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Notes

Contribution from the Department of Chemistry, East Texas State University, Commerce, Texas 75428

Tetraperoxychromate(V)-Diperoxychromate(VI) Equilibrium in Basic Aqueous Hydrogen Peroxide Solutions[1]

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In basic aqueous hydrogen peroxide solutions chromate is present as the red-brown tetraperoxychromate(V) ion, CrO_8^{3-}, and in neutral solutions as the violet diperoxychromate(VI) ion, $HCrO_6^-$.[2] It has been shown that interconversion reactions between these species take place readily on adjustment of the basicity of the solution.[2a,3] The structure of the tetraperoxychromate ion in the solid state has been firmly established on the basis of X-ray diffraction studies of the potassium salt.[4] Various formulas have been given for the violet species.[2] The uncertainty in identification of this species has been due to the instability of its solid salts. $HCrO_6^-$, now generally accepted as the correct formula, was proposed by Griffith[5] on the basis of analytical and spectroscopic data. The present spectrophotometric study of the equilibrium existing in aqueous hydrogen peroxide solutions between the tetraperoxy and diperoxy species provides supporting evidence for Griffith's formula.

Assuming that the structure of the violet peroxychromate is that proposed by Griffith, $HCrO_6^-$, two reaction schemes involving the interconversion of the two peroxides might be written. The first possibility involves oxygen evolution on conversion of the tetraperoxychromate to the diperoxy species.

$$CrO_8^{3-} + 2H^+ \rightleftarrows HCrO_6^- + {}^3/_4O_2 + {}^1/_2H_2O \qquad (1)$$

Rapid oxygen evolution has been observed on addition of K_3CrO_8 to neutral peroxide solutions.[3] However, once equilibrium is obtained, oxygen evolution at 0° is only slight, and the equilibrium relationship may also be represented by

$$HCrO_6^- + {}^3/_2H_2O_2 \rightleftarrows CrO_8^{3-} + 2H^+ + H_2O \qquad (2)$$

For both of these reaction schemes, at a given ionic strength and peroxide concentration (and for reaction 1, under constant partial pressure of oxygen), an apparent equilibrium constant would be given by the relationship

$$K_a = [CrO_8^{3-}][H^+]^2/[HCrO_6^-] \qquad (3)$$

from which the following relationship is derived.

$$pK_a = 2\ pH - \log([CrO_8^{3-}]/[HCrO_6^-]) \qquad (4)$$

It can be shown that in a given solution of absorptivity λ_ϵ at some arbitrary wavelength λ, the concentration ratio is given by

$$\frac{[CrO_8^{3-}]}{[HCrO_6^-]} = \frac{{}^\lambda\epsilon_A - {}^\lambda\epsilon}{{}^\lambda\epsilon - {}^\lambda\epsilon_B} \qquad (5)$$

where ${}^\lambda\epsilon_A$ is the absorptivity at λ of a solution containing only the diperoxychromate ion and where ${}^\lambda\epsilon_B$ is the absorptivity at λ of a solution containing only tetraperoxychromate. Thus, for a series of spectra run under identical conditions of solvent composition and ionic strength, a plot of $\log {}^\lambda\epsilon_A - {}^\lambda\epsilon/{}^\lambda\epsilon - {}^\lambda\epsilon_B$ *vs.* the pH of the solution should give a straight line with a slope of 2. Furthermore, where $\log {}^\lambda\epsilon_A - {}^\lambda\epsilon/{}^\lambda\epsilon - {}^\lambda\epsilon_B = 0$, the apparent p$K$ is equal to twice the pH at the intercept. Such plots were prepared at two wavelengths, one on either side of the isosbestic, at 500 and 425 nm, corresponding to the maximum and minimum, respectively, of the diperoxychromate absorption spectrum.

