Sonolytic Decomposition of Nitrous Oxide in Aqueous Solution

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Water was insonated with 300-kHz ultrasound under pure argon, pure nitrous oxide, and mixtures of the two gases. The products of decomposition of N_2O are N_2, O_2, NO_2^-, and small amounts of NO_3^-. Maximum yield of decomposition occurs at an Ar/N_2O vol % ratio of 85:15, the yield being comparable to that of the well-known CCl_4-KI reaction. N_2O is decomposed at a very low rate when water is insonated under pure nitrous oxide. H_2O molecules and N_2O molecules in argon bubbles containing a few percent N_2O are decomposed with similar rates, although N_2O is much more unstable than H_2O. This observation is explained by postulating that all H_2O molecules and N_2O molecules in an argon bubble are converted into radicals in the short time of the adiabatic compression phase of a bubble. The yield of N_2O decomposition increases with increasing gas pressure in a similar way as for other sonolytic reactions.

Introduction

It is generally believed that ultrasonic waves initiate chemical reactions in aqueous solution only in the presence of monoatomic or diatomic gases. The reactions are brought about by the high temperatures of several thousand kelvin that exist for a short time in the compression phase of oscillating or collapsing gas bubbles.[1,2,3] As these oscillations take place adiabatically, higher temperatures are produced in gases having a larger value of γ, the ratio of their specific heats. For example, iodine is generated in an iodide solution in the presence of argon, oxygen, or air but not in the presence of nitrous oxide or carbon dioxide. Recently, it was reported that the iodine yield in the irradiation under argon is drastically increased by a few percent of nitrous oxide. However, at N_2O concentrations of more than 50% in the $Ar-N_2O$ mixture, the iodine yield is practically zero.[4]

In the present studies water was irradiated with 300-kHz ultrasonic waves under various mixtures of argon and nitrous oxide, and the following products were analyzed: N_2, O_2, and H_2 as gaseous products and NO_2^-, NO_3^-, and H_2O_2 as condensed products. N_2O is more readily decomposed thermally than water. The latter is known to dissociate into H atoms and OH radicals.[5] Under cavitation conditions, where temperatures of several thousand kelvin occur, N_2O decomposes much more rapidly than water. Such conditions could be expected to exist in argon bubbles containing little N_2O. However, because of the great thermal instability of N_2O, one could also expect to have a chance of detecting its decomposition in the irradiation of water under pure N_2O, i.e., under conditions where the temperature possibly is not sufficient for the decomposition of water itself.

The irradiation conditions and methods of analysis were described in a preceding paper on the sonolysis of aqueous solutions containing $^{14,14}N_2$ and $^{15,15}N_2$.[6]

Results

Figure 1 shows the rate of formation of the gaseous products as a function of the concentration of nitrous oxide in the $Ar-N_2O$ gas mixture. In the irradiation under pure argon, H_2 is formed at a rate of 13.4 $\mu M \cdot min^{-1}$. In the presence of a few percent N_2O, the H_2 yield rapidly decreases to zero. At the same time, the yields of N_2 and O_2 steeply increase with increasing N_2O concentration,

reach maximum values at about 15 vol% N_2O, and rather steeply decrease at higher concentrations of this gas. However, even at 100% N_2O, nitrogen and oxygen can still be found, the rates of formation being 9.0 and 2.5 $\mu M \cdot min^{-1}$, respectively. Note that the yield of O_2 never amounts to 50% of that of N_2, which would be expected if the reaction $N_2O \rightarrow N_2 + \frac{1}{2}O_2$ was the only process occurring. The reason must lie in the fact that NO_2^- and NO_3^- are also formed. Figure 2 shows the yields of these products as functions of the N_2O concentration. Maxima in these curves are also observed. They lie at somewhat higher N_2O concentrations than the maxima for N_2 and O_2 in Figure 1. The NO_2^-/NO_3^- ratio of rates is not far from one for N_2O concentrations below 15% but then strongly increases with increasing N_2O concentration. Above 40% N_2O in the gas atmosphere NO_3^- is a trace product. NO_2^- is also formed in the irradiation under pure nitrous oxide, the yield being 0.87 $\mu M \cdot min^{-1}$.

