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Heptavalent Bromine Compounds

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Publications on heptavalent bromine compounds which have appeared during the last 10 years are reviewed. The discussion includes the preparation and analysis of perbromates, the physical and chemical properties of perbromic acid and its salts, the "hot atom" chemistry and radiation chemistry of perbromates, and the practical utilisation of heptavalent bromine compounds. 80 references.

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I. INTRODUCTION

Perbromates have long been classified among the compounds which cannot be prepared by ordinary chemical methods. However, the existence and widespread applications of their homologues (the perchlorates and the periodates) have stimulated renewed interest from theoreticians and experimentalists in the preparation of perbromates. The first attempts to prepare heptavalent bromine compounds were made in the middle of the 19th century. Experimental and theoretical work in this area is reviewed in Refs.1–4. The first successful preparation of perbromate (Appelman[5]) by the β^- disintegration of ^{83}Se in a selenate composition was described as recently as in 1968. By studying the chemical properties of microquantities of perbromate Appelman was able to develop[5] a macro-synthetic method for heptavalent bromine compounds.

Several dozen papers on heptavalent bromine compounds have appeared since the first successful synthesis of perbromate, but they do not include general reviews of the subject. The aim of this paper is to generalise existing information on heptavalent bromine compounds.

II. METHODS OF PREPARATION OF HEPTAVALENT BROMINE COMPOUNDS

The first successful synthesis of perbromate was carried out by the "hot atom" chemistry method, using the β^- disintegration of ^{83}Se in a selenate composition[5]. The resulting bromine-83 is radioactive, with a half-life of 2.4 h. Therefore the method does not yield weighable amounts of perbromates, but it does show that heptavalent bromine compounds are relatively stable and therefore can be prepared (in principle) in macro-amounts. The preparation was demonstrated by electrochemically oxidising lithium bromate in a neutral solution[5], using a partitioned cell with a platinum anode and an anodic current density of 10 A cm^{-2}. The yield of perbromate was ~2%.

The electrolytic oxidation of bromate was therefore not acceptable as a preparative method, because its yield was too low, and a search for more effective methods of preparing heptavalent bromine compounds was started. An aqueous solution of xenon difluoride, whose oxidation potential is 2.62 V, was added[6] to a fairly concentrated bromate solution, giving perbromate in 12% yield (calculated from the initial amount of xenon difluoride[7]).

Shortly after Appelman's preparation of heptavalent bromine compounds Brown and coworkers[8] demonstrated the formation of perbromate by irradiating caesium bromate with gamma-rays from ^{60}Co. The yield of caesium perbromate was 0.86% of the initial amount of caesium bromate. Irradiation of lithium bromate did not produce perbromate. No heptavalent bromine compounds were obtained by oxidising aqueous bromate solutions with sodium perxenate and persulphate at 100 °C,[5] or by treating bromate solutions with hydrogen peroxide in the presence of acid[9].

A more convenient method of preparing heptavalent bromine compounds relies[10] on the oxidation of sodium bromate by fluorine in an alkaline solution. This reaction gave a sodium perbromate yield of 20% of the initial amount of bromate:

$$F_2 + BrO_3^- + 2OH^- \rightarrow BrO_4^- + 2F^- + 2H_2O.$$

The preparation of sodium perbromate by this method is described in detail in Ref.11.

A simple method of separating sodium perbromate from the reaction mixture is extraction with acetone[12]. The sodium bromate solution after being oxidised with fluorine is evaporated to dryness under a heat lamp, and the residue is washed with acetone. Under these conditions the sodium perbromate is extracted into the liquid phase, and the sodium bromate and fluoride remain in the solid phase. The acetone is evaporated off, and the sodium perbromate is recrystallised first from acetone and then from ethanol.

The following perbromates have been prepared by neutralising perbromic acid with the appropriate hydroxide or oxide: lithium, sodium, potassium, rubidium, and caesium[13], magnesium, calcium, strontium, and barium[14], ammonium[15], silver[16], and uranyl[17]. Potassium, rubidium, caesium, and uranyl perbromates are recrystallised from aqueous solutions, silver perbromate by adding hexane to a benzene solution, and the other perbromates are usually recrystallised from acetone.

The reaction of potassium perbromate with antimony pentafluoride yields the highly reactive compound perbromyl fluoride[18–22], BrO_3F, which rapidly hydrolyses in air[23] and attacks glass even at room temperature. Isopropyl perbromate[16] also is unstable at room temperature, though it can be prepared by the reaction between isopropyl bromide and silver perbromate. On the other hand tetraphenylarsonium perbromate, prepared from tetraphenylarsonium chloride and sodium perbromate[8], is a very stable compound.

