film material	t _{max} , s	$D_{\rm e} \times 10^9$, cm ² /s	
		TOF	steady state ^a
Prussian Blue/White ^b	15.8	1.4	3.9 ± 1.3
Prussian Yellow/Blue ^c	0.5	45	29
$poly[Os(bpy)_2(vpy)_2](ClO_4)_2^d$	0.6	38	20 ± 8
$poly[Fe(DSB)_3](ClO_4)_2^e$	4.5	5.0	3.7 ± 1.4

"Steady-state measurement is by applying potentials that continuously reduce and oxidize opposing faces of the film. D_e calculated as in ref 16. ^bElectron transport by Fe(III/II,II/II) self-exchange. Steady-state measurements show that there are two closely spaced Fe-(III/II,II/II) couples which we have called²³ types A and B. The steady-state value given in the table, 3.9×10^{-9} cm²/s, is primarily type A; that for type B, 28×10^{-9} cm²/s, is thought²³ to correspond to more symmetrically (-NC) coordinated ferric sites. Initial film state is the Fe(III/II) form of Prussian Blue (ideal formula $Fe_4[Fe(CN)_6]_3$); potential pulse to -0.2 V vs SSCE to generate Fe(II/II), Prussian White, at generator electrode. Film deposited according to ref 17. Electron transport by Fe(III/III,III/II) self-exchange. Initial film state is the Fe(III/II) form of Prussian Blue; potential pulse to +1.0 V vs SSCE to generate Fe(III/III), Prussian Yellow, at generator electrode. Film deposited according to ref 17. d'Electron transport by Os(III,II) self-exchange. Initial film state is Os(II); potential pulse to +0.9 V vs. SSCE to generate Os(III). Film deposited according to ref 16. 'Electron transport by Fe(III,II) self-exchange. Initial film state is Fe(II); potential pulse to +1.1 V vs SSCE to generate Fe(III). Film deposited similar to ref 16.

film depth: 0.36 for a 0.3- μ m deep film and 0.44 for a 1.0- μ m film. Since we employ films of depth not much greater than the array finger height,¹⁷ θ = 0.36 in eq 1 should adequately represent our electrochemical time-of-flight experiment.

Results and Discussion

The collector current transient for electron time of flight of a pulse of (acceptor) poly[Os(bpy)₂(vpy)₂](ClO₄)₃ states generated in a film of poly[Os(bpy)₂(vpy)₂](ClO₄)₂ is shown ($\textcircled{\bullet}$) in Figure 2. Also shown ($\textcircled{\bullet}$) is the calculated $I/I_{\rm max}$ curve of Figure 1E, curve b, overlaid on the experimental one by normalizing it at $t_{\rm max}$ on the time axis. In this way we see that the collector currents calculated for the model of Figure 1D agree reasonably well with experiment and due to the reservoir effect are, beyond $t_{\rm max}$, larger than those calculated (O) for the Figure 1C geometry. Application of $\theta = 0.36$ in eq 1 to the observed $t_{\rm max} = 0.6$ s gives $D_e = 3.8 \times 10^{-8}$ cm²/s. This value is close to that obtained (2.0×10^{-8}

 cm^2/s) by our method^{9,10} of applying Fick's first law to the steady-state currents flowing between generator and collector electrodes when these are continuously maintained at oxidizing and reducing potentials.

Electron time-of-flight results from the above and from experiments with three other donor/acceptor couples are collected in Table I. In each case we see good agreement with results from steady-state currents. That electron hopping is slower²³ for the type A iron states in the Prussian Blue/Prussian White couple Fe(III/II,III/II) than for the ferro-ferricyanide states in the Prussian Yellow/Prussian Blue couple Fe(III/III,III/II) is confirmed by these results. That the M(III/II) electron self-exchange rates are larger in poly[Os(bpy)₂(vpy)₂](ClO₄)₂ than in poly-[Fe(DSB)₃](ClO₄)₂ probably reflects both a larger site-site spacing and the difference in central metal.¹⁹

In general, steady-state methods for determination of D_e are preferred¹⁰ over transient ones like chronoamperometry and chronocoulometry in order to minimize the possible consequences of slow diffusion of (electroneutrality-required) counterions and correspondingly maximize influence of electron hopping upon D_e . The time-of-flight experiment described here is a transient approach, but noteworthy is the fact that, in the array, the motions of electrons (between fingers) and of charge-compensating counterions (between solution and polymer film) are normal to one another. Since the ion motion is over a shorter distance (the polymer film depth) than that of the electron (the interfinger gap), effects of ion mobility again tend to be minimized.

