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Sensitizing Effect of Nitrous Oxide in the Radiolysis of Nickel(II) Iminodiacetate in Aqueous Solution

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Summary Nitrous oxide has been found to initiate a chain process in the radiolytic degradation of Ni^{II} iminodiacetate in aqueous solution.

THE role of N_2O in sensitizing the radiolytic degradation of methanol and isopropyl alcohol has recently been reported.[1,2] Such behaviour in the case of a metal complex containing a ligand with an abstractable hydrogen atom would be unique. Our study with Ni^{II} iminodiacetate (IDA) points towards such a possibility.

$Ni^{II}IDA$ undergoes ligand degradation on radiolysis into glycine and carbonyl compounds, *e.g.*, formaldehyde and glyoxalic acid. When an OH scavenger such as HCO_2^- or t-butanol is present during radiolysis, no such ligand degradation is observed. The OH radical, therefore, appears to be responsible only for causing damage to the ligand. As for Ni^{II} ethylenediaminetetra-acetate (EDTA),[3] Ni^{II} nitrilotriacetate (NTA),[4] or the ligand IDA[5] itself it seems pertinent to assume that OH reacts at the ligand site of the complex forming a C-centred radical [equation (1)], where $Ni^{II}RNHCH_2CO_2^-$ represents $Ni^{II}IDA$.

$$OH + Ni^{II}RNHCH_2CO_2^- \longrightarrow Ni^{II}RNHCHCO_2^- + H_2O \quad (1)$$

This radical may either undergo electron transfer with the metal centre of the metal complex or may disproportionate. However, the observed result that $G(\text{gly}) = G(>C{=}O) = 1{\cdot}3 = ca.\ 1/2G_{OH}$ supports disproportionation rather than electron transfer, [equation (2)].

$$2\,Ni^{II}RNHCHCO_2^- \xrightarrow{H_2O} Ni^{II}RNH_2 + CHOCO_2H + Ni^{II}RNHCH_2CO_2^- \quad (2)$$

This simple radiolytic model fails to account for the observed behaviour in the presence of N_2O. Thus in N_2O saturated solution, G(ligand) *i.e.* G(gly) or $G(>C{=}O)$ was found to be as high as 12·0 molecules per 100 eV (Table). If it is assumed that $k(e_{aq}^- + Ni^{II}IDA)$ is not very high, then it is to be expected that all the e_{aq}^- would be scavenged by N_2O, [equation (3)]. If this occurs G(gly) or $G(>C{=}O)$

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \quad (3)$$

should not be higher than $1/2[G_{OH} + G(e_{aq}^-)] = ca.\ 3{\cdot}0$ in any case (since N_2O scavenges[6] into the spurs giving an effective $G_{OH} = 6{\cdot}0$ in N_2O saturated solutions).

To trace the reason behind the enhanced yield, radiolysis was carried out using different concentrations of the complex under N_2O saturated conditions. It is evident from Figure 1 that the trend of enhanced degradation of the ligand occurs even at concentrations far below that at which $G(CHOCO_2H)$ starts increasing more gradually, $[Ni^{II}IDA]$ *ca.* 5 mM. The enhanced degradation at such

TABLE. Effect of N_2O on the observed G values in the radiolysis of Ni^{II}-IDA at neutral pH. $[Ni^{II}\text{-IDA}] = 1{\cdot}0 \times 10^{-2}$ M.

Scavenger S	[S]	$G(CHOCO_2H)$	$G(CH_2O)$	G(glycine)
None	—	1·1 ± 0·1	0·2	1·3 ± 0·2
N_2O	Saturated (*ca.* 2·5 × 10^{-2} M)	10·2 ± 0·4	1·9 ± 0·1	12·0 ± 0·4

low concentrations, *i e*, at *ca* 10^{-4} M, clearly indicates that Ni^I formed by reaction between e^-_{aq} and Ni^{II} can in no way be held responsible for this extra degradation of the ligand