Figure 3 shows on an enlarged scale how the H_2 yield decreases upon addition of small amounts of N_2O to the solution. Oxygen also decreases the H_2 yield. By comparing the two curves of Figure 3, one recognizes that O_2 is about 10 times more effective in decreasing the H_2 yield than N_2O. The decrease in the yield is attributed to the scavenging of H atoms. Experiments were also carried out in which water was irradiated under pure nitrous oxide at various pressures. Figure 4 shows the rates of formation of various products as functions of the N_2O pressure. An increase in yield by a factor of 1.5–2.0 is observed as the pressure is raised from normal conditions (i.e., 1000 mbar) by a factor of 1.5. Figure 5 finally shows the results of similar experiments where the gas atmosphere consisted of a 80%–20% mixture of Ar and N_2O. High yields were already observed at normal pressure (1000 mbar). The yields were about tripled by increasing the pressure to 1500 mbar.

Discussion

H atoms and OH radicals are formed in the irradiation of water under argon, and the final products H_2, H_2O_2, and O_2 arise from reactions among the radicals. The rapid decrease in the H_2 yield upon the addition of small amounts of N_2O (Figure 1) is attributed to the scavenging of H atoms. It is known that the reaction H + $N_2O \rightarrow N_2$ + OH rapidly takes place at higher temperatures.[7] The H_2O_2 yield is also decreased to practically zero, which may be explained by the reaction of N_2O with OH radicals. This reaction has been observed in the gas phase.[7] It should also be kept in mind that about 80% of the H and OH radicals primarily generated recombine to water.[4,8,9] However, in the presence of

(1) Noltingk, B. E.; Neppiras, E. A. *Proc. Phys. Soc., London, Sect. B* **1950**, *B63*, 674.

(2) Flynn, H. G. In *Physical Acoustics, Principles and Methods*; Mason, B. W. P., Ed.; Academic: New York, 1964; Vol. 1B, 57.

(3) Fitzgerald, M. E.; Griffing, V.; Sullivan, J. *J. chem. Phys.* **1956**, *25*, 926.

(4) Henglein, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 100.

(5) Makino, K.; Mossoba, M. M.; Riesz, P. *J. Phys. Chem.* **1983**, *87*, 1369.

(6) Hart, E. J.; Fischer, Ch.-H., Henglein, A. *J. Phys. Chem.*, preceding paper in this issue.

(7) Hampson, R. F.; Garvin, D. "Reaction Rate and Photochemical Data for Atmospheric Chemistry"; National Bureau of Standards Special Publication 513, Gaithersburg, MD, 1978.

(8) Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1985**, *89*, 4342.

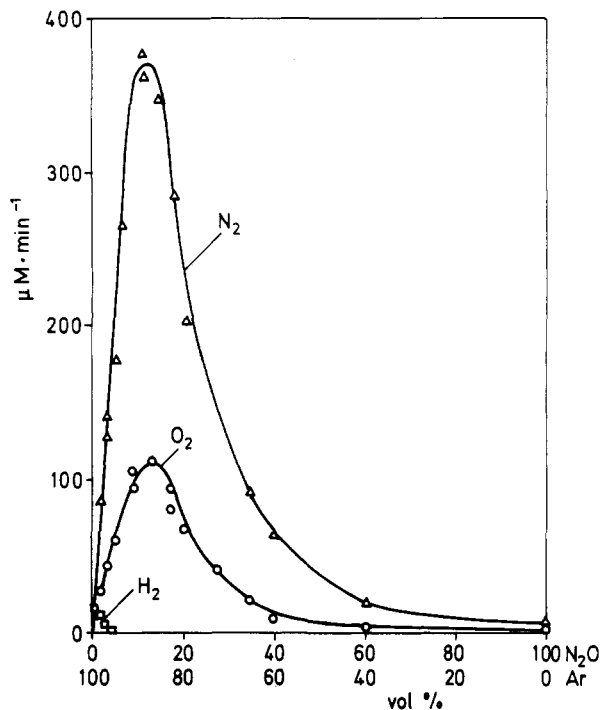(9) Fischer, Ch.-H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 222.