Thus, several compounds of heptavalent bromine have already been prepared.

III. PHYSICAL AND CHEMICAL PROPERTIES OF PERBROMIC ACID AND ITS SALTS

Perbromic acid is a strong monobasic acid. Potentiometric titration of 0.6 M $HBrO_4$ with a 0.6 M solution of sodium hydroxide gives a curve very similar to that of $HClO_4$ under the same conditions[10]. In aqueous solutions perbromic acid is stable up to a concentration of 55% (6 M), but it decomposes at higher concentrations. A 6 M solution of $HBrO_4$ is stable indefinitely at room temperature. When heated on a water bath the solution becomes weakly yellow after one hour, but its oxidising power is reduced by only 1%. Mass spectrometric measurements have shown[24] that perbromic acid is a very stable compound, and is less volatile than perchloric acid. Samples in which the concentration of perbromic acid is as high as 83% can be obtained by vacuum distillation at room temperature. Rapid removal of the water produces crystals of $HBrO_4 \cdot 2H_2O$, which quickly become liquid when stored in air.

Perbromic acid is a slow-acting oxidising agent. In dilute solutions it oxidises iodide and bromide ions quite slowly, and it does not react with chloride ions. This may explain early failures to detect perbromates, which were always sought among the most reactive (rather than the most inert) compounds. On the whole, perbromates are the least reactive of all oxy-halogen compounds (except the perchlorates). However, at high concentrations perbromic acid is no longer a slow-acting oxidiser. Thus, 12 M $HBrO_4$ rapidly oxidises chloride ions and reacts explosively with filter paper; 3 M $HBrO_4$ rapidly oxidises stainless steel, and 6 M $HBrO_4$ at 100 °C easily oxidises bivalent manganese to MnO_2, tervalent chromium to dichromate, and tervalent cerium to Ce(IV).[10] These reactions occur also at room temperature if the acid is dehydrated under vacuum.

Perbromic acid and its salts have the same u.v. and Raman spectra, showing that identical anions are present in both cases. The similarity between the Raman spectra of solid $KBrO_4$ and those of its solutions[25] confirms that these anions are also present in the crystals. By comparing the Raman and the i.r. spectra of solid $KBrO_4$ we find that two of the four Raman bands are active in the i.r.: assignment of these frequencies suggests a tetrahedral structure for $KBrO_4$. The fundamental vibrational frequencies of BrO_4^- [10] are compared with those of ClO_4^- and IO_4^- [26] in Table 1.

Table 1. Vibrational frequencies of ClO_4^-, BrO_4^-, and IO_4^- ions in the i.r. region.

Anions	Vibrational frequencies, cm^{-1}			
	ν_1	ν_2	ν_3	ν_4
ClO_4^-	935	460	1060	630
BrO_4^-	798	331	883	410
IO_4^-	791	256	853	325

The lack of fast oxygen exchange between the perbromate ion and water shows that this ion (unlike the periodate ion[27]) does not undergo the fast hydration reaction

$$IO_4^- + 2H_2O \rightleftarrows H_4IO_6^- .$$

The most fully investigated of the salts of perbromic acid is potassium perbromate: $KBrO_4$, a white crystalline substance with a density of 3.08 g cm^{-3}.[28] The enthalpy of formation of potassium perbromate is -68.74 ± 0.14 kcal $mole^{-1}$, and its enthalpy of dissolution is 11.61 kcal $mole^{-1}$.[29] The potassium perbromate crystals belong to the $BaSO_4$ structure type, with the rhombic lattice parameters $a = 8.930$, $b = 5.921$, and $c = 7.488$ Å. The BrO_4^- ion has a tetrahedral structure, with a Br–O bond length of 1.61 Å and an O–Br–O bond angle of 109–110°.[28] The bond order, calculated by the Long–Plane–Pauling formula, is 1.93,[30] as compared with a Br–O bond order of 1.56 [31] in perbromyl fluoride. The mean-square vibrational amplitudes and the Coriolis interaction constants have also been calculated[32–35].

The chemical shift in the photo-electronic spectra of potassium perbromate (as compared with potassium bromide) was lower than for the corresponding chlorine compounds but higher than for the iodine analogues[36]. This is consistent with the differences in bond energy for the three halogens calculated by the Hartree–Fock method. Quantum-chemical calculations[37,38] have shown that the perbromate ion can be less stable than the perchlorate and the periodate, but that the difference is very small. The standard electrode potential of the bromate–perbromate couple is variously reported as 1.74 V,[39] 1.76 V,[29,40] and 1.82 V,[41] which should be compared with 1.23 V for the chlorate–perchlorate couple and 1.64 V for the iodate–periodate couple.

