Iodination of Aromatic Compounds with a Mixture of Iodine and Peracetic Acid. III. Autocatalysis and Relative Rates

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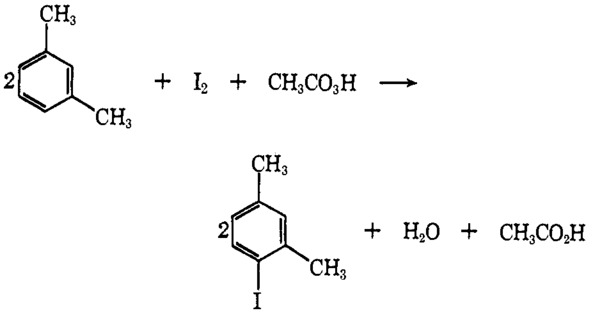
Abstract: In acetic acid solution, the rate of reaction of *m*-xylene with a mixture of iodine and peracetic acid to give 4-iodo-1,3-dimethylbenzene can be expressed as $v = k[I_2][CH_3CO_3H]$ and is independent of [*m*-xylene]. The reaction showed autocatalysis for aromatic compounds with reactivity greater than benzene. Addition of iodoaromatics to the system accelerates the reaction. Iodosobenzene and phenyl iodine diacetate are effective oxidizing agents for iodine, and a mixture of these materials and iodine can iodinate aromatic compounds. The autocatalysis seems to be due to the formation of aromatic iodoso compounds or aryl iodine diacetates by the oxidation of iodoaromatics with peracetic acid. The relative rates of this iodination of some aromatic compounds were measured by competitive reactions. Electron-releasing substituents accelerate the reaction, suggesting that the iodinating species is electrophilic in nature.

Iodination of aromatic compounds with elemental iodine is a slow reaction and usually requires the presence of oxidizing agents such as CH_3CO_3H,[1] HNO_3,[2] HIO_4,[3] HIO_3, $K_2S_2O_8$, SO_3, I_2O_5,[4] H_2O_2, $AgSO_4$,[5] CF_3COOAg, $AgClO_4$, HgO, and $Hg(OCOCH_3)_2$,[6] where Ag^+ is an oxidant because of the reaction $I_2 + Ag^+ \rightarrow I^+ + AgI$. Iodine monochloride is also used as an iodinating agent of aromatics.[7] Most of the kinetic studies on iodination have been done using phenols and anilines as substrates; hypoiodic acid or acetyl hypoiodite[1] have been postulated as probable iodinating agents.[8] A method for the iodination of aromatic compounds with a mixture of iodine and peracetic acid has been reported together with some kinetic results.[1,9]

The present paper describes some interesting features of this reaction, where *m*-xylene was chosen as a main substrate to follow the reaction



(1)

Experimental Section

Materials. *Ca.* 3.5 *M* peracetic acid was prepared by adding dropwise acetic anhydride (407 g, 3.99 mol) to a stirred solution of 60% hydrogen peroxide (100 g, 1.77 mol; H_2O, 2.22 mol) and concentrated sulfuric acid (1 ml) at 30° over a period of 3 hr. The solution contained a small amount (*ca.* 0.2 *M*) of diacetyl peroxide.[10] Acetic acid (99.5%) was used without further purification. Iodine of guaranteed grade (above 99.8%) was used for the kinetics and iodine of reagent grade (above 99.0%) for syntheses. *p*-Xylene (bp 138.2–139.5°), *o*-xylene (bp 144.5–145.2°), and chlorobenzene (bp 130.5–131.5°) were purified by duplicate rectifications. The following idoinated compounds for authentic samples of gas chromatographic analyses were synthesized by the reaction of appropriate aromatic compounds with a mixture of iodine and peracetic acid–iodobenzene (bp 182–185°), 4-iodo-1,3-dimethylbenzene (bp 111–112° (13.5 mm)), *p*-iodoanisole (mp 49.5–50.0°), *o*- and *p*-iodotoluene (bp 203–210°), *p*-iodochlorobenzene (mp 54.5°), *p*-iodobromobenzene (mp 90.0°), *p*-iodocumene (bp 113–114° (13.5 mm)), 1-iodonaphthalene (bp 160–162° (15 mm)). *p*-Diiodobenzene was prepared by the reaction of iodobenzene with a mixture of iodine and concentrated nitric acid (*d* 1.50), and purified by recrystallization from alcohol, mp 127–129° (lit.[11] mp 129.4°). Iodosobenzene was prepared from iodobenzene *via* iodobenzene dichloride.[12] Phenyl iodine diacetate was prepared by the peracetic acid oxidation of iodobenzene, mp 157–159° (lit.[13] mp 158°, 161.1–162.2° [14]). The authentic samples of *o*-[15] (bp 74–76° (4 mm)), *m*-[16] (bp 76–77.2° (4 mm)), and *p*-[17] (mp 33–35°) iodotoluenes were prepared from corresponding toluidines *via* the diazonium salts.

