

499. *The Blue Perchromic Acid.*

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The composition of the blue perchromic acid has been elucidated in several ways. Photometric measurements of ethyl acetate extracts show that in aqueous solutions it is formed from two molecules of hydrogen peroxide and one molecule of chromic acid. The determination of the residual hexivalent chromium in the aqueous solutions, after extraction, confirms the ratio $\text{H}_2\text{O}_2/\text{CrO}_3 = 2$.

75% Acetone-water and 75% dioxan-water (v/v) * solutions were examined by Job's method.¹ In both media the maxima of the Job curves correspond to the ratio $\text{H}_2\text{O}_2/\text{CrO}_3 = 2$ if equimolar solutions of hydrogen peroxide and sodium chromate are employed, but on using an equimolar solution of potassium dichromate the ratio $\text{H}_2\text{O}_2/\text{K}_2\text{Cr}_2\text{O}_7 = 3$ is obtained. The discrepancy is attributed to the slow formation and decomposition of the per-compound causing a small shift in the position of the maxima of the Job curves. This shift is more exaggerated in the dichromate variations. Hence, it is concluded that Schwarz and Giese's² formula CrO_5 for the blue perchromic acid is correct.

On evidence from the optical density of *ca.* 76% alcohol-water solutions, it has been concluded³ that the blue perchromic acid is formed from hydrogen peroxide and chromic acid in the ratio 3 : 2. It was, therefore, given the formula HCrO_5 , partial reduction of the chromium to the quinquevalent state being assumed. This concept was in accord with Riesenfeld's results.⁴ It also offered an explanation of the intense colour, instability, and spontaneous decomposition of the per-acid to one containing tervalent chromium. On the other hand, Schwarz and Giese's results,² and some properties of the per-compound, could not be explained on the basis of the given formula (for literature see refs. 1—4). More experimental evidence on the composition of this unusual per-compound has therefore been sought.

A new experimental approach has been opened by the findings that the blue perchromate ion is quite stable in ethyl acetate solutions⁵ and that chromium in either minerals or alloys can be determined quantitatively by measuring the optical density of the ethyl acetate extract of the blue per-acid formed in aqueous solutions.⁶ Besides,

* 75% Acetone-water, *e.g.*, in this paper refers to a solution made by diluting 75 parts by volume of acetone to 100 parts by volume.

¹ Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

² Schwarz and Giese, *Ber.*, 1932, **65**, 871; 1933, **66**, 310; 1936, **69**, 575.

³ Glasner, *J.*, 1950, 2795, see also Bobtelsky, Glasner, and Bobtelsky-Chaikin, *J. Amer. Chem. Soc.*, 1945, **67**, 966.

⁴ Riesenfeld *et al.*, *Ber.*, 1905, **38**, 1885, 3380, 3578, 4068; 1908, **41**, 2826, 3536, 3941; 1914, **47**, 584.

⁵ Brookshier and Freund, *Analyt. Chem.*, 1951, **23**, 1110.

⁶ Glasner and Steinberg, *ibid.*, 1955, **27**, 2008.

Job's method of "continuous variations" has been employed in the investigation of cooled acetone-water and dioxan-water solutions.

Our results indicate a ratio $\text{H}_2\text{O}_2/\text{CrO}_3 = 2$, and Glasner's previous conclusion² should be revised accordingly.

EXPERIMENTAL AND RESULTS

Materials.—Stock solutions of CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, and Na_2CrO_4 of analytical grade (Baker's Analysed, or May and Baker's) were diluted as required. The concentration of the dichromate solution was determined by accurate weighing of the powdered salt dried at 160° , and the concentration of the other chromium solutions was standardized potentiometrically against it, a solution of Mohr's salt being used as titrant.

Hydrogen peroxide (May and Baker, 100 vol.) was diluted as required, and its concentration determined by use of a permanganate solution standardized with the primary dichromate solution.

Dilute sulphuric, hydrochloric, and perchloric acid were prepared from reagents of analytical quality. Ethyl acetate, acetone, and dioxan were Baker's C.P., May and Baker's, and "AnalaR." The ethyl acetate from the three firms was equally good, and was occasionally redistilled for repeated use. Only freshly opened bottles of dioxan were usable, because the presence of peroxides had an understandably disturbing effect.

Apparatus.—Measurements were made with Unicam (Model S.P. 350), Beckman DU, and Beckman B spectrophotometers, as convenient. The maximum on the absorption spectra of ethyl acetate extracts⁶ as well as that of the mixed solvents occurred at $580 \text{ m}\mu$, and all results recorded were obtained at this wavelength.

