Radiation-induced Reactions of (2-Methyl-5-nitro-1*H*-imidazole-1-ethanol)nickel(II) in Aqueous Solution: A Flash-photolysis and Steady-state Gamma-radiolysis Study *

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On gamma radiolysis of the nickel(II) complex of metronidazole (2-methyl-5-nitro-1*H*-imidazole-1-ethanol), hydroxyl radicals and the hydrated electron e$^-$(aq) react with the complex leading to the destruction of the nitroimidazole structure. The loss of the complex and the production of nitrite have been followed by steady-state experiments, while the transient kinetics of the hydroxyl reactions have been probed by flash photolysis. The OH radicals react with the complex with a rate constant of $\approx 4.0 \times 10^9$ dm^3 mol^{-1} s^{-1}, resulting in elimination of the nitro group either by adding to the C^5 position or through generation of a nickel(III) species. The latter undergoes intramolecular electron transfer from the ring with a rate constant of $\approx (4.6 \pm 0.4) \times 10^3$ s^{-1}, while the imidazole radicals formed decay by second-order kinetics with a $2k/\varepsilon$ value of $(9.1 \pm 1.3) \times 10^5$ cm s^{-1}. The hydrated electrons generate the nitroanion radicals, a fraction of which undergoes denitration while the rest is reduced by a successive four-electron scheme to a hydroxylamino derivative.

Metronidazole (2-methyl-5-nitro-1*H*-imidazole-1-ethanol) has been found to be a good radiosensitizer of hypoxic cells.[1,2] Co-ordination of the 5-nitroimidazole ligand to metal ions can increase its sensitizing ability[3] and at the same time reduce the phototoxicity of the drugs.[4] Several approaches have been made at studying sensitizing effects of complexes of Pt,[5–7] Rh,[8] Ru[9–11] and other related metals with different nitroimidazoles. The radiation chemical behaviour of the copper complex of metronidazole has also been recently reported.[12]

In view of the excellent sensitization achieved with some nickel complexes in hypoxic cells,[13] it would be interesting to study the radiolytic behaviour of the nickel(II) complex of metronidazole. In this paper an attempt has been made to describe the reactions of the water-borne primary radicals OH and e$^-$(aq) with the nickel(II) complex as studied by steady-state gamma radiolysis and flash photolysis. The results are compared with those for free metronidazole and its copper(II) complex.

Experimental

Materials.—Metronidazole was obtained from Sigma. All other reagents were of analytical reagent grade. The 1:1 complex of Ni^{II} and metronidazole was prepared by mixing equimolar amounts of metronidazole and nickel(II) sulfate in aqueous medium at ≈ 50 °C. The solution was reduced to a smaller volume and allowed to stand for a few hours, when a pale green solid was precipitated. The solid complex obtained on filtration was washed with a little methanol, dried and then recrystallized from water–methanol. Formation of the complex was ascertained by studying its UV and IR spectra. From the results of elemental analysis, the molecular formula of the complex was found to be $C_6H_9N_3NiO_7S$ (C, 21.2; H, 2.2; N, 12.1; Ni, 17.5. Calc., C, 22.1; H, 2.8; N, 12.9; Ni, 18.0%). The λ_{max} of the complex was found to be 320 nm with $\varepsilon = 6862.74$ dm^3 mol^{-1} cm^{-1}. The predominant site of interaction of the metal in the complex is assigned to be N^3 of the ligand.[14]

Gamma Irradiations.—Aqueous solutions of nickel(II) metronidazole [Ni(metro)]$^{2+}$ (5×10^{-4} mol dm^{-3}) saturated with N$_2$ or N$_2$O and with or without *tert*-butyl alcohol (0.4 mol dm^{-3}) as OH scavenger were exposed to a gamma source (^{60}Co, dose rate 12 Gy min^{-1}). The dose rate was determined with the help of a Fricke dosimeter taking $G(\mathrm{Fe^{3+}}) = 15.6$. Measured G values are expressed as the number of molecules lost or formed per 100 eV of energy absorbed (1.036×10^{-7} mol J^{-1}). After radiolysis, the samples were analysed for nitrite and [Ni(metro)]$^{2+}$.

Analysis.—The disappearance of [Ni(metro)]$^{2+}$ after irradiation was followed spectrophotometrically by measuring the absorbance at 320 nm after appropriate dilution. The amount of HNO$_2$ produced was determined with sulfanilic acid and 1-naphthylamine reagent.[15] The difference spectra was taken immediately after irradiation by rapidly scanning the wavelength region (240 nm min^{-1}) on a Perkin Elmer 554 UV/VIS spectrophotometer.

