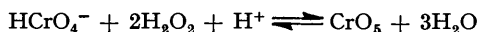


## 796. Blue Perchromic Acid.

By D. F. EVANS.

The formula of blue perchromic acid has been investigated by low-temperature spectrophotometry in aqueous methyl alcohol (Job's method), and, more satisfactorily, by rapid spectrophotometry of the equilibria in aqueous solution at 10° c. Both methods indicate that the basic formula is CrO<sub>5</sub>, thus agreeing with Glasner and Steinberg's work,<sup>1a</sup> and not HCrO<sub>5</sub> as originally claimed by Glasner.<sup>1b</sup> The predominant equilibrium in dilute aqueous solution is



with an equilibrium constant of  $5.4 \times 10^7$  at 10° and ionic strength 0.09.

A stable 1:10-phenanthroline-perchromic acid complex has been prepared whose analysis provides additional evidence for the formula CrO<sub>5</sub>.

The infrared spectra of the pyridine- and the 1:10-phenanthroline-perchromic acid complexes are also consistent with this formula.

Analysis of the brown peroxide CrO<sub>4</sub>·3NH<sub>3</sub> indicates that it is a diperoxide of quadrivalent chromium, in agreement with previous magnetic evidence, and not a monoperoxide of hexavalent chromium.

THERE has been considerable controversy concerning the composition of the well-known blue perchromic acid which is obtained on treating acidic solutions of chromates with hydrogen peroxide.<sup>2</sup> This compound quickly decomposes in aqueous solution, but can be extracted into organic solvents such as ethers, esters, alcohols, ketones, and nitriles, and these solutions are much more stable. If an ethereal solution is treated with organic bases such as pyridine, relatively stable solid adducts are obtained.

The early analytical work of Riesenfeld and his collaborators<sup>3</sup> indicated that the pyridine complex was C<sub>5</sub>H<sub>5</sub>N·HCrO<sub>5</sub>, corresponding to HCrO<sub>5</sub> for the acid. However, Schwarz and Giese<sup>4</sup> decomposed the pyridine complex with sulphuric acid and the blue ethereal solution of perchromic acid with silver oxide; they measured the amount of oxygen evolved in both cases, and also treated the pyridine complex with permanganate. Their results agreed much more closely with the alternative formula CrO<sub>5</sub>, a diperoxide of hexavalent chromium. Further evidence for this formulation is provided by (1) the thermochemical and spectrophotometric work of Rivenq<sup>5</sup> and Rumpf<sup>6</sup> which indicates that the blue perchromic acid is formed from two molecules of hydrogen peroxide and one molecule of chromate, and (2) the small paramagnetic moment of the pyridine complex at room temperature,<sup>7</sup> which is much less than that expected for one unpaired electron, and is similar to, though rather larger than, that shown by the chromates themselves (temperature-independent paramagnetism).

Glasner,<sup>1b</sup> by means of a filter photometer, studied the equilibrium between hydrogen peroxide, chromic acid, and blue perchromic acid in alcoholic solution at 0°, and concluded that the last compound is formed from one molecule of chromic acid and 1½ molecules of hydrogen peroxide, and hence is HCrO<sub>5</sub>. We have now studied the problem in a variety of ways, all of which indicate that the basic formula of blue perchromic acid is in fact CrO<sub>5</sub>, as has very recently been shown also by Glasner and Steinberg.<sup>1a</sup>

<sup>1</sup> (a) Glasner and Steinberg, *J.*, 1957, 2569; (b) Glasner, *J.*, 1950, 2795.

<sup>2</sup> Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, 1006.

<sup>3</sup> Riesenfeld, *Ber.*, 1908, **41**, 3946.

<sup>4</sup> Schwarz and Giese, *Ber.*, 1932, **65**, 871.

<sup>5</sup> Rivenq, *Bull. Soc. chim. France*, 1945, **12**, 283.

<sup>6</sup> Rumpf, *Ann. Chim. (France)*, 1937, **8**, 456.

<sup>7</sup> (a) Bhatnagar, Prakash, and Hamid, *J.*, 1938, 1428; (b) Asmussen, "Magnetochemical Investigations of Inorganic Complexes," J. Gjellerups, Copenhagen, 1944, 129 *et seq.*; (c) Klemm and Werth, *Z. anorg. Chem.*, 1933, **216**, 127.

