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One-electron reduction reactions of some inorganic nitrogen radicals in water

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The technique of pulse radiolysis and kinetic absorption spectrophotometry has been used to generate various inorganic nitrogen radicals and follow their one-electron reduction reactions. The method used is based on following the one-electron reduction of these free radicals ($R^{\bullet}$) by various electron donor compounds (DH) present in solution: the $R^{\bullet} + DH \rightarrow R^{-}$ (or RH) + $D^{\bullet} + H^{+}$. The efficiency of this reaction is usually monitored by observing the formation of the $D^{\bullet}$ radicals at the wavelength of their absorption The efficiency of reduction of $R^{\bullet}$ radicals is found to depend upon the known redox potentials (E_0^1 at *p*H 7.0, 25°C) of the donor compounds. Typical titration curves are obtained and from the midpoint (50% electron transfer) the "kinetic potentials" E_k^{01} of the $R^{\bullet}$ radicals can be derived. The E_k^{01} values for the one-electron reduction of the following inorganic nitrogen radicals have been determined: $^{\bullet}N_3$ (≥+0.41V), $^{\bullet}NH_3^+$ (+0.55V), $^{\bullet}NH_2$ (+0.20V), $CH_3{}^{\bullet}NH_2^+$ (+0.06V), $CH_3{}^{\bullet}NH$ (-0.05V), $^{\bullet}N_2H_4^+$ (+0.034V), $^{\bullet}N_2H_3$ (+0.20V), $^{\bullet}NHOH$ (-0.40V), and $^{\bullet}NHOCH_3$ (-0.45V). These values are based on the two-electron redox potentials of the donor compounds. The electron transfer kinetics leading to the formation of $D^{\bullet}$ radicals are determined and rate constants (≤6.0 x 10^9 $M^{-1}sec^{-1}$) have been obtained. The implications of the results with regard to the reaction mechanism and kinetics of these inorganic nitrogen free radicals are discussed.

Nitrogen is capable of exhibiting oxidation states from +5 to -3. For example, in ammonia N = -3, in hydrazine N = -2 and in hydroxylamine N = -1. A knowledge of the oxidation states and redox potentials of a compound and its corresponding free radical are most useful, especially in conjunction with reaction mechanisms, chemical kinetics and oxidation-reduction processes. A considerable amount of work has been done on ESR studies[1] of inorganic free radicals, but relatively little has been done on studying the chemistry of these radicals, particularly in solution.

The method[2] developed to study the kinetic potentials of organic free radicals in aqueous solutions, was applied to examine one-electron reduction of a number of simple inorganic nitrogen radicals. Presented below are the results on the azide ($^{\bullet}N_3$), ammonium ($^{\bullet}NH_3^+$), amino ($^{\bullet}NH_2$), methylammonium ($CH_3{}^{\bullet}NH_2^+$), methylamino ($CH_3{}^{\bullet}NH$), hydrazonium ($^{\bullet}N_2H_4^+$), hydrazyl ($^{\bullet}N_2H_4^+$), hydroxyamino ($^{\bullet}NHOH$) and methoxyamino ($^{\bullet}NHOCH_3$) radicals. These radicals were chosen based on their known properties and ionization constants in aqueous solution[3-7].

Materials and Methods

The inorganic nitrogen radicals studied were generated in aqueous solutions by reaction of the parent compounds with either hydroxyl radicals or hydrated electrons. The fast-reaction technique of pulse radiolysis was used to produce relatively high concentrations of these short-lived free radicals and to follow their subsequent one-electron redox reactions in the presence of various electron donor compounds (DH).