Generation of OH *Radicals under Flash-photolysis Conditions.*—Hydroxyl radical formation in the photolysis reaction cell was initiated by flash photolysis of H$_2$O$_2$[16] whereupon reactions (1)–(3) occur. In the presence of metronidazole or its

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad (1)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad (2)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (3)$$

complex [Ni(metro)]$^{2+}$, the OH radicals generated react with the solutes as in equations (4) and (5). The solute concentrations

$$OH + [\mathrm{Ni(metro)}]^{2+} \longrightarrow \mathrm{Products} \qquad (4)$$

$$OH + \mathrm{metro} \longrightarrow \mathrm{Products} \qquad (5)$$

were so chosen that almost quantitative reaction of the OH radicals takes place thereby minimizing the occurrence of reactions (2) and (3).

Flash Photolysis.—The apparatus consisted of a conventional kinetic spectrophotometer with flash energies of 200 J (Applied Photophysics, model KN 020) and a photolysis cell of path length 10 cm. Two flash lamps (LR 16) connected in series were

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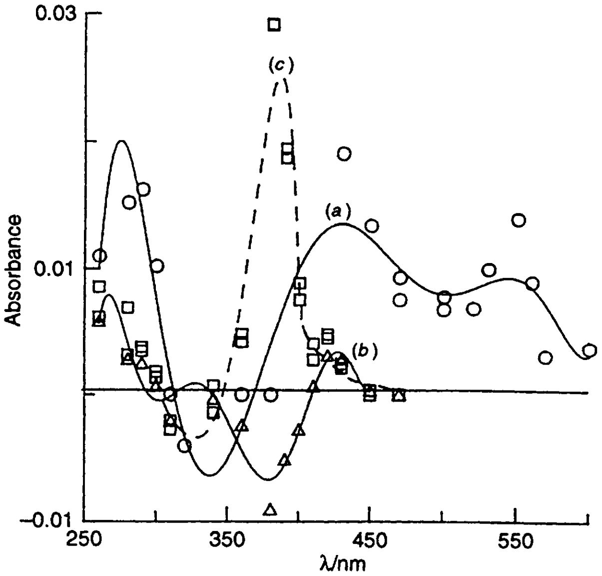


Fig. 1 Transient absorption spectra recorded after flash photolysis of a solution of H_2O_2 (10^{-2} mol dm^{-3}) in the presence of $[Ni(metro)]^{2+}$ under argon-saturated conditions: (*a*) 0.2, (*b*) 1.96 and (*c*) 19.6 ms after the flash

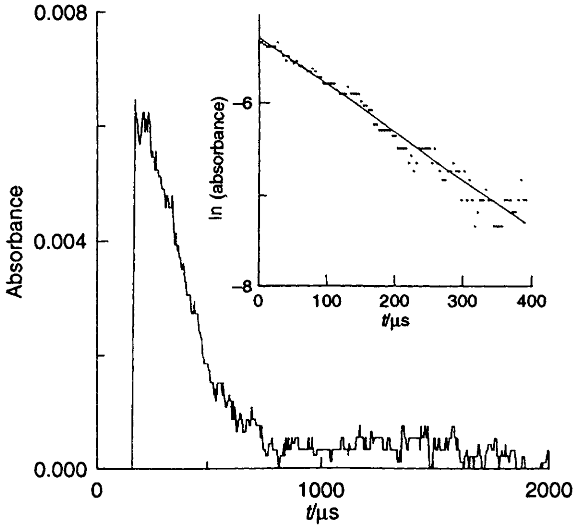


Fig. 2 Kinetic trace of the signal recorded at 550 nm in the flash photolysis of a solution of H_2O_2 (10^{-2} mol dm^{-3}) containing $[Ni(metro)]^{2+}$ (5×10^{-4} mol dm^{-3}). Insert: fitting of the data by first-order kinetics

operated at 15 kV which gave a flash of light of duration 10 µs. The digitized signal from the oscilloscope (Iwatsu TS-8123) was fed into a personal computer through a GPIB interace and the absorbance *vs.* time data were analysed for first- and second-order fits by least-squares methods.

