Studies of the Decomposition Products of Ethereal Blue Perchromate by Ion-exchange Resins. II. The Open Bottle Decomposition Product

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The blue perchromate decomposes in different manners, yielding different compounds under different conditions. Rai and Prakash(1) and Rajput and Rai(2) have shown, for instance, that in contact with water it gives $Cr_2(Cr_2O_7)_3$.

No serious attempt has, however, yet been made to ascertain the composition of and to assign a chemical formula to the decomposition product of the ethereal blue perchromate obtained when it is allowed to decompose in uncorked Erlenmeyer flasks (the open bottle decomposition product). According to Schwarz and Giese,(3) ethereal blue perchromate gives CrO_3 in presence of silver oxide. Rai, Rajput and Rai(4) have seen that if the ethereal blue perchromate is allowed to decompose under tightly-corked conditions (the closed bottle decomposition product), its titration value becomes nearly double when this product is oxidised with 30% hydrogen peroxide in a strongly alkaline medium (NaOH). They have thus tried to show that, under such conditions, a compound with the formula $CrCrO_4$ seems to be formed. The same compound has been reported by Vauquelin and others.(5)

In the present paper, the composition of the open bottle decomposition product of the ethereal blue perchromate will be studied, and, on the basis of the observations obtained, a chemical formula will be assigned to it. It will further be shown how the formation of this product supports the formula suggested by Rai for the ethereal blue perchromate.

Experimental

Blue perchromate was prepared by mixing ice-cold solutions of 5% w/v potassium dichromate (50 ml.), 2 N sulphuric acid (5 ml.) and 6% hydrogen peroxide. The blue compound thus formed was then extracted with ice-cold ethyl ether (100 ml.), washed several times with ice-cold distilled water, and placed in a tightly-corked flask in the refrigerator in order to freeze out the water. After about three hours, it was transferred to a previously-dried and cooled flask and kept in ice. Five milliliters of it was then allowed to decompose in each of two dry, 100-ml. Erlenmeyer flasks; the rest of it was allowed to decompose in a 250-ml. Erlenmeyer flask under open conditions. After about 12 to 14 hr., only a brown residue was left in all the flasks. The contents of one of the 100-ml. Erlenmeyer flasks were titrated after potassium iodide and sulphuric acid had been added; that of the other was so titrated after the contents had been oxidised with 30% hydrogen peroxide in an alkaline medium (NaOH). The excess peroxide was then removed by prolonged boiling. The brown residue left in the third flask was dissolved in water with the aid of a few milliliters of dilute sulphuric acid.

Several columns (6/75 mm.) were prepared for the different ion-exchangers and washed thoroughly with distilled water. Cations and anions separated from the solution of the open bottle decomposition product prepared above. It was found, with the aid of a spot test, that chromium was present in cationic as well as in anionic portions of the product solution. The amount was then estimated quantitatively iodometrically. In the case of cationic chromium, it was oxidised with 30% hydrogen peroxide as above after elution and then titrated iodometrically. Anionic chromium was titrated iodometrically, as usual. In the case of anion exchangers, a final elution was made with a few milliliters of 1 N hydrochloric acid in order to elute any chromium formed due to some reaction(6) between the resin and the anion of the effluent. The elutriant so obtained did not liberate iodine with acid; hence it was oxidised as above with 30% hydrogen peroxide and titrated iodometrically after the excess peroxide had been removed. The titration value so obtained was added to the titration value of the anionic portion of the product solution. The experimental results are noted in Tables I—III:

Discussion

According to Schwarz the ethereal blue perchromate decomposes in the presence of silver oxide, giving CrO_3:

$$CrO_5 \xrightarrow{Ag_2O} CrO_3 + 2O$$

When the ethereal blue perchromate is decomposed in an open bottle in the absence of any foreign substance, a brown substance is formed. It liberates iodine in the presence of acid; the

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1) R. C. Rai and S. Prakash, *Z. anorg. u. allgem. Chem.*, **275**, 94 (1954).

2) B. S. Rajput and R. C. Rai, *J. Indian Chem. Soc.*, **42**, 277 (1965).

3) R. Schwarz and H. Giese, *Ber.*, **65B**, 871 (1932).

4) R. C. Rai, B. S. Rajput and R. C. Rai, Paper presented at the Annual convention of I. C. S. at Allahabad 1964 and paper communicated to *J. Indian Chem. Soc.*

5) L. N. Vauquelin et al., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Ed. by J. W. Mellor, Longmans, Green and Co., London (1931), p. 208.

6) O. Samuelson, "Ion-exchangers in Analytical Chemistry," John Wiley & Sons, Inc., New York (1953).

Table I. Cation exchangers

Column : 6/75 mm.; Strength of thiosulphate solution used = N/97.58
Drop rate : 15 to 18 per minute ; Volume of the solution exchanged with resin each time = 5 ml.

