

Carbonyl dibromide: a novel reagent for the synthesis of metal bromides and bromide oxides †

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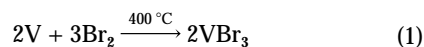
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Carbonyl dibromide reacted with a wide selection of d- and f-block transition-metal oxides to form either the metal bromide or bromide oxide; the reactions are driven by the elimination of carbon dioxide. In a typical reaction the metal oxide was treated with an eight-fold excess of COBr₂ in a sealed Carius tube at 125 °C for 10 d (to ensure complete reaction of the metal oxide). As COBr₂ and the reaction by-products (CO₂, CO and Br₂) are all volatile, the desired products were obtained in essentially quantitative yield and a high degree of purity. Under these conditions V₂O₅, MoO₂, Re₂O₇, Sm₂O₃ and UO₃ were converted into VOBr₂, MoO₂Br₂, ReOBr₄, SmBr₃ and UOBr₃, respectively. This route offers great potential for the preparation of many known bromide derivatives of the transition metals, lanthanides and actinides, in a very convenient manner, and also for the synthesis of new materials. A modified synthesis of carbonyl dibromide was elaborated, and its ¹⁷O NMR and electron impact mass spectra are reported for the first time.

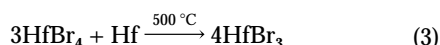
Although the routes to pure anhydrous metal chlorides are well established, versatile, and generally convenient,¹⁻³ the analogous routes to metal bromides and bromide oxides are poorly explored.¹⁻³ When appropriate, they can best be prepared by reaction of the element with either dibromine, *e.g.* equation (1),⁴



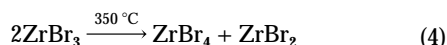
or hydrogen bromide, equation (2),⁵ by bromination of the



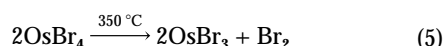
metal oxide with Br₂,^{6,7} BBr₃,⁸ AlBr₃,⁹ CBr₄,^{10,11} or SOBr₂,¹² or by halide exchange with HBr¹³ or BBr₃.¹⁴ In addition, less general routes include the reduction of high-oxidation-state bromides with the appropriate metal (aluminium or dihydrogen are alternative reductants in some cases),^{1,2} *e.g.* equation (3),¹⁵ or by



thermal disproportionation, equation (4),^{15,16} or thermal



decomposition, equation (5),¹⁷ of a higher-oxidation-state

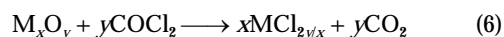


binary bromide. Metal-vapour synthesis has also been used to synthesize metal bromides:¹⁸ thus co-condensation of rhenium atoms with 1,2-dibromoethane (followed by extraction with tetrahydrofuran, thf) gave [Re₃Br₉(thf)₃].

As is apparent, there is no satisfactory general route to metal bromides and bromide oxides. The two main problems appear to be: (a) many of the synthetic routes require severe experi-

mental conditions, and (b) alternative syntheses, performed under milder conditions, frequently lead to product contamination, the contaminant often being extremely difficult to remove (see below).

Metal chlorides have long been prepared by treating metal oxides with phosgene, COCl₂, equation (6).¹⁹ These syntheses



are not only clean, high yielding, and performed under mild conditions, but also provide the basis of many patents (*e.g.* for dealuminating zeolites).^{20,21} It was somewhat surprising, therefore, that the analogous routes to metal bromides using carbonyl dibromide had not been investigated. The only report in the literature of a reaction between a metal oxide and COBr₂ is by Prigent,²² who proposed that heating UO₃ with COBr₂ in a sealed tube for 2 h at 126 °C produced uranium(v) bromide. In our hands, and those of others,²³ however, these observations were unrepeatable. Indeed, as uranium(v) bromide decomposes above 80 °C²⁴ it would have been a very surprising result. We report here on the reaction between a wide range of metal oxides with carbonyl dibromide, which offers great potential for the preparation of many known bromide derivatives of the transition metals, lanthanides and actinides, in a very convenient manner, and for the synthesis of new materials. Preliminary observations on this system have been reported previously in a communication²⁵ and patent applications.^{26,27}

Experimental

CAUTION: The physiological effects of carbonyl dibromide were judged (as a result of some rather amateur experiments on white mice) similar to those of phosgene,²⁸ but clearly a modern detailed evaluation is required if COBr₂ is to be used more widely. The following safety precautions were adopted on the assumption that its toxicity is similar to that of phosgene.

