

Interhalogens as Oxidimetric Titrants: Part VI*—Oxidimetric Determinations with Bromine Monochloride

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New analytical methods, employing bromine monochloride as an oxidimetric titrant, are described for the determination of isonicotinic acid hydrazide, triphenylphosphine, phosphorothioate, trithionate, xanthate, dithiocarbamate, reineckate, oxine and oxinates of Mg, Al, Mn, Fe, Co, Ni, Cu and Zn.

IN our previous communications¹⁻⁵ we had described some convenient excess-back titration oxidimetric methods for the determination of several technologically important compounds using iodine monochloride in 5N HCl medium as the oxidant. In the present paper, a more reactive interhalogen, viz. bromine monochloride, is suggested as an oxidimetric reagent. It has been shown that, in general, bromine monochloride effects a more extensive oxidation than iodine monochloride, giving larger equivalent consumption of the oxidant and therefore leading to an improved accuracy. Analytical methods using bromine monochloride are described for the determination of the following: isonicotinic acid hydrazide, triphenylphosphine, phosphorothioate, trithionates, xanthates, dithiocarbamates, reineckates, oxine and metallic oxinates.

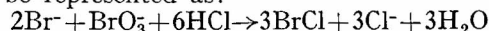
Pioneer work on the use of bromine monochloride as an analytical reagent has been done by Schulek and coworkers⁶. Schulek and Burger used bromine monochloride as a halogenating agent in the determination of antipyrine, phenol, *p*-nitrophenol and fluorescein. Other compounds which have been determined with bromine monochloride are hypophosphite⁷, hydroxylamine⁸, maleic and fumaric acids⁹, formic acid¹⁰, hydrazine¹¹, hexobarbital¹² and thiocyanate, urea and thiourea¹³. It is hoped that the present studies would extend the scope of BrCl as a versatile and convenient oxidimetric titrant.

Materials and Methods

Preparation of stock solutions of bromine monochloride—Preliminary studies showed that the presence of even small amounts of bromate in BrCl solution causes complications. Therefore, the method described in literature was slightly modified as follows, in order to ensure absence of any free bromate. Potassium bromide (3.976 g) and potassium bromate (2.7835 g) (molar ratio bromide/bromate = slightly more than 2) were dissolved together in water (125 ml). To this 100 ml of conc. hydrochloric

acid was added. The solution was shaken well with carbon tetrachloride (2 × 10 ml), in order to remove free bromine. Finally conc. hydrochloric acid (400 ml) was added and the solution diluted to one litre. The solution was stored in contact with a layer of carbon tetrachloride which served to extract any trace of bromine produced in the aqueous phase. Before use, the solution was shaken well and allowed to settle and the aqueous layer standardized by adding, to measured aliquots (20 ml), 10 ml 10% aqueous KI, diluting to 200 ml and titrating the liberated iodine with standard thiosulphate. It has been noted that under these conditions bromine monochloride exists as a complex¹⁴.

The formation of BrCl in the above preparation may be represented as:



The excess HCl taken serves to stabilize the BrCl, possibly by complex formation¹⁴. It may be noted that stock solutions of bromine monochloride are reasonably stable and undergo no change in titre even for periods up to two weeks.

Stock solutions of various compounds to be estimated—Solutions of potassium trithionate (prepared by the method of Goehring¹⁵), potassium ethyl xanthate (USSR), sodium diethyl dithiocarbamate (BDH), sodium phosphorothioate (prepared by the method of Kubierschky¹⁶), isonicotinic acid hydrazide (Koch-Light) and Reinecke salt (E. Merck) were prepared in distilled water while that of triphenylphosphine (Koch-Light) was prepared in carbon tetrachloride. All these solutions were standardized by procedures involving oxidation with chloramine-T¹⁷⁻²⁰ or iodine monochloride¹⁻⁵. Cadmium thiourea reineckate was prepared by the procedure of Rulf *et al.*²¹ and was used as such; the purity of the sample was checked by the chloramine-T procedure²². Oxine (Riedel) was dissolved in 2N HCl and the solution standardized by the bromate-bromide method. The oxinates of magnesium, aluminium, manganese, iron, cobalt, nickel, copper and zinc were prepared by standard methods involving the addition of a solution of oxine in 2N acetic acid to the hot aqueous solutions of the respective metal sulphates under specified conditions of pH²⁴. The precipitates were

*For Parts I to V, see references 1 to 5.

