CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 25, No. 1 January 1977

Regular Articles

[Chem. Pharm. Bull. 25(1) 1—5 (1977)]

UDC 546.763.04.08 : 543.544.6.062

Quantitative Studies on the Water Decomposition Product of Ethereal Blue Perchromate by Ion-Exchange Resins[1]

BUDHIMAN UPADHYAY[2a] and SATISH CHANDRA TRIPATHI[2b]

Department of Chemistry, Satish Chandra College,[2a] and University of Gorakhpur[2b]

(Received January 25, 1975)

Ion-exchange resins have been employed to separate Cr(III) and Cr(VI) present in the water decomposition product of ethereal blue perchromate prepared with 5-Sulphosalicylic acid. The quantitative estimations of Cr(III) and Cr(VI) present in cationic and anionic portions of the decomposition product have been determined by the usual Volumetric and Gravimetric methods. The experimental results and ratios between Cr(III) and Cr(VI) are in agreement with formula $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}_2O_7)_3]$ for the water decomposition product corresponding to parent blue perchromate, $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}_2O_{10})_3]$, where Su is bivalent Sulphosalicylate ion.

Keywords——ethereal blue perchromate; water decomposition product; sorption; effluent; elutriant; oxygenated Cr(VI); Rai's mechanism and formula

The ethereal blue perchromate decomposes yielding different species under various conditions. Rai and Prakash[3] and also Rajput and Rai[4] have shown that in water it furnishes chromium dichromate, $Cr^{III}_2(Cr_2O_7)_3$, a very stable Cr(III) compound. Presence of Cr(III) has also been reported by Tuck and Walters.[5] Authors[6] in analogy with Rai's formula,[7] $Cr^{III}_2(Cr^{VI}_2O_{10})_3$, for blue compound, have suggested $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}_2O_{10})_3]$ and $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}_2O_7)_3]$ for ethereal blue perchromate prepared with 5-sulphosalicylic acid and its water decomposition product respectively. The dichromate nature of water decomposition product has also been confirmed by pH[8] and Conductometric[9] studies. Infrared (IR)[10] spectra of solid complexes of this blue compound reveal the presence of peroxy and sulphonic groups while paramagnetic nature of the complexes shows the presence of Cr(III).

1) Paper presented at 58th Indian Science Congress, *Proc. Ind. Sc. Congr.*, **III**, 109 (1971)-Revised.
2) *a*) Location: *Ballia, India*; *b*) *Gorakhpur, India*.
3) R.C. Rai and S. Prakash, *Z. Anorg. Chem.*, **275**, 94 (1954).
4) B.S. Rajput and R.C. Rai, *J. Ind. Chem. Soc.*, **42**, 277 (1965).
5) D.G. Tuck and R.M. Walters, *J. Chem. Soc.*, **1964**, 3405.
6) B. Upadhyay and S.C. Tripathi, *Proc. Ind. Sc. Congr.*, **III**, 102 (1970); *Acta Ciencia Indica* **2**, 23 (1976).
7) R.C. Rai, *J. Ind. Chem. Soc.*, **34**, 59 (1957); Advances in Inorganic chemistry and Radio chemistry by H.J. Emeleus and A.G. Sharpe, Vol. VI Academic Press, New York, 1964, pp. 306—307.
8) B. Upadhyay, *Vijnan Anushandhan Patrika, Allahabad*, (India), **12**, 31 (1969).
9) B. Upadhyay and S.C. Tripathi, *Proc. Ind. Sc. Congr.*, **III**, 149 (1973).
10) B. Upadhyay and S.C. Tripathi, *Convention of Chemists, India, Abstract*, 1970, 59.

The behaviour of Cr(III) complexes[11] is complicated during ion-exchange separation but results are largely dependent upon the composition of the sample solutions and upon the working conditions. Literature[12] reveals that Cr(III) complexes containing $[Cr(CNS)_6]^{-3}$ and $[Cr(C_2O_4)_2]^{-1}$ anions when passed through the bed of cation exchangers no uptake of chromium occurs while these complex anions are taken up quantitatively by anion exchangers. Weakly acid cation exchangers in the hydrogen form and strongly basic anion exchanger in the chloride form have been employed[13,14] to separate Cr(III) and oxygenated Cr(VI).

Thus in order to ascertain the composition of water decomposition product of ethereal blue perchromate prepared with 5-Sulphosalicylic acid, authors thought it worth-while to estimate quantitatively Cr(III) and oxygenated Cr(VI) present in the decomposition product with the help of ion-exchange resins. This composition will further be a clue to justify the composition of parent blue perchromate.

Experimental

All the chemicals used were either A.R. or G.R. quality of Merck and were cooled in referigerator before use.