Handling carbonyl dibromide

Phosgene is a toxic gas, with a permissible UK Occupational Exposure Limit (OEL) of 0.08 mg m⁻³ of air (0.02 ppm v/v).²⁹ In the event of exposure, the victim may experience chest pain,

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† Non-SI unit employed: μ_B ≈ 9.27 × 10⁻²⁴ J T⁻¹.

coughing and rapid breathing associated with pulmonary oedema, and it may take over 24 h for symptoms to appear. There is no antidote to phosgene poisoning,¹⁹ and hence treatment is usually directed to the main symptom, toxic pulmonary oedema.³⁰ Hence, all manipulations involving carbonyl dibromide were carried out in a well ventilated fume cupboard with a face velocity of $>0.75 \text{ m s}^{-1}$, and in the presence of at least one other experienced research worker. The vacuum line was constructed within the fume cupboard. The atmosphere both inside and outside the fume cupboard was constantly checked using Dräger tubes³¹ and detector tape (Rimon Laboratories Ltd.). All glassware used greaseless taps, and joints were lubricated with Teflon sleeves. After use, carbonyl dibromide was destroyed by passage through a column containing moist activated charcoal. The fume cupboard was fitted with an alarm system, which was activated automatically if the extractor mechanism failed, or manually in the event of an accident. After use all equipment was washed with an aqueous solution of sodium hydroxide before removal from the fume cupboard.

Spectroscopic measurements

Carbon-13 and ^{17}O NMR spectra were recorded on a Bruker WM360 spectrometer operating at 90.55 and 48.82 MHz, respectively. The ^{13}C and ^{17}O chemical shifts were measured with respect to external tetramethylsilane and water, respectively. Mass spectra were recorded on a Kratos MS80RF spectrometer, and infrared spectra on a Perkin-Elmer 598 spectrometer. Gas-phase infrared spectra were recorded using a 10 cm gas cell fitted with CsI windows, those of solids were recorded as Nujol mulls, using CsI plates. All spectra were calibrated using polystyrene (1601 and 907 cm^{-1}) and indene (551.7 and 420.5 cm^{-1}). Magnetic susceptibilities were measured at room temperature on a Johnson Matthey magnetic susceptibility balance.

Preparation of carbonyl dibromide

Concentrated sulfuric acid (20 cm^3) was slowly added to molten tetrabromomethane (20 g , 60 mmol) at *ca.* 90°C . The reaction vessel, which was connected to a conventional distillation unit, fitted with a high-surface-area trap, was then heated to $150\text{--}170^\circ\text{C}$ for 2 h. The products were collected, as the reaction proceeded, in a -10°C trap. The deep red impure distillate was then transferred quickly to a vacuum line, held at -95°C and continuously evacuated for 1 h to remove the small amounts of SO_2 present. To remove the considerable quantities of free dibromine, the product was condensed into an ampoule (fitted with a greaseless tap) containing mercury, and allowed to warm to room temperature. The ampoule was then closed, removed from the vacuum line, and vigorously (but carefully) agitated within the fume cupboard for 5 min. It was then reconnected to the vacuum line, and the liquid was distilled into a storage bulb. The colourless liquid was redistilled into an ampoule fitted with a greaseless tap, and then stored at room temperature in the absence of light. The purity of the product was checked by gas-phase infrared, ^{13}C and ^{17}O NMR and mass spectrometry. Yield (based on CBr_4): 5.8 g (51%).

Preparations of metal bromides and metal bromide oxides

The procedure for performing the reaction of UO_3 with COBr_2 , and the subsequent isolation of the product, UOBr_3 , is described in detail. Exactly the same experimental procedures were followed for the other reactions. All reactions were performed at 125°C for 10 d and in all cases free dibromine was observed during them.

