

Radiolysis of Aqueous Solutions containing Nitrite Ions and Nitrous Oxide

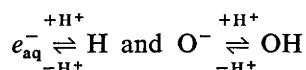
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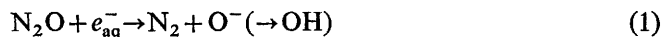
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In the radiolysis of aqueous solutions containing N_2O and nitrite ion, the yield of reducing radicals appears to increase with the solute concentrations. This increase is much greater than the decrease in G_{H_2} and therefore cannot be wholly attributed to increased scavenging within the spur of the reducing radicals which would otherwise have combined with another radical. The results are consistent with an initial yield, of G about unity, of a species which, if it were the excited water molecule H_2O^* would have a half-life of about 10^{-6} - 10^{-7} sec, which can react with N_2O to produce N_2 and whose relative rate constant with NO_2^- and N_2O is comparable with that of the solvated electron.

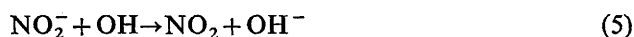
The radiation chemistry of aqueous solutions in the pH range 4-10 can be interpreted on the assumption that a short time after the passage of a fast charged particle there exist yields of the molecular products, H_2 and H_2O_2 and of very reactive oxidising and reducing species. From the absence of a kinetic salt effect¹ on its reaction with Br^- and from the similarity of the relative rate of reaction with H_2 and H_2O_2 to that of the radical produced by photolysis of H_2O_2 with 2537 Å radiation,² the oxidizing species is known to be mainly, or perhaps exclusively, the OH radical. The greater part of the yield of reducing species is the solvated electron, from the kinetic salt effects found in competitions involving charged scavengers in several different systems^{3, 4, 5, 6} and from the optical absorption which may be observed by pulse radiolysis,⁷ but there is also evidence that another reducing species is present which may dehydrogenate isopropanol, for example, to produce H_2 .⁸ Studies with systems which may be used over a range of pH values have indicated radical yield variations⁵ which cannot be adequately explained on the basis of the acid-base interconversions:



In this paper we describe experiments concerned with competitive reactions between N_2O and NO_2^- ions for the reducing species. N_2O can be reduced by e_{aq}^- and H according to eqn. (1) and (2):



for which $k_1 \approx 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ^{9, 10} and $k_2 \approx 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.^{11, 12} Nitrite ions are reduced by e_{aq}^- and H and oxidized by OH radicals:



and it is known that $k_3 \approx 3 \times 10^9$,¹⁰ $k_4 \approx 10^{10}$,¹³ and $k_5 \approx 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.¹⁴ The

NO_2 formed in reaction (5) is more than sufficient to oxidize NO_2^- to NO_2 and the excess NO_2 is hydrolyzed to form $\frac{1}{2}\text{NO}_2^- + \frac{1}{2}\text{NO}_3^-$. The nitrate ion is an efficient electron scavenger and in those experiments where the NO_3^- ions generated were sufficient to permit reaction (6)



to compete significantly with reactions (1) and (3), corrections were applied as described below.

If G_{e^-} and G_{H} denote the yields of e_{aq}^- and H the nitrogen yields from solutions containing both N_2O and NO_2^- should be given by eqn. (7):

$$G(\text{N}_2) = G_{e^-} \cdot k_1[\text{N}_2\text{O}] / (k_1[\text{N}_2\text{O}] + k_3[\text{NO}_2^-]) + G_{\text{H}} k_2[\text{N}_2\text{O}] / (k_2[\text{N}_2\text{O}] + k_4[\text{NO}_2^-]) \quad (7)$$

We have therefore studied the dependence of $G(\text{N}_2)$ on the composition of the solution and on the presence of sodium perchlorate.

EXPERIMENTAL

MATERIALS

Water was prepared from laboratory-distilled water which was distilled from acid dichromate and then refluxed overnight and distilled from alkaline permanganate. Nitrous oxide was obtained from a cylinder of anaesthetic-grade gas and was purified by passage through a column of KOH pellets, by trap-to-trap distillation and by several cycles of freezing at -196°C , pumping and revaporizing. One such cycle was completed just before each experiment. A.R. NaNO_2 was recrystallized from triply-distilled water and dried in a vacuum desiccator. A solution of NaClO_4 was prepared from redistilled A.R. HClO_4 and A.R. Na_2CO_3 , from which the solid was crystallized, collected and dried over P_2O_5 . Stock solutions were made up from this and the reaction adjusted to pH 7 by adding small quantities of dilute HClO_4 or NaOH solutions, made from A.R. reagents.