Results and Discussion

Flash Photolysis Study.—The reaction of OH radicals with metronidazole in aqueous solutions containing H_2O_2 was initially studied for comparison with the literature data. The bimolecular rate constant for the reaction, the spectra of the transients and their decay kinetics were followed under our conditions and the results found to agree quite well with those obtained earlier by pulse radiolysis.[17] The method was then extended to study the reactions of OH with $[Ni(metro)]^{2+}$. Fig. 1 shows the transient optical absorption spectra obtained on flash photolysis of a solution of H_2O_2 (10^{-2} mol dm^{-3}) and $[Ni(metro)]^{2+}$ (5×10^{-4} mol dm^{-3}) saturated with argon and recorded at different times after the flash. The initial spectrum recorded 300 µs after the flash shows an absorption extending up to 600 nm having one peak at ≈430 nm and another at ≈550 nm [Fig. 1(*a*)]. The signal at 550 nm decayed exponentially to its preflash level (Fig. 2) with a rate constant of $(4.6 \pm 0.4) \times 10^3$ s^{-1} and this rate was independent of the complex concentration. However, when the decay of the transient was monitored at 430 nm it could not be fitted by a single first- or second-order rate law. This decay could be well described by concurrent first- and second-order processes, the kinetics of which is shown in Fig. 3. The second-order process on analysis yielded a $2k/\varepsilon$ value of $(9.1 \pm 1.3) \times 10^5$ cm s^{-1} which remained unaltered on increasing the photon flash energy. Subtraction of the second-order component from the observed change in absorbance showed an exponential decay [Fig. 3(*c*)] the rate constant of which was $\approx(5.0 \pm 0.5) \times 10^3$ s^{-1}. Since this value is quite close to that observed for the decay observed at 550 nm, it appears that both these decay constants represent the same process. Thus, the spectrum in Fig. 1(*a*) obtained initially may be thought of as that of a mixture of two transient species, one of which decays by a first-order and the other by a second-order rate law.

It may be mentioned here that Zeigerson *et al.*[18] observed the spectra of nickel(III) complexes of tetraaza macrocyclic ligands ($Ni^{III}L_3$) obtained by the oxidation of $[NiL_3]^{2+}$ with OH. The initial transient spectrum observed by us [Fig. 1(*a*)] resembles the spectra reported by the above authors for tervalent nickel. Hence, the first-order process observed in our system may be ascribed to the decay of a nickel(III) species which causes the peak at 550 nm to disappear and the absorbance at 430 nm to decrease.

The transient spectrum [Fig. 1(*b*)] obtained 2 ms after the flash is similar to that obtained by reaction of OH with metronidazole as monitored by flash photolysis under similar conditions as well as that reported following pulse-radiolysis studies.[17] This spectrum has been reported to be due to the OH adducts of metronidazole as well as denitrated products.[17] Likewise, we attribute it to similar species but co-ordinated to Ni^{II}. The $2k/\varepsilon$ value observed here is somewhat higher than that with free metronidazole.[17] This difference may, in fact, be due to the co-ordination of the metal ion to the N^3 position of the imidazole ring in the case of $[Ni(metro)]^{2+}$.

This spectrum in turn decays to that in Fig. 1(*c*) which shows a strong absorption at ≈380 nm. This transient was sufficiently long lived and its decay could not be observed within several seconds, the available time limit of the flash-photolysis instrument. To see whether this absorption was due to a permanent product or whether it decayed over a still longer period, a difference spectrum was taken with the repeatedly flash-photolysed solution. This difference spectrum was identical to that obtained following γ-irradiation in a N_2O-saturated solution (Fig. 5). The absorbance at 380 nm of the difference spectrum was found to decrease gradually with time (Fig. 5) indicating again that it must be due to an intermediate decaying over the order of minutes. The spectrum in Fig. 1(*c*) thus represents the same long-lived intermediate as that obtained through reaction with OH radicals upon γ-irradiation which is discussed further later. Incidentally, such long-lived intermediates have been isolated after gamma radiolysis of metronidazole by Moore and Wilkins.[19]

It is important to mention here that due to the longer duration of the flash compared to the time of formation of the initial transient, we could not follow the formation kinetics of the initial transients. Hence, an attempt has been made to determine the rate constant for the reaction of OH with $[Ni(metro)]^{2+}$ using competition kinetics. Under the experimental conditions there exists a competition between H_2O_2 and complex for the OH radicals [reactions (2) and (4)]. Thus if A_α be the absorbance due to the transient monitored at 430 nm when the concentration of $[Ni(metro)]^{2+}$ is sufficiently large that reaction (2) is negligible and A_t be the observed absorbance at any