Uranium(v) tribromide oxide. Carbonyl dibromide (0.9 g , 4.84 mmol) was condensed into a Carius tube containing uranium(vi) oxide (0.18 g , 0.63 mmol), which was then sealed *in*

vacuo and heated at 125°C for 10 d. After this time the Carius tube was cooled to -95°C , and the top (which had been carefully scored with a glass knife) fitted with Portex tubing (which was attached to a ground-glass joint). The Carius tube was then connected to a high-vacuum line, opened carefully and, after removal of the excess of COBr_2 and gaseous reaction products, isolated, removed from the high-vacuum line, and taken into an inert-atmosphere dry-box where the contents were transferred into a Schlenk tube. The black powder was subsequently identified as uranium(v) tribromide oxide by bromide analysis (Found: Br, 50.05. Calc. for Br_3OU : Br, 48.9%), magnetic measurements [$\chi_g = 4.07 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, μ_{eff} (296 K) = $2.04 \mu_{\text{B}}$], and infrared spectroscopy [960m (br), 812m, 607w, 473m (br), 339s (br) and 281 cm^{-1}]. Yield (based on UO_3): 0.28 g (90%).

Samarium(III) bromide. Reaction of carbonyl dibromide (0.95 g , 5.05 mmol) and samarium(III) oxide (0.23 g , 0.66 mmol) at 125°C for 10 d gave a pale yellow powder which was shown to be samarium(III) bromide by bromide analysis (Found: Br, 61.1. Calc. for Br_3Sm : Br, 61.45%), magnetic measurements [$\chi_g = 3.29 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, μ_{eff} (294 K) = $1.64 \mu_{\text{B}}$] and infrared spectroscopy. Yield (based on Sm_2O_3): 0.47 g (92%).

Rhenium(vi) tetrabromide oxide. Reaction of carbonyl dibromide (0.91 , 4.84 mmol) and rhenium(vii) oxide (0.31 g , 0.65 mmol) at 125°C for 10 d gave a deep blue-black solid which was shown to be rhenium(vi) tetrabromide oxide by bromide analysis (Found: Br, 60.3. Calc. for Br_4ORe : Br, 61.25%), magnetic measurements [$\chi_g = 2.58 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, μ_{eff} (296 K) = $1.71 \mu_{\text{B}}$], infrared spectroscopy (1003s and 239 cm^{-1}), and mass spectrometry $\{m/z$ 522 ($[\text{ReOBr}_4]^+$, 46), 314 ($[\text{ReO}_3\text{Br}]^+$, 64), 283 ($[\text{ReOBr}]^+$, 37), 235 ($[\text{ReO}_3]^+$, 40), 187 (Re^+ , 58), 160 (Br_2^+ , 100) and 81 (Br^+ , 64%)}. Yield (based on Re_2O_7): 0.59 g (88%).

Molybdenum(vi) dibromide dioxide. Reaction of carbonyl dibromide (1.03 g , 5.48 mmol) and molybdenum(IV) oxide (0.09 g , 0.70 mmol) at 125°C for 10 d gave purple-brown crystals which were shown to be molybdenum(vi) dibromide dioxide by bromide analysis (Found: Br, 56.4. Calc. for Br_2MoO_2 : Br, 55.5%), magnetic measurements ($\chi_g = -3.90 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$), infrared spectroscopy [846s (br), 759s (br), 391w, 366w, 340m, 325m, 298m and 261 cm^{-1}], and mass spectrometry $\{m/z$ 209 ($[\text{MoO}_2\text{Br}]^+$, 82), 193 ($[\text{MoOBr}]^+$, 46), 177 ($[\text{MoBr}]^+$, 30), 160 (Br_2^+ , 15), 130 ($[\text{MoO}_2]^+$, 12), 114 ($[\text{MoO}]^+$, 22), 98 (Mo^+ , 36) and 79 (Br^+ , 100%)}. Yield (based on MoO_3): 0.18 g (87%).