Preparation of Blue Perchromate——Different samples of blue perchromate were prepared by the addition of 10 Vol. or 3% hydrogen peroxide (5 ml) to a mixture of 0.2% (w/v) potassium dichromate (20 ml), ether (60 ml) and 250 ml 5-sulphosalicylic acid (0.4N or 5.1%). Ethereal layer was separated and washed 3 to 4 times with ice cold water to ensure the complete removal of H_2O_2, excess of acid, *etc.*

Preparation of Water Decomposition Product——The water decomposition product of ethereal blue perchromate was prepared by decomposing different samples in water and finally it was made up to 50 ml in measuring flasks and 5 ml of this solution was taken for study each time.

Oxidising Power of Water Decomposition Product——The oxidising power of water decomposition product was determined iodometrically in unoxidised and oxidised conditions. Oxidation of decomposition product was carried out by treating it with 1N NaOH and 30% hydrogen peroxide. Excess of peroxide was boiled off by prolonged heating.

Ion-exchange Separation——Columns (12/125 mm) of different ion-exchangers were prepared and washed thoroughly with distilled water. Now decomposition product was allowed to percolate through each column at constant rate. Sorbed cation from cation exchangers and anion from anion exchangers were eluted with dil. sulphuric acid (1N,2N, and then 4N) and a mixture of 2% sodium hydroxide and sodium chloride.[15] The process of sorption and elution was repeated three to four times to check the results.

Volumetric Estimation——The effluent from the cation exchangers and elutriant from anion exchanger were titrated iodometrically before and after oxidation. The oxidising powers of the effluent from anion exchanger and elutriant from cation exchanger were determined after oxidation as in both cases only cationic Cr(III) was present. Its presence was confirmed by bluish green colour of the solution and by the negative results of diphenylcarbazide test.

As it has been observed[6] that part of the total Cr(III) is only oxidisable in alkaline medium and part of it forms probably stable complex (anionic) with sulphosalicylate ion. Therefore, to find out unoxidisable Cr(III) a set of experiments were performed separately as given in Table III. To convert oxidisable Cr(III) into Cr(VI) the water decomposition product was oxidised in alkaline medium as in previous cases and then it was treated with 4N hydrochloric acid and with little alcohol[16] to reduce Cr(VI) into Cr(III). Now this solution was exchanged with anion exchanger to separate out unoxidisable Cr(III) mentioned above. The effluent was oxidised and oxidation value was determined iodometrically. Sorbed anion, probably anionic portion of Cr–Su complex was eluted with a mixture of 2% NaOH and NaCl and then decomposed with conc. sulphuric acid. Liberated Cr(III) was converted into Cr(VI) and oxidation value was determined.

Gravimetric Estimation——The effluent from the anion exchanger and elutriant from cation exchangers containing cationic chromium were treated with conc. sulphuric acid to decompose Cr(III) complex with biva-

11) O. Samuelson, Ion-exchange Separation in Analytical Chemistry, John Wiley and Sons, New York, 1963, p. 240.
12) K.H. Gustavson, *Sevensk, Kem. Tid.*, **56**, 14 (1944).
13) B.S. Rajput and R.C. Rai, *Bull. Chem. Soc., Japan*, **38**, 2052 (1965).
14) O. Samuelson, Ion-exchange separation in Analytical chemistry John Wiley and Sons, New York, 1963, pp. 375—376.
15) R. Kunin, Ion-exchange Resins, John Wiley and Sons, New York, 1955, pp. 284—285.
16) A.I. Vogel, A text-Book of Quantitative Inorganic Analysis, ELBS, Longmans Green and Co., Ltd. London, 1961, p. 520.

lent sulphosalicylate anion. Solution was diluted and precipitated as $Cr(OH)_3$ by adding ammonia. It was boiled for few minutes, filtered and then estimated as Cr_2O_3.

In other set effluent from cation exchangers and elutriant from anion exchanger containing anionic chromium Cr(VI) were reduced[16] to Cr(III) and then again estimated as Cr_2O_3.

Table I. Cation Exchangers

Resins		Water decomposition unexchanged. Vol. (ml) Sod. thiosulphate solution. Unoxi. a	Oxi. b	Effluent Unoxi. c	Oxi. d	Elutriant Oxidised e	Ratios b/a f	a/c g	b/c+d h	b/d i	b/d+e j	d/e k	d/c l
Dowex	1	3.75	5.10	3.70	4.30	0.65	1.36	1.00	1.18	1.18	1.04	6.67	1.16
50 (H)	2	2.10	2.75	2.00	2.30	0.35	1.31	1.05	1.17	1.17	1.01	6.60	1.15
	3	5.30	7.10	5.25	6.00	0.90	1.34	1.00	1.15	1.18	1.02	6.67	1.14
Amberlite	1	3.75	5.10	3.70	4.25	0.65	1.36	1.00	1.18	1.18	1.01	6.55	1.14
IR 120 (H)	2	2.10	2.75	1.95	2.30	0.35	1.31	1.06	1.19	1.17	1.01	6.50	1.17
	3	5.30	7.10	5.30	6.05	0.90	1.33	1.00	1.13	1.18	1.03	6.73	1.14