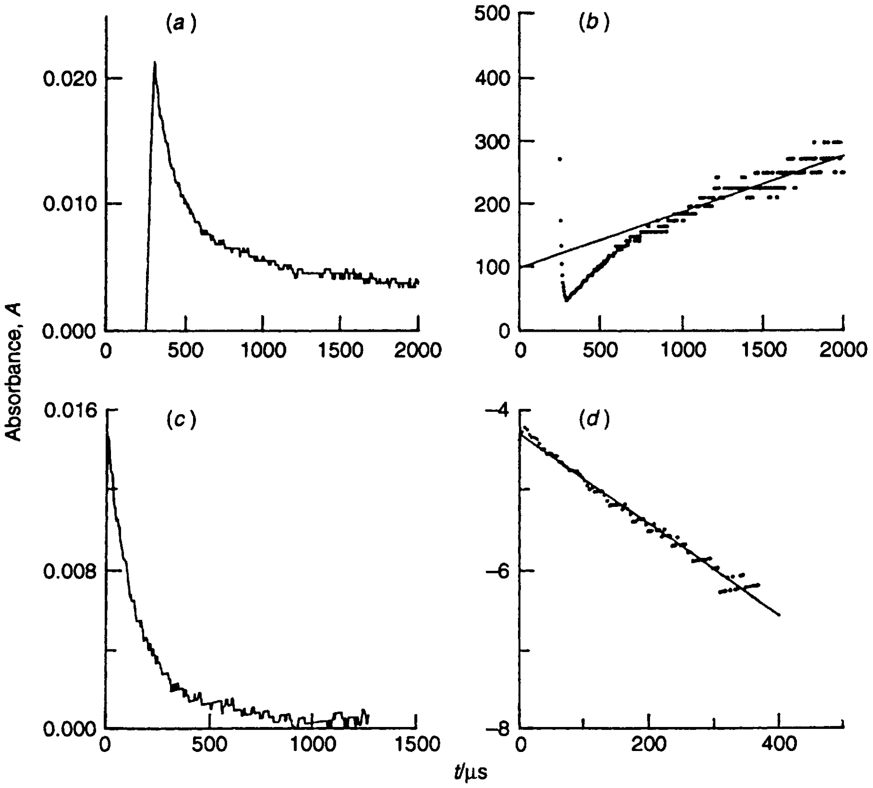


Fig. 3 (*a*) The change in absorbance at 430 nm with time after flash photolysis of a solution of H_2O_2 (10^{-2} mol dm^{-3}) and $[Ni(metro)]^{2+}$ (5×10^{-4} mol dm^{-3}). (*b*) Second-order kinetic fitting of the data in (*a*). (*c*) Absorbance *vs.* time curve for the decay at 430 nm after subtracting the contribution from the second-order component from the data in (*a*). (*d*) Fitting of data in (*c*) by first-order kinetics

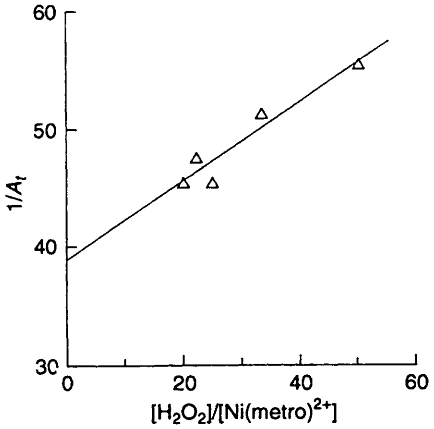


Fig. 4 Kinetic plot of the reaction of OH with $[Ni(metro)]^{2+}$ after flash photolysis of a solution of H_2O_2 (10^{-2} mol dm^{-3}) in the presence of different complex concentrations under argon-saturated conditions

intermediate concentration of $[Ni(metro)]^{2+}$ then the faction of OH reacting with $[Ni(metro)]^{2+}$ is $1/(1 + \{k_2[H_2O_2]/k_4[Ni(metro)^{2+}]\})$. Hence A_t is given by equation (6). A plot of $1/A_t$

$$A_t = \frac{A_\alpha}{1 + \{k_2[H_2O_2]/k_4[Ni(metro)^{2+}]\}} \qquad (6)$$

$$\frac{1}{A_t} = \frac{1}{A_\alpha} + \frac{1}{A_\alpha} \cdot \frac{k_2[H_2O_2]}{k_4[Ni(metro)^{2+}]} \qquad (7)$$

vs. $[H_2O_2]/[Ni(metro)^{2+}]$ (Fig. 4) yielded a slope of 0.338 ± 0.05 and intercept of 38.88 ± 1.6. Taking the value of k_2 from the literature,[20] the value of k_4 was determined to be $(3.1 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}.

Steady-state Gamma Radiolysis.—On gamma irradiation of a N_2O-saturated aqueous solution of $[Ni(metro)]^{2+}$ (5×10^{-4} mol dm^{-3}) the spectral nature of the complex remained unchanged while the absorbances decreased linearly with increasing dose indicating loss of the chromophoric group in the complex. At the same time there was evidence for the production of nitrite. In particular, the formation of nitrite was linearly dependent on the absorbed dose and the yields obtained under different conditions are shown in Table 1. Moreover, the $G[-Ni(metro)^{2+}]$ value was found to be independent of the complex concentration in the range (5–10) × 10^{-4} mol dm^{-3}. The change in the difference spectra of γ-irradiated N_2O-saturated solutions of the complex with time (Fig. 5) indicates that the reaction of OH with $[Ni(metro)]^{2+}$ leads to the formation of a long-lived intermediate which was also evidenced earlier in the flash-photolysis experiments. From a time-dependent study of the absorbance recorded at 380 nm, the half-life of the intermediate was found to be ≈5 min.

