Table III

Comparison between Experimental and Calculated Constants at 20°, $\mu = 0.1\ M$, and $(Cr(VI)) = 4 \times 10^{-4}\ M$

$10^3 (S_2O_3^{2-})_t$, M	$10^2(H^+)$, M	$10^3 (HS_2O_3^-)$, M	k_{exptl}, sec^{-1}	k_{calcd}, sec^{-1}	
				From eq 16	From eq 13
1.6	1.00	0.229	0.0104	0.0167	0.0226
3.0	0.94	0.402	0.034	0.025	0.038
6.0	0.50	0.457	0.032	0.0284	0.0334
6.0	0.80	0.700	0.058	0.0556	0.062
6.0	1.00	0.858	0.0825	0.0767	0.0839
6.0	1.20	0.990	0.106	0.100	0.108
6.0	1.50	1.189	0.145	0.139	0.148
6.0	2.00	1.487	0.229	0.212	0.224
9.0	0.80	1.05	0.078	0.086	0.093
12.0	0.726	1.28	0.102	0.1016	0.108

easily formed. The electron exchange deeply affects the structure of the chromium orbitals, and the symmetry changes from tetrahedral to octahedral.

Since the next step is very fast, there is little experimental support to make more assumptions on the mechanism.

The rate law derived from mechanism 14 and the stoichiometry $S_2O_3^{2-}:CrO_4^{2-} = 3:1$

$$-\frac{d(CrS_2O_6^{2-})}{dt} = \frac{K}{3}\frac{(HS_2O_3^-)^2}{1 + K(HS_2O_3^-)}\{k_2 + k_3(H^+)\}(CrS_2O_6^{2-}) \qquad (16)$$

is in agreement with empirical law 12 with $k_2 = 3k_2'$ and $k_3 = 3k_3'$, or, neglecting 1 in comparison to $K(HS_2O_3^-)$, with eq 13.

There is a good agreement between the experimental and calculated values of k, as shown in Table III. The equilibrium constant K calculated from kinetic data has the same order of magnitude as calculated previously from equilibrium measurements.[12]

Table IV

The Effect of Temperature on the Rate Constants at $\mu = 0.1\ M$

Temp, °C	$10^{-2}k_2$, M^{-1} sec^{-1}	$10^{-4}k_3$, M^{-2} sec^{-1}
15.4 ± 0.3	1.12 ± 0.18	1.34 ± 0.19
20.0 ± 0.2	1.42 ± 0.21	1.55 ± 0.22
25.0 ± 0.2	1.79 ± 0.36	1.85 ± 0.29
29.6 ± 0.2	2.13 ± 0.45	2.24 ± 0.05
34.4 ± 0.3	2.76 ± 0.54	2.63 ± 0.43

3.4. The Influence of the Temperature.—The velocity constants k_2 and k_3 were calculated from kinetic experiments carried out at five different temperatures between 15 and 35°, at acidities between 5×10^{-3} and $2 \times 10^{-2}\ M$, an ionic strength of 0.1 M, a Cr(VI) concentration of $4 \times 10^{-4}\ M$, and a thiosulfate concentration of $6 \times 10^{-3}\ M$. The straight lines in Figure 4 served to obtain k_2'' and k_3'' and by multiplying with 3 the values k_2 and k_3 as recorded in Table IV. Standard deviations were calculated by using for each point of the graph five to eight experimental data.

By means of the least-squares method, the activation enthalpies and entropies were obtained. For reaction 14b: $\Delta H^{\ddagger} = 8.2 \pm 0.7$ kcal and $\Delta S^{\ddagger} = -20.8 \pm 2.5$ eu. For the trimolecular reaction 14c: $\Delta H^{\ddagger} = 6.4 \pm 2.4$ kcal and $\Delta S^{\ddagger} = -17.7 \pm 8.0$ eu. Haight, *et al.*,[8] found for the reaction between SO_3^{2-} and Cr(VI) an activation entropy of −13 eu and an activation enthalpy of 4.5 kcal.

The proposed mechanism explains the formation of tetrathionate as the reaction product. At higher Cr(VI) concentrations and acidities sulfate is also formed and the mechanism could be quite different. This reaction path will be the subject of future investigations.

