

## KINETICS OF REACTION OF *p*-SUBSTITUTED PHENOLS WITH BROMINE IN WATER

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Bromination kinetics of six *p*-substituted phenols have been studied in water. The measurements carried out at various acidities enabled the separation of phenol and phenolate bromination rate constants. The rate constants could be measured up to  $2 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  by the stopped-flow method. The difference between the bromination rate constants of a phenol and the respective phenolate anion is increased by the presence of electron-withdrawing substituents, being  $6.3 \cdot 10^6$  in the case of the *p*-chloro derivative. *p*-Methoxyphenol gives *p*-benzoquinone under the bromination conditions used. The measurements of the reaction rate by both the bromine decrease and *p*-benzoquinone increase could support the reaction mechanism suggested by us previously.

A number of papers deal with the fast reaction of bromine with phenols in water<sup>1-3</sup> (and further references therein). In spite of this fact there are not enough reliable critical data. The reaction rate constants are differing even in the order of magnitude in some cases. The bromination rate was followed by a potentiometric method using the steady state treatment<sup>1</sup>, by the limit current measurements with the use of rotating platinum cathode<sup>2</sup>, and by measurements of redox potential of the system<sup>3</sup>. All these methods are based on the bromine decrease measurements.

In the present work the kinetics was measured by a spectrometric stopped-flow method allowing to follow the product increase besides the bromine decrease. The 4-substituted phenols were chosen in such a way that it was possible to correlate the  $\log k$  values with  $\sigma$  constants for bromination of both phenolate anions and undissociated phenols.

### EXPERIMENTAL

*The substances used.* *p*-Methylphenol (m.p. 34–35°C, ref.<sup>4</sup> 34.6°C), *p*-chlorophenol (m.p. 42–44°C, ref.<sup>6</sup> 43.2–43.7°C) and *p*-nitrophenol (m.p. 113–114°C, ref.<sup>6</sup> 113.1–113.8°C) were commercial products and were purified before further use. *p*-Methoxyphenol<sup>5</sup> (m.p. 55 to 56°C, purified by two distillations and crystallization from cyclohexane) and *p*-acetylphenol<sup>7</sup> (m.p. 107–108°C, crystallized from diethylether) were prepared by known methods. *p*-Methylsulphonylphenol: 0.05 mol *p*-methylsulphonylaniline was dissolved in 50 ml warm 50% sulphuric acid, cooled and diazotized with 0.05 mol sodium nitrite dissolved in 20 ml water. The diazonium salt solution was added drop by drop into 50 ml boiling 50% sulphuric acid. After the evolution

of nitrogen gas ceased, the solution was cooled and shaken with ether. The ether extract was evaporated, and the residue was twice recrystallized from benzene; m.p. 94°C, ref.<sup>8</sup> 95.5–96.5°C.

**Brominating agent.** The solution was prepared by acidification of a mixture potassium bromide and bromate (1 : 15 mol) with perchloric acid immediately before use. The desired bromine concentration was obtained by dilution. All the inorganic chemicals used were of p.a. purity grade.

**Kinetic measurements.** The rates of reactions of the *p*-substituted phenols with bromine were measured by the stopped-flow method (Durrum apparatus) whereby the milisecond half-lives were experimentally accessible. From the reaction half-life  $\tau_{1/2}$  (i.e. the time of decrease of the initial bromine concentration  $a = 10^{-4}$  mol/l to the value  $a/2$ ) the 2nd order rate constant  $k_{2, \text{obs}}$  was calculated according to Eq. (1) where  $b$  is the initial phenol concentration  $2 \cdot 10^{-4}$  mol/l.

