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Kinetics and Mechanism of the Reaction of 2(1*H*)-Pyrimidinone with Bromine. Reaction via Its Covalent Hydrate

Oswald S. Tee* and Martino Paventi

Department of Chemistry, Concordia University, Montreal, Quebec, Canada H3G 1M8

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The kinetics of the fast disappearance of bromine due to reaction with 2(1*H*)-pyrimidinone (**1a**) and with 1-methyl-2-pyrimidinone (**1b**) in aqueous solutions (pH 0–6) have been measured. The data support bromine attack upon the covalent hydrates (**3a** and **3b**) and a change in rate-determining step (rds) with acidity. At high acidity (pH <2) the rds is attack of bromine upon the covalent hydrate **3** (**a** or **b**), whereas at low acidity (pH >4) formation of **3** (**a** or **b**) from the appropriate cation **2** (**a** or **b**) is the rds. These results, together with those of earlier studies, provide a detailed mechanism for the bromination of **1a** in acidic aqueous solution. In addition, it is estimated that **1a** in aqueous solution exists as its covalent hydrate **3a** to the extent of about 0.05%.

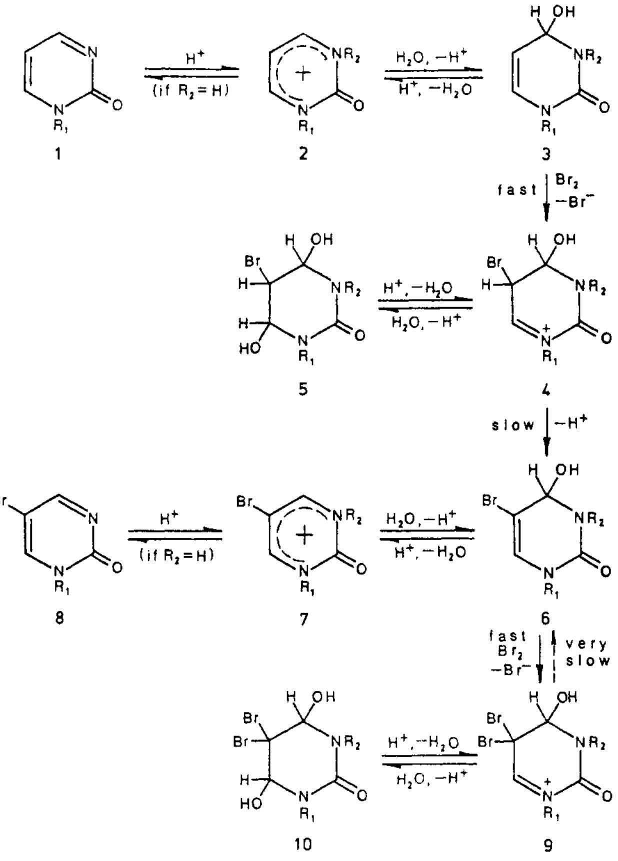
Sometime ago we proposed that the bromination of 2(1*H*)-pyrimidinones (**1**) in acidic aqueous solution proceeds by the various discrete steps shown in Scheme I.[1] Our initial study[1] afforded spectroscopic evidence of the pseudobases **3c** and **6c**, the intermediates **5**, and the ultimate products **10**. In addition, we obtained kinetic evidence for the steps **5** ⟶ **8**.[1] Subsequently, a kinetic study carried out in strong acid gave results consistent with the steps **8** ⟶ **10** shown for the second bromination.[2] More recently, a stopped-flow study of the reaction of bromine with the dimethyl cation **2c** fully supported the hypothesis that this reaction involves attack of bromine upon the pseudobase **3c**[3] (eq 1). Furthermore, the study[3]

$$H_2O + 2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + 3 \xrightarrow[Br_2]{k_2} 4 \rightarrow 5 \qquad (1)$$

showed that the rate-determining step (rds) in eq 1 changes with acidity. At high acidity, where $k_{-1}[H^+] \gg k_2[Br_2]$, the attack of bromine upon the pseudobase **3c** is the rds. On the other hand, at low acidity, where $k_2[Br_2] \gg k_{-1}[H^+]$, the rds is formation of the pseudobase **3c** from the quaternary cation **2c**. This interpretation of the bromination kinetics was supported by a separate kinetic study of the equilibration of **2c** and **3c**.[3]

In the present paper we report the results of a stopped-flow study of the reaction of bromine with 2(1*H*)-pyrimidinone (**1a**) and 1-methyl-2-pyrimidinone (**1b**). The kinetic behavior exhibited by these substrates is very similar to that previously observed for the quaternary cation **2c**[3] except that it is modified by the presence of the protonation equilibria between **1** (**a** or **b**) and their conjugate acids **2** (**a** or **b**). Accordingly, the present work provides concrete evidence that the substrates **1a** and **1b** react with bromine via their covalent hydrates **3a** and **3b**, respectively.