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N-Iodopyridinium Dichloroiodate(I)

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Mixing pyridine with an Andrews solution of dichloroiodate(I) in 5 M hydrochloric acid gives stable yellow crystalline material of formula $C_5H_5NI_2Cl_2$. Ultraviolet and infrared data supported by electrolytic, conductometric, and cryoscopic measurements suggest that this material is a double-charge-transfer complex of $C_5H_5NI^+$ and ICl_2^- ions. The rate and mechanism of aqueous hydrolysis to iodine and other unidentified material is discussed.

Introduction

Many molecular charge-transfer complexes can be prepared as crystalline solids by reaction of interhalogens with organic bases, particularly pyridine (py),[1-6] alkylpyridines,[2,7,8] halopyridines,[4] and dipyridyls.[9,10] Failkov and Musyka[11] concluded that the

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physical properties of nitrobenzene, with added pyridine and iodine monochloride, in molar ratios of 1 and 2, respectively, indicated the presence of N-iodopyridinium chloride, IpyCl, and N-iodopyridinium dichloroiodate(I), $IpyICl_2$. Popov and Pflaum[9] attempted to obtain compounds similar to those detected but not actually isolated by Failkov and Musyka.[11] Mixing iodine monochloride with pyridine in the vapor state or in carbon tetrachloride did not give $IpyICl_2$, although IpyCl could be readily isolated.[9] Similarly, quinoline forms only the 1:1 complex with iodine monochloride although iodine trichloride reacts with both pyridine and quinoline to give 1:2 and 2:1 complexes.[6]

A pyridine–iodine monochloride complex of 1:2 stoichiometry was successfully prepared by treatment of the solution remaining at the end point of an Andrews titration with excess pyridine. Such solutions are known to contain dichloroiodate(I) anions.[12,13] The material was obtained as a yellow crystalline precipitate in >90% yield, analyzing as pyI_2Cl_2.

Experimental Section

Reagents.—Chemicals were of AR quality. Solvents were purified and dried by standard techniques.

Preparation.—N-Iodopyridinium dichloroiodate(I) rapidly precipitated on adding excess pyridine (5 ml) to the solutions resulting from mixing 0.1 *M* potassium iodide (25 ml) in 1–10 *M* hydrochloric acid (50 ml) with 0.05 *M* potassium iodate (25 ml). The yellow product was recrystallized from 5 *M* hydrochloric acid. The melting point, 226–229°, taken in a sealed tube is much higher than the figure of 34° once predicted from phase studies.[11] *Anal.* Calcd for $C_5H_5NI_2Cl_2$: C, 14.9; H, 1.24; N, 3.46; Cl, 17.6; I, 62.9. Found: C, 15.0; H, 1.53; N, 4.05; Cl, 17.6; I, 62.7.

Molecular Weight.—The molecular weight (calculated for $C_5H_5NI_2Cl_2$: 404) was measured cryoscopically in nitrobenzene as 204 ± 5 (Beckmann) and in naphthalene as 411 ± 20 (Rast).

Electrical Measurements.—Conductivity measurements were made with a Mullard bridge on solutions in nitrobenzene.

The material dissolved in nitrobenzene was electrolyzed between platinum electrodes when iodine discharge was observed at both the cathode and the anode.

Infrared Spectra.—Data were obtained for N-iodopyridinium dichloroiodate(I) between 4000 and 400 cm^{-1} for saturated solutions in pyridine and carbon disulfide, in Nujol mulls, and as potassium bromide disks, using a Model 521 Perkin-Elmer instrument. No useful data resulted from scans between 2000 and 4000 cm^{-1}. Owing to very low solubility, scans in carbon tetrachloride, benzene, and cyclohexane provided little information. The neat pyridine spectrum was run against air. Except where noted, spectra were obtained with freshly prepared solutions or disks.

Visible and Ultraviolet Spectra.—These were run on a Unicam SP 800 which was fitted with a constant-temperature bath for the stability and hydrolysis studies.

