539. *The Formation and Constitution of the Perchromates.*

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Evidence is brought forward that the formulæ of the blue and the violet perchromate correspond to those given by Riesenfeld *et al.*. It is suggested that the ether-soluble blue perchromate is formed by addition of an HO_2 radical to chromium trioxide : $CrO_3 + HO_2 \rightleftharpoons HCrO_5$.

At a pH above 4·5, or on the addition of an excess of hydrogen peroxide, by which a reduction in the concentration of the chromic acid and consequently a rise in the pH is produced, the blue perchromate adds another molecule of hydrogen peroxide forming the violet perchromate : $HCrO_5 + H_2O_2 \rightleftharpoons H_3CrO_7$.

The quinquevalency of the chromium in the perchromates and the reduction of chromic acid by hydrogen peroxide in acid solution is thus considered to be due to the odd electron in the HO_2 radical. It is also considered that this radical is present in all hydrogen peroxide solutions owing to the equilibrium $3H_2O_2 \rightleftharpoons 2HO_2 + 2H_2O$.

Riesenfeld *et al.* (*Ber.*, 1905, **38**, 1885, 3380, 3578, 4068; 1908, **41**, 2826, 3536, 3941; 1914, **47**, 548) established that there are three series of perchromates which may be distinguished by their colours as blue, violet, and red, and may be represented by the typical formulæ $PyHCrO_5$ (Py = pyridine), KH_2CrO_7, and K_3CrO_8. The valency of these compounds is rather perplexing; Riesenfeld ascribed to them first septi- and later quinque-valency (" Lehrbuch der anorganischen Chemie," 1939, 2nd edn., p. 518).

Schwarz and Giese (*Ber.*, 1932, **65**, 871; 1933, **66**, 310; 1936, **69**, 575) concluded, on the evidence of oxidation power, that the pyridine complex is an addition compound of CrO_5 (the well-known, blue, ether-soluble perchromate), and that the formulæ of the other perchromates should be doubled ($K_2Cr_2O_{12},2H_2O$ and $K_6Cr_2O_{16}$), attributing sexivalency to each of these per-compounds. On the other hand, the X-ray diffraction (Wilson, *Arkiv Kemi, Min. Geol.*, 1941, **15**, *B*, No. 5, 7), the magnetic moment (Tjabbes, *Z. anorg. Chem.*, 1933, **210**, 385), and the isomorphism of the red perchromate K_3CrO_8 with K_3TaO_8 (Böhm, *Z. Krist.*, 1926, **63**, 319) indicate that the chromium in this case, at least, is quinquevalent and that the compound should be formulated as $K_3Cr(O_2)_4$. The constitution of the perchromates is therefore still in doubt and they are given quite different formulæ by various authors (Ephraim, " Inorganic Chemistry," 5th edn., p. 525).

Bobtelsky, Glasner, and Bobtelsky-Chaikin (*J. Amer. Chem. Soc.*, 1945, **67**, 966) reported the results of photometric measurements on the catalytic decomposition of hydrogen peroxide by chromic acid, and it is the purpose of the present paper to apply these and other data to the problem of the perchromates.

EXPERIMENTAL.

The Blue Perchromate.—When chromic acid is mixed with hydrogen peroxide in 80% ethyl alcohol at 0°, a blue colour develops which attains a maximum intensity after several minutes and then remains almost constant for some time. This stability had been noted by Wiede (*Ber.*, 1897, **30**, 2178; 1898, **31**, 516, 3139; 1899, **32**, 378), and in our experiments, too, scarcely any bubbles of oxygen were observed.

Measurements were made with a Hellige " panphotometer " and three colour filters, 530, 550, and 570 mμ., which showed slightly increasing extinctions in the order written. The extinction values of chromic acid solutions measured at these wave-lengths were small and were subtracted from the actual readings. The constant ratio of the three values thus obtained served as a control on the accuracy of the measurements as well as on any change in the hue of the solutions (for experimental details, see *J. Amer. Chem. Soc., loc. cit.*). Tables I and II show the maximum extinctions E (for a 10-mm. layer at 550 mμ.), as well as the equilibrium constants K_1, calculated as explained below, of two series of solutions containing various proportions of the reactants. From Table I, it may be seen that the extinction of the blue perchromate (Per), formed at a constant initial concentration of hydrogen peroxide in excess

