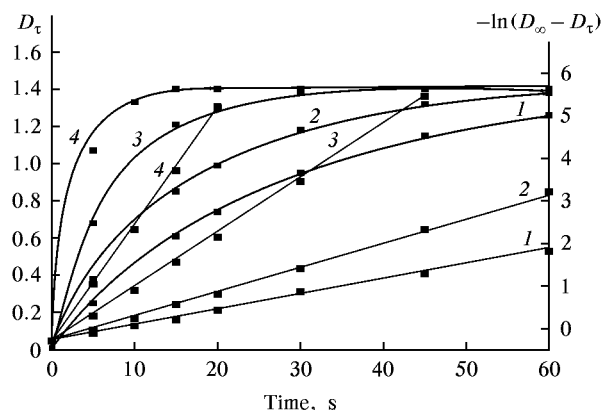

Fig. 1. Kinetic curves for accumulation of chloronitrobenzene in the nitration of chlorobenzene with 75.33% nitric acid and the corresponding semilog plots: (*1*) 72, (*2*) 75, (*3*) 78, and (*4*) 82°C.
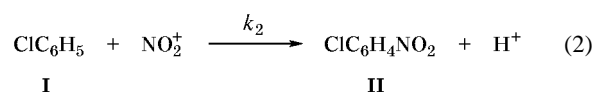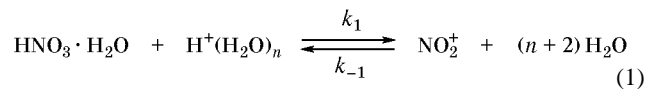
Table 1. Apparent rate constants $k'_{ap} \times 10^2$ (s^{-1}) and energies of activation for nitration of chlorobenzene in nitric acid[a]

[HNO$_3$], %	51°C	55°C	59°C	63°C	69°C	72°C	75°C	78°C	82°C	87°C	E, kJ/mol
70.36	–	–	–	–	–	–	3.6	5.9	12.6	27.5	178±2
75.33	–	–	–	–	–	7.6	13.3	26.2	56	83	170±2
80.44	–	–	–	–	8.7	16.2	25.2	45	75	–	167±2
90.50	12.7	16.7	30.1	45	81	112[b]	151[b]	202[b]	–	–	98±2

[a] In all experiments the concentration of chlorobenzene was 8.66×10^{-4} M.
[b] Obtained by extrapolation of the k'_{ap}—$1/T$ dependence (Fig. 3).

Taking into account that the formation of nitronium ion in both aqueous sulfuric acid and aqueous nitric acid is reversible and that it involves two water molecules [7, 8], the nitration process may be represented by the following scheme:

$$HNO_3 \cdot H_2O + H^+(H_2O)_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ + (n+2)H_2O \quad (1)$$

$$\underset{\textbf{I}}{ClC_6H_5} + NO_2^+ \overset{k_2}{\longrightarrow} \underset{\textbf{II}}{ClC_6H_4NO_2} + H^+ \quad (2)$$

Assuming that the concentration of nitronium ion is qausistationary, we obtain Eq. (3) for the rate of accumulation of the nitration product:

$$\frac{\partial[\textbf{II}]}{\partial\tau} = \frac{k_1 k_2 a_{H^+} a^n_{H_2O}}{k_{-1} a^2_{H_2O} a^n_{H_2O} + k_2[\textbf{I}]} [\textbf{I}] a_{HNO_3}, \quad (3)$$

where a is the activity of the corresponding species. At low chlorobenzene concentration $k_{-1} a^2_{H_2O} a^n_{H_2O} \gg k_2[\textbf{I}]$, and Eq. (3) can be transformed into

$$\frac{\partial[\textbf{II}]}{\partial\tau} = \frac{k_1 k_2 a_{H^+}}{k_{-1} a^2_{H_2O}} [\textbf{I}] a_{HNO_3} \quad (4)$$

with the second-order rate constant

$$k_{2\,ap} = k'_{ap}/a_{HNO_3} = \frac{K_{eq} k_2 a_{H^+}}{a^2_{H_2O}}, \quad (5)$$

where K_{eq} is the equilibrium constant (1). From Eq. (5) we obtain

$$\log k_{2\,ap} = \log(K_{eq} k_2) + \log(a_{H^+}/a^2_{H_2O}). \quad (6)$$

It is known that

$$\log(a_{H^+}/a^2_{H_2O}) = -(H_R + \log a_{H_2O}); \quad (7)$$

therefore,

$$\log k_{2\,ap} = \log(K_{eq} k_2) - (H_R + \log a_{H_2O}), \quad (8)$$

where H_R is the acidity function determined from the ionization equilibrium of triarylmethanols [9].

