The Bromination of *p*-Hydroxybenzoic Acid in Aqueous Solution. Reaction via the Minor *p*-Carboxyphenoxide Anion Tautomer

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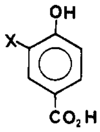
The kinetics of bromination of *p*-hydroxybenzoic acid have been measured in aqueous solution in the pH range 0–6. From the pH–log rate profile the reactive species appear to be the free acid (pH <1.5), the monoanion (pH 1.5–5), and the dianion (pH >5). However, the reactivity attributable to the monoanion is about 9 times higher than that predicted by a Hammett plot for the bromination of *p*-substituted phenols. This deviation is ascribed to reaction via the tautomeric *p*-carboxyphenoxide monoanion which is present to the extent of 1 in 3100. Support for this proposal comes from related studies on ethyl *p*-hydroxybenzoate, 3-bromo-4-hydroxybenzoic acid, and *p*-methoxybenzoic acid. In particular, the 3-bromo-4-hydroxybenzoate anion *appears* to be *5200 times more reactive* than predicted and *twice as reactive* as the *p*-hydroxybenzoate anion. These anomalies are removed if reaction occurs via the minor tautomeric anion.

Salicylate (*o*-hydroxybenzoate) anions have an intramolecular hydrogen bond between the ortho hydroxyl group and the adjacent carboxylate moiety.[1] This feature gives rise to anomalous pK_as and to low rates of protonation and deprotonation of such monoanions.[1]

We are studying the bromination of salicyclic acid (and derivatives) to see if the intramolecular hydrogen bond affects, in any way, the normal course of electrophilic attack. For comparative purposes we have also studied the analogous bromination of *p*-hydroxybenzoic acid (**1**) and some of its derivatives. We find that **1**, our "control", shows abnormal behavior, which is the subject of the present paper.

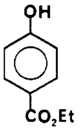
Results

We have measured the kinetics of aqueous bromination of **1** and of its derivatives **2**, **3**, and **4**. The experimental approach used was as in other recent publications from this laboratory.[2]



1 X = H

3 X = Br



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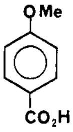

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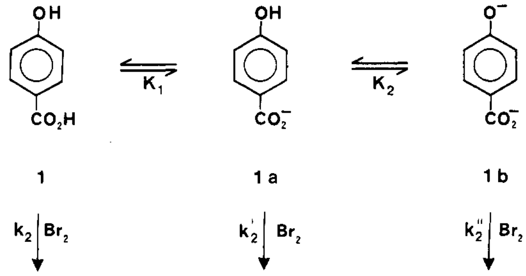
All four substrates exhibit second-order behavior: first order in substrate and in bromine. The variations of the observed second-order rate constants (k_2^{obsd}) with pH are displayed logarithmically in Figure 1; the actual data are listed in Table S1 (Supplementary Material). The shapes of the various pH–log rate profiles are, as expected, of various forms.

Ethyl *p*-hydroxybenzoate (**2**) shows a profile indicative of behavior similar to other para-substituted phenols.[3-5] There is a pH independent region (pH <2) and a region where the rate increases monotonically with the inverse of the acidity. The data may be represented by eq 1, where

$$k_2^{\mathrm{obsd}} = k_2 + k_2''K_2/[\mathrm{H}^+] \tag{1}$$

k_2 is the rate constant for the attack of bromine on **2** itself, k_2'' is for attack upon its anion, and K_2 is the dissociation constant of the phenolic OH of **2**. As will be discussed later, the values of k_2 and k_2'' (Table I) are quite reasonable, when compared to other phenols and phenoxides.[3-5]

Scheme I



Over the range studied the rate profile for *p*-anisic acid (**4**) (Figure 1) suggests that it reacts solely as its anion (eq 2), where k_2' is for bromine attack on the anion and K_1 is

$$k_2^{\mathrm{obsd}} = k_2'K_1/(K_1 + [\mathrm{H}^+]) \tag{2}$$

the dissociation constant of the carboxyl function. Likewise, the profile for the 3-bromo acid **3** can also be represented by eq 2. For both substrates (**3** and **4**) the values of k_2' and K_1 (expressed as pK_1) obtained from fitting eq 2 to the data are given in Table I.

