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IODINATION OF AROMATIC COMPOUNDS WITH A MIXTURE OF PEROXYACETIC ACID AND IODINE

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Abstract—A method for the iodination of water-insoluble aromatic compounds in a homogeneous system is reported; an acetic acid solution of peroxyacetic acid is introduced into a solution of iodine and excess aromatic compound. The yields of iodobenzene and iodotoluenes were 60·5 and 84·6%, respectively. Iodic acid is formed simultaneously, and is the main product in the absence of aromatic compounds. A kinetic study comparing the rate equation and rate constants for the iodination of benzene with those for the reaction of iodine with peroxyacetic acid under similar conditions has been made. The acidity of the solution has no appreciable effect on the rate and the data suggest a mechanism which involves a rate-determining formation of iodine acetate or hypoiodous acid followed by a rapid condensation with benzene to form iodobenzene.

IN CONTRAST to chlorination or bromination, the iodination of aromatic compounds is a mild reaction and generally requires some activating catalyst such as iodine pentoxide,[1] peroxysulfate,[2] sulfur trioxide,[3] nitric acid,[4] and hydrogen peroxide[5] which have been proposed for the iodination of aromatic compounds.

It has been reported that silver perchlorate[6] and trifluoroacetate[7] are also activating agents for the iodination and a mechanism was postulated, which involves an attack of the iodonium ion produced from molecular iodine on the aromatic compound.[8]

$$I_2 + Ag^+ \rightarrow AgI + I^+$$
$$I^+ + ArH \rightarrow ArI + H^+$$

No report has been published on the mechanism of iodination using a mixture of oxidizing agents and iodine. The difficulty in obtaining a homogeneous system and the severe reaction conditions in most of the reactions make kinetic and mechanistic studies difficult.

Iodination in a homogeneous system is possible by using an acetic acid solution of peroxyacetic acid as an oxidizing agent. The kinetic study of iodination was carried out in order to elucidate the mechanism in this system.

RESULTS AND DISCUSSIONS

The results of the iodination of benzene and other aromatic compounds are listed in Tables 1 and 2, respectively. The best yield of iodobenzene was 60·5%. In general,

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better yields were obtained if the solution of peroxyacetic acid is added dropwise and if the reaction is carried out at a higher temperature and a lower ratio of peroxyacetic acid to iodine is used, probably because peroxyacetic acid may be consumed more effectively to iodinate benzene than to form iodic acid which is also observed in the reaction of peroxyacetic acid with iodine alone. Toluene is iodinated more easily in the *o*- and *p*-positions than benzene, but it was difficult to iodinate nitrobenzene and benzoic acid. These facts suggest an electrophilic nature of the reagent.

TABLE 1. IODINATION OF BENZENE

Benzene mole	Iodine mole	Peroxyacetic acid mole	Temp °C	Time hr	Yield[a] %	Procedure[b]	HIO_3 mole
0·398	0·100	0·300	50	5	10·5	M	
1·28	0·110	0·0225	75	5	20·1	M	
1·59	0·110	0·128	81	4·5	25·8	M	
1·28	0·113	0·277	80	2	44·7	D	0·0091
1·54	0·0865	0·213	50	12	24·8	M	0·0236
1·36	0·106	0·196	70	4	60·5	D	0·0169
1·86	0·106	0·425	40	8·5	53·9	D	0·052

[a] Yield of iodobenzene on the basis of iodine.

[b] D is the procedure of dropping peroxyacetic acid solution and M is that of mixing of two solutions rapidly.

TABLE 2. IODINATION OF OTHER AROMATIC COMPOUNDS[a]

Reactant	Reactant mole	Iodine mole	Peroxyacetic acid mole	Temp °C	Time hr	Yield %
Toluene	1·10	0·0865	0·143	60	2	84·6[b]
Nitrobenzene	0·451	0·0985	0·384	60	4·5	0
Benzoic acid	0·205	0·0985	0·262	90	4	0

[a] All experiments were done by dropping a peroxyacetic acid solution.

[b] A mixture of *o*- and *p*-iodotoluenes.