Figure 1. Rate of formation of H_2, N_2, and O_2 as a function of the concentration of N_2O in the Ar–N_2O mixture.
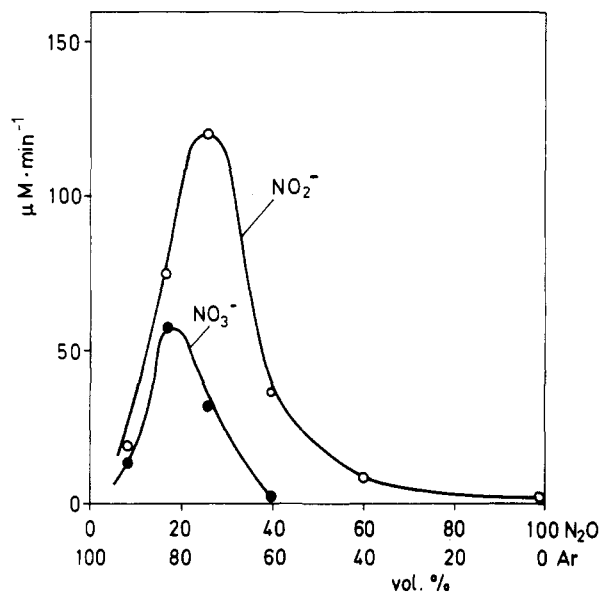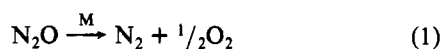

Figure 3. Rate of H_2 formation under argon in the presence of small concentrations of O_2 and N_2O in the solution.

Figure 2. Rate of formation of NO_2^- and NO_3^- as a function of the concentration of N_2O in the Ar–N_2O mixture.
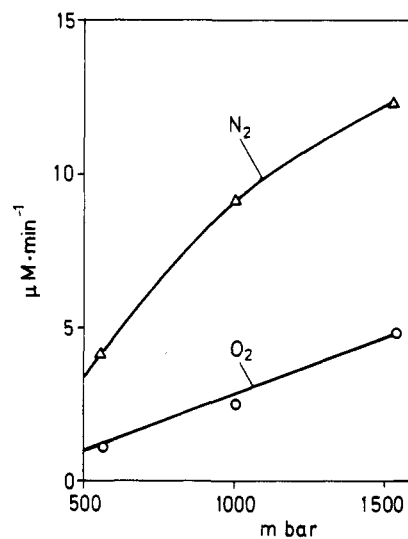
Figure 4. Irradiation of water under various pressures of N_2O.

a scavenger they may undergo other reactions. The yields of N_2 and O_2 in Figure 1 increase rapidly with increasing N_2O concentration and at concentrations of several volume percent N_2O the yields exceed by far those obtained for water in the presence of pure argon. A thermal decomposition of nitrous oxide according to the overall equation

$$N_2O \xrightarrow{M} N_2 + {}^1/_2O_2 \qquad (1)$$

has to be postulated. At larger N_2O concentrations the yields go through a maximum and finally decrease. This effect is attributed to the fact that lower temperatures are reached in the Ar–N_2O bubbles with increasing N_2O concentration.

