# 959. *Kinetics and Mechanism of Bromination of Phenol with Bromine and Iodine Bromide in Glacial Acetic Acid and Carbon Tetrachloride.*

By LOURDU M. YEDDANAPALLI and N. S. GNANAPRAGASAM.

The kinetics of reaction of phenol with (*a*) bromine and (*b*) iodine monobromide in acetic acid and carbon tetrachloride has been studied by a method applicable to short reaction times. Reaction (*a*) in acetic acid is of first order with respect to phenol and bromine severally. The other brominations are of first order with respect to phenol and of second order with respect to reagent. Activation energies are calculated. Reaction (*b*) in both solvents is catalysed by iodine monobromide (not by iodine). Reaction mechanisms are discussed.

THE main difficulty in the kinetic investigation of the bromination of phenol by bromine appears to be the extreme rapidity of the reaction even at low concentrations. Robertson *et al.*[1] reported that reaction of 0·001M-phenol and bromine in anhydrous acetic acid is 20% complete in 0·82 min. Two possible ways of rendering the reaction tractable seemed to be the use of a milder brominating agent, and the modification of the experimental procedure to permit of rate-measurements within intervals of seconds. Iodine monobromide was found, in our investigations of cashew phenols,[2] to be a mild brominating agent for the phenolic nucleus : it is known to react with phenol in non-aqueous solvents, such as glacial acetic acid and carbon tetrachloride, to give only *p*-bromophenol.[3, 4] Its use and a modified experimental procedure are now reported, reaction being carried out in acetic acid and in carbon tetrachloride. For additional information, bromination of anisole in the latter solvent was included. Fresh experimental data have also been obtained regarding the disputed rôle of iodine as catalyst in bromination of phenol.[4, 5]

## EXPERIMENTAL

*Procedure.*—The halogen and phenol solutions (5 c.c. each), in several glass-stoppered bottles and corked test-tubes respectively, were placed in a thermostat maintained within ±0·05°. After the solutions reached the bath-temperature, the phenol solution was quickly emptied into the halogen solution, and the mixture was allowed to react for a definite time, even as short as 5 sec., after which the reaction was arrested by quick addition of potassium iodide solution, the liberated iodine being titrated against standard sodium thiosulphate.

Glacial acetic acid (f. p. 15·8°) was used without treatment. Anhydrous carbon tetrachloride was prepared by fractionation of a sulphur-free B.P. quality sample (b. p. 76·5—76·7°/760 mm.).

Reproducibility is illustrated by the duplicate results 50·4 and 49·9 for the first entry in the second column of Table 3, and 55·8 (twice) for the second entry there.

### *Results in Acetic Acid.*

*Phenol–Bromine Reaction.*—(a) *Over-all order.* Rate-measurements were made with phenol and bromine in acetic acid over the concentration range 0·001—0·02M. Fig. 1 and Table 1 show the results. The total order of the reaction (see Table 1) is evidently two.

(b) *Individual orders.* Ostwald's isolation method was employed for evaluating the kinetic order with respect to bromine. The concentration of phenol was kept at a constant large excess, 0·02M, and that of bromine varied from 0·002 in the first to 0·001M in a second experiment. The time required for a definite fraction of the reaction was found to be independent of the initial concentration of bromine, so that the order with respect to bromine is one.

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[1] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

[2] Paul, M.Sc. Thesis, Madras, 1951; Yeddanapalli and Paul, *J. Sci. Ind. Res.* (*India*), 1953, **12**, *B*, 524.

[3] Militzer, *J. Amer. Chem. Soc.*, 1938, **60**, 256.

[4] Bennett and Sharpe, *J.*, 1950, 1383.

[5] Lambourne and Robertson, *J.*, 1947, 1167.

TABLE 1. *Total order of the reaction between phenol and bromine.*

Solvent : acetic acid. Temp. : 30°.

| Br reacted (%) | $a$ (mole/l.) | $b$ (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | $n$ (total order) | Br reacted (%) | $a$ (mole/l.) | $b$ (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | $n$ (total order) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 0·020 | 0·010 | 4 | 9 | 2·17 | 40 | 0·004 | 0·002 | 26 | 50 | 1·94 |
| 60 | 0·020 | 0·010 | 10 | 23 | 2·20 | 50 | 0·004 | 0·002 | 40 | 75 | 1·91 |
| 40 | 0·010 | 0·005 | 9 | 20 | 2·15 | 20 | 0·002 | 0·001 | 19 | 42 | 2·14 |
| 60 | 0·010 | 0·005 | 23 | 53 | 2·20 | 40 | 0·002 | 0·001 | 50 | 99 | 1·99 |

Rate-measurements were also made with phenol concentrations of 0·02—0·01M, that of bromine being constant at 0·001M. The rate of the reaction can be represented by

$$d[C_6H_4Br{\cdot}OH]/dt = k(a - x)^n(b - x) \qquad (1)$$

where *a* and *b* are the initial concentrations of phenol and bromine respectively, *x* the amount of each reacted in time *t*, and *n* the order with respect to phenol. When 40% of the bromine has reacted, *x* is only 0·0004M and therefore negligible when compared to *a*, 0·02 and 0·01M. Eqn. (1) then reduces to :

