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Microwave-Assisted Carbohydrohalogenation of First-Row Transition-Metal Oxides (M = V, Cr, Mn, Fe, Co, Ni, Cu) with the Formation of Element Halides

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Supporting Information

ABSTRACT: The anhydrous forms of first-row transition-metal chlorides and bromides ranging from vanadium to copper were synthesized in a one-step reaction using the relatively inexpensive element oxides, carbon sources, and halogen halides as starting materials. The reactions were carried out in a microwave oven to give quantitative yields within short reaction times.

In industry as well as in academia, element halides are widely used as starting materials for the synthesis of a variety of different products. Because of the element halide functionality, element chlorides and bromides serve as valuable precursors for the synthesis of transition-metal complexes.[1−3] Because of their moisture-sensitive and often highly reactive polar element halide bonds, these compounds are not available in nature and therefore have to be synthesized from their natural ores, which are abundant in nature as element oxides. For transformation of oxides into their corresponding halides, different processes are known. In principle, in a two-step synthetic route, the oxides are reduced to the respective element in oxidation state zero with the cheapest and most available reducing agent, carbon. The metals are then reoxidized to a higher oxidation state with chlorine or bromine to give the element halides (Scheme 1).[4]

Scheme 1. Conventional Two-Step Synthesis of Element Halides

$$M_yO_z + z\,C \longrightarrow y\,M + z\,CO$$

$$2y\,M + z\,X_2 \longrightarrow 2\,M_yX_z$$

$$(M = V, Cr, Mn, Fe, Co, Ni, Cu;\ X = Cl, Br)$$

On a laboratory scale, different routes for the synthesis of element halides in the lower oxidation states are known and most of them require long reaction times or multiple synthetic steps.[5] The direct conversion of the inert oxides can only be achieved by the highly reactive elemental halides.[6] For example, in the synthesis of water-free VCl_3, vanadium metal is oxidized with Cl_2.[7] The preparation of VBr_3 requires vanadium metal to be reacted with Br_2 for more than 3 days at 400 °C.[8] $CrCl_3$ is synthesized from the corresponding oxide with Cl_2 at 650 °C, with toxic phosgene being formed as a side product.[9] $CrBr_3$ is obtained from Br_2 and Cr_2O_3.[10] Anhydrous manganese halides are available upon reaction of the corresponding acetyl halide with manganese acetate.[11] Because of the inertness of Fe_2O_3, anhydrous iron(II) halides are also prepared from the metal.[12,13] The microwave-assisted synthesis of $FeCl_2$ under modified conditions is also described.[14] Cobalt(II) halides are produced starting from $CoCO_3$, and the acetyl halide[11] or alternatively $CoCl_2{\cdot}6H_2O$ is subsequently dehydrated with $SOCl_2$.[15] While $NiCl_2$ is prepared analogously, the bromide is obtained by reacting Br_2 with nickel powder in diethyl ether.[16] Copper(I) halides are available in solution from $CuSO_4$ and SO_2 with NaCl or KBr.[5]

According to our investigations, the synthesis of first-row transition-metal chlorides and bromides (M = V, Cr, Mn, Fe, Co, Ni, Cu) starting from the element oxides can be simplified using a microwave-assisted synthesis. This one-step reaction uses the carbohydrohalogenation reaction and is an attractive alternative to the conventional two-step process "metal oxide−metal−metal halide" described before. For performance, carbon is mixed with the relevant element oxide and gaseous HCl or HBr is passed through a quartz tube while the reaction chamber is heated by microwave absorption. The halogenation reactions occur according to Scheme 2.