Experimental details of the pulse radiolysis setup have been described[8,9] in literature. Single pulses of ~2.3MeV electrons and ~30nsec duration were provided by the Febetron (Field Emission Corporation) 705 pulsed radiation source.The radiation chemistry of water may be depicted as

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$H_2O \rightsquigarrow e^-_{aq}$ (2.8), $^{\bullet}OH$ (2.8), H (0.6), H_2: (0.45) and H_2O_2 (0.71) where the values in parentheses are G-values (yields of radicals produced per 100 eV of energy absorbed by the aqueous solution). The inorganic nitrogen radicals formed by reaction of the substrates (RH) with $^{\bullet}OH$ radicals were produced on irradiation in the presence of N_2O (1atm = ~2.5 x 10^{-2} *M*) in order to convert e^-_{aq} into $^{\bullet}OH$ radicals:

$$e^-_{aq} + N_2O \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad (1)$$

where k_1 = 8.7 x 10^9 $M^{-1}sec^{-1}$. (ref.10) The concentrations of RH were chosen such that $k(e^-_{aq} + N_2O) / k(e^-_{aq} + RH) \sim 20.0$.

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (2)$$

The chemicals used were the highest research grade commercially available samples from J. T. Baker, Aldrich, Eastman Chemicals, Baker and Adamson, Calbiochem and K and K Laboratories. The substrates were dissolved in air-free solutions, and the *p*H was adjusted with perchloric acid, potassium hydroxide, and ~1m*M* phosphate and tetraborate buffers. Solutions were made just prior to use and were protected from exposure to light.

Determination of kinetic potentials

Details of the method and the experimental conditions during the determination of the kinetic potentials of free radicals have been given elsewhere[2]. This method is based on the one-electron redox properties of the free radical $R^{\bullet}$. On reaction with electron donors, reaction (3) takes place:

$$R^{\bullet} + DH \rightarrow R^- \text{ (or RH)} + D^{\bullet} + H^+ \quad (3)$$

Such a transfer of electrons takes place provided the redox potential of the donor DH is lower (i.e. more negative) than that of the acceptor radical $R^{\bullet}$. The efficiency of electron transfer, expressed as a percentage, is found to be dependent on the potentials of the donor compounds, which are well known[12]. A plot of the percentage efficiency of electron transfer against the redox potentials of the donors gives typical "titration" curves.

Under the experimental conditions used, reaction (3) was found to irreversible. Hence, equilibrium conditions do not prevail and the Nernst equation cannot be applied. Since these potentials are not thermodynamic, they are referred to as kinetic the redox radicals can be obtained. These values are with reference to the two-electron redox potentials of the electron donor compounds.

Table 1- List of electron donor compounds used

Compounds	E_0^1(V[a])	λ(nm[b] monitored)
Fluorescein	-0.572	500*
Eosin	-0.500	520*
Methyl green	-0.395	610*
Crystal violet	-0.357	525*
Safranine T	-0.289	520*
Indigo disulphonate	-0.125	610*
Indigo tetrasulphonate	-0.046	610*
Methylene blue	+0.011	580*
Indophenol (*p*H 9.0)	+0.089	610*
Trimethyl *p*-hydroquinone	+0.109	430
Sodium thiosulphate	+0.110	380
Dimethylhydroquinone	+0.170	440
2,6-Dichloroindophenol	+0.217	600*
Potassium iodide	+0.230	385
p-Hydoquinone	+0.280	430
Methyl *p*-phenylenediamine	+0.330	520
p-Phenylenediamine	+0.363	470
Potassium bromide	+0.380	360
3-Dimethyl 4-aminophenol	+0.411	400
Potassium thiocyanate	+0.430	500
Potassium chloride	+0.510	350
2,3-Dicyano 4-hydroquinone	+0.510	430
p-Methoxyphenol	+0.564	400
2,4-Dimethylphenol	+0.611	400
Diphenyl amine	+0.655	680
p-Cresol	+0.755	405
Phenol	+0.805	400

[a]redox potentials obtained from ref. 12; [b]stars indicate that "bleaching" of the donor compounds was monitored.

The concentration of $D^{\bullet}$ radicals produced was monitored at the appropriate wavelengths, (see Table 1). When dyes were used, the "bleaching" or disappearance of the dyes was monitored since this is a more sensitive and convenient procedure.