TABLE 3. THE RATES OF THE REACTION OF PEROXYACETIC ACID WITH IODINE AND THE RATES OF IODINATION OF BENZENE AT 50·0 ± 0·2°

Iodine 10^{-3} M	Peroxyacetic acid 10^{-3} M	Benzene 10^{-3} M	$\frac{[AcO_3H]_0}{[I_2]_0}$[a]	k_2 10^{-3} l. mole^{-1} sec^{-1}	
7·85	23·2	120	2·96	1·18	Av. 1·26
7·62	25·1	150	3·25	1·24	
8·27	23·9	130	2·89	1·12	
6·76	23·9	138	3·54	1·40	
8·16	28·8	—	3·53	1·39	Av. 1·25
7·34	14·9	—	2·03	1·25	
8·02	32·0	—	4·00	1·21	
7·77	35·3	—	3·54	1·14	

[a] [ ]$_0$ represents the initial concentration.

The rate data for the iodination of benzene as seen in Table 3 show that the rates satisfy the second-order equation:

$$v = k[I_2][CH_3CO_3H]$$

The rate is independent of the concentration of benzene. A similar rate equation and rate constant was obtained in the reaction of peroxyacetic acid with iodine alone under similar conditions. The effect of acidity on the rate is negligible as shown in Fig. 1 and Table 4.

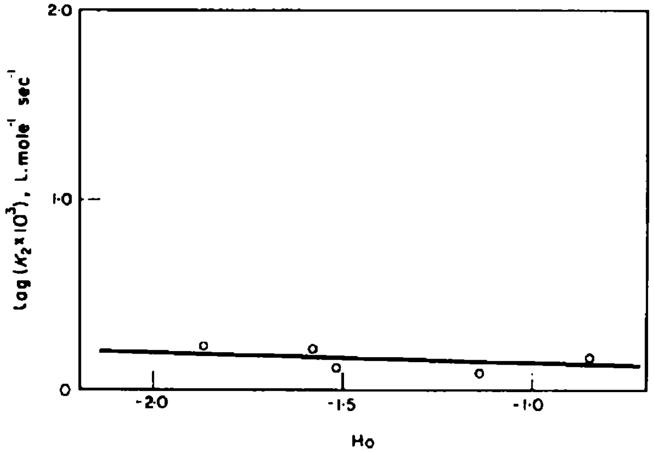

Fig. 1. Effect of acidity on the rate of iodination of benzene with peroxyacetic acid and iodine in acetic acid.

Table 4. Effect of acidity on the rate-determining step of the iodination of benzene with an acetic acid solution of peroxyacetic acid and iodine at 50·0 ± 0·2°

Iodine M	Peroxyacetic acid M	Benzene M	Sulfuric acid M	H_0	k_2 10^{-3} l. mole⁻¹ sec⁻¹	log 10^3k_2 l. mole⁻¹ sec⁻¹
0·0111	0·0133	0	0·089	−1·58	1·62	0·21
0·0111	0·0133	0	0·0178	−0·85	1·52	0·18
0·0104	0·0585	0·108	0·0845	−1·52	1·30	0·11
0·00734	0·0522	0·119	0·168	−1·87	1·72	0·24
0·00742	0·0290	0·111	0·0346	−1·135	1·24	0·09

The rate data suggest a mechanism which involves a rate-determining formation of hypoiodous acid followed by a fast reaction of the hypoiodous acid with benzene to form iodobenzene. The reaction of benzene competes with the reaction of hypoiodous acid to form iodic acid.

$$CH_3COO_2H + I_2 + H_2O \xrightarrow{\text{slow}} CH_3CO_2H + 2HIO \quad (1)$$

$$HIO + C_6H_6 \xrightarrow{\text{fast}} C_6H_5I + H_2O \quad (2)$$

$$HIO + 2CH_3COO_2H \xrightarrow{\text{fast}} HIO_3 + 2CH_3CO_2H \quad (3)$$

or

$$3HIO \xrightleftharpoons{\text{fast}} HIO_3 + 2I^- + 2H^+ \quad (4)$$

One of the other possible attacking agents is CH_3COOI which may be present in the reaction mixture according to the equilibrium:

$$CH_3COOH + HIO \rightleftarrows CH_3COOI + H_2O \tag{5}$$

Although there seems to be no decisive evidence to distinguish between hypoiodous acid and iodine acetate, the tendency to give an electrophilic agent should be greater in iodine acetate because of the stability of the acetate ion as compared with the hydroxide ion. Hence, CH_3COOI is more probable than HIO. However, there may be other iodinating species derived from hypoiodous acid such as H_2IO^+, I_2O and I^+, which are indistinguishable at present.

