Nitrogen Dioxide and Related Free Radicals: Electron-transfer Reactions with Organic Compounds in Solutions containing Nitrite or Nitrate

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The absolute rate constants for the reaction of $NO_3^{2-\bullet}$ (formed by one-electron reduction of nitrate) with oxygen, benzoquinone, and methyl viologen have been determined by pulse radiolysis. Experiments have shown that such reactions can occur in competition with the hydrolysis reaction leading to $NO_2^{\bullet}$ and that the formation of the latter can be catalysed by the presence of hydrogen or ammonium ions. Absolute rate constants for the oxidation of the phenothiazine derivative metiazinic acid, of 2,2'-azinobis-(3-ethyl-2,3-dihydrobenzothiazole-6-sulphonate), of ascorbate, and of dihydroxyfumarate by $NO_2^{\bullet}$ have also been measured.

Nitrogen oxides are being implicated increasingly in disease processes.[1-7] The major atmospheric pollutant nitrogen dioxide ($NO_2^{\bullet}$) can initiate the oxidation of lipids by adding to alkene groups or by abstracting allylic hydrogen atoms from unsaturated fatty acids. The carbon-centred free radicals so formed may react subsequently with oxygen to form organic peroxyl radicals.[6-8]

Radiation studies, particularly using the fast-reaction technique of pulse radiolysis, can provide much useful information concerning the chemical reactions of $NO_2^{\bullet}$ and related radicals in aqueous solution.[9-17] The hydroxyl radical ($^{\bullet}OH$) and the hydrated electron (e_{aq}^-) formed on radiolysis of water can react rapidly with nitrite and nitrate ions respectively[11-16] [reactions (1)—(7)]. Recently during pulse radiolysis studies of

$$OH^{\bullet} + NO_2^- \longrightarrow OH^- + NO_2^{\bullet} \qquad (1)$$
$$k_1 = 1.3 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

$$e_{aq}^- + NO_3^- \longrightarrow NO_3^{2-\bullet} \qquad (2)$$
$$k_2 = 1.0 \times 10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

$$NO_3^{2-\bullet} + H_2O \longrightarrow NO_2^{\bullet} + 2OH^- \qquad (3)$$
$$t_{1/2} = 12.5\ \mu s$$

$$NO_3^{2-\bullet} + H^+ \longrightarrow NO_3H^{-\bullet} \qquad (4)$$
$$pK_a = 7.5$$

$$NO_3H^{-\bullet} \longrightarrow NO_2^{\bullet} + OH^- \qquad (5)$$
$$t_{1/2} = 3\ \mu s$$

$$2NO_2^{\bullet} \rightleftharpoons N_2O_4 \qquad (6)$$
$$2k_6 = 9 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}};\ K_6 = 6.5 \times 10^4\ \mathrm{l\ mol^{-1}}$$

$$N_2O_4 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \qquad (7)$$
$$k_7 = 1.0 \times 10^3\ \mathrm{s^{-1}}$$

2,2-azinobis-(3-ethyl-1,2-dihydrobenzothiazole-6-sulphonate) (ABTS) it was found that when nitrate was used as a scavenger of hydrated electrons, a reaction product oxidised ABTS.[17] This was tentatively attributed to reaction (8). A similar observation

$$NO_2^{\bullet} + ABTS \longrightarrow NO_2^- + ABTS^{+\bullet} \qquad (8)$$

has been made during laser photolysis studies of solutions of the photosensitisers *N*-methylphenothiazine and *N,N,N',N'*-tetramethylbenzidine containing nitrate: two molecules of sensitiser were oxidised per photon absorbed: the triplet state of the photosensitiser can reduce nitrate and the $NO_2^{\bullet}$ formed on hydrolysis of $NO_3^{2-\bullet}$ [reaction (3)] can oxidise a second photosensitiser molecule.[18] Previous photochemical studies with solutions containing hexacyanoferrate(4−) and nitrate ion had shown that the hydrated electron formed on photolytic oxidation of hexacyanoferrate can reduce nitrate, and the $NO_2^{\bullet}$ formed can oxidise a second hexacyanoferrate ion[19] [reaction (9)]. Values for the absolute rate constant of this reaction, k_9 =

$$NO_2^{\bullet} + Fe(CN)_6^{4-} \longrightarrow NO_2^- + Fe(CN)_6^{3-} \qquad (9)$$