In order to improve the accuracy of the results, the absorbance due to 100% formation of $D^{\bullet}$ radicals (or 100% bleaching of the dyes) was determined in all cases immediately prior to carrying out the experiment under identical experimental conditions of dose, concentration, *p*H, monochromator slit-widths, etc[2,11]. The notation E_k^m is used to specify the kinetic potential at the stated *p*H of the experiment, and E_k^{01} the kinetic potential at *p*H 7.0 and 25°C. Equation (A) is used to

convert the redox potentials of the donor compounds from one *p*H to another,

$$E_m = E^0 - 0.059\, pH \quad (A)$$

where E^0 is the redox potential in 1.0*M* [H^+]. When dyes were used, the experimentally determined[12] E_m values were employed.

Results

The azide radical $N_3^{\bullet}$

The $^{\bullet}N_3$ radical has been observed on flash photolysis[3] of azide ions in aqueous solution, and is also formed by a one-electron oxidation[4] on reaction with $^{\bullet}OH$ radicals under pulse radiolytic conditions,

$$N_3^- + {}^{\bullet}OH \rightarrow N_3^{\bullet} + OH^- \quad (4)$$

with k_4 = 1.2 x 10^{10} $M^{-1}sec^{-1}$. ref.. 4 The azide radical[4,5] has an absorption maximum at 278nm, ε_{278}=2.3 x 10^3 $M^{-1}cm^{-1}$, and decays bimolecularly with $2k$=1.3 x 10^{10} $M^{-1}sec^{-1}$.

At very low [$^{\bullet}N_3$] and high [DH], reaction (5)

$$N_3^{\bullet} + DH \rightarrow N_3^- + D^{\bullet} + H^+ \quad (5)$$

was found to be 100% efficient with certain donor compounds (e.g. 2,6-dichloroindophenol, I^-, *p*-hydroquinone and *p*-phenylenediamine) whose redox potentials E_0^1 are more negative than ~+0.36V. With DH compounds having a more positive redox potential, no electron transfer could be observed under these experimental conditions, (see Fig.1.) From the midpoint of the curve, a kinetic potential $E_k^{01} \geq +0.41V$ can be obtained at *p*H 7.0 for the redox couple $N_3^{\bullet}/N_3^-$.

The ammonium $^{\bullet}NH_3^+$ and amino $^{\bullet}NH_2$ radicals

These radicals have been produced[5] from the one-electron reduction of hydroxylamine by hydrated electrons:

$$^{+}NH_3OH + e^-_{aq} \rightarrow {}^{\bullet}NH_3^+ + OH^- \quad (6)$$

$$NH_2OH + e^-_{aq} \rightarrow {}^{\bullet}NH_2 + OH^- \quad (7)$$

where k_6=1.2 x 10^{10} $M^{-1}s^{-1}$ and k_7=9.2 x 10^8 $M^{-1}s^{-1}$. These radicals have acid-base properties[5], (reaction 8),

$$^{\bullet}NH_3^+ \leftrightarrow {}^{\bullet}NH_2 + H^+ \quad (8)$$
$$pK_a \sim 6.7 \pm 0.2$$

The formation of the $^{\bullet}NH_3^+$ and $^{\bullet}NH_2$ radicals and the determination of their kinetic potentials were carried out by pulse radiolysis of $10^{-3}M$ aqueous solutions of hydroxylamine sulphate in presence of $10^{-2}M$ DH compounds in order to reduce these