HNO_2 is a product of irradiation in the presence of N_2O, and noticeable amounts of HNO_3 are found, too. These products are known to be formed in the irradiation of water under air[10-12] and
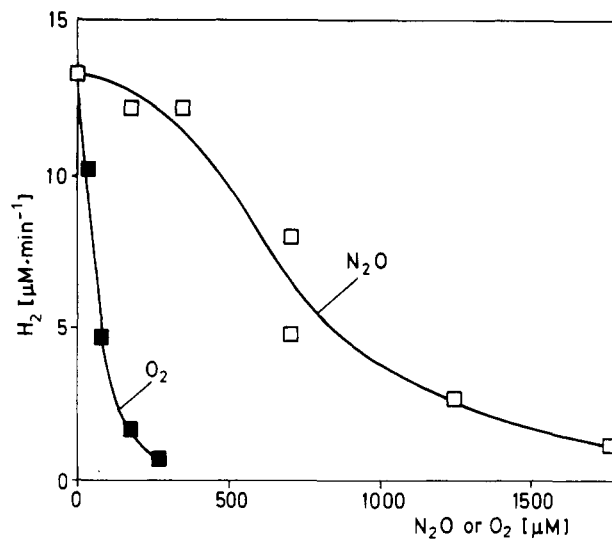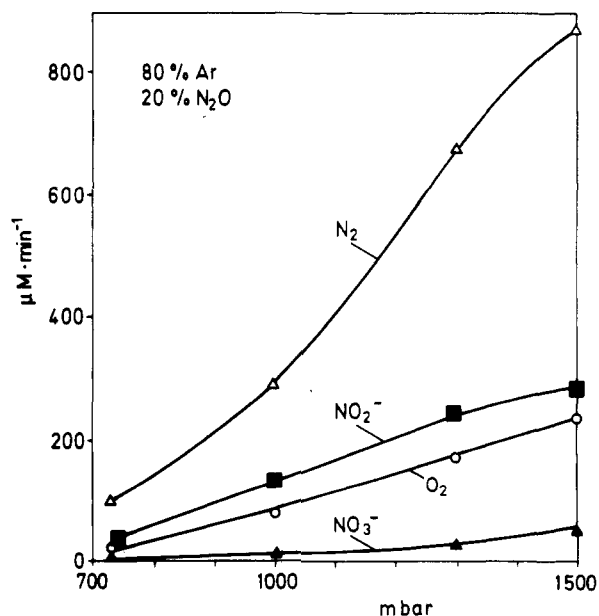

Figure 5. Irradiation of water under various pressures of an argon–N_2O (80%–20%) mixture.

under mixtures of nitrogen and argon.[6] However, the yields in the presence of N_2O are very much higher. There must exist a

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(10) Polotskii, I. G. *Zh. Obsch. Khim.* **1947**, *17*, 1048.

second overall process for the decomposition of N_2O

$$3N_2O + H_2O \rightarrow 2HNO_2 + 2N_2 \qquad (2)$$

Using the yields at 15% N_2O in Figures 1 and 2, one calculates that processes 1 and 2 occur in the ratio 4:1. Most interesting is the fact that nitrous oxide is still decomposed in the irradiation of water under a pure N_2O atmosphere. This seems to be the first observation of a sonolytic reaction in water under an atmosphere of a triatomic gas after the luminscence of water under NO_2 has already been reported.[13] The rate of formation of N_2 is only half the rate of H_2 formation under argon. As about 80% of the H and OH radicals formed in the irradiation under an argon atmosphere recombine, one can say that 10 times less N_2O molecules are decomposed in an N_2O bubble than water molecules are decomposed in an argon bubble. (An efficient back-reaction O + N_2 $\xrightarrow{M}$ N_2O for N_2O does not need to be postulated as this reaction is known to be very slow[7]). Further, the concentration of N_2O in an N_2O bubble is about 30 times higher than that of water vapor in an argon bubble. The specific rate of decomposition of N_2O in an N_2O bubble, therefore, is about 300 times lower than that of the decomposition of water in an argon bubble. This is explained by the much lower temperature that is reached in the adiabatic compression of an N_2O bubble.

