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On the Substituent Effects of Halogens in Aromatic Substitutions

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The general kinetic features of the bromination of 4-bromophenol by molecular bromine in acetic acid medium has been studied and *Arrhenius* activation energies for the bromination of four *para* substituted phenols of the general formula RC_6H_4OH ($R = CH_3$, F, Cl, and Br) have been accurately determined. These values, which indicate an anomalous order in substituent effect of halogens, are discussed.

(Keywords: Aromatic substitution; Bromination, kinetics; Kinetics)

Der Substituenten-Effekt von Halogenen bei der aromatischen Substitution

Die Bromierung von 4-Bromphenol mit Br_2 in Essigsäure wurde untersucht. Außerdem wurden die *Arrhenius*-Aktivierungs-Energien für die Bromierung von vier *p*-substituierten Phenolen RC_6H_4OH ($R = CH_3$, F, Cl und Br) genau bestimmt. Die beobachteten Substituenten-Effekte werden diskutiert und interpretiert.

Introduction

The electron-withdrawing properties of halogen substituents in aliphatic compounds are well established[1–3]. The values of their substituent constants show the same trend as the electronegativities of these elements[4,5]. On the contrary, the substituent effects of halogens in aromatic electrophilic substitutions have always presented a difficult hurdle for organic chemists. In addition to their electron-withdrawing powers, they are supposed to possess electron-releasing properties also[6,7]. This electron-releasing tendency order was never found to be constant. In fact the electronic effects of halogens in both *para*- and *meta*-positions cannot adequately be expressed in terms of single

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substituent constants[8]. Unusual resonance structures are invoked to explain *meta* activation[9]. It has been shown recently that in aromatic electrophilic substitutions involving neutral molecules of both aromatic substrate and halogen, the *Arrhenius* activation energies could be correlated with the electron-densities on the carbon atoms where halogenation takes place[10, 11]. In the light of this approach, we have reinvestigated the effects of halogen substituents in aromatic substitution. The chief object of this investigation was to evaluate accurately the *Arrhenius* activation energies (E) and the entropies of activation ($\Delta S^{\neq}$) for the bromination of four *para* substituted phenols* of the general formula RC_6H_4OH ($R = Me$, F, Cl, and Br) by molecular bromine in acetic acid medium and correlate them to the substituent effects of halogens. The general kinetic features of the reaction has also been studied in the case of a typical phenol, namely, 4-bromophenol.

Experimental

The broad experimental technique has already been described[11, 18]. Equal volumes (5 ml each) of the substrate and bromine solutions of known strength in acetic acid were mixed in specially designed ground glass-stoppered tubular reaction vessels (capacity 20 ml) provided with a cup at the mouth, as in an iodine flask, under thermostatic conditions. After the lapse of the desired time interval for each reaction vessel, the unreacted bromine was estimated iodometrically. Loss of bromine due to volatility during a run did not exceed 0.5% and hence quite accurate and reproducible kinetic parameters were obtained.

4-methylphenol (Naardan, Holland; bp 199.5 °C) and 4-chlorophenol (E. Merck; bp 217 °C) were distilled and used. 4-fluorophenol (Aldrich, mp 48-50 °C) and 4-bromophenol (Fluka; puriss; mp 62-64 °C) were used. Dry acetic acid was prepared according to the *Orton* and *Bradfield* method[34].

GC analysis of the products showed the formation of only one product. Thus in a typical case, bromination of 4-methylphenol, the product contained only 2-bromo-4-methylphenol. The GC analysis was carried out in a Varian model 1800 unit. A 20% silicone oil, DC 550 column of length 5 feet was used. Injection, column and detector temperatures were the same, i.e. 200 °C. Hydrogen was used as the carrier gas, with an input of 15 psi. The attenuator was set at 16. 10 μl of the sample was used for analysis. The sample itself was