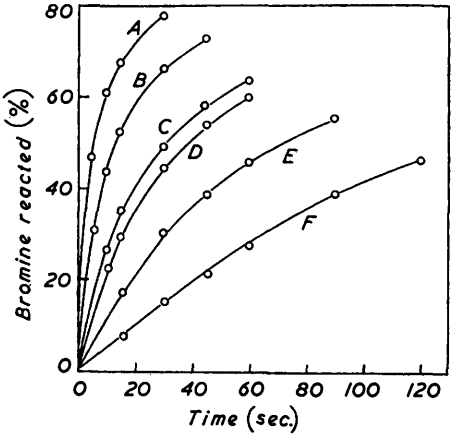


FIG. 1. *Rate of bromination of phenol at various initial equimolar concentrations. A,* 0·02M; *B,* 0·01M; *C,* 0·005M; *D,* 0·004M; *E,* 0·002M; *F,* 0·001M.

$$d[C_6H_4Br{\cdot}OH]/dt = k'(b - x) \qquad (2)$$

where $k'$ is a first-order rate constant and is equal to $ka^n$. The values of $k'$ are $8{\cdot}8 \times 10^{-2}$ and $4{\cdot}7 \times 10^{-2}$ at $a = 0{\cdot}02$ and 0·01M respectively. From this *n* is found to be 0·91, so that the order with respect to phenol is one.

(c) *Activation energy.* Rate constants corresponding to 20%, 25%, and 30% reaction were calculated for phenol and bromine (0·001M each) over the temperature range 20—40°. Fig. 2 shows plots of log *k* against $1/T°(\text{K})$. From the slopes the calculated activation energies are 4·81, 4·81, and 4·88 kcal. mole$^{-1}$ for 20, 25, and 30% reaction respectively, the average being 4·83 ± 0·05 kcal. mole$^{-1}$.

It may be noted that the time required for 20% bromine consumption at 0·001M at 25° in glacial acetic acid in our case, *viz.*, 0·80 min., agrees with the value 0·82 min. in anhydrous acetic acid reported by Robertson *et al.*[1]

*Phenol–Iodine Bromide Reaction.*—(a) *Over-all kinetic order.* Iodine bromide of the required concentration was prepared by mixing equal volumes of equimolar solutions of iodine and bromine in glacial acetic acid. The reaction between phenol and iodine bromide was found to be homogeneous (as tested by a four-fold increase of surface : volume ratio by addition of small pieces of glass tubing), and not light-sensitive. In order to evaluate the over-all kinetic order, rate-measurements were made with equimolar 0·001—0·1M-solutions of phenol and reagent. The percentage of halogen reacted at each concentration was plotted against time and from the curves the times required for definite fractions of the reaction at different initial concentrations were read off. These together with the calculated kinetic orders are represented in Table 2, from which it is seen that the over-all order is three.

(b) *Individual orders.* The order with respect to iodine monobromide was determined by keeping the phenol concentration at 0·1M and changing that of the reagent from 0·01 to 0·005M. The times required for 20% of the halogen to react in the two cases were 70 and 139 sec. respectively, from which the calculated kinetic order is 1·99. The kinetic order for phenol was determined by the same procedure as with bromine, the iodine bromide being 0·005M and phenol 0·1—0·05M. The values of the second-order rate constants $k'$ are 1·92 and 1·05 l. mole$^{-1}$ sec.$^{-1}$ at $a$ = 0·1 and 0·05M respectively, so that the order with respect to phenol is 0·87, close to unity.

TABLE 2. *Total order of reaction between phenol and iodine bromide.*

Solvent: acetic acid. Temp.: 30°.

| Halogen reacted (%) | $a$ (mole/l.) | $b$ (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | $n$ (total order) | Halogen reacted (%) | $a$ (mole/l.) | $b$ (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | $n$ (total order) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 0·100 | 0·050 | 7 | 26 | 2·89 | 12 | 0·020 | 0·010 | 51 | 216 | 3·08 |
| 20 | 0·100 | 0·050 | 21 | 91 | 3·12 | 16 | 0·020 | 0·010 | 156 | 645 | 3·05 |
| 12 | 0·050 | 0·025 | 8 | 29 | 2·86 | 8 | 0·010 | 0·005 | 69 | 276 | 3·00 |
| 16 | 0·050 | 0·025 | 26 | 100 | 2·94 | 4 | 0·002 | 0·001 | 810 | 3450 | 3·09 |

FIG. 2. *Plot of* log $k$ *against* $1/T$ (°K) *for different extents of the reaction between phenol and bromine* (0·001M *each*): *A*, 30%; *B*, 25%; *C*, 20%.