Results and Discussion

Previous failures to isolate pyI_2Cl_2 are possibly due to the high solubility in nitrobenzene, on the one hand,[11] and the use of anhydrous nonpolar solvents, on the other.[9] Indeed, all attempts to make pyI_2Cl_2 in benzene and carbon tetrachloride, as well as chloroform, have been unsuccessful.[8,9]

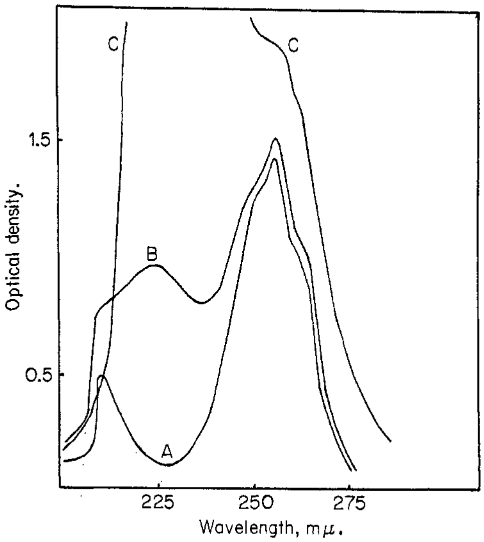

Figure 1.—Ultraviolet spectra of pyridine and pyridine–ICl_2^- mixtures in 5 *M* HCl: A, 2.35 × 10^{-4} *M* pyridine; B, 2.35 × 10^{-4} *M* pyridine and 2.35 × 10^{-5} *M* ICl_2^-; C, 2.35 × 10^{-4} *M* pyridine and 2.35 × 10^{-4} *M* ICl_2^-.

From viscosity, conductivity, and freezing point measurements, Failkov and Musyka[11] suggested that both the 1:2 and 1:1 pyridine–iodine monochloride complexes formed in nitrobenzene are ionized under dilute conditions

$$pyI_2Cl_2 \rightleftharpoons Ipy^+ + ICl_2^- \qquad (1)$$

$$pyICl \rightleftharpoons Ipy^+ + Cl^- \qquad (2)$$

Furthermore, transport experiments showed that while iodine concentrated at both the anode and the cathode on electrolyzing a pyI_2Cl_2 solution, iodine discharged only at the cathode in the case of pyICl.[11] Indeed, simultaneous discharge of iodine at a platinum mesh anode and cathode with the present material is as expected. The analytical results indicate the material to be a pyridine–iodine monochloride complex of 1:2 stoichiometry. Cryoscopic molecular weight values in naphthalene are close to the theoretical value of 404 required for $C_5H_5NI_2Cl_2$. In nitrobenzene, however, at concentrations of $<10^{-4}$ *M* with respect to complex, the molecular weight is essentially half that expected from the molecular formula, thus supporting complete ionization of the kind shown in eq 1. At concentrations exceeding about 10^{-4} *M*, conductivities in nitrobenzene, using a Mullard bridge, do not confirm complete ionization, but below this concentration the equivalent conductivity *vs.* $[pyI_2Cl_2]^{1/2}$ plot is approximately linear and consistent with the molecular weight observations in this solvent.

Ultraviolet Spectrum.—In hydrochloric acid (5 *M*), pyridine exhibits peaks at 212 and 257 mμ with inflections at 253 and 264 mμ (Figure 1, Table I), the high extinctions for the 212- and 257-mμ absorptions being those expected for $\pi \rightarrow \pi^*$ transitions in a strong acid.[14] The Andrews titration mixture, 5 *M* with respect to hydrochloric acid and known to contain ICl_2^- ions,[12,13] shows peaks at 225 and 343 mμ. The

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Table I

Molar Extinction Coefficients of pyI_2Cl_2, ICl_2^-, and Pyridine, each in 5 *M* Hydrochloric Acid

Wavelength, mμ	pyI_2Cl_2	ICl_2^-	Pyridine
212	. . .	. . .	2040
225[a]	70,500	50,000	. . .
253	. . .	. . .	5500
257	17,960	. . .	6130
264	*Ca.* 12,800	. . .	*Ca.* 4500
343	370	275	. . .