The initial slope of the curve for N_2 in Figure 1 is 36 μM·min^{-1}/vol % N_2O. At 3% N_2O, which roughly corresponds to the water vapor concentration in an argon bubble, the rate of decomposition is 108 μM·min^{-1}. This may be compared with the rate of the decomposition of water in a pure argon bubble. H_2 is formed at a rate of 13.4 μM·min^{-1}. Taking into account that about 80% of the initially decomposed water molecules are reformed one calculates an initial rate of water decomposition of 67 μM·min^{-1}. In other words, H_2O and N_2O molecules present in low concentrations in an argon bubble are decomposed within a factor of 2 with the same specific rate. At first sight, this fact seems surprising as it is known from combustion chemistry that the rate constants of the two decomposition processes are quite different[7]

$$k(N_2O \xrightarrow{M} N_2 + O) = 8.3 \times 10^{-10}e^{-29\,000/T}$$

$$k(H_2O \rightarrow H + OH) = 5.8 \times 10^{-9}e^{-52\,900/T}$$

For example, the specific rate of N_2O decomposition at 5000 K is greater by a factor of 17 than that of water. Since the rates appear to differ by only a factor of 2, one could be inclined to postulate that the temperature in an argon bubble is much higher. However, one should also consider the absolute conversions of water and nitrous oxide in an argon bubble. Perhaps at a lower temperature of, say, 4000 K, the rate of water decomposition is already fast enough to decompose all H_2O molecules during the short time of compression of the bubble. The same reasoning applies for added N_2O and an increase in temperature caused no further decomposition. Or, to express it in other words, if the thermodynamic equilibrium of water dissociation, which at 4000 K and 10 bar lies to only 25% on the side of undissociated molecules, is established in that short time, the observed specific rate of decomposition of another molecule with a lower activation energy can hardly be faster than that of water decomposition. Under these conditions almost all molecules in the bubble are dissociated. According to this explanation one expects a very high local concentration of decomposition products, such as free radicals and atoms, in the bubble and on its interface with the solution.

The data for N_2 formation of Figure 1 are presented in Figure 6 in a different form by plotting the logarithm of the product $Yc_0/(Y_0c)$ vs. the concentration c of N_2O in the liquid phase. c_0 = 2.3 × 10^{-2} M is the saturation concentration of N_2O and c/c_0 the fraction of N_2O in the Ar–N_2O mixture. Y is the N_2 yield
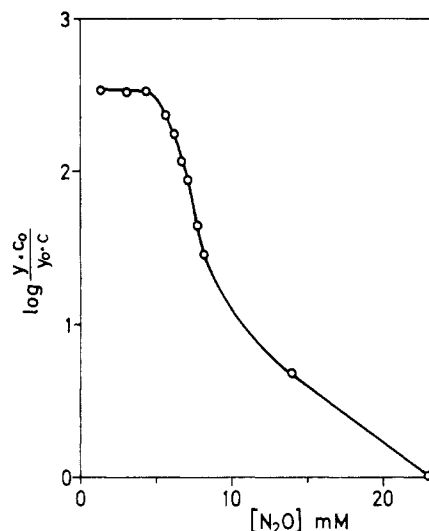

Figure 6. Semilogarithmic plot of the reduced yield/concentration ratio vs. the N_2O concentration (from the data of Figure 1).

and Y_0 that in the solution irradiated under pure nitrous oxide. The curve in Figure 6 is horizontal at small N_2O concentrations and later decreases with increasing c. At low N_2O concentrations, the temperature in the argon bubbles is not drastically lowered and all N_2O molecules in them are decomposed (i.e., Y/c = constant). At higher N_2O concentrations, the temperatures are lower and this results in less decomposition of N_2O.

