

## Bromination of Phenol and Substituted Phenols in Carbon Tetrachloride-Influence of Hydrogen Bromide

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Hydrogen bromide, one of the products of the bromination of aromatic substrates, acts as a catalyst as well as an inhibitor in carbon tetrachloride. A detailed investigation on the kinetics and mechanism of the bromination of phenols of different reactivities in carbon tetrachloride has revealed that structural features of the substrate determine the mechanism in these reactions.

### Introduction

It has been reported that for the bromination of *p*-bromophenol in carbon tetrachloride, the overall order is three, the individual orders being two in the substrate and one in bromine<sup>1</sup>. The second order in the substrate has been attributed to its participation as an electrophile assisting the removal of  $Br^-$  from the substrate-bromine complex. The bromination of phenol in carbon tetrachloride is also overall third order<sup>2</sup> but the individual orders have not been reported. Hydrogen bromide, one of the products of reaction, acts as an inhibitor in the bromination of *p*-bromophenol whereas in the bromination of anisole<sup>3</sup> in carbon tetrachloride, it acts as a catalyst. In the latter case it has

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<sup>1</sup> J. RAJARAM and J. C. KURIACOSE, Indian J. Chem. **1970**, 145.

<sup>2</sup> L. M. YEDDANAPALLI and N. S. GNANAPRAGASAM, J. chem. Soc. [London] **1956**, 4934.

<sup>3</sup> D. CHAYA RAO, J. RAJARAM and J. C. KURIACOSE, Chem. Comm. **1971**, 754.

been suggested that hydrogen bromide acts as an effective electrophile replacing a molecule of bromine in the rate determining step. The ambivalent behaviour of hydrogen bromide in carbon tetrachloride suggests a comparative study of the effect of hydrogen bromide on the bromination of phenols of varying reactivities in order to obtain any possible relationship between the structure of the phenol and the effective role of hydrogen bromide.

### Experimental

Carbon tetrachloride (AR BDH) dried over fused calcium chloride was distilled and the fraction boiling between 76–77 °C was used. Bromine (AR BDH ampoules) was used without further purification. Phenol, *p*-cresol, *o*-cresol, *p*-chlorophenol and *o*-chlorophenol were distilled before use. The samples used and their boiling points are tabulated below.

		B.pt in °C
Phenol	(BDH)	181–182
<i>p</i> -cresol	(Riedel)	202–203
<i>o</i> -cresol	(Riedel)	191–192
<i>p</i> -chlorophenol	(BDH)	216–217
<i>o</i> -chlorophenol	(BDH)	175–176
<i>p</i> -chloroanisole*		197–198
<i>o</i> -chloroanisole*		195–196

\* Both the samples were prepared from the respective phenols by methylation.

*p*-Bromophenol (BDH) was recrystallised from carbon tetrachloride (m.pt. 63 °C). The purity of the samples was ascertained by gas chromatography.

### Rate measurements

The bromination of phenol, *p*-cresol and *o*-cresol in carbon tetrachloride was investigated by following the disappearance of bromine spectrophotometrically using a Carl Zeiss DMR 21 spectrophotometer. The optical densities of the reaction mixtures at 520 nm were followed as a function of time. The optical densities at zero time were obtained through extrapolation of the optical density-time curve. The percentage of bromine reacted at different times were calculated using the differences in optical densities. The initial rates, calculated from the % bromine reacted in the first few minutes, have been used in determining the individual orders in the reactants.

The bromination of deactivated phenols like *p*-bromophenol, *p*-chlorophenol and *o*-chlorophenol was followed iodometrically by the batch method<sup>2</sup>. The orders have been determined by the isolation method<sup>2</sup> using the initial rates. The slopes at various concentrations were taken from the concentration-time curve by the mirror method<sup>4</sup> and the initial rates obtained from the double logarithmic plots of rate versus concentration.