Extractions.—Solutions of the various reagents were measured by microburettes into 50-ml. flasks, cooled in ice-water. Hydrogen peroxide was always added last with vigorous mixing for 30 sec. The solutions were allowed 120 sec. to separate, and the organic solvent was transferred by pipette into the photometric cuvette, to be measured soon. The periods indicated were found best by experiment and were strictly adhered to; they allowed sufficient time for complete reaction while anticipating the decomposition of the perchromic acid.

Ethyl acetate extracted the blue perchromic acid formed in acid solutions, but not the violet alkali perchromate formed in dichromate solutions to which no mineral acid had been added.

Composition of the Blue Perchromic Acid in Ethyl Acetate Extracts.—Several series of solutions were prepared in which the concentration of either chromic acid or hydrogen peroxide was kept constant, whilst the concentration of the other reagent was increased stepwise. The optical densities of the ethyl acetate extracts increased linearly to a maximum that slightly fluctuated on further additions of the varying reagent. A plot of the optical densities gave, therefore, two straight lines intersecting at a point that indicates the ratio of hydrogen peroxide to chromium in the per-compound.

In Table 1 the ratios $\text{H}_2\text{O}_2/\text{CrO}_3$ obtained from such series of measurements are summarized. The solutions were mostly acidified by hydrochloric acid, though extractions with other mineral acids were quite as good.⁸ Clearly, the ratios $\text{H}_2\text{O}_2/\text{CrO}_3$ approximate to 2, with a tendency to higher values in the series with fixed concentrations of chromium, and to lower values in the series with fixed concentrations of hydrogen peroxide, *i.e.*, the ratios deviate from 2 to the benefit of the varying reactant in a series. This is because the extraction of the perchromic acid is more favoured in the presence of an excess of any one of the reactants, and consequently, the inclination of the rising straight line is always somewhat less, and the point of intersection at somewhat larger concentrations of the reagent being varied, than the theoretical value.

Analysis of the Residual Chromium in the Aqueous Solution, after Extraction.—In a series of solutions the concentration of the chromate left in the aqueous solution after extraction was determined by the diphenylcarbazide method.⁹ Each solution contained initially 1 ml. of $\text{M}/75\text{-K}_2\text{Cr}_2\text{O}_7$ and x ml. of $2\text{M}/75\text{-H}_2\text{O}_2$. In Table 2 are shown the analytical results, together

⁷ Job, *Ann. Chim. (France)*, 1928, **9**, 113; 1936, **6**, 97; cf. Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, 1953, p. 29.

⁸ Troitskii, *Zhur. Analit. Khim.*, 1954, **9**, 51.

⁹ Sandell, "Colorimetric Determination of Traces of Metals," Interscience, New York, 1944, pp. 191—195.

TABLE 1. Molar ratios of hydrogen peroxide to chromic acid in ethyl acetate extract.

Total vol. of aqueous soln. (ml.)	Reagent not varied (ml.; M) *	Final concn. of HCl in aqueous layer (10 ⁻² M)	Pyridine added †	Ratio H ₂ O ₂ /CrO ₃
CrO ₃				
3	1.0; 0.00906	0.8	—	2.05
5	1.0; 0.00906	1.0	—	2.13
5	1.0; 0.00906	1.0	+	1.98
5	1.0; 0.00906	2.0	—	2.17
5	0.5; 0.00466	3.0	—	2.12
10	1.0; 0.00906	1.0	+	2.50
K ₂ Cr ₂ O ₇				
5	1.0; 0.005123	1.0	—	2.18
5	0.5; 0.005123	2.0	—	2.18
H ₂ O ₂				
5	1.0; 0.01859	1.0	—	1.99
5	1.0; 0.01927	1.0	+	1.82
10	2.0; 0.00887	1.0	+	1.99
10	1.0; 0.01030	1.0	+	1.75
10	1.5; 0.01269	0.75	—	1.94

* I.e., Quantity (ml.) of a solution of molarity M taken. † 0.5 ml. of a 0.04M-soln. in water.

TABLE 2. Hydrogen peroxide/chromic acid ratio by the determination of the residual chromate.

x	0.5	1.0	1.5	2.0	2.5	3.0
K ₂ Cr ₂ O ₇ in residue (ml. of M/75 soln.)	0.77	0.52	0.247	0.007	0.00	0.00
H ₂ O ₂ /CrO ₃ in extract	2.17	2.08	1.99	2.01	—	—

FIG. 1. Job curves of 75% acetone-water mixtures.