[a] This band in water is at 206 mμ.

intense 225-mμ absorption is characteristic of a charge-transfer peak and corresponds to the transition involved in the formation of ICl_2^- from Cl^- and ICl.[15] Popov and Swenson[16] suggested that the similar absorption at 227 mμ of dichloroiodate(I) in acetonitrile (ε 54,500) is due to a $\sigma \rightarrow \sigma^*$ transition. A solution of N-iodopyridinium dichloroiodate(I) in hydrochloric acid (5 *M*) also absorbs at 225 and 343 mμ, while, in addition, inflections are present at 257 and 264 mμ.

The 225- and 343-mμ absorptions are common to both dichloroiodate(I) and N-iodopyridinium dichloroiodate(I) species and support the presence of the ICl_2^- anion in the pyridine complex as suggested by eq 1. However, this equation presumes the formation of the Ipy^+ cation for which spectral evidence is less easily gleaned. In this respect Reid and Mulliken[17] suggested that the 235-mμ band (ε 50,000) of a solution of iodine in pyridine blanked against pyridine was due to a charge-transfer band, probably of the Ipy^+ ion. Close examination of this band reveals asymmetry in the manner recently noted,[18] similar asymmetry being evident for a number of strong charge-transfer complexes formed by iodine and N-heterocyclics with absorptions between 230 and 240 mμ.[19] This band is not evident in the spectrum of N-iodopyridinium dichloroiodate(I) although it might well be submerged within the 225-mμ absorption. However, the formation of a strong charge-transfer complex involving pyridine, and with the same geometry since there is no wavelength shift, is suggested by the enhanced absorptions at 257 and 264 mμ for N-iodopyridinium dichloroiodate(I) compared with pyridine itself.

Formation Constants.—Reid and Mulliken[17] have proposed the equation

$$I_3^- + py \rightleftharpoons Ipy^+ + 2I^- \qquad (3)$$

for the reaction between pyridine and triiodide. The ultraviolet spectra of various pyridine–dichloroiodate(I) mixtures are not inconsistent with the similar equation

$$ICl_2^- + py \rightleftharpoons Ipy^+ + 2Cl^- \qquad (4)$$

for which the formation constant $K = [Ipy^+]/[py] \cdot [ICl_2^-]$ may be evaulated by the Benesi–Hildebrand

Table II

Infrared Bands[a,b] of Pyridine, $py(ICl)_2$, and pyICl in Various Media between 400 and 2000 Cm^{-1}

As Nujol mull		As KBr disk			In pyridine				In carbon disulfide		Neat pyridine	
			pyICl		py(ICl)$_2$[c]		PyICl					
py(ICl)$_2$[c]	pyICl[d]	py(ICl)$_2$[c]	e		Fresh	24-hr old	e	d	py(ICl)$_2$[c]	pyICl[d]	c	d
	426 s							424 s		421 sh	400 s	405
	428[g]							434				
						600 s					600 s	605
		622 sh			625 s	622 s						
	636 s		630		629 s		627	632 s		627 s		
	649 w								650 s	655 w	650 s	652
660 s		660 s			660 s							
675 s										675 w	672 s	
	689 s		684		682 s	682 s						
				693						692 s		
	704 w					700 b	701			702 w	700 b	700
		730 s										
	752 s		748	751	745 sh		746			748 s	745 s	749
768 b					757 s							

