

SODIUM AZIDE AS A REAGENT FOR SOLID STATE METATHESIS PREPARATIONS OF REFRACTORY METAL NITRIDES

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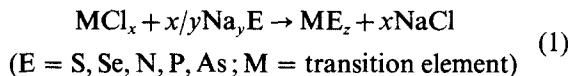
Abstract—Thermal initiation ($\sim 300^\circ\text{C}$) of a reaction between sodium azide and anhydrous metal chlorides (LaCl_3 , SmCl_3 , TiCl_3 , ZrCl_4 , HfCl_4 , VCl_3 , TaCl_5 , CrCl_2 , WCl_6 and MnCl_2) in sealed evacuated ampoules rapidly produces binary metal nitrides, dinitrogen and sodium chloride. The metal nitrides were purified by trituration with methanol and characterized by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and FT-IR.

Metal nitrides of various formulations are known for all the transition and lanthanide elements with the exception of the platinum group metals.¹ Nitrides are traditionally divided into two groups, the salt-like nitrides in which the bonding can be thought of as almost purely ionic (groups 1, 2, 9 and 10), and interstitial nitrides, in which the nitrogen atoms occupy vacancies in the metal lattice (groups 4–8). The interstitial nitrides have a wide range of stoichiometries and properties, the most useful of which, hardness, reflectance and high melting point, are utilized for a number of industrial applications.² Titanium nitride, for example, is used as a hardness coating for steel, as a decorative coating for jewellery and as a coating for the modification of optical transmission through glass.³

Metal nitrides have been synthesized both as bulk powders and thin films. They have traditionally been made by the reaction of a metal powder or metal hydride with nitrogen, a nitrogen/hydrogen mix or ammonia at elevated temperatures for extended time periods.⁴ Commercial coatings of titanium nitride have been made by the reaction of TiCl_4 and ammonia at 800°C .⁵ More recently, molecular precursor routes to metal nitrides have been developed. In this process a molecule with

an inherent chemical trigger is made to thermally decompose, sometimes in the presence of another co-reactant such as ammonia.⁶ A problem with the precursor route is the contamination of other elements in the product from side reactions. Nevertheless, Maya *et al.*⁷ have shown that group 4 nitrides can be made by the action of ammonia on homoleptic metal amides and Chisholm and co-workers⁸ have extended a similar methodology to the synthesis of a range of early transition metal nitrides by the thermolysis of precipitates from the reaction of ammonia with metal halides.

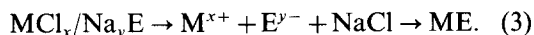
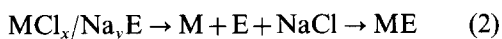
Recently, solid state routes to a number of materials have been reported by Kaner *et al.*⁹ and subsequently developed by others¹⁰ to the synthesis of metal nitrides. These are self-propagating reactions of alkali metal pnictides or chalcogenides with metal halides:



The reactions sometimes initiate on mixing and on other occasions can be initiated by grinding, heating with a small resistive filament, addition of a drop of solvent or by microwave induction. The reactions are typified by a thermal flash for 2–3 s where temperatures have reached in excess of 1000°C and rapid cooling. The reactions are extremely exothermic, primarily due to the lattice energy of the

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co-produced alkali metal halide. Reaction mechanisms are yet to be resolved but in simplistic terms the reaction can be thought of as occurring by one of two means. Reductive recombination requires reduction to the elements followed by high temperature recombination [eq. (2)].¹¹ Ionic metathesis involves direct exchange of ions with no accompanying reduction/oxidation chemistry, possibly followed by thermal decomposition to stable phases of material [eq. (3)].¹²



In an attempt to enlarge the scope of materials available from the synthesis and to try to contribute to the reaction mechanism, in this paper we report our findings for the reaction of metal halides with sodium azide. Sodium azide has been used previously by Russian workers in self-propagating high temperature synthesis of group 3 and 4 nitrides¹³ by reaction with finely divided metal powders.