Vanadium(IV) dibromide oxide. Reaction of carbonyl dibromide (0.98 g , 5.21 mmol) and vanadium(v) oxide (0.13 g , 0.71 mmol) at 125°C for 10 d gave olive-brown leaflets which were shown to be vanadium(IV) dibromide oxide by bromide analysis (Found: Br, 69.7. Calc. for Br_2OV : Br, 70.5%), magnetic measurements [$\chi_g = 5.34 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, μ_{eff} (293 K) = $1.57 \mu_{\text{B}}$], and infrared spectroscopy [881s (br), 361m, 290s and 238 cm^{-1}]. Yield (based on V_2O_5): 0.30 g (92%).

Results and Discussion

Carbonyl dibromide

The early attempts³²⁻³⁷ to prepare COBr_2 , and the claims and counterclaims of success and failure, are summarized elsewhere.¹⁹ By 1906, von Bartsch³⁴ had demonstrated that COBr_2 could be prepared in 50-60% yield by the oxidation of CBr_4 with concentrated sulfuric acid at $150\text{--}170^\circ\text{C}$, equations (7) and (8), although oleum is too vigorous a reagent, oxidizing the

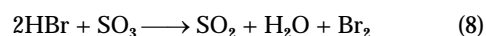
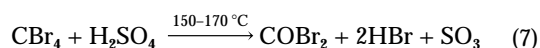


Table 1 Mass spectral data for COBr₂

<i>m/z</i>	Relative intensity	Assignment
190, 188, 186	—	<i>M</i> ⁺
162, 160, 158	37	[Br ₂] ⁺
109, 107	100	[COBr] ⁺
93, 91	12	[CBr] ⁺
81, 79	86	Br ⁺
28	4	[CO] ⁺

COBr₂ through to CO₂ and Br₂. By the nature of all the known synthetic routes, COBr₂ is always produced contaminated with elemental bromine, and von Bartal³⁴ proposed a two-step purification technique. Crude COBr₂ is initially shaken with mercury at 0 °C, and then distilled, collecting the 62–65 °C fraction. This distillate is then treated with powdered antimony, and redistilled to yield colourless COBr₂. If the first stage of the reaction with mercury is omitted the reaction with antimony is too vigorous, and some COBr₂ is lost through decomposition. Slight modifications of this procedure were later published by Schumacher and Lenher,²⁸ and this has become the most commonly used procedure.³⁸

The procedures used here are derived from von Bartal's preparation,³⁴ followed by Schumacher and Lenher's purification,²⁸ but they differ in some significant details (especially in the procedure for the removal of Br₂). The antimony step has been eliminated, as the heat generated was observed to cause decomposition of the carbonyl dibromide.

The infrared spectrum of gaseous COBr₂ did not differ significantly from that reported elsewhere,³⁸ and showed no detectable traces of CO₂, CO, COCl₂ or COBrCl. The ¹³C and ¹⁷O NMR spectra (in CD₂Cl₂ at –50 °C) of COBr₂ gave chemical shifts at δ 106.9 and 549.2, respectively [*cf.* δ(C) 103.4 in CCl₃F],^{39,40} and its mass spectrum (Table 1) is discussed in the preceding paper.⁴¹ These data highlight the purity of the product produced.

The pure COBr₂ was stored in the dark, since it was found that, in the presence of light, the colourless liquid became straw-coloured within 1 d due to decomposition to carbon monoxide and dibromine, equation (9). Over a prolonged



period this would result in a hazardous build-up of pressure in the storage vessel.

Reactions of carbonyl dibromide with metal oxides

The yields of the metal-containing products from the reactions of UO₃, Sm₂O₃, Re₂O₇, MoO₃, or V₂O₅ with COBr₂ at 125 °C were all greater than 87%, and it can be assumed that, neglecting manipulative losses, conversion of the oxide was essentially quantitative. Attempted reactions with WO₃, PbO₂, Al₂O₃ and CaO led to incomplete reaction, products being heavily contaminated with unreacted metal oxide; as convenient syntheses of the desired products already existed, the use of alternative reaction conditions was not explored, although the reaction with WO₃ had clearly produced significant amounts of WO₂Br₂.