Analyses of Reaction Products. The products were analyzed by glpc employing a Yanagimoto Model GCG 550 F with a flame ionization detector operated with a 2 m × 3 mm column packed with Apiezon L grease 15% on Celite 545 of 80–100 mesh using nitrogen as a carrier (15–20 cc/min) at 80–200°, hydrogen flow rate 20–30 cc/min, injection temperature 260°, and detector temperature 320°.

The ratio of the products was calculated from the peak area obtained from the known mixtures of authentic samples. The

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[13] K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

[14] J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967).

[15] H. J. Lucas, E. R. Kennedy, and C. A. Wilmot, *ibid.*, **58**, 158 (1936), bp 95.5° (24 mm).

[16] J. W. Baker and H. B. Hopkins, *J. Chem. Soc.*, 1096 (1949), bp 96° (21 mm).

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Table I. Iodination of Aromatic Compounds with a Mixture of Iodine and Peracetic Acid at 60°

Substrate (mol)	Iodine, mol	Peracetic acid, mol × 10	Time, min	Yield,[a] %	Product	Bp (mm) or mp, °C	Lit. bp (mm) or mp, °C
p-Xylene (0.5)	0.1	1.61	70	72	2-Iodo-*p*-xylene	92–93.2 (5)	106–108 (13)[d]
o-Xylene (0.5)	0.1	1.57	75	75	Iodo-*o*-xylene[c]	99–100.5 (5)	111 (11)[d]
Durene (0.1)	0.05	0.58	60	86	Iododurene	78	80[e]
Mesitylene (0.05)	0.025	0.31	30	80	Iodomesitylene	29–31	31[f]
Toluene (0.5)	0.1	1.83	170	85	*o*- and *p*-Iodotoluene[b]	105–107 (30)	. . .
4-Iodo-*m*-xylene (0.02)	0.01	0.44	350	21	4,6-Diiodo-*m*-xylene	71–72	72[g]

[a] Based on iodine used. [b] *ortho/para* ratio was estimated to be 0.73 by infrared spectrophotometry. [c] The ratio of isomers has not yet been determined. A strong absorption band at 803 cm^{-1} indicates that 4-iodo-1,2-dimethylbenzene is the main isomer. [d] See ref 18. [e] A. Töhl, *Ber.*, **25**, 1522 (1892). [f] R. L. Datta and J. C. Bhoumik, *J. Amer. Chem. Soc.*, **43**, 315 (1921). [g] A. Töhl and E. Bauch, *Ber.*, **26**, 1105 (1893).

Table II. Competitive Iodination of Aromatic Compounds with a Mixture of Iodine and Peracetic Acid at 60°

Substrates (mol × 10)	Iodine, mol × 10^2	Peracetic acid, mol × 10^2	Time, min	Ratio of iodinated products
Anisole–toluene (1:1)	2.5	3.7	40	1:0.00061
Toluene–benzene (2:2)	2.5	12.5	120	1:0.023
Benzene–chlorobenzene (2:2)	2.5	18.3	240	1:0.062[b]
Chlorobenzene–bromobenzene[a] (1:1)	1.0	3.0	100	1:0.54[b]
Mesitylene–durene (0.1:0.1)	0.1	0.5	20	1:0.030
Durene–*m*-xylene (0.1:0.1)	0.1	0.5	20	1:0.85[c]
m-Xylene–*o*-xylene (1:1)	1.0	3.0	45	1:0.051
o-Xylene–*p*-xylene (1:1)	1.0	3.1	45	1:0.82
p-Xylene–toluene (0.1:0.1)	0.1	0.5	25	1:0.48[c]
Biphenyl–toluene (1:1)	1.0	5.3	70	1:0.95
Toluene–cumene (1:1)	2.5	10.3	120	1:0.76
Naphthalene–toluene (1:1)	1.0	5.6	120	1:0.14

[a] H_2SO_4 (0.0188 mol) was added. [b] Iodic acid was produced in considerable amount as by-product. [c] Yields of iodinated products were quantitative.

yields were estimated by glpc by using iodinated aromatics as an internal standard.