Ammonium perbromate is another salt of perbromic acid which has been adequately studied[15]. It is a white crystalline compound, indefinitely stable in air. Its density is 2.5 g cm^{-3}, and its crystal lattice has a rhombic unit cell with lattice parameters $a = 9.20$, $b = 6.04$, and $c = 7.63$ Å.[15] NH_4BrO_4 is very much less hygroscopic than ammonium perchlorate. Thus at 95% relative humidity ammonium perbromate absorbs only 4% of water, after which its weight remains constant, whereas ammonium perchlorate absorbs 23% of water and becomes visibly wet. The solubility of ammonium perbromate in water increases with temperature[15] (9.5, 13.9, 17.8, and 26.3 g per 100 g of solution at 0, 15, 25, and 45 °C respectively). Ammonium perbromate is soluble in methanol, acetone, ethanol, and acetonitrile.

In the alkali metal perbromates the solubility in water decreases in the sequence from lithium perbromate to caesium perbromate. Whereas lithium and sodium perbromates are very soluble in water, the solubility of $KBrO_4$ is only 0.2 mole $litre^{-1}$, and rubidium and caesium perbromates are only sparingly soluble at room temperature. On the other hand the perbromates of the alkaline earth metals, magnesium, silver, and uranyl are very soluble in water as well as in acetone.

When stored in air the anhydrous perbromates of lithium and sodium are converted into crystal hydrates of composition $LiBrO_4 \cdot 2H_2O$ and $NaBrO_4 \cdot H_2O$ respectively, but potassium, rubidium, and caesium perbromates are much less hygroscopic. Crystals of alkaline-earth, magnesium, and uranyl perbromates deliquesce very rapidly in the air, and have to be handled in a dry-box.

Alkali, alkaline-earth, and magnesium perbromates decompose to the bromates, after losing all their water, when heated[13,14], whereas the decomposition products of ammonium perbromate are N_2, Br_2, H_2O, and small amounts of N_2O and NO_2.[15] Temperature ranges and decomposition temperatures of the alkali, alkaline-earth, magnesium, and ammonium perbromates are listed in Table 2.

It is clear from Table 2 that the thermal stability of the alkali metal perbromates increases in the sequence $LiBrO_4 < NaBrO_4 < KBrO_4 < RbBrO_4 < CsBrO_4$, whereas the alkaline-earth and magnesium perbromates are indistinguishable as regards thermal stability (within experimental error). The alkali metal perbromates decompose at higher temperatures than the perbromates of the alkaline-earth metals, but the decomposition temperatures are very sensitive to the purity

of the sample. Thus, a sample of $KBrO_4$ which had been prepared without recrystallisation began to decompose at 150 °C, whereas a recrystallised sample remained unchanged up to 260 °C.[10] Obviously, even traces of bromate impurity are able to catalyse the thermal decomposition of perbromates.

Table 2. Temperature ranges and decomposition temperatures of alkali, alkaline-earth, magnesium, and ammonium perbromates.

Compound	Decompn. temperature range, °C	Decompn. temperature, °C	References
$LiBrO_4$	185—220	210±10	13
$NaBrO_4$	246—289	226±10	13
$KBrO_4$	255—282	271±5	13
$KBrO_4$	260—280	275	10
$RbBrO_4$	272—300	291±5	13
$CsBrO_4$	200—319	302±5	13
NH_4BrO_4	180—260	—	15
$Mg(BrO_4)_2$	181—199	191±5	14
$Ca(BrO_4)_2$	180—201	193±5	14
$Sr(BrO_4)_2$	180—207	192±5	14
$Ba(BrO_4)_2$	174—203	187±5	14

Other salts of perbromic acid, such as silver and uranyl perbromates, have been much less fully investigated. Baum and coworkers[16] prepared $AgBrO_4$ as a white, hygroscopic salt which was stable for several months at room temperature. Silver perbromate is soluble in benzene but insoluble in saturated hydrocarbons. Uranyl perbromate is a light-green, very hygroscopic salt. As in the case of the uranyl perchlorates[42], samples of $UO_2(BrO_4)_2 \cdot nH_2O$ containing up to 7 moles of water per mole of salt can be prepared[17]. Uranyl perbromate pentahydrate (unlike the perchlorate) can be obtained only in a narrow range of water vapour pressures. From the i.r. and Raman spectra of the uranyl perbromates we may conclude[17] that the force constants of the UO_2^{2+} bonds in $UO_2(BrO_4)_2$ are similar to the corresponding values for $UO_2(ClO_4)_2$. The i.r. spectra of the hydrated uranyl perbromates indicate the existence of different types of bond in these compounds [as in the case of $UO_2(ClO_4)_2 \cdot .nH_2O$].[43]

IV. ANALYTICAL CHEMISTRY OF HEPTAVALENT BROMINE COMPOUNDS

Various methods can be used to detect and to determine perbromates. For qualitative analysis the main reaction is a drop test with an acidified solution of potassium iodide. The perbromate spot, unlike that of many other oxidising agents, does not appear at once: the rate of development of the spot increases with the concentration of potassium iodide and with the acidity of the solution. The perbromate ion can be detected by a Methylene Blue drop reaction, which produces a crimson spot of perbromate on a blue background[44], and also by the reaction with manganese sulphate in phosphoric acid, which produces a violet colour[45].

