occurs in high yield (≥85%, Figure 2) even at micromolar levels of reactants.

The present results do not allow us to distinguish the relative reactivities of O_2^- and HO_2 with NO. Experiments to measure the pH dependence of the kinetics of reaction 1 are in progress. However, a calculation based on the assumptions that (1) HO_2 is the only reactive species and (2) $pK_a(HO_2) = 4.7$ in our reaction medium[13] and on the observation that reaction 1 is complete within 15 s in 0.1 M KOH indicates that the second-order rate constant for the reaction of HO_2 with NO would be above the diffusion-controlled limit. This argues strongly that O_2^- itself reacts with NO at a significant rate.

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Registry No. O_2^-, 11062-77-4; NO, 10102-43-9; ^-OONO, 19059-14-4.

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Versatility and Low-Temperature Synthetic Potential of Ammonium Halides

Sir:

The obvious successes of the so-called ceramic approach to the synthesis of inorganic solids have led to the conclusion that solid-state *synthesis* is simple and that just brute force, high temperature and/or pressures, and patience have to be applied. However, under such severe reaction conditions, important information on the reaction pathways ("mechanisms"), on intermediates, and on metastable or less stable compounds is almost completely lost. The application of compound or solid-solution precursors[1] has brought considerable improvement in that reaction temperatures are reduced by several hundred degrees because diffusional limitations are overcome by mixing on the atomic scale.

A different approach to the lower temperature synthesis of inorganic solids is the use of highly mobile reagents such as ammonium compounds. We wish to report here the synthetic potential and the versatility of the reactions with ammonium halides, NH_4X (X = Cl, Br, I), as part of a more general program in which ammonium sulfate, nitrate, phosphates, and carbonate are used. The ammonium halides react with rare-earth-metal sesquioxides at temperatures as low as 230 °C (NH_4Cl), 280 °C (NH_4Br), and 360 °C (NH_4I), for example with Y_2O_3 to yield $(NH_4)_3YCl_6$ or with La_2O_3 to yield $(NH_4)_2LaCl_5$.

A variety of different reactants may be applied, not only oxides, but also sulfides, selenides, phosphides, carbides, and the metals themselves. Some of the results are summarized in Table I. The reactants are intimately ground and loaded under dry argon (not mandatory) into Pyrex ampules that have a capillary opening. Optimal reaction temperatures are easily detected by sight when water is one of the products, as it condenses in the capillary, or via the basic reaction of ammonia, which is evolved in many of the reactions, or by reactions of the phosphanes or sulfane with copper sulfate solution. In many cases, the reaction temperature as observed was confirmed by high-temperature X-ray powder patterns (the Guinier–Simon technique[2]) recorded subsequently with the same reaction mixture.

Table I. Survey of the Lower Temperature Syntheses with Binary and Complex Ammonium Halides

reactants	conditions	products
	Redox Reactions	
Li, NH_4Cl	1:2, 270 °C	LiCl, NH_3, H_2
Zn, NH_4Cl	1:4, 270 °C	$(NH_4)_2ZnCl_4$, ...[a]
La, NH_4Cl	1:5, 280 °C	$(NH_4)_2LaCl_5$, ...
Y, NH_4Cl	1:6, 270 °C	$(NH_4)_3YCl_6$, ...
Y, NH_4Br	1:6, 300 °C	$(NH_4)_3YBr_6$, ...
Y, NH_4I	1:6, 390 °C	$(NH_4)_3YI_6$, ...
Cu, NH_4Cl	1:3, 280 °C	$(NH_4)_2CuCl_3$, ...
UH_3, NH_4Cl	1:6, 250 °C	$(NH_4)_2UCl_6$, ...
NH_4ReO_4, NH_4Cl	6:8, 400 °C	Re, N_2, HCl, H_2O
	Acid–Base Reactions	
Li_3N, NH_4Cl	1:3, 250 °C	LiCl, NH_3
$LiYO_2$, NH_4Cl	1:6, 260 °C	$(NH_4)_2LiYCl_6$, NH_3, H_2O
Y_2O_3, NH_4Cl	1:12, 230 °C	$(NH_4)_3YCl_6$, NH_3, H_2O
Y_2S_3, NH_4Cl	1:12, 230 °C	$(NH_4)_3YCl_6$, NH_3, H_2S
YP, NH_4Cl	2:3, 250 °C	$(NH_4)_3YCl_6$, NH_3, PH_3 (P_2H_4)
Y_2O_3, NH_4Br	1:12, 280 °C	$(NH_4)_3YBr_6$, NH_3, H_2O
Y_2O_3, NH_4Br	1:2, 280 °C	YOBr, NH_3, H_2O[b]
Y_2O_3, NH_4I	1:2, 360 °C	YOI, NH_3, H_2O
	Reactions of Complex Ammonium Halides	
$(NH_4)_3YCl_6$, $H_2O(g)$[c])	350 °C	YOCl, HCl, NH_4Cl
$(NH_4)_3YCl_6$, $H_2S(g)$	400 °C	YSCl, HCl, NH_4Cl
$(NH_4)_3YCl_6$, Y_2O_3	2:5, 330 °C	YOCl, NH_3, H_2O
$(NH_4)_3YBr_6$, Y_2O_3	2:5, 260 °C	YOBr, NH_3, H_2O
$(NH_4)_3YI_6$, Y_2O_3	2:5, 340 °C	YOI, NH_3, H_2O
$(NH_4)_3YCl_6$, Y_2S_3	2:5, 300 °C	YSCl[d], NH_3, H_2S
$(NH_4)_2EuCl_5$, LiCl	1:2, 280 °C	$(NH_4)_2LiEuCl_6$
	Decompositions	
$(NH_4)_2LiEuCl_6$	350 °C, vac	$LiEuCl_4$, NH_4Cl
$(NH_4)_2UCl_6$	300 °C, vac	UCl_4, ...[e]
$(NH_4)_3YCl_6$	360 °C, GS[f]	$NH_4Y_2Cl_7$, ...
$NH_4Y_2Cl_7$	380 °C, GS	YCl_3, ...
$(NH_4)_3SmBr_6$	365 °C, GS	$(NH_4)_2SmBr_5$, NH_4Br
$(NH_4)_2SmBr_5$	420 °C, GS	$NH_4Sm_2Br_7$, ...
$NH_4Sm_2Br_7$	560 °C, GS	$SmBr_3$, ...