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* Kinetics of bromination of 4-iodophenol has not been dealt with here, because it was found that the kinetics was complicated and did not fit into any of the standard rate expressions. *Ganesan* and *Kalachandra*[17], who studied the kinetics of chlorination of 4-iodoanisole have also reported that the results were abnormal, and may be due to the formation of an addition compound *p*-iodoanisoledichloride in addition to substitution in the ring. It is also likely that an "*ipso*" attack at iodine by bromine molecule may take place[22], as in the case of nitration of 4-iodoanisole and 4-iodophenols, as it is believed[23] that the leaving ability of I^+ is almost equal to that of H^+.

obtained as follows. 25 ml of the solution of 4-methylphenol in acetic acid ($0.5\,M$) was mixed with 25 ml of bromine in acetic acid ($0.25\,M$) in an 100 ml quickfit flask. The reaction was allowed to proceed to completion. The contents of the flask were then treated with water and a calculated amount of solid $NaHCO_3$ was added, in small amounts at a time, with stirring to neutralise the acetic acid. The organic material was then completely extracted with ether and the extracts dried over anhydrous sodium sulphate.

Results and Discussion

The bromination of 4-bromophenol in dry acetic acid was found to be of the second order, in the concentration range examined. The overall reaction obeyed the integrated second order rate equation. The reaction was first order in 4-bromophenol (p-BrP) and first order in bromine and the rate of disappearance of bromine could be expressed by the equation:

$$-\frac{\mathrm{d}\,[\mathrm{Br_2}]}{\mathrm{d}\,t} = k_2\,[p\text{-Br}P]\,[\mathrm{Br_2}] \qquad (1)$$

where k_2 is the second order rate constant. When $[p\text{-Br}P] \gg [\mathrm{Br_2}]$, the reaction was pseudo first order and could be expressed by the equation

$$-\frac{\mathrm{d}\,[\mathrm{Br_2}]}{\mathrm{d}\,t} = k_1'\,[\mathrm{Br_2}] \qquad (2)$$

where k_1' is the pseudo first order rate constant. Hence it follows

$$k_1' = k_2\,[p\text{-Br}P] \qquad (3)$$

The validity of equations (1), (2) and (3) was established by the following plots. Figure 1 shows a plot of pseudo first order kinetics, the integrated rate equation used being

$$\log\,(a—x) = -\frac{k_1'}{2.303}\,t + \log a \qquad (4)$$

Plots of log (a—x) against t were linear with slopes equal to k_1' and intercept log a. The linear plot of slope 1.2 in Fig. 2 (B) confirms equation (3). Further Fig. 2 (A) shows a plot of log $(-\mathrm{d}\,[\mathrm{Br_2}]/\mathrm{d}t)_0$ i. e. logarithm of the initial rates against log $[p\text{-Br}P]$. This is also linear with a slope of 1.2, thus confirming by a differential method that the order with respect to the aromatic compound is unity. Figure 3 (A) shows, by a differential method, that the reaction is first order in bromine; that is, a plot of the logarithm of the initial rates, $(-\mathrm{d}\,[\mathrm{Br_2}]/\mathrm{d}t)_0$, against log $[\mathrm{Br_2}]$ is linear with a slope of 0.9. Further a plot of $(-\mathrm{d}\,[\mathrm{Br_2}]/\mathrm{d}t)_0$ against $[\mathrm{Br_2}]$ is also linear and passes through the origin (Fig. 3 B).