The infrared spectra were determined by a Perkin-Elmer Model 333 spectrophotometer. The iodinated product of toluene contains *o*- and *p*-iodotoluenes, but virtually no *meta* isomer (ν_{max} 766 cm^{-1}). The *ortho/para* ratio of iodotoluenes was estimated by measuring the absorbance at ν_{max} 741 (*ortho*) and 795 cm^{-1} (*para*) with the total concentration of iodotoluenes 2.5 w/v % in CS_2 solution using a 0.1-mm KBr cell.

Iodination of Aromatic Compounds. 2-Iodo-1,4-dimethylbenzene. A typical procedure for the iodination is described with *p*-xylene. An acetic acid solution (47 ml) of 3.42 *M* peracetic acid (0.161 mol) was added dropwise into a mixture of *p*-xylene (53.1 g, 0.5 mol) and iodine (25.4 g, 0.1 mol) at 60–65° over a period of 70 min. At the end of the reaction the mixture became pale yellow and transparent, a small amount (*ca.* 3%) of iodic acid being precipitated. The mixture was washed with water and then with 5% aqueous $Na_2S_2O_3$ to remove acetic acid and peracetic acid. The oily layer was dried over Na_2SO_4 and distilled, giving recovered *p*-xylene (bp 47.5–48.5° (29 mm), 23.5 g) and then 2-iodo-1,4-dimethylbenzene; bp 92–93.2° (5 mm) (lit.[18] bp 106–108° (13 mm)), $n^{19.5}$D 1.5922, 33.4 g (72%).

These results together with those of other aromatic compounds are listed in Table I.

Competitive Iodination of Aromatic Compounds. An excess of an equimolar mixture of two aromatic compounds was iodinated with a mixture of iodine and peracetic acid. A typical procedure for toluene and benzene is as follows. An acetic acid solution (37 ml) of 3.39 *M* peracetic acid (0.125 mol) was added dropwise to a mixture of toluene (18.4 g, 0.2 mol), benzene (15.6 g, 0.2 mol), and iodine (6.35 g, 0.025 mol) at 60° over a period of 120 min. After the usual work-up of washing and drying the oily layer, the products were analyzed by glpc to determine the ratio of iodotoluene and iodobenzene. The conditions for glpc are as follows: temperature 80–200° (6°/min), nitrogen flow rate 20–30 cc/min, a 2 m × 3 mm column packed with Apiezon L grease 15% on Celite 545 of 80–100 mesh. Retention times for iodotoluene and iodobenzene were 13.8 and 10.5 min, respectively. The results together with those of other aromatic compounds are listed in Table II.

A Typical Procedure for the Rate Measurements. A. Reaction of *m*-Xylene with a Mixture of Iodine and Peracetic Acid. An acetic acid solution (98 ml) of iodine (1.00 × 10^{-2} *M*) with *m*-xylene (8.01 × 10^{-2} *M*) was placed in a 200-ml flask equipped with a thermometer and a stirrer, which was allowed to stand at 60.0 ± 0.2° to reach temperature equilibrium. An acetic acid solution (2 ml) of 2.61 *M* peracetic acid was added to the solution to start the reaction. Aliquots (each 10 ml) were pipetted out at known intervals of time and placed in a separatory funnel containing distilled water (50 ml) and benzene (20 ml). The benzene extract, after being washed with 5% aqueous $Na_2S_2O_3$, was dried over Na_2SO_4 and analyzed by glpc using iodotoluene as an internal standard. The conditions for glpc analysis are as follows: column temperature 160°, carrier gas N_2 17 cc/min, Apiezon L grease 15% on Celite 545 of 80–100 mesh 2 m × 3 mm column. Retention times for iodotoluene and 4-iodo-1,3-dimethylbenzene were 4.3 and 7.1 min, respectively.