Name of resin	Vol. in ml. of thiosulphate solution used in titrating the open bottle decomposition product solution					Ratios					
	5 ml. unexchanged with resin and unoxidised	5 ml. unexchanged with resin but oxidsed	Effluent unoxidised	Effluent oxidised	Elutriant oxidised	$\frac{b}{a}$;	$\frac{a}{c}$;	$\frac{a}{d}$;	$\frac{d}{c}$;	$\frac{b}{c+e}$, $\frac{b}{d+e}$ or $\frac{b}{a+e}$;	$\frac{a}{e}$, $\frac{c}{e}$ or $\frac{d}{e}$
	a	b	c	d	e	f	g	h	i	j	k
Amberlite IR 120(H)	8.25	13.95	7.80	8.00	5.80	1.69	1.05	1.03	1.02	1.02	1.42
	8.25	13.90	7.80	8.00	5.70	1.68	1.05	1.03	1.02	1.03	1.45
	8.10	13.80	7.85	8.00	5.50	1.70	1.03	1.01	1.01	1.03	1.47
	8.40	14.00	8.00	8.00	5.80	1.66	1.04	1.04	1.00	1.01	1.45
	8.60	14.00	8.10	8.30	6.00	1.62	1.06	1.03	1.02	1.00	1.43
Dowex 50(H)	8.10	13.80	8.00	8.20	5.50	1.70	1.01	0.99	1.02	1.02	1.47
	8.10	13.75	8.00	8.15	5.45	1.70	1.01	0.99	1.01	1.02	1.47
	8.40	14.00	8.15	8.30	5.80	1.66	1.01	1.01	1.01	1.00	1.45
	8.25	13.95	8.10	8.40	5.75	1.69	1.01	0.98	1.03	1.00	1.42
	8.30	13.95	8.10	8.20	5.75	1.69	1.01	1.01	1.01	1.00	1.42

Table II. Anion exchangers

Column : 6/75 mm.; Strength of thiosulphate solution used = N/97.58
Drop rate : 15 to 18 per minute ; Volume of the solution exchanged with resin each time = 5 ml.

Name of resin	Vol. in ml. of thiosulphate solution used in titrating open decomposition product solution					Ratios			
	5 ml. unexchanged with resin and unoxidised	5 ml. unexchanged with resin but oxidised	Effluent oxidised	Elutriant (a) unoxidised	Elutriant (b) oxidised	$\frac{b}{a}$ or $\frac{b}{d+e}$;	$\frac{a}{c}$ or $\frac{d+e}{c}$;	$\frac{a}{d+e}$;	$\frac{b}{c+d+e}$ or $\frac{b}{a+c}$
	a	b	c	d	e	f	g	h	i
Dowex-1(Cl)	5.75	9.80	3.60	5.50	0.30	1.70	1.59	0.99	1.05
	8.30	13.90	5.75	7.50	0.60	1.67	1.44	1.02	1.00
	8.40	14.00	5.80	7.50	0.60	1.66	1.44	0.99	0.99
	8.40	14.00	5.80	7.90	0.40	1.66	1.44	1.01	1.00
Dowex-21(Cl)	5.75	9.80	3.60	5.45	0.40	1.70	1.59	0.99	1.03
	5.90	9.95	3.80	5.30	0.50	1.67	1.55	1.01	1.02
	5.85	9.90	3.80	5.35	0.40	1.69	1.53	1.02	1.03
	8.40	14.00	5.80	8.00	0.20	1.66	1.45	1.02	1.00
Amberlite IR 400(Cl)	6.10	10.10	3.90	5.00	1.50	1.65	1.56	0.91	0.97
	6.15	10.10	3.90	5.20	1.00	1.65	1.56	0.99	0.97
	5.75	9.80	3.55	4.00	1.30	1.70	1.60	1.08	1.10

TABLE III.

5% w/v $K_2Cr_2O_7$ solution = 50 ml. 2N H_2SO_4 = 5 ml. Ethyl ether = 100 ml.
6% H_2O_2 = varying quantities Strength of $Na_2S_2O_3$ solution = N/40

Sample No.	Vol. of 6% H_2O_2 used ml.	Vol. in ml. of $Na_2S_2O_3$ soln. used in titrating			Ratios	
		Blue perchromate 5 ml. blue perchromate	Open decomp. product			
			unoxidised	oxidised	$\frac{b}{c}$	$\frac{b}{d}$
	a	b	c	d	e	f
1	20	50.40	18.20	31.60	2.76	1.58
2	15	43.00	15.10	26.00	2.84	1.65
3	10	43.35	16.30	28.05	2.64	1.54
4	10	27.80	10.00	16.80	2.78	1.65
5	5	18.00	6.50	11.20	2.76	1.60

quantity of iodine liberated increases if the product is oxidised with 30% hydrogen peroxide in a strongly alkaline medium (NaOH) before the iodometric titration. This increase in titration value can be understood if the product is considered to have chromium in the cationic portion as well. In an attempt to verify this, the product was dissolved in water with the aid of dilute sulphuric acid, and then cationic and anionic portions were separated with the help of different ion-exchangers. Chromium was found to be present in both portions; when this was estimated quantitatively and iodometrically, it was found that the cationic and anionic chromium are present in the ratio of 1 : 1.5 (Tables II and III). The increase in the titration value of the unexchanged product solution may, therefore, be considered to be due only to the conversion of chromium(III) to chromium(VI).