APPARATUS AND PROCEDURE

The Pyrex cells used for runs with N_2O pressures less than and greater than 1 atm were as shown in fig. 1(a) and 1(b). They were cleaned using permanganic acid followed, after

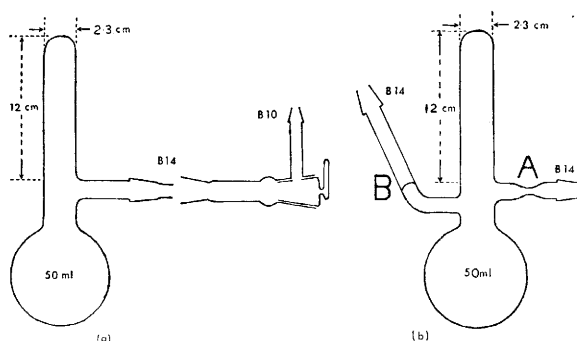


FIG. 1.—The irradiation cells. On cell (b), A indicates a seal-off point and B a break-seal.

rinsing, by nitric acid+hydrogen peroxide. After some hours with the latter liquid the cells were rinsed 10 times with doubly-distilled water, then with triply-distilled water and finally dried in an oven at 120°C . All cells were pre-irradiated before runs were carried out.

The 25 ml samples of solution were thoroughly degassed by standard methods and the desired concentration of N_2O was obtained by (i) for very low concentrations, condensing into the cell the N_2O contained in a 3.69 ml volume at a known pressure of 50-700 mm Hg, (ii) for moderate concentrations, equilibrating with a suitable pressure of N_2O between 50-750 mm Hg, making a correction for the saturated water vapour pressure at 20°C, the temperature of the solution, or (iii) for high concentrations, condensing into cell (b) the N_2O contained in a volume of 577 ml at a known pressure of several hundred mm Hg and sealing off at A. Volumes of, in case (i) the cell and sidearm including the tap and, in case (ii) the sealed-off cell, were measured subsequently and N_2O concentrations were calculated using Boyle's law and the known solubility⁵ of 3.73×10^{-5} M per mm Hg in water at 20°C. In all cases, the solution was maintained at 20°C with intermittent shaking for the 10 min before the cell was inverted and the sample irradiated in the finger.

Irradiation was performed using a (nominal) 1750 curie ^{60}Co γ -ray source, using doses of between 3.0 and 4.7×10^{19} eV. The dose-rate was measured by the Fricke dosimeter assuming $G(Fe^{3+}) = 15.55$ ions per 100 eV,¹⁵ and corrections were applied for the 1.1 % difference in electron densities and for the ^{60}Co decay. The only gaseous products obtained were N_2 and H_2 , which were measured by the normal gas micro-analytical methods.¹⁶

RESULTS

For each nitrite solution, a number of runs were carried out in which the N_2O concentration was varied over that range in which N_2O and NO_2^- compete comparably for the reducing species, giving $G(N_2)$ values in the range 1-2. A plot was then made of $\{G(N_2)\}^{-1}$ against

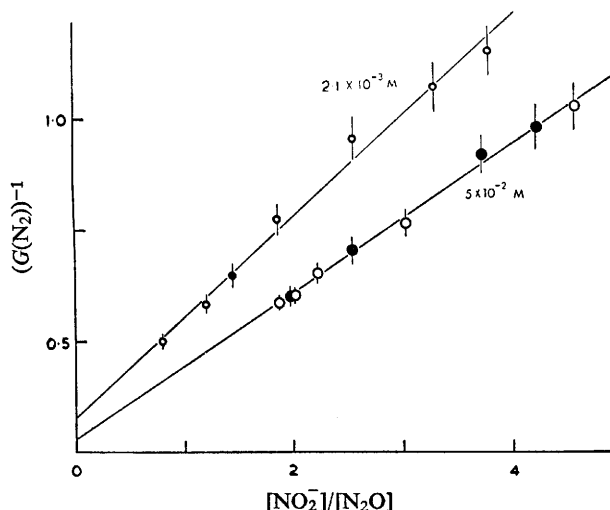


FIG. 2.—Plots of $G(N_2)^{-1}$ against $[NO_2^-]/[N_2O]$ from the experiments with $[NO_2^-] = 2.1 \times 10^{-3}$ (○) and 5×10^{-2} M (●). Filled symbols indicate that the sample was used for the second time.