Although free Br₂ was observed in all the reactions, its presence can give no information concerning the stoichiometry of the reactions, since pure COBr₂, if heated to 125 °C, undergoes some dissociation to CO and Br₂, equation (9).²⁸ The presence of Br₂ raises the possibility of the formation of [Br₃][–]; however, the satisfactory bromide analyses together with the appropriate magnetic moments mean that [Br₃][–] contamination of the product can be safely discounted.

Uranium(v) tribromide oxide. The reaction of UO₃ and COBr₂ at 125 °C gave UOBr₃, as a black powder, presumably

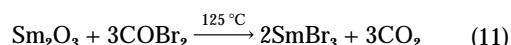
according to equation (10). Unfortunately, the colour of UOBr₃



is not reported in the literature, nor are there any reports of its magnetic moment or infrared spectrum. The effective magnetic moment of 2.04 μ_B (at 296 K) reported here is similar to values obtained for other uranium(v) compounds, *e.g.* UO₂Cl [μ_{eff} (295 K) = 1.86 μ_B]⁴² and UCl₅ [μ_{eff} (300 K) = 2.00 μ_B].⁴³ The infrared spectrum of UOCl₃ has been reported twice (1000–450 cm^{–1} only),^{44,45} with the bands at 965, 845, 615 and 450 cm^{–1} analogous to the bands at 960, 812, 607 and 473 cm^{–1} for UOBr₃. Attempts to record the electron impact (EI) mass spectrum of UOBr₃ were unsuccessful due to its involatility, and the positive-ion fast-atom bombardment (FAB) technique failed to give a spectrum due to reaction of the UOBr₃ with the matrix. Interestingly, the proposal by Russian workers⁴⁶ that UOBr₃ slowly evolved Br₂ at room temperature was not vindicated.

The only reproducible synthesis of UOBr₃ in the literature is by Prigent,¹⁰ who heated UO₃ in a stream of N₂ and CBr₄ vapour at 110 °C. It has been reported, also by Prigent,^{22,47} that reaction of UO₃ and COBr₂ in a sealed tube at 126 °C (*i.e.* the same conditions as used here) gave UBr₅, although attempts to repeat this by other workers have been unsuccessful.²³ Furthermore, work by Blair and Ihle²⁴ has shown that UBr₅ readily decomposes at >80 °C, and hence Prigent's claim^{22,47} to have prepared UBr₅ must be regarded as incorrect. It was hoped that performing the reaction of UO₃ and COBr₂ at a lower temperature, *viz.* 70 °C, might give a different product (perhaps even UBr₅); unfortunately, under these milder conditions, no reaction occurred.

Samarium(III) bromide. The reaction of Sm₂O₃ and COBr₂ at 125 °C gave SmBr₃, as a pale yellow powder (the same colour as reported in the literature),³ presumably according to equation (11). The effective magnetic moment of 1.64 μ_B (at 294 K) was in



reasonable agreement with the 1.51 μ_B (at 293 K) obtained by Selwood.⁴⁸ The infrared spectrum showed no bands in the range 1000–200 cm^{–1}, indicating the absence of Sm₂O₃ and SmOBr.

The existing syntheses of anhydrous SmBr₃ involve either dehydration of SmBr₃·6H₂O in the presence of HBr at high temperature (>640 °C),⁴⁹ or reaction of Sm₂O₃ and NH₄Br, again at high temperature.^{50–52} The synthesis reported here required less severe conditions, and more importantly did not produce unwanted SmBr₂ and SmOBr, the latter being a frequent contaminant when synthesizing SmBr₃ from SmBr₃·6H₂O.^{3,53}

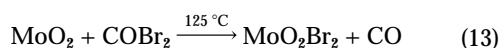
Rhenium(vi) tetrabromide oxide. The reaction of Re₂O₇ and COBr₂ at 125 °C gave ReOBr₄, as a deep blue-black solid (the same colour as reported in the literature^{54,55}), presumably according to equation (12). The effective magnetic moment of



1.71 μ_B (at 296 K) and infrared spectral bands at 1003s and 239s cm^{–1} were in reasonable agreement with those reported by Edwards and Ward [μ_{eff} = 1.80 ± 0.1 μ_B (at 294 K), infrared bands at 1005s, 364m and 242s cm^{–1}],⁵⁵ although they report a band at 364 cm^{–1} in their infrared spectrum which was not observed here. The previously unrecorded mass spectrum of ReOBr₄ shows a strong molecular ion.

