265. *The Kinetics of the Reduction of Aromatic Iodo-compounds by Hydriodic Acid in Solution.*

By V. Gold and Mary Whittaker.

The replacement of the iodine atom by hydrogen through the action of hydriodic acid on some substituted *p*-iodophenols has been studied kinetically in acetic acid–water mixtures. The effect of methyl and chloro-groups on the reaction velocity is very similar to the known effect of these substituents on the velocity of nitration of aromatic compounds. It is concluded that the reduction is an electrophilic replacement of iodine.

The iodine atom in an organic iodide may often be replaced by hydrogen by the use of hydriodic acid, $RI + HI \longrightarrow RH + I_2$. Some observations on the structural factors affecting the velocity of this reaction were made by Shoesmith and Slater (*J.*, 1924, **125**, 1312, 2278), who showed that the ease of reduction of the three isomeric iodophenols followed the sequence $p > o \gg m$, that iodoresorcinol was more reactive than any of the iodophenols, and that the series of iodo-hydrocarbons *o*-iodotoluene, *p*-iodotoluene, *m*-iodotoluene, iodobenzene was reduced with increasing difficulty in that order. A few facts have also been recorded on the related topics of the relative ease of reduction of some substituted benzyl bromides by means of hydriodic acid (Lapworth and Shoesmith, *J.*, 1912, **101**, 1391; Shoesmith and Slater, *loc. cit.*) and of the reduction of substituted aromatic halogeno-compounds by the use of hydrogen chloride alone and with stannous chloride (Nicolet *et al.*, *J. Amer. Chem. Soc.*, 1921, **43**, 2081: 1927, **49**, 1796, 1801, 1806, 1810). The reduction of some alkyl iodides by hydriodic acid in the gas phase has also been investigated kinetically (Ogg, *ibid.*, 1934, **56**, 526), but this probably constitutes a problem which has little in common with the solution reactions studied by us.

The present investigation deals with velocity measurements on the reduction of some further-substituted 4-iodophenols by means of hydriodic acid in aqueous acetic acid. The effects of changes in the structure of the aromatic iodide, and in solvent, temperature, and concentrations of the reactants were studied.

Experimental.

Materials.—*p*-Iodophenol was prepared from *p*-aminophenol (Dains and Eberley, *Org. Synth.*, Coll. Vol. II, 1943, p. 355) and purified by steam distillation and crystallisations from benzene. 4-*Iodo*-2-*methylphenol* (5-iodo-*o*-cresol) was synthesised from *o*-cresol by nitrosation (Bridge and Morgan, *J. Amer. Chem. Soc.*, 1898, **20**, 766), followed by reduction to 5-amino-*o*-cresol by use of ammoniacal hydrogen sulphide, and subsequent replacement of the amino-group by iodine by the Gattermann reaction as used for *p*-iodophenol. It was crystallised from carbon tetrachloride and finally from light petroleum (b. p. 60—80°); m. p. 64° (Found: C, 35·8; H, 3·0; I, 56·0. C_7H_7OI requires C, 35·9; H, 3·0; I, 54·3%).

4-Iodo-3-methylphenol (6-iodo-*m*-cresol) and 4-iodo-3-methyl-6-*iso*propylphenol (6-iodothymol) were prepared by analogous sequences of reactions starting from *m*-cresol and thymol (Kremers, Wakeman, and Hixon, *Org. Synth.*, Coll. Vol. II, p. 511), respectively : preparation by direct iodination of thymol (Datta and Prosad, *J. Amer. Chem. Soc.*, 1917, **39**, 444) was abandoned because of the unsatisfactory yield. Both substances were recrystallised from light petroleum.

2-Chloro-4-iodophenol was obtained by chlorination of *p*-iodophenol (Brazier and McCombie, *J.*, 1912, **101**, 968), followed by steam-distillation and crystallisation from carbon tetrachloride. It was also prepared from *o*-chlorophenol by the above sequence of nitrosation, reduction, and Gattermann replacement of the amino-group by iodine.

4-Iodo-2-nitrophenol, prepared from *p*-aminophenol by nitration of the acetyl derivative (Girard, *Bull. Soc. chim.*, 1924, **35**, 772), hydrolysis to 4-amino-2-nitrophenol, and introduction of iodine in place of the amino-group, was crystallised from light petroleum.