Other aliquots (each 10 ml) were pipetted out at the same intervals of time and placed into a separatory funnel containing distilled water (50 ml) and CCl_4 (25 ml). The content of iodine in CCl_4 and the content of peracetic acid in the aqueous layer were measured iodometrically. The concentration of iodine in the reaction mixture is also measurable by diluting aliquots with methanol and measuring the absorption maximum at 450 mμ. Both estimations of iodine agreed within experimental error.

B. Reaction of *m*-Xylene with a Mixture of Iodine and Iodosobenzene. The reaction was carried out in an acetic acid solution (100 ml) at 60°. The initial concentrations were 8.01 × 10^{-2} *M* *m*-xylene, 1.00 × 10^{-2} *M* iodine, and 2.07 × 10^{-2} *M* iodosobenzene. Aliquots (each 10 ml) were taken out at known intervals of time and worked up as usual. The amount of products in the benzene extract was estimated similarly as in case A by glpc using iodotoluene as an internal standard. The retention times of iodobenzene, iodotoluene, and 4-iodo-1,3-dimethylbenzene were 4.0, 7.0, and 12.3 min, respectively.

C. Reaction of *m*-Xylene with a Mixture of Iodine and Phenyl Iodine Diacetate. An acetic acid solution (100 ml) of 8.01 × 10^{-2} *M* *m*-xylene and 1.00 × 10^{-2} *M* iodine was kept standing at 60° to reach temperature equilibrium. Phenyl iodine diacetate (0.647 g, 2.01 × 10^{-3} mol) was added to the solution to start the reaction. Aliquots (each 10 ml) were taken out into a separatory

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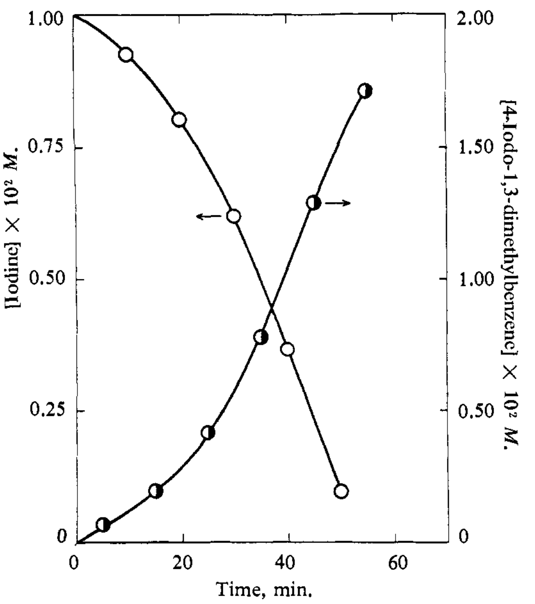

Figure 1. Conversion curves for iodination of *m*-xylene with a mixture of iodine and peracetic acid in acetic acid at 60°. Initial concentrations: *m*-xylene, 8.01×10^{-2} *M*; I_2, 1.00×10^{-2} *M*; CH_3CO_3H, 5.22×10^{-2} *M*.

funnel containing water (50 ml) and benzene (20 ml). The benzene layer was worked up and analyzed similarly as in case A by glpc to estimate 4-iodo-1,3-dimethylbenzene. Retention times of iodobenzene, iodotoluene, and 4-iodo-1,3-dimethylbenzene were 4.6, 7.9, and 13.5 min, respectively.

Attempted Reaction of Aromatic Iodocompounds and Hydriodic Acid. In acetic acid (10 ml) under an atmosphere of nitrogen, a mixture of 54% hydriodic acid (*d* 1.65, 0.1 ml) and an aromatic iodo compound (0.1 ml), such as iodobenzene, 4-iodo-1,3-dimethylbenzene, 2-iodo-1,4-dimethylbenzene, or *o*- and *p*-iodotoluenes, did not liberate iodine on standing at 60° or at room temperature for several days. Therefore, the present iodination is irreversible.

Ultraviolet Spectrum of a Charge-Transfer Complex. A methanolic solution of a nixture of *m*-xylene (8.01×10^{-2} *M*) and iodine (1.00×10^{-2} *M*) in acetic acid at 60° shows λ_{max} 290 mμ characteristic for a charge-transfer complex,[19] but when peracetic acid (6.15×10^{-2} *M*) was added to start the reaction, it disappeared immediately.