Experimental Section

Reagents and Glassware. Hydrogen peroxide (90%), obtained from the FMC Corp., was diluted to the desired concentration using deionized distilled water. All other chemicals were standard, reagent grade. Sodium perchlorate solutions were standardized by pipeting a known volume into a flask, evaporating to dryness, and weighing the residue. Carbonate-free sodium hydroxide was prepared according to the method of Kolczynski, Roth, and Shanley.[6] All glassware used was cleaned several times using the method recommended by Easton, Mitchell, and Wynne-Jones[7] in order to minimize peroxide decomposition during the course of the measurements.

Spectrophotometric Measurements. The following procedure was used for preparing solutions for spectrophotometric measurements of the tetraperoxy-diperoxy equilibria. Neutral and 0.10 *M* sodium hydroxide stock solutions were prepared having the desired peroxide concentration and total ionic strength (sodium perchlorate was used as the ionic medium). A series of solutions of varying basicity was prepared using differing ratios of the two stock solutions. The neutral solution containing no added base was generally the least basic solution in the series. In some series (those at 1.0 *M* total ionic strength) it was necessary to add perchloric acid in order to obtain a solution in which the equilibrium was shifted to complete diperoxychromate formation. Preparation of solutions was carried out in volumetric flasks immersed in an ice-salt bath to minimize peroxide decomposition. A weighed amount of J. T. Baker reagent grade K_2CrO_4 was added to each of eight 50-ml volumetric flasks. The flasks were then filled to 50 ml with each of a set of eight peroxide solutions, prepared as described above, the chromate was dissolved, and the resulting solution was placed in an ice bath at 0°. The solutions were allowed to sit for about 1.5–2 hr to achieve equilibrium. The spectrum of each solution was then recorded from 600 to 350 nm using a Cary Model 15 recording spectrophotometer whose sample compartment was continuously purged with nitrogen to prevent fogging of the cell. As quickly as possible after recording the spectrum, the pH of each solution was determined using a Beckman Research Model pH meter using a glass electrode and a calomel reference electrode containing 4 *M* NaCl. The observed readings were corrected using the empirical correction factors determined by Kolczynski, Roth, and Shanley for aqueous hydrogen peroxide solutions.[6]

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(1) Taken from the B.S. Honors Thesis of B. L. B., East Texas State University, 1972; presented, in part, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) Reviews of, and extensive references to, earlier work on chromium peroxide systems can be found in (a) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964); (b) S. B. Brown, P. Jones, and A. Suggett, *Progr. Inorg. Chem.*, **13**, 159 (1970).

(3) D. Quane and B. Bartlett, *J. Chem. Phys.*, **53**, 4404 (1970).

(4) R. Stomberg, *Ark. Kemi*, **24**, 283 (1965).

(5) W. P. Griffith, *J. Chem. Soc.*, 3948 (1962).

(6) J. R. Kolczynski, E. M. Roth, and E. S. Shanley, *J. Amer. Chem. Soc.*, **79**, 531 (1957).

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The chromium concentration of these solutions was determined spectrophotometrically using a Beckman DU spectrophotometer[8] after peroxide decomposition was completed. In order to ensure complete oxidation of any chromium(III) to chromate, the solutions were made basic and sodium peroxide was added. Decomposition of excess sodium peroxide was ensured by boiling the solution.

Peroxide Determination. Aliquots of the stock peroxide solutions used in preparing the chromate solutions were set aside at 0° and the peroxide contents determined by titration with potassium permanganate. The titration was done *after* the spectra of the chromate solutions had been obtained, in order to obtain comparable degrees of peroxide decomposition. It is expected that the peroxide contents so determined are slightly higher than that actually present in the chromate systems, since some chromium-catalyzed peroxide decomposition cannot be avoided even at 0°. The amount of decomposition (judging by oxygen evolution) is small and no serious error due to this should be present.