## EXPERIMENTAL

*Materials.*—"AnalaR" potassium dichromate, hydrogen peroxide (100 vol.), and perchloric acid (72%) were used. Sodium chromate was recrystallised from water. In any series of experiments the ionic strength was kept approximately constant by the addition, if necessary, of sodium perchlorate.

The pyridine complex of perchromic acid was prepared by Wiede's method,<sup>8</sup> and dried in a vacuum desiccator ( $H_2SO_4$ ) for several days to remove the last traces of pyridine which seem to be tenaciously retained (Found: Cr, 24.4. Calc. for  $C_5H_5N, CrO_5$ : Cr, 24.7%). A few days later the sample exploded spontaneously.

The 1:10-phenanthroline complex was obtained similarly by adding saturated ethereal 1:10-phenanthroline to a cooled solution of perchromic acid in ether. The light blue powder was filtered off, thoroughly washed with ether, and dried in a vacuum desiccator ( $H_2SO_4$ ) (Found: C, 47.3, 47.1; H, 2.69, 2.63; N, 9.15, 9.4; Cr, 16.1.  $C_{12}H_8N_2, CrO_5$  requires C, 46.1; H, 2.58; N, 9.0; Cr, 16.7.  $C_{12}H_8N_2, HCrO_5$  requires H, 2.88%). Unlike the pyridine complex it is stable for a long time at room temperature, non-explosive, and almost insoluble in most organic solvents. It is appreciably soluble in acetone and the solution can be boiled without

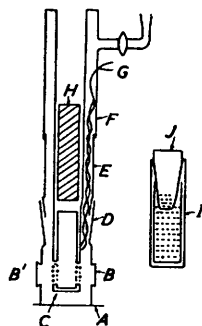


FIG. 1.

- A, Metal base plate to fit spectrometer 5 cm. cell compartment.  
 B, B', Fused silica windows.  
 C, Copper frame to hold stoppered cell. A little Silicone grease provides good thermal contact and a sliver of cork holds the stopper in place. The stoppered cell is vacuum-tight, and hence no evaporation can occur when the assembly is evacuated.  
 D, E, B.34 socket and cone, silvered internally.  
 F, Brass Dewar flask.  
 G, Copper-constantan thermocouple.  
 H, Copper block to increase heat capacity.  
 I, Unicam 1 cm. stoppered cell.  
 J, Hollow stopper.

All glass-metal and glass-silica joints were made with "Araldite."

undue decomposition. However, it resembles the pyridine complex in reacting with concentrated sulphuric acid, to give oxygen and  $Cr^{3+}$ , and with (boiling) alkali, to give oxygen and  $CrO_4^{2-}$ .

$CrO_4 \cdot 3NH_3$  was prepared by Riesenfeld's<sup>9</sup> method (Found: Cr, 31.3. Calc. for  $CrO_4 \cdot 3NH_3$ : Cr, 31.1%). It was analysed for peroxidic groups by addition to excess of dilute potassium permanganate solution (3N in  $H_2SO_4$ ). Similar results were obtained in both the presence and absence of traces of manganous sulphate and ammonium molybdate as catalysts. When all the solid had dissolved, ferrous sulphate solution was added, and the excess back-titrated with potassium permanganate.

Some difficulty was experienced in determining separately the  $Cr^{VI}$  produced in the presence of excess of permanganate,  $Cr^{3+}$ , and  $Mn^{2+}$ . Eventually a more convenient modification of Fales and Roller's<sup>10</sup> method was used. The solution obtained after the  $CrO_4 \cdot 3NH_3$  had dissolved was diluted with an equal volume of water, potassium bromide solution added, and the bromine liberated by the permanganate removed with excess of phenol. The residual dichromate was then estimated iodometrically as usual. Blank tests showed that this method was quite accurate even in the presence of a large excess of permanganate.

*Spectroscopic Measurements.*—Ultraviolet and visible spectroscopic measurements were made on a Unicam S.P. 500 spectrophotometer with cells of length 2 mm.—4 cm.

*Low-temperature spectra.* The low-temperature cell shown in Fig. 1 is an adaptation of the well-known conduction-cooling type. Standard "Unicam" 1 cm. stoppered silica cells are used, and the stopper greased with Silicone grease (for polar solvents such as methyl alcohol or water) or glycerol-based greases such as glycerol-mannitol-dextrin<sup>11</sup> (for non-polar solvents). The low-temperature spectrum of blue perchromic acid was studied in 87% (v/v) methyl

<sup>8</sup> Wiede, *Ber.*, 1897, **30**, 2178.