Finally, we should note an advantage common to both timeof-flight and steady-state^{9,10} determinations of D_e with interdigitated electrodes, which is that absolute values of donor/acceptor site concentrations and of film thicknesses are not required in the determination of D_e . This is significant because solvent-induced swelling changes (vs dry films) are difficult to assess in these ultrathin films.

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Registry No. $Poly[Os(bpy)_2(vpy)_2](ClO_4)_2$, 88080-25-5; $poly[Os-(bpy)_2(vpy)_2](ClO_4)_3$, 88080-24-4; $poly[Fe(DSB)_3](ClO_4)_2$, 110682-71-8; $poly[Fe(DSB)_3](ClO_4)_3$, 110698-00-5; Prussian Blue, 12240-15-2; Prussian White, 81681-39-2.

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Track Effects in Radiation Chemistry: Production of HO₂ in the Radiolysis of Water by High-LET ⁵⁸Ni Ions¹

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The yields of HO₂[•] produced in the radiolysis of water by ⁵⁸Ni ions having energies up to 460 MeV have been determined. For these radiations the differential yields for HO₂[•] production increase from 0.26 to 0.43 molecules/100 eV over an LET range of 260–520 eV/Å. From these measurements a limiting yield of 0.57 molecules/100 eV is estimated for HO₂[•] production by energy deposited in the track core at very high LETs. These studies demonstrate the feasibility of carrying out significant radiation-chemical studies with beams of particles having LETs in excess of 200 eV/Å.

Introduction

In studies of the radiolysis of water with heavy ions it is found that intratrack radical combination processes become increasingly more important as the density of energy deposited along the track increases.² The dependences noted are usually characterized in terms of the linear energy transfer (LET = -dE/dx, i.e., stopping power) of the irradiating particle, but it is clear that other factors

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Figure 1. Radiation-chemical beam targeting system. Beam current (I_B) was collected from the cell and accelerator exit window. Backscattered electron current (I_i) was collected from the suppression tube across which a 2-kG magnetic field was applied.

also enter into these dependences. Most of our ideas on the importance of intratrack processes are derived from studies with protons and helium ions³ which have maximum LETs at their Bragg peaks of only ~ 8 and $\sim 20 \text{ eV/Å}$, respectively. There is great need for determining quantitatively the yields of radiolytic products at much higher LETs, particularly to test models proposed to describe the intratrack processes but also to provide the basis for estimating the relative importance of radical and molecular products produced by heavy ion radiations in, for example, radiobiological studies^{4,5} and in radiolysis with fission fragments.^{6,7} To reach appropriately higher LETs, one must carry out studies with low energy ions of high charge. Previously we have shown⁸ that it is practical to carry out detailed studies of the LET dependence of HO₂[•] production from water with ions such as ¹²C and ²⁰Ne which have maximum LETs of 100 and 200 eV/Å, respectively. Since in irradiations with heavy ions HO₂[•] is produced in yields considerably higher than the low yield observed in fast-electron radiolysis ($G \sim 0.02$ molecules/100 eV),⁹ it provides a direct measure of the importance of intratrack processes. We have now extended these earlier studies to irradiations with ⁵⁸Ni ions accelerated at the Argonne National Laboratory ATLAS facility. These studies, which are reported here, provide information for radiation with LETs in the range 260-520 eV/Å. They represent radiation-chemical measurements at the highest particle LETs made to date.

Experimental Section

Irradiation methods and analytical procedures were essentially as previously described.^{8,10} Because ⁵⁸Ni ions accelerated at ATLAS are only partially stripped, they have a maximum energy of only ~ 11 MeV/nucleon as compared to ~ 17 MeV/nucleon available with ions of lower atomic number. Particle energies (up to 640 MeV) were determined with a time-of-flight energy ana-

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Figure 2. Yield of HO_2° as a function of energy deposited for 444-MeV ⁵⁸Ni ions.

lyzer recently installed at ATLAS and are known to better than 1%. The charge state accelerated (+20) was determined by magnetic analysis. A vacuum of $< 2 \times 10^{-8}$ Torr was maintained between the analyzing magnet and accelerator exit window (3.6 mg/cm² titanium) to assure integrity of this charge state. Beam currents were $\sim 10^{-9}$ A (particle fluxes $\sim 10^{10}$ cm⁻² s⁻¹). The beam targeting system is illustrated in Figure 1. For studies with ⁵⁸Ni ions the targeting arrangement used is particularly critical since there is appreciable electron backscattering from the accelerator exit window. The beam current (I_B) was collected from the sample cell and exit window. The backscattered current (I_s) was confined magnetically and collected from the electron suppression tube indicated in Figure 1. For ⁵⁸Ni ions I_s was found to be ~20% of the beam current, which is appreciably greater than the few percent found in our previous studies with lighter ions.⁸ Absolute dosimetry was in terms of the product of the integrated beam current and particle energy, taking into account the particle charge, the backscattered current, and the energy lost in the window system. The range tables of Hubert et al.¹¹ were used to make corrections for the latter. Because of the very short range of ⁵⁸Ni ions, at least 40% of the initial ion energy was loss in the window