Processes 1 and 2 are composed of several elementary reactions. The first step probably is the dissociation[14]

$$N_2O \rightarrow N_2 + O \qquad (3)$$

The most probable reaction of the O atom is

$$O + N_2O \rightarrow N_2 + O_2 \qquad (4)$$
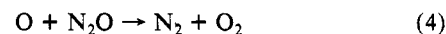
which is known from combustion chemistry.[7] Reactions 3 and 4 explain the overall process 1. Some of the oxygen atoms may undergo the well-known reaction with nitrous oxide.[7]

$$O + N_2O \rightarrow 2NO \qquad (5)$$

HNO_2 and HNO_3 are formed by further oxidation of NO. These products would be formed in equal amounts if NO was oxidized to NO_2 and NO_2 subsequently hydrolized. However, the HNO_2/HNO_3 ratio was quite different at the various N_2O concentrations (Figure 2). HNO_2 generally was formed in a higher yield than HNO_3. Various reaction paths are conceivable for the direct oxidation of NO to HNO_2. It could be that H_2O_2 formed in the sonolysis of water oxidizes NO to HNO_2. We have recently given reasons for O atoms and OH radicals being interconvertible: O + H_2O ⇌ 2OH.[15,16] Oxidation of NO by OH would be another explanation for HNO_2 formation

$$NO + OH \xrightarrow{M} HNO_2 \qquad (6)$$
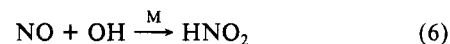
Another possibility would consist of the reaction

$$NO + NO_2 \rightarrow N_2O_3 \qquad (7)$$
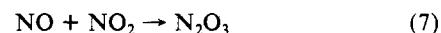
(which requires that the reactants are cooled down) and subsequent hydrolysis of N_2O_3. We do not see a possibility at the present time to distinguish between these different reaction paths.

An increase in yield with increasing pressure up to about 2 bar of the gas atmosphere, under which water is irradiated, was also observed by Polotskii for the formation of HNO_2 and HNO_3 in

(11) Virtanen, A. J.; Ellfolk, N. *J. Am. Chem. Soc.* **1950**, *72*, 1046.
(12) Mead, L.; Sutherland, R. G.; Verrall, R. E. *Can. J. Chem.* **1976**, *54*, 1114.
(13) Sehgal, C.; Sutherland, R. G.; Verrall, R. E. *J. Phys. Chem.* **1980**, *84*, 396.

(14) Olschewski, H. A.; Troe, J.; Wagner, H. Gg. *Ber. Bunsen-ges. Phys. Chem.* **1966**, *70*, 450.
(15) Fischer, Ch.-H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 1954.
(16) Gutiérrez, M.; Henglein, A.; Fischer, H.-J. *Int. J. Radiat. Biol.* **1986**, *50*, 313.

aerated water.[10] We find an increase in yield by a factor between 1.5 and 3.0 for practically all reactions (under argon, xenon, oxygen, and mixtures of argon and other gases) when the pressure is raised from 1 to 1.5 bar. The results shown by Figures 4 and 5 follow this general line of observations. The increase in yield with increasing pressure could be due to (1) higher temperatures in the gas bubbles, (2) a larger number of gas bubbles, and (3) a larger size of the bubbles. In the first case, it could be difficult to understand why all reactions should be accelerated in the same way by increased pressures. The third case would at least semi-quantitatively be understood in terms of the theory of pulsating gas bubbles,[3,17] according to which the volume of a resonating

bubble is proportionate to the 1.5 power of pressure. At much higher pressures, the yields decrease again, and above about 5 bar no more sonochemistry takes place.[10] Further work is necessary to understand the yield vs. pressure curves.

(17) Minnaert, M. *Philos Mag.* **1933,** *16,* 235.

Track Effects in Water Radiolysis with High-Energy Heavy Ions[1]

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While the differential yield for $HO_2^{\bullet}$ production in the radiolysis of water with 100–200-MeV carbon ions (~0.05 molecules/100 eV) is more than twice the yield observed for fast electrons there is little dependence of yield on particle energy or linear energy transfer (LET). This observation suggests that the density of initial events in the spurs produced by highly charged ions is somewhat greater than in electron radiolysis. Detailed examination of the effect of particle charge on track structure is in order.