The most recent synthesis of ReOBr₄ was by the reaction of rhenium metal, Br₂ and SO₂ in a sealed tube at 400 °C:⁵⁵ the preparation reported here was performed under far milder conditions.

Molybdenum(vi) dibromide dioxide. The reaction of MoO₂ and COBr₂ at 125 °C gave MoO₂Br₂, as purple-brown crystals (the same colour as reported in the literature),² presumably according to equation (13). The diamagnetism of the product is



consistent with a d⁰ molybdenum(vi) compound. The infrared and mass spectra were in good agreement with those reported by Barraclough and Stals,⁵⁶ the only significant difference being the absence of the molecular ion in the mass spectrum reported here.

This compound is usually prepared by passing a mixture of O₂ and Br₂, diluted with N₂, over the metal at 300 °C.⁵⁷ The method reported here was performed under milder conditions, and may be considered a more accessible synthesis.

Vanadium(IV) dibromide oxide. The reaction of V₂O₅ and COBr₂ at 125 °C gave VOBr₂, as olive-brown leaflets (the same colour as reported in the literature),^{6,58} presumably according to equation (14). The magnetic moment of 1.57 μ_B (at 293 K) was

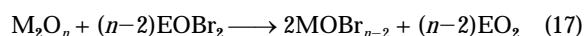
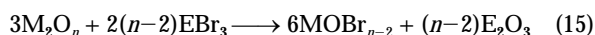


reasonable for a d¹ halide oxide with an extended lattice. The infrared spectrum was in very good agreement with that reported by Dehnicke⁶ [bands at 871s (br), 360m and 293m cm⁻¹], although he did not report the spectrum below 250 cm⁻¹ and thus did not observe the band at 238 cm⁻¹.

There are several syntheses of VOBr₂ reported in the literature,^{1,58} the two most widely used being bromination of V₂O₃ at 600 °C in a flow system⁶ and thermal decomposition of VOBr₃ at 180 °C.⁵⁹ The synthesis employed here has an obvious advantage over the bromination reaction, and is also preferable to the alternative method, since synthesis of VOBr₃ is itself not trivial.^{1,58}

Thermodynamic comparison of brominating agents

The thermodynamics of the reactions of EBr₃ (E = B or Al), CBr₄ and EOBBr₂ (E = S or C) with metal oxides [equations (15)–(17)], derived from the JANAF Thermochemical Tables⁶⁰



and the NBS Tables,⁶¹ are compared in Table 2. As the metal oxide, M₂O_n, and metal-containing product, MOBr_{n-2}, are assumed to be the same in each case, only the differences in free energy of formation, ΔG_{diff} (and enthalpy of formation, ΔH_{diff}) of the brominating agent and the product derived from the brominating agent are listed, expressed per mol of MOBr_{n-2} formed. Dibromine was not included in this table since no thermodynamic data were available for Br₂O (the 'expected' by-product of the reaction of Br₂ with metal oxides). However, as Br₂O is unstable above -40 °C⁶² it is unlikely to provide a significant thermodynamic driving force, and this is reflected in the observation that conversion of metal oxides into metal bromide oxides using Br₂ often requires the use of very high temperatures and/or the presence of reducing agents.¹⁻³

Thermodynamically, SOBr₂ (which decomposes above 80 °C)¹² and CBr₄ are the poorest brominating agents listed in Table 2 and, not surprisingly, are rarely used in this way (*cf.* CCl₄, which is a significantly better halogenating agent, and is commonly used in the synthesis of metal chlorides and chloride oxides¹⁻³).