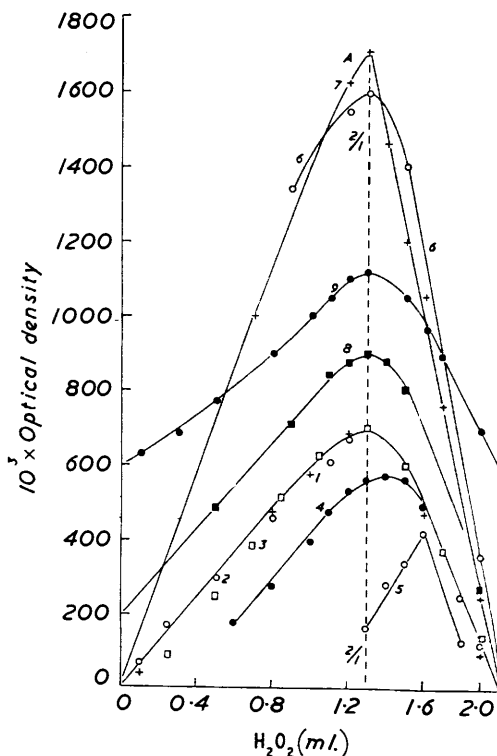
Curves 1—5: Variations with M/50 solutions of Na₂CrO₄ and H₂O₂, acidified by HClO₄; final concn. of acid: 1, 0.05M; 2, 0.01M; 3, 0.005M; 4, 0.0038M; 5, 0.0019M.

Curve 6: Variations with M/25 solutions of CrO₃ and H₂O₂, with final concn. of HClO₄ = 0.01M.

Curve 7(A): Variations with M/50-K₂Cr₂O₇ and M/25-H₂O₂, with final concn. of HClO₄ = 0.02M.

Curve 8: Variations with M/50 solns. of Na₂CrO₄ and H₂O₂, with final concn. of H₂SO₄ = 0.01N (reduce scale on ordinate by 200 units).

Curve 9: Variations with M/75 solns. of Na₂CrO₄ and H₂O₂, with final concn. of HClO₄ = 0.01M (reduce scale on ordinate by 600 units).



with the ratios H_2O_2/CrO_3 calculated therefrom. The value 2 thus obtained confirms the previous results of the extraction experiments.

The Rate of Formation and Composition of the Per-compound in Acetone-Water Mixtures.—When the solutions were mixed the optical density reached a maximum only after 5–10 min.;

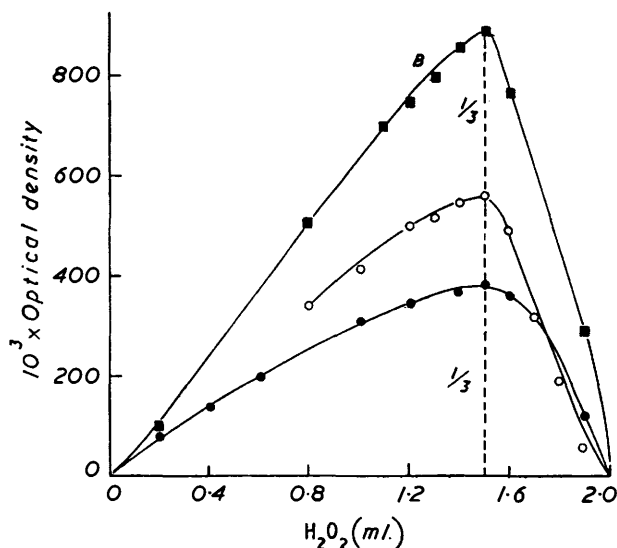


FIG. 2. Job curves of 75% acetone-water mixtures.

Variations with $M/75$ solns. of $K_2Cr_2O_7$ and H_2O_2 ; final acid concns.: \circ , $0.01N-H_2SO_4$ (Unicam); \bullet , $0.04M-HCl$ (Beckman DU); \blacksquare (B), $M/25-CrO_3$ and $M/50-H_2O_2$, $0.025M-HClO_4$.

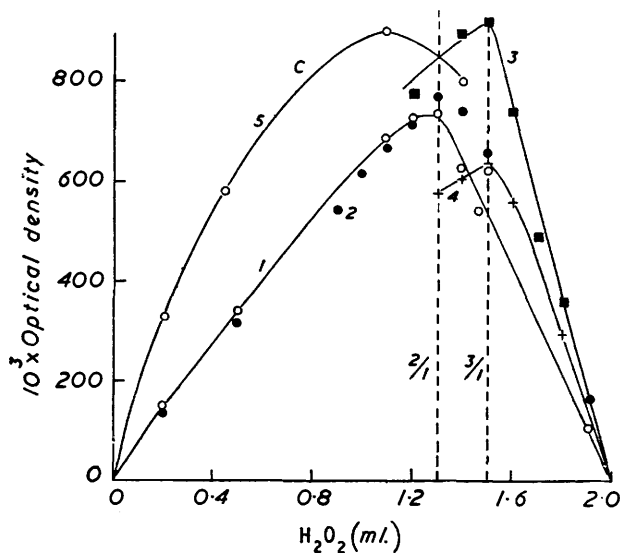
FIG. 3. Job curves of 75% dioxan-water mixtures.