Results

Typical plots of molar absorptivity *vs.* wavelength are shown in Figure 1. The spectrum of the "neutral" solution corresponds to that previously reported for the diperoxy species,[3,5] with a maximum near 500 nm and a minimum at 425 nm; the tetraperoxychromate shows no absorption maximum in the visible. The presence of an isosbestic point indicates that these two species are the only chromate-containing species present in any appreciable concentration over the pH range studied and suggests the existence of an equilibrium relationship between them. Similar results are obtained at peroxide concentrations from 7 to 50%, at ionic strengths of 0.2 *M* and 1.0 *M*, and in solutions in which the ionic medium was not controlled. At low peroxide concentrations (below about 10%) the isosbestic is not clearly marked, probably due to the presence of nonperoxychromate species. At higher peroxide concentrations (above 50%) oxygen evolution becomes too great to permit obtaining satisfactory spectra.

Figure 2 shows a plot of the absorptivity ratio (eq 5) calculated from the spectra of Figure 1. The points give a reasonably straight line with a slope equal to 1.88 and an intercept indicating that $\mathrm{p}K_a = 2\ \mathrm{pH} = 14.0$. Table I shows the values of the slopes and apparent p*K*'s for all sets of spectra run. In all cases the line slopes and intercepts were calculated using a least-squares program on a Hewlett-Packard Model 9100 A desk calculator. In some cases the points for the two wavelengths resulted in two distinctly separate lines. When this occurred, the average value of the intercept was used in calculating $\mathrm{p}K_a$.

Discussion

If eq 2 correctly represents the equilibrium reaction, then the thermodynamic equilibrium constant is given by

$$K_T = \frac{(a_{\mathrm{CrO_8}^{3-}})(a_{\mathrm{H_2O}})(a_{\mathrm{H^+}})^2}{(a_{\mathrm{HCrO_6}^-})(a_{\mathrm{H_2O_2}})^{3/2}} \qquad (6)$$

If ideal solution behavior for the aqueous peroxide mixture ($\gamma_{\mathrm{H_2O_2}} = \gamma_{\mathrm{H_2O}} = 1$) is assumed, then, after taking the logarithm of both sides, rearranging, and substituting for equivalent terms, eq 6 becomes

$$\mathrm{p}K_T = \mathrm{p}K_a - \log(\gamma_{\mathrm{CrO_8}^{3-}}/\gamma_{\mathrm{HCrO_6}^-}) - \log\ [\mathrm{H_2O}]/[\mathrm{H_2O_2}]^{3/2} \qquad (7)$$

where $\mathrm{p}K_a$ has the same meaning as in eq 3 and 4, and [H_2O] and [H_2O_2] represent the mole fractions of these substances. Since the concentrations of water and hydrogen peroxide were constant for each set of spectra, and can be calculated, the apparent p*K*'s can be corrected by subtraction of the term $\log([\mathrm{H_2O}]/[\mathrm{H_2O_2}]^{3/2})$. This was done with the results shown in the last column of Table I. This procedure greatly improves the agreement of the several p*K*'s for a

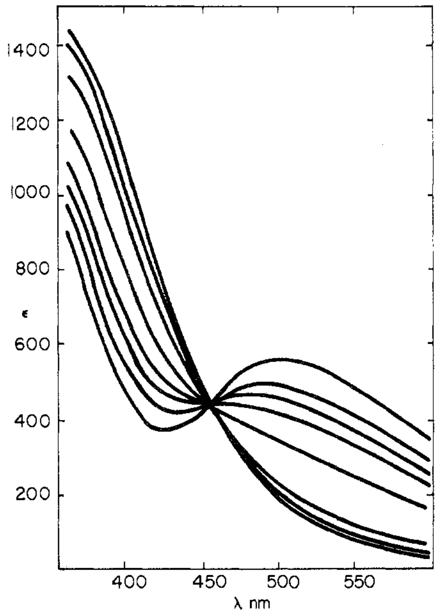

Figure 1. Variation in visible spectra of basic chromium peroxide solutions with changing pH. Series of solutions in 22.7% H_2O_2, 0.2 *M* total ionic strength.