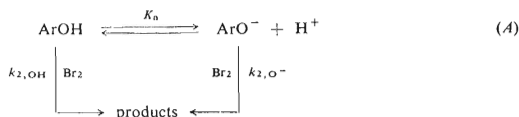
$$k_{2, \text{obs}} \tau_{1/2} = (2 \cdot 303 / (b - a)) \log ((2b - a) / b). \quad (1)$$

The required pH was adjusted by addition of perchloric acid and determined by titration with 0.2M sodium hydroxide using the Tashiro indicator. The following perchloric acid concentrations were used: 0.08, 0.225, 0.42, 0.61, 0.8 mol/l. The dependence of  $k_{2, \text{obs}}$  vs pH for *p*-chlorophenol was studied in 0.2, 0.05, 0.01 and 0.007M perchloric acid, the acidity of the last two solutions being determined by pH measurements. The ionic strength 0.8 was adjusted by addition of sodium perchlorate.

The same methods were applied for kinetic measurements in deuterium oxide. In all the experiments the constant concentration of 95% D<sub>2</sub>O was adjusted due to the perchloric acid being only available as a 70% aqueous solution.

## RESULTS AND DISCUSSION

Two substrates must be considered in reactions of bromine with phenols in water viz. undissociated phenol and phenolate anion. Both the substrates can react with two reagents – molecular bromine and tribromide ion. It was found experimentally<sup>3</sup> that undissociated phenol did not react with tribromide ion. Hence the brominations kinetics can be described by three rate constants:  $k_{2, \text{OH}}$  (for the reaction of phenol with bromine),  $k_{2, \text{O}^-}$  and  $k_{2, \text{Br}_3^-}$  (for the reactions of phenolate with bromine resp. tribromide anion). As the reaction of phenolate with tribromide ion does not constitute more than 1–3% of that with bromine<sup>3</sup>, the following scheme (A) can be written for the reaction of phenols with bromine:



Ar = aryl

Eq. (2) derived from the Scheme (A) can be modified by introduction of the equilibrium constant  $K_a$  of the phenol dissociation to give Eq. (3) where the term in brac-

kets represents  $k_{2,obs}$ . If the proton concentration is higher than  $K_a$  ( $[H^+] \gg K_a$ ), the term for  $k_{2,obs}$  is simplified (Eq. (4)), which allows to separate the bromination rate constants of phenol and phenolate anion.

$$-d[Br_2]/dt = k_{2,0H}[Br_2][ArOH] + k_{2,0-}[Br_2][ArO^-] \quad (2)$$

$$-d[Br_2]/dt = [Br_2][ArOH](k_{2,0H} + k_{2,0-} \cdot K_a/(K_a + [H^+])) \quad (3)$$

$$k_{2,obs} = k_{2,0H} + k_{2,0-} \cdot K_a/[H^+] \quad (4)$$

Rate constants of the reaction of the investigated phenol series with bromine were determined at various pH values (Table I), and from the pH-dependence of these  $k_{2,obs}$  values the individual rate constants  $k_{2,0H}$  and  $k_{2,0-}$  were computed according to Eq. (4) for *p*-nitro-, *p*-methylsulphonyl-, *p*-chloro- and *p*-acetylphenol (Table II).

The values of  $\log k_{2,0H}$  were correlated with  $\sigma_m$  constants. In the case of *p*-methylphenol the average value was used of the  $k_{2,obs}$  values measured in 0.08, 0.225 and 0.8M perchloric acid. The  $\log k_{2,0H}$  value of the reaction of *p*-methoxyphenol with bromine was not included in the correlation, because this substrate reacted by a different mechanism (formation of *p*-benzoquinone) as compared with the other

TABLE I

Results of Direct Measurements of Rate Constants  $k_{2,obs}$  ( $l \text{ mol}^{-1} \text{ s}^{-1}$ ) of Reaction of Bromine with *p*-Substituted Phenols in Water at 20°C and Ionic Strength 0.3

Initial concentrations: phenols  $2 \cdot 10^{-4} \text{ mol/l}$ , bromine  $10^{-4} \text{ mol/l}$ .