Scheme I[a]



[a] a, $R_1 = R_2 = H$; b, $R_1 = Me$, $R_2 = H$; c, $R_1 = R_2 = Me$.

Results and Discussion

We monitored the disappearance of bromine due to reaction with an excess of the substrates **1a** and **1b** in aqueous solutions of pH 0–6. The kinetic order varies with acidity, being pseudo first order at pH <2 and pseudo zero order at pH >4. In the region pH 2–4 there is a gradual changeover between these orders. This behavior, which matches that previously observed for the cation **2c**,[3] is explicable by the rate law expressed by eq 2 which is derived from eq 1 by assuming a steady-state concentration of the species **3**.[3] The observed change in kinetic order is thus attributed to a change in the relative magnitudes of the two terms in the denominator of eq 2 with pH.

$$\text{rate} = \frac{k_1 k_2 [2][Br_2]}{(k_{-1}[H^+] + k_2[Br_2])} \qquad (2)$$

At high acidity, when $k_{-1}[H^+] \gg k_2[Br_2]$, eq 3 holds, and

$$\text{rate} = k_1 k_2 [2][Br_2]/k_{-1}[H^+] \qquad (3)$$

so for an excess of substrate at fixed pH (buffer) pseudo-first-order behavior is observed. Conversely, at low acidity, when $k_2[Br_2] \gg k_{-1}[H^+]$, eq 4 holds, and pseudo-zero-order

$$\text{rate} = k_1[2] \qquad (4)$$

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[1] O. S. Tee and S. Banerjee, *Can. J. Chem.*, **52**, 451 (1974).

[2] S. Banerjee, O. S. Tee, and K. D. Wood, *J. Org. Chem.*, **42**, 3670 (1977).

[3] O. S. Tee, D. C. Thackray, and C. G. Berks, *Can. J. Chem.*, **56**, 2970 (1978).

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Table I. Second-Order Rate Constants for the Reaction of Bromine with 2-Pyrimidinones 1 at High Acidity[a]

substr	pH	$10^3[1]_s$, M	k_1^{obsd}, s^{-1}	$10^{-3}k_2^{obsd}$, $M^{-1}\,s^{-1}$
1a	−0.035[b,c]	2.0	0.140	1.50
	0.264[b,d]	2.0	0.285	3.16
	0.614[b,e]	2.0	0.658	6.96
	0.908[b,f]	2.0	1.37	14.6
	0.96	0.50	2.74	17.1
		0.954	5.44	16.9
	1.22[g]	2.0	2.65	28.3
	1.55	1.0	19.3	57.0
		2.0	39.5	56.8
	1.99	1.0	51.7	153
		2.0	106	152
	2.52	1.0	113[h]	334
	2.99	1.0	156[h]	461
		2.0	318[h]	457
	3.51	1.0	154[h]	455
1b	−0.035[b,c]	2.0	0.0371	0.396
	0.264[b,d]	2.0	0.0714	0.792
	0.614[b,e]	2.0	0.173	1.83
	0.908[b,f]	2.0	0.365	3.89
	0.97	1.0	1.62	5.09
		2.0	3.36	5.14
	1.22[g]	2.0	0.755	8.05
	1.50	1.0	5.49	16.2
		2.0	11.2	16.1
	1.97	1.0	13.7	40.5
		2.0	28.5	41.0
	2.21	1.0	23.7	70.0
		2.0	48.4	69.6
	2.42	1.0	33.4[h]	98.6
		2.0	67.3[h]	96.8
	2.90	1.0	48.6[h]	144
		2.0	98.9[h]	142
	3.12	1.0	57.9[h]	171
		2.0	119[h]	171
	3.83	1.0	71.2[h]	210

[a] At 30 °C, $[Br_2]_0 = 5.0 \times 10^{-5}$ M. [KBr] = 0.1 M and $\mu = 0.11$ M except where noted otherwise. [b] pH = −log [HBr]. [c] [HBr + KBr] = 1.100 M. [d] [HBr + KBr] = 1.144 M. [e] [HBr + KBr] = 1.088 M. [f] [HBr + KBr] = 1.098 M. [g] [HBr + KBr] = 1.097 M. [h] k_1^{obsd} from mixed-order analysis. See text.

kinetics are observed for an excess of **2**.