[a] NH_3 and H_2 are evolved, as above. [b] $(NH_4)_3YBr_6$ is produced as an intermediate but reacts promptly with excess Y_2O_3, which is also the case for the reaction of Y_2O_3 with NH_4I (see below). [c] Argon saturated with H_2O vapor at room temperature. [d] Under preparative conditions more or less $NH_4Y_2Cl_7$ is also produced. [e] NH_4Cl is set free, as above. [f] Under the conditions of a temperature-controlled powder pattern study, Guinier–Simon (GS) technique,[2] typical heating rates were 10 °C/h and film speeds were 2 mm/h.

The reactions as summarized in Table I may be divided into two groups, redox and acid–base reactions. In certain cases, NH_4Cl may react as a reductant. For example, when NH_4ReO_4 is heated with NH_4Cl to 400 °C, finely divided Re metal is obtained as the only solid, and N_2, H_2O, and HCl are evolved. Ammonium halides may also react as oxidizing agents with metals, not only the rare-earth metals but also lithium, zinc, and copper, to name only a few. To be specific, it is the H^+ ion that oxidizes the metal. This is interesting because of the relative inertness of copper, but it may be explained by the fact that a stable complex halide, $(NH_4)_2CuCl_3$, is formed simultaneously with the oxidation. Complex formation is also believed to be the driving force of the reactions where, e.g., NH_4Cl reacts as an acid. Again, the H^+ ion is the actual acid and not simply hydrogen chloride that may be formed via the facile dissociation of NH_4Cl.

In either case, NH_4X reacts quantitatively with the appropriate amounts of the reactant used. This has been systematically investigated for the NH_4Cl/Y_2O_3 system: Equimolar amounts within the ranges 2:3 to 12:1 yield $(NH_4)_3YCl_6$ in the first step at 230 °C. When a ratio of 12:1 is used, subsequent decomposition in vacuo around 350 °C yields finely divided, highly active YCl_3, pure on a Guinier basis. The reaction passes through the intermediate $NH_4Y_2Cl_7$. Therefore, the so-called and long known "ammonium chloride route"[3,4] to anhydrous rare-earth-metal

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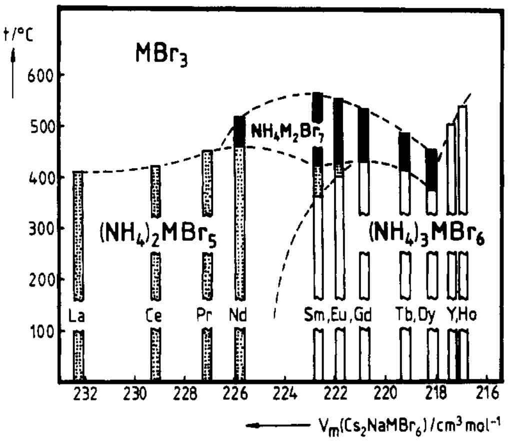

Figure 1. Survey of the ammonium bromide route to anhydrous rare-earth-metal bromides, MBr_3, showing the complex ammonium bromides stable at room temperature for M = La–Ho and their decomposition pathways as determined by Guinier–Simon X-ray patterns. Instead of the ionic radii of the trivalent rare-earth-metal cations, the molar volumes of the elpasolites Cs_2NaMBr_6 (see: Meyer, G.; Gaebell, H.-Chr. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1476) are used as abscissa.