Substituent	$\lambda$ nm	$k_{2,obs} \cdot 10^{-3}$ at HClO <sub>4</sub> conc., M				
		0.80	0.61	0.42	0.225	0.08
CH <sub>3</sub>	250 <sup>a</sup>	425	—	—	458	425
	390 <sup>b</sup>	467	—	—	486	458
CH <sub>3</sub> O	390 <sup>b</sup>	274	—	—	257	281
CH <sub>3</sub> CO	240 <sup>a</sup>	2.26	—	—	3.13	4.52
	410 <sup>b</sup>	2.32	2.71	2.90	3.25	4.62
CH <sub>3</sub> SO <sub>2</sub>	410 <sup>b</sup>	0.232	0.262	0.296	0.405	0.920
NO <sub>2</sub>	250 <sup>a</sup>	—	—	0.368	0.623	1.59
	410 <sup>b</sup>	0.253	0.289	0.379	0.586	—
Cl <sup>c</sup>	250 <sup>d</sup>	3.30	3.52	4.03	4.38	—
	410 <sup>b</sup>	3.15	—	—	—	—

<sup>a</sup> Extinction increase at the wavelength corresponding to the product. <sup>b</sup> Extinction decrease at the wavelength corresponding to bromine. <sup>c</sup> The values of  $k_{2,obs}$  are given for 0.2, 0.05, 0.01 and 0.007M-HClO<sub>4</sub>, respectively. <sup>d</sup> Extinction decrease.

phenols (formation of the respective bromo derivatives). The regression analysis gave the following results:  $\log k_{2,0H} = 5.3 - 5.0\sigma_m$ , standard deviation  $s_\sigma = 0.22$ , correlation coefficient  $r = -0.997$ .

The values of  $\log k_{2,0-}$  were also correlated with  $\sigma_m$  constants, the value of *p*-bromophenol bromination obtained by Bell and Rawlinson<sup>3</sup> being included, too (Fig. 1). With respect to the small number of derivatives the slope can only be roughly estimated ( $\rho \approx -3.5$ ). In all the cases investigated the velocity of the reaction of bromine with phenol measured at the wavelength corresponding to the bromine decrease agreed with that measured at  $\lambda_{max}$  of the bromo derivative formed.

We found previously that *p*-methoxyphenol reacts with bromine in water to give *p*-benzoquinone. Now we have compared the reaction rate curves obtained by either the bromine decrease or benzoquinone increase measurements and found that increasing\* of perchloric acid concentration accelerated the benzoquinone formation whereas the bromine decrease was acidity-independent in the range studied.

The reactions of *p*-nitrophenol, *p*-methylsulphonylphenol and *p*-acetylphenol with bromine were followed in 0.08–0.80M perchloric acid, whereas in the case of *p*-chlorophenol, which has a higher  $pK_a$ , the range of 0.007–0.2M perchloric acid was adopted. At higher proton concentrations  $k_{2,obs}$  did not change, the reaction of bromine with *p*-chlorophenolate anion was insignificant due to low phenolate concentration ( $k_{2,obs}$  and  $k_{2,0H}$  were  $3.3 \cdot 10^3$  and  $3.25 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ , respectively, in 0.2M perchloric acid). A similar situation is encountered in determination of the dependence of reaction rates of *p*-methoxy- and *p*-methylphenols with bromine on the acidity of reaction medium (the measured  $k_{2,obs}$  is practically identical with

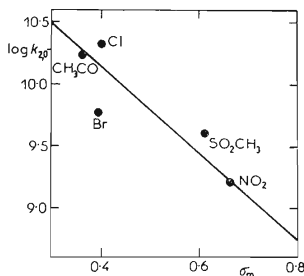


FIG. 1  
Dependence of  $\log k_{2,0-}$  on  $\sigma_m$  for Reaction of *p*-Substituted Phenolate Anions with Bromine

\* With respect to the complexity of the reaction, however, it is not possible to use the half-life method for calculation of the rate constant from the product increase.