(4.3 ± 1) × 10^6 and (3.0 ± 0.5) × 10^6 l mol^{-1} s^{-1}, have been obtained using flash photolysis and pulse radiolysis techniques respectively.[19,20] The rate constant for the reaction (10) of $NO_2^{\bullet}$ with iodide ion has also been measured recently by pulse radiolysis: $k_{10} = 1.1 \times 10^5\ \mathrm{l\ mol^{-1}\ s^{-1}}$.[20]

$$NO_2^{\bullet} + I^- \longrightarrow NO_2^- + I^{\bullet} \qquad (10)$$

In the light of these observations it was decided to investigate further the redox and kinetics properties of $NO_2^{\bullet}$ and related species with a selection of organic compounds of biological interest.

Experimental

The pulse radiolysis experiments were undertaken with the Brunel University 4 MeV linear accelerator, and associated equipment for kinetic spectroscopy and computer analysis of data.[21,22] A 0.2 μs electron pulse producing a radiation dose of *ca.* 2—10 J kg^{-1} in an irradiation cell of 1.5 cm optical path was used. All solutions were prepared in doubly distilled or Millipore-filtered water. When required, t-butyl alcohol, purified by fractional crystallisation, was added to scavenge hydroxyl radicals [reaction (11)]. The resulting radical has been

$$OH^{\bullet} + (CH_3)_3COH \longrightarrow H_2O + {}^{\bullet}CH_2C(CH_3)_2OH \qquad (11)$$

found to be relatively unreactive towards organic oxidants.

Solutions were purged and saturated with oxygen-free nitrogen, nitrous oxide, or oxygen (British Oxygen) using the syringe bubbling technique.[23] Metiazinic acid and hydroquinone (May and Baker), ABTS (diammonium salt; Boehringer), potassium hexacyanoferrate(4−), potassium iodide, sodium nitrate, sodium nitrite, ascorbic acid, potassium hydroxide (B.D.H. AnalaR), cysteine, DL-α-tocopherol, linoleic acid, and dihydroxyfumaric acid (Sigma) were used as supplied.

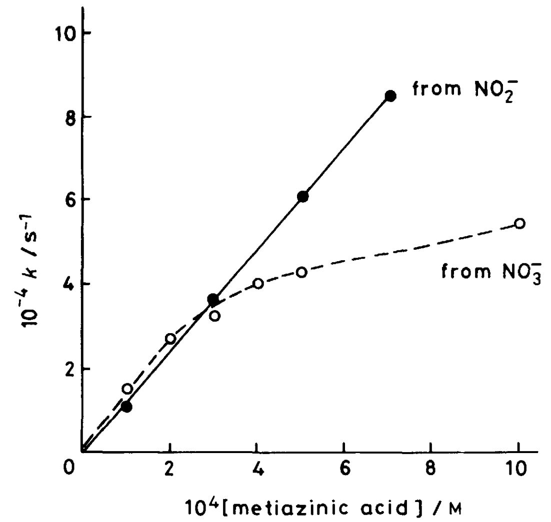

Figure 1. Plot of first-order rate constant for the formation of the transient absorption at 530 nm against metiazinate concentration on pulse radiolysis of solutions containing (a) t-butyl alcohol and nitrate, (b) nitrous oxide and nitrite

Benzoquinone and duroquinone (Aldrich) were purified by sublimation.

Results and Discussion

(1) *Oxidation of Metiazinic Acid* by* $NO_2^{\bullet}$ *but not by* $NO_3^{2-\bullet}$ *or* HNO_3.—It was shown recently that the free radicals $(SCN)_2^{-\bullet}$, $CO_3^{-\bullet}$, and $N_3^{\bullet}$ can oxidise stoicheiometrically the anion of the phenothiazine derivative metiazinic acid (MZ^-) to a long-lived zwitterion-radical ($\lambda_{max.}$ 530 nm; $\varepsilon_{max.}$ 11 000 l mol^{-1} cm^{-1}).[24] We observed a similar absorption when N_2-saturated solutions (pH 7) containing $NaNO_3$ (0.1M), t-butyl alcohol (1M), and metiazinic acid (1—5 × 10^{-3}M) were pulse-irradiated. The rate of formation of the radical absorption was exponential and first-order in phenothiazine concentration up to 0.4mM (Figure 1), in agreement with reaction (12). However,

$$NO_2^{\bullet} + MZ^- \longrightarrow NO_2^- + MZ^{+-\bullet} \qquad (12)$$

at concentrations greater than 0.4mM the first-order rate constant no longer increased linearly with the metiazinic anion concentration, suggesting that $NO_3^{2-\bullet}$ or $HNO_3^{-\bullet}$ was not able to oxidise the drug, and that their hydrolysis to $NO_2^{\bullet}$ according to reactions (3)—(5) becomes rate-determining at higher MZ^- concentrations (Figure 1).