The rate profile for *p*-hydroxybenzoic acid (**1**) is more complex than those already discussed. At low pH the rate levels off, suggestive of reaction upon the undissociated substrate. Over most of the pH range the profile is consistent with reaction upon the *p*-hydroxybenzoate monoanion (**1a**). However, the data do not show a distinct plateau above pH 4.7 ($\simeq$pK_1), as required by eq 2. We propose, therefore, that the rise in the data at the highest pHs is due to the onset of reaction upon the dianion **1b**. The overall situation is summarized is Scheme I and the appropriate form of k_2^{obsd} is given in eq 3. Values of k_2,

$$k_2^{\mathrm{obsd}} = \frac{k_2[\mathrm{H}^+] + k_2'K_1}{K_1 + [\mathrm{H}^+]} + \frac{k_2''K_2}{[\mathrm{H}^+]} \tag{3}$$

k_2', k_2'', and K_1 were obtained by fitting eq 3 to the data, the literature value of K_2 being assumed. These quantities are collected in Table I together with those derived from the other rate profiles. As will be discussed in the next

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[1] (a) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1. (b) Perrin, D. D. *Nature (London)* **1958**, *182*, 741. (c) Hibbert, F. *Acc. Chem. Res.* **1984**, *17*, 115 and references therein.

[2] (a) Tee, O. S.; Paventi, M. *J. Am. Chem. Soc.* **1982**, *104*, 4142. (b) Tee, O. S.; Paventi, M. *Can. J. Chem.* **1983**, *61*, 2556. (c) Tee, O. S.; Kornblatt, M. J.; Berks, C. G. *J. Org. Chem.* **1982**, *47*, 1018. (d) Tee, O. S.; Berks, C. G. *J. Org. Chem.* **1980**, *45*, 830.

[3] Bell, R. P.; Rawlinson, D. J. *J. Chem. Soc.* **1961**, 63.

[4] Kulic, J.; Vecera, M. *Collect. Czech. Chem. Commun.* **1974**, *39*, 171.

[5] (a) Tee, O. S.; Paventi, M., manuscript in preparation. (b) Tee, O. S.; Bennett, J. M., unpublished results. (c) Tee, O. S.; Iyenger, N. R., unpublished results. (d) Paventi, M. Ph.D. Thesis, Concordia University, 1984.

0022-3263/85/1950-0973$01.50/0

Table I. Constants for the Bromination of *p*-Hydroxybenzoic Acid and Derivatives[a]

	1	2	3	4
k_2'	3500	2200		
k_2'	2.6×10^{6} [b]		5.6×10^{6} [b]	260
k_2''	3.5×10^9	8.2×10^9		
k_2'''	8.2×10^9		3.3×10^9	
pK_1	4.80 (4.61)[c]		3.97 (4.03)[d]	4.26 (4.52)[c]
pK_2	(9.31)[c]	(8.50)[e]	?	
pK_3	8.30		6.74	
K_3/K_1	3.2×10^{-4}		1.7×10^{-3}	

[a] A 25 °C, $I = 0.11$ M. Units of k_2s are $M^{-1}\ s^{-1}$. Values of p*K*s in parentheses are measured; those without parentheses are from fitting rate profiles or estimated from $\rho\sigma$ plots (see text). [b] This is an "apparent" value (see text). [c] Kortum, G.; Vogel, W.; Andrussow, K. *Pure Appl. Chem.* 1961, *1*, 190. [d] Measured spectrophotometrically. [e] Jencks, W. P.; Regenstein, J. In "Handbook of Biochemistry and Molecular Biology"; Vol. I, 3rd ed., Fasman, G. D., Ed.; CRC Press: Cleveland, OH, 1976; p 314.