Table 2 Thermodynamic comparison of some brominating agents, at 600 K^a

Brominating agent	Product derived from the brominating agent	ΔH _{diff} ^b /kJ mol ⁻¹	ΔG _{diff} ^b /kJ mol ⁻¹
BBr ₃ (g)	B ₂ O ₃ (s)	-128 ^c	-112 ^c
Al ₂ Br ₆ (g)	α-Al ₂ O ₃ (s)	-108 ^c	-101 ^c
CBr ₄ (g)	COBr ₂ (g)	-53 ^d	-79 ^d
SOBr ₂ (g)	SO ₂ (g)	-91 ^e	-75 ^e
COBr ₂ (g)	CO ₂ (g)	-140 ^e	-154 ^e

^a Enthalpies and free energies of formation of the brominating agents and the products derived from the brominating agent were obtained from the JANAF Thermochemical Tables,⁶⁰ except for COBr₂¹⁹ and SOBr₂⁶¹. ^b ΔH_{diff} is the difference in enthalpy of formation (ΔH_f) of the product derived from the brominating agent and the brominating agent itself, expressed per mol of MOBr_{n-2} formed. Thus, for COBr₂, ΔH_{diff} = ½ [ΔH_f(CO₂) - ΔH_f(COBr₂)]. ΔG_{diff} is the analogous free-energy difference. ^c Calculated for a general reaction (15). ^d Calculated for a general reaction (16). ^e Calculated for a general reaction (17). ^f The free energy of formation of SOBr₂ was estimated assuming that ΔH_f(SOBr₂) is independent of temperature.

The remaining brominating agents listed in Table 2, BBr₃, AlBr₃ and COBr₂, are all thermodynamically excellent, with COBr₂ being the best. The driving force for the first two reactions is the large enthalpy of formation of the extended solids B₂O₃ and Al₂O₃, respectively, whilst for COBr₂ both the enthalpy of formation of CO₂ and the concomitant favourable increase in entropy provides a significant part of the driving force. However, although BBr₃ and AlBr₃ are thermodynamically excellent brominating agents, the generation of E₂O₃ (E = B or Al) as by-products often causes experimental difficulties, *viz.* separation of the E₂O₃ from the metal bromide or bromide oxide. Sublimation (providing, of course, the product is volatile) often leads to decomposition (*e.g.* FeBr₃ and TaOBr₃),⁶³ while other separation techniques, such as dissolution in methanol (often used to remove B₂O₃),^{8,63} are often unsuitable since many metal bromides and bromide oxides react with donor solvents (*e.g.* UOBr₃^{10,64,65} and TiBr₄⁵⁸) giving both solvation and solvolysis products.

Alternative syntheses of metal bromides and bromide oxides usually involve the use of high temperatures and pressures, one of the few exceptions being the halogen-exchange reaction with BBr₃.¹⁴ The advantage of this halogen-exchange method is that the reaction can be carried out under mild conditions, and, more importantly, since the by-products are volatile purification is straightforward. The only problem with it is the possibility of mixed-halide formation (*e.g.* WOCl₃Br and WCl₃Br₂ are well known,⁶⁶ and are possible products of the reaction of BBr₃ with WOCl₄ and WCl₅, respectively).

In the light of this discussion, it is apparent that existing syntheses of metal bromides and bromide oxides are, on the whole, performed under very forcing conditions, and in many cases yield impure products. The use of COBr₂ offers a new synthetic route under mild conditions. The synthesis of a pure 3d, 4d, 5d and 5f bromide oxide, together with a pure 4f bromide illustrates the widespread applicability of COBr₂ as a brominating agent. There is a strong thermodynamic driving force (*viz.* formation of CO₂) and, more importantly, purification of the metal-containing product is trivial providing reaction has gone to completion. Given the efficacy of COBr₂ in synthesizing metal bromides and bromide oxides, its toxicity is not of major significance. Indeed, current synthetic routes frequently involve the use of toxic (but less emotive) compounds, and COBr₂ appears to be no more toxic than O₃, and is considerably less toxic than [Ni(CO)₄].

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