### Results and discussion

The equilibrium constant for the formation of  $HBr_3$  in carbon tetrachloride was first determined spectrophotometrically. A series of solutions of varying concentrations of hydrogen bromide [0.1 M to 0.04 M] and bromine [0.005 M] in carbon tetrachloride were prepared and the optical densities of these solutions and those of the mixtures were recorded at wavelengths ranging from 290–310 nm at 30 °C, a region in which the absorption by the complex was intense and that of free bromine weak as observed in trial runs. The data at each wavelength were analysed graphically using the equation<sup>5</sup>

$$\frac{1}{\epsilon_{(Br_2)_T} - \epsilon_{(Br_2)}} = \frac{1}{(HBr) K [\epsilon_{(HBr_3)} - \epsilon_{(Br_2)}]} + \frac{1}{\epsilon_{(HBr_3)} - \epsilon_{(Br_2)}} \quad (1)$$

where  $\epsilon_{(Br_2)_T}$  is the experimentally measured apparent extinction coefficient of bromine (both free and complexed),  $\epsilon_{(Br_2)}$  is the extinction coefficient of bromine and  $K$  is the equilibrium constant for the formation of  $HBr_3$ . The values of  $K$  and  $\epsilon_{(HBr_3)}$  at different wavelengths as determined from the linear plots are tabulated below (Table 1).

Table 1. *Equilibrium constant for the formation of HBr<sub>3</sub>*

Solvent:  $CCl_4$

Temperature: 30 °C

Wavelength nm	$K$	$\epsilon_{(HBr_3)}$
290	0.39	1666
300	0.36	1250
310	0.36	1110

Bromination of phenol in carbon tetrachloride was autocatalytic and subject to an induction period which was independent of the concentration of bromine but dependent on the concentration of the substrate (Table 2). The individual orders, as determined from the rates

<sup>4</sup> W. H. PEARLSON and J. H. SIMONS, *J. Amer. chem. Soc.* **67** (1945) 352.

<sup>5</sup> R. M. KEEFER and L. J. ANDREWS, *J. Amer. chem. Soc.* **78** (1956) 3637.

Table 2. *Autocatalysis in the bromination of phenol*Solvent:  $CCl_4$ 

Temperature: 30°C

Concentration (mole · l <sup>-1</sup> )		Approximate induction period (minutes)	Initial rate × 10 <sup>5</sup>	Order in reactants	10 <sup>-4</sup> <i>k</i> (l <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup> )
[ <i>ArH</i> ] × 10 <sup>3</sup>	[ <i>Br</i> <sub>2</sub> ] × 10 <sup>4</sup>				
11.18	11.78	6	2.95	1.10	2.01
11.18	7.99	6	2.00	( <i>Br</i> <sub>2</sub> )	1.76
11.18	5.05	6	1.26		1.99
8.94	5.05	8	1.00		1.56
6.91	5.05	10	0.63	1.92	1.97
4.88	5.05	20	0.25	( <i>ArH</i> )	1.92

obtained from the initial portions of the autocatalytic curves were two in substrate and one in bromine respectively (Table 2). The rate of formation of hydrogen bromide is not affected to the same extent by the variation in the concentration of bromine as by the variation in the concentration of *ArH* because the order in bromine is one and that in *ArH* is two. The induction periods for constant concentration of bromine increase with the decrease in substrate concentration. The induction period may therefore be related to the accumulation of an optimum amount of hydrogen bromide. The results suggest that a minimum concentration of hydrogen bromide must be formed in the bromination reaction before the reaction rate becomes appreciable.

The reaction curves for the autocatalysed reaction appear to conform to the rate expression,

$$-\frac{d[Br_2]}{dt} = k' [Br_2] [HBr] \quad (2)$$

which on integration gives

$$k't = \frac{2.303}{a+b} \log \frac{a}{b} + \frac{2.303}{(a+b)} \log \frac{(b+x)}{(a-x)} \quad (3)$$

where  $x' = b + x$ ,  $b$  = concentration of hydrogen bromide accumulated at the end of the induction period,  $x$  = concentration of hydrogen bromide produced after the induction period,  $a$  = initial concentration of bromine,  $(a - x')$  = concentration of bromine remaining after a time ' $t$ ' and  $k'$  = the apparent rate constant for the autocatalysed reaction.