All the iodophenols prepared were free from iodine. Where necessary the last traces of iodine were removed by extraction of a solution in chloroform with dilute aqueous thiosulphate solution. Stock solutions in acetic acid were stable and produced no visible colour even on storage for several months.

Acetic acid was purified and made anhydrous by treatment with acetic anhydride as described by Orton and Bradfield (*J.*, 1927, 983) and fractionally distilled. Acetic anhydride was the AnalaR reagent.

Constant-boiling hydriodic acid (May and Baker) was freed from iodine by refluxing with red phosphorus and distillation in all-Pyrex apparatus immediately before use, the vapour being passed over a copper spiral. The constant-boiling fraction was collected and made into a stock solution in acetic acid, with additions of acetic anhydride when it was desired to reduce the water content of the reaction mixture below the amount introduced with the constant-boiling hydriodic acid. The exact concentration of hydriodic acid was checked by a Volhard titration.

FIG. 1.

Illustration of procedure for evaluation of initial rates. (*Expt.* 109; *see Table I.*)

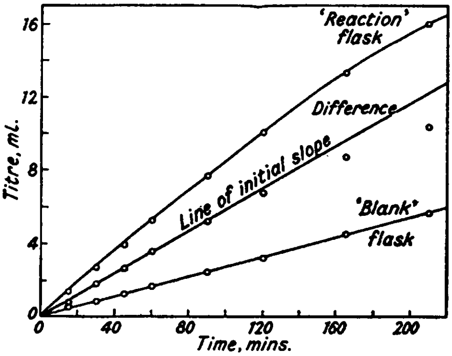
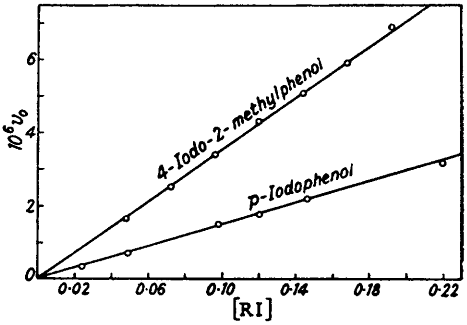


FIG. 2.

Dependence of initial rates upon concentration of aromatic iodide.



Kinetic Measurements.—The reactions were carried out in stoppered round-bottom flasks (150 ml.), coated black on the outside to exclude light and shaken mechanically in a thermostat bath. Each run was paralleled by a blank experiment with identical amounts and samples of solvents and hydriodic acid, but with the omission of the organic iodide. Both reactions were started by the final addition of a freshly prepared stock solution of hydriodic acid to the solutions in the reaction vessels. The progress of the reactions in both flasks was followed by periodically pipetting samples (7 ml.) into water (100 ml.), thus arresting the reaction, and titrating the liberated iodine with standard (~N/20) thiosulphate solution.

In most cases the amount of reaction in the blank vessel was appreciable, sometimes constituting more than half of the total reaction. This was allowed for in the following way. Let the velocity of the increase in iodine concentration in the reaction flask and in the blank flask be given by $(\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t)_{\text{reaction}} = -\mathrm{d}[\mathrm{RI}]/\mathrm{d}t + k_{\mathrm{B}}[\mathrm{HI}]^n$ and $(\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t)_{\text{blank}} = k_{\mathrm{B}}[\mathrm{HI}]^n$, respectively. Since the concentration of hydriodic acid in the reaction flask will not be exactly the same as that in the blank flask at any time except at the start of the reaction, the velocity of reduction at any particular moment during the course of the reaction cannot be obtained by simple subtraction of these two equations. However, subtraction of these two sets of titres (corresponding to the same moment of time) from each other should lead to a rate of iodine formation which will approximate to the rate of disappearance of iodophenol the more closely the nearer are the points to the start of the reaction (provided that the iodophenol exerts no large effect on the " blank " oxidation of hydriodic acid). Initial rates (v_0) of iodophenol reduction were accordingly obtained from the relation

$$\begin{aligned} v_0 &= -(\mathrm{d}[\mathrm{RI}]/\mathrm{d}t)_{t\to 0} \\ &= \{(\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t)_{\text{reaction}} - (\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t)_{\text{blank}}\}_{t\to 0} \\ &= \{\mathrm{d}([\mathrm{I}_2]_{\text{reaction}} - [\mathrm{I}_2]_{\text{blank}})/\mathrm{d}t\}_{t\to 0} \end{aligned}$$

The procedure is illustrated by a typical experiment in Table I and Fig. 1.

