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

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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 $COBr_2$ in a sealed Carius tube at 125 °C for 10 d (to ensure complete reaction of the metal oxide). As $COBr_2$ and the reaction by-products (CO_2, CO and Br_2) are all volatile, the desired products were obtained in essentially quantitative yield and a high degree of purity. Under these conditions V_2O_5, MoO_2, Re_2O_7, Sm_2O_3 and UO_3 were converted into $VOBr_2$, MoO_2Br_2, $ReOBr_4$, $SmBr_3$ and $UOBr_3$, 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 ^{17}O 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]

$$2V + 3Br_2 \xrightarrow{400\ ^\circ C} 2VBr_3 \qquad (1)$$

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

$$Cr + 2HBr \xrightarrow{750\ ^\circ C} CrBr_2 + H_2 \qquad (2)$$

metal oxide with Br_2,[6,7] BBr_3,[8] $AlBr_3$,[9] CBr_4,[10,11] or $SOBr_2$,[12] or by halide exchange with HBr[13] or BBr_3.[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

$$3HfBr_4 + Hf \xrightarrow{500\ ^\circ C} 4HfBr_3 \qquad (3)$$

thermal disproportionation, equation (4),[15,16] or thermal

$$2ZrBr_3 \xrightarrow{350\ ^\circ C} ZrBr_4 + ZrBr_2 \qquad (4)$$

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

$$2OsBr_4 \xrightarrow{350\ ^\circ C} 2OsBr_3 + Br_2 \qquad (5)$$

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 $[Re_3Br_9(thf)_3]$.

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 experimental 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, $COCl_2$, equation (6).[19] These syntheses

$$M_xO_y + yCOCl_2 \longrightarrow xMCl_{2y/x} + yCO_2 \qquad (6)$$

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 $COBr_2$ is by Prigent,[22] who proposed that heating UO_3 with $COBr_2$ 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 °C[24] 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 communication[25] 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 $COBr_2$ 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 permissable 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:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

coughing and rapid breathing associated with pulmonary œdema, 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 œdema.[30] Hence, all manipulations involving carbonyl dibromide were carried out in a well ventilated fume cupboard with a face velocity of >0.75 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 tubes[31] 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 150–170 °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 [$\chi_g = 4.07 \times 10^{-8}$ m^3 kg^{-1}, μ_{eff} (296 K) = 2.04 μ_B], and infrared spectroscopy [960m (br), 812m, 607w, 473m (br), 339s (br) and 281m 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 [$\chi_g = 3.29 \times 10^{-8}$ m^3 kg^{-1}, μ_{eff} (294 K) = 1.64 μ_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 [$\chi_g = 2.58 \times 10^{-8}$ m^3 kg^{-1}, μ_{eff} (296 K) = 1.71 μ_B], infrared spectroscopy (1003s and 239s cm^{-1}), and mass spectrometry {*m/z* 522 ($[ReOBr_4]^+$, 46), 314 ($[ReO_3Br]^+$, 64), 283 ($[ReOBr]^+$, 37), 235 ($[ReO_3]^+$, 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 ($\chi_g = -3.90 \times 10^{-8}$ m^3 kg^{-1}), infrared spectroscopy [846s (br), 759s (br), 391w, 366w, 340m, 325m, 298m and 261w cm^{-1}], and mass spectrometry {*m/z*: 209 ($[MoO_2Br]^+$, 82), 193 ($[MoOBr]^+$, 46), 177 ($[MoBr]^+$, 30), 160 (Br_2^+, 15), 130 ($[MoO_2]^+$, 12), 114 ($[MoO]^+$, 22), 98 (Mo^+, 36) and 79 (Br^+, 100%)}. Yield (based on MoO_2): 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 [$\chi_g = 5.34 \times 10^{-8}$ m^3 kg^{-1}, μ_{eff} (293 K) = 1.57 μ_B], and infrared spectroscopy [881s (br), 361m, 290s and 238s cm^{-1}]. Yield (based on V_2O_5): 0.30 g (92%).

Results and Discussion

Carbonyl dibromide

The early attempts[32–37] to prepare $COBr_2$, and the claims and counterclaims of success and failure, are summarized elsewhere.[19] By 1906, von Bartal[34] had demonstrated that $COBr_2$ could be prepared in 50–60% yield by the oxidation of CBr_4 with concentrated sulfuric acid at 150–170 °C, equations (7) and (8), although oleum is too vigorous a reagent, oxidizing the

$$CBr_4 + H_2SO_4 \xrightarrow{150\text{–}170\ ^\circ C} COBr_2 + 2HBr + SO_3 \qquad (7)$$

$$2HBr + SO_3 \longrightarrow SO_2 + H_2O + Br_2 \qquad (8)$$

Table 1 Mass spectral data for $COBr_2$

m/*z*	Relative intensity	Assignment
190, 188, 186	—	M^+
162, 160, 158	37	$[Br_2]^+$
109, 107	100	$[COBr]^+$
93, 91	12	$[CBr]^+$
81, 79	86	Br^+
28	4	$[CO]^+$

CBr_4 through to CO_2 and Br_2. By the nature of all the known synthetic routes, $COBr_2$ is always produced contaminated with elemental bromine, and von Bartal[34] proposed a two-step purification technique. Crude $COBr_2$ 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 $COBr_2$. If the first stage of the reaction with mercury is omitted the reaction with antimony is too vigorous, and some $COBr_2$ 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 Br_2). The antimony step has been eliminated, as the heat generated was observed to cause decomposition of the carbonyl dibromide.