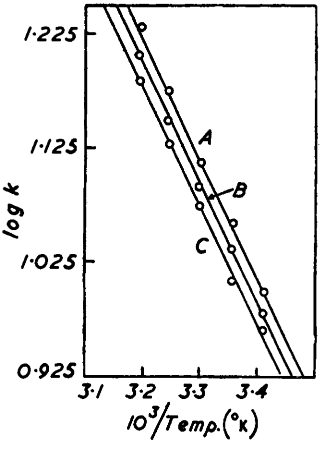
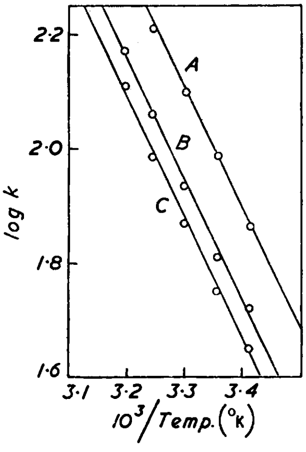


FIG. 3. *Plot of* log $k$ *against* $1/T$ (°K) *for different extents of the reaction between phenol and* IBr (0·01M *each*): *A*, 12%; *B*, 14%; *C*, 15%.



(c) *Activation energy.* Rate constants for the reaction at 0·01M-concentrations at 20—40° were calculated from experimental data for different extents of the reaction. The activation energies calculated from the slopes for 12, 14, and 15% reaction (Fig. 3) are 9·76, 9·71, and 9·69 kcal. mole$^{-1}$ respectively, average 9·72 ± 0·04 kcal. mole$^{-1}$.

(d) *Iodine bromide catalysis.* In order to examine the effect of iodine on the rate of bromination experiments were made in which the concentration of iodine was progressively increased from 0 to 0·01M, the phenol and bromine solutions being constantly 0·01M and 0·005M respectively. The results are summarised in Table 3. Column 2 gives the percentage of bromine reacted within the first 15 sec. for varying amounts of added iodine, and column 3 the

TABLE 3. *Effect of iodine on rate of bromination of phenol.*

Solvent: acetic acid. Temp.: 30°. Initial concns.: phenol, 0·01M; bromine, 0·005M.

| Concn. of added iodine (M) | Br reacted (%) in first 15 sec. | $\frac{\text{Total I}}{\text{Total Br}}$ | Concn. of added iodine (M) | Br reacted (%) in first 15 sec. | $\frac{\text{Total I}}{\text{Total Br}}$ |
|---|---|---|---|---|---|
| 0·0000 | 50·4 | 0·0 | 0·0040 | 21·2 | 0·8 |
| 0·0005 | 55·8 | 0·1 | 0·0050 | 7·5 | 1·0 |
| 0·0010 | 59·9 | 0·2 | 0·0075 | 2·0 | 1·5 |
| 0·0020 | 55·5 | 0·4 | 0·0100 | 0·5 | 2·0 |
| 0·0030 | 37·0 | 0·6 | | | |

ratio of total iodine to bromine. From Fig. 4, which represents the plot of the percentage of bromine reacted against the iodine : bromine ratio, it is seen that the rate of bromination is a maximum when this ratio is 0·31. The significance of this maximum rate may be brought out by the following considerations. It is known that the equilibrium constant for the reaction $I_2 + Br_2 \rightleftharpoons 2IBr$ in an acid medium is quite large, *e.g.*, 5·26 × $10^4$ at 25° in 4N-hydrobromic acid.[6] It may therefore be assumed that in acetic acid the iodine added to bromine will be present almost wholly as IBr. Since the concentration of total bromine is 0·005M and the ratio of total iodine to bromine at the catalytic maximum is 0·31, the iodine concentration corresponding to this maximum will be 0·31 × 0·005, *i.e.*, 0·00155M. Given that each iodine molecule $I_2$, gives two IBr, the concentration of the latter is 0·0031, so that free bromine is equal to total bromine 0·005 minus the bound bromine 0·00155, *i.e.*, 0·00345M. The ratio, then, of IBr to free bromine becomes 0·0031/0·00345, equal to 0·9, approximately one. It may therefore be concluded that the maximum rate corresponds to the presence of equimolar amounts of IBr and free bromine. In other words, IBr appears to be the catalyst in this bromination.

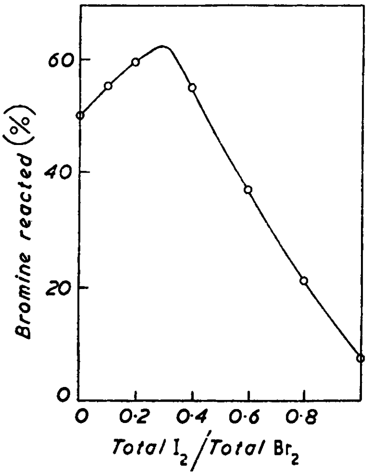


FIG. 4. *Plot of the percentage of bromine reacted in the first* 15 *seconds against the ratio of total iodine to bromine.*

### *Results in Carbon Tetrachloride.*

*Phenol–Iodine Bromide Reaction.*—(a) *Kinetic order.* The reaction is not light-sensitive and not sensibly affected by a four-fold increase in surface : volume ratio and so essentially homogeneous. The kinetic order of the reaction is three in the concentration range 0·02—0·002M (see Table 4). Experiments with 0·05M-, 0·05M-, and 0·025M-phenol and 0·005M-, 0·0025M-, and 0·0025M-iodine bromide respectively showed that the time required for 6% halogen consumption in the three cases was 30, 60, and 123 sec. respectively, from which the kinetic order was found to be two with respect to iodine bromide and 1·04 with respect to phenol.