The most sensitive spot test for perbromate ions on paper is the benzidine reaction[46]. The chromatograms are sprayed with a 2% solution of benzidine in 10% acetic acid, and heated in a jet of hot air. The spot due to the perbromate ion is initially blue, but on being heated it becomes dark grey. The sensitivity of the reaction is 0.01 μg of potassium perbromate. The main drawback of all these qualitative reactions is their lack of specificity: many oxidising agents will seriously interfere with the detection of heptavalent bromine compounds.

Perbromates can be determined quantitatively by a variety of methods. One of the simplest is the reduction of perbromate to bromide ions, using 12 M HBr.[10] A five-fold (by volume) excess of concentrated HBr is added to the sample for analysis, and the resulting solution is allowed to stand for 10 min in a closed vessel. The reaction goes to completion in this time if the concentration of HBr is not less than 11.5 M: at an HBr concentration of 10.4 M 40 min are required to complete the reaction. The solution is then diluted 10-fold with a 2% solution of sodium iodide containing NaH_2PO_4, and titrated with thiosulphate. If the perbromate solution contains substantial amounts of lower oxygen compounds of bromine it is first reduced with dilute HBr, and the resulting bromine is swept out of the solution by a stream of argon. If the concentration of HBr is held between 0.5 and 1 M the perbromate is practically unaffected by this operation.

An alternative oxidation–reduction method uses $SnCl_2$ for the determination of perbromate ions[5]. The perbromate solution is made 6 M in hydrochloric acid, and Mo(VI) is added to it to a 0.04 M concentration. After adding an excess of $SnCl_2$ an aliquot of the solution is heated for 30 min on the water bath, in order to reduce the perbromate to bromide, and the latter is oxidised by chlorine to BrCN in a neutral solution of cyanide. The solution thus obtained is acidified and titrated with thiosulphate after adding KI.

Another method of determining perbromate in the presence of bromate includes the reduction of BrO_4^- to BrO_3^- by iodine in a weakly alkaline medium (pH 7–9) at 100 °C.[47] Evolution of free iodine is prevented by adding a known amount of Na_3AsO_3, and the excess of this reagent is titrated with iodine with starch indicator. The total amount of bromate is determined by titration with acidified thiosulphate. The perbromate ion can be reduced to bromate simply by adding a solution of KI, but in this case two weeks must be allowed for the reaction to go to completion, whereas with hydroiodic acid the reduction of BrO_4^- to Br^- is instantaneous at room temperature[48].

In addition to the redox methods, gravimetry methods of determining perbromate have been described. They involve precipitation of the perbromate as $RbBrO_4$ [5] or as tetraphenylarsonium perbromate[8]. The latter is precipitated by adding tetraphenylarsonium chloride to the solution containing perbromate and bromate ions. The precipitate is washed with water to remove traces of bromate and with 50% aqueous ethanol, and dried in a vacuum desiccator at room temperature.

As an alternative to the gravimetric end-determination, perbromate can be determined as tetraphenylarsonium perbromate by potentiometric titration with a solution of tetraphenylarsonium chloride[49]. Anions such as chlorate, chloride, bromate, bromide, fluoride, sulphate, and chromate do not interfere with the titration. However, in the presence of periodate ions this method cannot be used.

Polarographic measurements have given a single wave for solutions containing bromate and perbromate ions in 0.05 M $HClO_4$, corresponding to the reduction of BrO_4^- and BrO_3^- to Br^-, whereas in neutral or in alkaline media two distinct waves are observed. The first corresponds to the reduction of perbromate ions to bromate, and the second to the reduction of bromate to bromide, thus allowing the method to be used for the determination of BrO_4^- in the presence of BrO_3^-.[50] The error of the determination of perbromate by this method is 2%. The electrochemical reduction of BrO_4^- is discussed also in Refs. 51–54.

