[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Preparation of Ammonium Trinitride from Dry Mixtures of Sodium Trinitride and an Ammonium Salt

BY W. J. FRIERSON AND A. W. BROWNE

Ammonium trinitride may be prepared in the pure state by the metathetical reaction between sodium trinitride and an ammonium salt such as the sulfate or the nitrate

$$NaN_3 + (NH_4)_2SO_4 \longrightarrow NH_4N_3 + NaHSO_4 + NH_3 \tag{I}$$

$$NaN_3 + NH_4NO_3 \longrightarrow NH_4N_3 + NaNO_3 \tag{II}$$

Equimolecular mixtures of the dry reagents were heated either statically in a sealed tube, *in vacuo*, or dynamically in a simple sublimation apparatus through which was passed a continuous current of dry air.

Mixtures containing 1 g. of ammonium sulfate and 0.4924 g. of sodium trinitride repeatedly were found to yield 87% of the theoretical amount of ammonium trinitride when heated to 300° for forty-five minutes in the current of air. The amounts of free ammonia were found to correspond closely to the theory based upon Equation I. Because of the relatively low melting point of ammonium nitrate, mixtures containing one gram of this reagent with 0.8125 g. of sodium trinitride gave consistent yields of over 93% of the volatile salt when heated to 190° for thirty minutes. In a series of experiments with the nitrate mixtures *in vacuo* a maximum yield of 95.7% was obtained after a five-hour period at 190°. The dynamic method with ammonium nitrate was adjudged most satisfactory, in view of the lower temperature and the shorter time required.

The white, crystalline sublimate was shown by the standard qualitative tests,[1] and by quantitative analysis involving repeated determinations of both ammonia and the trinitride ion, to be ammonium trinitride of a high degree of purity. Experiments with mixtures of the reagents in other than equimolecular proportions led to no improvement in the yields of ammonium trinitride.

Failure to obtain strictly quantitative yields is in no case attributable to loss of the N_3 radical by decomposition, but rather to the difficulty of securing satisfactory contact between the reagents. In a number of experiments the amounts of N_3 left in the reacting mass have been determined, with the result that it was found possible to account for over 99% of the trinitride originally taken.

In the opinion of the authors the reaction between sodium trinitride and an ammonium salt, or a suitable eutectic mixture of two or more ammonium salts, might readily be adapted for use on a larger scale, with certain precautions to minimize danger of detonation.

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(1) Browne, THIS JOURNAL, **27**, 551 (1905).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Further Studies of the Oxides of Potassium

BY CHARLES A. KRAUS AND ELLIS F. PARMENTER[1]

Of the various oxides of potassium reported in the literature, only K_2O, K_2O_2, K_2O_3 and K_2O_4 seem actually to exist. Of these, K_2O_4 has been established definitely by Vernon-Harcourt[2] and Holt and Sims[3] and has been confirmed by Kraus and Whyte.[4] Holt and Sims report a buff-colored oxide, K_2O_3, but without analytical details. They also report a yellow product whose oxygen content corresponded roughly to that of K_2O_2, but Kraus and Whyte report K_2O_2 as white.

Rengade[5] reports an oxide, K_2O, but its behavior toward liquid ammonia indicates that it may have been impure. While Kraus and Whyte obtained K_2O_2 and K_2O_4 by oxidation of potassium in liquid ammonia, they could obtain no evidence of the formation of an intermediate oxide, K_2O_3.

In the present investigation K_2O_2 and K_2O_4

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(1) Du Pont Fellow in Chemistry at Brown University.

(2) Vernon-Harcourt, *J. Chem. Soc.*, **14**, 267 (1861).

(3) Holt and Sims, *ibid.*, **65**, 432 (1894).

(4) Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926). The earlier literature is reviewed by these authors.

(5) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907).