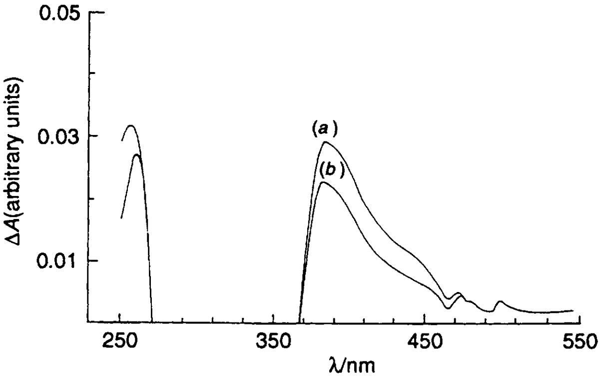
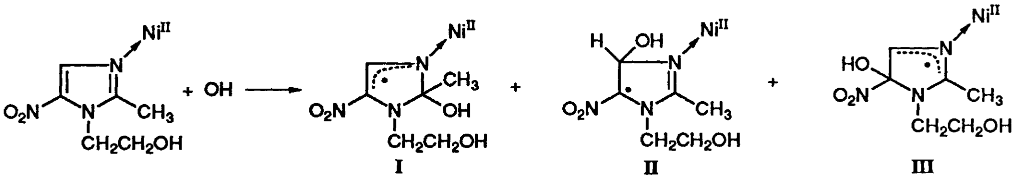


Fig. 5 Difference absorption spectra of irradiated and unirradiated N_2O-saturated aqueous solutions of $[Ni(metro)]^{2+}$; absorbed dose ≈140 Gy. (*a*) Recorded immediately after irradiation and (*b*) recorded 10 min after (*a*)

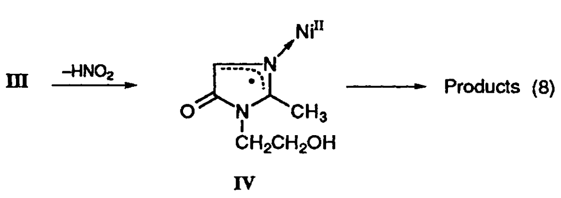
Table 1 The G values for the conversions of $[Ni(metro)]^{2+}$, $[Cu(metro)]^{2+}$ and metronidazole and for the formation of nitrous acid

	Metronidazole		$[Cu(metro)]^{2+}$ (ref. 12)		$[Ni(metro)]^{2+}$ *	
Reaction system	$G(-metro)$	$G(HNO_2)$	$G[-Cu(metro)^{2+}]$	$G(HNO_2)$	$G[-Ni(metro)^{2+}]$	$G(HNO_2)$
N_2O saturated		1.6[12]	3.2	2.4	5.6	3.3
Argon saturated	2.1[21]	2.0[21]	2.0	0.9	4.1	2.4
Aerated			2.0	1.2	2.8	2.1
Argon saturated + 0.4 mol dm^{-3} Bu^tOH			0.4	0.0	2.3	1.6
N_2O saturated + 0.4 mol dm^{-3} Bu^tOH					1.9	1.4

* Maximum error in the determination of G is ± 10%.



(4)



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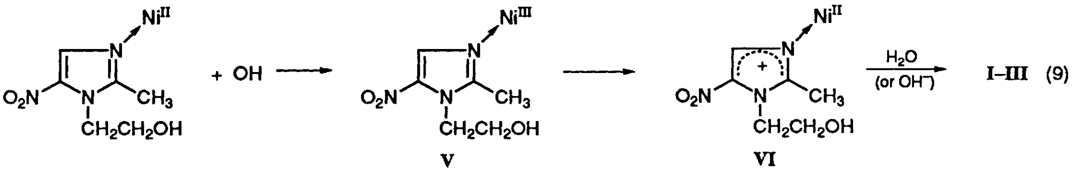


(9)