The infrared spectrum of gaseous $COBr_2$ did not differ significantly from that reported elsewhere,[38] and showed no detectable traces of CO_2, CO, $COCl_2$ or COBrCl. The ^{13}C and ^{17}O NMR spectra (in CD_2Cl_2 at −50 °C) of $COBr_2$ gave chemical shifts at δ 106.9 and 549.2, respectively [*cf.* δ(C) 103.4 in CCl_3F],[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 $COBr_2$ 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.

$$COBr_2 \rightleftharpoons CO + Br_2 \qquad (9)$$

Reactions of carbonyl dibromide with metal oxides

The yields of the metal-containing products from the reactions of UO_3, Sm_2O_3, Re_2O_7, MoO_2, or V_2O_5 with $COBr_2$ 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 WO_3, PbO_2, Al_2O_3 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 WO_3 had clearly produced significant amounts of WO_2Br_2.

Although free Br_2 was observed in all the reactions, its presence can give no information concerning the stoichiometry of the reactions, since pure $COBr_2$, if heated to 125 °C, undergoes some dissociation to CO and Br_2, equation (9).[28] The presence of Br_2 raises the possibility of the formation of $[Br_3]^-$; however, the satisfactory bromide analyses together with the appropriate magnetic moments mean that $[Br_3]^-$ contamination of the product can be safely discounted.

Uranium(V) tribromide oxide. The reaction of UO_3 and $COBr_2$ at 125 °C gave $UOBr_3$, as a black powder, presumably according to equation (10). Unfortunately, the colour of $UOBr_3$ 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.* UO_2Cl [μ_{eff} (295 K) = 1.86 μ_B][42] and UCl_5 [μ_{eff} (300 K) = 2.00 μ_B].[43] The infrared spectrum of $UOCl_3$ 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 $UOBr_3$. Attempts to record the electron impact (EI) mass spectrum of $UOBr_3$ 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 $UOBr_3$ with the matrix. Interestingly, the proposal by Russian workers[46] that $UOBr_3$ slowly evolved Br_2 at room temperature was not vindicated.

$$2UO_3 + 4COBr_2 \xrightarrow{125\,°C} 2UOBr_3 + 4CO_2 + Br_2 \qquad (10)$$

The only reproducible synthesis of $UOBr_3$ in the literature is by Prigent,[10] who heated UO_3 in a stream of N_2 and CBr_4 vapour at 110 °C. It has been reported, also by Prigent,[22,47] that reaction of UO_3 and $COBr_2$ in a sealed tube at 126 °C (*i.e.* the same conditions as used here) gave UBr_5, although attempts to repeat this by other workers have been unsuccessful.[23] Furthermore, work by Blair and Ihle[24] has shown that UBr_5 readily decomposes at >80 °C, and hence Prigent's claim[22,47] to have prepared UBr_5 must be regarded as incorrect. It was hoped that performing the reaction of UO_3 and $COBr_2$ at a lower temperature, *viz*. 70 °C, might give a different product (perhaps even UBr_5); unfortunately, under these milder conditions, no reaction occurred.

Samarium(III) bromide. The reaction of Sm_2O_3 and $COBr_2$ at 125 °C gave $SmBr_3$, 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 Sm_2O_3 and SmOBr.

$$Sm_2O_3 + 3COBr_2 \xrightarrow{125\,°C} 2SmBr_3 + 3CO_2 \qquad (11)$$

The existing syntheses of anhydrous $SmBr_3$ involve either dehydration of $SmBr_3{\cdot}6H_2O$ in the presence of HBr at high temperature (>640 °C),[49] or reaction of Sm_2O_3 and NH_4Br, again at high temperature.[50–52] The synthesis reported here required less severe conditions, and more importantly did not produce unwanted $SmBr_2$ and SmOBr, the latter being a frequent contaminant when synthesizing $SmBr_3$ from $SmBr_3{\cdot}6H_2O$.[3,53]

Rhenium(VI) tetrabromide oxide. The reaction of Re_2O_7 and $COBr_2$ at 125 °C gave $ReOBr_4$, 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 $ReOBr_4$ shows a strong molecular ion.