EXPERIMENTAL

All reactions and reagent preparations were carried out under anaerobic conditions using either glove box or Schlenk line techniques. Glass ampoules (greater than 35 cm³ internal volume) were annealed prior to use and thoroughly flame dried *in vacuo*. Anhydrous metal chlorides and NaN₃ were obtained from Aldrich Chemical Co. and Strem chemicals and used as supplied. Methanol was used as supplied. IR spectra were recorded on a Nicolet 205 FT-IR spectrometer using KBr discs. Powder X-ray diffraction (XRD) measurements were performed on a Siemens Diffractometer D5000 in transmission mode using germanium monochromated Cu-K_{α1} (λ = 1.5406 Å) radiation. Scanning electron microscopy (SEM) profiles and energy dispersive X-ray analyses (EDXA) were obtained on a Jeol JSM 820 instrument using a Kevex detector and software. EDXA was performed on various regions across the sample surface, using point analyses to determine regional homogeneity. A Lenton Thermal Designs programmable tube furnace was used to initiate the reactions.

Reaction of NaN₃ with MCl_n (M = La, Sm, Ti, Zr, Hf, V, Ta, Cr, Mo, W, Mn)

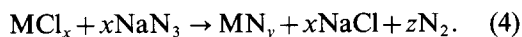
Sodium azide (0.050 g, 0.77 mmol) and metal chloride (equivalent amounts of chloride to sodium) were carefully ground together and sealed *in vacuo* in a large Pyrex ampoule. The ampoule

was placed into a tube furnace and the temperature ramped at 25°C per minute from room temperature until a reaction was observed (300–400°C) by a thermal flash and the appearance of material at the end wall of the ampoule. After cooling, the ampoule was broken open and the material was washed with methanol and dried *in vacuo*. The residual black materials were analysed by powder XRD (Table 1), SEM/EDXA and FT-IR.

CAUTION! These reactions are extremely exothermic and produce large quantities of nitrogen. Large ampoules should be used to minimize the risk of pressure explosions and reactions should be conducted behind a safety screen.

RESULTS AND DISCUSSION

Heating preground mixtures of sodium azide and metal chloride in sealed ampoules to temperatures between 300 and 400°C induces an exothermic reaction with the production of dinitrogen and a black solid [eq. (4)]. The black solid was analysed by SEM/EDXA and showed the presence of nitrogen, metal, sodium and chlorine. The powder XRD pattern of the solid revealed a mixture of sodium chloride and metal nitride or metal (Table 1) of various formulations.¹⁴ Trituration of the black solid with water and methanol left, in most cases, a single phase of metal nitride by XRD and only metal and nitrogen by EDXA.



The IR spectra of the metal nitrides showed a broad absorption at *ca* 600 cm⁻¹, assignable to a metal–nitrogen stretch.¹⁵

The reactions of sodium azide with metal chlorides are exothermic as assessed by Hess' law,¹⁶ with typical exothermicities of –900 kJ mol⁻¹. The primary driving force in the reaction is the formation of the sodium chloride by-product. Indeed, it is the exothermic nature of the reaction that accounts for the crystallinity of metal nitride products. Typically, when metal nitrides are synthesized by molecular precursor routes, normally from metal amides, the product is annealed at 850–1000°C for a few hours to induce sufficient crystallinity to be readily identified by powder XRD. The products were not annealed and the oven temperature was raised to a maximum of 400°C purely to initiate the reaction. Even so, products were sufficiently crystalline to allow powder XRD characterization. Initiation was judged by the dispersion of material throughout the ampoule and the furnace was immediately turned off. This indicates that the exothermic reaction is very rapid and probably high temperatures are generated. A ther-

Table 1. Phases detected by X-ray powder diffraction from the reactions of Na_3N and Li_3N with MCl_n