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Figure 3. Production of HO₂[•] ($G_0E_0(\text{HO}_2^{\bullet})$ molecules/particle) as a function of initial ion energy (E_0) for (\bullet) ⁵⁸Ni, this work; (\Box) ²⁰Ne, ref 8; and (Δ) ¹²C, ref 8. The dashed line shows the limit found with fast electrons ($G(\text{HO}_2^{\bullet}) = 0.020$; see ref 9). The solid lines were obtained by appropriate integration of the differential yields of Figure 4.

system. Irradiations were typically for a ~ 1 -min period with energy deposition in the radiolysis cell of $\sim 5 \times 10^{18}$ eV in 30 cm³ of solution.

The production of HO_2^{\bullet} was determined by measuring the yield of oxygen produced in 1 mM ferrous sulfate-10 mM cupric sulfate solutions by using an electrolytic oxygen detector (Hersch cell) as described previously.⁸ The solutions were made up in 0.01 N sulfuric acid with triply distilled water.

Results and Discussion

The production of HO₂[•] by 444-MeV ⁵⁸Ni ions (LET = 260 eV/Å) is shown in Figure 2 to be linearly dependent on the total energy deposited in the solution over the range of $(0.5-10) \times 10^{18}$ eV (0.25-5 krad). From the slope of the line a radiation-chemical yield of 0.35 molecules/100 eV is obtained for the production of HO₂[•]. The yield is accurate on an absolute basis to better than 5%. It is a factor of ~15 greater than that for fast electrons and considerably higher than observed for less massive ions even near to their maximum LETs.

The energy dependence for HO₂• production (G_0E_0) by ⁵⁸Ni ions of initial energy E_0 is shown in Figure 3. Also shown are analogous results previously obtained with ²⁰Ne and ¹²C ions⁸ and fast electrons.⁹ The LET of these ⁵⁸Ni ions increases from ~260 eV/Å at the highest energy (~450 MeV) to ~520 eV/Å at the Bragg peak (~40 MeV) so that the LETs covered in these experiments are greater than the maximum LET for all of the particles previously studied. They even exceed the LET of 400 eV/Å usually considered to describe fission fragment radiations.^{6,7} We particularly note that there is observable curvature of the data for ⁵⁸Ni ions in Figure 3 so that even at the high LETs involved the radiation-chemical yield is still somewhat dependent on the particle energy. The slope at low energies corresponds to a limiting yield at the Bragg peak of 0.43 molecules/100 eV.

In Figure 3 the ordinate corresponds to the total number of product molecules produced by particles of energy E_0 and is measurable to a few percent. The principal uncertainty in determining the radiation-chemical yield is in knowing the energy at which the chemical observation is made. At the higher energies correction for energy lost in the window system can be made with reasonable accuracy so that the absolute values of these yields are known quite well (~5%). At lower energies, however, de-



Figure 4. Differential HO_2^{\bullet} yields for the various ions as a function of ion energy. The dashed line is the high-energy limit as obtained with fast electrons.

termination of the energy incident to the solution is critically dependent on the stopping powers used to correct for energy loss in the window materials. For ⁵⁸Ni ions of 176 MeV incident on the solution we found that the range, using chemical dosimetry to determine energy deposition after addition of absorbers, was 7.2 mg/cm² of aluminum. This range is in accord with values obtained from the tables of Hubert et al.¹¹ and indicates that the stopping powers given by them are applicable. By use of ranges determined from these chemical measurements, the absolute energy scale is known with reasonable accuracy at all energies above ~50 MeV. Ranges for 58 Ni ions estimated from the tables of Northcliffe and Schilling¹² are somewhat in excess (by ~ 1.5 mg/cm²) and cannot be reconciled with our results. The present studies, therefore, suggest that the stopping powers given in Northcliffe and Schilling for ⁵⁸Ni ions in the 100-400-MeV range are somewhat small. We also note that in our studies any effect of straggling appears to be at a minimum and that there is no evidence for any significant contribution from ion fragmentation which would be indicated by chemical effects beyond the range of the primary particle.