<sup>9</sup> Riesenfeld, *Ber.*, 1905, **38**, 4068.

<sup>10</sup> Fales and Roller, *J. Amer. Chem. Soc.*, 1929, **51**, 345.

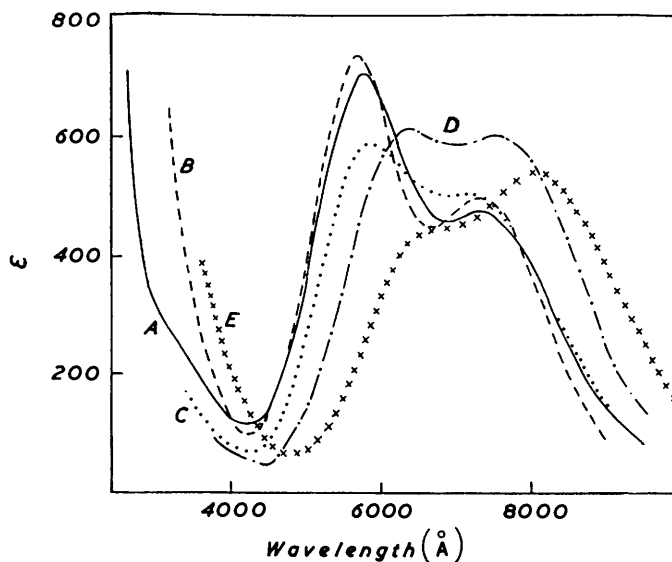
<sup>11</sup> Meloche and Fredrick, *J. Amer. Chem. Soc.*, 1932, **54**, 3264.

alcohol-water (0.1M in perchloric acid). The stopper contained a known volume (0.13 c.c.) of a freshly prepared methyl-alcoholic solution of sodium chromate, and the hydrogen peroxide and perchloric acid solution was placed in the silica absorption cell. After the apparatus had been pumped out and cooled to about  $-40^\circ$  with liquid air, the two solutions were mixed by inverting the whole assembly several times and shaking. The blue colour slowly formed, and after a few minutes the optical density at  $-40^\circ$  remained constant to within 1% for at least 1 hr. The solution was still fluid, though very viscous, at  $-120^\circ$ . Corrections were applied for the absorption of the alcohol and for the contraction of the solution on cooling. The temperature of the cell was kept constant  $\pm 2^\circ$  by additions of liquid air. After evacuation for a few minutes with a mercury-vapour pump, the apparatus could be removed from the vacuum line and spectroscopic measurements carried out for several hours without repumping. Blank tests showed that the temperature of the solution was within  $1^\circ\text{C}$  of that of the copper framework, even at  $-183^\circ$  (liquid-oxygen cooling).

*Rapid spectrophotometric measurements.* Owing to the instability of perchromic acid in aqueous solution at  $10^\circ$ , it was necessary to read the optical density of the solution as soon as possible after mixing the reactants, and at definite intervals shortly afterwards. The readings were then extrapolated back to the time of mixing (the formation of the blue compound is virtually instantaneous at  $10^\circ$ ). A small correction was applied for the absorption of the  $\text{Cr}^{3+}$  produced.

In practice, a cell containing an acidified solution of potassium dichromate and a perforated Polythene paddle-type stirrer was placed in a cell holder at  $10^\circ \pm 0.3^\circ$ . A known small volume of hydrogen peroxide was quickly squirted in from a constant-volume pipette, the stirrer removed, and the optical density of the solution at  $5800 \text{ \AA}$  recorded. A reading could be taken within 10 sec. of first adding the hydrogen peroxide. The subsequent optical densities were

FIG. 2.



- A,  $\text{CrO}_5$  in ether at  $10^\circ$ .  
 B,  $\text{Py.CrO}_5$  in benzene at ca.  $22^\circ$ .  
 C,  $\text{CrO}_5$  in 87% methyl alcohol at  $-40^\circ$ .  
 D,  $\text{CrO}_5$  in 87% methyl alcohol at  $-120^\circ$ .  
 E, 1 : 10-Phenanthroline,  $\text{CrO}_5$  in acetone at ca.  $22^\circ$ .

obtained by setting the transmission dial at various values, and recording the times at which the meter needle crossed the zero. In general, except for very fast or slow reactions, the random errors in any one run did not usually exceed 0.001 unit in optical density and 0.5 sec. in time. Good first-order plots were normally obtained for the initial part of the reaction. The molar extinction coefficient of perchromic acid at  $5800 \text{ \AA}$  was found by steadily increasing the concentration of hydrogen peroxide. At ratios of  $[\text{H}_2\text{O}_2]/[\text{Cr}^{\text{VI}}]$  of about 10 : 1 or greater a constant value of 500 was obtained. As Beer's law was obeyed ( $\pm 1\%$ ) over a wide range

of concentration, the initial concentration of perchromic acid in any solution could easily be calculated. The absorption of the  $\text{HCrO}_4^-$  ion at  $5800 \text{ \AA}$  is extremely small.