TABLE 4. *Total order of the reaction between phenol and iodine bromide.*

Solvent : carbon tetrachloride. Temp. : 30°.

| Halogen reacted (%) | *a* (mole/l.) | *b* (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | *n* (total order) | Halogen reacted (%) | *a* (mole/l.) | *b* (mole/l.) | $t_1$ (sec.) | $t_2$ (sec.) | *n* (total order) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 0·020 | 0·010 | 39 | 170 | 3·12 | 6 | 0·010 | 0·004 | 76 | 458 | 2·96 |
| 12 | 0·020 | 0·010 | 90 | 360 | 3·00 | 2 | 0·004 | 0·002 | 60 | 245 | 3·03 |
| 3 | 0·010 | 0·004 | 22 | 140 | 3·02 | 4 | 0·004 | 0·002 | 205 | 720 | 2·81 |

(b) *Activation energy.* The halogen consumption on reaction of phenol and iodine bromide (0·01M each) in the temperature range 0—40° is represented in Fig. 5, which shows a slight increase in rate from 0° to 20°, but a marked decrease between 20° and 40°. To determine the exact temperature of this rate inversion, third-order rate constants for 10% of the reaction at different temperatures (Table 5) are plotted against temperature in Fig. 6 which shows the inversion to occur at 19°. The apparent activation energy calculated from the rate constants at 0—10° for 10, 14, and 18% reaction is 3·38, 3·46, and 3·49 respectively, the average being

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[6] Faull, *J. Amer. Chem. Soc.*, 1934, **56**, 522.

TABLE 5. *Rate constants at various temperatures for phenol–iodine bromide reaction.*

Solvent: carbon tetrachloride. Phenol and IBr, 0·01M each. Extent of reaction: 10%.

| Temp. | 0° | 5° | 10° | 20° | 30° | 35° | 40° |
|---|---|---|---|---|---|---|---|
| $k_3$ (l.$^2$ mole$^{-2}$ sec.$^{-1}$) | 79·8 | 88·6 | 99·6 | 112·6 | 48·5 | 30·7 | 18·3 |

3·44 ± 0·06 kcal. mole$^{-1}$. Similarly at 30—40° $E$ for 6, 8, and 10% reaction is −18·55, −18·42, and −18·42 respectively (average −18·46 ± 0·10 kcal. mole$^{-1}$).

FIG. 5. *Rate of halogen consumption at various temperatures for phenol–*IBr *reaction at* 0·01M-*concentration.*

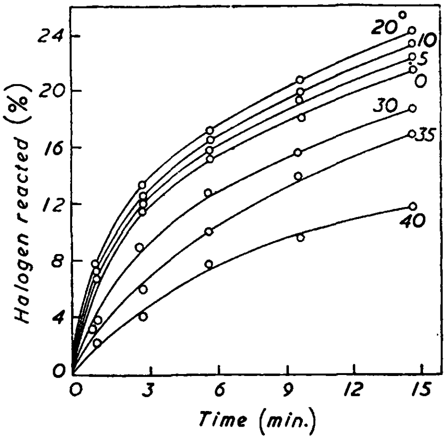


FIG. 6. *Plot of third-order rate-constants for phenol–*IBr *reaction against temperature.*

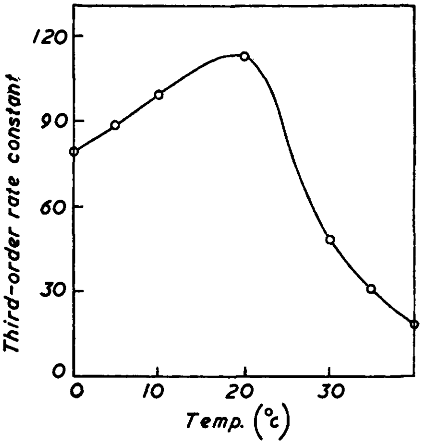


FIG. 7. *Plot of the percentage of bromine reacted in the first* 15 *seconds against the ratio of total iodine to bromine.*

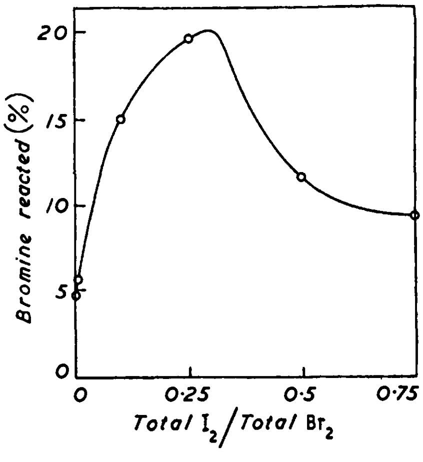
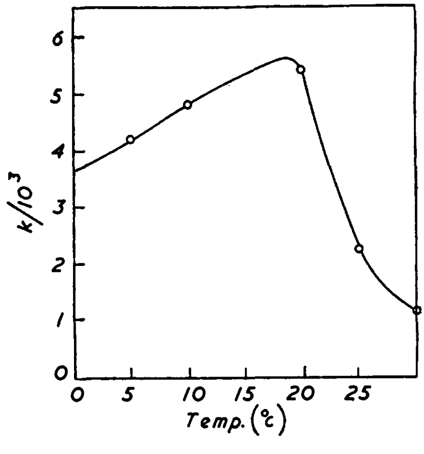