To confirm this suggestion, $NO_2^{\bullet}$ was produced directly through the oxidation of nitrite by $OH^{\bullet}$ according to reaction (1). Spectrophotometric measurements indicated that nitrite did not react directly with the phenothiazine under the experimental conditions required for pulse radiolysis studies. Solutions were saturated with nitrous oxide (N_2O) to scavenge hydrated electrons and increase the yield of $OH^{\bullet}$, through reaction (13). When N_2O-saturated solutions containing

$$e_{eq}^- + N_2O \longrightarrow N_2 + {}^{\bullet}OH + OH^- \qquad (13)$$

$NaNO_2$ (0.01M) and MZ^- (1—7 × 10^{-4}M) (pH 6.8) were pulse-irradiated, exponential formation of the absorption at 530 nm was again observed. The first-order rate constant was proportional to MZ^- concentration and remained so at concentrations above 0.4mM, in contrast to the system containing nitrate (Figure 1). The maximum absorbance in the NO_2–nitrite system was 1.9 times greater than that in the N_2–t-butyl alcohol–nitrate system, in agreement with hydroxyl radicals and hydrated electrons being produced in approximately equal amounts during the radiolysis of water. Indeed when N_2-saturated solutions containing MZ^- (3 × 10^{-4}M), $NaNO_3$ (0.1M), and $NaNO_2$ (0.01M) were pulse-irradiated, the maximum absorbance was 1.97 times greater than that observed with the N_2–t-butyl alcohol–nitrate system, and the rate constant obtained was the same as that found in the separate NO_2^- and NO_3^- systems, $k_{12} = (1.2 \pm 0.1) \times 10^8$ l mol^{-1} s^{-1}. This value can be compared with the value $k = 6.6 \times 10^7$ l mol^{-1} s^{-1} reported for *N*-methylpromethazine in 2:1 v/v ethanol–water.[18]

A value for the acid dissociation constant of metiazinic acid, pK_a = 7.2, has been published; thus, under the conditions used in these experiments both the free acid and conjugate base forms would have been present.[24] However, the rate of formation of the phenothiazine radical did not change on increasing the pH to 9.3, showing the rate constant to be insensitive to the state of protonation of the side-chain.

(2) *Reactions of* $NO_2^{\bullet}$ *with Hydroquinone, α-Tocopherol, and Cysteine.*—Studies of the rates of oxidation of hydroquinone and α-tocopherol at pH 12 and of cysteine at pH *ca.* 8 in the N_2–t-butyl alcohol–nitrate system provides further support for the view that it is only $NO_2^{\bullet}$ and not $NO_3^{2-\bullet}$ which acts as the oxidising radical in these systems. On pulse radiolysis of N_2-saturated solutions containing $NaNO_3$ (0.1M) and hydroquinone (QH_2) at pH *ca.* 12 the characteristic absorption of the semiquinone radical $Q^{-\bullet}$ was formed.[25] At this pH the substrate is in the form QH^-. However, at concentrations of 10mM, 1mM, and 0.1mM, the yield of $Q^{-\bullet}$ was the same and the half-life of its formation only changed slightly in spite of the 100-fold concentration range (values were 10, 14, and 20 μs, respectively). These results are consistent with a rapid reaction between $NO_2^{\bullet}$ and the hydroquinone anion, but with the hydrolysis of $NO_3^{2-\bullet}$ to $NO_2^{\bullet}$ [reaction (3)] being the rate-controlling process and $k_{14} > 5 \times 10^8$ l mol^{-1} s^{-1}. At pH 7 no product absorption was

$$NO_2^{\bullet} + QH^- \longrightarrow NO_2^- + Q^{-\bullet} + H^+ \qquad (14)$$

observed, implying at this point that the reaction between QH_2 and $NO_2^{\bullet}$ is too slow to be followed under the experimental conditions used.