$$Re_2O_7 + 5COBr_2 \xrightarrow{125\,°C} 2ReOBr_4 + 5CO_2 + Br_2 \qquad (12)$$

The most recent synthesis of $ReOBr_4$ was by the reaction of rhenium metal, Br_2 and SO_2 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 MoO_2 and $COBr_2$ at 125 °C gave MoO_2Br_2, as purple-brown crystals (the same colour as reported in the literature),[2] presumably according to equation (13). The diamagnetism of the product is

$$MoO_2 + COBr_2 \xrightarrow{125\ ^\circ C} MoO_2Br_2 + CO \qquad (13)$$

consistent with a d^0 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 O_2 and Br_2, diluted with N_2, 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 V_2O_5 and $COBr_2$ at 125 °C gave $VOBr_2$, 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

$$V_2O_5 + 3COBr_2 \xrightarrow{125\ ^\circ C} 2VOBr_2 + 3CO_2 + Br_2 \qquad (14)$$

reasonable for a d^1 halide oxide with an extended lattice. The infrared spectrum was in very good agreement with that reported by Dehnicke[6] [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 $VOBr_2$ reported in the literature,[1,58] the two most widely used being bromination of V_2O_3 at 600 °C in a flow system[6] and thermal decomposition of $VOBr_3$ 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 $VOBr_3$ is itself not trivial.[1,58]

Thermodynamic comparison of brominating agents

The thermodynamics of the reactions of EBr_3 (E = B or Al), CBr_4 and $EOBr_2$ (E = S or C) with metal oxides [equations (15)–(17)], derived from the JANAF Thermochemical Tables[60]

$$3M_2O_n + 2(n-2)EBr_3 \longrightarrow 6MOBr_{n-2} + (n-2)E_2O_3 \qquad (15)$$

$$M_2O_n + (n-2)CBr_4 \longrightarrow 2MOBr_{n-2} + (n-2)COBr_2 \qquad (16)$$

$$M_2O_n + (n-2)EOBr_2 \longrightarrow 2MOBr_{n-2} + (n-2)EO_2 \qquad (17)$$

and the NBS Tables,[61] are compared in Table 2. As the metal oxide, M_2O_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 Br_2O (the 'expected' by-product of the reaction of Br_2 with metal oxides). However, as Br_2O is unstable above −40 °C[62] 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 Br_2 often requires the use of very high temperatures and/or the presence of reducing agents.[1–3]

Thermodynamically, $SOBr_2$ (which decomposes above 80 °C)[12] and CBr_4 are the poorest brominating agents listed in Table 2 and, not surprisingly, are rarely used in this way (*cf.* CCl_4, which is a significantly better halogenating agent, and is commonly used in the synthesis of metal chlorides and chloride oxides[1–3]).

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

Brominating agent	Product derived from the brominating agent	$\Delta H_{diff}{}^b$/kJ mol^{-1}	$\Delta G_{diff}{}^b$/kJ mol^{-1}
BBr_3 (g)	B_2O_3 (s)	− 128[c]	− 112[c]
Al_2Br_6 (g)	α-Al_2O_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[f]
$COBr_2$ (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 $COBr_2$[19] and $SOBr_2$[61]. [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 $COBr_2$, $\Delta H_{diff} = \frac{1}{2}\ [\Delta H_f\ (CO_2) - \Delta H_f\ (COBr_2)]$. 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 $SOBr_2$ was estimated assuming that ΔH_f ($SOBr_2$) is independent of temperature.

The remaining brominating agents listed in Table 2, BBr_3, $AlBr_3$ and $COBr_2$, are all thermodynamically excellent, with $COBr_2$ being the best. The driving force for the first two reactions is the large enthalpy of formation of the extended solids B_2O_3 and Al_2O_3, respectively, whilst for $COBr_2$ both the enthalpy of formation of CO_2 and the concomitant favourable increase in entropy provides a significant part of the driving force. However, although BBr_3 and $AlBr_3$ are thermodynamically excellent brominating agents, the generation of E_2O_3 (E = B or Al) as by-products often causes experimental difficulties, *viz*. separation of the E_2O_3 from the metal bromide or bromide oxide. Sublimation (providing, of course, the product is volatile) often leads to decomposition (*e.g.* $FeBr_3$ and $TaOBr_3$),[63] while other separation techniques, such as dissolution in methanol (often used to remove B_2O_3),[8,63] are often unsuitable since many metal bromides and bromide oxides react with donor solvents (*e.g.* $UOBr_3$[10,64,65] and $TiBr_4$[58]) 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 BBr_3.[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.* $WOCl_3Br$ and WCl_3Br_2 are well known,[66] and are possible products of the reaction of BBr_3 with $WOCl_4$ and WCl_5, 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 $COBr_2$ 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 $COBr_2$ as a brominating agent. There is a strong thermodynamic driving force (*viz.* formation of CO_2) and, more importantly, purification of the metal-containing product is trivial providing reaction has gone to completion. Given the efficacy of $COBr_2$ 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 $COBr_2$ appears to be no more toxic that O_3, and is considerably less toxic than $[Ni(CO)_4]$.

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