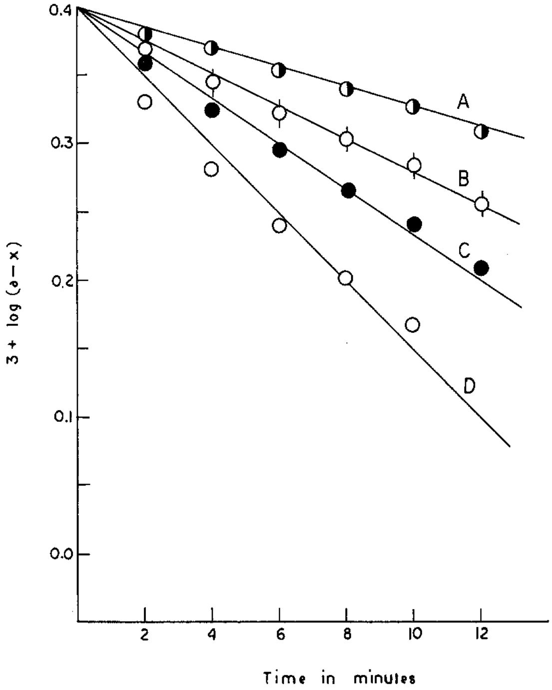

Fig. 1. Plots showing pseudo-first order kinetics; [p-BrP] = 2.5 × 10^{-3}, 3.75 × 10^{-3}, 5.00 × 10^{-3} and 7.5 × 10^{-3} M for A, B, C, and D respectively; [Br_2] = 2.5 × 10^{-3} M; Temperature 34 °C

For the overall second order kinetics observed, the following mechanism can be written (*Ar*H denotes the aromatic substrate in general)

$$ArH + Br_2 \underset{}{\overset{K,\ \mathrm{fast}}{\rightleftharpoons}} \underset{(\pi\text{-complex})}{ArH \cdot Br_2} \tag{5}$$

$$ArH \cdot Br_2 + \mathit{Solvent} \xrightarrow{k,\ \mathrm{slow}} \underset{(\sigma\text{-complex})}{ArH \cdot Br^+} + \mathit{Solvent} \cdot Br^- \tag{6}$$

$$ArH \cdot Br^+ \xrightarrow{\mathrm{fast}} ArBr + H^+ \tag{7}$$

$$H^+ + Br^- \xrightarrow{\mathrm{fast}} HBr \tag{8}$$

The mechanism is similar to the one for overall third order kinetics, proposed by *Robertson*[12], in which a second molecule of bromine attacks the π-complex. Quinoid type intermediates, believed to be obtained by

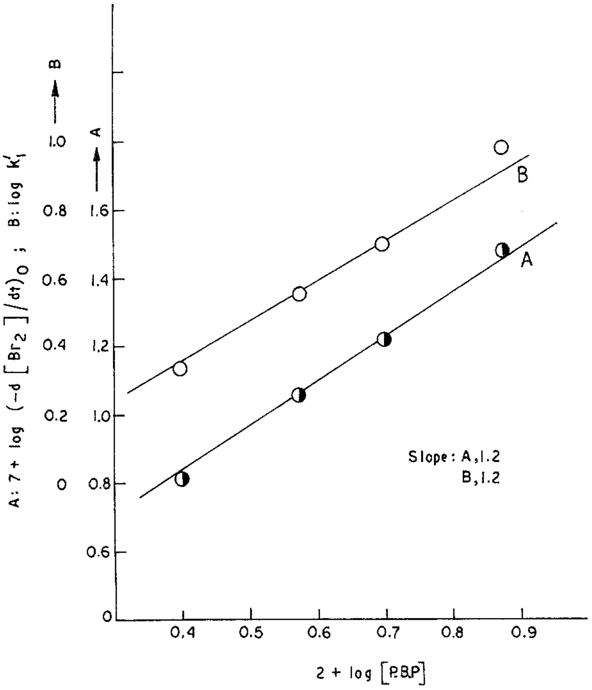

Fig. 2. Plots to determine the order with respect to 4-bromophenol; values of k_1' are from Fig. 1

the expulsion of the phenolic proton[13,14], could not be detected by spectrophotometric studies. In the present mechanism, instead of a second bromine molecule, a solvent molecule aids the polarisation and anionisation of the bromine-bromine bond in $ArH \cdot Br_2$, by forming the activated complex. Reaction step (6) should be ratedetermining, since the other steps are known to be fast, and the observed activation energies (Table 1) should be associated with this step. The existance of the aromatic-bromine-π-complex and its intermediacy in aromatic substitutions are now generally accepted[15]. The nature of the π-complex and the σ-complex formed are also fairly well known[15,16]. The structures of the π-complex, the activated complex and the σ-complex in aromatic halogenation have already been discussed[17,18]. For the mechanism consisting of steps (5), (6) and (7) we may write the following expression