It has been reported that iodobenzene was formed in 12% yield by the reaction of iodine and hydrogen peroxide with benzene in the presence of strong acid.[5] Recently, it has been reported[9] that iodobenzene may be prepared in 83% yield by the reaction of benzene with a mixture of iodic acid and iodine in acetic acid containing 10% water at ca. 90°. It is probable that these iodinations go by way of similar attacking species, i.e., hypoiodous acid or iodine acetate formed via the reverse step of Eq. 4 or the combination of Eqs. 4 and 5, because it has been confirmed that iodic acid itself cannot be the iodinating agent as no reaction takes place between benzene and iodic acid in pure acetic acid at 90° for 4 hr. Further, no peroxyacetic acid could be detected by the paper chromatography in the reaction between iodic acid and acetic acid.

Since no acid-catalysis was observed (see Fig. 1), the slow step (1) is not acid-catalysed. The formation of iodic acid from hypoiodous acid has been reported.[10]

By analogy, these results imply that most iodinations by means of iodine and oxidizing agents such as peroxysulfuric acid, iodine pentoxide, nitric acid, iodine chloride, hydrogen peroxide, mercuric oxide and silver salts may proceed by way of hypoiodous acid or related species as stated previously, since the following reactions are possible:

$$I_2 + H_2S_2O_8 \rightarrow HIO_3 \tag*{(6)[11]}$$

$$I_2 + I_2O_5 + H_2O \rightarrow I_2 + 2HIO_3 \overset{H_2O}{\rightleftarrows} HIO \tag*{(7)[12]}$$

$$I_2 + HNO_3 \rightarrow HIO \tag*{(8)[13]}$$

$$ICl + H_2O \rightarrow I_2 + HIO_3 + HCl \tag*{(9)[14]}$$

$$H_2O_2 + I_2 \rightarrow 2HIO \tag*{(10)[15]}$$

$$HgO + 2I_2 + H_2O \rightarrow HgI_2 + 2HIO \tag*{(11)[16]}$$

$$AgClO_4 + I_2 + H_2O \rightarrow AgI + HClO_4 + HIO \tag*{(12)[17]}$$

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EXPERIMENTAL

Materials. Peroxyacetic acid was prepared by the reaction of 30% H_2O_2 aq. (40 g) and acetic anhydride (180 g) with an addition of catalyst, H_2SO_4 (2 g), at 30–35°.[18]

Iodination of benzene. A mixture of iodine (27 g) and benzene (105 g) was heated with stirring to ca. 70° until a homogeneous solution was obtained, then a 1·6 M solution of peroxyacetic acid in acetic acid (170 ml) was added slowly (1 ml per min) to the benzene solution during 3–4 hr. After the brown colour of iodine had disappeared at the end of the reaction, the stirring was continued for an additional 10 min.

The reaction product was diluted with water (1 l.), the oily layer separated and $Na_2S_2O_3$ aq. added to decompose the peroxides, especially acetyl peroxide which may be formed from peroxyacetic acid.[19] The separated oily layer was washed with water, dried ($CaCl_2$) and distilled, yielding iodobenzene b.p. 182–185°. Iodobenzene was identified by nitration and by the mixed m.p. determination of the *p*-nitroiodobenzene (m.p. and mixture m.p. 176°).

The precipitation of iodic acid observed during the iodination also occurs in the reaction of peroxyacetic acid with iodine alone. The precipitate had the known chemical and physical properites of iodic acid (iodine test, solubility, heating test etc.). Mol. wt. calc. for HIO_3:175·9. Found: 175·9 and 172·9, on the basis of acidimetry and redox titration, respectively.

Iodination of toluene and other aromatic compounds. A similar procedure was applied to the iodination of toluene and other aromatic compounds. The results are shown in Table 2.

Kinetic experiments. Solutions of iodine and benzene in acetic acid and a solution of peroxyacetic acid in acetic acid were brought to equilibrium temp at 50° and were then mixed in a thermostat to start the reaction. Aliquot volumes (each 10 ml) were pipetted out at known intervals of time and poured into a separatory funnel containing CCl_4 (25 ml) and cold water (50 ml), the funnel being shaken rapidly to extract iodine. After two extractions, the combined extracts were washed with water and separated. The CCl_4 solution was titrated with 0·01 N thiosulfate solution. Blank tests showed that the experimental error for the estimations of iodine and of peroxyacetic acid were within 0·3%.

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