In case of observation No. 1, 2 and 3, four, two and six samples were decomposed in water respectively.
The results are tabulated above: 0.2% $K_2Cr_2O_7$=20 ml, ether=50 ml, H_2O_2 (10 Vol.)=5 ml, 0.4N 5-sulphosalicylic acid=250 ml, drops=15/min column=12/125 mm, Vol. of water decomposition product exchanged each time=5 ml, Sod. thiosulphate sol.=N/200.

Table II. Anion Exchanger

Resins		Water decomposition unexchanged Vol. (ml) Sodium thiosulphate solution Unoxi. a	Oxi. b	Effluent Oxi. c	Elutriant Unoxi. d	Oxi. e	Ratios b/a f	a/d g	b/c+d h	b/e i	b/c+e j	e/c k	e/d l
Amberlite	1	3.80	5.10	0.60	3.80	4.35	1.35	1.00	1.14	1.18	1.04	7.16	1.13
IR 400 (Cl)	2	2.10	2.75	0.30	2.10	2.30	1.31	1.00	1.14	1.17	1.05	7.60	1.10
	3	5.30	7.05	0.85	5.35	6.05	1.33	1.01	1.14	1.14	1.02	7.10	1.13

In case of observation No. 1, 2 and 3, four, two and six samples were decomposed in water respectively.

Table III. Water Decomposition Product Oxidised, reduced in Acidic Medium and then Exchanged with Anion Exchanger

Resin		Effluent a Vol. (ml) Sod. thiosulphate	Elutriant b Vol. (ml) Sod. thiosulphate	a/b c Ratios	a+b/b d Ratios	a+b/a e Ratios
Amberlite IR 400 (Cl)	1	30.6	6.85	4.5	5.4	1.22
	2	15.5	3.55	4.3	5.4	1.22
	3	32.6	7.50	4.3	5.3	1.23

Four, two and four samples decomposed in water for observation No. 1, 2 and 3 respectively.

TABLE IV. (Gravimetric) Vol. of Water Decomposition Product Exchanged Each Time 25 ml

Resins		Effluent wt. of Cr as Cr_2O_3 a	Elutriant wt. of Cr as Cr_2O_3 b	Ratios a/b c	b/a d	a+b/b e
Dowex 50 (H)	1	0.0062	0.0028	2.23	0.45	3.22
	2	0.0076	0.0034	2.24	0.44	3.26
	3	0.0050	0.0024	2.08	0.48	3.26
Amberlite IR 400 (Cl)	1	0.0028	0.0058	0.48	2.08	1.48
	2	0.0032	0.0066	0.48	2.06	1.48
	3	0.0022	0.0048	0.45	2.18	1.45

In case of observation No. 1, 2, 3, five, six and four samples were decomposed in 50 ml water respectively.

Discussion

It may be seen from the titration values obtained in Col. a and b of Table I and II that the oxidation value of unexchanged water decomposition product increases after oxidation. This increase in oxidation value leads to the conclusion that chromium is present as Cr(III) along with Cr(VI) and the ratio between oxidisable Cr(III) and Cr(VI) is 1: 3 (Col. f) *i.e.* two oxidisable Cr(III) and six Cr(VI). The oxidation values of effluent of cation exchangers and elutriant of anion exchanger also increase on the oxidation. From this it is evident that oxidisable Cr(III) is also present in the anionic part of the water decomposition product and ratio between this Cr(III) and Cr(VI) is 1: 6 as shown in Col. l *i.e.* one oxidisable Cr(III) with six Cr(VI). The oxidation values of elutriant of cation exchangers and effluent of anion exchanger come nearly seven times lower than oxidation value of total chromium present in anionic part of the decomposition product (Col. k). Hence it is evident that one oxidisable Cr(III) is present in cationic portion as well. The slight low results in Col. k are probably due to take up of chromate by cation exchangers.