Results and Discussion

Some examples of iodination of aromatic compounds by a mixture of iodine and peracetic acid are listed in Table I.

Iodination of *m*-Xylene and the Effect of Initial Concentrations of Reactants. The reaction of *m*-xylene with a mixture of iodine and peracetic acid in acetic acid at 60° is shown in Figure 1. As is evident from the sigmoid conversion curve, the reaction is autocatalytic. The consumption of iodine results in the formation of 4-iodo-1,3-dimethylbenzene but no diiodo compound as confirmed by glpc using an authentic specimen. The absence of 4,6-diiodo-1,3-dimethylbenzene shows that the acceleration of reaction is not due to further iodination of the 4-iodo-1,3-dimethylbenzene formed. The yield of 4-iodo-1,3-dimethylbenzene in eq 1 was 86% on the basis of iodine. Since the conversion was almost 100%, the rate of consumption of iodine, which was measured in most cases, approximated the rate of iodination.

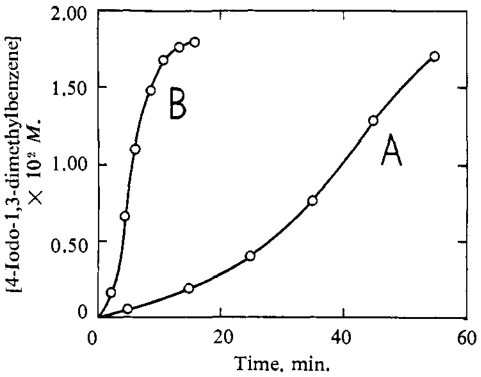

Figure 2. Effect of addition of iodobenzene on the iodination of *m*-xylene with a mixture of iodine and peracetic acid in acetic acid at 60°. A, initial concentrations: *m*-xylene, 8.01×10^{-2} *M*; I_2, 1.00×10^{-2} *M*; CH_3CO_3H, 5.22×10^{-2} *M*. B, iodobenzene of initial concentration 8.95×10^{-2} *M* was added to system A.

All conversion curves were identical for the reactions with a constant initial concentration of iodine (1.00×10^{-2} *M*) and peracetic acid (6.15×10^{-2} *M*) but varying initial concentrations of *m*-xylene (2.00, 4.00, or 8.01×10^{-2} *M*) in an acetic acid solution at 60°. This result shows that the rate of the reaction is independent of initial concentration of *m*-xylene as reported for the iodination of benzene.[1,9]

The conversion curves were drawn for the reaction with a constant initial concentration of *m*-xylene (8.01×10^{-2} *M*) and iodine (1.00×10^{-2} *M*) but various initial concentrations of peracetic acid (1.51, 3.03, 6.15, and 12.1×10^{-2} *M*) in acetic acid at 60°. The rate of iodine consumption was calculated at 25, 50, and 75% conversion from them and was plotted against the initial concentration of peracetic acid, giving straight lines through the origin. Apparently, the rate is first order in peracetic acid.

The conversion curves with constant initial concentration of *m*-xylene (8.01×10^{-2} *M*) and peracetic acid (6.15×10^{-2} *M*) but various initial concentrations of iodine (0.50, 1.00, 2.00, 3.00, and 4.00×10^{-2} *M*) were drawn. The rate of the reaction was calculated at 25, 50, and 75% conversion and was plotted against initial concentration of iodine, giving straight lines through the origin. Therefore, the rate is first order in iodine. Thus the rate law is $v = k[I_2][CH_3CO_3H]$. The value of *k* at an early stage of reaction is calculated to be *ca.* 2.1×10^{-3} l. mol^{-1} sec^{-1} at 60°.

Effects of the Addition of 4-Iodo-1,3-dimethylbenzene and Iodobenzene. The addition of 4-iodo-1,3-dimethylbenzene (0.345, 0.695, and 1.38×10^{-2} *M*) to the reaction system at 60° accelerates the reaction. The rate of reaction increased linearly with an increase of added 4-iodo-1,3-dimethylbenzene. Figure 2 shows the effect of addition of iodobenzene to the reaction system for the iodination of *m*-xylene which gave a 90% yield of 4-iodo-1,3-dimethylbenzene. Apparently, iodobenzene and its dimethyl derivative are marked catalysts.

