Further work directed toward the generalization of these themes with the help of other examples is in progress. We strongly suspect that the relative paucity[1] of synthetic sulfur-ligated nickel(III) species may actually be due more to the lack of a systematic search than to inherent instability.[23,24]

Acknowledgment is made for financial support received from the Council of Scientific and Industrial Research and Department of Science and Technology, New Delhi, India.

---

(23) One reason for this situation is no doubt the inertia of the prevalent view that only hard donors are suited for binding higher oxidation states. The recent discovery[24] of thiolato complexes of, e.g., manganese(III) and cobalt(III) is a good indication of things to come.

(24) Dorfman, J. R.; Rao, C. P.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 453-454. Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311-3312. Seela, J. L.; Folting, K.; Wang, R. J.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N.; *Inorg. Chem.* **1985**, *24*, 4454-4456.

Department of Inorganic Chemistry
Indian Association for the Cultivation of Science
Calcutta 700032, India

Debashis Ray
Samudranil Pal
Animesh Chakravorty*

Received March 11, 1986

Photolysis of the N=N Bond in Trioxodinitrate: Reaction between Triplet NO$^-$ and O$_2$ To Form Peroxonitrite

Sir:

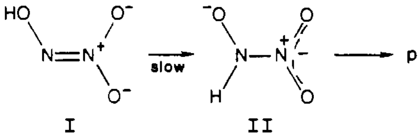
Studies on the reaction of $Na_2N_2O_3$ (sodium trioxodinitrate, N-N) with hemoglobin[1] have led to the suggestion that the anion $HN_2O_3^-$ decomposes by the formation of NO and HNO_2^- rather than nitrosyl hydride (HNO) and NO_2^- (eq 1, 2) as previously reported.[2-7] This proposal was advanced without reference to

$$HN_2O_3^- \rightleftharpoons HNO + NO_2^- \qquad (1)$$

$$2HNO \rightarrow N_2O + H_2O \qquad (2)$$

extensive kinetic and isotopic evidence[5,6] that shows the existence of an equilibrium between $HN_2O_3^-$ and its primary decomposition products (eq 1). Furthermore, the only reported evidence for occurrence of HNO_2^- in aqueous solution is as a transient product of the pulsed radiolysis of nitrite.[8] In this paper we report studies on the photochemical decomposition of trioxodinitrate that provide further support for the mechanism of eq 1 and 2 and also show that the reactive intermediate NO$^-$ can appear in solution in singlet and triplet states exhibiting distinct chemical properties, analogous to the isoelectronic case of O_2.

Important mechanistic implications arise from the reversibility of the decomposition of trioxodinitrate.[5] Homolytic cleavage of the -N=N- bond would generate biradical NO_2^-, but the reverse recombination reaction is observed upon addition of normal reagent nitrite, which cannot be in an excited, triplet electronic state. Therefore, by the principle of microscopic reversibility, the cleavage of trioxodinitrate must involve the generation of ground-state NO_2^- by the heterolytic cleavage of a -N—N- bond. The overall scheme must therefore include a tautomerization step (eq 3).[5] Furthermore, the tautomerization step must be slow, as otherwise



(3)

substantial deviations from the observed first-order kinetics of decomposition would occur due to the buildup of nitrite in solution.[5]

The reported results of kinetic studies on the trioxodinitrate–hemoglobin reaction[1] provide support for eq 3, since they show the reaction to be first order in $HN_2O_3^-$ and zero-order in hemoglobin, with rate constants similar to those found for the normal self-decomposition.[4] Thus these authors were, in all probability, measuring the rate of tautomerization of trioxodinitrate. Hollocher et al.[9,10] have also suggested a rate-determining conversion between two forms of trioxodinitrate to account for the kinetics of the trioxodinitrate–hemoglobin reaction.

Studies of different reactions in which HNO is an intermediate have led to the conclusion that it may exist in solution in two different forms[11,12] and that these may correspond to the anions of HNO and NOH. The molecule HNO is known to have a singlet ground state,[13] while that of NOH is expected to be a triplet.[14,15] Both species should deprotonate rapidly in the pH range of interest here ($pK_a = 4.7$ for HNO;[16] NOH should be more acidic); the multiplicity difference would be preserved in the two forms of the anion NO$^-$. Heterolysis of tautomer II of $HN_2O_3^-$ (eq 3) should produce singlet NO$^-$ as well as singlet NO_2^-; the former is known to be excited relative to its triplet ground state,[17] in an energy level spacing similar to the isoelectronic case of O_2.[18] Normal self-decomposition of $HN_2O_3^-$ is thus expected to form singlet NO$^-$, consistent with previously reported evidence that the undeprotonated intermediate in this reaction is HNO.[19] Decomposition of the species tautomer I would lead to formation of triplet NO$^-$, and this has now been shown photochemically.