Small amounts of perbromate in the presence of traces of other bromine anions have been determined by colorimetric methods[55] and by extraction photometry, using Crystal Violet[56]. In the latter method the presence of bromate at concentrations up to 10^{-3} g-ion litre^{-1} does not interfere with the determination of perbromate, whereas bromide at concentrations greater than 5×10^{-4} M lowers the optical density of solutions of Crystal Violet containing BrO_4^-. The method is suitable for determining perbromate ions at concentrations between 10^{-6} and 10^{-5} M.

Perbromate ions can be separated from mixtures with other anions by ion-exchange, thin-layer, and paper chromatography methods. Lederer and Sinibaldi[44] studied the chromatographic behaviour of perbromate ions on paper and on thin cellulose and silica gel layers, using the ethanol–water–ammonia and butanol–pyridine–1 M NH_4OH systems. BrO_4^- was found to be more mobile than BrO_3^- under these conditions. The same is true in the isopropanol–1.5 M NH_4OH system[45], but in this case substantial reduction of the perbromate ion occurs, and therefore the system is not suitable for the quantitative determination of perbromate.

Table 3. Chromatographic separation of chemical forms of bromine by thin-layer and paper chromatography.

Chemical form	R_f values for chromatography on Al_2O_3		R_f values for paper chromatography	
	Acetone–water (8:1)	Acetone–water–ethanol (6:2:1)	Acetone–water–ethanol (6:2:1)	Acetone–water–pyridine (6:1:2)
BrO_4^-	0.60±0.02	0.68±0.02	0.89±0.02	0.82±0.02
BrO_3^-	0.08±0.01	0.14±0.02	0.39±0.01	0.26±0.02
Br^-	0.27±0.02	0.41±0.02	0.53±0.05	0.14±0.01

A method free from this drawback is described in Ref. 57. Bromine compounds were separated on thin layers of Al_2O_3 and on paper by using the following solvent systems: acetone–water, acetone–water–ethanol, and acetone–water–pyridine. The R_f values were determined by measuring the ^{82}Br activity with an MST-17 end-window counter: the results are summarised in Table 3.

Separation of bromate and perbromate ions on a thin layer of Al_2O_3 has been achieved also by using aqueous solutions of the salts, acids, and bases[58]. As in the case of paper electrophoresis, the perbromate ion has the higher mobility. The sharpest separation was obtained with solutions of thorium nitrate and zirconyl chloride[44].

A reliable method of separating the different chemical forms of bromine is ion-exchange chromatography on the strongly basic anion exchangers AV-17 and Dowex-1.[57] Selective separation of bromine compounds in different states of oxidation was achieved by elution with potassium bicarbonate and nitrate solutions. Bromite ions were washed out by elution with 0.5 M $KHCO_3$, bromate ions with 1 M $KHCO_3$, bromide ions with 1 M KNO_3, and perbromate ions with 2 M KNO_3. On the other hand, hypobromite ions were absorbed at the top of the column and were not eluted: apparently, these ions react with the anion exchange resin by brominating it.

On anion-exchange paper the perbromate ions are adsorbed as strongly as perchlorate and periodate ions: the Rf values of all these ions are very similar[45]. The best separation of BrO_4^- from BrO_3^- is obtained by using diethylaminocellulose.

V. "HOT ATOM" CHEMISTRY OF CRYSTALLINE PERBROMATES

The "hot atom" chemistry of crystalline perbromates has great theoretical and practical interest. Its theoretical importance stems from the possibility of predicting chemical forms and of setting up a kinetic theory of chemical reactions involving atoms with an excess of energy. The practical interest lies in the preparation of sources of radioactive bromine with a high specific activity.

One possible way of obtaining radioactive isotopes of bromine is to irradiate perbromates in a nuclear reactor. The radioactive isotopes are usually stabilised in chemical forms different from the original compound. The distribution of atoms of the radioactive isotope ^{82}Br over the different chemical forms after irradiation with thermal neutrons is shown in Table 4 for the perbromates of alkali[59] and alkaline-earth metals, and of magnesium and ammonium[60].

Table 4. Yield of chemical stabilisation forms of ^{82}Br in neutron-irradiated perbromates.

Irradiated compound	Yield of bromine-82, %				
	BrO_4^-	BrO_3^-	BrO_2^-	BrO^-	Br^-
$LiBrO_4 \cdot H_2O$	2.1±0.3	44±2	4.4±0.5	4.4±0.5	45±2
$NaBrO_4$	2.1±0.4	36±1	1.0±0.6	0.8±0.3	60±1
$KBrO_4$	2.3±0.4	44±3	1.1±0.3	1.7±0.3	51±3
$RbBrO_4$	2.6±0.4	33±1	3.0±0.3	2.0±0.3	59±2
$CsBrO_4$	2.2±0.4	31±1	5.1±0.5	3.5±0.5	58±2
NH_4BrO_4	1.6±0.4	<0.3	<0.3	0.4±0.3	98±1
$Mg(BrO_4)_2 \cdot 6H_2O$	4.4±0.4	68±2	1.8±0.5	1.7±0.5	24±1
$Ca(BrO_4)_2 \cdot 6H_2O$	9.2±0.7	42±2	3.8±0.5	2.2±0.5	43±2
$Sr(BrO_4)_2 \cdot 3H_2O$	8.0±0.3	26±1	1.9±0.3	1.7±0.3	62±1
$Ba(BrO_4)_2 \cdot 2H_2O$	6.0±0.3	27±1	1.1±0.3	3.1±0.3	63±1