FIG. 8. *Plot of third-order rate-constants for phenol–bromine reaction against temperature* ($k$ at 0° C = 3·7 × 10$^{-3}$).



(c) *Iodine bromide catalysis.* The rate of bromination of phenol in presence of 0—0·01M-iodine, phenol and bromine being constant at 0·01M and 0·005M respectively, was determined in the same manner as in the case of acetic acid. The percentage of bromine which reacted in the first 15 sec. for various amounts of added iodine is represented in Fig. 7 from which the maximum rate is seen to correspond to an iodine : bromine ratio of 0·30. The equilibrium constant at 25° for the reaction $I_2 + Br_2 \rightleftharpoons 2IBr$ in carbon tetrachloride is reported by Yost *et al.*[7] as 363·1, and its heat of reaction[8] as −3260 cal. mole$^{-1}$. The value of $K$ at 30° calculated from these data is 331·6, so that the concentrations of iodine bromide and free bromine at the catalytic maximum are, respectively, 0·0030M and 0·0035M, from which the ratio of iodine bromide to free

[7] Yost, Anderson, and Skoog, *J. Amer. Chem. Soc.*, 1933, **55**, 552.

[8] Blair and Yost, *ibid.*, p. 4489.

bromine is 0·85, approximately unity. Hence, it may be concluded that the rate of bromination of phenol in carbon tetrachloride is a maximum when iodine bromide and free bromine are in equimolar concentrations, as in the case of acetic acid.

*Phenol–Bromine Reaction.*—The over-all kinetic order of this reaction between 0·002M and 0·001M is three. It shows the same peculiar temperature effect as the phenol–iodine bromide reaction, with an inversion point at 19° (Fig. 8). The value of $E$ at 0—10° is 3·24 and at 25—30° $-24{\cdot}37$ kcal. mole$^{-1}$.

*Anisole–Iodine Bromide Reaction.*—This reaction, which is also kinetically of the third order, has a negative temperature coefficient at 20—40°. The third-order rate constants for 2% reaction at 0·01M-anisole and -iodine bromide are 0·90, 0·70, and 0·56 l.$^2$ mole$^{-2}$ sec.$^{-1}$ at 30°, 35°, and 40° respectively, from which $E$ is found to be $-8{\cdot}89$ kcal. mole$^{-1}$.

## DISCUSSION

*Mechanism in Glacial Acetic Acid.—Phenol–bromine reaction.* The general mechanism of aromatic bromination in acetic acid solution proposed by Robertson [9] involves a direct electrophilic attack by a neutral bromine molecule on the aromatic compound, forming an intermediate of the type ArH·Br$_2$, in which the bromine molecule is polarised into Br$^+$Br$^-$. This is followed by the slow rate-determining step, namely, the removal of the bromide ion Br$^-$ from the intermediate complex, leading to ArHBr$^+$. The final step, elimination of a proton from ArHBr$^+$, is a fast reaction, as was demonstrated earlier by Melander.[10] The following is the sequence of reactions :

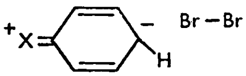
$$\mathrm{ArH} + \mathrm{Br_2} \rightleftharpoons \mathrm{ArH,Br_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{ArH{\cdot}Br_2} \xrightarrow{\text{Slow}} \mathrm{ArHBr^+} + \mathrm{Br^-} \quad . \; . \; . \; . \; . \; . \quad (4)$$

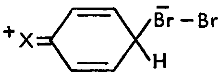
$$\mathrm{ArHBr^+} \xrightarrow{\text{Fast}} \mathrm{ArBr} + \mathrm{H^+} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\mathrm{H^+} + \mathrm{Br^-} \xrightarrow{\text{Fast}} \mathrm{HBr} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

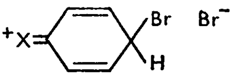
The intermediate molecular complex shown in eqn. (3) is supposed to have the following resonance structures :



(I)



(II)



(III)

It is rather difficult to see how (I)—(III) can be called resonance structures at all. Structure (I) represents a polarised benzene molecule and a neutral bromine molecule, there being no chemical bond between them. Structure (III) again represents two separate entities, namely, the positively charged ion C$_6$H$_5$X$^+$Br and a bromide ion Br$^-$. Structures (I) and (III) therefore correspond to the configuration of the molecular species on the left-hand side of eq. (3) and the right hand side of eqn. (4) respectively. Hence we have to conclude that the intermediate proposed by Robertson must have structure (II).