TABLE I.*

Solutions : x ml. of 0·02069M-CrO_3 + 5 ml. of 0·0637M-H_2O_2 + 40 ml. of
96% EtOH ÷ (5 − x) ml. of H_2O.

x.	10^3E.	$\dfrac{[CrO_3]}{[Per]}$.	$10^3[H_2O_2]$.	10^5K_1.	x.	10^3E.	$\dfrac{[CrO_3]}{[Per]}$.	$10^3[H_2O_2]$.	10^5K_1.
1	260	0·115	5·81	5·09	3 †	768	0·134	4·73	4·36
2	506	0·146	5·29	5·62		(758)	(0·149)		(4·80)
	(516)	(0·124)		(4·77)	4	980	0·184	4·27	5·13
						(990)	(0·172)		(4·80)
								Mean	(5·05)

* For significance of data in parentheses, see p. 2796.
† 3 Ml. $CrO_3 = 1·241 \times 10^{-3}$M.

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TABLE II.

$10^3[H_2O_2]_i$	10^3E	$\dfrac{[CrO_3]}{[Per]}$	$10^3[H_2O_2]$	10^5K_1	$10^3[H_2O_2]_i$	10^3E	$\dfrac{[CrO_3]}{[Per]}$	$10^3[H_2O_2]$	10^5K_1
1·450	310	2·06	0·787	4·55	5·248	780	0·218	3·578	4·66
2·900	568	0·672	1·684	4·65	5·800	815	0·166	4·056	4·29
3·496	640	0·484	2·126	4·74	8·700	880	0·080	6·816	4·48
4·374	723	0·314	2·826	4·71				Mean	4·63

is proportional to the concentration of the chromic acid. The initial concentration of the chromic acid in the series of solutions presented in Table II was kept constant at $1·3536 \times 10^{-3}$M-CrO_3 and that of the hydrogen peroxide ($[H_2O_2]_i$) was varied, as shown. There is a steady increase in the extinction, which attains a maximum of $E = 0·950$ (for a 10-mm. layer of solution) at a molecular ratio of hydrogen peroxide to chromic acid of about 12 : 1 (see also figure). On further increase in the concentration of hydrogen

Extinction–time curves of blue and violet perchromates in 80% alcoholic solution.
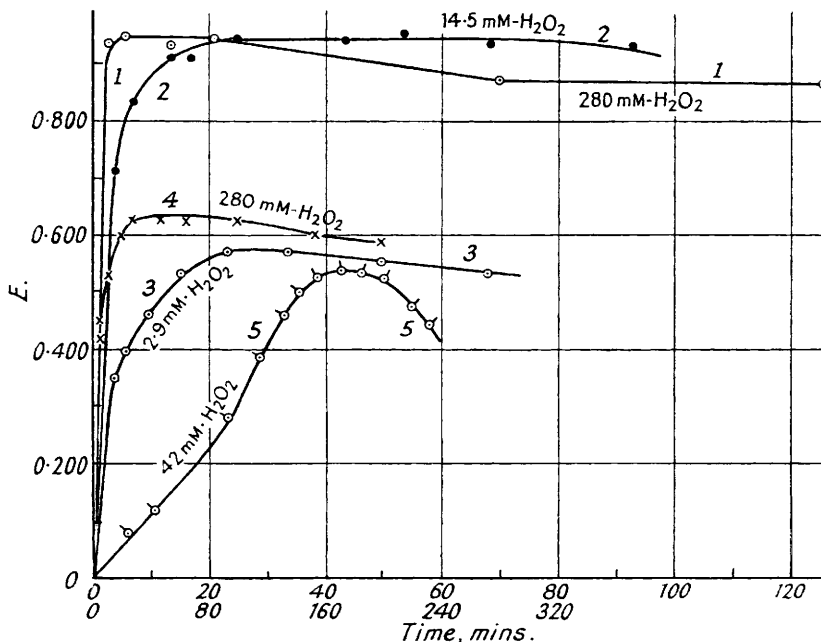
Curves 1, 2, 3 for 1·3536mM-CrO₃. Curves 4, 5 for 1·2094mM-Na₂Cr₂O₇ (*lower time scale*).

peroxide, even to 100-fold excess, the extinctions at 530 and 550 mμ. did not change, but those at 570 mμ. decreased; at the same time the solutions acquired a slight violet tint, indicating the presence of the violet perchromate. (The violet perchromate has a slightly higher extinction at 530 mμ. than at 550 mμ., and its optical density at 570 mμ. is low.) This should have been expected, for, with the consumption of the chromic acid the pH of the solution rises, creating conditions necessary for the formation of the violet perchromate. Therefore, it was assumed that in solutions containing more than 12-fold excess of hydrogen peroxide, the chromic acid initially present has been converted quantitatively into the blue perchromate and the extinction measured was that of a blue $1·3536 \times 10^{-3}$ M-perchromate solution.