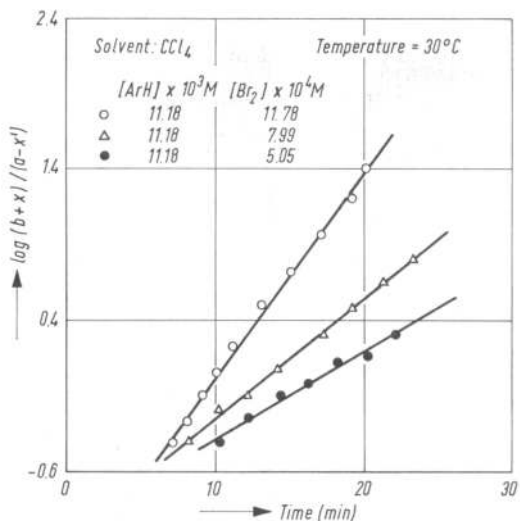


Fig. 1. Evaluation of rate constants using the rate expression

$$k't = \frac{2.303}{a+b} \log \frac{a}{b} + \frac{2.303}{a+b} \log \frac{(b+x)}{(a-x')}$$

in the autocatalysed bromination of phenol

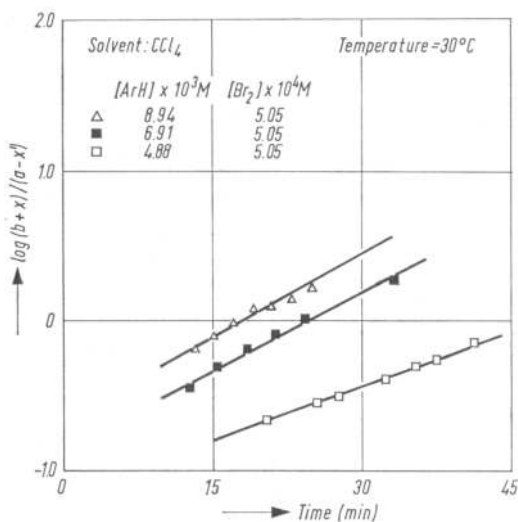


Fig. 2. Evaluation of rate constants using the rate expression

$$k't = \frac{2.303}{a+b} \log \frac{a}{b} + \frac{2.303}{a+b} \log \frac{(b+x)}{(a-x')}$$

in the autocatalysed bromination of phenol

The apparent rate constant  $k'$  contains the concentration of  $ArH$  which could be considered to be constant, since isolation conditions are maintained for the reaction, i.e.:

$$k = k'/ArH . \quad (4)$$

The kinetic equation (3) can be rearranged to give

$$\log \frac{(b+x)}{(a-x')} = \frac{k't(a+b)}{2.303} - \log \frac{a}{b} . \quad (5)$$

Plots of the left hand side of equation (5) against time were linear, confirming the applicability of the above expression to the reaction under study (Fig. 1 and 2).  $k'$  can be obtained from the slope as follows:

$$k' = \frac{2.303 \cdot \text{Slope}}{(a+b)} . \quad (6)$$

From equations (4) and (6), the rate constant for the autocatalysed reaction can be written as

$$k = \frac{2.303 \cdot \text{Slope}}{[ArH] \cdot (a+b)} . \quad (7)$$

The rate constants obtained by using an expression involving a first order each in substrate, bromine and hydrogen bromide are tabulated in Table 2. The reasonable agreement in the values of the rate constants

Table 3

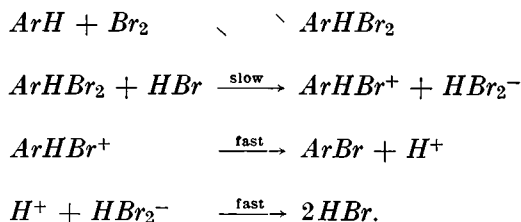
*Data on the bromination of phenol in the presence of added hydrogen bromide*  
Solvent:  $CCl_4$  Temperature:  $30^\circ C$