Now, 1 : 1 molecular complexes between aromatic compounds and halogens, similar to structure (II), have been shown to exist in an inert solvent such as carbon tetrachloride by Keefer and his co-workers [11] by spectrophotometric studies. But there is no experimental evidence for such complexes in a polar solvent such as acetic acid : in fact, experimental evidence shows that in acetic acid the halogens are polarised into X$^+$X$^-$ by solvation.[12] Nevertheless, one may consider structure (II) to represent the configuration of the activated complex in the reaction.

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[9] Robertson, *J.*, 1954, 1267.

[10] Melander, *Arkiv Kemi*, 1950, **2**, 213.

[11] (*a*) Keefer and Andrews, *J. Amer. Chem. Soc.*, 1950, **72**, 4677, 5170; Andrews and Keefer, *ibid.*, 1951, **73**, 462; (*b*) Keefer, Blake, and Andrews, *ibid.*, 1954, **76**, 3062; (*c*) Keefer and Andrews, *ibid.*, 1955, **77**, 2164; (*d*) Ogimaschi, Andrews, and Keefer, *ibid.*, p. 4202.

[12] Fairbrother, *J.*, 1948, 1051; Bayliss, *Nature*, 1949, **163**, 764; Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

In view of these considerations, the following scheme is proposed for the mechanism of bromination of phenol in glacial acetic acid :

$$C_6H_5{\cdot}OH + Br_2 \xrightarrow[\text{Slow}]{k} \underset{\text{Activated complex}}{[C_6H_5{\cdot}OH^+Br^-Br]} \longrightarrow C_6H_5{\cdot}OH^+Br + Br^- \quad . \quad (7)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \ . \ . \ . \ . \ . \quad (8)$$

$$H^+ + Br^- \xrightarrow[\text{Fast}]{} HBr \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

The rate of production of monobromophenol is given by :

$$d[C_6H_4Br{\cdot}OH]/dt = k[C_6H_5{\cdot}OH][Br_2] \quad . \ . \ . \ . \ . \ . \quad (9)$$

in agreement with the observed second-order kinetics for the reaction and the orders with respect to phenol and bromine, namely, one each. The experimental value of 4·83 kcal. mole$^{-1}$ for the activation energy evidently refers to the rate-determining step, eqn. (7). The small value of the energy of activation is in keeping with the extremely fast rate of bromination of phenol by bromine (cf. Fig. 1).

*Phenol–iodine bromide reaction.* As pointed out above, iodine bromide is a brominating agent for phenol in glacial acetic acid and in carbon tetrachloride; it is so even in nitrobenzene, so that the reacting halogen seems to be bromine. The mechanism proposed by Militzer [3] for this reaction in carbon tetrachloride, as represented by :

$$C_6H_5{\cdot}OH + IBr \longrightarrow p\text{-}C_6H_4Br{\cdot}OH + HI \quad . \ . \ . \ . \quad (10)$$

$$HI + IBr \longrightarrow I_2 + HBr \quad . \ . \ . \ . \ . \ . \ . \ . \quad (11)$$

has been criticised by Bennett and Sharpe [4, 13] on the ground that it involves polarisation into $I^-Br^+$, contrary to the greater electropositive character of iodine than of bromine. They suggested therefore that bromine arising by thermal dissociation of iodine bromide is the actual brominating agent, iodine probably acting as catalyst.

Iodine bromide is known to dissociate to about 9·5% at 25° in carbon tetrachloride,[7] but to a much smaller extent in an acid medium such as hydrobromic acid.[6] In acetic acid also, dissociation will be small, as shown by the fact that bromination by bromine is much faster than that by iodine monobromide (the times required for 16% reaction at 0·01M-concentration in acetic acid are about 2 sec. for bromine, cf. curve *B*, Fig. 1, and 645 sec. for iodine bromide, cf. Table 2). But Bennett and Sharpe's suggestion that iodine may be a catalyst in this reaction is against our experimental results (cf. above) that the addition of iodine beyond a critical amount retards the reaction and that in fact iodine bromide is the effective catalyst, as also suggested earlier by Robertson [5] in connection with his criticism of Militzer's mechanism.

In keeping with the above considerations and our experimental results, the following mechanism is suggested :

$$2IBr \rightleftharpoons I_2 + Br_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (12)$$

$$Br_2 + C_6H_5{\cdot}OH \xrightarrow[\text{Slow}]{k} [C_6H_5{\cdot}OH^+Br^-Br] \xrightarrow{IBr} C_6H_5{\cdot}OH^+Br + IBr_2^- . \quad (13)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \ . \ . \ . \ . \ . \quad (8)$$

$$H^+ + IBr_2^- \xrightarrow[\text{Fast}]{} HBr + IBr \quad . \ . \ . \ . \ . \ . \ . \ . \quad (14)$$

Taking into account eqns. (13), (8), and (14) the rate of bromination is given by :

$$d[C_6H_4Br{\cdot}OH]/dt = k[C_6H_5{\cdot}OH][Br_2][IBr] \quad . \ . \ . \ . \quad (15)$$

This rate equation, including equimolar concentrations of iodine monobromide and free bromine, accounts for the catalytic maximum observed when the ratio of iodine bromide to free bromine is unity. With iodine bromide as the brominating agent, as in the present

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[13] Sharpe, *J.*, 1953, 3713.

case, eqn. (12) must also be taken into account, so that the concentration of bromine is evidently given by the expression $[\mathrm{IBr}]\sqrt{K}$, and eqn. (15) then becomes

$$d[C_6H_4Br{\cdot}OH]/dt = [C_6H_5{\cdot}OH][IBr]^2k\sqrt{K} \quad . \quad . \quad . \quad . \quad (16)$$

in agreement with the experimental finding that the total kinetic order is three, two with respect to iodine monobromide and one with respect to phenol.