TABLE I.

Illustration of procedure for evaluation of initial rates.

(Expt. 109.) [4-Iodo-2-methylphenol]$_0$ = 0·096M. [H_2O] = 5·94M. [HI]$_0$ = 1·02M. Temp. = 40°.

Titres refer to ml. of 0·0482N-$Na_2S_2O_3$ per 7-ml. sample.

Time, mins.	Titres. Reaction (*R*).	Titres. Blank (*B*).	*R* – *B*.	Time, mins.	Titres. Reaction (*R*).	Titres. Blank (*B*).	*R* – *B*.
15	1·41	0·60	0·81	90	7·72	2·49	5·23
30	2·73	0·88	1·85	120	10·04	3·25	6·79
45	3·97	1·30	2·67	165	13·34	4·58	8·76
60	5·30	1·70	3·60	210	16·01	5·67	10·34

Initial slope of graph in Fig. 1 = 0·0594 ml. min.$^{-1}$.

$$v_0 = 0{\cdot}0594 \times 0{\cdot}0482/(2 \times 7 \times 60) \text{ moles l.}^{-1} \text{ sec.}^{-1}$$
$$\doteq 3{\cdot}41 \times 10^{-6} \text{ moles l.}^{-1} \text{ sec.}^{-1}.$$

TABLE II.

Initial rates (v_0) *and first-order rate constants* (k_1).

Temp.	[H_2O].	[RI]$_0$.	[HI]$_0$.	10^6v_0.	10^5k_1.	
		RI = *p*-Iodophenol.				
40°	5·94	0·0240	1·02	0·35	1·48	Mean, 1·49
,,	,,	0·0490	,,	0·73	1·49	
,,	,,	0·0980	,,	1·52	1·55	
,,	,,	0·120	,,	1·78	1·48	
,,	,,	0·146	,,	2·20	1·51	
,,	,,	0·220	,,	3·16	1·44	
,,	9·05	0·120	,,	0·37	0·31	
,,	7·50	,,	,,	0·79	0·66	
,,	6·71		,	1·05	0·87	
,,	6·06	,,	,,	1·40	1·17	
,,	5·63	,,	,,	2·20	1·83	
,,	5·26	,,	,,	4·43	3·69	
,,	4·49	,,	,,	12·7	10·6	
30	5·26	,,	,,	1·41	1·17	
50	5·94	,,	,,	5·59	4·70	
		RI = 2-Chloro-4-iodophenol.				
40	5·94	0·120	1·02	~0·15	~0·12	
,,	1·53	,,	,,	2·48	2·06	
,,	0	,,	,,	8·91	7·42	
30	0	,,	,,	3·94	3·28	
50	0	,,	,,	19·6	16·3	
,,	[Ac_2O] =2·94	,,	,,	3·6	3·0	
		RI = 4-Iodo-3-methyl-6-*iso*propylphenol.				
20	5·94	0·120	1·02	~33	~28	
30	,,	,,	,,	~98	~82	
,,	9·09	,,	,,	~86	~72	