Metal halide	Phase identified ¹⁴ from reaction with NaN_3	Phase identified from reaction with Li_3N ¹⁰
LaCl_3	LaN	LaN
SmCl_3	SmN	SmN
TiCl_3	TiN	TiN
ZrCl_4	ZrN	ZrN
HfCl_4	HfN	HfN
VCl_3	VN, V_2N	VN (V_2N)
TaCl_5	TaN, Ta_2N	TaN, Ta_2N
CrCl_2	Cr, Cr_2N	Cr_2N
MoCl_3	Mo (Mo_2N)	Mo (Mo_2N)
WCl_6	W (W_2N)	W
MnCl_2	Mn_4N (Mn)	Mn_4N

Note: Where two phases are listed, the major phase is listed first; parentheses indicate trace amounts only of a phase.

mal flash was generally observed for the reactions of sodium azide, accompanied by the spread of material through the ampoule. The product was obtained as a fine powder.

Previously, we have studied the self-propagating reaction of lithium nitride and metal halides under comparable conditions to the reactions of sodium azide and metal halides.¹⁰ In these reactions a thermal flash is evident and the product is obtained as a fused mass rather than a fine powder. The calculated heats of reaction as determined by Hess' law are higher for the reactions of sodium azide than of lithium nitride, but the crystallinity as estimated by the Scherrer equation¹⁷ (based on the X-ray powder pattern line widths) is less in the sodium azide case. This can be explained by the evolution of large quantities of nitrogen gas, which takes away heat and spreads out the reaction mixture allowing faster cooling. It also accounts for the product being powdered rather than fused. These points are illustrated in the powder diffraction patterns for samples of titanium nitride (Fig. 1). The reactions of lithium nitride or sodium azide with titanium trichloride have calculated heats of reaction of -676 and -912 kJ mol^{-1} , respectively.

However, the product from the lithium nitride reaction is considerably more crystalline. Calculations from the half-width of the 2, 0, 0 reflection yield average crystallite sizes of $490 \text{ \AA}$ using lithium nitride and $250 \text{ \AA}$ using sodium azide.* Both reactions were performed on the same molar scale (50 mg titanium trichloride). This is of interest as some nitrides have been found to exhibit some interesting properties as heterogeneous catalysts (VN, Mo_2N , W_2N).²

The phases of material observed in the reactions of sodium azide with metal chlorides are shown in Table 1.¹⁴ In the reactions of the group 3 and 4 metal chlorides with sodium azide, only a single phase of metal nitride is observed and these are the nitrides of rock-salt structure MN (face-centred cubic; $\text{M} = \text{La, Sm, Ti, Zr, Hf}$). On moving across a period, the amount of nitrogen detected in the product is significantly decreased. This is well illustrated by the series $\text{TiN} \rightarrow \text{VN} + \text{V}_2\text{N} \rightarrow \text{Cr} + \text{Cr}_2\text{N}$. Similar patterns of detected phases were observed in the reactions of Li_3N with metal halides (Table 1). This can be explained by the thermal instability of the latter transition metal nitrides, which have decomposition points below the temperatures generated in the self-propagating reactions. The reactions of the rare earths proceed without any reduction at the metal and the reduction becomes more important on moving right in the periodic table.

The reactions of lithium nitride with metal halides have been envisaged mechanistically as either

* Calculations performed using the 2, 0, 0 reflection of TiN and using the 1, 0, 1 reflection of zinc as a standard. Crystallite sizes for the products from reactions of sodium azide and metal halides were all in the region of $250 \text{ \AA}$ as assessed by the Scherrer equation.