Curves 1 and 2: Variations with $M/50$ solns. of Na_2CrO_4 and H_2O_2 . Final acid concns.: 1, $0.05M-HClO_4$; 2, $0.005M-HClO_4$; 3 and 4, $0.01N-H_2SO_4$.

Curve 3: Variations with $M/50$ solns. of $K_2Cr_2O_7$ and H_2O_2 .

Curve 4: Variations with $M/75$ solns. of $K_2Cr_2O_7$ and H_2O_2 .

Curve 5 (c): as curve 1 but with dioxan that contained peroxides.



the maximum remained constant for some time and then decreased according to an approximately first-order law.¹⁰ For the experiments reported in the following section maximum values of the optical densities for each solution were recorded.

Composition of the Blue Per-compound in 75% Acetone-Water Solutions.—In Fig. 1 some curves obtained by Job's "continuous variations" method^{1,7} are recorded. If sufficient acid ($5 \times 10^{-3}M-HClO_4$, final concn.) is present, the maxima of the curves is at 65% H_2O_2 , corresponding to a ratio $H_2O_2/CrO_3 = 2$. In solutions weaker in acid the maxima move towards

¹⁰ Prakash and Rai, *Proc. Indian Acad. Sci.*, 1943, 18, A, 1.

higher ratios, up to $\text{H}_2\text{O}_2/\text{CrO}_3 = 4$; also in the last solutions the colour develops rather slowly, impairing greatly the ease of measurements.

When the "variations" were made with equimolar solutions of hydrogen peroxide and potassium dichromate (Fig. 2), the maxima of the Job curves were at 75 mole-% H_2O_2 , corresponding to the ratio $\text{H}_2\text{O}_2/\text{K}_2\text{Cr}_2\text{O}_7 = 3$, *i.e.*, $\text{H}_2\text{O}_2/\text{CrO}_3 = 1.5$. Similar results were obtained with a chromium trioxide solution having twice the molar concentration of the hydrogen peroxide (curve B, Fig. 2). On the other hand, with a hydrogen peroxide solution of twice the molar concentration of the dichromate, the maximum of the curve occurred again at 65 mole-% H_2O_2 (curve A, Fig. 1).

Composition of the Blue Per-compound in 75% Dioxan-Water Solutions.—Job curves obtained in dioxan-water solutions are recorded in Fig. 3. The results were identical with those of the corresponding acetone solutions, with respect to variations with either chromate or dichromate solutions. Similar experiments¹¹ with dichromate in dioxan-water mixtures were made here previously by Avinur; his Job curves were identical with those now recorded.

Great care was taken to use peroxide-free dioxan; for example, in a mixture prepared from an old sample of dioxan, appreciable amounts of the perchromate were formed on acidifying the solution before any hydrogen peroxide had been added; with this sample the maximum on the Job curve shifted from 65 to 55 mole-% H_2O_2 (curve C, Fig. 3).

DISCUSSION

The results with ethyl acetate extracts leave no doubt that the blue perchromic acid in this solvent is composed of two molecules of hydrogen peroxide to one molecule of chromium trioxide. The analyses of the hexavalent chromium in the aqueous residues confirm this conclusion.

The blue per-compound formed in acidified acetone-water or dioxan-water mixtures shows identical absorption spectra with that of the ethyl acetate extract. Hence, one may assume that the per-compound in the mixed solvents is identical with that in the acetate extract. Yet the Job curves are apparently conflicting: the chromate-hydrogen peroxide "variations" indicate a ratio $\text{H}_2\text{O}_2/\text{CrO}_3 = 2$, and the dichromate-hydrogen peroxide "variations" a ratio of 1.5. Several possible causes for the discrepancy were tested and disproved: (a) The disturbing effect of peroxides in the organic solvents; (b) the acidity of the solutions (in less acid solutions the indicated ratio $\text{H}_2\text{O}_2/\text{CrO}_3$ rises, but does not fall below 2); (c) the original form of the stock solution of the chromium, whether monomeric (chromate) or dimeric (dichromate), does not affect the Job curves.

Recalling that the formation of the per-compound is a time-dependent reaction, we have no doubt that a considerable portion of the chromium present in the solution is not in the per-acid state at the moment of maximum optical density. This would cause the maximum of the Job curves to move towards a lower percentage of hydrogen peroxide, the shift being twice as large in the case of the dichromate variations. More precise measurements in greater volumes of solution support this view but do not prove it, owing to experimental difficulties. In fact, the exact maxima of the Job curves were blurred in these experiments.

Glasner's previous results in alcohol-water mixtures³ seem to have suffered from a similar complication. It may therefore be concluded that the blue perchromic acid is composed of two molecules of hydrogen peroxide and one molecule of chromic acid, and that Schwarz and Giese's formulation² of the blue per-compound as CrO_5 (solvated) is correct.

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¹¹ Avinur, personal communication.