$[NO_2^-]/[N_2O]$ and in all cases the data lay on straight lines as exemplified by fig. 2, indicating that eqn. (8) is valid:

$$G(N_2) = Ak[N_2O]/(kN_2O + k^1[NO_2^-]). \quad (8)$$

is valid: table 1 obtained for the constants in eqn. (8) from a series of nitrite solutions in which the ionic strength was kept constant at 0.145 by the addition of sodium perchlorate. At three of these nitrite concentrations, runs were also carried out at one or two other values of ionic strength to find the effect on k^1/k and these results are listed in table 2.

At moderate concentrations of nitrite, the effect on the scavenging power for the reducing species of the products of irradiation or of the NO_2^- used up is entirely negligible at such

doses, and after collecting the gases from a first run, the same sample was used for a second. However, in the experiments with low scavenger concentrations this is no longer so and corrections were applied. The mean N_2O concentration was taken as the initial known value less half (N_2 yield/vol. of solution). If the only irradiation products are NO_3^- , N_2 , H_2 and H_2O_2 then, from eqn. (9),

$$G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} = G_{\text{e}^-} + G_{\text{H}} + 2G_{\text{H}_2} \quad (9)$$

and reactions (1)-(5) eqn. (10) may be shown to be valid. Since the relative rate constants of the solvated electron with NO_3^- and H_2O_2 are approximately 2 and 3 times those with

TABLE 1.—SOLUTIONS OF VARIABLE $[\text{NO}_2^-]$, WITH IONIC STRENGTH OF 0.145

$[\text{NO}_2^-](\text{M})$	range of $[\text{N}_2\text{O}](\text{M})$	no. of runs	$G(\text{H}_2)$	k^1/k	A
1.6×10^{-4}	0.7 to 4.5×10^{-4}	7	0.48 ± 0.02	0.82 ± 0.2	2.6 ± 0.3
5.0×10^{-4}	2.1 to 9.5×10^{-4}	9	0.46 ± 0.02	0.59 ± 0.15	2.75 ± 0.2
2.1×10^{-3}	0.6 to 2.5×10^{-3}	7	0.42 ± 0.02	0.67 ± 0.1	3.05 ± 0.2
1.0×10^{-2}	0.3 to 1.1×10^{-2}	10	0.39 ± 0.02	0.59 ± 0.1	3.3 ± 0.2
2.0×10^{-2}	0.5 to 2.5×10^{-2}	6	0.40 ± 0.02	0.62 ± 0.1	3.6 ± 0.25
5.0×10^{-2}	1.1 to 2.6×10^{-2}	9	0.36 ± 0.02	0.60 ± 0.04	3.7 ± 0.2
1.45×10^{-1}	0.3 to 1.4×10^{-1}	10	0.33 ± 0.02	0.54 ± 0.1	3.85 ± 0.3

TABLE 2.—DEPENDENCE OF k^1/k ON IONIC STRENGTH AT CERTAIN VALUES OF $[\text{NO}_2^-]$

$[\text{NO}_2^-](\text{M})$	μ	no. of runs	A	k^1/k	$\frac{d[\log(k^1/k)]}{d(\frac{\sqrt{\mu}}{1+\sqrt{\mu}})}$
5.0×10^{-4}	0.0155	6	2.7 ± 0.15	0.39 ± 0.08	1.14 ± 0.2
	0.145	9	2.75 ± 0.2	0.59 ± 0.15	
	0.330	7	2.8 ± 0.15	0.77 ± 0.06	
5.0×10^{-2}	0.050	9	3.85 ± 0.2	0.54 ± 0.05	0.60 ± 0.2
	0.145	9	3.7 ± 0.2	0.60 ± 0.04	
	0.350	8	3.8 ± 0.2	0.70 ± 0.04	
1.45×10^{-1}	0.145	10	3.8 ± 0.3	0.54 ± 0.1	0.85 ± 0.5
	0.322	9	3.9 ± 0.3	0.64 ± 0.1	