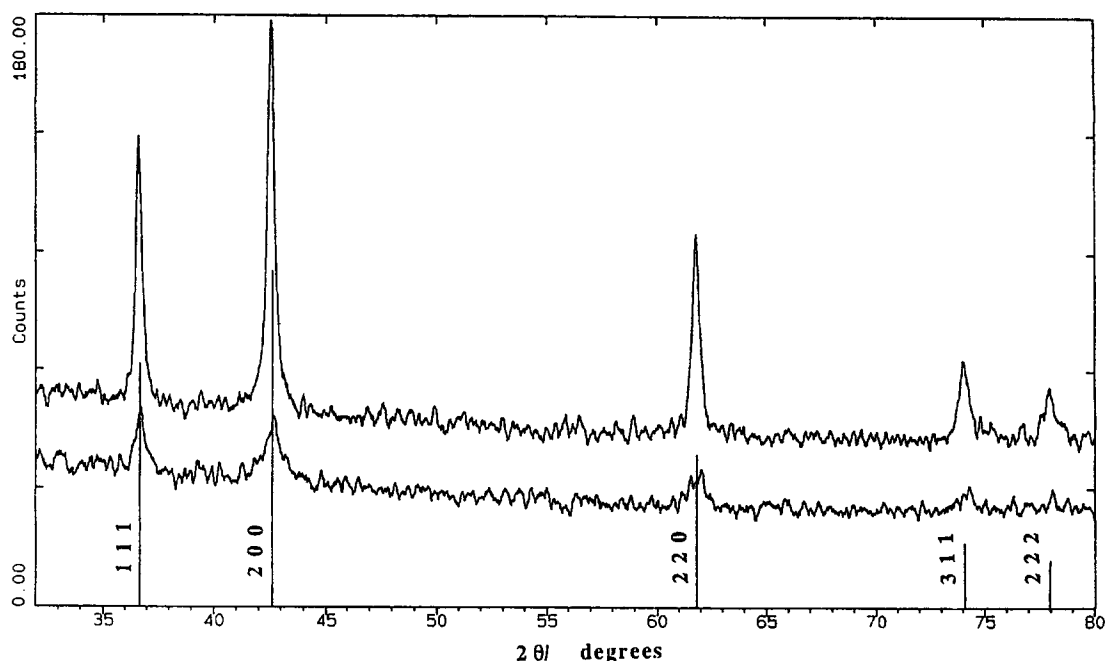


Fig. 1. Top trace: X-ray powder diffraction pattern from the reaction of Li_3N and TiCl_3 . Bottom trace: X-ray powder diffraction pattern of the material from reaction of NaN_3 and TiCl_3 (on the same scale as the top trace). Stick pattern is the standard pattern for TiN, Osbornite syn.¹⁴

a reductive recombination or a metathesis reaction. Some electron transfer is required in the reaction of sodium azide and metal chlorides to form metal nitrides if the nitrides are regarded as M^{n+} and N^{3-} . If the reaction of sodium azide with metal halides occurred via a reduction to the elements followed by a combination (this must presumably involve nitrogen radicals), then it might be expected that a more nitrogen-rich phase would be produced in the reaction compared with those of Li_3N (providing the nitrogen-rich phase is thermally robust, e.g. Ta_3N_5 is stable to 900°C). An alternative mechanism is a direct ionic metathesis reaction to form a metal azide which would then decompose with consequent loss of dinitrogen. This would have to involve either more than one azide on the metal or electron transfer between the azides before the metathesis reaction. Both of these pathways seem unlikely. In the reactions of sodium azide with metal chlorides to form metal nitrides, the mechanism for the reaction is not well described by either of the two simplistic extremes of reductive combination or ionic metathesis.

The reaction of sodium azide and metal chlorides forms an efficient rapid synthesis of refractory metal nitrides at lower temperature than conventional synthetic pathways. The co-production of large amounts of nitrogen, however, make this reaction unsuitable for large scale nitride synthesis unless

suitable pressure vessels and containment systems are employed.

CONCLUSION

The thermally initiated solid state reaction of sodium azide with metal chloride rapidly forms a single phase of metal nitride for the early transition metals and a mixture of metal and metal nitride for the latter transition metals. The reactions are exothermic, proceed with a visible thermal flash, are almost instantaneous and are accompanied by the spraying of material throughout the reaction container. The mechanism for the reaction is unlikely to follow either a simple reductive combination or ionic metathesis pathway. Products are considerably less crystalline than those obtained from comparable reactions of Li_3N and metal halides.

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