Temp.	[H_2O].	[RI]$_0$.	[HI]$_0$.	10^6v_0.	10^5k_1.	
		RI = 4-Iodo-2-methylphenol.				
40°	5·94	0·0480	1·02	1·67	3·48	Mean, 3·55
,,	,,	0·0720	,,	2·54	3·53	
,,	,,	0·0960	,,	3·41	3·56	
,,	,,	0·120	,,	4·31	3·59	
,,	,,	0·144	,,	5·09	3·53	
,,	,,	0·168	,,	5·92	3·52	
,,	,,	0·192	,,	6·90	3·59	
,,	,,	0·120	0·408	0·28	0·23	
,,	,,	,,	0·510	0·41	0·34	
,,	,,	,,	0·612	0·81	0·67	
,,	,,	,,	0·714	1·35	1·12	
,,	,,	,,	0·816	2·00	0·67	
,,	,,	,,	0·918	3·14	2·62	
,,	9·09	,,	1·02	0·81	1·67	
,,	8·26	,,	,,	1·35	1·12	
,,	7·50	,,	,,	1·98	1·65	
,,	7·11	,,	,,	2·36	1·97	
,,	6·71	,,	,,	3·36	2·80	
,,	6·06	,,	,,	4·11	3·42	
,,	5·63	,,	,,	5·66	4·71	
,,	5·23	,,	,,	7·22	6·01	
30	5·94	,,	,,	1·47	1·23	
50	,,	,,	,,	14·2	11·8	
		RI = 4-Iodo-3-methylphenol.				
20	5·94	0·120	1·02	9·03	7·5	
30	,,	,,	,,	28·5	23·7	
40	,,	,,	,,	85·1	71	

Results.—A summary of the experiments is given in Table II. The initial reaction velocity was found to be (*a*) proportional to the concentration of the iodophenol used; (*b*) approximately proportional to the cube of the stoicheiometric concentration of hydriodic acid used; (*c*) approximately inversely proportional to the 3·5th power of the molarity of water, at least at the high concentrations of water used; (*d*) unaffected by a large increase in surface area by packing the reaction vessel with glass-wool or by the presence of free iodine or the organic reaction product; and (*e*) decreased by the presence of free acetic anhydride in an anhydrous solvent. The proportionality (*a*) was verified for *p*-iodophenol ([HI]$_0$ = 1·02M.; [H_2O] = 5·94M.; 40°) and for 4-iodo-2-methylphenol under the same conditions (Fig. 2); (*b*) was found for 4-iodo-2-methylphenol ([H_2O] = 5·94M.; [RI]$_0$ = 0·120M.; 40°) (Fig. 3), and (*c*) for the same substance ([HI]$_0$ = 1·02M.; [RI]$_0$ = 0·120M.; 40°) (Fig. 4); (*d*) was verified for *p*-iodophenol and (*e*) for 2-chloro-4-iodophenol. These conclusions may be combined in the experimental rate equation

$$v_0 = k_0[\mathrm{RI}][\mathrm{HI}]_0^{3}/[\mathrm{H_2O}]^{3\cdot5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Experimental first-order rate coefficients, as listed in Table II, are defined as $k_1 = v_0/[\mathrm{RI}]_0$, the units of v_0 being moles l.$^{-1}$ sec.$^{-1}$. The first-order dependence of the rate on the iodophenol concentration during the major portion of an experiment was also verified by evaluating first-order rate coefficients in the usual manner from the integrated form of the rate equation in an experiment in which $[\mathrm{HI}]_0 \gg [\mathrm{RI}]_0$ and for which the iodine liberation in the blank flask was very slow, so that [HI] could be taken as constant for the run.

The liberation of iodine by the action of hydriodic acid on 4-iodo-2-nitrophenol was found to be considerably more rapid than with any other compound used. However, the reaction occurring in this case is the reduction of the nitro-group, and no information could be obtained about the speed of the iodine replacement, if it occurs at all.

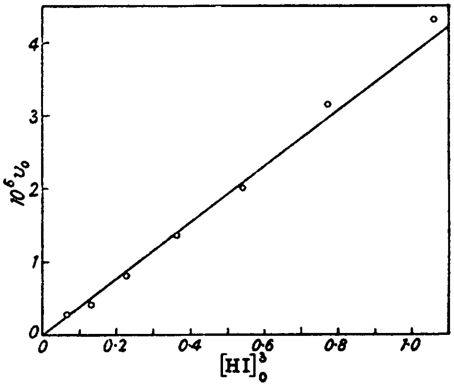


FIG. 3.
Dependence of initial rate upon concentration of hydriodic acid.

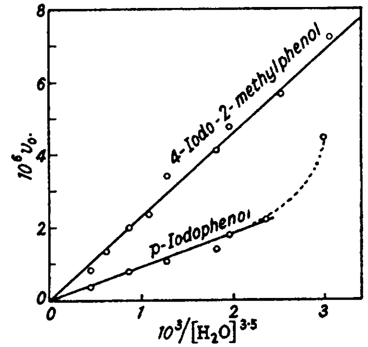


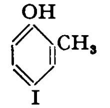
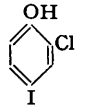
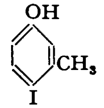
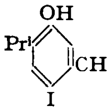
FIG. 4.
Dependence of initial rates upon concentration of water.