The distribution of ^{82}Br over the different chemical forms in alkali metal perbromates irradiated with neutrons was studied also by Hassan and Heitz[61], who found that 74% of the ^{82}Br was present as bromide, 24% as bromate, and 1% as perbromate, in general agreement with other workers[59,60], but (surprisingly) they claim that the $^{82}BrO_4^-$ ions remained in the original spot in their paper electrophoresis method of analysis whereas $^{82}BrO_3^-$ had a much higher mobility (in contrast to earlier reports[44,58]).

After thermal annealing of neutron-irradiated perbromates the yields of the chemical forms of ^{82}Br show some major changes[60–62]. In the alkali metal perbromates the content of ^{82}Br as BrO_4^- increases initially to a maximum, and then decreases, but in this case the changes are not very great. The main reaction occurring when alkali metal perbromates are annealed is the oxidation of $^{82}Br^-$ to $^{82}BrO_3^-$, the size of the effect being very dependent on the nature of the cation. For example, in neutron-irradiated lithium perbromate the yield of $^{82}BrO_3^-$ was 98% at the end of the heat treatment, for $NaBrO_4$ it was 93%, for $KBrO_4$ 89%, for $RbBrO_4$ 80%, and for $CsBrO_4$ 58%. Similar effects are reported in Ref. 63, but thermal annealing of neutron-irradiated potassium perbromate near its decomposition temperature (275 °C) was found to give a sudden increase in retention, similar to the increased retention of ^{128}I produced by heating irradiated potassium periodate[64]. The maximum retention of ^{82}Br (80%) was reached after heating $KBrO_4$ for 1 h at 275 °C. Above 300 °C all the bromine oxy-anions decompose.

In the alkaline-earth metal and magnesium perbromates the retention of ^{82}Br decreases, and at the end of the heat treatment it is as low as 2.0%. The changes in yield of $^{82}BrO_3^-$ caused by thermal annealing again depend on the nature of the cation[60]. The bromine and oxygen recoil atoms recombine with formation of bromate ions during thermal annealing of neutron-irradiated perbromates. On the other hand, the oxygen atoms can recombine together to give oxygen molecules. Therefore the oxidation of $^{82}Br^-$ to $^{82}BrO_3^-$ is not usually quantitative, in spite of the fact that stable perbromate molecules give off oxygen atoms during radiolysis.

Table 5. Yield of chemical stabilisation forms of ^{82}Br and ^{80m}Br recoil atoms in neutron-irradiated lithium and sodium perbromates.

Irradiated compound	Isotope	Yield of radioactive bromine, %				
		BrO_4^-	BrO_3^-	BrO_2^-	BrO^-	Br^-
$LiBrO_4$	^{82}Br	2.1±0.2	45±1	3.4±0.8	4.8±0.6	46±1
	^{80m}Br	1.9±0.2	60±2	2.9±0.6	4.2±0.9	31±1
$NaBrO_4$	^{82}Br	2.0±0.1	41±2	1.5±0.3	0.7±0.2	55±2
	^{80m}Br	1.1±0.1	55±2	0.9±0.2	1.2±0.5	41±1

Irradiation of perbromates with thermal neutrons produces, in addition to ^{82}Br, also ^{80m}Br, and this allows us to compare the yields of the chemical forms of these isotopes, i.e. to look for an isotope effect. The results of these experiments, made with lithium and sodium perbromates[65], are shown in Table 5.

During thermal annealing the yield of $^{82}BrO_3^-$ in neutron-irradiated sodium perbromate increases from 41 to 91% in 15 min at 150 °C, whereas the yield of $^{80m}BrO_3^-$ increases from 55 to 86% during the same time. Longer heating times have no effect, and at the end of the anneal the isotope effect amounts to 5%. In lithium perbromate the yields of ^{82}Br and ^{80m}Br as bromate ion are equal at the end of the anneal, possibly as a result of the production of fission fragments from ^6Li by the thermal neutrons. These fragments cause strong ionisation of their surroundings and tend to mask any differences in the dislocation regions where the ^{82}Br and ^{80m}Br recoil atoms are accommodated.