While studying the effect of medium acidity on the rate of nitration of a large number of aromatic and heterocyclic compounds with HNO$_3$–H$_2$SO$_4$ mixtures, it was found that a slope close to unity (0.95–1.08) is observed only for the linear correlation of $\log k_{2\,ap}$ with $-(H_R + \log a_{H_2O})$. According to [7, 8], these data indicate that in aqueous sulfuric acid the nitrating agent is nitronium ion generated by reaction (1). There are no published data on the existence of analogous correlations for nitration of aromatic hydrocarbons with aqueous nitric acid.

Unlike HNO$_3$–H$_2$SO$_4$ mixtures, H_R values for aqueous nitric acid were determined only at 20 and 25°C [10]; therefore, in our calculations we used the second-order rate constants $k_{2\,ap}$ derived from the pseudofirst-order rate constants k'_{ap} extrapolated to a temperature of 25°C by the formula

$$k_{2\,ap} = k'_{ap}/a_{HNO_3}.$$

The activity of nitric acid was calculated by the equation

$$\log a_{HNO_3} = 2\log(f x),$$

where f and x, are, respectively, the coefficient of activity and molar concentration of nitric acid in the system nitric acid–water [11]. The values of H_0 were taken from [10]. The results are given in Table 2.

Figure 4 shows that only the correlation of $\log k_{2\,ap}$ with the acidity function $(H_R + \log a_{H_2O})$ has a slope close to unity (0.96). This fact supports the assumption that the formation of nitronium ion in both aqueous sulfuric acid and aqueous nitric acid follows the same mechanism involving reaction of nitric acid
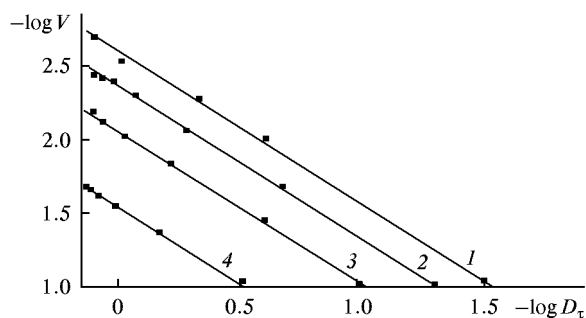
Fig. 2. Logarithmic plots of the rate ($V = D_\tau/\tau$) of nitration of chlorobenzene with nitric acid versus optical density of chloronitrobenzene solutions. Nitric acid concentration, %: (*1*) 70.36, 75°C ($n = 0.99$); (*2*) 75.33, 72°C ($n = 1.01$); (*3*) 80.44, 69°C ($n = 1.05$); (*4*) 90.50, 51°C ($n = 0.97$); n is the order of reaction.
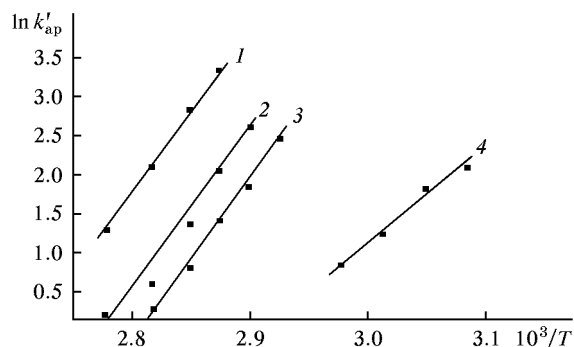

Fig. 3. Arrhenius plots for the nitration of chlorobenzene with nitric acid of various concentrations. The numbers of plots correspond to those given in Fig. 2.
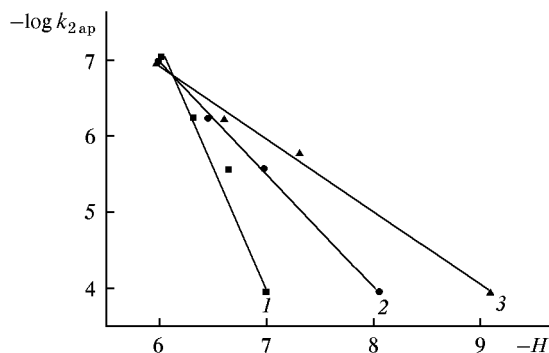