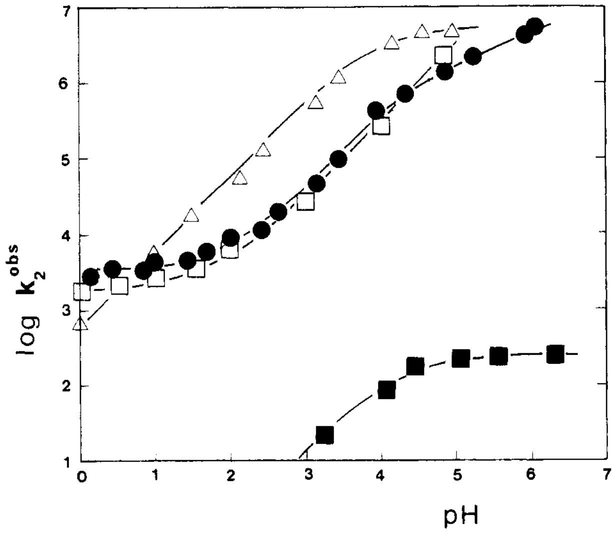

Figure 1. pH–rate profiles for the reaction of bromine with *p*-hydroxybenzoic acid (●), 3-bromo-4-hydroxybenzoic acid (△), ethyl *p*-hydroxybenzoate (□), and *p*-anisic acid (■).

section, most of them seem reasonable *except* for the values of k_2' for the *p*-hydroxybenzoate anion and its 3-bromo analogue which are about *9 times and 5200 times larger* than expected, respectively.

In response to a point raised by a referee we have checked the products of bromination of **1** (see Experimental Section). Under kinetic conditions (10-fold excess of **1**) at pH 4 the products were 94% of the 3-bromo acid **3** and 6% of 3,5-dibromo-4-hydroxybenzoic acid (**5**). Thus, the apparent rate constant for the anion **1a** largely reflects monobromination and is not significantly elevated due to substantial dibromination and bromodecarboxylation (cf. below).

In contrast, the principal product (at least 78%) obtained from mixing equimolar amounts of **1** and bromine was 2,4,6-tribromophenol (**6**). We presume that it arises from two successive brominations and a bromodecarboxylation (**1** → **3** → **5** → **6**) since the rate constants for these three steps are very similar. For the reaction of **5** with bromine we have measured rate constants (k_2^{obsd}) of 584 and 6140 $M^{-1}\ s^{-1}$ at pH 0 and 1, respectively. Thus, the apparent reactivity of the anion of the 3,5-dibromo acid **5** toward bromine is only slightly less than that of the anions of the 3-bromo acid **3** and the parent acid **1**.

Discussion

There are three striking features of the rate profiles in Figure 1. First, the profile for *p*-anisic acid (**4**) is well below that for **1** such that it implies that the *p*-hydroxybenzoate anion is 10 000 times more reactive toward bromine than the *p*-anisate ion (see k_2' values, Table I). This ratio is unusually high; for other phenol/anisole pairs the ratios are in the range 12–1200.[6]

The second and most striking feature of Figure 1 is that the rate profile for 3-bromo-4-hydroxybenzoic acid (**3**) lies *above* that of its parent, **1**. It implies that the monoanion of **3** is *more* reactive in bromination than the anion of **1**, contrary to the normal effect of a *m*-bromo substituent on electrophilic attack ($\sigma_m^+ = 0.405$).[9]

The third feature of note in Figure 1 is that, over most of the pH range, the profile for the ethyl ester **2** lies almost on top of that for the parent acid **1**. At low pH, where the rate is essentially invariant, this simply implies that these two substrates have very similar reactivities toward bromine, as one expects. However, the closeness of the rate profiles for **1** and **2** at pH 2–4, where the reactive form is an anion, means that it is quite feasible that the *p*-hydroxybenzoate anion (**1a**) reacts as its tautomer **1c** (Scheme II). Before discussing this mechanism in detail

Scheme II

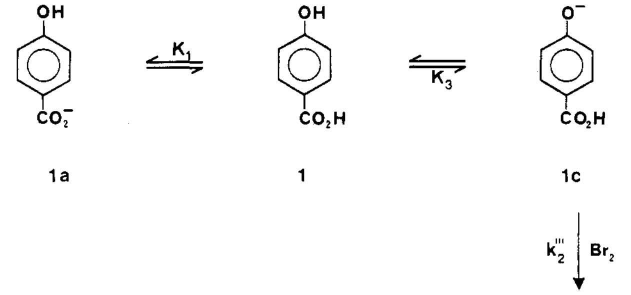

Table II. Second-Order Rate Constants for the Attack of Bromine on *p*-X-Substituted Phenols[a]