The rate law in eq 2 and its derivatives (eq 3 and 4) fully describe the behavior of the dimethyl cation **2c**.[3] For application to the substrates **1a** and **1b** of the present work, account must be taken of the fraction of 1 existing in the cationic form **2**. For the equilibrium in eq 5 the concentration of **2** is given by eq 6, where $[1]_s$ is the stoichiometric

$$1 + H^+ \overset{K_1}{\rightleftharpoons} 2 \tag{5}$$

$$[2] = [1]_s[H^+]/(K_1 + [H^+]) \tag{6}$$

concentration of the substrate 1 (**a** or **b**), and K_1 is the acid dissociation constant of the protonated form **2** (**a** or **b**). Substitution of eq 6 into eq 2, 3, and 4 leads to equations which account for the pH dependence of the rate constants observed for the substrates **1a** and **1b**.

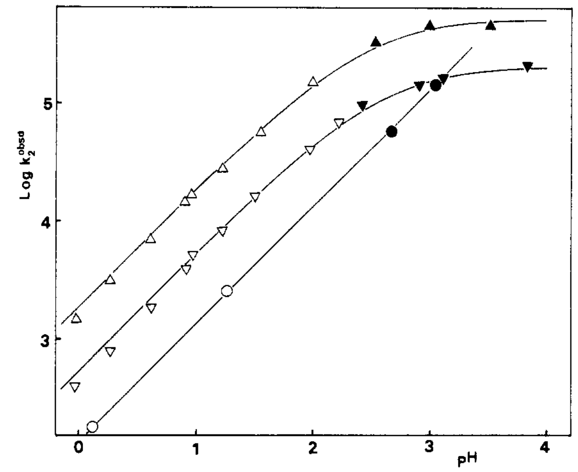

Figure 1. pH dependence of second-order rate constants for bromination of **1a** (△, ▲), **1b** (inverted triangles), and **2c** (○, ●). The open symbols are for rate constants derived from pseudo-first-order behavior, and the closed ones for values derived from mixed-order behavior (see text).

Table II. First-Order Rate Constants for the Reaction of Bromine with 2-Pyrimidinones 1 at Low Acidity[a]

substr	pH	$10^3[1]_s$, M	$10^5k_0^{obsd}$, $M\,s^{-1}$	$k_1^{obsd'}$, s^{-1}
1a	2.52	1.0	387[b]	3.87
	2.99	1.0	185[b]	1.85
		2.0	366[b]	1.83
	3.51	1.0	84.5[b]	0.845
	4.00	1.0	27.5	0.275
		2.0	56.4	0.282
	4.52	1.0	11.4	0.114
		2.0	22.8	0.114
1b	2.42	1.0	283[b]	2.83
		2.0	558[b]	2.79
	2.90	1.0	133[b]	1.33
		2.0	266[b]	1.33
	3.12	1.0	106[b]	1.06
	3.83	1.0	21.9	0.219
		2.0	43.3	0.217
	4.53	1.0	6.14	0.0614
		2.0	12.4	0.0620
	5.00	1.0	2.04	0.0204
		2.0	4.14	0.0207
	5.45	1.0	0.736	0.00736
		2.0	1.54	0.00770
	6.02	1.0	0.263	0.00263

[a] As for footnote *a* in Table I. [b] From mixed-order analysis. See text.

pH 0–2. For an excess of the substrate 1 (**a** or **b**) the disappearance of bromine shows good first-order behavior. Pseudo-first-order rate constants (k_1^{obsd}) vary linearly with substrate concentraton (Table I), indicating overall second-order behavior (eq 7).[4a] Second-order rate constants (k_2^{obsd}), derived[4b] from k_1^{obsd}, vary with pH as shown by the open symbols in Figure 1.

$$\text{rate} = k_1^{obsd}[Br_2]_s = k_2^{obsd}[1]_s[Br_2] \tag{7}$$

The acidity dependence of k_2^{obsd} is given by eq 8. This is obtained by setting eq 3 equal to eq 7 and substituting for [**2**] from eq 6.

$$k_2^{obsd} = (k_1k_2/k_{-1})/(K_1 + [H^+]) \tag{8}$$

In this region of pH (<2 < $pK_1 \approx 2.5^5$) the substrates **1a** and **1b** exist largely as their conjugate acids **2a** and **2b**, and they display reactivities very similar to the dimethyl cation **2c** (see Figure 1). The value of k_2^{obsd} for **2** increases with pH as the equilibrium concentration of **3** increases.