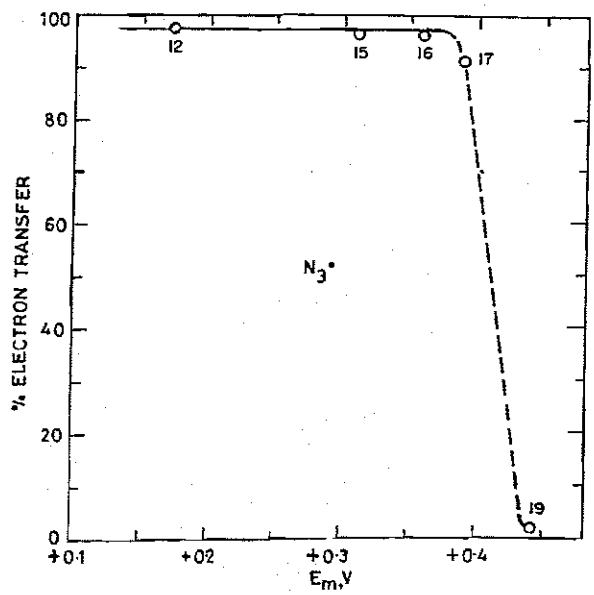


Fig 1- Dependence of the one-electron reduction of the azide radical $^{\bullet}N_3$ upon the redox potential of the electron donor compounds (DH)[.Experimental conditions: NaN_3, ($10^{-1}M$), ($10^{-3}M$) DH, N_2O (1atm), *p*H 6.5, [$^{\bullet}N_3$](~10μM). See Table 1 for listing of donors used].

radicals, as well as to scavenge all the $^{\bullet}OH$ radicals produced from the radiolysis of water:

$$^{\bullet}NH_3^+ + DH \rightarrow NH_3 + D^{\bullet} + H^+ \quad (9)$$

$$^{\bullet}NH_2 + DH \rightarrow NH_3 + D^{\bullet} \quad (10)$$

$$^{\bullet}OH + DH \rightarrow D^{\bullet} + H_2O \quad (11)$$

When reactions (9) and (10) do not take place, an absorbance due to $D^{\bullet}$ radicals [reaction (11)] is observed with 50% yield, since [e^-_{aq}] ~ [$^{\bullet}OH$]. The experiments were carried out in argon (1atm) at *p*H 5.0 and *p*H 8.0. The results are shown in Fig.2 and Table 2.

A kinetic potential E_k^{01}=+0.55V is observed for the $^{\bullet}NH_3^+/NH_3$ couple, and E_k^{01}=+0.20V for the $^{\bullet}NH_2/NH_3$ redox couple. These results clearly indicate that the ammonium radical is a powerful oxidizing agent and it is stronger than the amino radical.

This difference in the oxidizing powers of the acid-base forms of these radicals was shown by "titrating" these radicals against iodide ion (E_0^1=+0.23V) as the electron donor, as a function of *p*H. Figure 3(a) shows the titration curve obtained from which a pK_a value of 6..5 ± 0.2 canbe derived for equilibrium (8), which is in good agreement with the value of 6.7 ± 0.2

Table 2- Kinetic potentials of some inorganc nitrogen radicals in aqueous solution at ~25°C

Radical	pK_a (radical)	pH	Redox couple	E_k^m, V[a]	E_k^{01}, V[b]
$^{\bullet}N_3$	-	6.5	$^{\bullet}N_3/N_3^-$	≥ +0.41	≥ +0.41
$^{\bullet}NH_3^+$	-	5.0	$^{\bullet}NH_3^+/NH_3$	+0.67	+0.55
-	6.7[c]				
$^{\bullet}NH_2$	-	8.0	$^{\bullet}NH_2/NH_3$	+0.14	+0.20
$CH_3{}^{\bullet}NH_2^+$	-	5.0	$CH_3{}^{\bullet}NH_2^+/CH_3NH_2$	+0.18	+0.06
-	7.2[d]				
$CH_3{}^{\bullet}NH$	-	9.0	$CH_3{}^{\bullet}NH/CH_3NH_2$	-0.10	-0.05
$^{\bullet}N_2H_4^+$	-	5.5	$^{\bullet}N_2H_4^+/N_2H_4$	+0.43	+0.34
-	7.1[e]				
$^{\bullet}N_2H_3$	-	9.2	$^{\bullet}N_2H_3/N_2H_4$	+0.07	+0.20
$^{\bullet}NHOH$	4.2[c]	8.0	$^{\bullet}NHOH/NH_2OH$	-0.46	-0.40
$^{\bullet}NHOCH_3$	2.9[c]	8.0	$^{\bullet}NHOCH_3/NH_2OCH_3$	-0.51	-0.45

[a]Values derived at the stated pH from the midpoint (50% electron transfer) of the "titration curves"; [b]values are at pH 7.0 to ± 0.03V; [c]from reference 5; [d]this work; [e]from reference 7.