TABLE II

Rate Constants  $k_{2,\text{OH}}$  and  $k_{2,\text{O}^-}$  ( $1 \text{ mol}^{-1} \text{ s}^{-1}$ ) of Reaction of Bromine with Undissociated *p*-Substituted Phenols resp. Corresponding Phenolate Anions in Water at 20°C and Ionic Strength 0.3

Initial concentrations: phenols  $2 \cdot 10^{-4} \text{ mol/l}$ , bromine  $10^{-4} \text{ mol/l}$ .

Substituent	$pK_{\text{a}}^a$	$k_{2,\text{OH}} \cdot 10^{-3}$	$k_{2,\text{O}^-} \cdot 10^{-9}$	$(k_{2,\text{O}^-}/k_{2,\text{OH}}) \cdot 10^{-6}$
CH <sub>3</sub>	—	453	—	—
CH <sub>3</sub> O	—	273	—	—
Cl	9.42	3.25	20.7	6.37
CH <sub>3</sub> CO	8.05	2.50	17.2	6.86
CH <sub>3</sub> SO <sub>2</sub>	7.83	0.15	4.00	26.7
NO <sub>2</sub>	7.39	0.11	1.61	15.1

<sup>a</sup> Ref.<sup>8</sup>.

$k_{2,\text{OH}}$ ). As the reactions of the both phenols with bromine are too fast to be easily measured even in the range of 0.08–0.8M perchloric acid, we did not work at higher pH values.

For the sake of completion, the rates of reactions of *p*-methyl-, *p*-methoxy-, *p*-chloro and *p*-nitrophenols with bromine were also measured in 0.2M perchloric acid in 95% deuterium oxide at 20°C and ionic strength 0.3 (the initial concentrations of phenols and bromine were  $2 \cdot 10^{-4}$  and  $10^{-4} \text{ mol/l}$ , respectively):

Substituent	CH <sub>3</sub>	CH <sub>3</sub> O	Cl	NO <sub>2</sub>
$k_{2,\text{obs}} \cdot 10^{-3}, 1 \text{ mol}^{-1} \text{ s}^{-1}$	225–289	109	1.59	0.192

The reactivity order of the first two phenols is the same as that for the reaction with bromine in water. The  $k_{2,\text{obs}}$  measured are about 2–3 times lower in deuterium oxide than in water.

On the basis of our measurements the following can be stated: a) Direct measurements of the reaction rates of *p*-methoxy- and *p*-methylphenols with bromine confirmed the results obtained by measurements of this reaction rate by competition technique<sup>9,10</sup>. *p*-Methylphenol reacts with bromine about 1.5–1.6 times faster than *p*-methoxyphenol, whereas by the competition method the reactivity ratio 1.4–1.8 was found. As the mechanism is different in the two cases, it is impossible to discuss the reactivity in the terms of the Hammett equation. b) The direct measurement made it possible to follow the reaction of *p*-methoxyphenol with bromine by both the decrease of bromine and the increase of the reaction product (*p*-benzo-

quinone). The reaction rate obtained from the *p*-benzoquinone increase depended on acidity whereas the  $k_{2,obs}$  determined from the bromine decrease did not change in the acidity range studied. This observation agrees with the reaction mechanism suggested by us previously<sup>9</sup>; the last step of this mechanism consists in an acid-catalyzed splitting of the hemiacetal bond which is rate-limiting at higher pH values. c) Our results agree with the rate constant values of phenol bromination found by Bell and Rawlinson<sup>3</sup>. The measurement of the pH dependence of bromination rate made it possible to separate the rate constants of reactions of bromine with phenol and phenolate and estimate the values of the Hammett reaction constant  $\rho$ . Bromination of phenol is more selective than that of phenolate ( $\rho = -5.11$  resp.  $-3.5$ ). The undissociated phenols react substantially slower than phenolate anions. The negatively charged oxygen activates strongly the benzene nucleus towards electrophilic reagents, at the same time, however, it decreases the sensitivity of the reaction centre towards the other substituent effects.

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