On pulse radiolysis of a N_2-saturated solution containing $NaNO_3$ (0.1M), t-butyl alcohol (40%), α-tocopherol (5.6 × 10^{-4}M), and NaOH (0.02M), a transient species appeared rapidly with $t_{1/2}$ 19 μs. The spectrum of the species was identical with that obtained from oxidation of α-tocopherol by $CCl_3O_2^{\bullet}$ in neutral solution and attributed to the corresponding phenoxyl radical.[26] When similar experiments were undertaken in neutral solution, little change in absorption was observed, indicating that, as with hydroquinone, $NO_2^{\bullet}$ only reacts with the ionised form of the phenol.

Interestingly, no phenoxyl radical absorption was observed from phenol itself, even in alkaline solution. This is in agreement with the simple phenoxide ion being less readily oxidisable than the *para*-substituted hydroxy or alkoxy derivatives.[27]

With cysteine (CySH) in the pH range 7.9—9.0 the transient absorption characteristic of the disulphide radical anion, $CySSCy^{-\bullet}$, was detected.[28] This radical is formed when thiyl radicals are produced in the presence of thiolate anions with the

$$CyS^{\bullet} + CyS^- \rightleftharpoons CySSCy^{-\bullet} \qquad (15)$$

equilibrium constant K_{15} *ca.* 6.5 × 10^3 l mol^{-1}.[29,30] Over the

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* 10-Methylphenothiazin-2-ylacetic acid.

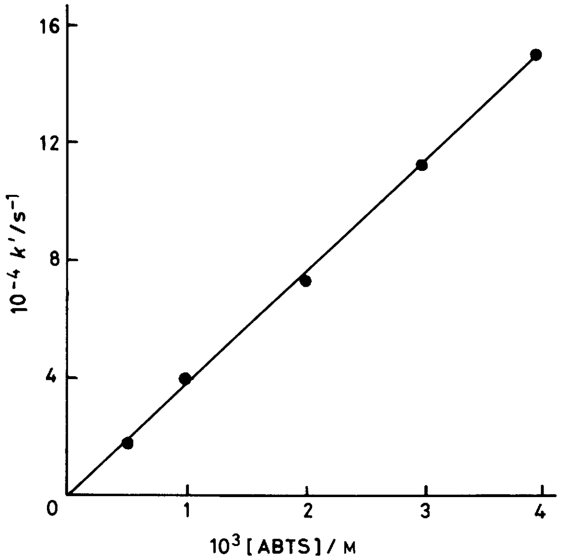

Figure 2. Plot of the first-order rate constant for the formation of the transient absorption at 415 nm against ABTS concentration on pulse radiolysis of solutions containing t-butyl alcohol and nitrate (pH 7)

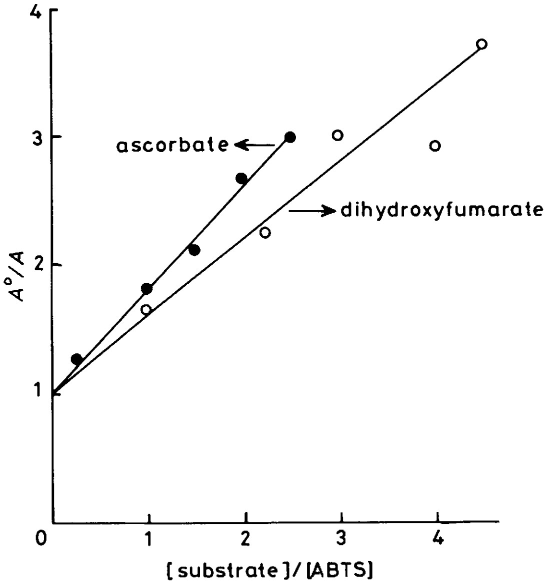

Figure 3. Kinetic competition plots (see text) for the effect of increasing concentrations of ascorbate and dihydroxyfumarate on the magnitude of the $ABTS^{+\bullet}$ absorption at 415 nm