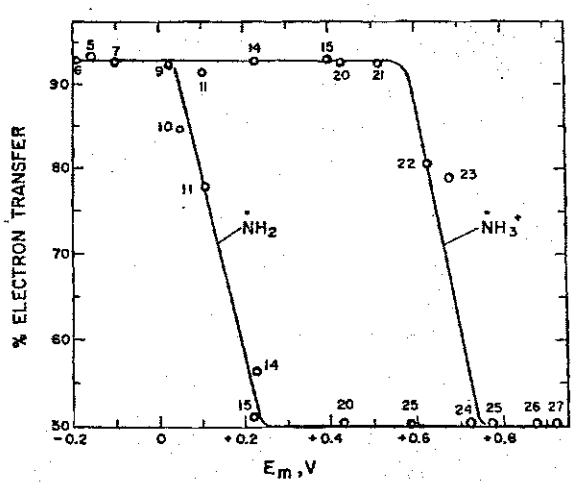


Fig 2- Dependence of the one-electron reduction of ammonium ($^{\bullet}NH_3^+$) and amino ($^{\bullet}NH_2$) radicals upon the redox potential of the electron donor compounds (DH). [Experimental conditions: hydroxylamine($10^{-3}M$), DH ($10^{-2}M$) (2.5 x $10^{-5}M$ dyes), argon (1atm), at pH 5.0, 0 and pH 8.0, [radical]~10μM. See Table 1 for listing of donors used].

obtained earlier[5].

The $CH_3{}^{\bullet}NH_2^+$ and $CH_3{}^{\bullet}NH$ radicals

These radicals were generated by the one-electron reduction of N-methyl hydroxylamine by e_{aq}, similar to the conditions described above for the $^{\bullet}NH_3^+$ and $^{\bullet}NH_2$ radicals:

$$CH_3{}^{+}NH_2OH + e^-_{aq} \rightarrow CH_3{}^{\bullet}NH_2^+ + OH^- \quad (12)$$

$$CH_3NHOH + e^-_{aq} \rightarrow CH_3{}^{\bullet}NH + OH^- \quad (13)$$

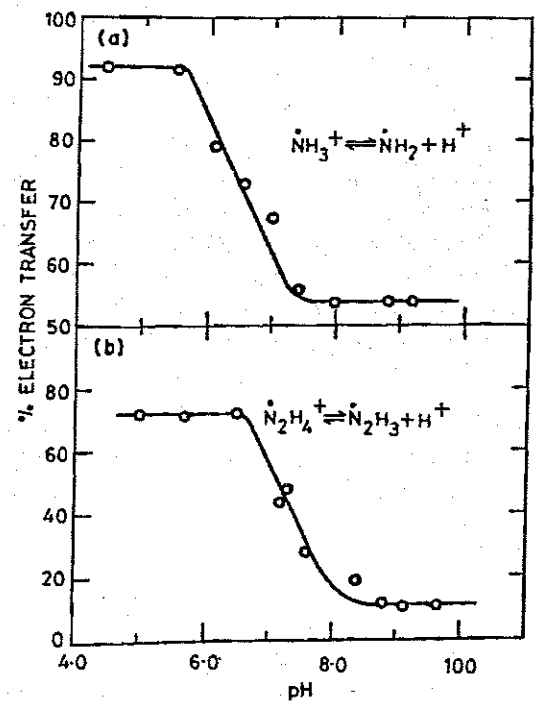
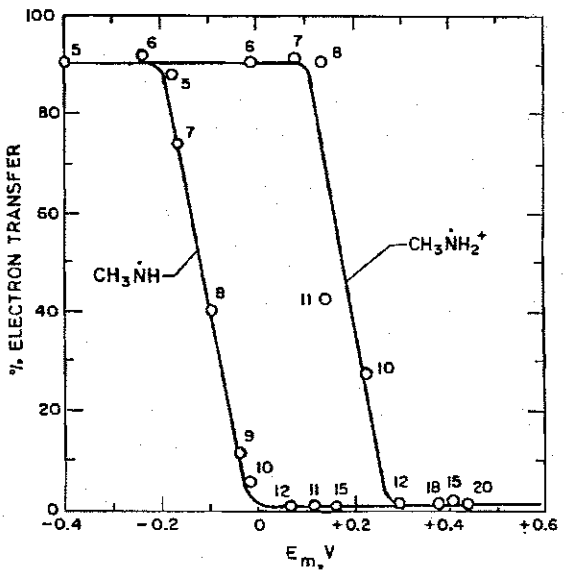