X	σ_m^+	k_2 ($M^{-1}\ s^{-1}$)	ref/note
Me	−0.066	6.2×10^5	5b
t-Bu	−0.059	5.9×10^5	5b
CO_2^-	−0.028	2.6×10^6	*b*
H	0.000	76000	*c*
CO_2H	0.322	3500	*b*
CO_2Et	0.366	2200	*b*
Br	0.405	3900	5b
CN	0.562	155	5b

[a] At 25 °C, $I = 0.11$ M (KBr + buffer). Values of k_2 are corrected for tribromide ion formation. σ_m^+ from ref 9a. [b] This work. [c] Based on $k_2 = 420000\ M^{-1}\ s^{-1}$ for phenol[7] and the *o*/*p* ratio of 18/82.[5a,d]

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(6) The second-order rate constants ($M^{-1}\ s^{-1}$) for phenol[7] and anisole[8] are 420 000 and 36 000 (ratio 12). Those for *p*-bromophenol[5b] and *p*-bromoanisole[8] are 3900 and 3.3 (ratio 1200).

(7) Tee, O. S.; Iyengar, N. R.; Paventi, M. *J. Org. Chem.* **1983**, *48*, 759.

(8) Aaron, J. J.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1971**, 603.

(9) (a) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 203–210. (b) Stock, L. M. "Aromatic Substitution Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1968; pp 60–69.

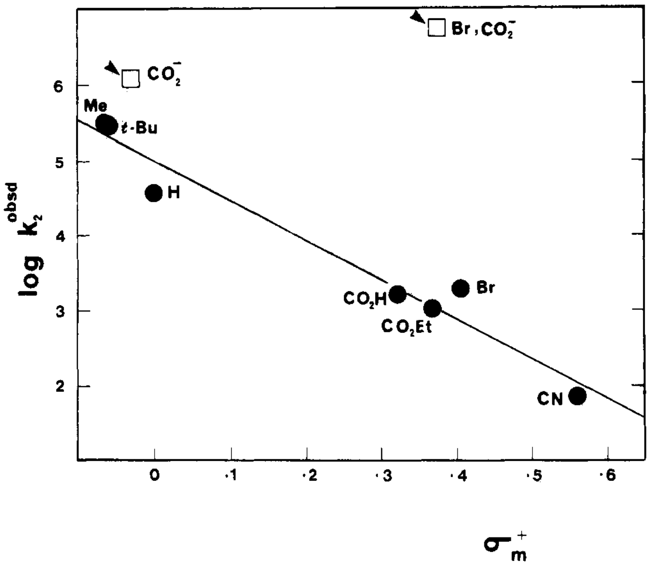

Figure 2. Hammett plot for the attack of bromine on *p*-substituted phenols. The correlation line is eq 4 *less* 0.30 so that it (and the points) is statistically corrected for *one* ortho position. The open squares represent the apparent points for the anions of *p*-hydroxybenzoic acid and 3-bromo-4-hydroxybenzoic acid. These points were not included in the calculation of eq 4.

we will briefly consider the apparent reactivities of the substrates and their reactive forms.

As remarked earlier, ethyl *p*-hydroxybenzoate (**2**) behaves as a typical phenol. Table II contains second-order rate constants for the bromination of various *p*-substituted phenols, obtained in this laboratory.[10] They give a reasonable Hammett plot, as shown in Figure 2. The correlation line[11] based on all the points except that for X = CO_2^-, which we believe is anomalous (vide infra), is

$$\log k_2 = 5.30 - 5.21\sigma_m^+ \tag{4}$$

The rate constants for *p*-hydroxybenzoic acid (X = CO_2H) and its ester (X = CO_2Et) correlate well with those of the other phenols. In contrast, the point for the anion **1a** (X = CO_2^-) is decidely above the correlation line. The observed value for this anion (k_2' for **1a**, Table I) is 9.3 times larger than that predicted by eq 4 ($k_2' = 2.8 \times 10^5$ M^{-1} s^{-1}).