Crystal defects play an important role in determining the fate of the bromine recoil atoms during thermal annealing of neutron-irradiated perbromates. In order to quantify the influence of crystal defects on the annealing operation the effect of previous heat treatment of the crystals (before neutron irradiation) has been investigated[66]. These experiments showed that in sodium perbromate which has been heat treated before irradiation the retention of ^{82}Br is unchanged by annealing, and the yield of bromate ions is lower than in ordinary samples which have been similarly annealed. Since all the samples had been irradiated under identical conditions, differences in behaviour of the recoil atoms during annealing can be interpreted as differences between the crystals, i.e. as differences in the relative distribution over energy levels with activation energies corresponding to different temperatures.

Whereas the retentions of ^{82}Br and ^{80m}Br formed by neutron irradiation of crystalline perbromates of the alkali metals seldom exceed 2.6%, the retention of the radioactive bromine isotopes formed by isomeric transition and β^- disintegration is substantially higher. Thus, the retention of ^{80}Br formed by isomeric transition from ^{80m}Br in a lithium perbromate composition is 31 ± 1%,[60] and the retention of ^{83}Br formed by β^- disintegration from ^{83}Se in potassium selenate is 24%.[67]

Whereas irradiation of perbromates in a nuclear reactor produces radioactive bromine isotopes, the interaction of stable bromine atoms with high-energy protons produces a whole series of radioactive isotopes of different elements. Radiochemical and gamma-spectroscopic analyses have shown that the irradiation of crystalline sodium perbromate with 1 GeV protons leads to the formation of oxygenated krypton compounds, produced from bromine by a (p, xn) reaction[68]. The retention of radioactive krypton isotopes in a chemically bound state was 30 ± 9% for krypton-74, 7 ± 3% for krypton-76, and not more than 0.3% for krypton-77 and krypton-79. No attempt was made to identify the krypton compounds formed. However, by analogy with the formation of xenon compounds by β^- disintegration of ^{131}I, ^{133}I, and ^{135}I in periodate, iodate, and iodine pentoxide compositions[69], in which the preferred chemical form of the bound xenon is XeO_3, we may assume the formation of KrO_3. Krypton trioxide may be formed by the interaction of krypton recoil atoms with various fragments, produced in sodium perbromate by the radiolytic interaction of the proton beam, secondary particles, gamma radiation, and the recoil atoms themselves. One possible fragment is O_3^-, which has been detected by ESR in potassium perbromate irradiated with X-rays[70]. The interaction of these ions with krypton recoil atoms can stabilise the latter in the form of KrO_3. The formation of oxygen compounds of krypton, xenon, and radon has been observed also after irradiation of uranyl sulphate with high-energy protons[71].

Thus, previously unknown oxygen compounds of krypton have been prepared by studying perbromates. The perbromates themselves, on the other hand, can be prepared by using xenon difluoride[7] and krypton difluoride[72].

VI. RADIATION CHEMISTRY OF HEPTAVALENT BROMINE COMPOUNDS

Boyd and Brown[73] have studied the stable radiolysis products formed in crystalline potassium perbromate irradiated with gamma rays from ^{60}Co. The irradiation was carried out at ~35 °C with two sources, having activities of 3 and 11.5-kCi respectively. The dose of radiation absorbed was 9.3×10^{17} eV g^{-1} H_2O min^{-1} for the first source and 3.8×10^{18} eV g^{-1} H_2O min^{-1} for the second source. The dose absorbed by crystalline potassium perbromate was calculated by multiplying the dose for water by the ratio of the number of electrons per gramme of $KBrO_4$ to the number of electrons per gramme of H_2O: it was found to be 1.5×10^{23} eV $mole^{-1}$. The i.r. spectrum of $KBrO_4$ irradiated with this dose contains, in addition to the BrO_4^- absorption bands, only the absorption bands due to BrO_3^-. No bands which could be assigned to BrO_2^- were detected. A possible explanation[73] is that the dose to which the sample was exposed was too small.

However, even at higher doses the bromate ion is practically the only product of the radiolysis of crystalline potassium perbromate (4.36×10^{24} eV $mole^{-1}$) and sodium perbromate (3.98×10^{24} eV $mole^{-1}$).[60] The preferential formation of bromate ions during radiolysis of perbromates is explained by the far higher probability of breaking one bromine–oxygen bond than two, three, or (especially) all four bonds in a perbromate ion irradiated with gamma rays from ^{60}Co.