The chromium in the cationic and anionic ingredients (effluent and elutriant) separated with the help of ion-exchangers from decomposition product on estimation gravimetrically comes in the ratio of 1: 2.24 or nearly 3: 7 (Col. c Table IV). This indicates that three Cr(III) are present in the cationic part of the decomposition product out of which only one is oxidisable. The two unoxidisable Cr(III) separated with the help of anion exchanger on treatment gave the oxidation value which is nearly 1/5th of the total oxidation value (Col. d Table III) *i.e.* total chromium. The ratio between oxidisable and unoxidisable Cr(III) has been further confirmed by Colorimetric determination.[17]

Several papers[18–22] on complexes of 5-sulphosalicylic acid reveal that this acid ionizes as $[OOCCH_3(OH)\ SO_3]^{-2}$ between pH 3—5 and phenolic hydrogen is also replaceable at increased pH *i.e.* in alkaline medium. Liebman and Anderson have investigated that if the ratio of Cr(III) and sulphosalicylic acid is increased some complexes other than Cr(III) and sulphosalicylic acid in the ratio 1: 1 are also available in the system even at low pH. Banks and Singh[22] have shown that more stable complexes of Be(II) and sulphosalicylic acid are formed in alkaline medium (pH above 7) when part of Be(II) precipitates as $Be(OH)_2$.

17) S.C. Tripathi, B. Upadhyay and Km. A. Upadhyay, Presented at convention of chemists (India)-Abstract Proceeding 20 (1975); *Israel J. Chem.*, communicated.
18) R.T. Foley and R.C. Anderson, *J. Am. Chem. Soc.*, **70**, 1195 (1948).
19) S.E. Turner and R.C. Anderson, *J. Am. Chem. Soc.*, **71**, 912 (1949).
20) C.V. Banks and J.H. Patterson, *J. Am. Chem. Soc.*, **73**, 3062 (1951).
21) A.M. Liebman and R.C. Anderson, *J. Am. Chem. Soc.*, **74**, 2111 (1952).
22) C.V. Banks and R.S. Singh, *J. Am. Chem. Soc.*, **81**, 6159 (1959).

$$2[BeSu]^{-} + 2OH^{-} \longrightarrow [Be(Su)_2]^{-4} + Be(OH)_2$$

where Su is sulphosalicylate ion.

Thus, in analogy of the above cited works the decomposition and oxidation of Cr(III) in cationic part $[(CrSu)_3]^{+3}$ of the water decomposition product is discussed. When it is treated with sodium hydroxide solution, cationic complex is decomposed first into Cr(III) and phenolic hydrogen is replaced changing $(Su)^{-2}$ into $(Su)^{-3}$. Simultaneously two Cr(III) form stable complex with $(Su)^{-3}$ and one Cr(III) gets precipitated as hydroxide which ultimately oxidises into Cr(VI) on treatment with H_2O_2. The reactions are proposed here in:

In earlier communication[6] on the assumption of Rai's mechanism and formula three possible formulae for water decomposition product corresponding to three formulae for parent ethereal blue perchromate were suggested as given below:

	Blue perchromate		Water decomposition product
I	$(Cr^{III}Su)_2[Cr_2{}^{VI}O_{10}]$	$\xrightarrow{\text{decomp.}}$	$(Cr^{III}Su)_2[Cr_2{}^{VI}O_7] + 3O$
II	$(Cr_2Su)[(Cr_2O_{10})_2]$	$\xrightarrow{\text{decomp.}}$	$(Cr_2Su)[(Cr_2O_7)_2] + 6O$
III	$(Cr^{III}Su)_3[Cr^{III}(Cr_2{}^{VI}O_{10})_3]$	$\xrightarrow{\text{decomp.}}$	$(Cr^{III}Su)_3[Cr^{III}(Cr_2{}^{VI}O_7)_3] + 9O$

Oxidation values before and after oxidation of unexchanged water decomposition product: (when formula III taken into consideration)

$$2(CrSu)_3[Cr(Cr_2O_7)_3] \xrightarrow{\text{oxi. value}} 3(CrSu)_2O + 7Cr_2O_3 + 18O \qquad \text{(Table I, Col. a)}$$

$$2(CrSu)_3[Cr(Cr_2O_7)_3] + 38NaOH + 3H_2O_2 \xrightarrow{\text{oxi.}} 2Na_3[Cr_2(Su)_3]^{23)} + 16Na_2CrO_4 + 22H_2O$$

$$16Na_2CrO_4 \xrightarrow{\text{oxi. value}} 8Cr_2O_3 + 16Na_2O + 24O \qquad \text{(Table I, Col. b)}$$

$$2[(CrSu)_3]^{+3} + 6NaOH \longrightarrow 2Na_3[Cr_2(Su)_3]^{23)} + 2Cr(OH)_3$$

Hence experimental results and inferences are only in agreement with formula, $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}{}_2O_7)_3]$, for the water decomposition product corresponding to parent ethereal blue perchromate, $(Cr^{III}Su)_3[Cr^{III}(Cr^{VI}{}_2O_{10})_3]$.

Acknowledgement One of the authors (B.U.) expresses his sincere thanks to Shri Paras Nath and Shri S.S. Upadhyay, Principal and Secretary of the college respectively for providing various facilities and also to U.G.C. for financial assistance.

23) Composition not ascertained.