chlorides must be interpreted as a two-step procedure with acid–base reaction *and* complex formation first and decomposition second.[5] This method also functions beautifully for the analogous bromides and iodides. The ammonium bromide route was particularly explored. Reaction of NH_4Br and rare-earth-metal oxide, M_2O_3, yields $(NH_4)_2MBr_5$ for M = La–Nd, and $(NH_4)_3MBr_6$ for M = Sm–Lu. Decomposition of the latter passes through $(NH_4)_2MBr_5$ for M = Sm and Eu, and $NH_4M_2Br_7$ is observed as an intermediate for M = Nd–Dy. Figure 1 summarizes the results. The crystal structures of the halides $(NH_4)_2MX_5$ (X = Cl, Br, I) are that of K_2PrCl_5,[6,7] and the halides $NH_4M_2X_7$ are isotypic with KDy_2Cl_7 or $RbDy_2Cl_7$.[8,9]

The versatility of the ammonium halide reactions is furthermore reflected by the fact that the complex halides themselves, especially $(NH_4)_2MX_5$ and $(NH_4)_3MX_6$, are useful starting materials. For example, $(NH_4)_3YCl_6$ reacts at temperatures as low as 300–400 °C with both gases (H_2O, H_2S) or solids (Y_2O_3, Y_2S_3) to yield YOCl and YSCl, respectively. This is particularly interesting because Y_2O_3 does not react at these temperatures with HCl gas at all. The usual route to YOCl is the reaction of YCl_3 with H_2O, air, or Y_2O_3 around 500 °C. It is then obtained in the PbFCl type structure. The reaction of $(NH_4)_3YCl_6$ with Y_2O_3, however, provides an easy access to YOF-type[10] YOCl. Its close relationship to the novel monochloride YCl with its rich interstitial chemistry has been particularly emphasized.[11] Thermal analyses of Y_2O_3 and NH_4Cl mixtures (1:2 molar ratio) that have recently been interpreted in terms of intermediates such as $[M(NH_3)_3]Cl_3$[12,13] are certainly misinterpreted.

Additionally, the complex ammonium halides react not only with chalcides (Y_2O_3, Y_2S_3, YSe), but also with pnictides such as YP (yielding Y_2PCl_3). Furthermore, alkali-metal halides like LiCl react with, for example, $(NH_4)_2EuCl_5$ to yield via the intermediate $(NH_4)_2LiEuCl_6$ the new scheelite-type[14] compound $EuLiCl_4$. Such methods seem particularly important as routes to metastable compounds or those of borderline stability. Another ternary halide that is obtained by a similar route is KYb_2Cl_7.[9]

It is expected that the solid-state reactions of other ammonium compounds with various metals and their compounds follow similar pathways and that their investigation will provide important insights in the production of industrially and technologically useful products.

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Registry No. NH_4Cl, 12125-02-9; NH_4Br, 12124-97-9; NH_4I, 12027-06-4; Li, 7439-93-2; Zn, 7440-66-6; La, 7439-91-0; Y, 7440-65-5; Cu, 7440-50-8; UH_3, 13598-56-6; NH_4ReO_4, 13598-65-7; Li_3N, 26134-62-3; $LiYO_2$, 12169-03-8; Y_2O_3, 1314-36-9; Y_2S_3, 12039-19-9; YP, 12294-01-8; $(NH_4)_3YCl_6$, 59230-45-4; $(NH_4)_3YBr_6$, 98218-63-4; $(NH_4)_3YI_6$, 98218-64-5; $(NH_4)_2EuCl_5$, 97253-02-6; $(NH_4)_2LiEuCl_6$, 98218-65-6; $(NH_4)_2UCl_6$, 22949-76-4; $NH_4Y_2Cl_7$, 84556-33-2; $(NH_4)_3SmBr_6$, 98218-66-7; $(NH_4)_2SmBr_5$, 98244-73-6; $NH_4Sm_2Br_7$, 98218-67-8; H_2O, 7732-18-5; H_2S, 7783-06-4; LiCl, 7447-41-8; NH_3, 7664-41-7; $(NH_4)_2ZnCl_4$, 14639-97-5; $(NH_4)_2LaCl_5$, 78476-14-9; $(NH_4)_2CuCl_3$, 61288-98-0; Re, 7440-15-5; N_2, 7727-37-9; HCl, 7647-01-0; H_2, 1333-74-0; $(NH_4)_2LiYCl_6$, 98218-68-9; PH_3, 7803-51-2; YOBr, 15923-89-4; YOI, 66923-06-6; YOCl, 13759-29-0; YSCl, 98218-69-0; $LiEuCl_4$, 98218-70-3; UCl_4, 10026-10-5; YCl_3, 10361-92-9; $SmBr_3$, 13759-87-0.

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Configurational Processes in Coordinated Ligands. Extremely Facile Phosphorus Inversion in the Pyramidal Terminal Phosphide Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRR')$

Sir:

Although configurational processes at coordinated sulfur and selenium have been studied extensively,[1] little is known regarding inversion barriers at coordinated phosphorus.[2,3] Complexes with terminal pyramidal phosphide ligands have been of considerable recent interest,[4] and in a brief note Malisch has indicated that $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(P(i\text{-}Pr)_2)$ has a phosphide phosphorus inversion barrier of 14.4 kcal/mol.[2] We have become interested in the structure and reactivity of chiral pyramidal phosphide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRR')$,[5] and we report here their dynamic NMR behavior and configurational stability at rhenium. These data establish inversion barriers that are among

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