$$-\mathrm{d}[Br_2]/\mathrm{d}t = k\,K\,[ArH]\,[Br_2] \tag{9}$$

Equation (9) is identical with equation (1) and hence

$$k_2 = k\,K. \tag{10}$$

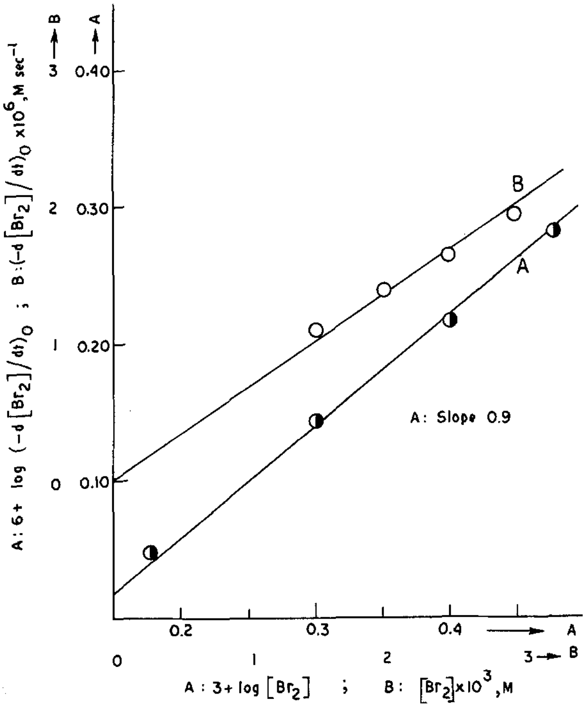

Fig. 3. Plots to determine the order with respect to bromine; $[Br_2] = 1.5 \times 10^{-3}$, 2×10^{-3}, 2.5×10^{-3} and $3.0 \times 10^{-3} M$; $[p\text{-BrP}] = 5 \times 10^{-2} M$; Temperature 34 °C

Table 1. *Kinetic parameters for the bromination of 4-substituted phenols in dry aceticacid* $[ArH] = [Br_2] = 2.5 = 10^{-3} M$

Compound	$k_2 \times 10^2$ l mol^{-1} s^{-1}				E[a]/kcal mol^{-1}	$\Delta S^{\neq}$/eu[b]
	18 °C	26 °C	34 °C	42 °C		
4-methylphenol	233.33	322.22	433.33	533.33	6.3 ± 0.16	—35.2
	244.44	300.00	422.22	544.44		
4-fluorophenol	0.75	1.19	1.94	2.44	9.0 ± 0.28	—37.3
	0.83	1.14	1.83	2.56		
4-chlorophenol	0.51	0.94	1.64	2.44	12.0 ± 0.05	—28.6
	0.53	1.03	1.67	2.42		
4-bromophenol	0.51	0.81	1.30	1.94	10.7 ± 0.50	—32.3
	0.49	0.76	1.13	2.18		

[a] *E* values obtained by applying the method of least squares.

[b] Entropy unit; 26 °C; concentration, mol l^{-1}.

The reactive species are neutral molecules of the phenol and bromine. Formation and participation of the phenoxide ion in the system can be ruled out, because the Ka values of the phenols under investigation are of the order 10^{-10}, whereas that of acetic acid is 1.75×10^{-5}.

Kinetic parameters for the bromination of certain phenols in acetic acid are given in Table 1. Kinetic runs were carried out at least in triplicate at each temperature (18°, 26°, 34° and 42 °C) with equimolar initial concentrations of bromine and the aromatic compound ($2.5 \times 10^{-3} M$). At each temperature, the two most concordent values of k_2, the *Arrhenius* activation energy (E) and the "probable error" in E were calculated for each substrate by the method of least squares[19]. Values of k_2, E and $\Delta S^{\neq}$ are given in Table 1.