CySH concentration range 0.2—1.8mM at pH 8.7—9.0 the yield of $CySSCy^{-\bullet}$ increased with cysteine concentration, though the rate of formation did not follow simple kinetics: the half-life only decreased from 4.9 to 3.4 μs. In the lower pH range (7.9—8.3) the half-life again only decreased from 4.2 to 2.0 μs over the same concentration range, suggesting that the rate constant for $NO_2^{\bullet}$ plus Cys^- is large ($k_{16} > 5 \times 10^8$ l mol^{-1} s^{-1}) and that of hydrolysis of $NO_3^{2-\bullet}$ is again the rate-controlling step. The increase in yield with increasing CySH concentration can be attributed to equilibrium (15). It was not possible to carry out

$$NO_2^{\bullet} + CyS^- \longrightarrow NO_2^- + CyS^{\bullet} \qquad (16)$$

the reaction at lower pH since here the quantity of thiolate ion would be negligible and $CysS^{\bullet}$ cannot be readily detected under these conditions.

(3) *Reaction of* $NO_2^{\bullet}$ *with ABTS.*—As already stated, the present studies were stimulated by the finding that $ABTS^{+\bullet}$ can be formed by pulse radiolysis of solutions in which nitrate ions are used to scavenge hydrated electrons. On repeating these experiments, we observed the characteristic absorption of $ABTS^{+\bullet}$ ($\lambda_{max.}$ 415 nm), identical with that formed on oxidation of ABTS by the free radicals $Br_2^{-\bullet}$, $(SCN)_2^{-\bullet}$, and $CCl_3O_2^{\bullet}$[17] The rate of formation of the absorption was exponential and first-order in ABTS for both the N_2O–nitrite–nitrate and N_2–t-butyl alcohol–nitrate systems, leading to $k_8 = 2.2 \times 10^7$ l mol^{-1} s^{-1} (Figure 2).

$$NO_2^{\bullet} + ABTS \longrightarrow NO_2^- + ABTS^{+\bullet} \qquad (8)$$

Taking [$\varepsilon_{ABTS^{+\bullet}}$] = 3.6×104 l mol^{-1} cm^{-1} at 415 nm the absorption in the nitrate system corresponded to 100% of the hydrated electrons reacting in this manner. However unlike the metiazinic acid–N_2–t-butyl alcohol–nitrate system, the formation of the product radical was first-order in ABTS over the whole concentration range studied, at both pH 6.5 and 9, with a half-life as low as 6 μs recorded, indicating that in this system the hydrolysis of $NO_3^{2-\bullet}$ is faster and not rate-determining. As will be described later, this is due to the fact that the ammonium salt of ABTS was used in all the experiments reported here.

(4) *Reactions of* $NO_2^{\bullet}$ *with Ascorbate and Dihydroxyfumarate.*—When solutions containing $NaNO_3$ (0.1M), ABTS (2mM), and Bu^{t}OH (1M) at pH 6.5 were irradiated in the presence of ascorbate (AH^-) or dihydroxyfumarate (DHF), the yields of $ABTS^{+\bullet}$ were reduced in agreement with reactions (17) and (18) competing with reaction (8). If we assume simple

$$NO_2^{\bullet} + AH^- \longrightarrow NO_2^- + A^{-\bullet} + H^+ \qquad (17)$$

$$NO_2^{\bullet} + DHF \longrightarrow NO_2^- + DHF(-H)^{\bullet} + H^+ \qquad (18)$$

competition, we obtain equation (i), where $A°$ and A are the

$$A°/A = 1 + k[S]/k_8[ABTS] \qquad (i)$$

absorbances in the absence and presence of competing substrate, respectively; then the slopes of the plots shown in Figure 3 correspond to $k_{17}/k_8 = 0.81$, and $k_{18}/k_8 = 0.60$, respectively, and hence $k_{17} = 1.8 \times 10^7$ and $k_{18} = 1.3 \times 10^7$ l mol^{-1} s^{-1}.

In analogous experiments where the effect of added linoleic acid (3×10^{-2}M) was investigated, no decrease in yield of $ABTS^{+\bullet}$ was observed, pointing to the rate constant for the reaction between $NO_2^{\bullet}$ and linoleate being less than 5×10^4 l mol^{-1} s^{-1}.

