The authors are thankful to the Head of Pulse Section, Department of Plant Breeding, for providing seeds and to ICAR, New Delhi for financial assistance.

21 April 1986

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INTERACTION OF NITROGEN MOLECULES WITH PRE-ADSORBED H_2O_2 ON RUTILE TiO_2

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THE presence of hydrogen peroxide on the surface of TiO_2[1] and its interaction with molecular nitrogen has shown the formation of nitric oxide species[2,3]. This can occur only when the nitrogen molecule is fixed on the surface. Molecular nitrogen has been shown[4] to react with water vapour in the presence of TiO_2 under the stimulus of near UV radiation to produce ammonia and hydrazine. A direct relationship has been proposed to exist between the amount of NO formed and the initial pressure of nitrogen[5]. In this communication, a relationship that exists further between NO formation and the concentration of H_2O_2 on the surface of TiO_2 is considered.

Adsorption–desorption experiments were carried out in a conventional high vacuum system. Nitrogen gas ($P_{N_2} = 20\ Nm^{-2}$) was kept in contact with the sample before addition of H_2O_2. The change in pressure of nitrogen was monitored by using the mass spectrometer (V.G. Micromass 2A). After attaining a steady pressure of nitrogen in contact with TiO_2, vapour/liquid H_2O_2 was added to the sample. H_2O_2 was subjected to several freeze-pump-thaw cycles prior to admitting the nitrogen gas to the bulb containing the frozen H_2O_2. No significant change in the pressure of nitrogen was observed under this condition. Solid H_2O_2 was then melted so that H_2O_2 (vapour) came in contact with the surface of TiO_2. This position is represented by a in figure 1. The subsequent addition of H_2O_2 to the TiO_2 surface is represented by b in figure 1. In a blank experiment (in the absence of TiO_2), no significant change in the nitrogen pressure was observed during the melting procedure.

The decomposition of H_2O_2 into water and oxygen was found to be significant only when the liquid H_2O_2 was in contact with the surface TiO_2. Figure 1 demonstrates that vapour H_2O_2 when in contact with the surface (point a), produces very little evolution of oxygen. This may be due to the small probability of recombination of the reactive oxygen species (O*) to form oxygen molecules. In other words, more adsorbed NO is being preferentially formed by scavenging of the reactive oxygen species by molecular nitrogen, as shown:

$$H_2O_2 \rightarrow H_2O + O^*,$$
$$O^* + N_2 \rightarrow NO + N^*,$$
$$O^* + O^* \rightarrow O_2.$$

The direct addition of liquid H_2O_2 produced an enormous increase in the evolution of oxygen (point b, figure 1). This suggests that by the time nitrogen molecule diffuses through the liquid medium to

