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Kinetics of Low-Temperature Oxidative Chlorination of Benzene in Aqueous Acetic Acid

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Abstract — The kinetics of chlorination of benzene with a mixture of sodium peroxide with hydrochloric acid in aqueous acetic acid at 298 K was studied. The chlorination rate is the highest when the AcOH concentration in the binary solvent is 49.4 – 40.6 mol % and the ratio of the initial cocentrations of water and sodium peroxide, 18.5–20.2. The linear dependences of $\log k_{app}$ on the AcOH concentration and $[H_2O]_0/[Na_2O_2]_0$ ratio were obtained.

Arenes are usually chlorinated by a direct reaction of molecular chlorine with an aromatic compound. Another procedure used in production of chlorobenzene is high-temperature oxidative chlorination of benzene with chlorine generated by catalytic oxidation of HCl with oxygen [1]. However, the low-temperature (at 273–353 K) oxidative halogenation with hydrohalic acids and hydrogen peroxide (or metal peroxides) is studied insufficiently. As shown in [2–9], low-temperature halogenation allows preparation of chloro- and bromotoluenes, monochloro-*p*-xylene, 1-bromonaphthalene, and other compounds in fairly high yields without using toxic molecular halogens.

Taking into account the urgency of theoretical studies of oxidative halogenation, in this study we examined the solvent effect on the kinetics of the benzene chlorination in the system Na_2O_2–HCl–AcOH–H_2O. The simplified scheme of the process includes reactions (I)–(III):

$$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2, \quad (I)$$

$$H_2O_2 + 2HCl \longrightarrow Cl_2 + 2H_2O, \quad (II)$$

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl. \quad (III)$$

The experiment was performed at 298 K in aqueous AcOH of various concentrations. The reactant ratio $C_6H_6 : Na_2O_2 : HCl$ was 1 : 1 : (4–5). The benzene–chlorobenzene mixtures obtained were analyzed by GLC. Preliminary experiments showed that, under the experimental conditions, the yield of benzene dichlorination products was insignificant.

As in [10], the reaction rate is satisfactorily described by a second-order reaction equation. Table 1 shows that, as the AcOH concentration (N_{AcOH}) in the binary solvent AcOH–H_2O is decreased from 91.9 to 40.6 mol %, k_{app} increases (run nos. 1–7 in Table 1). A similar trend was observed in chlorination with molecular chlorine of benzene in trifluoroacetic acid [11] and of toluene in acetic acid [12].

In the N_{AcOH} range from 4.06 to 91.9 mol %, linear correlation (1) is valid (r –0.989):

$$\log k_{app} = -(2.33 \pm 0.11) - (2.36 \pm 0.14)N_{AcOH}/100. \quad (1)$$

At $N_{AcOH} \leq 40.6$ mol %, the constants decrease, and correlation (1) is no longer observed (Fig. 1).

Since, according to reactions (I) and (II), under the experimental conditions $[Na_2O_2]_0$ corresponds to $[Cl_2]_0$ and the chlorinating power of the system H_2O_2–HCl depends on the water concentration in the reaction mixture, decreasing with an increase in $[H_2O]$ [4], it could be expected that the ratio of the initial H_2O and Na_2O_2 concentrations q would affect the rate constant more significantly than does the AcOH concentration in the binary solvent. Indeed, in run nos. 7 and 12 (Table 1), at virtually equal N_{AcOH} (40.6 and 40.2 mol %), the rate constants are essentially different. In run nos. 15 and 16, at equal q (40.6 and 40.7) and different N_{AcOH} (42.6 and 30.5 mol %), the constants are virtually equal. The influence of the concentration ratio q on the rate constant is seen from Fig. 2.

The ascending and descending portions of the $\log k_{app}$–q dependence can be described by Eqs. (2) and (3), respectively:

$$\log k_{app} = (0.075 \pm 0.005)q - (4.932 \pm 0.065), \; r \; 0.989, \quad (2)$$

$$\log k_{app} = -(0.059 \pm 0.002)q - (2.010 \pm 0.093), \; r \; -0.997. \quad (3)$$

In the range of q from 18.5 to 21.1, the reaction

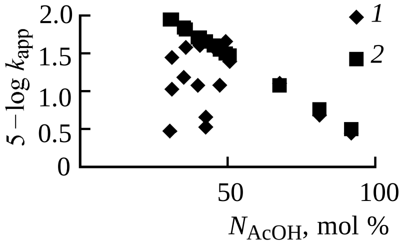

Fig. 1. Influence of the AcOH concentration in the binary solvent on k_{app}: (*1*) experimental data and (*2*) results of calculations by Eq. (1).