The iodinations of iodobenzene and 4-iodo 1,3-dimethylbenzene under similar conditions were carried out and their conversion curves were drawn. Both reactions were fast but the yields of diiodo compounds were low (below 5% for *p*-diiodobenzene and 21% for 4,6-diiodo-1,3-dimethylbenzene) because of the forma-

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[19] (a) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949); (b) R. S. Mulliken, *ibid.*, **72**, 600 (1950); (c) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

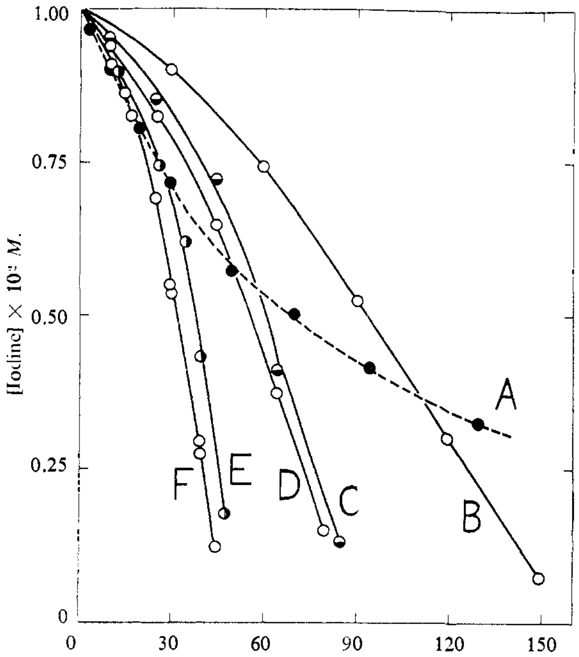


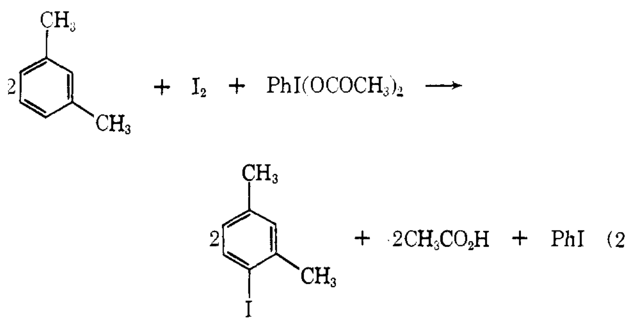
Figure 3. Conversion curves of iodine in the iodination of various aromatic compounds with a mixture of iodine and peracetic acid in acetic acid at 60°. Initial concentrations: I_2, 1.00 × 10^{-2} *M*; CH_3CO_3H, 6.15 × 10^{-2} *M*. Initial concentration of aromatics (× 10^2 *M*): A, none, benzene (11.0), cholorbenzene (9.80) or bromobenzene (9.52); B, toluene (18.6); C, *p*-xylene (8.06); D, *o*-xylene (8.26); E, mesitylene (7.18); F, *m*-xylene (8.01).

tion of iodic acid as a by-product. It is evident that iodo aromatics can accelerate the reaction, but they are very slowly iodinated and are little consumed under kinetic conditions.

Role of Iodosobenzene and Phenyl Iodine Diacetate in the Iodination of *m*-Xylene. Since it has been known that aromatic iodo compounds are oxidized by peracetic acid to form aryl iodine diacetate[13,14] $ArI(OCOCH_3)_2$, the iodination of aromatic compounds with a mixture of iodine and iodosobenzene or phenyl iodine diacetate was examined. The reaction of *m*-xylene with a mixture of iodine and iodosobenzene in acetic acid at 60° gave a high yield (97%) of monoiodinated *m*-xylene. Iodobenzene was recovered. The rate of this reaction is expressed as $v = k_2[I_2][PhIO]$ and it is independent of *m*-xylene. Second-order rate constant k_2 was *ca.* 5.5 × 10^{-2} l. mol^{-1} sec^{-1}. The reaction of iodine with iodosobenzene alone under the same conditions proceeded to *ca.* 50% conversion of iodine at the same rate, but the consumption of iodine then stopped probably because of the formation of phenyl iodine diacetate and water and then acetyl hypoiodite and iododobenzene (see eq 10 and 11).