Treatment of iodobenzene and *p*-chloroiodobenzene (0·12M.) [in which the iodine atom is known to be replaceable by a nitro-group in preference to nitration at another position (Holleman, *Rec. Trav. chim.*, 1913, **34**, 222)] with anhydrous hydriodic acid (1·02M.) in acetic acid at 40° produced only a negligible amount of reduction after three days.

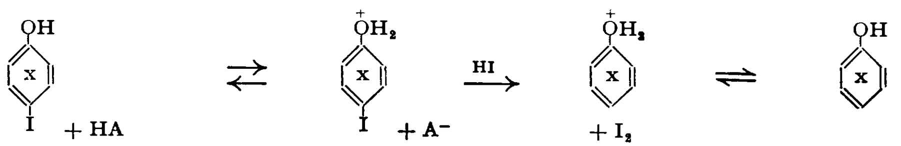
DISCUSSION.

The structures studied (Table III) are all derived from *p*-iodophenol, and a comparison of the effect of different substituent groups introduced into this parent molecule is possible. The strong influence exerted by substituent groups on the reaction velocity is, in fact, the most notable feature of the reaction. It is particularly significant that chlorine and methyl groups, introduced into the 2-position of *p*-iodophenol (where steric effects should be of minor importance), influence the reaction velocity in opposite senses, as they do, for example, in aromatic nitration. The reaction is, therefore, clearly not homolytic in character.

TABLE III.

Formula					
Relative rate of reduction	1	2·4	0·08	48	160

We may next ask whether the increase in reactivity on introducing an electron-repelling group (and the converse effect) can be due to an increased (decreased) basicity of the phenolic hydroxyl group, the compound reacting in the strongly acid media considered *via* the formation of its conjugate acid in a low concentration, *i.e.* :



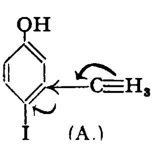
Although such a mechanism would help to explain the high reaction order with respect to hydriodic acid, it seems to be ruled out by Shoesmith and Slater's observation that the velocity of reduction is increased by introducing a methyl group also into iodobenzene, and in this case the methyl group cannot act by strengthening a basic grouping. The polar effect of the substituents must therefore be concerned with the actual substitution stage.

As has been pointed out by Hughes and Ingold on a number of occasions (*e.g.*, Hughes, Ingold, and Shapiro, *J.*, 1936, 225), the electronic requirements of a bimolecular heterolytic reaction cannot *a priori* be predicted with certainty, since attachment of the new group and detachment of the replaced group are helped by the movement of electrons in opposite directions.

Thus a substitution reaction which is accelerated by the introduction of electron-repelling methyl groups and retarded by the introduction of chlorine into the nucleus, like the reductions considered in this paper, may be brought about either by electrophilic attack, if the electronic effect on the proton attachment phase is more important, or by nucleophilic attack if the electronic effect on the iodide detachment phase is the bigger effect. It is found that, for substitution reactions in general, the electronic requirements of the attachment are more often decisive; those of the detachment only dominate the situation for reactions which, if the structure of the molecule were changed but slightly, would proceed according to a unimolecular mechanism in which the rate-determining stage of the reaction is the heterolytic detachment of the outgoing group. However, the nucleophilic replacement of iodine in substituted aryl iodides is known (*e.g.*, the hydrolysis of *p*-iodonitrobenzene by hydroxide ions) and its features are entirely different from those of the reduction reactions. Thus the iodine atom in the iodophenols cannot be removed through the agency of hydroxide ions, nor can iodobenzene with strong electron-attracting groups be reduced with hydriodic acid. This, in addition to the inherent improbability of a mechanism which would introduce hydrogen as H^-, leaves little doubt that the reaction is effected by electrophilic attack upon the carbon atom : *

$$R - \vdots I + H \vdots - X \longrightarrow R - H + I^+X^-$$

The same conclusion, namely, that the substituent group exerts its effect mainly on the approach phase of the reaction, is also supported by a comparison of the rates for 4-iodo-2- and -3-methylphenol. The effect of the methyl group is seen to be much greater when it is *ortho* to the iodine atom than when it is in the *meta*-position, the operation of the electron release increasing the electron availability at the carbon atom next to the iodine atom (see A). It is remarkable that 4-iodo-3-methylphenol is the more easily reduced compound in spite of the fact that methyl substitution in the *ortho*-position relative to the substitution centre of the reaction may introduce some steric hindrance. This interpretation also explains the sequence found by Shoesmith and Slater for the reduction of the isomeric iodotoluenes and iodophenols.