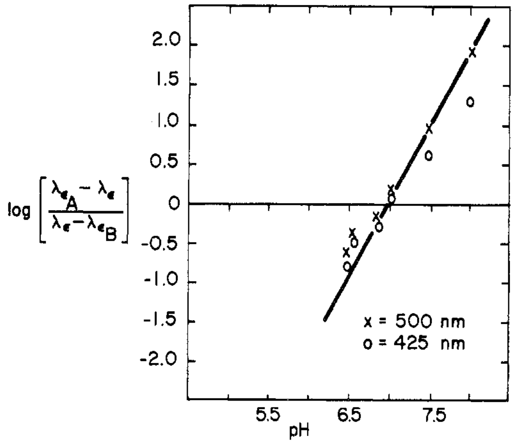

Figure 2. Plot of eq 5 for the series of spectra shown in Figure 1.

Table I. Equilibrium Data from Spectroscopic Measurements

Ionic medium	H_2O_2, %	Slope 425 nm	Slope (combined)	Slope 500 nm	$\mathrm{p}K_a$	$\mathrm{p}K_{\mathrm{cor}}$[a]
Uncontrolled	52.8		(2.2)		14.4	14.4
	30.1		(2.1)		14.4	13.4
	16.3		(2.2)		15.6	14.1
	12.1		(2.4)		15.7	14.0
						Av 13.9
0.2 *M* $NaClO_4$	27.9	1.8		1.7	14.0	12.9
	22.7		(1.9)		14.0	12.8
	22.1	2.0		1.8	13.4	12.1
	15.7		(1.9)		13.8	12.5
	13.8		(2.3)		14.3	12.7
	6.95	2.2		2.2	15.0	12.9
						Av 12.6
1.0 *M* $NaClO_4$	26.9		(1.8)		11.8	10.7
	16.7		(1.8)		12.4	10.9
	11.2		(2.0)		12.8	10.9
						Av 10.8

[a] $\mathrm{p}K_{\mathrm{cor}} = \mathrm{p}K_a - \log([\mathrm{H_2O}]/[\mathrm{H_2O_2}]^{3/2})$.

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(8) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).

given ionic strength, and this fact strongly suggests that eq 2 is in fact the equation governing the equilibrium. Subtraction of log $(1/[H_2O]^{1/2})$, the equivalent correction factor for reaction scheme 1, does not give similar agreement.

That eq 2 correctly represents the equilibrium in turn implies that the structure proposed by Griffith[5] for the violet perchromate, $HCrO_6^-$, is correct. Any of the other possible structures which have been proposed (*e.g.*, $M^IOCrO_4 \cdot H_2O$, $M^IH_2CrO_7$, and the binuclear $Cr_2O_{12}{}^{2-}$)[5] would have resulted in different overall proton, water, peroxide, and, in the case of the binuclear complex, chromium stoichiometries.[9] A recent report[10] has claimed that a product isolated from neutral chromium peroxide systems has the formula K_2HCrO_6, although it was too unstable for accurate analysis. The results reported here are inconsistent with the possibility that this formula correctly represents the species existing in neutral chromium peroxide solutions. The same paper has also reported an additional chromium peroxide, K_3CrO_7, isolated from peroxide solutions of intermediate basicity. The present spectrophotometric study, indicating that $CrO_8{}^{3-}$ and $HCrO_6^-$ are the only chromium peroxy species present in any appreciable concentration in basic aqueous hydrogen peroxide solutions, casts doubt on the possibility of isolating a triperoxy compound. Other work in this laboratory[11] has failed to obtain any product other than tetraperoxychromate under the conditions reported in ref 10.