Concentration (mole l <sup>-1</sup> )			(Initial rate) $\times 10^5$	Order in reactants	$10^{-4} k$ (l <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup> )
$[ArH] \times 10^3$	$[Br_2] \times 10^4$	$[HBr] \times 10^4$			
8.94	5.05	9.90	5.75		
6.91	5.05	9.90	3.98	1.18	1.98
4.88	5.05	9.90	2.40	( $ArH$ )	
3.25	5.05	9.90	1.45		
6.91	9.79	9.90	9.33		
6.91	7.35	9.90	5.75	1.06	1.79
6.91	5.05	9.90	3.98	( $Br_2$ )	
6.91	5.05	14.9	7.24		
6.91	5.05	9.90	3.98	1.17	1.85
6.91	5.05	6.00	2.82	( $HBr$ )	

obtained in different experiments therefore suggests the participation of hydrogen bromide as a catalyst in one of the steps.

Externally added hydrogen bromide accelerated the rate of bromination of phenol in carbon tetrachloride considerably. The individual orders were one each in substrate, bromine and hydrogen bromide. The rate constants in the presence of externally added hydrogen bromide have been obtained from the intercepts of the double logarithmic plots of initial rates versus initial concentrations for the determination of order (Table 3).

A first order in hydrogen bromide agrees with the suggested intervention of a molecule of hydrogen bromide as an electrophile in the rate determining step. In the presence of hydrogen bromide, the following mechanism for the bromination of phenol in carbon tetrachloride is proposed.



The agreement between the values of the rate constants obtained using the rate expression for autocatalysis (Table 2) and the ones obtained when hydrogen bromide is previously added (Table 3) supports the suggested mechanism.

Further studies on the bromination of a number of substituted phenols in carbon tetrachloride in the absence and presence of hydrogen bromide have revealed some interesting features (Tables 3, 4 and 5). Phenols and substituted phenols can be classified into three groups on the basis of the kinetics of their bromination in carbon tetrachloride.

1. Reactive substrate (phenol);
2. Substrates more reactive than phenol (*p*-cresol and *o*-cresol);
3. Substrates less reactive than phenol (*p*-bromophenol, *p*-chlorophenol and *o*-chlorophenol).

A common feature observed with all the phenols except *o*-chlorophenol is the occurrence of a second order in substrate and a first order in bromine. A second order in substrate could arise in two ways.

Table 4. Data on the bromination of substrates more reactive than phenol  
 Solvent:  $CCl_4$  Temperature:  $30^\circ C$

Substrate	Concentration (mole $l^{-1}$ )			(Initial rate) $\times 10^5$	Orders in reactants
	$[ArH] \times 10^3$	$[Br_2] \times 10^4$	$[HBr] \times 10^4$		
<i>p</i> -cresol	21.30	7.01	—	6.03	
	13.30	7.01	—	2.82	1.85
	10.60	7.01	—	1.74	( <i>ArH</i> )
<i>p</i> -cresol	16.30	15.10	—	12.02	
	16.30	11.30	—	8.51	1.04
	16.30	9.30	—	6.61	( <i>Br</i> <sub>2</sub> )
<i>p</i> -cresol	16.30	7.20	9.80	8.13	
	13.20	7.20	9.80	3.98	1.80
	10.90	7.20	9.80	3.09	( <i>ArH</i> )
<i>p</i> -cresol	10.90	9.60	9.80	4.07	
	10.90	7.20	9.80	3.09	1.20
	10.90	4.80	9.80	2.04	( <i>Br</i> <sub>2</sub> )
<i>p</i> -cresol	10.90	7.20	13.10	5.75	
	10.90	7.20	9.80	3.09	1.00
	10.90	7.20	4.90	2.09	( <i>HBr</i> )
<i>o</i> -cresol	10.26	7.10	—	10.72	
	8.20	7.10	—	5.01	2.17
	6.15	7.10	—	3.55	( <i>ArH</i> )
<i>o</i> -cresol	10.26	11.80	—	18.62	
	10.26	9.40	—	14.99	1.05
	10.26	7.10	—	10.72	( <i>Br</i> <sub>2</sub> )
	10.26	4.80	—	8.51	
<i>o</i> -cresol	10.26	7.20	9.80	24.55	
	8.20	7.20	9.80	15.85	2.20
	6.10	7.20	9.80	8.71	( <i>ArH</i> )
	4.10	7.20	9.80	3.46	
<i>o</i> -cresol	8.20	9.60	9.80	19.55	
	8.20	7.20	9.80	15.85	1.03
	8.20	4.80	9.80	10.00	( <i>Br</i> <sub>2</sub> )
<i>o</i> -cresol	8.20	7.20	13.10	23.44	
	8.20	7.20	9.80	15.85	0.80
	8.20	7.20	4.90	11.48	( <i>HBr</i> )