Fig. 4. Correlations of $\log k_{2\,ap}$ with acidity functions at 25°C: (*1*) H_0, $n = 2.92$; (*2*) H_R, $n = 1.44$; (*3*) $H_R + \log a_{H_2O}$, $n = 0.96$; n is the slope.

monohydrate with hydroxonium ion. An additional support of the role of nitronium ion as active nitrating species in aqueous nitric acid was obtained by studying the relation between the acidity of the medium

and the apparent second-order rate constant ($\log k_{2\,ap}^*$) for nitration of chlorobenzene, calculated with regard to the nitronium ion concentration. As follows from equilibrium (1), the activity ratio of nitronium ion and nitric acid can be expressed by Eq. (9):

$$\frac{a_{HNO_3}}{[NO_2^+]} = \frac{a_{H_2O}^2 f_{NO_2^+}}{K_{eq}\, a_{H^+}}. \qquad (9)$$

Substituting a_{HNO_3} into Eq. (3) for the reaction rate gives Eq. (10) for the bimolecular rate constant:

$$k_{2\,ap}^* = k_{ap}'/[NO_2^+] = \frac{k_2 f_{NO_2^+}}{K_{eq}}\, \frac{a_{H_2O}^2}{a_{H^+}}, \qquad (10)$$

then

$$\log k_{2\,ap}^* = \log\frac{k_2 f_{NO_2^+}}{K_{eq}} + \log\frac{a_{H_2O}^2}{a_{H^+}} = \frac{k_2 f_{NO_2^+}}{K_{eq}}$$
$$+ (H_R + \log a_{H_2O}). \qquad (11)$$

If Eq. (11) is applicable to nitration of chlorobenzene with aqueous nitric acid, we could expect a linear correlation between $\log k_{2\,ap}^*$ and $-(H_R + \log a_{H_2O})$ with a slope close to unity. The concentrations of nitronium ion were obtained by extrapolation of the data in [7]. The plot of $\log k_{2\,ap}^*$ versus $-(H_R + \log a_{H_2O})$ is shown in Fig. 5; it is linear, and its slope is 0.99.

Thus the results of our kinetic study lead us to conclude that the rate-determining stage in the nitration of chlorobenzene with aqueous nitric acid is the reaction of the aromatic substrate with nitronium ion generated by the reversible reaction of nitric acid monohydrate with hydroxonium ion.

Cox and Strachan [2] reported the pseudofirst-order rate constant k_{ap}' for nitration of chlorobenzene in 70.2% sulfuric acid at 25°C to be 3.3×10^{-5} s^{-1}. Comparison of this value with the data in Table 1 shows that the nitration of chlorobenzene with 70–80% nitric acid proceeds at approximately the same rate, but in 90.5% nitric acid the reaction rate increases by almost two orders of magnitude.

Analysis of the activation parameters (Table 1) shows that increase in the concentration of nitric acid is accompanied by reduction of the activation energy, which becomes especially significant in going from 80% to 90% nitric acid. An analogous pattern was observed in the nitration of aromatic hydrocarbons with mixtures of sulfuric and nitric acids [2]: The energy of activation decreases by about 3.1 kJ/mol as

Table 2. Second-order rate constants $k_{2\,ap}$ for the nitration of chlorobenzene with nitric acid and acidity functions of aqueous nitric acid at 25°C

[HNO$_3$], %	$k'_{ap} \times 10^5$, s^{-1}	$k_{2\,ap} \times 10^5$, l mol^{-1} s^{-1}	$-\log k_{2\,ap}$	$-H_0$	$-\log a_{H_2O}$	$-H_R$	$-(H_R + \log a_{H_2O})$
70.36	0.12	0.012	6.93	4.01	0.99	5.00	5.99
75.33	0.65	0.063	6.21	4.32	1.14	5.46	6.60
80.44	1.02	0.286	5.55	4.65	1.33	5.98	7.31
90.50	464	11.3	3.95	5.00	2.05	7.05	9.10

the sulfuric acid concentration rises by 1 mol %. According to our data, the reduction in the activation energy for nitration of chlorobenzene with 70–80% nitric acid is 0.82 kJ/mol per 1 mol % of nitric acid, and in going from 80% to 90% nitric acid this value increases to 3.61 kJ/mol per 1 mol % of nitric acid.