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(4) (a) $[Br_2]_s = [Br_2] + [Br_3^-]$. (b) Derived from k_1^{obsd} by taking into account $[1]_s$ and the depletion of free bromine due to the formation of tribromide ion[4a] (see Experimental Section).

(5) D. J. Brown, E. Hoerger, and S. F. Mason, *J. Chem. Soc.*, 211 (1955). These authors give $pK_1 = 2.24$ and 2.50 for **1a** and **1b**, respectively, at $\mu = 0.01$ M and at an unspecified temperature.

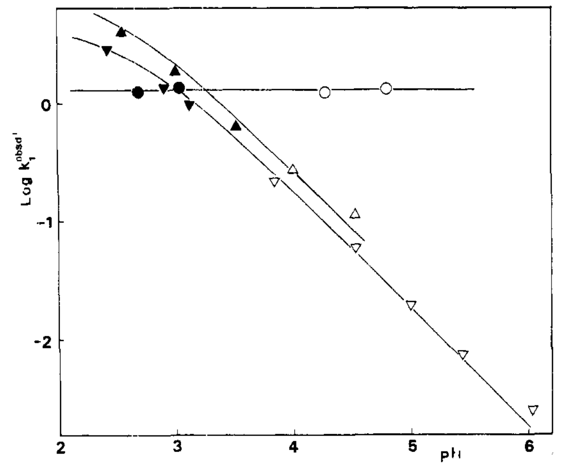

Figure 2. pH dependence of first-order rate constants for bromination of **1a** (△, ▲), **1b** (inverted triangles), and **2c** (○, ●). The open symbols are for rate constants derived from pseudo-zero-order behavior and the closed ones for values derived from mixed-order behavior (see text).

pH 4–6. In the presence of an excess of the substrate **1a** or **1b** the disappearance of bromine exhibits pseudo-zero-order kinetics, and observed rate constants (k_0^{obsd}) show a linear dependence upon substrate concentration (Table II), indicating a first-order consumption of the substrate (eq 9). The variation of the first-order rate

$$\text{rate} = k_0^{obsd} = k_1^{obsd'}[1]_s \qquad (9)$$

constants $k_1^{obsd'}$ with acidity is shown by the open symbols in Figure 2. About pH 5 the order of reaction for **1a** changes again, and the rate increases with pH, indicating that a new mechanism takes over.[6] However, for the 1-methyl derivative **1b** pseudo-zero-order kinetics were obtained up to pH 6.

The results in this region are consistent with the rate law in eq 4 and the variation of [**2**] as given by eq 6. From these equations and the observed rate law (eq 9) eq 10 is

$$k_1^{obsd'} = k_1[H^+]/(K_1 + [H^+]) \qquad (10)$$

obtained. For the dimethyl cation **2c** the rate is invariant with acidity (Figure 2) since its concentration is invariant with acidity in this region. However, for the substrates **1a** and **1b** the rates are diminishing since the concentrations of their respective cations, **2a** and **2b**, are decreasing with pH, since pH > pK_1 ~ 2.5.[5] Overall, the results are understandable in terms of rate-determining formation of the covalent hydrates (**3a** or **3b**) or the pseudobase **3c** from the appropriate cation **2**.

pH 2–4. In this region there is a gradual changeover between the two types of behavior just described, with the order changing from pseudo first order to pseudo zero order as the pH is raised. Analysis of the mixed-order kinetics which are observed may be carried out by making use of the full rate law in eq 2 and its integrated form,[3] eq 11. As it stands, this equation contains a logarithmic

$$\frac{k_{-1}[H^+]}{k_2} \ln \frac{[Br_2]_0}{[Br_2]} + ([Br_2]_0 - [Br_2]) = k_1[2]t \qquad (11)$$

(first-order) term and a linear (zero-order) term and so cannot be analyzed by conventional means.[7] However, eq 11 may be rearranged to a form[8] (eq 12a) which may be analyzed by linear least-squares.[9]

The slope of the left hand side of eq 12a vs. Rt provides

$$R \ln \frac{[Br_2]_0}{[Br_2]} = -\frac{k_2[Br_2]_0}{k_{-1}[H^+]} + \frac{k_1k_2[2]}{k_{-1}[H_+]}(Rt) \qquad (12a)$$

$$R = [Br_2]_0/([Br_2]_0 - [Br_2]) \qquad (12b)$$

a value of "k_1^{obsd}" (cf. eq 3 and 7) from which "k_2^{obsd}" may be derived in the normal way.[4b] Values of k_2^{obsd} obtained in this way for substrates **1a** and **1b** are given in Table I and plotted in Figure 1 as solid symbols. These data continue the trends evident in k_2^{obsd} values obtained at pH <2 by analysis of pseudo-first-order data.