The p*K*'s listed in Table I are still not thermodynamic equilibrium constants, as they include the term log $\gamma_{CrO_8{}^{3-}}/\gamma_{HCrO_6{}^-}$. There are various expressions allowing, at least, an approximate calculation of the values for activity coefficients. One of the most accurate is the semiempirical relationship of Davies.[12] This law states that for any ionic species, *i*, present in a solution of ionic strength μ, the activity coefficient is given by the following equation

$$\log \gamma_i = -\left(\frac{e^2}{\epsilon kT}\right)^{3/2} \sqrt{\frac{2\pi N}{1000}}\, Z_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\,\mu\right) \qquad (8)$$

where *T* is the absolute temperature, ϵ is the dielectric constant of the solvent, e is the electronic charge, *k* is the Boltzmann constant, and *N* is Avogadro's number. This law is valid to within 1% in solutions of ionic strength below 0.01 *M* and thus can readily be applied to those solutions which have thus far been referred to as of uncontrolled ionic strength. The actual ionic strength of these solutions lies between 10^{-2} and 10^{-3} *M*. Since the values of the dielectric constants of water and hydrogen peroxide are so close ($\epsilon = 88$ for H_2O, $\epsilon = 84$ for H_2O_2 at 0°),[13] it was assumed that for all solutions concerned, $\epsilon = 87$. Upon substitution of the appropriate values for the ionic strength ($10^{-3} < \mu < 10^{-2}$), the additional correction term for the pK_{cor} is found to be bounded by $0.12 \leqslant$ correction term < 0.35. Thus, it may be concluded that the thermodynamic p*K* lies between 14.0 and 14.2 for the uncontrolled ionic strength studies.

Furthermore, the variation in the corrected p*K*'s of Table I as a function of total ionic strength can be understood in terms of eq 8. Calculations of the correction term for those solutions of 0.200 *M* ionic strength yield a value of approximately 1.1. If this value is added to the pK_{cor}'s of Table I for such solutions, it gives an approximate value of 13.9 for the thermodynamic constant, which is in good agreement with the values calculated for the solutions of uncontrolled ionic strength. Inherent inaccuracy of the Davies law in solutions above 0.5 *M* total ionic strength[12] prevents a similar application to the data for the 1 *M* solutions; however, it is a logical assumption that the deviation of these p*K*'s from about 14.0 is accounted for by the variation in the activity coefficients of tetraperoxychromate and diperoxychromate.

Registry No. $CrO_8{}^{3-}$, 12526-97-5; $HCrO_6^-$, 40330-52-7.

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[9] A referee has suggested, correctly, that this conclusion assumes that the tetraperoxychromate ion, in solution, has the same composition as in the solid state, namely $CrO_8{}^{3-}$. If this is not the case then the conclusion as to the structure of the diperoxy species must be changed. It is clear, however, that (1) the two species are related by a reaction involving two protons and (2) *both* must be mononuclear or *both* binuclear (otherwise straight line plots would not be obtained).

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Mossbauer Spectroscopy and Electron Paramagnetic Resonance Study of Some Iron(III)-Tris(diimine) Complexes

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A recent interpretation of the electron paramagnetic resonance (epr) and Mossbauer spectral data of potassium ferricyanide reveals that $\langle r^{-3}\rangle_{t_{2g}}$ and the spin-orbit coupling constant are reduced to about 15% of their free ion values.[1] We have examined the electronic structure of some tris(1,10-phenanthroline) (phen) and tris(2,2′-bipyridyl) (bipy) complexes of iron(III) in order to determine if extensive delocalization is typical of low-spin iron(III) complexes.

Experimental Section

Preparation of Complexes. The complexes $Fe(phen)_3(PF_6)_3$ and $Fe(bipy)_3(PF_6)_3$ were prepared by the methods of DeSimone and Drago.[2] $Fe(phen)_3(ClO_4)_3$ and $Fe(bipy)_3(ClO_4)_3$ were prepared by the methods of Burstall and Nyholm.[3]

Physical Measurements. The Mossbauer spectrometer and associated cryostat have been described previously.[1] The spectra were fit with a least-squares fitting program and the accuracy was determined statistically.[4] Epr spectra were measured at X-band frequencies at 77°K. The magnetic field was measured with a gaussmeter and checked with DPPH.

Results

Epr. Spectra were obtained with pure powdered samples of $Fe(phen)_3(PF_6)_3$, $Fe(bipy)_3(PF_6)_3$, $Fe(phen)_3(ClO_4)_3$, and

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