Carbonyl Dibromide: a Novel Reagent for the Synthesis of Metal Bromides and Oxide Bromides

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Carbonyl dibromide reacts with a wide selection of d- and f-block transition metal oxides to form either the metal bromide or metal oxide bromide; the reactions are driven by the elimination of carbon dioxide.

In contrast to the many convenient and versatile synthetic routes to metal chlorides and oxide chlorides, there are no general and convenient synthetic routes to their d- and f-block bromide analogues.[1—6] Apart from the direct reactions of the metals with elemental bromine or hydrogen bromide at elevated temperatures, the known routes either require rather extreme experimental conditions or yield impure products (particularly a problem with the preparation of oxide bromides). We report here the use of carbonyl dibromide, $COBr_2$,[7] as a novel reagent for the one-step reproducible

syntheses of either metal bromides or metal oxide bromides under mild conditions from metal oxides.

$$V_2O_5 + 3COBr_2 \longrightarrow 2VOBr_2 + 3CO_2 + Br_2 \quad (1)$$

$$COBr_2 \rightleftharpoons CO + Br_2 \quad (2)$$

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 ten days (to ensure complete reaction of the metal oxide). As $COBr_2$ and the reaction by-products [CO_2, CO, and Br_2; see, for example, equations (1) and (2)] are all volatile, the desired products were obtained in essentially quantitative yields and with 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, and in all cases this method should now represent the synthetic method of choice.† The reactions are driven thermodynamically, under such mild conditions, by the elimination of carbon dioxide. 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 for the synthesis of new materials.

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† All products were characterized by microanalysis, IR spectroscopy, magnetic susceptibility measurements, and mass spectrometry.

References

1 R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals,' Wiley, London, 1969.
2 J. H. Canterford and R. Colton, 'Halides of the Second and Third Row Transition Metals,' Wiley, London, 1968.
3 D. Brown, 'Halides of the Lanthanides and Actinides,' Wiley, London, 1968.
4 P. M. Druce, M. F. Lappert, and P. N. K. Riley, *J. Chem. Soc., Chem. Commun.*, 1967, 486.
5 M. F. Lappert and B. Prokai, *J. Chem. Soc. (A)*, 1967, 129.
6 P. M. Druce and M. F. Lappert, *J. Chem. Soc. (A)*, 1971, 3595.
7 A. von Bartal, *Liebigs Ann. Chem.*, 1906, **345**, 334.