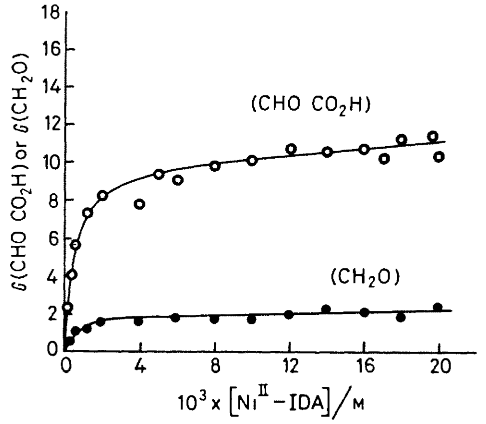

FIGURE 1 Effect of initial concentration of Ni^{II}IDA on $G(CHOCO_2H)$ and $G(CH_2O)$ in the radiolysis of aqueous solution of Ni^{II}IDA at neutral pH under N_2O saturated conditions

The role of the C-centred radical formed by reaction (1) above seems to be more decisive in this regard It is reasonable to assume that the ligand radical undergoes electron transfer with the N_2O molecule, thereby initiating a chain reaction, with the continuing formation of OH radicals in the process, [equation (4)]

$$Ni^{II}RNHCHCO_2^- + N_2O \xrightarrow{H_2O} Ni^{II}RNH_2 + CHOCO_2H + OH + N_2 + OH^-$$
$$\xrightarrow{H_2O} Ni^{II}RNH_2 + CH_2O + CO_2 + OH + N_2 + OH^- \quad (4)$$

Since G(ligand) is not very high, a short chain mechanism must be considered It is possible to assume that the disproportionation of C-centred radicals as discussed earlier, constitutes the chain termination step The reaction mechanism would then comprise the following reactions,

$$RH_2 + OH \longrightarrow RH\cdot \quad (1)$$
$$RH\cdot + N_2O \longrightarrow P_1 + OH \quad (4)$$
$$RH\cdot + RH\cdot \longrightarrow P_2 + RH_2 \quad (2)$$

where RH_2 represents Ni^{II}IDA and P_1 and P_2 are products such that the total products $P = P_1 + P_2$ An estimate of the ligand radical (RH•) which induces the chain process may be made from the relation

$$G(P) = G(Gly) = G(>C{=}O) = \frac{1+\alpha}{2(1-\alpha)} \quad G_{OH}$$

where α represents the distribution of RH between reactions (4) and (2) and $G_{OH} = G_{OH} + Ge^-_{aq}$ Since $G(P) = 12\ 0$ and $G_{OH} = 6\ 0, \alpha = ca\ 0\ 6$ which is a reasonable value for the chain propagation step

From a kinetic analysis of the above reaction scheme one can easily visualize that G(P) should be proportional to the inverse square root of dose rate (D_r) following equation (5)

$$G(P) = \tfrac{1}{2}G_{OH} + k_4[N_2O]\sqrt{(G_{OH}/2k_2)}\sqrt{(1/D_r)} \quad (5)$$

where G_{OH} is again equal to $G_{OH} + G(e^-_{aq})$ This expectation is corroborated by the observed results shown in Figure 2 where a smooth straight line with the required intercept of $1/2\ G_{OH}$ is obtained

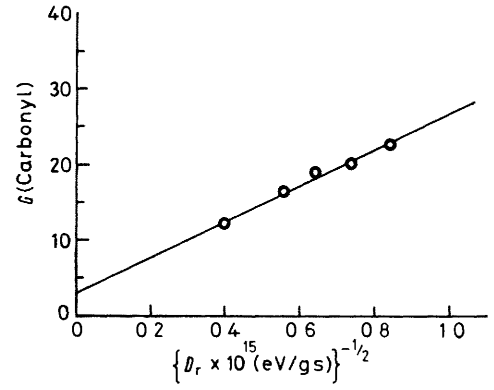

FIGURE 2 Product yields plotted against (dose rate)$^{0\ 5}$ [N_2O] *ca* $2\ 5 \times 10^{-2}$ M [Ni^{II} IDA] *ca* $1\ 0 \times 10^{-2}$ M

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