

NOTES AND CORRESPONDENCE

On the Decomposition of Ammonium Nitrate in the Atmosphere

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1. Introduction

Ammonium nitrate is known to form a substantial part of naturally occurring atmospheric aerosols. It is formed generally by the oxidation of biologically released ammonia or by the reaction of ammonia with nitrogen oxides or their corresponding acids. Because of its highly exothermic decomposition to either nitrous oxide and water or oxides of nitrogen and water, ammonium nitrate is widely used in the manufacture of explosives and propellents. It is also extensively used as a synthetic fertilizer. Because of this, considerable attention has been focused on this compound and its chemical properties are still subject to extensive research. In the field of the atmospheric sciences, several original contributions dealing with the distribution and air chemistry of ammonia (and hence partly also of ammonium nitrate), have been made by Junge (1963) who also summarizes much of that part of the present knowledge of atmospheric ammonium nitrate; this chemical is also known to be hygroscopic and hence a source of condensation nuclei.

Atmospheric aerosols are subject to a wide range of chemical reactions, including those which are induced by ultraviolet radiation. These have been described, in part, by Leighton (1961). Although both solid and aqueous nitrates account for a substantial part of the natural inorganic aerosol which may be altered by long-wave UV radiation, and although such processes may be expected to contribute to the occurrence of chemical changes in products which have been dissolved with nitrates in the aerosol droplets, not much work on the subject appears to be available in the literature. This lack seems to be only partly filled by earlier contributions which deal with nucleation phenomena induced by UV radiation in air such as, for example, the work of Farley (1951), Atkinson (1955) and Verzar and Kunz (1957), or by contributions of more direct interest to

atmospheric chemistry, such as the investigations of Robbins *et al.* (1959), Goetz and Pueschel (1967) and Schuck *et al.* (1966).

An extensive program of applied research on the photolysis both of nitrates in solution and of solid ammonium nitrate salts has been carried out in this laboratory for the past several years. This work stemmed from our earlier qualitative observation that when aqueous sodium chloride, which contained dissolved nitrates, was irradiated in a 450 W, high-pressure mercury UV immersion reactor under vigorous stirring, traces of chlorine were carried away by the inert gas carrier dispersed in the solution. Contrary to earlier thought, this observation implied the occurrence of highly oxidative steps during such photolytic processes. It was subsequently found by Papee and Petriconi (1964) that UV photolysis of aqueous alkali nitrates yielded substantial amounts of highly oxidizing transients. This was the first reported synthesis of pernitrites by the action of ultraviolet light on nitrate solutions. We have later found (Petriconi and Papee, 1966, 1968 a,b) that the formation of the pernitrous species was here concurrent to the well-known photo-production of nitrites from nitrates in solution. Gori *et al.* (1968) and Petriconi *et al.* (1968) have also shown recently that sunlight is sufficient to decompose aqueous alkaline nitrates, and that the reaction is enhanced by dissolved chlorides. It is therefore apparent that ammonium nitrate, which is known to decompose under ultraviolet light in the solid phase (Zawidzki *et al.*, 1965), will also photodecompose when dissolved in water. This yields nitrites which, in turn, undergo spontaneous decomposition into nitrogen and water (Kolarow *et al.*, 1965). The possibility that such a photolytic process occurs under sunlight was, in fact, confirmed by Petriconi *et al.* (1967) and by Gori *et al.* (1969) in a series of experiments performed outdoors and at different elevations above sea level.

2. Experimental measurements

Because of the importance of these reactions in defining the composition of atmospheric aerosols, a series of more rigorous experiments was begun under controlled laboratory conditions. Aside from a general interest in a process by which an atmospheric component, which carries biologically assimilable nitrogen, is being slowly eliminated, and besides the possibility of release of hygroscopic material ("secondary" condensation nuclei such as yielded by NO and NO₂) from large and giant nuclei which contain ammonium and nitric ions, there are two further points of interest:

1) Junge and Manson (1961) discovered substantial amounts of sulfur in the stratospheric aerosol layer, while Friend *et al.* (1961) and Friend (1966) found that a large part of this element is in the form of ammonium sulfate and persulfate. No nitrate was found by these workers in this aerosol. Since a portion of the nitrates which are formed in the atmosphere result from the oxidation of ammonia, and since stratospheric sulfur also appears to be of terrestrial origin as pointed out by Junge and Manson (1961), one would normally expect to find the presence of some nitrate ions in these stratospheric ammonium salts. An explanation for their absence is that the nitrates are being photolytically destroyed during their ascent and that sulfates are at

the same time being oxidized to persulfates. We did find, in fact, that small amounts of persulfates are formed when aqueous ammonium nitrate is photolyzed in the presence of sulfate.