#### RESULTS AND DISCUSSION

*Formula of Perchromic Acid.*—(i) *Job's method of continuous variations.*<sup>12</sup> The interaction of hydrogen peroxide and  $\text{Cr}^{\text{VI}}$  was first studied at  $-40^\circ$  in 87% methyl alcohol-water (0.1M in perchloric acid). The absorption spectrum of perchromic acid under these conditions is shown in Fig. 2, and optical-density measurements were made at 5800 and 7300  $\text{\AA}$ . Unfortunately both monomeric and dimeric species are present in aqueous acidic solutions of chromates<sup>13,14</sup> (predominantly the  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions in not-too-acid solutions), and this is presumably also true in alcoholic solutions. This point, incidentally, was neglected in earlier work by Glasner.<sup>15</sup> However, the equilibrium constant for the formation of perchromic acid is so high at  $-40^\circ$  that well-defined maxima at  $[\text{H}_2\text{O}_2]/[\text{Cr}^{\text{VI}}]$  ratios of approximately 2 : 1 were obtained on plotting optical density against this function, either entirely monomeric or entirely dimeric species being assumed. The basic formula  $\text{CrO}_5$  requires  $[\text{H}_2\text{O}_2]/[\text{Cr}^{\text{VI}}]$  to be 2 : 1, and the alternative formula  $\text{HCrO}_5$  1.5 : 1.

(ii) *Aqueous equilibria.* It is theoretically more satisfactory to work with aqueous solutions, since the equilibrium  $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$  has been carefully studied<sup>13,14</sup> and it is possible to work under conditions where the predominant species is the  $\text{HCrO}_4^-$  ion. Also, the equilibrium constant for the formation of perchromic acid is much smaller, and can therefore be more easily evaluated. The practical difficulty arising from the much more rapid decomposition of perchromic acid in aqueous solution at  $10^\circ$  was largely overcome by using our extrapolation procedure.

The results so obtained for various concentrations of  $\text{Cr}^{\text{VI}}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}^+$  are shown in the Table for ionic strength 0.09. Equilibrium "constants" were calculated by assuming either  $\text{CrO}_5$  ( $K_1 = [\text{CrO}_5]/\{[\text{H}_2\text{O}_2]^2[\text{HCrO}_4^-][\text{H}^+]\}$ ) or  $\text{HCrO}_5$  ( $K_2 = [\text{HCrO}_5]/\{[\text{H}_2\text{O}_2]^{3/2}[\text{HCrO}_4^-][\text{H}^+]\}$ ) as the basic formula of perchromic acid, and are given in the last two columns. The average values, with the standard deviations, are

$10^3[\text{Cr}^{\text{VI}}]$ initial (M)	$10^3[\text{H}_2\text{O}_2]$ initial (M)	$10^3[\text{H}^+]$ final (M)	$10^3$ [perchromic acid] (M)	$10^{-7}K_1$	$10^{-5}K_2$
0.696	1.392	1.73	{ 0.267 } { 0.270 }	5.3 <sub>0</sub>	1.25
0.696	1.392	3.48	0.342	5.7 <sub>9</sub>	1.12
0.696	2.09	3.47	0.487	5.5 <sub>9</sub>	1.40
0.348	1.052	3.50	0.167	5.3 <sub>9</sub>	1.21
0.928	1.856	3.47	0.518	5.7 <sub>2</sub>	1.08
1.392	2.79	3.43	{ 0.889 } { 0.897 }	5.64	1.02
0.464	0.928	3.50	0.173	5.2 <sub>3</sub>	1.03
0.696	2.79	3.47	0.574	5.1 <sub>0</sub>	1.63
0.464	1.392	3.49	0.266	5.3 <sub>3</sub>	1.27
0.696	0.696	3.50	0.150	5.3 <sub>6</sub>	0.82 <sub>6</sub>

$10^{-7}K_1 = 5.44 \pm 0.23$  and  $10^{-5}K_2 = 1.18 \pm 0.22$ . Corrections were applied to allow for the presence of  $\text{Cr}_2\text{O}_7^{2-}$  ions, the data of Tong and King<sup>13</sup> and Davies and Prue<sup>14</sup> (extrapolated to  $10^\circ$ ) being used. Although these corrections are known only very approximately, since they were never greater than about 10% no serious errors are involved.