From the intercept and slope of eq 12 and knowing $[Br_2]_0$, one may calculate a value of "k_0^{obsd}" = $k_1[2]$ (cf. eq 4 and 9), from which $k_1^{obsd'}$ is obtained by division by $[1]_s$. Such values are given in Table II and plotted as closed symbols in Figure 2. They follow the same pattern of behavior as values obtained at pH >4 by the analysis of pseudo-zero-order data.

Despite the deficiencies inherent in the approach,[9] analysis of the mixed-order data by using eq 12 provides rate constants k_2^{obsd} and $k_1^{obsd'}$ which agree well with those obtained outside the region of pH 2–4. Accordingly, the analysis supports the contention that the region of mixed-order kinetics results from $k_{-1}[H^+]$ being of similar magnitude to $k_2[Br_2]$ in eq 2.

The data from all three pH regions are consistent with the substrates **1** (**a** or **b**) reacting via their covalent hydrates **3** (**a** or **b**) formed from the conjugate acids **2** (**a** or **b**) (eq 1, 2, and 5 and Scheme I). At high acidity, bromine attack upon **3** is rate limiting, but at low acidity, when $k_{-1}[H^+] \ll k_2[Br_2]$ (eq 1), formation of **3** is rate determining.

Quantitative Aspects. On the basis that the experimental data (Tables I and II) are compatible with the mechanism in eq 1 and the rate law given in eq 2, one can consider the magnitudes of the various rate constants k_1, k_{-1}, and k_2. Also, one can estimate the degree to which **1a** and **1b** exist as their covalent hydrates and set an upper limit for the rate of direct attack by bromine[10] upon **1a** or **1b**.

The theoretical curves in Figure 1 drawn through the data for **1a** and **1b** were calculated from eq 8 by using k_1k_2/k_{-1} = 1900 and 550 s^{-1} and pK_1 = 2.44 and 2.58, respectively.[11] In Figure 2 the curves for **1a** and **1b** were calculated from eq 10 by using k_1 = 10 and 4.9 s^{-1} and the same pK_1 values. By way of comparison, the dimethyl cation **2c** has k_1k_2/k_{-1} = 135 s^{-1} and k_1 = 1.3 s^{-1}.

The equilibrium constant between the cation **2c** and the pseudobase **3c** can be measured, and it was found[3] that $K_{R^+} = k_1/k_{-1} = 6.92 \times 10^{-8}$ M. Accordingly, the rate constant for attack of bromine[10] upon **3c** is $k_2 = 2 \times 10^9$ M^{-1} s^{-1}. The covalent hydrate **3b** differs from the pseu-

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[6] The nature of this mechanism is currently under investigation.

[7] Our previous approach[3] was to assume the zero-order term and find the first-order term by fitting, or the converse. The assumed values were derived from the studies at higher and lower pH.

[8] G. F. Sheats and A. N. Strachan, *Can. J. Chem.*, **56**, 1280 (1978). These authors use a similar equation in the treatment of mixed-order nitration data.

[9] Strictly speaking, eq 12 is not well suited to analysis by linear least-squares methods in that both sides of the equation contain the observable having the major error, $[Br_2]$. However, most of our data is sufficiently free from noise, and eq 12 give good fits (r > 0.999) to this data.

[10] It is implicit in subsequent discussion that the only significant brominating species under our experimental conditions is molecular bromine. The justification for this assumption is given at length elsewhere.[12]

[11] Obtained from analyses of the reciprocal plots of $1/k_2^{obsd}$ vs $[H^+]$ (from eq 8). The correlation coefficients obtained were 0.999 and 0.998. For experimental pK_1 values see ref 5.

[12] O. S. Tee and C. G. Berks, *J. Org. Chem.*, **45**, 830 (1980).