On the basis of the above ratio (1 : 1.5) between cationic and anionic chromium, it can easily be found that the compound formed is $Cr_2(CrO_4)_3$, as otherwise this ratio can not be explained. Moreover, the insolubility of the compound in water also agrees with the known properties of $Cr_2(CrO_4)_3$.

An attempt will now be made to show how this product can be formed from the blue compound, and in what manner it is related to the parent compound (blue perchromate). It will also be seen which formula, the CrO_5 of Schwarz or the $Cr_2(Cr_2O_{10})_3$ and $CrCrO_8$ of Rai best explains the results obtained above.

If the blue perchromate is CrO_5, it is difficult to presume the formation of trivalent chromium from it without the presence of any reducing agent. However, omitting all this and admitting that it does happen, CrO_5 may be taken to decompose in the following manner to give chromium chromate:

$$10CrO_5 \rightarrow 2Cr_2(CrO_4)_3 + 26O \qquad (1)$$

and the total oxidising capacity of the blue compound as expressed in the number of available oxygen atoms may be given in this case as:

$$10CrO_5 \rightarrow 5Cr_2O_3 + 35O \qquad (2)$$

and from chromium chromate:

$$2Cr_2(CrO_4)_3 \rightarrow 5Cr_2O_3 + 9O \qquad (3)$$

The ratio between the total available oxygen atoms from the blue perchromate and chromium chromate will, in this case, be 35 : 9, i. e., 3.88 : 1 (Eqs. 2 and 3). However, the ratio obtained in Table III, Column 'e' does not exceed 2.84 : 1.

On the contrary, if the formulae suggested by Rai are accepted, the above relation can be shown as follows:

$$5Cr_2(Cr_2O_{10})_3 \rightarrow 8Cr_2(CrO_4)_3 + 54O \qquad (4)$$

and

$$20CrCrO_8 \rightarrow 8Cr_2(CrO_4)_3 + 64O \qquad (5)$$

The total available oxygen atoms in these cases will be:

$$5Cr_2(Cr_2O_{10})_3 \rightarrow 20Cr_2O_3 + 90O \qquad (6)$$

and

$$20CrCrO_8 \rightarrow 20Cr_2O_3 + 100O \qquad (7)$$

and from chromium chromate:

$$8Cr_2(CrO_4)_3 \rightarrow 20Cr_2O_3 + 36O \qquad (8)$$

The corresponding ratios in these cases will be 90 : 36 and 100 : 36, i. e., 2.5 : 1 and 2.77 : 1 (Eqs. 6, 7 and 8), values which agree fairly well with the ratios obtained in Table III, Column 'e' on the basis of experimental results.

When the open bottle decomposition product is oxidised with hydrogen peroxide in an alkaline medium, it is converted into sodium chromate:

$$8Cr_2(CrO_4)_3 + 80NaOH + 24H_2O_2 \rightarrow 40Na_2CrO_4 + 64H_2O \qquad (9)$$

When titrated iodometrically, this gives:

$$40Na_2CrO_4 \rightarrow 40Na_2O + 20Cr_2O_3 + 60O \qquad (10)$$

The ratios between the available oxygen atoms of the blue perchromate and those obtained from the sodium chromate so formed will be:

1) on the basis of CrO_5: 35 : 15, i. e., 2.33 : 1
2) on the basis of $Cr_2(Cr_2O_{10})_3$: 90 : 60, i. e., 1.50 : 1
3) on the basis of $CrCrO_8$: 100 : 60, i. e., 1.66 : 1

The values obtained in Column 'f' of Table III are, again, nearer to those obtained by Rai's formulae.

The formula, $Cr_2(Cr_2O_{10})_3$, suggested by Rai⁷⁾ for the blue perchromate has been shown by him⁸⁾ to be in equilibrium with the other formula, $CrCrO_8$:

$$Cr_2(Cr_2O_{10})_3 + 2H_2O_2 \rightleftarrows 4CrCrO_8 + 2H_2O$$

He has further shown that $CrCrO_8$ is formed when hydrogen peroxide is present in excess.

The observations noted above, therefore, prove that the ethereal blue perchromate gives chromium chromate, $Cr_2(CrO_4)_3$, when decomposed in an open bottle and that its formation can be explained on the basis of Rai's formulae for the blue perchromate.

Summary

The composition of the open bottle decomposition product has been studied and a chemical formula $Cr_2(CrO_4)_3$ has been assigned to it. It has been shown that the formation of this product can be explained successfully if we accept the formula suggested by Rai for the ethereal blue perchromate.

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7) R. C. Rai, *J. Indian Chem. Soc.*, **34**, 193 (1957).

8) R. C. Rai, D. Sc. Thesis, University of Allahabad, 1962 on On the Constitution of Blue Peroxy Chromic Acid,' page 214.