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As Nujol mull		As KBr disk			In pyridine				In carbon disulfide		Neat pyridine	
			pyICl		py(ICl)$_2^c$		PyICl					
py(ICl)$_2^c$	pyICl^d	py(ICl)$_2^c$	*e*	*f*	Fresh	24-hr old	*e*	*d*	py(ICl)$_2^c$	pyICl^d	*c*	*d*
									786 s			
									807 s		808 sh	
	851 vw											
890 b	869 vw										880 s	886
920 b	948 w				931 b					941 vw	938 s	942
975 b						990 sh	992				990 s	992
1008 s					1004 s	1000 b			1004 b	1009 s		
	1013 s		1012	1012			1012	1011 s				
1025 s		1021 s										
	1035 m		1033	1033			1032			1030 b	1028 s	1030
1040 b		1039 s			1040 s							
1060 s	1056 s	1055 s	1055	1054	1056 s							
							1067			1067 s	1065 s	1068
	1087 w				1100 b		1148					1085
1155 s	1154 w	1150 s	1153		1160 s					1150 s	1144 s	1148
1190 s												
1205 sh	1197 s	1183 s			1197 s	1197 s		1209 s				
	1209 s		1201				1213 sh			1209 s		
			1211				1219				1215 s	1218
1230 b		1229 b										
1250 b	1247 s	1245 b	1248		1251 s	1250 s	1246	1244 w		1239 b		
							1294				1290 s	
1320 s		1317 s										
		1352 s	1348		1348 s					1347 b	1350 s	
	1344 s	1360 s					1356					
							1374				1370 s	1375
	1390 w	1392 s										
							1442	1449 s			1434 b	1439
	1449 s		1452		1450 b		1454					
		1472 s	1481		1463 s		1487				1480 b	1482
1525 b		1520 s			1488 s	1485 s						
					1530 b	1530 s						
	1569 m										1575 b	1572
						1580 b	1584					1583
	1597 s	1594 s									1595 s	
		1605 s	1601				1602					
		1625 s			1634 s	1630 s	1634				1630 s	
	1647 w										1680 s	
1840 b	1838 w	1840 s									1865 s	
	1915 w				1900 b				1912 b	1910 w	1915 s	
		1950 b			1960 b							
	1980 vw					1978 b					1980 s	

[a] Abbreviations: s, strong; w, weak; vw, very weak; b, broad; sh, shoulder. Intensities not available for some columns. [b] All runs taken in fresh solutions except for one in the 24-hr old pyridine solvent. [c] Present work. [d] Reference 28. [e] Reference 29. [f] Reference 3 (KCl disk). [g] Reference 7.

method at 225 mμ.[20,21] Recent doubts[22,23] cast on the validity of this classical method[20,21] are inapplicable since steric hindrance is remote, and the complex is not weak ($K_{25°} = 4.40 \times 10^4$ l. mol^{-1}) and is of the order shown by other pyridine and substituted-pyridine complexes with halogen.[8] A plot of $L[\mathrm{A}]/d$ against $1/[\mathrm{D}]$, where L is the cell path length, [A] is the acceptor concentration, d is the optical density at 225 mμ, and [D] is the donor concentration, gave a series of straight lines at four different temperatures. From their respective slopes, formation constants, and hence free energy ($\Delta G° = -6.35$ kcal mol^{-1}), enthalpy ($\Delta H° = -2.01$ kcal mol^{-1}), and entropy ($\Delta S° = 15.9$ cal deg^{-1} mol^{-1}) changes were calculated. This entropy change value is consistent with complex formation by eq 4, and the free energy change is compatible with values given by Mulliken[24] for nν complexes.

Infrared Spectra.—Mulliken's[17,25] charge-transfer theory proposes that marked infrared changes should appear in the acceptor molecule, while the majority of the donor-band positions, except for some intensity enhancement, remain unchanged,[25] particularly with weak complexes. With regard to the present study, the available infrared evidence excludes the far-infrared acceptor halogen frequencies of N-iodopyridinium dichloroiodate(I) and is confined mainly to the pyridine donor frequencies. For pyridine, the fundamental modes lie at frequencies above 400 cm^{-1}, and in keeping with Mulliken's theory the infrared spectra of 1:1 pyridine–interhalogen complexes closely resemble that of pyridine, although new bands, assigned to shifted pyridine bands, are also observed.[8,10,26–30] As can be seen from Table II, which summarizes relevant total infrared character, between 400 and 2000 cm^{-1}, the present complex also shows new bands.