Scheme 2. Alternative One-Step Carbohydrohalogenation for the Synthesis of Element Halides

$$2\,M_aO_b + 2b\,C + 2c\,HX \longrightarrow 2\,M_aX_c + 2b\,CO + c\,H_2$$

Excess water from the water-containing oxides or released from the reduction process is split under the reaction conditions into hydrogen (H_2) and carbon monoxide (CO) and thus avoids hydrolysis of the often water-sensitive element halides formed.[17,18]

When the carbohydrohalogenation experiments are performed, anhydrous dark-blue $CoCl_2$ is formed; the formation of red-purple $CoCl_2{\cdot}6H_2O$ is not observed. Analogously, the formation of anhydrous dark-green $CoBr_2$ in contrast to red-purple $CoBr_2{\cdot}6H_2O$ excludes the formation of water upon reduction even in the cold zones of the reaction vessels (Figure 1). This convincingly demonstrates the absence of water due to reduction by carbon to CO and H_2 at temperatures above 800 °C. The formation of H_2 was proven by bubbling the reaction gas through deuterated benzene and detected by ^1H NMR spectroscopy of the resulting solution (C_6D_6, $\delta = 4.48$ ppm).

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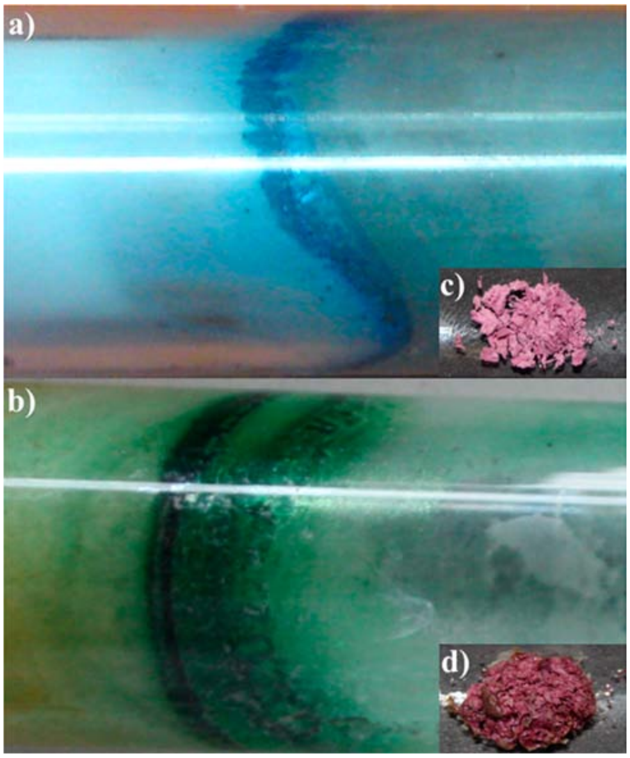

Figure 1. Anhydrous products (a) $CoCl_2$ and (b) $CoBr_2$. For comparison, the hydrolyzed products $CoCl_2{\cdot}6H_2O$ (c) and $CoBr_2{\cdot}6H_2O$ (d) are shown.

For the reduction of element oxides, different kinds of carbon sources can be applied. Because of its very attractive microwave absorption coefficient, the use of graphite gives the best results.[19] For the use of different carbon sources with a lower microwave absorption coefficient, graphite might be admixed to the oxide/carbon mixture to reach reaction temperatures of about 1000−1400 °C. For achievement of the quantitative yields of halides with respect to their metal oxides, an excess of carbon is required. In case carbon is depleted, the reduction stops and excess element oxide remains. This complicates a separation of the pure halogenated products. Because of the high reaction temperatures required and the transparency against microwave irradiation[20,21] needed for halogenation, the reaction vessel consists of quartz. A side reaction giving $SiCl_4$ from SiO_2 is not observed. Carbon does not react with the smooth inner surface of the quartz tube; for tetrachlorosilane formation the SiO_2 sources have to be carefully mixed with the reducing agent.[14]

Instead of microwave heating, carbohydrohalogenation can also be performed in conventional ovens but then require significantly longer reaction times. For comparison, for equal molar amounts of metal oxides, the microwave-assisted reaction needs about 15 min for complete consumption of the material, while in conventional ovens at 1000 °C, most of the starting material is still left after the same time period. Besides, other disadvantages of conventional heating are the higher energy costs and the longer heating and cooling times.[22] When microwave irradiation of the reaction mixtures is performed, a colored plasma or white sparks and high energetic arcs are visible in most reactions. In these reaction zones, the temperatures are obviously much higher, leading to high or quantitative yields of the products.