Irradiation of alkali metal perbromates in a reactor also leads to extensive radiolysis with formation of bromate ions, the radiation-chemical yield $G(-BrO_4^-)$ being 3.9 ± 0.3 for

lithium perbromate, 2.8 ± 0.3 sodium, potassium, and rubidium perbromates, and 3.2 ± 0.3 for caesium perbromate. These yields are very large in comparison with $G(Br^-)$, which is never greater than 0.02.[60]

Hassan and Heitz[74] studied the radiolytic reduction of potassium perbromate in aqueous solutions (both aerated and de-aerated) under the influence of gamma rays from ^{60}Co. In acid solutions only one reaction is observed: $H^{\bullet}(HO_2^{\bullet}) + BrO_4^-$ [with a yield $G(-BrO_4^-) = 3.5$]. In a neutral solution the perbromate ion is reduced by solvated electrons. However, the yield of this reaction [$G(-BrO_4^-) = 5.3$] suggests that species other than solvated electrons are also involved in the reduction. The photolysis and the radiolysis of potassium perbromate solutions are discussed also by Byberg and Linderberg[75].

Irradiation of potassium perbromate single crystals with X-rays (of 50 kV energy) at 10, 26, and 77 K produces four types of centre [A, BrO_4^{2-}; C, $BrO_4^{\bullet}$; D, $(BrO_4)_2^-$; G, O_3^-] which can be detected by ESR. At 10 K only BrO_4^{2-}, $BrO_4^{\bullet}$, and $(BrO_4)_2^-$ are observed, but at temperatures above 20 K O_3^- is produced by thermal processes from BrO_4^{2-}, and BrO_2 from $BrO_4^{\bullet}$. As a result of these annealing effects only O_3^- and BrO_2 can be detected in the potassium perbromate single crystal at 240 K.

The ESR method has been used also to study the radiolysis products of frozen solutions of potassium perbromate[76]. $BrO_3^{\bullet}$, $BrO_4^{\bullet}$, and BrO_4^{2-} were identified in an irradiated polycrystalline solution of potassium perbromate; the $KBrO_4$ reacted with electrons even in a frozen (glassy) solution in 10 M NaOH, but under these conditions bromine-containing radicals could not be detected.

The pulsed radiolysis of aqueous solutions of potassium perbromate with electrons of 10 MeV energy in a neutral solution saturated with argon produced the reaction

$$BrO_4^- + e^-_{hybr} = BrO^- + O^-,$$

whose rate constant was 7×10^9 litre mole^{-1} s^{-1}.[77] Measurements of the yield of $OH^{\bullet}$ radicals in acid or neutral argon-saturated solutions and of the yield of O_3^- in alkaline oxygen-saturated solutions of potassium perbromate showed that interactions of $H^{\bullet}$, $OH^{\bullet}$, and O^- with BrO_4^- all have rate constants smaller than 10^7 litre mole^{-1} s^{-1}.

Polarographic, optical spectroscopy, and ESR methods have been used to study the photolysis products of aqueous solutions of potassium perbromate at room temperature and at 77 K.[78] Irradiation was carried out at a wavelength $\lambda = 253.7$ nm. At 77 K the O^- centre was detected, but this centre disappears at 160 K with formation of O_2^- and O_3^-. BrO_3^-, BrO_2^-, HO_2^-, and molecular oxygen were detected when a solution of potassium perbromate in 0.1 M NaOH was irradiated.

VII. PRACTICAL APPLICATIONS OF PERBROMIC ACID AND ITS SALTS

Perbromates are still laboratory compounds, and are not yet handled on an industrial scale. However, they are beginning to find wide uses in the laboratory, for example in studies of the electrical double layer[79,80] and of the synthesis of oxygen compounds of krypton[68]. Perbromic acid and its salts can be used as special oxidising agents, and also for the quantitative determination of rubidium and caesium (whose perbromates are sparingly soluble in water at 0 °C). Mixed with nitric acid, $HBrO_4$ has been used for wet ashing organic compounds. Concentrated perbromic acid is one of the strongest oxidising agents, whereas dilute perbromic acid (like perchloric acid) can be used as a reaction medium. Since most perbromates are fairly soluble, perbromic acid and its salts can be used in metal treatment processes such as electroplating, etching, and polishing. Perbromic acid can also be used in organic synthesis for separating alcohols, ketones, and amines from resinous materials.

Perbromates can be used as sources of radioactive bromine (in the form of bromide ions) with a high specific activity, because most of the radioactive bromine isotopes in neutron-irradiated perbromates are stabilised as bromide ions, and the yield of Br^- during radiolysis is negligible. A high specific activity is important in medical and biological investigations, in which the application of radioactive bromine isotopes is increasing every year.

Thus, heptavalent bromine compounds will undoubtedly find increasingly wide applications in industry and in the national economy as well as in scientific research.

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