It can be seen that much more satisfactory equilibrium "constants" are obtained when it is assumed that the formula of blue perchromic acid is  $\text{CrO}_5$ . The scatter of the values is no greater than would be expected from the errors involved in the measurement of  $[\text{CrO}_5]$ , especially since the equilibrium constants are normally rather sensitive to this quantity.

<sup>12</sup> Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

<sup>13</sup> Tong and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.

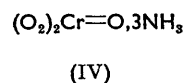
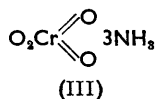
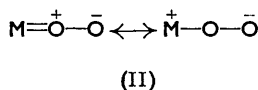
<sup>14</sup> Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

(iii) *Analysis of the 1 : 10-phenanthroline complex.* It is very difficult to make an accurate hydrogen analysis of the pyridine complex of perchromic acid, because of its extreme instability (Wiede's analysis<sup>8</sup> indicated slightly more hydrogen than corresponds to  $\text{Py}\cdot\text{HCrO}_5$ ). For the 1 : 10-phenanthroline complex, prepared in the hope that it would prove to be more stable, it was in fact found that hydrogen, carbon, and nitrogen analyses could be carried out normally, the hydrogen analysis agreeing more closely with the formula  $\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{CrO}_5$  than with  $\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{HCrO}_5$ . It is also significant that the H, C, and N analyses are all slightly high, and the Cr analysis slightly low, probably owing to slight contamination with excess of 1 : 10 phenanthroline; in agreement with this the ratios H/C and H/N are almost exactly those in 1 : 10-phenanthroline (Found: H/C, 0.0563; H/N, 0.288. Calc. for  $\text{C}_{12}\text{H}_8\text{N}_2$ : H/C, 0.0560; H/N, 0.288).

(iv) *Infrared spectra.* The infrared spectra of the pyridine and 1 : 10-phenanthroline complexes, and also of pyridinium nitrate ( $\text{PyH}^+\text{NO}_3^-$ ) and  $\text{Ag}(\text{Py})_2\text{NO}_3$ , were measured in Nujol or hexachlorobutadiene mulls over the region 2—15  $\mu$ . If the basic formula of perchromic acid is  $\text{HCrO}_5$ , then the pyridine and the 1 : 10-phenanthroline complex will almost certainly\* contain either an OH or an  $\text{N}^+\text{—H}$  group. However, in the region 2—4  $\mu$  the infrared spectrum of the pyridine complex closely resembled those of pyridine itself and also  $\text{Ag}(\text{Py})_2\text{NO}_3$ , and was very different from that found for pyridinium nitrate. The very broad  $\text{N}^+\text{—H}$  band around 3.5  $\mu$  shown by the latter compound, and also any band that could be assigned to an O—H stretching frequency, were both absent. Similarly the spectrum of the 1 : 10-phenanthroline complex around 3  $\mu$  was very similar to that of 1 : 10-phenanthroline itself. These results therefore provide additional evidence for the basic formula  $\text{CrO}_5$ .

*Ultraviolet and Visible Spectra.*—The ultraviolet and visible spectra of  $\text{CrO}_5$  and its derivatives under various conditions are shown in Fig. 1. Except for the 1 : 10-phenanthroline complex the spectra are very similar, with two maxima ( $\epsilon \approx 500$ ) at about 5800 Å and 7500 Å. Maxima at 5800 Å and  $\sim 7500$  Å were also observed by Glasner and Steinberg<sup>16</sup> for  $\text{CrO}_5$  dissolved in ethyl acetate.

It is noteworthy that the peroxides of other transition metals in Groups IV, V, and VI such as Ti, V, Nb, and Mo have absorption bands with molar extinction coefficients of the same order of magnitude ( $\sim 10^3$ ). These bands are intermediate in intensity between the very weak ones associated with  $d\text{—}d$  transitions [*e.g.*,  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ], and the very strong ones which are normally regarded as essentially charge-transfer in type (*e.g.*,  $\text{FeCNS}^{2+}$ ).<sup>17</sup> It seems likely that appreciable charge-transfer (from the  $\text{O}_2$  group to the metal atom) is involved, since for the peroxides of Group IV, V, and VI elements there is a fairly good correlation between the position of the absorption maximum and the oxidising power of the metal valency state involved.