(5) $NO_3^{2-\bullet}$ *as a One-electron Reducing Agent.*—The foregoing results, which indicate that in some cases the rate of oxidation of substrates in the Bu^{t}OH–nitrate–N_2 system is controlled by the rate of hydrolysis of $NO_3^{2-\bullet}$, imply that $NO_3^{2-\bullet}$ itself is not an oxidising agent. It was therefore of interest to see if it could act as a reducing agent. Studies of the effect of oxygen on the yield of nitrite ion when aqueous alkaline solutions of nitrate and hydrogen peroxide are irradiated had already led to the suggestion that $NO_3^{2-\bullet}$ can react with oxygen in competition with its hydrolysis [reaction (19)]. Indeed an estimate for k_{19}/k_3 (2×10^5) had been obtained.[13] When solutions containing Bu^{t}OH (1M), nitrate (0.5M), and ABTS (5×10^{-4}M) were saturated with air or oxygen instead of nitrogen, the yield of $ABTS^{+\bullet}$ obtained on pulse radiolysis was

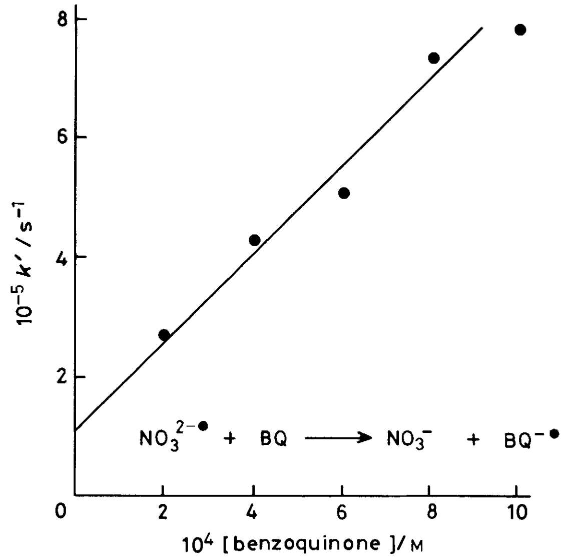

Figure 4. Plot of first-order rate constant for the formation of the benzosemiquinone absorption at 430 nm against benzoquinone concentration on pulse radiolysis of solutions containing t-butyl alcohol and nitrate

lowered, in agreement with reaction (19) competing with

$$NO_3^{2-\bullet} + O_2 \longrightarrow NO_3^- + O_2^{-\bullet} \quad (19)$$

reaction (3). The air/N_2 yield ratios were 0.81 at pH 6 and 0.49 at pH 10.6, and the corresponding O_2/N_2 ratios were 0.51 and 0.34, respectively.

The greater effect of oxygen at the higher pH is consistent with the lower rate of hydrolysis in alkaline solution. Taking a value for $k_3 = 5.5 \times 10^4\ \mathrm{s}^{-1}$ derived from the half-life of $NO_3^{2-\bullet}$ (12.5 μs) at pH 10.6, the foregoing results in air- and oxygen-saturated solutions correspond to $k_{19} = 2.3 \times 10^8$ and $8.5 \times 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}$, respectively. Although the decrease in yield of $NO_2^{\bullet}$ on going from air to oxygen is not as great as predicted in terms of simple competition, the results do show directly that the reaction with oxygen does occur. Furthermore the rate constants obtained are in close agreement with a value of $k_{19} = 2 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ derived from the previous studies.[13]

The reducing nature of $NO_3^{2-\bullet}$ was confirmed by using solutions containing benzoquinone (BQ), duroquinone (DQ), and methyl viologen (MV^{2+}), all of which give strong visible transient absorptions when reduced. On pulse radiolysis of a nitrogen-saturated solution containing t-butyl alcohol (10%), $NaNO_3$ (0.2M), and benzoquinone (0.2—1mM) at pH 7, the formation of the characteristic semiquinone radical was observed. The rate of appearance of the absorption was exponential and increased with increasing benzoquinone concentration (Figure 4). The maximum yield of the semiquinone following the pulse increased with increasing benzoquinone concentration, and this, together with the intercept of the kinetic plot (Figure 4), is consistent with $NO_3^{2-\bullet}$ being oxidised by benzoquinone in competition with its hydrolysis (3) to yield $NO_2^{\bullet}$, which does not reduce benzoquinone.

$$NO_3^{2-\bullet} + BQ \longrightarrow NO_3^- + BQ^{-\bullet} \quad (20)$$

From the slope of the plot, $k_{20} = 7.6 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$. When similar experiments were undertaken with duroquinone, it was clear that the corresponding rate constant was considerably lower. No appreciable durosemiquinone absorption was seen under the conditions used for benzoquinone. Only by raising the quinone concentration to 2mM in 40% t-butyl alcohol (duroquinone is less water-soluble than benzoquinone) could a semiquinone absorption be observed, in the region of 430 nm with a formation half-life of 9 μs and a yield corresponding to 30% of e_{aq}^-, and then only at pH 11. At pH 6 no absorption was detected suggesting that in neutral solution $k < 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}$.