Next, the value of x in the assumed equilibrium $CrO_3 + xH_2O_2 \rightleftharpoons CrO_3,(H_2O_2)_x$ was found by trial to be equal to 1·5, yielding the constants :

$$K_1 = [CrO_3][H_2O_2]^{1·5}/[Per] = 4·63 \times 10^{-5} \text{ (mean)},$$

as shown in the tables ; [Per] is the molar concentration of the blue perchromate as calculated from the extinction measured, [CrO_3] the initial concentration of chromic acid less the fraction converted into the per-compound, [H_2O_2] the initial concentration of hydrogen peroxide less one and a half times the concentration of the per-compound in moles.

Large deviations from the average, especially in Table I, were obtained in solutions containing a relatively big excess of hydrogen peroxide. These may be accounted for by experimental mistakes in the photometric readings ($\pm 0·01E$) as shown by the corrected data given in Table I in parentheses.

The Violet Perchromate.—It was proved in our previous paper (*loc. cit.*) that in dichromate solutions, or generally in solutions above pH 4·5, the violet perchromate is formed. When the reagents are mixed in alcoholic solutions in this case, too, extinction–time curves showing maxima were obtained, but the attainment of these maxima took rather a long time even at 18° (1—2·5 hours). Meanwhile the hydrogen peroxide decomposed and some of the alcohol was oxidised to acetaldehyde, though no evolution of oxygen

was observed. Therefore the concentration of the hydrogen peroxide at the point of maximum extinction cannot be calculated, though the symmetry of the extinction curves allows one to assume that just half of the original amount of hydrogen peroxide has been consumed.

Treating a $1 \cdot 2094 \times 10^{-3}$M-sodium dichromate solution in 80% alcohol with a very large excess (100-fold) of hydrogen peroxide, and measuring the extinction of a 5-mm. layer with a 530 mμ. filter, gave the value $E = 0 \cdot 632$. This extinction did not increase on a further addition of hydrogen peroxide and remained constant for a long time, giving, unlike the solution with lower concentrations of hydrogen peroxide, an extinction–time curve with a steady maximum ; the figure shows a number of typical curves. Therefore it was assumed that this is the extinction of the violet perchromate corresponding to the above concentration of dichromate.

The $E_{max.}$ values of two series of solutions (the concentration of dichromate being varied in one case, and that of hydrogen peroxide in the other), together with the calculated equilibrium constants K_2, are given in Tables III and IV.

TABLE III.			
$4 \cdot 200 \times 10^{-2}$M-H$_2O_2$; 18°.			
10^3[Na$_2$Cr$_2$O$_7$]$_i$.	E.	$\dfrac{[Cr_2O_7'']^{0 \cdot 5}}{100[Per]^2}$.	K_2.
1·2094	0·550	113	0·723
1·8141	0·720	110	0·703
2·4188	0·850	106	0·681
3·0235	0·938	109	0·695
3·6282	1·010	110	0·705
		Mean	0·702

TABLE IV.		
$2 \cdot 4188 \times 10^{-3}$M-Na$_2Cr_2O_7$; 18°.		
10^2[H$_2$O$_2$]$_i$.	E.	K_2.
2·657	0·526	0·754
4·212	0·830	0·735
5·616	0·995	0·827
7·020	1·135	0·768
	Mean	0·752

As may be seen in Table III, a 3-fold increase in the concentration of the dichromate less than doubles the extinctions. This suggests that the reaction with the hydrogen peroxide is preceded by dissociation of the dichromate. This surmise is confirmed by the constancy of the quotient $[Cr_2O_7'']^{0 \cdot 5}/[Per]^2$, indicating, also, that the oxidation of the alcohol is bimolecular with respect to the violet perchromate.