(A.)

The possible reaction mechanism

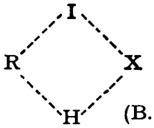
$$R \vdots - I + X \longrightarrow R^+ + IX^-$$

in which the rate-determining stage is a bimolecular electrophilic replacement on iodine would not be expected to lead to RH as final product, since H^- is not easily abstracted from the reaction medium and other bases are present in the solvent (phenyl acetate could be a product, for example). The same objection would not apply to the alternative scheme

$$R - \vdots I + X \longrightarrow R^- + IX^+$$

and certain features of it are used in the following paragraph. It is unlikely to be a good description of the reaction by itself, since it again leads to difficulties concerning the effect of substituent groups on the velocity. Also, the reducing power of the reagent X should then follow its general nucleophilic activity, which is not observed.

Although the electrophilic attack on the aromatic molecule appears to account for the most structure-sensitive contribution to the activation energy of the reaction, the same or another reagent molecule appears to be involved in the transition state (as a nucleophilic reagent) for the removal of the ejected I^+. If this were not so, the efficiency of the reagent should merely depend on its potency as a proton donor and therefore other strong acids besides hydriodic acid should be deiodinating reagents, whereas in fact hydriodic acid is an exceptionally good reagent and sulphuric acid in acetic acid, for example, is quite useless for the purpose. However, hydriodic acid or any species derived from it in the medium is unlikely to be as powerful a nucleophilic reagent as the bases derived from the solvent system. A reason why it may nevertheless be more important that these other species may lie in the greater entropy of activation for its reaction, such as would arise if electrophilic and nucleophilic reactivity were combined in a single reagent molecule to give a transition state as shown in (B). Intervention of another molecule for the purpose of removing I^+ would involve either a reaction with two successive bimolecular stages or a termolecular process, and both these alternatives would have a lower *a priori* probability. For a highly organised transition state like (B), geometrical factors, such as the relative bond lengths of R–I and H–X may be very critical and



(B.)

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* On our picture the phenoxide ion should be most readily reduced but its concentration in our acidic reaction medium must be quite insignificant.

thus lead to maximum reactivity in a molecule which would not have been regarded as the most efficient reagent on purely electrostatic considerations.

The identity of the reagent HX which is believed to effect the reduction in a single-stage process is not certain. It seems improbable that the curious kinetic relationship (1) is related to the mechanism of the reaction in a straightforward way; it is more likely to be a complex consequence of employing a solvent system of several components. In dry acetic acid hydrogen iodide may, in the main, be in the form of HI molecules, but the addition of an excess of water probably results in a high degree of conversion into H_3O^+ and I^- ions, leaving only a small amount of HI molecules. For various reasons the species I^-, I_3^-, H_3O^+, $AcOH_2^+$, HI_2^- can all be ruled out as feasible reagents, so that the effect of water must be to reduce the concentration of the effective reagent which is either hydrogen iodide or a species derived from it by a reaction other than the loss of a proton (cf. the experimentally observed strong retardation of the reaction by the addition of water). The chemical species which appear to be the most likely reagents are HI and H_2I^+, but we cannot decide between them on our experimental evidence. Both these reagent molecules would fit into kinetic schemes involving the concentration of hydriodic acid to a power higher than unity. The scheme involving H_2I^+, in particular, leads to a rate equation which is very similar to the experimental one (1), but it would be unjustifiable to rule out HI on this ground alone.