The deviation for the 3-bromo-4-hydroxybenzoate anion is much more pronounced since, as pointed out earlier, it appears to be more reactive than its parent **1a**. If we assume that its rate constant should lie on the line expressed by eq 5,[12] then the observed value is *5200 times larger* than the predicted value.

$$\log k_2 = 5.00 - 5.21 \sum\sigma_m^+ \tag{5}$$

The rate constant ascribed to the anion of ethyl *p*-hydoxybenzoate (k_2'' for **2**, Table I) is at the diffusion-controlled limit,[13] as found for other simple phenoxide ions.[3-5,7] Similarly, the value for the dianion **1d** appears reasonable.

We now show that the apparently anomalous reactivities of the *p*-hydroxybenzoate anion and its 3-bromo analogue can be quantitatively explained by the mechanism in Scheme II. For reaction via the minor tautomeric anion **1c**, the expected form of the observed rate constants is[14]

$$k_2^{obsd} = k_2'''K_3/(K_1 + [H^+]) \tag{6}$$

This equation is algebraically equivalent to eq 2, which is appropriate for reaction via the major anion **1a**, since the reaction of the two tautomeric anions **1a** and **1c** are kinetically indistinguishable. In other words, eq 2 or eq 6 will fit the observed data equally well in the region of pH where reaction via the free acid **1** or the dianion **1d** is unimportant. Therefore the product $k_2'K_1 = 41.2$ s^{-1}, obtained earlier by fitting eq 3 to the data, can be equated with $k_2'''K_3$. A value of pK_3 = 8.30 is estimated from the Hammett correlation for phenols,[15] using $\sigma^- = 0.728$ for the *p*-carboxy substituent.[16] This p*K* is completely reasonable since the analogous p*K* for the ethyl ester **2** is 8.50 (Table I). Using then $K_3 = 10^{-8.3}$ M, the value of k_2''' required to fit the data is 8.2×10^9 M^{-1} s^{-1}. This value fully validates the mechanism in Scheme II since it is the same as the analogous rate constant for the anion of the ethyl ester **2** (k_2'', Table I).

The apparent reactivity of the 3-bromo-4-hydroxybenzoate ion can be rationalized in exactly the same way. For this anion $k_2'K_1 = 600$ s^{-1} was obtained by fitting eq 2 to the kinetic data (see Table I). Equating this to $k_3'''K_3$ and estimating pK_3 = 6.74 for the phenolic OH of **3**[17] leads to $k_3''' = 3.3 \times 10^9$ M^{-1} s^{-1} for the 3-bromo analogue of the anion **1c**. Again, this value is within the range of those observed for other phenoxides.[3-5]

The tautomeric ratio [**1c**]/[**1a**] may be estimated by using pK_1 and pK_3: it equals $K_3/K_1 = 0.00032$. Thus, the monoanion **1c** is estimated to be present only to the extent of 1 molecule in 3100 but reaction proceeds through it because it is 29 000 times[18] more reactive than the predominant anion **1a**.

Likewise, the tautomeric ratio for the 3-bromo monanions is estimated to be 0.0017. This larger value arises because the effect of the bromo substituent on the acidity of the phenol OH is larger ($\rho = 2.23$)[15] than on that of the carboxylic acid group ($\rho = 1.00$). Clearly, the tautomeric ratio has an effective ρ of 1.2 and so the electron-withdrawing bromo substituent increases the proportion of the minor anion. In the present case, the higher tautomeric ratio (3-Br-**1c**/3-Br-**1a**), coupled with the much greater reactivity of 3-Br-**1c** over 3-Br-**1a** (3 million times)[19] results in the apparently anomalous rate profile for 3-bromo-4-hydroxybenzoic acid, noted earlier.

Finally, we return to the question of why the *p*-hydroxybenzoate anion **1a** seems to be 10 000 times more reactive toward bromine than its methoxy analogue, the *p*-anisate ion. Since **1a**, reacting via **1c**, is 9 times more reactive than expected, a truer ratio is 1110. This is still high for a phenol/anisole ratio[20] and it appears that the reactivity of the *p*-anisate ion is low. With respect to a Hammett correlation line for the aqueous bromination of other *p*-substituted anisoles,[8] the point for the CO_2^- substituent is low by a factor of 13. Moreover, this substituent also gives low points in correlations for the aqueous bro-

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(10) Rather than use data from several sources obtained by different methods under various conditions,[3-5] we have chosen to use recent data from our laboratory measured in a uniform manner.