There is good evidence that NO$^-$ reacts with O_2 to give peroxonitrite (ONOO$^-$), as has been demonstrated for the autoxidation of hydroxylamine.[20,21] However, ONOO$^-$ does not form when O_2 is bubbled through self-decomposing $HN_2O_3^-$ solution,[22] in which the form of NO$^-$ produced is expected to be singlet. Since we expect O_2 to react with triplet NO$^-$, the photolysis of trioxodinitrate has been studied both in O_2-free and in oxygenated solutions, in anticipation that peroxonitrite should form in the latter case.

The photochemical decomposition of trioxodinitrate was carried out in a reactor utilizing a Hanovia low-pressure mercury lamp, emitting light of wavelengths 253.7 and 184.9 nm. The latter line was screened by the use of a water jacket. Reaction was initiated by adding weighed $Na_2N_2O_3$ to the reaction solution, which was either O_2-saturated or N_2-saturated. The solution was stirred by the gas flow. The reaction was followed by withdrawing samples and measuring the trioxodinitrate concentration by UV absorption at either 248 or 233 nm, depending upon the pH.[3,4]

---

(1) Doyle, M. P.; Mahapatro, S. N. *J. Am. Chem. Soc.* **1984**, *106*, 3678.
(2) Angeli, A. *Gazz. Chim. Ital.* **1903**, *33*, 245.
(3) Bonner, F. T.; Ravid, B. *Inorg. Chem.* **1975**, *14*, 558.
(4) Hughes, M. N.; Wimbledon, P. *J. Chem. Soc., Dalton Trans.* **1976**, 703.
(5) Hughes, M. N.; Wimbledon, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1650.
(6) Akhtar, M. J.; Lutz, C. A.; Bonner, F. T. *Inorg. Chem.* **1979**, *18*, 2369.
(7) Veprek-Siska, J.; Pliska, V.; Smirous, F.; Vesely, F. *Collect. Czech. Chem. Commun.* **1959**, *24*, 687.
(8) Grätzel, M.; Henglein, A.; Lilie, J.; Beck, G. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 646.
(9) Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.
(10) Bazylinski, D. A.; Goretski, J.; Hollocher, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7986.
(11) Bonner, F. T.; Dzelzkalns, L. S.; Bonucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487.
(12) Bonner, F. T.; Akhtar, M. J. *Inorg. Chem.* **1981**, *20*, 3155.
(13) Ishawata, T.; Akimoto, H.; Tanaka, I. *Chem. Phys. Lett.* **1974**, *27*, 260.
(14) Gallup, G. A. *Inorg. Chem.* **1975**, *14*, 563.
(15) (a) Wu, A. A.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1975**, *35*, 316. (b) Bruna, P. J.; Marian, C. M. *Chem. Phys. Lett.* **1979**, *67*, 109.
(16) Grätzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003.
(17) Huber, K. P.; Hertzberg, G. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; p 484.
(18) Reference 17, p 490 ff.
(19) Bonner, F. T.; Degani, H.; Akhtar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3739.
(20) Hughes, M. N.; Nicklin, H. G. *J. Chem. Soc. A* **1971**, 164.
(21) Yagil, G.; Anbar, M. *J. Inorg. Nucl. Chem.* **1964**, *26*, 453.
(22) Wimbledon, P. E. Ph.D. Thesis, University of London, 1977.

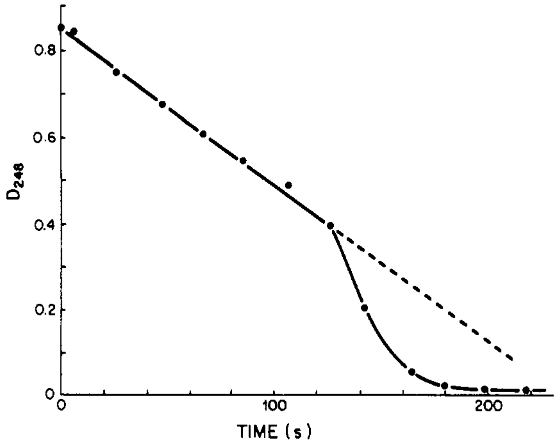


Figure 1. Photolysis of an oxygenated solution of trioxodinitrate (10^{-4} M) at pH 10.75 and 25 °C: onset of an additional decomposition pathway.

