SPONTANEOUS EXPLOSION OF A NORMALLY STABLE COMPLEX SALT

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AN IMPURE sample of trihydrazinenickel(II)nitrate was prepared several years ago in this laboratory by the simple method of adding a concentrated hydrazine-hydrate solution to an aqueous nickel-nitrate solution.[1] The product was apparently a mixture of the di- and trihydrazine complexes containing approximately 2.7 moles of hydrazine. The mixture was found to be stable and safe to handle under ordinary conditions, but was fairly sensitive to impact and friction.

Because of this laboratory's interest in extending the range of stable and nonhygroscopic, pyrotechnically active compounds which are sufficiently active to qualify as possible prime flame-producing, initiating, or similar agents, the pure compound was made and studied using the method of Franzen and von Mayer.[2] The method consists of the preparation of the tetramminenickel(II)nitrate as an intermediary with the subsequent replacement of ammonia by hydrazine when the ammine is heated with a hydrazine hydrate solution. The resulting trihydrazinenickel(II)nitrate was a pure salt which was prepared on several occasions by this method in quantities of 5 to 180 grams. On one occasion the moist product produced by this method spontaneously deflagrated. Its drop-weight sensitivity under a 2-kg. weight was 100 per cent at $16^1/_2$ inches, which classifies it as a moderately impact-sensitive compound to be treated with circumspection though with fewer precautions than are reserved for primary explosive mixtures containing such compounds as azides and fulminates.

RECENT WORK

Upon learning of the method of Medard and Barlot,[3] this laboratory produced a small amount of the nickel compound as well as the hydrazine complexes of manganese, zinc, and cadmium as described in the reference. A solution of nickelous nitrate in ethanol was added slowly and with agitation to a 40 per cent solution of hydrazine hydrate in ethanol. The hydrazine was in excess by approximately 5 per cent. The extremely fine pink powder was washed with ethanol and then dried for 16 hours in a vacuum desiccator containing calcium chloride and powdered ethyl cellulose. After drying, approximately 1.5 g. of the product remained in a 120-mm. porcelain evaporating dish.

DESCRIPTION OF ACCIDENT

The dish, containing the powder in the form of a dry cake, was removed from the desiccator and was examined visually without being disturbed. The dish was carried in the person's hand with his index finger extended above it. During this handling, the contents exploded with a deafening report, shattering the dish. About ten minutes had elapsed since the compound had been exposed to the atmosphere. Injuries consisted of a badly bruised finger tip and of a few small scratches on the face. Safety glasses were worn by the victim, this being a requirement for every person engaged in any kind of laboratory work at this installation.

HYPOTHETICAL CAUSES

It appears likely that notwithstanding the thorough washing of the compound on a Büchner funnel, hydrazine was occluded or was present in the form of an unstable higher complex. The presence of filter fibers or of residual alcohol after drying at room temperature is possible. Exposure to air may have initiated a spontaneous decomposition reaction between some uncombined hydrazine and combustible contaminants. These explanations are entirely speculative. However, they agree with similar though less spectacular experiences in this laboratory during the course of synthesis of similar compounds.

RECOMMENDATIONS

Complex salts which contain oxygenated anions of a pyrotechnically active type such as nitrite, nitrate, chlorate, perchlorate, and others in conjunction with a "fuel," such as ammonia, hydrazine, hydroxylammine, organic amines, etc., as a complexing agent are all potential explosives because of the presence of a strong oxidizer and a fuel within the molecule. Some of them are not explosive, but others may detonate more or less violently. Chlorate, perchlorate, and nitrate form a series of decreasing explosive potential; and of the complex-formers, hydrazine is especially dangerous.

Therefore, any of these compounds should be prepared, handled, and stored as if they were initiating explosives until proved otherwise by repeated preparation in an identical manner and by physical tests commonly used for the testing of explosives.

[1] FRANZEN, H., AND O. VON MAYER, *Z. anorg. Chem.*, **60**, 247 (1908).

[2] FRANZEN, H., AND O. VON MAYER, *Z. anorg. Chem.*, **60**, 248 (1908).

[3] MEDARD, L., AND J. BARLOT, *Chem. Abstracts*, **48**, 6125 (1954).