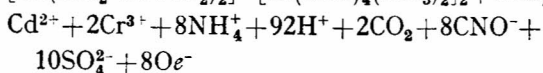
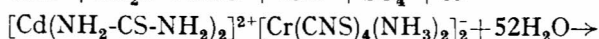
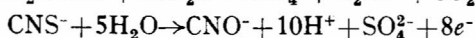
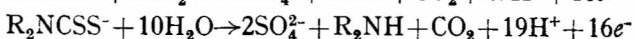
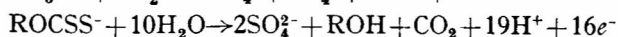
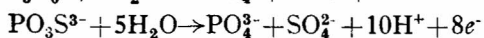
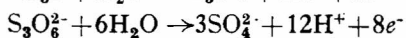
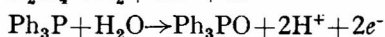
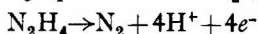
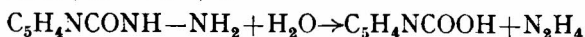
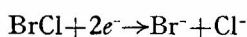
dried as recommended. Solutions of these oxinates were prepared in 2*N* HCl and were standardized using the bromate-bromide method.

General procedure—All the experiments were carried out at room temperature (28 ± 2°C). (It may be noted that, unlike solutions of iodine monochloride² in 5*M* hydrochloric acid, solutions of bromine monochloride in 5*M* hydrochloric acid decompose on heating). To measured volumes (20-40 ml) of the bromine monochloride solution taken in stoppered conical flasks, measured aliquots (5 to 12 ml) of the reductant solutions or a known weight of the reductant (in the case of cadmium thiourea reineckate) were introduced. The contents were shaken and were allowed to stand, in separate experiments, for different time intervals (5 min to 24 hr) at the end of which the unconsumed bromine monochloride was determined by adding 20 ml 10% aqueous potassium iodide and titrating the liberated iodine with standard thiosulphate. A standing time of 10 min is recommended for the oxidation of all the reductants studied, except for oxinates (15 min) and cadmium thiourea reineckate (30 min). A longer standing time (up to 12 hr) did not lead to any increased consumption of the oxidant in any case. Blanks were done concurrently for each experiment. Blank corrections were negligible (less than 0.1 ml) even on keeping for 24 hr.

Results and Discussion

Typical results are presented in Tables 1 and 2. For convenience, these results could be evaluated under two categories:

(a) *Oxidations*—It may be seen from the data in Tables 1 and 2 that the number of equivalents of bromine monochloride consumed per mole of the reductant is 4 for isonicotinic acid hydrazide, 2 for triphenylphosphine, 8 for trithionate and phosphorothioate, 16 for xanthate and dithiocarbamate, 32 for reinecke salt and 80 for cadmium thiourea reineckate. These values agree with the following oxidation reactions.



On comparing these results with the results of iodine monochloride oxidation it may be noted that in the case of four of the compounds in this study, i.e. triphenylphosphine, phosphorothioate, trithionate and isonicotinic acid hydrazide, the number of equivalents of oxidant consumed per mole of reductant is the same for both the reagents. In these

cases the bromine monochloride method has no specific advantage over the iodine monochloride method and it is simply a useful alternative method.