A similar reaction using phenyl iodine diacetate instead of iodosobenzene was conducted at 60°, giving 96% yield of iodinated *m*-xylene. The rate follows the equation: $v = k_2'[I_2][PhI(OCOCH_3)_2]$. The value of k_2' was *ca.* 1.1 × 10^{-1} l. mol^{-1} sec^{-1}. Iodobenzene was recovered. The over-all reaction is as in eq 2.

The comparison of these rate constants indicates that phenyl iodine diacetate is *ca.* twofold more effective than iodosobenzene for oxidizing iodine to iodinated aromatics. Iodosobenzene may give phenyl iodine diacetate in acetic acid.



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Effect of Sulfuric Acid and Water. The consumption of iodine in the reaction of *m*-xylene (8.01 × 10^{-2} *M*), iodine (1.00 × 10^{-2} *M*), and peracetic acid (6.15 × 10^{-2} *M*) in acetic acid at 60° was retarded by the addition of sulfuric acid (1.83, 3.66, and 7.32 × 10^{-2} *M*), probably because of the suppression of autocatalysis. Sulfuric acid, 7.32 × 10^{-2} *M*, resulted in the disappearance of autocatalysis, and the rate equation was $v = k_2[I_2][CH_3CO_3H]$, where k_2 is *ca.* 2.6 × 10^{-3} l. mol^{-1} sec^{-1} at 60°.

The rate of the reaction of *m*-xylene, iodine, and peracetic acid under the same condition was increased by the addition of 5 vol % of water to the system. Water may promote the reaction of iodine and peracetic acid.

Reaction of Various Aromatic Compounds with a Mixture of Iodine and Peracetic Acid and Their Relative Rates. The conversion curves for the reaction of various aromatic compounds with a mixture of iodine (1.00 × 10^{-2} *M*) and peracetic acid (6.15 × 10^{-2} *M*) in acetic acid at 60° are shown in Figure 3. As already stated,[1,9] the initial concentration of aromatics does not affect the rate.

The over-all rates of reaction with aromatics of low reactivities such as benzene, chlorobenzene, and bromobenzene (curve A) were found to be determined by the rate of iodine with peracetic acid to form acetyl hypoiodite. The second-order rate constant, k_2, calculated from the equation $v = k_2[I_2][CH_3CO_3H]$ on the basis of iodine consumption was *ca.* 2.6 × 10^{-3} l. mol^{-1} sec^{-1} at 60°.

Aromatics having higher reactivity than benzene showed an autocatalysis as shown in B–F of Figure 3. It is interesting to note that the initial rate of consumption of iodine of aromatics of low reactivities (curve A) is faster than those of high reactivities (curves B, C, D, . . .). This fact might seem to be inconsistent with the reactivities of aromatic compounds determined by competitive iodination, but it may show the lower reactivity of charge-transfer complex between substrates having electron-releasing groups and iodine. A large amount of by-product iodic acid is formed and the yields of iodinated aromatics are lower in case A.

Since the rates of iodination are almost independent of the concentration of aromatic compounds, the relative rates of iodination cannot be obtained from the rates of iodine consumption or from the rates of formation of iodo aromatics. Therefore, the relative rates of iodination of aromatic compounds were determined by competitive reaction.

An excess of an equimolar mixture of two aromatic compounds was iodinated with a mixture of iodine and peracetic acid. The results are listed in Table II.

Assuming that the second-order rate equation, $v = k$[substrate][iodinating agent], is applied in an excess of substrates, the relative rates of iodination of aromatics, k/k_0, calculated by Ingold's equation from Table II are: for anisole, 1×10^5; toluene, 5×10; benzene, 1; chlorobenzene, 0.06; and bromobenzene, 0.03. The relative rates of iodine consumption, v/v_0, calculated from Figure 3 at 50% conversion differ by a factor of *ca.* 3. The second-order rate constant, k, at an early stage of reaction is calculated to be *ca.* 0.7×10^{-3} l. mol^{-1} sec^{-1} for toluene, *ca.* 1.5×10^{-3} l. mol^{-1} sec^{-1} for *o*-xylene, and *ca.* 2.1×10^{-3} l. mol^{-1} sec^{-1} for *m*-xylene. The reactivities of monosubstituted benzenes are in the ordinary order of substituent effect on electrophilic substitution:[20] $CH_3O > CH_3 > H > Cl > Br$. The application of Hammett's equation, however, needs more precise determination of the rates and isomer distributions. This iodination of toluene is *ortho* and *para* directing, the *ortho/para* ratio being 0.73. A considerable amount of *ortho* isomer was formed in spite of the expected steric effect by a large iodine atom. The reactivities of polymethylbenzenes also fit the ordinary order:[7,21] mesitylene > durene > *m*-xylene > *o*-xylene > *p*-xylene > toluene > benzene. These results suggest an electrophilic nature for this reaction.