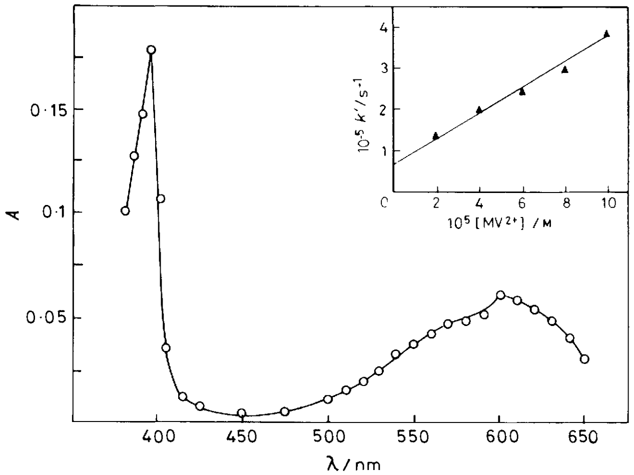

Figure 5. Spectrum of the transient produced on pulse radiolysis of solution containing methyl viologen, t-butyl alcohol, and nitrate at pH 11. Inset: Plot of first-order rate constant for the formation of the absorption against methyl viologen concentration

On pulse radiolysis of a nitrogen-saturated solution containing t-butyl alcohol (1M), $NaNO_3$ (0.1M), and methyl viologen (1mM) at pH 11, the characteristic absorption of the methyl viologen radical cation ($\lambda_{max.}$ 395 and 600 nm) was observed, as shown in Figure 5. The appearance of the absorption was first-order in [methyl viologen], in agreement with reaction (21), with $k_{21} = 3.3 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$.

$$NO_3^{2-\bullet} + MV^{2+} \longrightarrow NO_3^- + MV^{+\bullet} \quad (21)$$

Methyl viologen is a weaker oxidising agent than benzoquinone, and the greater value of the rate constant is presumably due to its being a doubly charged cation, whereas benzoquinone is uncharged. The intercept on the kinetic plot can again be attributed to the minor competing hydrolysis reaction (Figure 3).

(6) *Catalysis of the Formation of* $NO_2^{\bullet}$ *from* $NO_3^{2-\bullet}$ *by the Ammonium Cation.*—The diammonium salt of ABTS was used throughout this work, and the fact that the hydrolysis of $NO_3^{2-\bullet}$ did not limit the rate of oxidation of ABTS at pH 6.5 or 9, whereas it did with metiazinic acid, can be explained in terms of reaction between $NO_3^{2-\bullet}$ and NH_4^+. Previous studies[16] have shown that $NO_3^{2-\bullet}$ reacts with $H_2PO_4^-$ with $k = 5 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$, and it was thought that similar proton-transfer reaction with the ammonium ion could explain the apparent increase in the rate of formation of $NO_2^{\bullet}$ [reactions (22) and (5)]. To confirm this, the effect of the addition of ammonium chloride (5mM) on the rate of formation of $MZ^{+\bullet}$ on pulse radiolysis of the N_2–Bu^{t}OH–nitrate–metiazinate system (pH 7.5) was investigated. The rate of $MZ^{+-\bullet}$ formation was then