Table III. Summary of Rate Constants for the Reaction of Bromine with 1a, 1b, and 2c[a]

const	unit	value of const 1a	 1b	 2c[b]
k_1k_2/k_{-1}	s^{-1}	1900	550	135
k_1	s^{-1}	10	4.9	1.3
k_2/k_{-1}		190	112	104
k_2	$M^{-1}\ s^{-1}$	$\sim 10^9$ [c]	$\sim 2 \times 10^9$ [c]	2×10^9
k_{-1}	$M^{-1}\ s^{-1}$	$\sim 5 \times 10^6$	$\sim 1.8 \times 10^7$	2×10^7
$K_{R^+} = k_1/k_{-1}$[d]	M	$\sim 2 \times 10^{-6}$	$\sim 2.7 \times 10^{-7}$	6.92×10^{-8}
pK_1		2.44	2.58	
pK_{R^+}		~ 5.7	~ 6.6	7.16
$K_1/K_{R^+} =$ [1]/[3]		~ 1800	~ 9700	

[a] At 30 °C and $\mu = 0.11$ M. [b] Data either directly from ref 3 or derived therefrom. [c] Estimated. See text. [d] $K_{R^+} = [3][H^+]/[2]$. See ref 3 and 13.

dobase **3c** only by a hydrogen in place of a methyl at N-3, remote from the site of attack. Therefore, for **3b** we estimate $k_2 \approx 2 \times 10^9$ M^{-1} s^{-1} also. For **3a**, having hydrogens at N-1 and N-3, the rate is probably somewhat less, say, $k_2 \sim 10^9$ M^{-1} s^{-1}.

These various constants, and others derived therefrom, are collected in Table III. They appear quite reasonable for the proposed mechanism (eq 1 and Scheme I). The value of k_1 diminishes with methyl substitution upon cation **2** as expected since methyls should inductively stabilize **2** somewhat and, for steric reasons, impede slightly the attack of water.[13] Likewise, k_{-1} increases in that methyl substitution should facilitate expulsion of hydroxyl from **2** for electronic and steric reasons. The combined effect of methyl substitution is then to diminish $K_{R^+} = k_1/k_{-1}$ from $\sim 2 \times 10^{-6}$ to 6.92×10^{-8} M, that is, to reduce the ease of equilibrium formation of **3** from **2**.

The rate constants k_2 for attack of bromine upon the species **3** are $\sim 10^9$ M^{-1} s^{-1}, close to the diffusion-controlled limit. This is to be expected since **3** is essentially a substituted enamine which should be very susceptible to electrophilic attack.[3] Also it should be noted that the high values of k_2 and k_{-1} ($\sim 10^7$ M^{-1} s^{-1}) compared to k_1 (1–10 s^{-1}) justify the use of the steady-state approximation in deriving eq 2. In the present instance this justification seems post facto, but in the earlier work[3] on the quaternary cation **2c** and its pseudobase **3c** values of k_1, k_{-1}, and k_2 were obtained independent of one another, which allowed our initial derivation and use of eq 2.[3]

The extent of covalent hydration of the 2-pyrimidinones **1** can be estimated from the apparent pK_1 values and the estimated K_{R^+}. Since $K_1 = [1][H^+]/[2]$ and $K_{R^+} = [3][H^+]/[2]$, then $[1]/[3] = K_1/K_{R^+}$. From the values in Table III it appears that [1]/[3] is ~ 1800 for **1a** and $\sim 10\,000$ for **1b**. Thus we estimate that 2(1*H*)-pyrimidinone (**1a**) in aqueous solution exists as its covalent hydrate **3a** to the extent of $\sim 0.05\%$.

The value of $pK_{R^+} \approx 5.7$ for **1a** given in Table III derives from our kinetic determination of k_1 and k_2/k_{-1} and the estimate of $k_2 \sim 10^9$ M^{-1} s^{-1}. An independent estimate of pK_{R^+} may be obtained by extrapolation of the correlation noted earlier between pK_{R^+} and Taft's σ^* for symmetrical cations **2** ($R_1 = R_2 =$ Me, Et, *n*-Pr, *n*-Bu, *i*-Pr).[13] From this extrapolation $pK_{R^+} \approx 5.0$ (at 24 °C). Also, the literature gives a value of $pK_1 = 2.24$ for **1a**.[5] Therefore, we feel that our estimate of 0.05% for the extent of hydration of **1a** is probably correct within an order of magnitude.[14]

We now consider the question of an upper limit for the rate of direct attack of bromine upon **1a** and **1b**. For this, of course, eq 13 applies, where k_2' is the second-order rate

$$\text{rate} \le k_2'[\mathbf{1}][\mathrm{Br_2}]_0 \qquad (13)$$

constant of interest. At the highest pH studied (6.02) **1b** is still reacting via its covalent hydrate **3b** with rate $= k_0^{\text{obsd}} = 0.263 \times 10^{-5}$ M s^{-1} (for $[\mathbf{1b}] = 10^{-3}$ M and $[\mathrm{Br_2}]_0 = 5 \times 10^{-5}$ M; vide supra). Therefore, $0.263 \times 10^{-5} \gg k_2'[\mathbf{1b}][\mathrm{Br_2}]_0$ and so $k_2' \ll 50$ M^{-1} s^{-1}. The corresponding value for **1a** should be slightly less.