Table 5. Data on the bromination of substrates less reactive than phenol  
 Solvent:  $CCl_4$  Temperature:  $30^\circ C$

Substrate	Concentration (mole l <sup>-1</sup> )			(Initial rate) × 10 <sup>4</sup>	Orders in reactants
	[ArH] × 10 <sup>2</sup>	[Br <sub>2</sub> ] × 10 <sup>3</sup>	[HBr] × 10 <sup>3</sup>		
<i>p</i> -bromophenol	15.00	4.63	—	37.15	
	10.00	4.63	—	12.59	1.91
	5.00	4.63	—	5.01	(ArH)
<i>p</i> -bromophenol	10.00	9.09	—	31.62	
	10.00	6.87	—	22.39	1.17
	10.00	4.63	—	12.59	(Br <sub>2</sub> )
<i>p</i> -bromophenol	10.00	4.79	8.88	7.94	
	7.50	4.79	8.88	6.31	1.00
	5.00	4.79	8.88	3.98	(ArH)
<i>p</i> -bromophenol	10.00	9.19	8.88	13.18	
	10.00	6.86	8.88	10.00	1.07
	10.00	4.79	8.88	7.94	(Br <sub>2</sub> )
<i>p</i> -bromophenol	10.00	9.19	13.49	8.32	
	10.00	9.19	8.88	13.18	— 0.57
	10.00	9.19	5.00	15.85	(HBr)
	10.00	9.19	2.50	21.88	
* <i>p</i> -chlorophenol	24.27	12.20	—	53.30	—
* <i>p</i> -chlorophenol	24.27	12.20	9.60	46.50	—
<i>o</i> -chlorophenol	40.00	9.80	—	7.59	
	30.00	9.80	—	5.75	0.90
	20.00	9.80	—	3.98	(ArH)
	10.00	9.80	—	2.29	
<i>o</i> -chlorophenol	30.00	30.03	—	19.05	
	30.00	20.02	—	10.47	1.07
	30.00	9.80	—	5.75	(Br <sub>2</sub> )

\* Individual orders in the reactants have not been determined.

(a) The substrate molecule can act as an electrophile and remove the  $Br^-$  from the  $ArHBr_2$  complex in the rate determining step or  
 (b) Hydrogen bonded phenol dimers formed under these conditions may react with a molecule of bromine in the rate determining step. The

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existence of phenol dimers in carbon tetrachloride has been established by both NMR<sup>6</sup> and IR<sup>7</sup> spectroscopic studies.

For phenol in carbon tetrachloride the value of the extinction coefficients of the first overtone of the free *O—H* stretching vibration does not change with the concentration<sup>7</sup> and therefore it is not likely that there is an appreciable dimer formation. Hence for a reactive substrate like phenol the mechanism could be the one discussed earlier.