$$NO_3^{2-\bullet} + NH_4^+ \longrightarrow NO_3H^{-\bullet} + NH_3 \quad (22)$$

$$NO_3H^{-\bullet} \longrightarrow NO_2^{\bullet} + OH^- \quad (5)$$

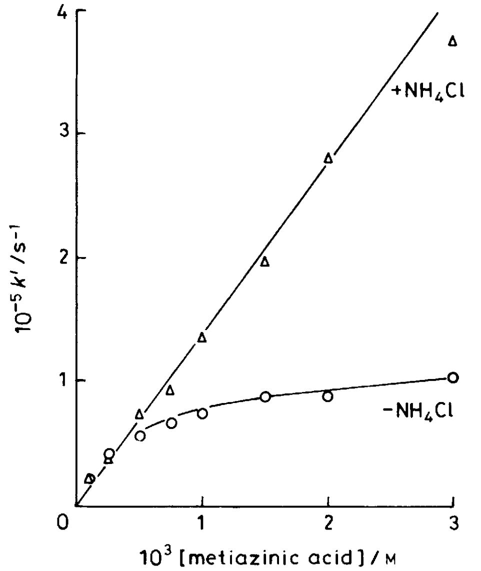

Figure 6. Plot of first-order rate constant for the formation of the transient absorption at 530 nm against metiazinic acid concentration at pH 7.5 for solutions containing t-butyl alcohol and nitrate in the absence and presence of ammonium chloride

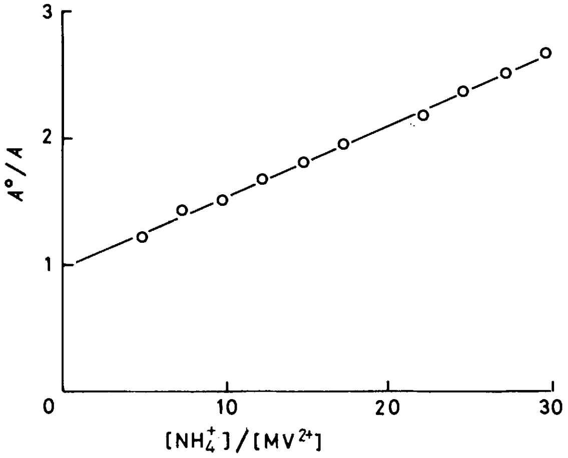

Figure 7. Kinetic competition plot for the effect of increasing the ammonium ion concentration on the magnitude of the $MV^{+\bullet}$ absorption at 600 nm

first-order in metiazinate acid concentration up to 2×10^{-3}M with a half-life of 3 μs (Figure 6). Furthermore, when the pH of a solution containing 5×10^{-3}M-ABTS was raised to 11 by addition of sodium hydroxide, converting all the NH_4^+ into NH_3 (for $[NH_4^+]$, $pK_a = 9.24$), the half-life for $ABTS^{+\bullet}$ formation was found to be reduced to 16 μs.

Finally, when increasing amounts of NH_4Cl were added to nitrogen-saturated solutions containing Bu^{t}OH (1M), $NaNO_3$ (0.1M), and methyl viologen (0.1mM) the yield of $MV^{+\bullet}$ was decreased, in agreement with competition between reactions (21) and (22). A plot of A°/A against $[NH_4^+]/[MV^{2+}]$ was linear (Figure 7). From the slope of the plot (0.061) $k_{22} = 2 \times 10^8$ l mol^{-1} s^{-1} was derived, close to that (5×10^8 l mol^{-1} s^{-1}) reported for the corresponding reaction with $H_2PO_4^-$.

Conclusions

The present work shows $NO_2^\bullet$ to be a moderately reactive oxidising agent towards a number of substances, but rather less reactive than species such as $(SCN)_2^{-\bullet}$, $CCl_3O_2^\bullet$, $Br_2^{-\bullet}$, $RS^\bullet$, $(R_2S)^{+\bullet}$, $CO_3^{-\bullet}$, and $N_3^\bullet$, reactions of which with ABTS, ascorbate, dihydroxyfumarate, and various phenol and phenothiazine derivatives have been studied previously.[17,24,31-38]

While there is good evidence from other studies [6-8] that $NO_2^\bullet$ can add to or abstract hydrogen atoms from unsaturated hydrocarbons, the present studies indicate that the rate constants for these reactions are likely to be several orders of magnitude lower than those for the electron-transfer reactions studied. In contrast to nitrogen dioxide, $NO_3^{2-\bullet}$ appears not to be a strong oxidising agent, but can itself be oxidised by compounds such as oxygen and methyl viologen.

Nitrate ion has often been used in radiation studies as a selective scavenger of hydrated electrons.[39] Clearly care is needed because of the additional reactions that $NO_3^{2-\bullet}$ or $NO_2^\bullet$ may undergo.

Acknowledgements

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