Both py(ICl)$_2$ and pyICl contain the pyI$^+$ cation; hence their infrared spectra should be essentially identical exept for the enhancement of certain bands according to the strength of the respective complex. Pyridine–iodine monochloride absorptions not present in pyridine include bands at 625–636, 1004–1013, 1190–1209, 1239–1251, 1317–1320, 1392, and 1520–1530 cm^{-1}. Of these, the bands located at 625–636 and 1004–1013 cm^{-1} are interesting in that they have been noted to parallel electronegativities in various pyridine–iodine monohalide systems.[3,29] For example, Zingaro and Tolberg[3] noted that the shift in their 989-cm^{-1} band of pyridine was directly related to the electronegativity of the anionic component, the maximum frequencies being 1014, 1012, 1011, and 1005 cm^{-1} for fluoride, chloride, bromide, and iodide, respectively. The shift to 1004–1008 cm^{-1} with the more complex anionic ICl$_2^-$ of N-iodopyridinium dichloroiodate(I) is consistent with the simple halide shifts of the 1:1 pyridine–interhalogen complexes.

On the basis of absorptions at 636, 434, and 172 cm^{-1}, assigned to (py)$_2$I$^+$, Wood and coworkers[28,31] proposed that 1:1 py–IX complexes ionize in polar solvents according to

$$2\mathrm{pyIX} \rightleftharpoons (\mathrm{py})_2\mathrm{I}^+ + \mathrm{IX}_2^- \qquad (5)$$

For N-iodopyridinium dichloroiodate(I), the formation of this cation is feasible only in pyridine medium

$$\mathrm{py} + \mathrm{pyI}^+ \rightleftharpoons (\mathrm{py})_2\mathrm{I}^+ \qquad (6)$$

However, it is unlikely that the absorption at 629 cm^{-1} is due to this cation because there is no related absorption near 434 cm^{-1} (Table II).

Equilibrium 6 is unlikely to be extensive, for otherwise the 1:1 pyridine–iodine monochloride complex would be expected on adding excess pyridine to the solution remaining at the end point of an Andrews titration

$$\mathrm{pyI}^+ + \mathrm{ICl}_2^- + \mathrm{py} \longrightarrow 2\mathrm{pyICl} \qquad (7)$$

No such 1:1 material was found.

Hydrolysis.—Solutions of the complex in 5 *M* hydrochloric acid are stable over several days but in water rapidly turn brown and give a positive starch test. Simultaneously a new absorption shows at 460 mμ which increases in intensity, while the absorptions of the complex at 206 and 343 mμ fall in intensity. The absorptions at 343 and 460 mμ being of similar magnitude and attributed to ICl$_2^-$ and I$_2$, respectively,[13] facilitate rate measurements at each wavelength on just one sample.

Small samples, in 1-cm silica cells, were dissolved in water and examined at three different pH values at 25° and at three different temperatures at pH 7.0 (Table III).

Table III

First-Order Rate Constants (min^{-1}) for IpyICl$_2$ Hydrolysis in Aqueous Media

Temp, °C	pH	10^4k_1 (from 343-mμ peak)	10^3k_2 (from 460-mμ peak)
15.20	7.0	3.06	1.35
25.00	5.0	2.52	1.62
25.00	7.0	3.08	1.62
25.00	9.0	8.13	1.62
35.00	7.0	3.08	1.89

Hydrolysis rates, calculated from the respective absorptions, are first order for each absorption (Table III) but numerically different ($k_2 > k_1$) suggesting that the reactions associated with each change, although related, are not successive and dependent reactions.

Reaction in water occurs in two distinct stages. The first, and slower, as indicated by the fading 343-mμ peak is temperature independent with associated zero activation energy. It is, however, pH dependent and k_1 increases with rising pH. This reaction probably

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involves decomposition of the ICl_2^- formed by a rapid water-complex reaction

$$IpyICl_2 + 2H_2O = IpyOH + H_3O^+ + ICl_2^- \quad \text{(rapid)}$$

$$ICl_2^- \overset{k_1}{\rightleftharpoons} I^- + Cl_2 \quad \text{(rate determining)}$$

Long and Skoog[32] reported a similar aqueous hydrolysis for $I(SCN)_2^-$

$$I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2$$

which is contrary to the mechanism proposed by Creemer and Duncan[33] for thermal and aqueous dissociation of polyhalide ions

$$IX_2^- \rightleftharpoons IX + X^-$$

This reaction rather than $IX_2^- \rightleftharpoons I^- + X_2$ would be expected to predominate in acid solution since X^- is generally a stronger base than I^-. On the other hand, for the pH range of this study, the latter mode is consistent with the above rate-determining proposal and is in line with the view of Long and Skoog.[32]