As seen from the above reaction scheme, the observed activation energy is made up of the heat of dissociation of two moles of iodine bromide [eqn. (12)] and the true activation energy of the rate-determining step [eqn. (13)]. The latter value may be assumed to be the same as for the phenol–bromine reaction, namely, 4·83 kcal. mole$^{-1}$, since the rate-determining step is essentially the same in both cases. The heat of dissociation of 2 moles of iodine bromide is then equal to the observed activation energy minus the true activation energy, *i.e.*, 9·72—4·83 = 4·89, *i.e.*, 2·45 kcal. per mole. This is of the same order of magnitude as found from vapour-pressure determinations [8] in carbon tetrachloride, *viz.*, 1·63 kcal. mole$^{-1}$.

*Mechanism in Carbon Tetrachloride.*—The bromination of benzene and toluene in carbon tetrachloride has been explained by Tsurata *et al.*[14, 15] by a mechanism in which the rate-determining step involves the removal of hydrogen bromide from a 1 : 1 bromine–hydrocarbon complex under the catalytic influence of iodine bromide :

$$C_6H_6 + Br_2 \rightleftharpoons C_6H_6{,}Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$C_6H_6{,}Br_2 + m\mathrm{IBr} \xrightarrow[\text{Slow}]{} C_6H_5Br + HBr + m\mathrm{IBr} \quad . \quad . \quad . \quad (18)$$

Experimentally *m* is found to be 3 for benzene [14] and toluene,[15] and 2 for mesitylene.[16] In the case of phenol, we find that the rate is a maximum when iodine bromide and free bromine are present in equimolar concentrations, so that for IBr-catalysed bromination of phenol in carbon tetrachloride *m* is unity, and the rate-determining step may be represented by :

$$C_6H_5{\cdot}OH{,}Br_2 + IBr \xrightarrow[\text{Slow}]{} C_6H_5{\cdot}OH^+Br + IBr_2^- \quad . \quad . \quad . \quad (19)$$

The observed decrease in the over-all rate of the reaction between 20° and 40° must be attributed to the decrease, with temperature, of the concentration of one of the two reactants in the above rate-determining step. This cannot be iodine bromide, since the same effect is observed for bromination by bromine. Hence the other reactant, namely, the phenol–bromine complex, must be responsible for the negative temperature coefficient. Experimental evidence for the thermal decomposition of hydrocarbon–halogen complexes has recently been provided by spectrophotometric studies,[11b, c] *e.g.*, the value of equilibrium constant for mesitylene–bromine complex at 20° and 25° is 0·398 and 0·381 respectively. It is reasonable to conclude that the phenol–bromine complex begins to dissociate sensibly above 19°, in order to account for the observed negative temperature coefficient. It may be recalled that the negative temperature coefficient in the well-known third-order gas-phase reaction between nitric oxide and oxygen is also attributed [17] to the thermal decomposition of the intermediate $(NO)_2$.

*Phenol–bromine reaction.* In the light of the above discussion, the following mechanism is proposed for the phenol–bromine reaction in carbon tetrachloride :

$$C_6H_5{\cdot}OH + Br_2 \overset{K'}{\rightleftharpoons} C_6H_5{\cdot}OH{,}Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$C_6H_5{\cdot}OH{,}Br_2 + Br_2 \xrightarrow[\text{Slow}]{k} C_6H_5{\cdot}OH^+Br + Br_3^- \quad . \quad . \quad . \quad . \quad (21)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + Br_3^- \xrightarrow[\text{Fast}]{} HBr + Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

[14] Tsuruta, Sasaki, and Farukawa, *J. Amer. Chem. Soc.*, 1952, **74**, 5995.

[15] *Idem, ibid.*, 1954, **76**, 994.

[16] Blake and Keefer, *ibid.*, 1955, **77**, 3707.

[17] Bodenstein, *Helv. Chim. Acta*, 1935, **18**, 743; Rice, *J. Chem. Phys.*, 1936, **4**, 53.

The rate of formation of monobromophenol is given by:

$$d[C_6H_4Br{\cdot}OH]/dt = kK'[C_6H_5{\cdot}OH][Br_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

which agrees with the observed third-order kinetics of the reaction.