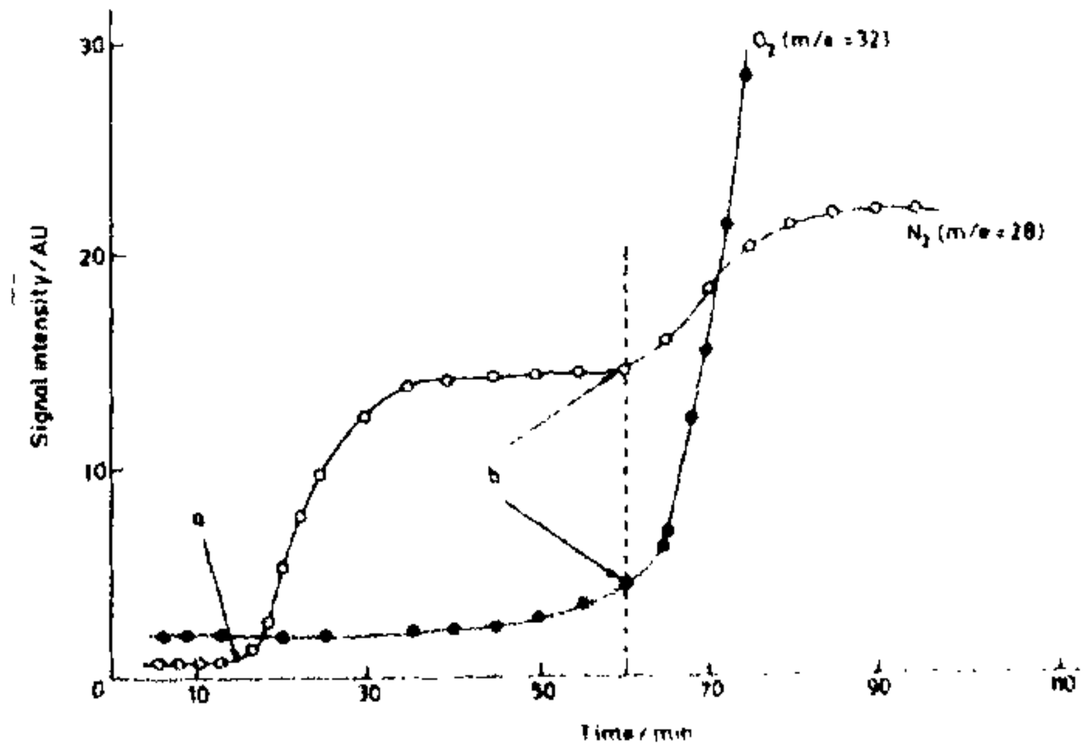

Figure 1. The simultaneous adsorption of nitrogen (m/e 28) and evolution of oxygen (m/e = 32) from the surface of TiO_2 moistured with H_2O_2. Point a–H_2O_2 (vapour) in contact with TiO_2 + N_2 (gas); point b–H_2O_2 (liquid) in contact with TiO_2 + N_2 (gas).

contact the surface of TiO_2, recombination of oxygen atoms occurred thus minimizing the rate of uptake of nitrogen and causing the increased evolution of oxygen.

In conclusion, it is suggested that molecular nitrogen reacts with atomic oxygen originating from hydrogen peroxide, as the interaction of molecular nitrogen with hydroxyl radicals is energetically very unfavourable[6]. The quantity of NO formed is directly related to the pressure of nitrogen as well as the concentration of hydrogen peroxide on the surface of TiO_2.

The author thanks the University of Bradford, England, (UK), for providing research facilities to carry out this work and Dr R. I. Bickley for encouragement and valuable discussions.

7 March 1986

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ACTIVITIES OF ALDOLASE, LACTATE DEHYDROGENASE, GLUCOSE-6-PHOSPHATASE AND ARGINASE IN PERCHLORATE TOXICITY

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PERCHLORATE is one of the toxic effluents in space research. Addition of perchlorate to the medium has been observed to reduce the growth rate of microorganisms[1,2]. Perchlorates as potassium or ammonium salt caused decreased food intake and loss of body weights in rats[3–5]. Ammonium perchlorate administered to chicks in their food was found to increase the glycolysis in erythrocytes[6]. Although these studies could prove the toxic effects of perchlorate, a study on the perchlorate toxicity in relation to carbohydrate metabolism and protein catabolism has not been carried out so far. It is, therefore, proposed to study the effect of perchlorate feeding to rats on the blood glucose level (a parameter of carbohydrate metabolism) and blood urea level (a parameter of protein catabolism). A few enzymes related to these parameters were also studied. In order to make a comparative study, potassium and ammonium perchlorates were used in the present investigation.

Weanling albino rats derived from the Wistar strain were purchased from Veterinary College, Madras. Glucose-6-phosphate, fructose-1,6-diphosphate and nicotinamide adenine dinucleotide were obtained from V.P. Chest Institute, Delhi. Bovine serum albumin was the product of Fluka Buchs, Switzerland. Sodium pyruvate was obtained from E. Merck, W. Germany. L-arginine monohydrochloride was purchased from Koch-Light, England. DL-glyceraldehyde was obtained from Sigma Chemical Co., St. Louis, USA. All other chemicals used were of analytical grade.

The animals were fed with commercial rat feed with paired feeding and water *ad libitum* along with oral administration (500 mg/kg body weight/day) of potassium or ammonium perchlorate for 45 days (chronic treatment). The dosage was selected based on the report of Spreca *et al*[7]. The animals were then sacrificed by stunning and decapitating and the blood was collected from jugular vein with potassium oxalate as an anticoagulant. Blood glucose was estimated by the method of Dubowski[8] modified by Sasaki and Matsui[9] and urea was estimated according to the method described by Geyer and Dabich[10]. The liver, kidney and intestine were dissected out immediately, washed with ice-cold saline and stored in ice. The appropriate amounts of the tissues were taken and homogenized in 0.1 M tris-HCl buffer pH 7.4. The homogenates were centrifuged at 2,500 rpm for 10 min at 4°C. The supernatants were used as the enzyme source. Aldolase and lactate dehydrogenase were assayed according to the methods prescribed by King[11]. Glucose-6-phosphatase and arginase were assayed by the methods of