(11) All eight rate constants in Table II give $\rho = -5.68$ (SD = 0.66) and $r = 0.962$. However, omitting the point X = CO_2^- yields $\rho = -5.21$ (SD = 0.47) and $r = 0.980$.

(12) With respect of eq 4 the intercept is reduced by 0.30 to reflect that there is only one ortho position available in the anion of **3**.

(13) Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1.

(14) The derivation of eq 6 assumes $K_1 \gg K_3$, as is reasonable (see later).

(15) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. "pK_a Prediction for Organic Acids and Bases"; Chapman and Hall: London, 1981; p 47.

(16) Reference 9, p 211.

(17) Using the correlation equation for phenols[15] and a special σ for the *o*-bromo substituent. See ref 15, p 137.

(18) It is assumed that **1c** reacts at 8.2×10^9 M^{-1} s^{-1} and **1a** reacts at 2.8×10^5 M^{-1} s^{-1}, as estimated from eq 4 (see earlier).

(19) It is assumed that 3-Br-**1c** reacts at 3.3×10^9 M^{-1} s^{-1} and 3-Br-**1a** reacts at 1100 M^{-1} s^{-1}, as estimated from eq 5.

(20) Since $\sigma_m^+ \sim 0$ for CO_2^- one expects a ratio of about 12, as for unsubstituted phenol/anisole.[6]

mination of *o*-substituted anisoles[8] (factor of 8.5)[5c] and 2-substituted furans (factor of 48).[21] For the anisate ions (*o* and *p*) a more appropriate value of σ_m^+ for CO_2^- is about 0.10, rather than −0.028, as normally cited.[9] This is close to $\sigma_m = 0.09$, based on the ionization of the substituted benzoic acid,[24] which seems reasonable since generally speaking $\sigma_m^+ \simeq \sigma_m$.[9] Perhaps, as Hine stresses "values of σ for electrically charged groups are relatively unreliable."[25]

If, indeed, a more realistic value of σ_m^+ for CO_2^- is about 0.10, then our estimated rate constants for bromine attacking **1** and 3-Br-**1a** should be reduced, in which case, the apparent rate constants for these anions (k_2', Table I) would be even more anomalous, lending further weight to our proposal that they react via their minor tautomers **1c** and 3-Br-**1c**.

Conclusions

The rate constants for the aqueous bromination of the *p*-hydroxybenzoate anions **1a** and 3-Br-**1a** are abnormally high. The anomalies are explicable if reaction occurs via the minor tautomeric anions **1c** and 3-Br-**1c** (Scheme II). The σ^+ value normally cited for *m*-CO_2^- may be too low.

Experimental Section

The following substrates, obtained from commercial sources, were recrystallized before use: 4-hydroxybenzoic acid (Matheson, Coleman and Bell), *p*-anisic acid (Aldrich), and ethyl 4-hydroxybenzoate (Aldrich). 3,5-Dibromo-4-hydroxybenzoic acid was available from earlier work.[5d]

3-Bromo-4-hydroxybenzoic Acid (3). Bromine (7.99 g, 0.05 mol) in dioxane was added dropwise, with stirring, to **1** (6.91 g, 0.05 mol) in dioxane over 15 min. In the dioxane medium the reaction was slow and the solution was allowed to stand for 3 days at room temperature, after which time the bromine color had disappeared. The solvent was evaporated and the residue was recrystallized from aqueous EtOH to give crude **3** (10.1 g, 93%). A second recrystallization from water gave purer material, mp 175–178 °C (lit. mp 177 °C).[26] The structure of the product was confirmed by proton NMR spectroscopy.

All kinetics solutions were 0.1 M in KBr and normally had I = 0.11 M (= [KBr] + buffer). At higher acidities (pH <2) solutions of HCl were used and ionic strengths were higher (= [KBr] + [HCl]). Buffer solutions were made following Perrin.[27] Bromine solutions were made by dilution of a fresh stock solution in aqueous KBr, made up by weight.