NO_2^- 6, 9, 10 the mean effect of the radiation yields of those products on scavenging of e_{aq}^- in reactions which do not produce N_2 is equivalent to a $G(\text{NO}_2^-)$ of $G(\text{NO}_3^-) + 3G_{\text{H}_2\text{O}_2}$, which, from eqn. (10),

$$\begin{aligned} G(\text{NO}_3^-) &= \frac{1}{2}(G_{\text{OH}} - G_{\text{e}^-} - G_{\text{H}}) + G(\text{N}_2) \\ &= G_{\text{H}_2} - G_{\text{H}_2\text{O}_2} + G(\text{N}_2) \end{aligned} \quad (10)$$

is equal to $G_{\text{H}_2} + G(\text{N}_2) + 1.5$. At the lowest concentrations used, these (maximum) corrections altered the ratio $[\text{NO}_2^-]/[\text{N}_2\text{O}]$ by 10-15 %.

In the runs with N_2O pressures greater than 1 atm a correction was also applied for the gas-phase decomposition of N_2O , assuming $G(\text{N}_2) = 11.0^{17}$ and estimating the dose-rate of the gas phase from the relative electron density and from the geometry of bulb, solution and source during irradiation. At the highest pressures used, 4 atm, the correction was about 2 % of the observed nitrogen yield.

Some runs were also carried out using a large pressure of N_2O and a small non-competitive concentration of NO_2^- , to scavenge the hydroxyl radicals. The results, listed in table 3, show that $G(\text{N}_2)$ agrees fairly well with the value of A , obtained by extrapolation, at similar concentrations.

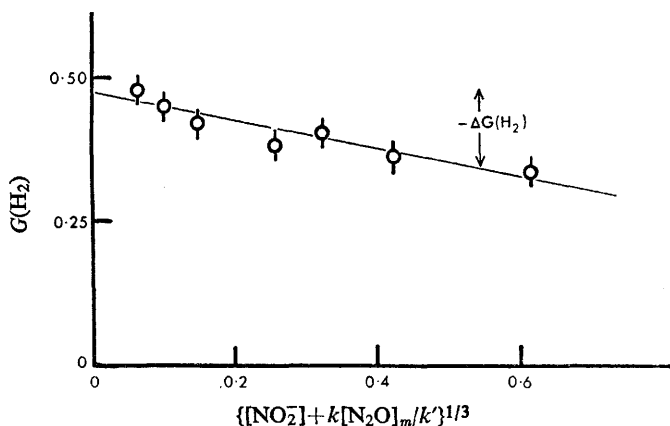
TABLE 3.—N₂ YIELDS FROM RUNS WITH [N₂O] ≫ [NO₂⁻]

[NO ₂ ⁻] (M)	[N ₂ O] (M)	G(H ₂)	G(N ₂)
5 × 10 ⁻⁴	2.26 × 10 ⁻²	0.40	3.26
5 × 10 ⁻⁴	2.26 × 10 ⁻²	0.37	3.33
11 × 10 ⁻⁴	1.67 × 10 ⁻¹	0.35	3.82
9 × 10 ⁻⁴	2.04 × 10 ⁻¹	0.36	3.90

DISCUSSION

Comparison of eqn. (8) with (7) suggests that one of the following may be true: (i) only one reducing species is produced, i.e., only e_{aq}^- ; (ii) if H is produced in addition to e_{aq}^- , that k_1/k_3 is much greater than k_2/k_4 and since G_e easily exceeds G_H the contribution of the second term in eqn. (7) would be negligible and $A = G_e$; (iii) if e_{aq}^- and H are produced, that $k_1/k_3 \approx k_2/k_4$; or if the second species is not H, that the corresponding relative rate constant is nearly equal to that of e_{aq}^- .

Of these possibilities, (i) may be discarded for the reasons⁸ mentioned above; (ii) appears to be true, in that the value of k_2 is so much less than k_4 that H atoms, if formed, would react almost exclusively with NO₂⁻ in our experiments and so would not contribute towards A , which is thus a measure of the yield of reducing species for which N₂O is competing. Thus the first part of (iii) is excluded, but it will be shown that the second part may apply.

FIG. 3.—Plot of $G(H_2)$ against $([NO_2^-] + k[N_2O]_{mean}/k_1)^{1/3}$.