It is more advantageous for modeling purposes to obtain the differential yields $(G_i = d(G_0 E_0)/dE_0)$ pertinent to the production of HO2' in a track segment at a given particle energy. These values can be obtained from the slopes of dependences given in Figure 3. A set of differential yields was obtained in a manner similar to that used in previous studies,^{8,13-15} subject to the condition that appropriate integration faithfully reproduced the data. The line through the ⁵⁸Ni ion data in Figure 3 was obtained by such an analysis, and the corresponding differential yields are shown in Figure 4. It is seen in the latter that the differential HO₂• yields for ⁵⁸Ni ions are very much greater than those observed for the other ions. The differential HO_2^* yields increase from 0.26 at the highest energy studied to a maximum of 0.43 at the Bragg peak. Unfortunately, the LET of the particles available in these experiments varies by only a factor of 2 so that it cannot be ascertained to what extent the yield will decrease at very much higher energies.

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Figure 5. Differential HO_2^* yields as a function of LET for the various ions.

The differential yields for the various ions are shown as a function of LET in Figure 5. For ⁵⁸Ni ions these LETs reflect not only the energy but the equilibrium charge state which decreases from about +22 at ~500 MeV to about +11 as one approaches the Bragg peak (~40 MeV). It is seen by extrapolation of the data of Figure 5 that at a given LET the yield of HO₂[•] produced by ⁵⁸Ni ions is considerably less than that obtained with lighter ions. This difference follows the trend previously noted and is as expected since the ⁵⁸Ni ion tracks have a larger radius and therefore a lower density of energy deposition within the track core. It is not currently feasible for us to compare directly the data with ⁵⁸Ni ions and, for example, ¹²C ions of similar LETs. Such a comparison requires ⁵⁸Ni ions with LETs <100 eV/Å (energies >3 GeV), at which point ion fragmentation becomes a problem in data interpretation.

The differential yield at low energies, which approximates the yield in the vicinity of the Bragg peak, is somewhat larger than that noted for the lighter ions. Because the LET of the 5^8 Ni ions is more than a factor of 2 greater than that for previously used radiations, the present data allow a more accurate estimation of the limiting yield at very high LET. As in our previous studies,⁸ it is found that a plot of the inverse of the difference between the observed yield at the Bragg peak and that for fast electrons as a function of the inverse of LET is reasonably linear. A limiting yield of 0.38 molecules/100 eV at infinite LET is found by extrapolation of such a plot. This value is only slightly higher than that (0.37) previously estimated.⁸

Because the yield of HO_2^* is relatively small with fast electrons, it is possible to estimate the yield of HO_2^* pertinent to the track core.⁸ For low-energy particles the production of HO_2^* in the track core appears to be a singular function of the energy remaining in the track core (LET_c, eV/Å) for all particles. This dependence is described quite well by

$$G_{i}(HO_{2}^{\bullet})_{core} = 0.57 \frac{LET_{c} + 2.14}{LET_{c} + 61}$$

in units of radicals per 100 eV. The limiting yield of 0.57 molecules/100 eV at high LETs is somewhat greater than our previous estimate of 0.47.⁸ It has been found in other studies with the Fricke dosimeter¹⁶ that the net water decomposition at very high LETs is only 2.4 molecules/100 eV.¹⁶ Since at least two water molecules are needed to produce one HO₂[•] radical, a major fraction (>40%) of the oxidizing intermediates produced in the track of these densely ionizing radiations are converted to this product. This observation could have very important biological consequences, especially since the yields of all other radicals are expected to be negligible.

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Registry No. H₂O, 7732-18-5; HO₂[•], 3170-83-0; Ni, 7440-02-0.

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Boron Atom Reactions with the Bromomethanes

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Rate constants have been measured for the reactions of boron atoms with a series of bromomethanes and bromofluoromethanes. The experiments were performed in a linear flow apparatus at 300 K. The bimolecular rate constants were obtained by measuring the density of boron along the flow tube as a function of reactant gas density. The measured rate constants in units of cubic centimeters per molecule per second are for CBr_4 , 4.2×10^{-11} ; for CBr_3H , 8.1×10^{-11} ; for CBr_2H_2 , 1.3×10^{-10} ; for $CBrH_3$, 5.7×10^{-11} ; for CBr_3F , 3.8×10^{-11} ; for CBr_2F_2 , 9.2×10^{-11} ; for CBr_3 , 1.4×10^{-11} ; for CH_3F , $<8 \times 10^{-14}$; and for CBr_2Cl_2 , 1.4×10^{-10} . These results are compared to the previously published work on the chlorofluoromethanes where the reactivity of the chlorine site was substantially reduced by fluorine substitution. The corresponding decrease in reactivity of the bromine site is not present in the bromofluoromethanes.

Introduction

In a previous publication,¹ the reaction rates of boron atoms with the chloromethanes and chlorofluoromethanes were presented. An interesting pattern of reactivity was observed in that work.

The substitution of fluorine in those systems produced a notable reduction on the reactivity of the chlorine site. In the extreme, comparing the reactivity of CCl_4 to $CClF_3$, the reaction cross section of the chlorine site in the latter was reduced by 2 orders

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