It has been shown that, in aromatic electrophilic halogenations, the values of E give a true indication about the electron-densities on the carbon atom where substitution takes place[10; 20, 21]. The lower the value of E, the greater is the electron-density at the carbon atom where substitution takes place. Subsequently it has been further pointed out[11] that the values of E give the correct indication about the electron-releasing or attracting capacities of substituents attached to the benzene ring.

The value of E for 4-fluorophenol is markedly less than those of 4-chloro and 4-bromophenols, which are nearly equal. This shows that the electron-densities at the ortho position with respect to the OH group in 4-chloro- and 4-bromophenols are almost equal, but in 4-fluorophenol it is higher. E for 4-methylphenol is the lowest among the phenols and hence the electron-density at the *ortho* position with respect to the OH group in 4-methylphenol should be the greatest. It is possible that there is a net inductive withdrawal of electrons from the benzene ring, because the activation energies for the three halogenophenols (Table 1) are greater than that for 4-methylphenol. But the observed trend in activation energies and hence in electron-densities are not in the anticipated order. They do not show the same trend as the electronegativities of halogens. We are faced with the anomaly that the less electronegative bromine and chlorine appear to provide a more powerful electron-withdrawing influence than the fluorine atom. It has been argued[7, 24–26] that the outer $p\pi$ orbitals of halogens are capable of overlapping with the 2 $p\pi$ orbitals of the aromatic ring carbon atom, to which they are bonded. This overlap, it is claimed, should increase in the order F > Cl > Br due to the decreasing carbon-halogen bond length and the increasing disparity between the sizes of the carbon and the halogen $p\pi$ orbitals. Since C—F bond is, by far, the shortest, and since the $p\pi$ orbitals of fluorine are supposedly the most similar to those of carbon, there is a better overlap and hence a greater feed back of electrons to the benzene ring. But an actual evaluation[27] of overlap integrals did not support this view. The C—F overlap integral was in fact found to be smaller than the C—Cl and C—Br values. The orbital overlap and feed back theory thus seem to be not valid. It has also been suggested[28–30] that the repulsive interactions between the outer $p\pi$ electrons of the halogens and the $2p\pi$ electrons of the aromatic ring, especially those associated with the carbon to which the halogen is substituted, has the effect of pushing the aromatic electrons into the ring and build up some π-charge at the various carbon atoms. The *Coulomb* energy of repulsions have been actually evaluated and they show the desired trend i. e. in the case of fluorine it is maximum[27].

Mulliken and others[31–33] have pointed out that Cl, Br and I may use their *d*-orbitals for electron-acceptor action and this becomes significant when strong electron-donating groups such as OH (as in the present case) are present, *ortho* or *para* to the halogens. This view also seems to be applicable here. Accordingly, chlorine and bromine substituents in 4-chloro and 4-bromophenol are able to accept electrons into their *d*-orbitals in addition to their usual inductive electron withdrawal. Fluorine, on the other hand, can be presumed to show no such acceptor-tendency because the 3*d*-orbitals of fluorine lie at energies far above those of the flourine valence shell. Hence chloro- and bromophenols have lower electron-densities and higher activation energies.

In conclusion, it may be said that the halogens withdraw electrons from the benzene ring (*ortho*, *meta* and *para*) and thus deactivate it by the inductive mechanism and this, probably, is the predominating effect. But the actual order of electron-withdrawing effect i.e. $\mathrm{Cl} \simeq \mathrm{Br} > \mathrm{F}$, as indicated by the activation energies measured in the present study can only be explained in terms of a concomitant activation of the benzene ring as a result of repulsive interactions between outer $p\pi$ electrons of the halogen and the $2p\pi$ electrons of the carbon atom to which it is bonded or as a consequence of the electron-acceptor action of the *d*-orbitals of Cl and Br. It is quite likely that both these processes may operate simultaneously.

The $\Delta S^{\neq}$ values (Table 1) are all negative indicating probably the solvation of the activated complex which is more polar than the reactants.

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