The high reaction order *may* arise in the following way. In the presence of water the equilibrium $HI + H_2O \rightleftharpoons H_3O^+ + I^-$ (equilibrium constant, K_1) probably lies largely over on the right-hand side, and since, under the conditions for which the high reaction order with respect to the stoicheiometric concentration of hydrogen iodide ($[HI]_{st}$) was found,

$$[H_2O] \gg [HI]_{st}$$
$$[H_3O^+] \sim [I^-] \sim [HI]_{st} \quad \ldots\ldots\ldots\ldots \quad (2)$$

if we make the assumption that the reaction $H_2O + AcOH \longrightarrow H_3O^+ + OAc^-$ is relatively unimportant. This may be regarded as a fair first approximation in view of the poor conductivity of slightly wet acetic acid. Therefore,

$$[HI] = \frac{1}{K_1}\cdot\frac{[HI]^2_{st}}{[H_2O]}\cdot\frac{f_\pm^{\,2}}{f_{H_2O}\cdot f_{HI}} \quad \ldots\ldots\ldots\ldots \quad (3)$$

and

$$v = k[RI][HI] = \frac{k}{K_1}[RI]\frac{[HI]^2_{st}}{[H_2O]}\cdot\frac{f_\pm^{\,2}}{f_{H_2O}\cdot f_{HI}}$$

For a reaction involving the hypothetical species H_2I^+ we must also consider the equilibrium $2HI \rightleftharpoons H_2I^+ + I^-$ (equilibrium constant, K_2), which certainly would lie largely on the left-hand side, and hence obtain for the velocity of the reaction

$$v = k[H_2I^+][RI] = \frac{kK_2}{K_1^{\,2}}\frac{[RI][HI]^3_{st}}{[H_2O]^2}\cdot\frac{f_{H_3O^+}}{f_{H_2I^+}}\cdot\frac{f_{H_3O^+}\cdot f_{I^-}}{f^2_{H_2O}} \quad \ldots\ldots \quad (4)$$

which, apart from the solvent effect on the reaction velocity, is a good description of the experimental kinetic relationship (1). Although we believe the explanation of the high reaction order to lie somewhere along these or similar lines, we cannot claim, on the present data and the approximate treatment given, to have established a proof for either HI or H_2I^+ molecules as reagents. Having regard to the structure of the probable transition state (B), the HI molecule itself would appear to be the more plausible reagent species. Also, it must be admitted that there seems to be little evidence for the existence of H_2I^+ from any other field.

The activation energies for different substances (Table IV) follow the reverse sequence of the rates but the series is not quite isentropic. The activation energy for *p*-iodophenol is seen to increase with the water content of the medium. The low activation energy for 2-chloro-4-iodophenol need therefore not be anomalous, since it alone refers to an anhydrous solvent. The values given have therefore only comparative significance.

TABLE IV.

Activation energies.

Substance.	$[H_2O]$, M.	*E.*	Temp. range.	Substance.	$[H_2O]$, M.	*E.*	Temp. range.
p-Iodophenol	5·94	22·8	40—50°	4-Iodo-3-methylphenol	5·94	20·7	20—40°
	5·26	22·0	30—40	6-Iodothymol	5·94	19	20—30
4-Iodo-2-methylphenol	5·94	22·2	30—50	2-Chloro-4-iodophenol	0	15·7	30—50

It is noteworthy that the electronic requirements for iodine replacement and the replacement of a hydrogen atom by a nitro-group are also quantitatively very similar, as is seen if the effects of a substituent group on deiodination and nitration ***at a given position*** relative to a substituent group are compared, *e.g.*, by considering the following partial rate factors in the case of nitration.

Comparison of influence of substituent groups on rates of deiodination reduction and aromatic nitration.

Group X and its position relative to replaced I and H.	Reduction (replacement of I).	Nitration (replacement of H).
H (standard)	1	1
m-Methyl	2·4	3·0 [1]
o-Methyl	48	40 [1]
m-Chloro	0·08 [*]	0 [2]

[1] Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959.

[2] Bird and Ingold, *J.*, 1938, 918.

[*] This value is the least accurate result for reduction velocities owing to the importance of the "blank" correction in experiments using the same solvent as for the other iodophenols. The other measurements on 2-chloro-4-iodophenol reported in this paper relate to a dry solvent in which a study of the more reactive iodophenols is impossible.

KIMG'S COLLEGE, LONDON, W.C.2.

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