But, with the remaining compounds, viz. xanthate, dithiocarbamate, reinecke salt and cadmium thiourea reineckate, bromine monochloride effects a more extensive oxidation than iodine monochloride. The numbers of equivalents of iodine monochloride consumed for the above compounds are respectively 14, 14, 24 and 64 whereas, with bromine monochloride, the values are 16, 16, 32 and 80 respectively. This increased consumption of BrCl here may be traced to the ability of this oxidant to oxidize the formate ion to carbonate (in the case of oxidations of xanthate and dithiocarbamate) and the cyanide ion to cyanate (in the case of reinecke salt and cadmium thiourea reineckate). For the above-mentioned compounds the bromine monochloride method is therefore intrinsically more accurate than the iodine monochloride method.

It is noteworthy in this context that in many other oxidimetric methods for the determination of xanthates and dithiocarbamates, the number (*n*) of equivalents of oxidant consumed per mole of the reductant is <16. Thus for xanthate, *n* = 14 with chloramine-T¹⁷ and potassium iodate²⁵ and *n* = 1 with iodine²⁶. For dithiocarbamate, *n* = 14 with chloramine-T²⁷ and potassium iodate²⁵, *n* = 1 with iodine²⁸, ICN²⁹ and BrCN²⁹. On this basis, it would appear that BrCl should find preference over these

TABLE 1 — OXIDIMETRIC DETERMINATIONS WITH BROMINE MONOCHLORIDE

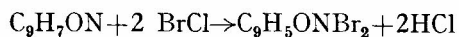
Substance	No. of determinations	Eq. BrCl consumed/mole reductant (mean value)	% relative mean error
Isonicotinic acid hydrazide	6	4.009	+0.23
Triphenylphosphine	5	2.002	+0.12
Sodium phosphorothioate	6	7.992	-0.10
Potassium trithionate	5	7.993	-0.09
Potassium ethyl xanthate	7	16.02	+0.15
Sodium diethyl dithiocarbamate	6	16.08	+0.48
Reinecke salt	5	32.05	+0.19
Cadmium thiourea reineckate	6	80.27	+0.32

TABLE 2 — DETERMINATION OF OXINE AND METALLIC OXINATES WITH BROMINE MONOCHLORIDE

Compound	No. of determinations	Eq. BrCl consumed/mole reductant (mean value)	% relative mean error
Oxine	8	4.022	+0.55
Mg (oxine) ₂	7	7.993	-0.10
Al (oxine) ₃	7	11.980	-0.17
Mn (oxine) ₂	6	7.991	-0.12
Fe (oxine) ₃	6	11.010	+0.07
Co (oxine) ₂	6	8.036	+0.45
Ni (oxine) ₂	4	8.031	+0.38
Cu (oxine) ₂	6	6.972	-0.40
Zn (oxine) ₂	5	8.024	+0.29

oxidants for the determination of xanthates and dithiocarbamates.

(b) *Halogenations (brominations)*— It was found that in dil. hydrochloric acid medium oxine reacts with bromine monochloride to give dibromooxine, consuming 2 moles (4 equivalents) of BrCl per mole of oxine.



It may be seen from Table 2 that the number of equivalents of BrCl consumed per mole of the oxinates of Mg(II), Mn(II), Co(II), Ni(II) Zn(II) etc. is 8 and that for Al(III) $n = 12$; for copper oxinate $n = 7$ and for iron oxinate $n = 11$. The apparent deviations in the case of Cu(II) and Fe(III) are due to the fact that during subsequent addition of KI (for estimating the unconsumed BrCl), there is a concomitant reduction of Cu(II) to Cu(I) and Fe(III) to Fe(II).

Oxine and metallic oxinates have been determined by Cihalik³⁰ using iodine monochloride as the oxidant, in a medium whose acidity is carefully controlled by the addition of ammonia in suitable amounts. If excess ammonia is added, oxine is thrown out. Further, increase of acidity was reported to slow down the rate of this reaction considerably. In the present investigation, it is found that the reaction of oxine with bromine monochloride takes place very quickly in the acidic media employed. Increase of acidity does not decrease the rate of the reaction. The present method is also superior to the conventional bromate-bromide method, in which special precautions have to be taken to preclude loss of bromine.

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