2) It is generally assumed (Bates and Hays, 1967) that atmospheric nitrous oxide originates through bacterial action in the soil. While this may be the major source of this gas, it has also been shown by Harteck and Dondes (1959) that this substance may be generated from atmospheric nitrogen and oxygen under suitable experimental conditions. As mentioned previously, Zawidzki *et al.* have also shown that nitrous oxide is evolved when solid ammonium nitrate undergoes photolytic destruction.

The research quoted above is strongly indicative of a natural process whereby ammonium salts are destroyed in the atmosphere, with ultimate conversion to oxygen, nitrogen and its oxides, and water. In order to evaluate the broad trends of this process, conditions under which the reaction takes place have been studied in the laboratory, using unfiltered light obtained from a Hanovia immersion lamp. The effects of nitrate concentration, temperature and radiation intensity were evaluated both by analysis for nitrite in the irradiated solutions and by volumetric measurements of the gases evolved, both during irradiation and during the dark decomposition.

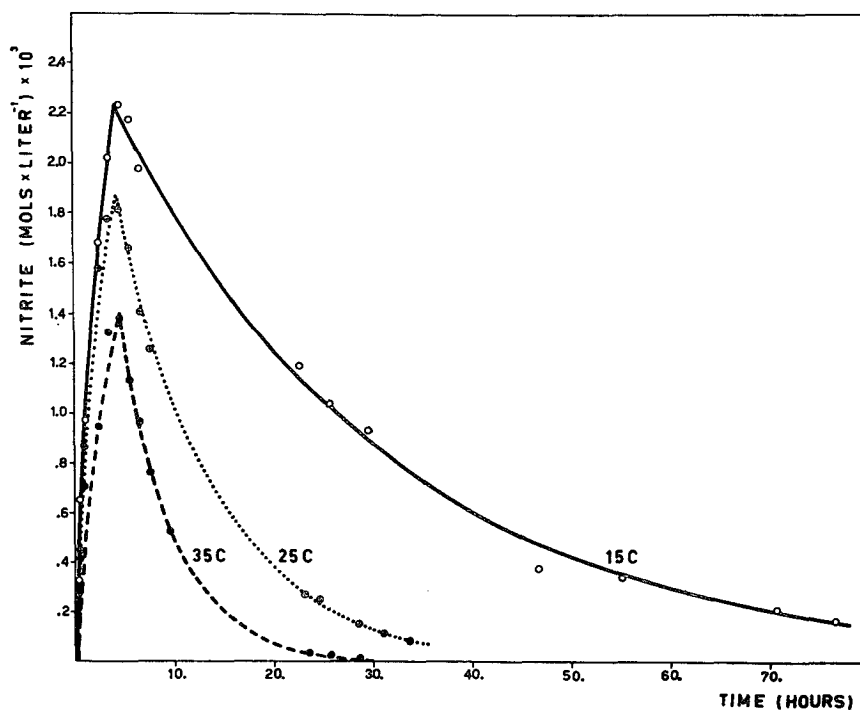


FIG. 1. Yields of nitrite as a function of time, from aqueous ammonium nitrate at concentrations of 60 gm per 100 cm³ of solution at temperatures indicated, during and after photolysis with $6.83 \cdot 10^{-5}$ UV quanta sec⁻¹N⁻¹. Curves were fitted by least squares according to Eqs. (2), (6) and (7) given by Petriconi and Papee (1969a).

A full account of this work is given elsewhere by Petriconi and Papee (1969 a,b,c). An example of the reaction course, at three different temperatures, is given in Fig. 1. Under experimental conditions described in the above papers, the overall effect of apparent nitrite formation is enhanced by increases in the intensity of the radiation and is inhibited by increases in nitrate concentration and temperature. The concurrent decomposition of nitrite and, hence, its dark decomposition, are enhanced by low *pH* values and high temperatures. Also, a concurrent oxidation of the ammonium ion by transient species developed during photolysis of nitrate, leads to a substantial increase in acidity of the photolyzed solutions. Therefore, under suitable conditions, hygroscopic nitrous anhydride may be released from those solutions.

3. Conclusions

Since both ammonia and ammonium nitrate are predominantly of terrestrial origin, the natural processes involving their formation and photolysis will occur primarily over land. Since the process is a function of both temperature and radiation flux, these reactions are strongly dependent on the geographic position of the land mass. Since the apparent yields of the photolytic reaction described above are also influenced by co-dissolved halide ions, this reaction should be of interest in the field of sea-land interaction chemistry. Keenan and Dimitriades (1962) have, in fact, shown that the thermal decomposition of ammonium nitrate is catalyzed by chloride ions; Gori *et al.* (1968) and Petriconi *et al.* (1969) have recently found that photolytic yields of nitrites, from irradiated sodium nitrate solutions, are enhanced by the presence of chlorides.

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