The second hydrolysis stage, also first order, is unlikely to concern ICl_2^-, and the iodine may form by decomposition of IpyOH

$$IpyOH \overset{k_2}{\rightleftharpoons} IOH + py \quad \text{(rate determining)}$$

$$5IOH = 2I_2 + HIO_3 + 2H_2O \quad \text{(rapid)}$$

These reactions involve the formation of the weak acid HIO, and thus k_2 should be, and is, pH independent. An activation energy of -3.53 kcal mol^{-1} has been calculated for this stage from a k_2 *vs.* $1/T$ plot.

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The Thermodynamic Properties of the Perbromate and Bromate Ions[1]

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The energies of decomposition of $KBrO_4$(c) and $KBrO_3$(c) to KBr(c) plus O_2(g) were measured in a bomb calorimeter. These data were used to derive the standard enthalpy of formation ($\Delta H_f°_{298.15}$) of $KBrO_4$(c), -68.74 ± 0.14 kcal mol^{-1}, and of $KBrO_3$(c), -86.02 ± 0.12 kcal mol^{-1}. The enthalpies of solution of $KBrO_4$(c) in 2144 mol of water and of $KBrO_3$(c) in 1808 mol of water were measured to be 11,606 ± 20 and 9765 ± 42 cal mol^{-1}, respectively, at 25°. The above values were combined with other data to derive standard thermodynamic properties at 25° for the perbromate ion: $\Delta H_f° = 3.19 \pm 0.15$ kcal mol^{-1}, $S° = 44.7 \pm 2.0$ cal deg^{-1} mol^{-1}, and $\Delta G_f° = 29.18 \pm 0.63$ kcal mol^{-1}; and for the bromate ion: $\Delta H_f° = -15.95 \pm 0.13$ kcal mol^{-1}, $S° = 38.6 \pm 0.3$ cal deg^{-1} mol^{-1}, and $\Delta G_f° = 4.55 \pm 0.14$ kcal mol^{-1}. The standard electrode potential of the bromate-perbromate couple in acid solution was calculated to be 1.763 ± 0.014 V at 25°. Selected values for the thermodynamic properties of the halates and perhalates of chlorine and iodine are also tabulated. Although the perbromate ion is more oxidizing than either perchlorate or periodate ion, the difference is not great enough to explain why the synthesis of perbromates has been so difficult.

Introduction

The recent discovery of preparative methods[2,3] for perbromic acid and perbromates has ended a long search for these compounds. This study was undertaken to determine some of the key thermochemical data for potassium perbromate and the perbromate ion. Such information should be helpful in exploiting these new and interesting compounds and may help to explain past difficulties encountered in their synthesis. The results of this study also bear on the contention that the highest oxidation states of the nonmetals of the first long period are less stable than the corresponding oxidation states of the preceding and succeeding periods.

Of the possible reactions of $KBrO_4$ suited to calorimetric study, thermal decomposition of the solid was chosen. The simplicity and directness of the reaction

$$KBrO_4(c) \longrightarrow KBr(c) + 2O_2(g) \quad (1)$$

leads to a reliable value for the enthalpy of formation of $KBrO_4$(c); the only auxiliary information required is the enthalpy of formation of KBr(c), which is well established. By also determining the enthalpy of solution of $KBrO_4$(c) in water, the standard thermodynamic properties of the perbromate ion could be computed.

Similar measurements were made on $KBrO_3$ to enable comparison of the bromate and perbromate ion stabilities, after finding that the existing thermodynamic data for the bromate ion, which had been obtained by aqueous-reaction calorimetry, were excessively discordant. In addition, it was desired to compare the results for the bromate and perbromate ions with those for the halates and perhalates of iodine and chlorine. Accordingly, a review and selection of data for these additional systems was made. A few calorimetric measurements of the thermal decomposition of $KClO_3$(c) were made to aid us in selecting from among the various values published for the enthalpies of formation of $KClO_3$(c) and $KClO_4$(c).

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