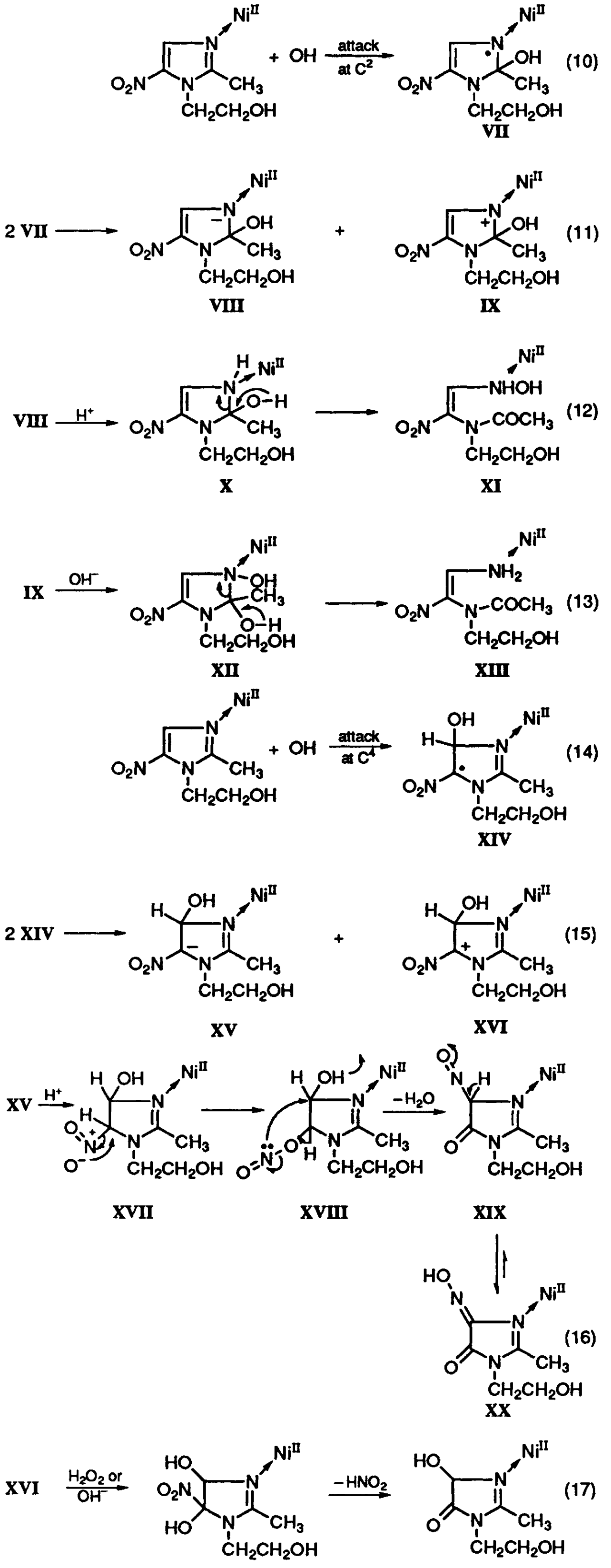
The magnitude of $G[-Ni(metro)^{2+}]$ under N_2O-saturated conditions is nearly equal to the yield of OH in the system ($G_{OH} = 5.4$) which indicates that all the OH radicals react with the complex leading to the loss of the chromophore. However, the lower yield of HNO_2 ($G_{HNO_2} = 3.3$) under these conditions suggests that the loss of the chromophoric group is not always preceded by nitrite elimination. A comparison of the results with those for free metronidazole[21] or its copper(II) complex[12] reveals that in these systems the loss of the chromophore was only due to the denitrated products formed by reaction with OH as opposed to that in the case of $[Ni(metro)]^{2+}$.

Since reactions of OH radicals with aromatic and heterocyclic compounds proceed mostly by addition to unsaturated carbon atoms[22,23] the OH adducts **I**–**III** would be produced as reaction intermediates in the present system [reaction (4)]. (C^5) Adduct **III** is expected to undergo nitrite elimination [reaction (8)] in accordance with the results obtained for nitrofurans,[24] nitrouracils[25] and $[Cu(metro)]^{2+}$.[12] However, the higher yield of HNO_2 in this system compared to that of metronidazole or $[Cu(metro)]^{2+}$ under similar conditions is indicative of other denitration pathways.

In this context it is instructive to recall our results of flash-photolysis experiments where the OH adducts decay by a second-order process which may be indicative of radical–radical reactions. It can then be surmised that the C^2- and C^4–OH adducts **I** and **II** undergo disproportionation reactions (10)–(17) leading to destruction of the nitroimidazole structure. The cation **XVI** formed from the C^4 adduct can react with H_2O_2 formed in the medium to yield HNO_2[26] [reaction (17)], thus, accounting partially for the higher HNO_2 yield observed in this system. Moreover, the C^4 adduct also leads to the formation of a 4-hydroxyimino 5-ketone [reaction (16)]. This mechanism is consistent with the results obtained with metronidazole where a similar product was isolated after gamma irradiation.[19] Thus it appears that the mode of reaction of OH with $[Ni(metro)]^{2+}$ may be similar to that of metronidazole. However, it is interesting that the fates of the C^2- and the C^4–OH adducts of $[Cu(metro)]^{2+}$ are quite different.[12] In this case the chromophore group is retained either by intramolecular electron transfer to Cu^{II} (in the case of the C^2 adduct) or by reaction with Cu^I formed (in the case of the C^4 adduct). This difference in the mode of reaction of the copper complex may be due to the higher redox potential of the couple $E°(Cu^{2+}–Cu^+) = 0.16$ V,[27] so that electron transfer to Cu^{II} is more feasible than in the case of $[Ni(metro)]^{2+}$ where the nickel(II) ion has much less probability of being reduced [$E°(Ni^{2+}–Ni^+) = -0.27$ V]).[28]