As scavenger concentrations are increased, A rises and the yield of hydrogen undergoes a decrease. If $G(H_2)$, for each solution of NO₂⁻, is plotted against the one third power of $\{[NO_2^-] + k[N_2O]_{mean}/k_1\}$, which will represent the concentration of NO₂⁻ which would be equivalent to the NO₂⁻ + N₂O mixture in scavenging power for e_{aq}^- and H, then as shown in fig. 3 a straight line is obtained, of the type found by Sworski¹⁸ for the dependence of $G_{H_2O_2}$ on scavenger concentration. The decrease indicates that a perceptible fraction of the precursors of molecular hydrogen are now being scavenged within the spur.

Since it has been shown that $e_{aq}^- + e_{aq}^-$ may react to produce H₂^{9, 19} and that an increase in ionic strength causes an increase in G_{H_2} ,²⁰ it is probable that a large portion of the H₂ yield is formed by bimolecular reaction of e_{aq}^- , the predominant reducing species. If we assume merely that the precursors are reducing radicals of the same

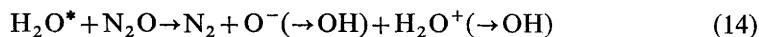
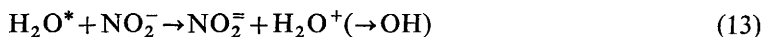
kind as those which are competed for by solutes outside the spur, then from the decrease in $G(\text{H}_2)$ an estimate may be made of the expected increase in the yield of reducing radicals reacting with solute as solute concentrations are increased. This will be at least twice the observed decrease in $G(\text{H}_2)$ and if the reaction of oxidizing + reducing radicals were twice as frequent as that of reducing + reducing radicals, (which would be expected if the G values and initial distributions of the two radicals and the rates of these two reactions were the same) then the expected change in reducing radical yield would be four times the decrease in $G(\text{H}_2)$. However, the distribution of solvated electrons in the spur is so much broader than that of OH radicals¹⁶ that the reaction $e_{\text{aq}}^- + e_{\text{aq}}^-$ might be expected to be more probable than $e_{\text{aq}}^- + \text{OH}$, even though the latter has a higher reaction rate. In addition, we are concerned not with the total occurrence of these reactions, but with the difference in their occurrence under the range of conditions employed. Thus it would seem that a factor of around three should be used, but it can easily be seen that the expected increase in $G_e^- + G_{\text{H}}$, calculated as 0.6 ± 0.2 if a factor of 4 is used, is much less than the observed increase in A of 1.2 ± 0.4 , over the range of NO_2^- concentrations listed in table 1. Thus variations in A can be only partially attributed to scavenging within the spur.

In interpreting the effects of pH on the observed radical yields, it has been suggested^{5, 11} that some of the excited water molecules H_2O^* produced by the energy input in excess of that required to cause the amount of ionization which may be calculated to occur, may react with H^+ or OH^- according to (11) or (12),



to give reducing radicals which are sufficiently long-lived to react with a much lower concentration of solute.

The ionization potential I^* of an excited state lying E eV above the ground state is $I^\circ - E$, where I° is the ionization potential of the ground state, and likewise $EA^* = EA^\circ + E$, where EA denotes electron affinity, and therefore H_2O^* should be both a better reducing and a better oxidizing agent than H_2O . In this system H_2O^* may be regarded as a source of an electron and is likely to react with NO_2^- or N_2O according to eqn. (13) and (14).



Since H_2O^* may also be quenched (reaction (15))



the observed yield of reducing equivalents derived from H_2O^* , ΔG_r will be given by eqn. (16).

$$\Delta G_r = G_{\text{H}_2\text{O}^*} (k_{13}[\text{NO}_2^-] + k_{14}[\text{N}_2\text{O}]) / (k_{15} + k_{13}[\text{NO}_2^-] + k_{14}[\text{N}_2\text{O}]) \quad (16)$$