The experimental energy of activation in homogeneous nitration is the sum of the energy of activation (E_a) of reaction (2) and the change in the enthalpy (ΔH) of equilibrium (1):

$$E = E_a + \Delta H. \qquad (12)$$

The quantity E_a is determined mainly by the substrate nature rather than by properties of the medium; therefore, the observed variation of E is caused by decrease of ΔH with rise in the nitric acid concentration, and it reflects increasing contribution of self-ionization to the formation of nitronium ion and weakening of its solvation as the activity of water in the reaction system decreases. This is supported by the fact that ionization of water in the system HNO$_3$–H$_2$O becomes appreciable when its concentration reaches 10 wt % [12]. Presumably, in nitric acid with a concentration lower than 90% ΔH sharply increases due to increase of the contribution of reaction (1) to formation of nitronium ion. As a result, the energy of activation in the nitration of chlorobenzene with 70–80% nitric acid is almost twice as high as that found for 90% nitric acid.

It should be noted that the experimental energy of activation $E = 98.64$ kJ/mol for nitration with 90.5% nitric acid is fairly consistent with the value 85 kJ/mol found for homogeneous nitration of chlorobenzene in 70.2% sulfuric acid.

Chloronitrobenzene obtained in experiments with 90% nitric acid at 55–69°C contained 68–70% of the *para* isomer, 29.5–31.9% of the *ortho* isomer, and 0.1–0.5% of the *meta* isomer. Thus, the nitration with aqueous nitric acid is characterized by formation of

a greater fraction (by about 5%) of *p*-chloronitrobenzene and smaller fraction (by 1.5–2%) of the *meta* isomer, as compared with reactions in HNO$_3$–H$_2$SO$_4$ mixtures, which may be explained in terms of the different activities of the nitrating agent in these media [13].

EXPERIMENTAL

The kinetics of nitration of chlorobenzene were studied by spectrophotometry using a Perkin–Elmer 402 spectrometer (1-cm quartz cells). The isomer composition of the product was determined by GLC on a Tsvet-500M chromatograph equipped with a thermal conductivity detector; stationary phase 5% of XE-60 on Chromaton-N-AW-DMC (0.315–0.400 nm); column length 3 m; carrier gas helium; injector and detector temperature 360°C; oven temperature programming: 40 s at 90°C, 90 s at 180°C, and 150 s at 320°C.

Reagent-grade nitric acid ($d_4^{20} = 1.501$ g/cm^3) containing 98% of the main substance was distilled under reduced pressure from a mixture with sulfuric acid and was then diluted at 0°C with twice distilled water to a required concentration. To remove nitrogen oxides, sulfamic acid was added to the mixture of nitric and sulfuric acids prior to distillation. The concentration of nitric acid was determined by titration
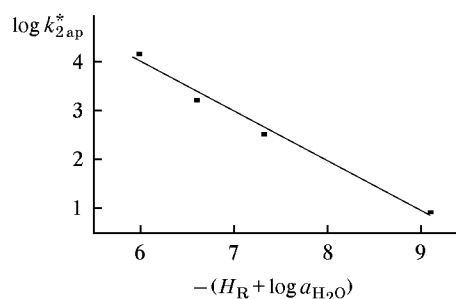
Fig. 5. Plot of $\log k^*_{2\,ap}$ versus $-(H_R + \log a_{H_2O})$ at 25°C.

with alkali. Chlorobenzene was purified by distillation just before use, and its purity was checked by GLC.

The nitration was performed using nitric acid with a concentration of 70.36 to 90.50%. For each concentration the temperature range was selected so as to ensure homogeneous reaction mixture. The reactions were carried out in a cell maintained at a constant temperature (within ±0.1°C) by injecting chlorobenzene into nitric acid heated to a required temperature. Samples of the mixture were withdrawn at specified time intervals and were transferred to a fixed amount of ethanol, and the optical density of the solution was measured.

The concentration of chloronitrobenzene was determined at a wavelength corresponding to the UV absorption maximum of chloronitrobenzene isomers ($\lambda = 340$ nm) in the presence of a 20-fold molar amount of nitric acid. The pseudofirst-order rate constants k'_{ap} were calculated by the equation

$$k'_{ap} = \tau^{-1} \ln[(D_\infty - D_\tau)/(D_\infty - D_0)],$$

where D_0, D_∞, and D_τ are the optical densities at the initial moment, by the end of the reaction, and at time τ. The error in determination of k' did not exceed ±5%. The concentration of chloronitrobenzene was calculated by the equation

$$c_\tau = D_\tau V \varepsilon^{-1} V_s^{-1},$$

where V (l) is the amount of ethanol used for dilution of the reaction mixture, V_s (l) is the amount of the sample withdrawn, and ε is the molar absorption coefficient, $6620 \ \text{l mol}^{-1} \ \text{cm}^{-1}$.

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