The flash-photolysis study clearly indicates the formation of a nickel(III) species. Such a species may be generated by direct attack of the highly oxidising OH radicals [$E°(OH) = 2.8$ V][29] on the metal centre [reaction (9)]. The first-order decay observed for this species shows that the transient undergoes intramolecular electron transfer from the imidazole ring which would generate a π cation **VI** [reaction (9)]. This π cation after solvolysis can give rise to **I**–**III**. However, the presence of the electron-deficient nitro group in the ring would facilitate attack at the C^5 position so as to give rise to **III** which in turn would undergo rapid denitration thereby accounting for the higher nitrite yield observed. Since solvolysis of the π cation is very fast, the intramolecular electron transfer is the rate-determining step.

From the results obtained in argon-saturated media it can be argued that nitrite is produced from the reaction of both OH and $e^-(aq)$ with $[Ni(metro)]^{2+}$. Since in this medium the yield of OH is half of that in N_2O, the amount of nitrite generated from OH under argon-saturated conditions is $\frac{1}{2}\,G(HNO_2)_{N_2O}$ =



1.6. The magnitude of $G(\text{HNO}_2)$ in an argon-saturated medium being 2.4, the rest of the nitrite equivalent to a G value of ≈ 0.8 must have resulted from reaction with e$^-$(aq). Similarly, the yield for the loss of $[\text{Ni(metro)}]^{2+}$ due to reaction with e$^-$(aq) should be $G[-\text{Ni(metro)}^{2+}]_{\text{Ar}} - \frac{1}{2}\, G[-\text{Ni(metro)}^{2+}]_{\text{N}_2\text{O}} = 1.3$.

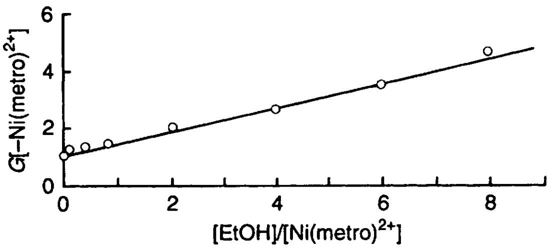


Fig. 6 Competition kinetic plot for the reaction of OH with EtOH and $[\text{Ni(metro)}]^{2+}$ (1×10^{-4} mol dm^{-3}) in an aerated medium

The reactions of e$^-$(aq) with the complex have been studied in the presence of Bu^{t}OH which is an efficient OH scavenger. However, under N_2O-saturated conditions where all the primary radicals are scavenged there was still an appreciable loss of the complex (Table 1). This can only be explained by considering that the *tert*-butyl alcohol radicals (generated by reaction with OH) undergo some sort of reaction with the complex although such reactions have not been reported earlier either with free metronidazole or with its copper(II) complex. The loss of the chromophore due to reaction with e$^-$(aq) should then correspond to a value of $G[-\text{Ni(metro)}^{2+}]_{\text{Ar+Bu}^t\text{OH}} - \frac{1}{2}\, G[-\text{Ni(metro)}^{2+}]_{\text{N}_2\text{O+Bu}^t\text{OH}} = 1.3$ in agreement with the results observed under argon-saturated conditions. Similarly, the value of $G(\text{HNO}_2)$ resulting from reaction with e$^-$(aq) would be $1.6 - 0.7 = 0.9$ and this is close to the observed value of 0.8. Thus 61% of the complex after reaction with e$^-$(aq) undergoes denitration. Although exactly the same results were obtained with metronidazole,[21] no denitration was reported following e$^-$(aq) reaction with $[\text{Cu(metro)}]^{2+}$. Here it may be noted that in the latter case a fraction of the nitroanion radicals undergoes intramolecular electron transfer to the metal centre. Presumably, the reduction of the metal centre being less probable in $[\text{Ni(metro)}]^{2+}$ it follows a pathway similar to that of the free metronidazole.