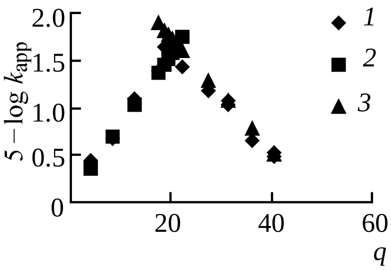

Fig. 2. Influence of the ratio *q* of the H_2O and Na_2O_2 concentrations on k_{app}: (*1*) experimental data and (*2, 3*) results of calculations by Eqs. (2) and (3), respectively.

rate is the highest, which is apparently due to the lowest activation energy under these conditions (Table 2).

To explain why the $\log k_{app}$–q dependence passes through a maximum, we can suggest that oxidative chlorination of benzene under the experimental conditions occurs with different limiting steps depending on *q* and on AcOH content in the binary solvent. At $q < 18$, in media with a high AcOH concentration, the reaction occurs by a common mechanism of electrophilic substitution [11, 12]. As the water concentration is increased, at $q > 20$, dissociation of HCl apparently starts to prevail, equilibria (4) and (5) are shifted to the right, and the formation of the chlorinating agent becomes the limiting step:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-, \qquad (4)$$

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl. \qquad (5)$$

Our results allow us to formulate certain practical recommendations concerning the synthesis of chlorobenzene. In particular, in chlorination of benzene with the system Na_2O_2–HCl–AcOH–H_2O at 298 K, the following conditions are the most favorable for the formation of chlorobenzene: initial concentration ratio $[H_2O]/[Na_2O_2]$ 18.5–21.1 and AcOH concentration in the binary solvent 40.6–49.4 mol %. Under these conditions, the chlorobenzene content in a mixture with benzene is 65.1–70.3 wt % in 2 h.

Table 1. Rate constants of oxidative chlorination of benzene

Run no.	N_{AcOH}, mol %	q^a	$k_{app} \times 10^4$, kg mol^{-1} s^{-1}
1	91.9	3.9	0.28 ± 0.02
2	80.9	8.4	0.48 ± 0.04
3	67.6	12.8	1.06 ± 0.10
4	50.8	17.3	2.53 ± 0.15
5	49.4	18.5	4.52 ± 0.29
6	45.1	19.3	3.83 ± 0.28
7	40.6	20.2	4.03 ± 0.35
8	35.9	21.1	3.70 ± 0.32
9	30.8	22.2	2.74 ± 0.18
10	34.8	27.3	1.53 ± 0.12
11	31.0	31.3	1.08 ± 0.09
12	40.2	31.3	1.18 ± 0.06
13	47.2	31.3	1.19 ± 0.08
14	42.5	36.2	0.45 ± 0.03
15	42.7	40.6	0.34 ± 0.02
16	30.5	40.7	0.30 ± 0.04

[a] (*q*) Ratio of the initial concentrations of water and sodium peroxide.

EXPERIMENTAL

The reaction mixtures were analyzed on an LKhM-8MD chromatograph as described in [10]. The determination error was ±(2–3)%, as judged from the check measurements with reference benzene–chlorobenzene mixtures.

Benzene chlorination. To a temperature-controlled (298 K) mixture of 0.02 mol of benzene, 7 cm^3 of

Table 2. Rate constants and activation energies at various *q*

q	*T*, K	$k_{app} \times 10^4$, kg mol^{-1} s^{-1}	E_a, kJ mol^{-1}
12.8	298	1.06 ± 0.10	38.0
12.8	303	1.52 ± 0.15	
12.8	313	2.33 ± 0.21	
19.3	298	3.81 ± 0.28	12.1
19.3	303	4.29 ± 0.38	
19.3	313	4.90 ± 0.46	
31.3	298	1.18 ± 0.06	70.2
31.3	303	2.95 ± 0.18	
31.3	313	5.29 ± 0.45	

concentrated HCl (~0.08 mol of HCl), and ~1/3 of the total volume of the solvent, we added with stirring a solution of 0.02 mol of sodium peroxide in the solvent (2/3 of the total volume). As solvent we used glacial acetic acid and acetic anhydride. In most cases, water was introduced with concentrated HCl, but in some experiments additional H_2O was introduced to attain the required q. The total solvent volume was varied from 10 to 25 cm^3. From the reaction mixture, at definite intervals, we took samples, from which we extracted the organic layer; this layer was analyzed by GLC. Benzene and acetic acid were purified as described in [13]. The concentration of acetic acid was monitored by alkalimetric titration. The content of the main substance in sodium peroxide was determined according to [14]. The other chemicals were of chemically pure or pure grade and were used without additional purification.

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