For performance of the halogenation reactions described, the use of elemental chlorine or bromine gas is, in principle, possible but is combined with experimental disadvantages: chlorine is an inherent toxic and corrosive gas that forms phosgene and tetrachloromethane under the required reaction conditions. In the case of bromine as the bromination agent, separation and transfer of the products is critical because unreacted bromine will stick on the products formed and has to be removed in a separate purification step. In contrast, the use of the less corrosive and at room temperature gaseous hydrogen halides HX (X = Cl, Br) simplifies the experimental procedure and is thus strongly recommended over the use of other mostly liquid or solid element halides that are technically used for halogenation reactions (e.g., PCl_5, $SbCl_3$).[1] Furthermore, no reaction of HCl with CO to give phosgene and tetrachloromethane is known in the literature.

After completion of carbohydrohalogenation, separation of the products from impurities such as remaining excess carbon or oxide residues is very simple. Because of the high temperature gradient within the quartz tube, the products sublime into the colder zones and are then mechanically collected as pure compounds. Alternatively, for quantitative isolation, the product is washed off with water to yield the hydrated form of the halides. In the case of CuBr, isolation with water has to be replaced by aqueous HBr as the solvent.

All products were formed in the crystalline state and identified and characterized by a combination of powder X-ray diffraction (PXRD) and energy-dispersive X-ray (EDX) analyses (Table 1).

Table 1. Products of Carbohalogenation

element oxide	halogenating agent	product (PXRD)	ratio M:X (EDX)[a]
V_2O_5	HCl	VCl_3	1:2.4 ± 0.2[b]
	HBr	$VOBr_2$[c]	1:2.1 ± 0.3[b]
Cr_2O_3	HCl	$CrCl_3$	1:3.2 ± 0.3
	HBr	$CrBr_3$	1:3.1 ± 0.3
MnO_2	HCl	$MnCl_2$	1:2.0 ± 0.1
	HBr	$MnBr_2$	1:3.0 ± 0.2[b]
Fe_2O_3	HCl	$FeCl_2$	1:2.0 ± 0.1
	HBr	$FeBr_2$	1:2.9 ± 0.3[b]
Co_3O_4	HCl	$CoCl_2$	1:2.0 ± 0.1
	HBr	$CoBr_2$	1:2.2 ± 0.1
CuO	HCl	$CuCl/CuCl_2$[c]	1:1.1 ± 0.2
	HBr	$CuBr/CuBr_2$[c]	1:2.0 ± 0.1[b]
Ni_2O_3	HCl	$NiCl_2$	1:2.0 ± 0.1
	HBr	$NiBr_2$	1:2.2 ± 0.1

[a] Value of four measurements. [b] The product was partly oxidized prior to EDX measurements. [c] The product was partly oxidized prior to PXRD measurements.

Representative samples showed no carbon impurities, as confirmed by CHN combustion analysis. Generally, the anhydrous forms of the salts are isolated. The products formed show the metal atoms in the lower oxidation states: V^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{+}, and Ni^{+}. For the oxidation-sensitive compounds of Fe^{2+} and Cu^{+}, PXRD analysis proves the lower oxidation state, but prior to the EDX analyses, the salts were readily oxidized under air to form the respective Fe^{3+} and Cu^{2+} species. For verification of a unified product formation, the residues of the reaction mixtures were checked by EDX and only excess carbon and traces of the halides could be identified.

In summary, we have described the syntheses of anhydrous element chlorides and bromides of the first-row transition metals (V, Cr, Mn, Fe, Co, Ni, and Cu). Compared to conventional methods, the microwave-assisted syntheses provide shorter reaction times, simple product isolation, and higher yields of the desired products. Carbon, graphite, or carbon-containing materials were applied as reducing agents; hydrogen halides were used for halogenations. The use of the latter is recommended because of lower costs, lower toxicity, and lower corrosivity compared to element halides. In all experiments, the water-free metal salts were isolated in lower oxidation states and characterized by PXRD and EDX spectroscopy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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