The initial species resulting from the reaction of e$^-$(aq) with $[\text{Ni(metro)}]^{2+}$ would be the nitroanion radical similar to that observed with nitroaromatic compounds.[30] A fraction of these nitroanion radicals ($G = 0.8$) undergoes denitration while the rest ($G = 2.7 - 0.8 = 1.9$) undergoes the usual reduction mechanism involving nitroso and hydroxylamine derivatives, similar to that suggested for free metronidazole.[21] Since, the ratio of the $[\text{Ni(metro)}]^{2+}$ molecules undergoing denitration to the magnitude of $G[-\text{Ni(metro)}^{2+}] = 1.9:0.5 \approx 4.0:1$, the reduction mechanism involves four electrons, as was observed with all N^1-substituted nitroimidazoles.[31]

Competition Kinetics with Alcohols.—Although under N_2O-saturated conditions, $G[-\text{Ni(metro)}^{2+}]$ attained a limiting value in the presence of an excess of alcohol, the loss of $[\text{Ni(metro)}]^{2+}$ was nearly zero in aerated media. This means that in the latter case the alcohol radicals disappear by preferential reaction with O_2 so that there is a competition for the OH radicals between the alcohols and $[\text{Ni(metro)}]^{2+}$ as shown in equations (18), (4) and (19). The bimolecular rate

$$\text{RH} + \text{OH} \longrightarrow \text{R}^{\bullet} + \text{H}_2\text{O} \qquad (18)$$

$$\text{OH} + [\text{Ni(metro)}]^{2+} \longrightarrow \text{I} + \text{II} + \text{III} \qquad (4)$$

$$\text{R}^{\bullet} + \text{O}_2 \longrightarrow \text{Products} \qquad (19)$$

constant for the reaction of OH with $[\text{Ni(metro)}]^{2+}$ was hence determined using the competition kinetic equation (20). The

$$\frac{G[-\text{Ni(metro)}^{2+}]_0}{G[-\text{Ni(metro)}^{2+}]} = 1 + \frac{k_{20}[\text{RH}]}{k_4[\text{Ni(metro)}^{2+}]} \qquad (20)$$

Table 2 Rate constant (dm^3 mol^{-1} s^{-1}) for the reaction of OH with [Ni(metro)]$^{2+}$ determined by competition kinetics using alcohols and by flash photolysis

Alcohol	k_{20} (ref. 18)	$10^{-9}k_4$
Methanol	9.7×10^8	4.8
Ethanol	1.9×10^9	3.8
Pr^{i}OH*	1.9×10^9	3.9
Bu^{t}OH	5.1×10^8	4.4
Flash photolysis (k_2)	2.7×10^7	3.1

* Average $k_1 = (4.0 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1}.

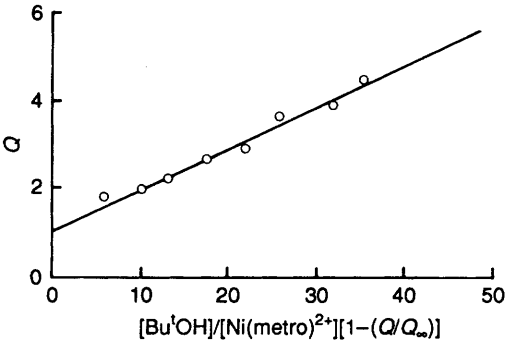


Fig. 7 Competition plot for the reaction of OH with [Ni(metro)]$^{2+}$ and Bu^{t}OH on γ-radiolysis of a solution of the complex (1×10^{-4} mol dm^{-3}) containing increasing concentrations of Bu^{t}OH in N_2O

kinetic plot is shown in Fig. 6 and the observed rate constants, are given in Table 2. However, under N_2O-saturated conditions there exists an additional competition as shown in equations (21) and (22). Under such circumstances the kinetic equation

$$\mathrm{R}^\bullet + [\mathrm{Ni(metro)}]^{2+} \longrightarrow \text{Products} \qquad (21)$$

$$\mathrm{R}^\bullet + \mathrm{R}^\bullet \longrightarrow \text{Products} \qquad (22)$$

takes the form[32] (23) where Q_∞ is the value of Q at infinitely

$$\frac{G[-\mathrm{Ni(metro)}^{2+}]_0}{G[-\mathrm{Ni(metro)}^{2+}]} = Q = 1 + \frac{k_{20}}{k_4} \cdot \frac{[\mathrm{RH}]}{[\mathrm{Ni(metro)}^{2+}]}\left(1 - \frac{Q}{Q_\infty}\right) \qquad (23)$$

high concentrations of alcohol so that the OH radicals are totally scavenged and the chromophore loss is only due to reaction (21). The kinetic plot is shown in Fig. 7 and the value of k_4 was determined to be 4.3×10^9 dm^3 mol^{-1} s^{-1}, in agreement with the result obtained by flash photolysis.

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