Mechanism. The simple oxidation of aromatic compounds by peracetic acid may afford oxidation products such as phenols or quinones,[22] which may be, however, slow and negligible under these conditions. Practically no reversible reaction[23] occurs under the present conditions. This fact and the kinetics suggest that the following mechanism is less probable.

$$ArH + I_2 \underset{}{\overset{\text{slow}}{\rightleftarrows}} ArI + HI \qquad (3)$$

$$2HI + CH_3CO_3H \xrightarrow{\text{fast}} I_2 + H_2O + CH_3CO_2H \qquad (4)$$

The rate of iodination of aromatic compounds of higher reactivity than benzene with a mixture of iodine and peracetic acid is determined by the reaction of iodine and peracetic acid, forming an active reagent such as acetyl hypoiodite.

$$I_2 + CH_3CO_3H \xrightarrow{\text{slow}} CH_3COOI + HOI \qquad 5)$$

$$I_2 + CH_3CO_3H \xrightarrow{\text{slow}} I_2O + CH_3CO_2H \xrightarrow[CH_3CO_2H]{\text{fast}} 2CH_3COOI + H_2O \qquad (5')$$

$$HOI + CH_3CO_2H \overset{\text{fast}}{\rightleftarrows} CH_3COOI + H_2O \qquad (6)$$

$$ArH + CH_3COOI \xrightarrow{\text{fast}} ArI + CH_3CO_2H \qquad (7)$$

However, since electron-attracting groups retard the reactivity of aromatics, the iodination of aromatics of lower reactivity competes with the formation of iodic acid.

$$HOI + 2CH_3CO_3H \xrightarrow{\text{fast}} HIO_3 + 2CH_3CO_2H \qquad (8)$$

In general, the rate of the aromatic halogenation is often first order in aromatic substrate, but this is not the case in the present iodination, although the reaction of iodine with peracetic acid is affected a little by the presence of different aromatic compounds (Figure 3). This effect on the rate may be ascribed to the formation of a charge-transfer complex between iodine and aromatics.[19] But the true nature is not yet clear, because an absorption maximum at 290 mμ corresponding to the complex disappears when the reaction is started by the addition of peracetic acid to the system.

The autocatalysis, observed with substrates of higher reactivities, may be due to the intermediary formation of aromatic iodoso compounds or more probably aryl iodine diacetates, formed by the peracetic acid oxidation of iodo aromatics.

The following mechanism involving eq 7 is postulated.

$$ArI + CH_3CO_3H \longrightarrow ArIO + CH_3CO_2H \qquad (9)$$

$$ArIO + 2CH_3CO_2H \rightleftarrows ArI(OCOCH_3)_2 + H_2O \qquad (10)$$

$$I_2 + ArI(OCOCH_3)_2 \longrightarrow 2CH_3COOI + ArI \qquad (11)$$

As the reaction proceeds, the contribution of these pathways becomes important and the reaction is autocatalyzed. It is not clear why sulfuric acid depresses the autocatalysis.

One evidence for the intermediary formation of acetyl hypoiodite is that the Prévost type of product of acetyl hypoiodite addition to olefin has been found in the reaction of propylene with a mixture of iodine and phenyl iodine diacetate.[24] Recently,[6] acetyl hypoiodite, formed by the reaction of mercuric acetate with iodine, has been postulated as an iodinating agent for pentamethylbenzene. Although a kinetic hydrogen isotope effect has been observed in the iodination of anilines[25] or azulene,[26] suggesting a rate-determining proton removal, the present reaction does not seem to be determined by the proton removal.

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