In previous radiolytic studies with heavy ions it has generally been assumed that as the particle energy increases the radiation chemical yields will approach those observed in radiolysis with fast electrons and γ-rays and be independent of particle type.[2] For this to be the case the structure within the heavy particle track must become essentially identical with that for high-energy electrons, i.e. the track must consist of isolated spurs which are of similar size for the different radiations. We have recently carried out studies with carbon ions of energies up to 200 MeV at the ATLAS facility of Argonne National Laboratory which lead us to question the second part of this requirement and which point to the possible importance of particle charge in determining the characteristics of spurs. In particular it is found that the radiation chemical yield of $HO_2^{\bullet}$ produced in the radiolysis of water by carbon ions decreases only slightly on increase of the particle energy from 100 to 200 MeV even though the differential yield is more than twice that observed for fast electrons. Extrapolation of this data appears to indicate that for particles having a LET less than a few electronvolts per angstrom the yield of $HO_2^{\bullet}$ produced by carbon ions is greater than that produced by protons. This result suggests that the limiting yields for high-energy heavy ions will be somewhat dependent on the charge of the irradiating particle and implies that as Z increases there is an increased importance of spurs with a high density of energy deposition. Such a dependence could have a profound importance in macromolecular and especially biological systems where concerted effects can control the overall consequences of radiolysis.

Although the present results are far from conclusive they suggest very strongly that discussions of track structure in radiation chemical processes do not adequately take into account the effect

of particle charge on the distribution of spur sizes at high velocities. It is therefore important to examine in considerable detail, from both the theoretical and experimental viewpoints, how track structure is affected by charge on the irradiating particle. The study reported here represents only a preliminary experimental attempt in this direction so that this report is intended primarily to provoke more experimental and theoretical investigations of this subject.

Experimental Section

Irradiations were carried out at the ATLAS facility of Argonne National Laboratory with carbon ions of energies up to 200 MeV using the second linear accelerator booster stage which has recently become operational. Experiments were generally similar to those previously reported [3-5] with the yield of O_2 produced from a 10 mM cupric sulfate–1 mM ferrous sulfate solution in 10 mM sulfuric acid taken as a measure of $HO_2^{\bullet}$ formation. O_2 production was measured with a Hersh electrochemical cell.[3] Particle energies, as measured with a scintillation detector,[3] were corrected for energy absorption in the window system and beam currents were integrated to give absolute doses. With improvements in targeting, current monitoring, and measurement of O_2 production, the precision of these measurements has been improved considerably over our previous studies. Because relatively little energy is lost in the window system the particle energies are known quite accurately and the overall accuracy of the reported yields is of the magnitude of the precision, i.e. ~2%.

Results and Discussions

Because $HO_2^{\bullet}$ does not appear to be produced to any appreciable extent outside spurs or tracks[3-5] its yield is a particularly

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2849 from the Notre Dame Radiation Laboratory.
(2) While this assumption does not appear to have been explicitly stated in the literature it is implied in many previous works; see, for example, Burns, W. G.; Barker, R. In *Aspects of Hydrocarbon Radiolysis*, Gäumann, T., Hoigne, J., Eds.; Academic: New York, 1968; p 33. Schuler, R. H. *Trans. Faraday Soc.* **1965,** *61,* 100.

(3) Burns, W. G.; May, R.; Baverstock, K. F. *Radiat. Res.* **1981,** *86,* 1.
(4) LaVerne, J. A.; Burns W. G.; Schuler, R. H. *J. Phys. Chem.* **1985,** *89,* 242.
(5) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1985,** *89,* 4171. LaVerne, J. A.; Schuler, R. H.; Burns, W. G. *J. Phys. Chem.* **1986,** *90,* 3238.
(6) Hart, E. J. *Radiat. Res.* **1955,** *2,* 33. Bjergbakke, E.; Hart, E. J. *Radiat. Res.* **1971,** *45,* 261.