At the point of maximum extinction, the velocity of formation of the violet perchromate and the velocity of its reduction by ethanol are equal; therefore the expression $[Cr_2O_7'']^{0 \cdot 5}[H_2O_2]^x/[Per]^2 = K_2$ should be a constant. From this equation x was obtained by trial. With $x = 2 \cdot 5$, the constants K_2 shown in the tables were obtained. (As the exact concentration of hydrogen peroxide is unknown, it has been assumed to have been reduced to half of its initial value in each case.)

The relation between the perchromates obtained from dichromate and from chromic acid is illustrated by the following qualitative experiment. On addition of a calculated amount of 0·1N-sodium hydroxide in 80% alcohol to a blue alcoholic solution of perchromic acid, the solution becomes violet in a few seconds without any noticeable evolution of oxygen, although the direct formation of the violet perchromate would require a few hours. Further, on neutralization of the sodium hydroxide by an equivalent amount of an alcoholic solution of hydrochloric acid, the blue colour reappears almost instantaneously. If the experiment is carried out at 0° these titrations can be repeated for several hours, always with the same results, until the hydrogen peroxide is entirely decomposed. Also there is no difference whether the " titration experiment " is started with a violet solution obtained from dichromate or with a blue solution obtained from chromic acid. These experiments leave no doubt that the two perchromates can be interconverted just by changing the hydrogen-ion concentration of the solution, without the intermediate formation of chromic acid.

DISCUSSION.

The extinction values of the alcoholic solutions measured and the equilibrium constants K_1 show that the blue perchromate is formed from one molecule of chromic acid and 1½ molecules of hydrogen peroxide. This may be expressed by the equation $2CrO_3 + 3H_2O_2 \rightleftharpoons 2HCrO_5 + 2H_2O$, in agreement with the formula proposed by Wiede and Riesenfeld (*loc. cit.*). The dimeric formula $H_2Cr_2O_{10}$, or the participation of the dichromate ion, is rejected, for it has been proved by all the authors mentioned that the blue perchromate, or more exactly its pyridine compound PyHCrO$_5$, is a monomer containing only one chromium atom. Thus the strange fact that a molecule of hydrogen peroxide should be divided between two molecules of chromic acid calls for an explanation, especially as it may be the cause of the peculiar properties of the perchromates.

On neutralization, the blue perchromate is readily converted into the violet form. The smooth change of colour from blue to violet on the addition of a mild alkali had been observed by Wiede (*loc. cit.*), and later Hofmann and Hiendelmaier (*Ber.*, 1904, **37**, 1663, 3405; 1905, **38**, 3059, 3066) suggested that the blue colour characterizes the per-acid whilst the salts have a reddish tint. The violet perchromate is formed, as the " equilibrium constants " K_2 show, from 0·5 molecule of dichromate and 2·5 molecules of hydrogen peroxide. Therefore the difference between the blue and the violet per-compounds should be only the addition of another molecule of hydrogen peroxide : $CrO'_5 + H_2O_2 \rightleftharpoons H_2CrO_7'$ (a reaction which seems to be possible only at pH above 4·5, *i.e.*, when the weak acid HCrO$_5$ is ionised).

The direct formation of the violet perchromate is comparatively slow. This may be connected with the observed participation of only half a molecule of dichromate in the reaction, indicating that the dichromate ion dissociates according to the equation $Cr_2O_7'' + 2H' \rightleftharpoons 2CrO_3 + H_2O$, and the small concentration of the chromium trioxide present at any moment is responsible for the slow reaction. Hence, there is evidence that the violet perchromate, too, is monomeric and that it contains half a molecule of hydrogen peroxide.

For the explanation of these results the dissociation of hydrogen peroxide suggests itself : $3H_2O_2 \rightleftharpoons 2H_2O + 2HO_2$. This kind of disproportionation of hydrogen peroxide in alkaline solutions has already been proposed by Calvert (*Z. physikal. Chem.*, 1901, **38**, 513). The HO_2 radicals would then add simply to the chromic acid molecules thus : $CrO_3,aq. + HO_2 \rightleftharpoons HCrO_5 + H_2O$.

The above representation is not only simple, but also explains the reduction of the chromium to the quinquevalent state by the odd electron of the HO_2 radical. Moreover, the intense coloration of the perchromate, and the analytically peculiar behaviour of the peroxidic oxygen, are also better understood.

As similar phenomena are typical for many per-compounds of the transition elements, the proposed interpretation may be quite general for this body of compounds as well as for the reducing action of hydrogen peroxide on such compounds as permanganate or ferric iron.