The photochemical decomposition of trioxodinitrate in N_2-saturated solutions was observed to be zero order in trioxodinitrate, with a zero-order rate constant at 25 °C of about 5.5×10^7 M s^{-1}, which was independent of $[Na_2N_2O_3]$ (10^{-5}–10^{-4} M) and pH (6.6–13.3). The zero-order kinetics arise as all the radiation is absorbed independent of the concentration of trioxodinitrate. Reaction products were nitrite (formed on a 1:1 basis with loss of trioxodinitrate) and N_2O.

In experiments carried out in O_2-saturated solutions, similar values of k_{obsd} were found, and the UV spectra similarly showed the loss of trioxodinitrate and formation of nitrite. At pH >11, however, the spectra also showed the formation and subsequent decay of peroxonitrite (λ_{max} = 302 nm, $\epsilon 302$ = 1670 M^{-1} cm^{-1}).[23] Peroxonitrite was not observed in experiments carried out at pH 8, as consistent with its increasing protonation in the interval pH 11–8 and the known instability of peroxonitrous acid.[23,24] The apparent yield of peroxonitrite was found to increase with pH, and in 0.1 M NaOH its formation was observed to occur on a very nearly 1:1 basis with the consumption of $N_2O_3^{2-}$. From this evidence we conclude that the NO^- produced in photochemical decomposition of trioxodinitrate is converted quantitatively to peroxonitrite.

The photolysis of trioxodinitrate in oxygenated solutions at $[Na_2N_2O_3] > 10^{-4}$ M showed an additional feature over the pH range 8.48–10.75. The zero-order rate constant for the first part of the reaction was identical with the usual value, but about halfway through the reaction there is a rapid increase in reaction rate (see Figure 1). The presence of 10% v/v ethanol had no effect on this phenomenon. The additional reaction pathway was seen only in the presence of O_2, suggesting that peroxonitrous acid is involved.

This additional pathway is probably a free-radical chain reaction, initiated by radical species formed in the decomposition or photochemical decomposition of peroxonitrous acid. Peroxonitrous acid isomerizes in aqueous solution to nitric acid via the formation and recombination of $^\bullet OH$ and NO_2 radicals.[25] The self-decomposition of peroxonitrous acid is very rapid in the pH range 8.48–10.75, and so the possibility of photolysis of peroxonitrous acid under these conditions was not readily amenable to investigation. However, we have shown in preliminary experiments at higher pH that peroxonitrite is photolyzed with production of about 50% nitrite. The presence of this additional pathway for the decomposition of trioxodinitrate is associated with enhanced production of nitrite (up to a maximum of $\Delta[NO_2^-]/\Delta[N_2O_3^{2-}] = 1.7$). It appears therefore that photolysis of intermediate peroxonitrous acid is responsible for initiation of the additional decomposition pathway, but these processes require further investigation.

Acknowledgment. We acknowledge the award of an SERC research studentship to C.E.D. and a NATO grant to F.T.B and M.N.H. We also thank Professor Thomas Hollocher for valuable discussions.

Registry No. $Na_2N_2O_3$, 13826-64-7; N_2O, 10024-97-2; $ONOO^-$, 19059-14-4; O_2, 7782-44-7; ONOOH, 14691-52-2; NO_2^-, 14797-65-0.

Department of Chemistry
King's College London
London W8 7AH, U.K.

Caroline E. Donald
Martin N. Hughes*
Janet M. Thompson

Department of Chemistry
State University of New York
at Stony Brook
Stony Brook, New York 11794

Francis T. Bonner*

Received February 27, 1986

---

(23) Hughes, M. N.; Nicklin, H. G. *J. Chem. Soc. A* **1968**, 451.
(24) Keith, W. G.; Powell, R. E. *J. Chem. Soc. A* **1969**, 90.
(25) Mahoney, L. R. *J. Am. Chem. Soc.* **1970**, *92*, 5263.