The molecular complex, $C_6H_5{\cdot}OH,Br_2$, may be assumed to suffer little dissociation between 0° and 10°. It is reasonable therefore to regard the observed activation energy of 3·24 kcal. mole$^{-1}$ in this temperature range as the real activation energy of the rate-determining step [eqn. (21)]; but beyond the inversion point (19°) the complex undergoes thermal dissociation with a consequent decrease of the reaction rate; hence the observed negative activation energy of $-24{\cdot}37$ kcal. mole$^{-1}$ between 25° and 30°. This value, as seen from the above reaction scheme, represents the sum of the activation energy of the rate-determining step [eqn. (21)] and the heat of formation of the complex [eqn. (20)], so that we have

$$-24{\cdot}37 \text{ (obs. } E) = 3{\cdot}24 \text{ (true } E) + \Delta H \text{(heat of formation of the complex)} \qquad (24)$$

from which $\Delta H$ is $-27{\cdot}61$ kcal. mole$^{-1}$. This seemingly high value is not unreasonable in view of the extreme reactivity of phenol in bromination, and the known direct relation between the rate of halogenation of aromatic compounds and the negative heats of formation of their halogen complexes.[11c]

*Phenol–iodine bromide reaction.* The mechanism of this reaction must include the thermal dissociation of iodine bromide and also its participation, as catalyst, in the rate-determining step. The following scheme seems to satisfy these requirements:

$$2IBr \xrightleftharpoons{K} I_2 + Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$C_6H_5{\cdot}OH + Br_2 \xrightleftharpoons{K'} C_6H_5{\cdot}OH,Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$C_6H_5{\cdot}OH,Br_2 + IBr \xrightarrow[\text{Slow}]{k} C_6H_5{\cdot}OH^+Br + IBr_2^- \quad . \quad . \quad . \quad (19)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + IBr_2^- \xrightarrow[\text{Fast}]{} HBr + IBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The rate of the reaction as given by eqns. (20), (19), (8), and (14) is

$$d[C_6H_4Br{\cdot}OH]/dt = kK' [C_6H_5{\cdot}OH][Br_2][IBr] \quad . \quad . \quad . \quad . \quad (25)$$

which agrees with the experimental finding that the catalytic maximum occurs at equimolar concentrations of bromine and iodine bromide.

Taking into account eqn. (12), in which bromine and iodine are produced in equal amounts from iodine bromide, the concentration of bromine is given by $[IBr]\sqrt{K}$. Insertion of this expression for bromine in eqn. (25) leads to

$$d[C_6H_4Br{\cdot}OH]/dt = (kK'\sqrt{K}) [C_6H_5{\cdot}OH][IBr]^2 \quad . \quad . \quad . \quad . \quad (26)$$

which accounts for the over-all kinetic order of three, one for phenol and two for iodine bromide.

The observed activation energy of this reaction at 0—10° (3·44 kcal. mole$^{-1}$) is almost identical with the true activation energy of the phenol–bromine reaction (3·24 kcal. mole$^{-1}$), and may therefore be assumed to be the true activation energy in the present case. On the other hand, the negative activation energy, $-18{\cdot}46$ kcal. mole$^{-1}$, observed between 30° and 40° is the sum of the heat of dissociation of two moles of iodine bromide [eqn. (12)], the heat of formation of the phenol–bromine complex [eqn. (20)], and the activation energy, just deduced, of the rate-determining step [eqn. (19)]. Hence:

$$\begin{aligned}-18{\cdot}46 \text{ (obs. } E) = 3{\cdot}44 \text{ (true } E) - 27{\cdot}61 \;(\Delta H &\text{ of formation of the complex)} \\ &+2\Delta H \text{ (dissocn. of IBr)} \quad . \quad . \quad (27)\end{aligned}$$

from which $\Delta H$ (heat of dissociation of IBr) is 2·86 kcal. mole$^{-1}$. The substantial agreement of this value with that deduced from vapour-pressure data[8] (1·63 kcal. mole$^{-1}$) may be regarded as providing some justification for the proposed mechanism.

Additional evidence for the mechanism is furnished by a consideration of the activation energy of the anisole–iodine bromide reaction, which is —8·89 kcal. mole$^{-1}$ at 30—40°. Given the similarity of the kinetics of this reaction to that of phenol (cf. Experimental section), it is justifiable to ascribe the same activation energy to the rate-determining step in the two cases. It follows then that for the anisole–iodine bromide reaction, we have:

$$-8{\cdot}89 \text{ (obs. } E) = 3{\cdot}44 \text{ (true } E) + \Delta H \text{ (heat of formn. of anisole–bromine complex)} \\ + 2 \times 2{\cdot}86 \text{ (heat of dissocn. of IBr)} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so that $\Delta H$ is —18·05 kcal. mole$^{-1}$. This is less than the value for phenol–bromine complex (—27·61 kcal. mole$^{-1}$), as it should be since anisole is less reactive than phenol in bromination; the rate constant for 2% reaction at 30° for phenol is 77·36 and for anisole 0·90 l.$^2$ mole$^{-2}$ sec.$^{-1}$.

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LOYOLA COLLEGE, MADRAS, INDIA. [*Received, May* 31*st*, 1956.]