For substrates more reactive than phenol like *o*-cresol and *p*-cresol (Table 4), the orders were two in substrate and one in bromine. The order in hydrogen bromide was one. Here again the concentration of the dimer is not likely to be appreciable<sup>7</sup>. In these cases a substrate-hydrogen bromide complex may be a better electrophile than either the substrate or hydrogen bromide. The formation of  $\pi$ -complexes between hydrogen bromide and cresols may be more facile because of the enhanced  $\pi$ -basicity. The interaction can also be through the oxygen atom of the hydroxyl group. In either case, the electrophilicity of the substrate could be increased and hence a molecule of the substrate-hydrogen bromide complex may be an effective electrophile in the rate determining step.

Deactivated para substituted phenols and ortho substituted phenols behave differently in the bromination reaction in carbon tetrachloride in the presence of hydrogen bromide.

i) For para substituted halophenols, the added hydrogen bromide inhibited the reaction.

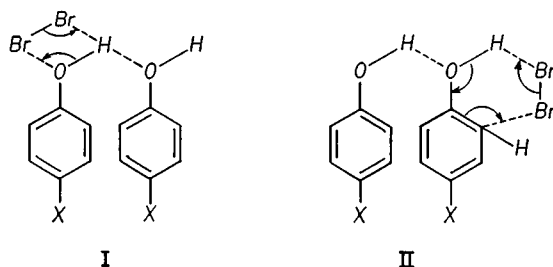
ii) For *o*-chlorophenol, there is no effect by the added hydrogen bromide.

For the concentrations used in the bromination of *p*-bromophenol, the second order in substrate could be attributed to the existence of dimers. The existence of dimers has been established in the case of *p*-chlorophenol under comparable concentration conditions<sup>7</sup>. Hydrogen bromide inhibits the bromination of *p*-bromophenol and *p*-chlorophenol. In the case of *p*-bromophenol, the order in substrate is reduced to one and that in bromine remained one under these conditions. One might interpret this as resulting from a reduction in the free substrate concentration due to complexing with hydrogen bromide and consequent reduction in the concentration of the substrate-dimer.

<sup>6</sup> J. A. POPLE, W. G. SCHNEIDER and H. J. BERNSTEIN, High resolution nuclear magnetic resonance, McGraw Hill, Chap. 15, p. 414 (1959).

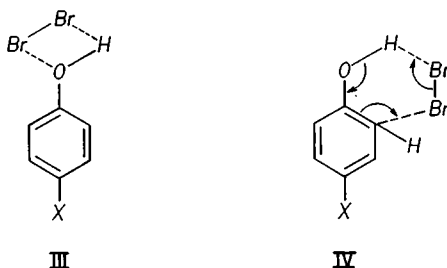
<sup>7</sup> M. M. MAGUIRE and R. WEST, Spectrochim. Acta 17 (1961) 373.

The decomposition of the complexes formed between *p*-substituted phenol dimers and bromine (I and II) may be rate determining.



Hydrogen bromide, in both the cases, can reduce the rate by breaking down the dimer molecule through hydrogen bonding with the oxygen atom. There is, however, no reason why the order in the substrate should be decreased to one under the experimental conditions when the concentration of hydrogen bromide is not large enough to convert all the substrate dimer into monomer. Though hydrogen bromide complexes with the substrate, the reduction in the concentration of the substrate is so small that even at this concentration one can expect the existence of dimers. At least a mixed order in substrate should have been observed. Since the order in *ArH* is clearly one in the presence of added hydrogen bromide, much importance cannot be given to the mechanism in which a substrate dimer is involved.

An attempt was made to explain the observed results through the general mechanism in which a substrate-bromine complex undergoes an attack by an electrophile in the rate determining step. The complexes formed between the substrate and bromine can be III or IV



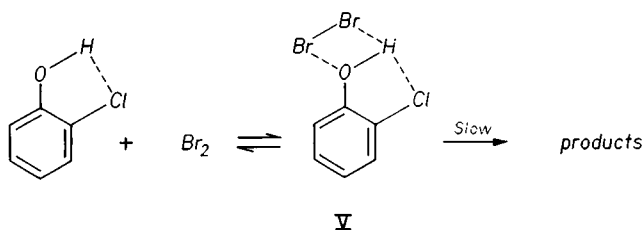
These complexes can undergo an electrophilic attack by a molecule of the substrate, so that a second order in substrate could be obtained. Hydrogen bromide can inhibit this reaction by hydrogen bonding with

the substrate and thereby preventing the formation of the complex. It is reasonable to expect that the substrate should have acted as the electrophile even under these conditions, where hydrogen bromide is added, since the reduction in the concentration of the substrate will be so small. But still only a first order in substrate is observed.