These considerations serve to emphasize the dramatic effect that covalent hydration may have upon the reactivity of a heterocyclic system. Even though 2(1*H*)-pyrimidinone (**1a**) exists as its covalent hydrate **3a** to only a limited extent ($\sim 0.05\%$), the covalent hydrate is much more reactive than **1a** toward bromine ($k_2 \approx 10^9$ M^{-1} s^{-1} vs. $k_2' \ll 50$ M^{-1} s^{-1}), and so **1a** in aqueous solution consumes bromine $>10^4$ times faster than it would if its covalent hydrate were not present.[16]

Conclusions

The results reported above provide strong evidence that 2(1*H*)-pyrimidinone (**1a**) in aqueous solution exists as its covalent hydrate (**3a**) to a limited extent ($\sim 0.05\%$) and that bromination of **1a** ensues by way of attack of bromine upon **3a**. Thus the initial steps $\mathbf{1} \rightleftarrows \mathbf{2} \rightleftarrows \mathbf{3} \rightarrow \mathbf{4}$ of the detailed mechanism in Scheme I are supported. Since the remaining steps in Scheme I have been justified by earlier studies,[1,2] the entire sequence $\mathbf{1} \rightarrow\rightarrow\rightarrow \mathbf{10}$ is placed on a firm footing.

In addition, the present work provides rate constants for the formation and decomposition of the covalent hydrates **3a** and **3b** and sets an upper limit for the rate constant for direct attack of bromine on **1a**.

Experimental Section

The substrates for this study, **1a** and **1b**, were employed in the form of their hydrobromides **2a** and **2b** (counterion Br^-). They were made by cyclization of urea or 1-methylurea with malonaldehyde tetramethyldiacetal (Aldrich) according to literature procedures[17,18] for the hydrochlorides but by using hydrobromic acid in place of hydrochloric acid. The hydrobromides gave ^1H NMR spectra identical with those of the corresponding hydrochlorides.

Solutions for kinetic experiments were mainly the same as those used previously,[3] being 0.1 M in potassium bromide and having $\mu = 0.01$ M derived from buffer components.[19] Thus in most cases the total ionic strength was $\mu = 0.11$ M. For pH <2, solutions of hydrobromic acid were used, and in some cases the total bromide concentration and ionic strength were much higher (see the footnotes to Table I). The reasons for employing high bromide ion concentrations have been discussed elsewhere.[12]

Kinetics experiments were carried out (at 30 °C) by using the stopped-flow apparatus described in other recent work.[3,12] The acquisition and treatment of data also followed established practice[3,12] except for the use of eq 12 described in the text. Each

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[13] The effect of substituents upon the pseudobase behavior of various quaternary cations **2** ($R_1, R_2 \neq H$) has been studied previously. O. S. Tee and M. Endo, *Can. J. Chem.*, **54**, 2681 (1976).

[14] An earlier estimate of 0.1–1.0% was based upon more intuitive considerations.[15]

[15] A. R. Katritzky, M. Kingsland, and O. S. Tee, *Chem. Commun.*, 289, (1968); *J. Chem. Soc. B*, 1484 (1968).

[16] **1a** undergoes hydrogen-deuterium exchange in acidic D_2O at $\sim$100 °C about 10^4 times faster than 2(1*H*)-pyridinone, whereas one would expect it would be considerably slower.[15]

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rate constant (k_1^{obsd} or k_0^{obsd}) in Tables I and II is the average of 3–5 runs.