Kinetic experiments were carried out at 25.0 ± 0.1 °C by using the stopped-flow apparatus, data acquisition system, and data analysis methods described earlier.[2,28] The disappearance of bromine was measured as the decrease in absorbance at 275 nm (relative to 340 nm).[2]

Kinetics were measured under pseudo-first-order conditions with the substrate in tenfold (or more) excess. Normally the substrate concentration was 5×10^{-4} M and that of bromine was 5×10^{-5} M. For the fastest reactions these concentrations were reduced by a factor of 5. First-order rate constants were obtained as averages of 3–5 runs differing <5%. They were converted to second-order rate constants (k_2^{obsd}) by taking into account the substrate concentration and the reduction of free molecular bromine due to the formation of tribromide ion and, at pH >5, of hypobromous acid.[2]

Rate profiles were fitted to the experimental data by using standard nonlinear least-squares techniques.[29] To correspond to the way in which the data is plotted (Figure 1) and to accommodate its range, logarithmic forms of eq 1–3 were employed.

To determine the reaction products under kinetic conditions, equal volumes of bromine (2.5 mM) and *p*-hydroxybenzoic acid (25 mM), each in acetate buffer (pH 4.0) containing 0.1 M KBr, were mixed. The water was slowly evaporated and the residual solids were analyzed. TLC on silica, using 90% MeOH + 10% aqueous KH_2PO_4 as eluent, showed no spot for 2,4,6-tribromophenol (**6**) (cf. below) but did not clearly separate the mono and dibromo acids **3** and **5**. A sample of the solids was trimethylsilylated and analyzed by GC/MS. It showed only **1**, **3**, and **5**, as their bis-Me_3Si derivatives. The ratio of monobromo to dibromo products (**3** to **5**) was ca. 15:1. Accordingly, the apparent rate constant obtained for the anion **1a** corresponds largely to monobromination.

Interestingly, the product obtained under 1:1 conditions was 2,4,6-tribromophenol (**6**). *p*-Hydroxybenzoic acid (10 mmol) was dissolved in 150 mL + 10 mL of 1 N NaOH. This solution was stirred continuously while bromine (10 mmol) in 100 mL of 0.1 M aqueous KBr was slowly added. The product, which precipitated during addition, was filtered off and dried in air. It was identified as **6**, formed in 78% yield. The same product was obtained by using acetate buffer (pH 4.0) as the reaction medium.

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Registry No. **1**, 99-96-7; **2**, 120-47-8; **3**, 14348-41-5; **4**, 100-09-4.

Supplementary Material Available: Table of rate constants for reaction of bromine with 4-hydroxybenzoic acid and its derivatives (2 pages). Ordering information is given on any current masthead page.

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(21) For the aqueous bromination of furan[22] (one position), 2-furoic acid, ethyl 2-furoate, and the 2-furoate anion[23] values of k_2 ($M^{-1}\,s^{-1}$) are 7.0×10^5, 60, 10, and 25 000, respectively. The first three values give a correlation line: $\log k_2 = 5.85 - 9.82\,\sigma_p^+$. This equation predicts $k_2 = 1.2 \times 10^6\ M^{-1}\,s^{-1}$ for the 2-furoate ion. The observed k_2 corresponds to $\sigma_p^+ = 0.148$ for CO_2^-.

(22) Tee, O. S.; Swedlund, B. E. *Can. J. Chem.* **1983**, *61*, 2171.

(23) Tee, O. S.; Ostrowski-Janik, E., unpublished results.

(24) Reference 15, p 111.

(25) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Kreiger: New York, 1981; p 67.

(26) Leulier, A.; Pinet, L. *Bull. Soc. Chim. Fr.* **1927**, *41*, 1369.

(27) Perrin, D. D. *Aust. J. Chem.* **1963**, *16*, 572.

(28) Tee, O. S.; Trani, M.; McClelland, R. A.; Seaman, N. E. *J. Am. Chem. Soc.* **1982**, *104*, 7219.

(29) Bevington, P. R. "Data Reduction and Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969.