Though no definite conclusions could be drawn about the mechanism of the bromination of *p*-halophenols in carbon tetrachloride in the presence of added hydrogen bromide, the involvement of the  $-O-H$  group in these reactions is clear. If the inhibition observed in these reactions is due to the interaction between  $-O-H$  group and hydrogen bromide, then catalysis should be observed for the bromination of *p*-chloroanisole. In fact catalysis is observed (Table 6).

An attempt was made to study the shift in the frequency of the  $-O-H$  overtone in the near infrared region. The  $-O-H$  group of *p*-bromophenol in carbon tetrachloride was found to have an absorption at  $7037\text{ cm}^{-1}$  which corresponds to the first overtone of the  $-O-H$  group. Addition of hydrogen bromide in carbon tetrachloride shifted the  $-O-H$  overtone absorption from  $7037\text{ cm}^{-1}$  to  $7022\text{ cm}^{-1}$  which may be indicative of an interaction between the  $-O-H$  group of *p*-bromophenol and hydrogen bromide.

*o*-Chlorophenol behaves differently from other phenols in that the overall order of the bromination is two, the individual orders being one in each. Since *o*-chlorophenol is internally hydrogen bonded one can envisage a complex of the type V for the interaction of bromine with *o*-chlorophenol.



The added hydrogen bromide should have prevented the formation of such a complex by hydrogen bonding with the  $-O-H$  group of the substrate. Hydrogen bromide does not have any effect in the bromination of *o*-chlorophenol (Table 7) but it does catalyse the bromination of *o*-chloroanisole (Table 6). Though the mechanism is not very clear, it is evident that internal hydrogen bonding in this case plays a significant role.

Table 6. Data on the bromination of chloroanisoles

Solvent:  $CCl_4$ Temperature:  $30^\circ C$ 

Substrate	Concentration (mole $l^{-1}$ )			(Initial rate) $\times 10^5$
	$[ArH] \times 10^1$	$[Br_2] \times 10^2$	$[HBr] \times 10^2$	
<i>p</i> -chloroanisole	41.3	2.00	—	4.57
<i>p</i> -chloroanisole	41.3	2.00	$2.50 \times 10^{-2}$	8.71
<i>o</i> -chloroanisole	42.0	2.00	—	4.36
<i>o</i> -chloroanisole	42.0	2.00	$2.50 \times 10^{-2}$	6.76

Table 7. Effect of hydrogen bromide on the bromination of *o*-chlorophenolSolvent:  $CCl_4$ Temperature:  $30^\circ C$ 

Concentration (mole $l^{-1}$ )			% reaction at different times	
$[ArH] \times 10^2$	$[Br_2] \times 10^2$	$[HBr] \times 10^2$	1 min	5 min
26.75	1.26	—	6.5	13.3
26.75	1.26	1.01	6.8	13.5

The investigations on the bromination of phenols in carbon tetrachloride in the absence and in the presence of hydrogen bromide thus reveal that the structural features of the substrate determine the mechanisms of these reactions. In the case of substrates of average reactivity and those of higher reactivity, it is suggested that a molecule of the substrate and the substrate-hydrogen bromide complex respectively can act as an electrophile in the rate determining step. The inhibition caused by externally added hydrogen bromide for less reactive substrates apparently involves the participation of the  $-O-H$  group. This is supported by the observation that while there is inhibition by hydrogen bromide for *p*-halophenols, for chloroanisoles there is catalysis (Table 6).

### Acknowledgement

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