The increase in A as the scavenger concentration is increased will thus be $\Delta G_r + 3(-\Delta G(\text{H}_2))$, where $-\Delta G(\text{H}_2)$ is the decrement in the hydrogen yield due to solute reacting with reducing species which would otherwise react bimolecularly to form H_2 or H_2O . Hence, eqn. (17)

$$\{A - G_e^- - 3(-\Delta G(\text{H}_2))\}^{-1} = (G_{\text{H}_2\text{O}^*})^{-1} \{1 + k_{15} / (k_{13}[\text{NO}_2^-] + k_{14}[\text{N}_2\text{O}])\} \quad (17)$$

should be applicable to our data. Fig. 4 shows a graph of $\{A - G_e^- - 3(-\Delta G(\text{H}_2))\}^{-1}$, where $-\Delta G(\text{H}_2)$ is taken from fig. 3 and alternative values of 2.3^{21} and 2.8^5 are used

for G_{e^-} , plotted against $\{[\text{NO}_2^-] + k[\text{N}_2\text{O}]_{\text{mean}}/k^1\}^{-1}$. (This assumes that k_{14}/k_{13} is, at least, approximately equal to k/k^1 . The results suggest that $G_{\text{H}_2\text{O}^*} \approx 1$ and $k_{15}/k_{13} \approx 10^{-2}$ M. Since k_{13} is the rate of reaction of H_2O^* with NO_2^- which, for reasons given above, is likely to be slower than $e_{\text{aq}}^- + \text{NO}_2^-$, which has a rate constant of $3.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$,¹⁰ a value of 10^8 to $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ might be assumed, which would indicate that k_{15} is of the order 10^6 – 10^7 sec^{-1} , i.e., that the lifetime of the excited state is around 10^{-6} – 10^{-7} sec .

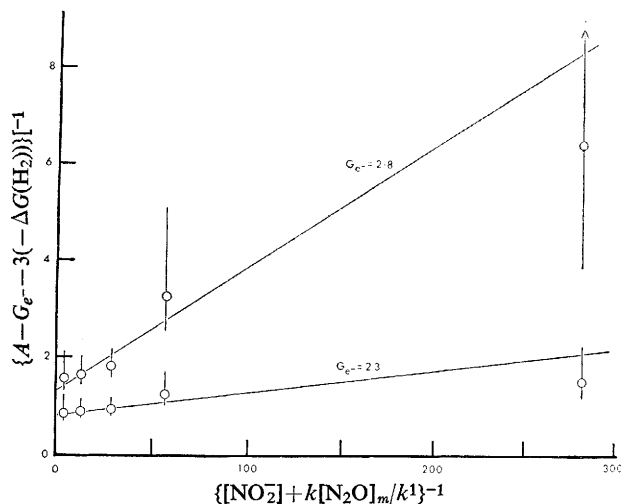


FIG. 4.—Plots of $\{A - G_{e^-} - 3(-\Delta G(\text{H}_2))\}^{-1}$ against $\{[\text{NO}_2^-] + k[\text{N}_2\text{O}]_{\text{mean}}/k^1\}^{-1}$ for $G_{e^-} = 2.3$ (lower) and 2.8 (upper) curve.

H_2O^* might also be expected to react with H^+ more slowly than does e_{aq}^- and on this basis the observed increase in the conventional yield G_{H} which begins at $\sim \text{pH } 2.5$ is entirely reasonable. Likewise the conclusion of Dainton and Watt⁵ that half the H_2O^* is scavenged by OH^- at $\text{pH } 12.5$ is in accord with the fact²² that H is rapidly converted to e_{aq}^- at $\text{pH } 12$.

The supposition that the reducing radicals scavenged at low concentrations are mostly solvated electrons is supported by the observed salt effect. The smaller enhancement of the relative rate constant with increasing ionic strength that is observed at higher scavenger concentrations may be partly due to the tendency for the electrons to react with solute before acquiring their equilibrium ion atmosphere,²³ and partly because at high concentrations the scavenger may react in a stoichiometrically equivalent manner with some uncharged species. Similarly, there will be two effects operating on the observed relative rate constant, k^1/k , that due to the change in the half-life of the electron with respect to its ionic relaxation time and that due to differences between k_3/k_1 and k_{13}/k_{14} . At $[\text{NO}_2^-] = 0.145 \text{ M} = \mu$, with $[\text{N}_2\text{O}] = 0.10$, the half-life of the electron and the ionic relaxation time are both calculated as being about $5 \times 10^{-10} \text{ sec}$, which would indicate that the first effect should contribute most of the theoretical decrease of 0.14 to k^1/k and, since only such a change is found, it would follow that e_{aq}^- and H_2O^* have similar relative rates of reaction with N_2O and NO_2^- .

This work was carried out whilst S. R. L. was an I.C.I. Research Fellow in the University of Leeds.

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