Each pseudo-first-order rate constant, k_1^{obsd} (Table I), was converted to a second-order rate constant, taking into account the substrate concentration $[1]_s$ and the difference between the actual bromine concentration, $[Br_2]$, and the stoichiometric concentration of bromine, $[Br_2]_s$.[12]

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Aryl Radical Departure Aptitudes in Reactions of Diaryliodonium Fluoroborates with Sodium Ethoxide

Jacek J. Lubinkowski,* Cecilia Giménez Arrieche, and William E. McEwen*

Departments of Chemistry, Universidad Simon Bolivar, Apartado 80659, Caracas, Venezuela, and The University of Massachusetts, Amherst, Massachusetts 01003

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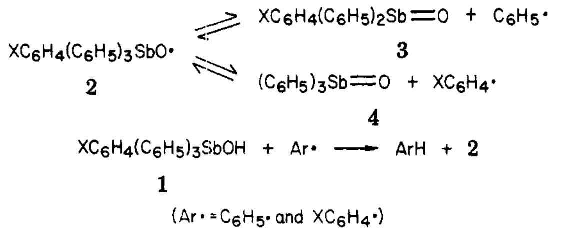
Several unsymmetrical diaryliodonium fluoroborates have been prepared and subjected to reaction with sodium ethoxide in ethanol solution at 71 °C. From quantitative determinations of products, it has been possible to calculate apparent departure aptitudes of several common aryl radicals from radical cations of type **6**. These results are compared with similar data obtained from thermolysis reactions of hydroxytetraarylstiboranes.

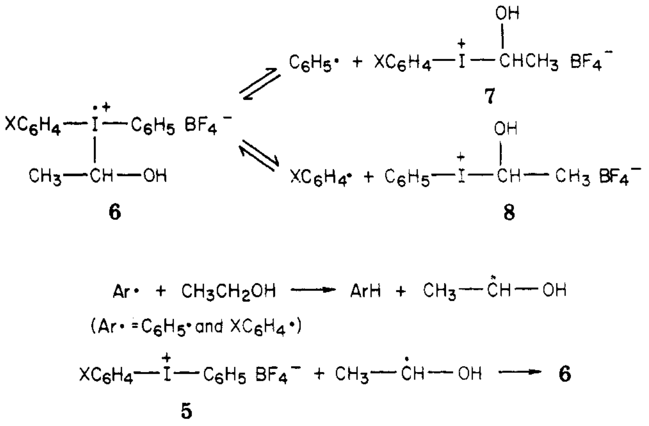
Hydroxytetraarylstiboranes of the type $XC_6H_4(C_6H_5)_3SbOH$ (1) have been reported[1-4] to undergo thermolysis at 30–50 °C by a radical chain mechanism. Evidence has been presented that the following competitive reactions occur in the propagation stage of each decomposition:



Since material balances were realized in these reactions, the ratios $3C_6H_5X/C_6H_6$ could be used as a measure of the apparent relative departure aptitudes of the various aryl radicals from 2. These departure aptitudes, corresponding to each of the substituents X in 1, were determined to be as follows: X = p-NO_2, 5.6; m-NO_2, 9.4; p-Cl, 2.5; m-Cl, 4.6; p-CH_3, 1.3; m-CH_3, 0.78; p-OCH_3, 2.6; m-OCH_3, 2.5.

A plot of log (departure aptitude) vs. σ° was found to be linear for the meta-substituted aryl groups; $\rho = 1.40$, correlation coefficient = 0.94. The σ° values are derived from reactions of compounds in which the aromatic ring is shielded from the reaction center (e.g., ionization of phenylacetic acids) or where the substituent is located in the meta position only. Taft[5] believes that these values are the best for use where only nonconjugative effects are involved. Most of the departure aptitudes for the para-substituted aryl groups cannot be correlated by use of the Hammett equation utilizing σ° values, and this suggests that there is a conjugative interaction of some type between the para substituent and the odd electron. This conjugative effect apparently causes an incremental decrease in stability of the radical when a strongly electron-withdrawing substituent (e.g., p-NO_2) is present, but an incremental increase in stability when an electron-donating substituent (e.g., p-MeO or p-Me) is present. For example, the departure aptitude of the p-methoxyphenyl group would be 0.76 based on the plot and the σ° value of the p-MeO group. Thus, the observed departure aptitude of the p-methoxyphenyl radical is apparently 3.4-fold greater than that expected if no conjugative influence were operative. In like manner, the departure aptitude of the p-methylphenyl radical would be 0.71 based on the plot and the σ° value of the p-Me group, and the observed departure aptitude of the p-methylphenyl group is 1.8-fold greater than that expected if no conjugative interaction were operative.

Scheme I



The reaction of a diaryliodonium salt with a metal alkoxide to give an alkyl aryl ether plus an aryl iodide is considered to be of synthetic utility; however, an aromatic hydrocarbon, an aryl iodide, and an aldol resin (or a ketone if the alkoxide is derived from a secondary alcohol) are frequently the major products. A mechanism which has been proposed for the formation of the latter set of

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