*Structure of Perchromic Acid.*—The peroxide grouping in  $\text{CrO}_5$  and other transition-metal peroxides is frequently written as (I).<sup>18</sup> It was pointed out by Sidgwick<sup>2</sup> that this structure involves considerable strain, and he accordingly suggested an alternative formulation (II). However, the structure of the red peroxide  $\text{K}_3\text{Cr}^{\text{V}}\text{O}_8$  has been examined by X-ray diffraction (powder photograph).<sup>19</sup> The four  $\text{O}_2$  groups are arranged round the central chromium atom in a manner reasonably consistent with structure (I) but not with structure (II), although the formation of 8 covalent bonds by chromium seems very

\* It is just possible that a hydrogen atom could be associated with the metal atom, as in  $\text{Co}(\text{CO})_4\text{H}$  and similar compounds.<sup>16</sup>

<sup>15</sup> Cotton and Wilkinson, *Chem. and Ind.*, 1956, 1305.

<sup>16</sup> Glasner and Steinberg, *Analyt. Chem.*, 1955, 27, 2008.

<sup>17</sup> Orgel, *Quart. Rev.*, 1954, 8, 422.

<sup>18</sup> Barnett and Wilson, "Inorganic Chemistry," Longmans, London, 1953, p. 421.

<sup>19</sup> Wilson, *Arkiv Kemi, Min., Geo.*, 1942, 15, B, No. 5.

unlikely. Clearly, an accurate X-ray analysis of a peroxide such as  $\text{Py}, \text{CrO}_5$  would be of considerable interest.

The nature of the bonding between the two components in  $\text{Py}, \text{CrO}_5$  is also not known. This compound is normally written <sup>2</sup> as  $\text{Py} \rightarrow \text{CrO}_5$ , with a co-ordinate link between the pyridine and the central chromium atom. It seems more likely, however, that it is merely a particularly strong Lewis acid-Lewis base (donor-acceptor) type of complex,<sup>20</sup> in which the  $\text{CrO}_5$  group as a whole acts as acceptor. It is significant that all the organic solvents in which  $\text{CrO}_5$  is soluble can function as Lewis bases.

*Structure of  $\text{CrO}_4 \cdot 3\text{NH}_3$ .*—This compound can be obtained as stable brown crystals from ammoniacal solutions of chromates in the presence of hydrogen peroxide, and several derivatives such as  $\text{K}_3[\text{CrO}_4(\text{CN})_3]$  are known.<sup>8, 21</sup> It is sometimes formulated as a monoperoxide (III) of hexavalent chromium, although magnetic measurements<sup>7a, b</sup> indicate the presence of two unpaired electrons, as expected for a diperoxide (IV) of quadrivalent chromium.

Decomposition of the peroxide group(s) with excess of acid permanganate should *increase* the oxidising capacity of the solution relative to ferrous ion by 1 equiv. per mole if formula (III) is correct, and decrease it by 3 equiv. if formula (IV) is correct. In three separate experiments, decreases of 2.92, 2.96, and 2.87 equiv. per mole were obtained, in good agreement with formula (IV). If the quadrivalent chromium merely disproportionated and did not react with the peroxide groups,  $\frac{2}{3}$  mole of  $\text{Cr}^{\text{III}}$  and  $\frac{1}{3}$  mole of  $\text{Cr}^{\text{VI}}$  would be produced. Analysis of the solution after decomposition of the excess of permanganate, however, indicated only about one third of the expected  $\text{Cr}^{\text{VI}}$ . This is clearly due to preferential reaction between the peroxide groups and the quadrivalent chromium in the acid solution, but will not affect the conclusions above.

The possibility that  $\text{CrO}_4 \cdot 3\text{NH}_3$  contains chromium atoms in two different valency states ( $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$ ), while not excluded by these measurements, seems very unlikely in view of its reactions and those of its derivatives. Moreover, this formulation agrees poorly with the magnetic evidence.

A fair number of quadrivalent chromium compounds are now known. Their comparative rarity can be attributed to the ready disproportionation into  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  which can occur, and which is probably largely due to the great stability of  $\text{Cr}^{\text{III}}$  complexes.

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<sup>20</sup> Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

<sup>21</sup> Wiede, *Ber.*, 1899, **32**, 378.