Fig 3- (a) Titration of the $^{\bullet}NH_3^+$ radical using iodide ions as the electron donor. [Experimental conditions: hydroxylamine($10^{-3}M$), KI ($10^{-3}M$), argon (1atm)]. (b) Titration of the $^{\bullet}N_2H_4^+$ radical using p-hydroquinone as the electron donor. [Experimental conditions: (8 x $10^{-2}M$) hydrazine, (5 x $10^{-4}M$) p-hydroquinone, N_2O (1atm)].

where =1.3 x 10^{10} $M^{-1}sec^{-1}$ and k_{13}=2.4 x 10^8 M^{-1} sec^{-1}.

$$CH_3{}^{\bullet}NH_2^+ \leftrightarrow CH_3{}^{\bullet}NH + H^+ \quad (14)$$

pK_a~7.2



Fig·4- Dependence of the one-electron reduction of the methyl amino radicals $^{\bullet}CH_3NH_2^+$ and $CH_3{}^{\bullet}NH$ upon the redox potential of the electron donors. [Experimental conditions: ($10^{-3}M$) N-methyl hydroxylamine,(1.0 M) t-BuOH, ($10^{-3}M$) DH (2.5 x $10^{-5}M$ dyes), Ar (1atm), at pH 5.0, 0 and pH 9.0, [radical]~10μM (~2μM when dyes are used). See Table 1 for listing of donors used].

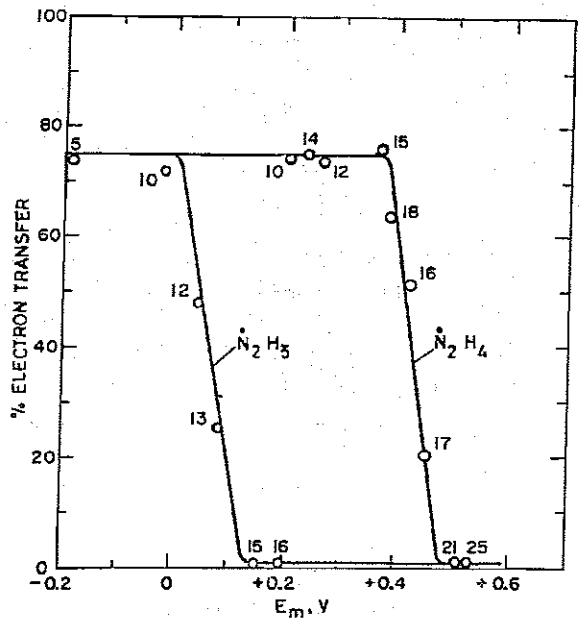


Fig 5- Dependence of the one-electron reduction of the hydrazyl radicals $^{\bullet}N_2H_4^+$ and $^{\bullet}N_2H_3$ upon the redox potential of the electron donor compounds. [Experimental conditions: hydrazine, (8 x $10^{-2}M$) DH, (5 x $10^{-4}M$) (2.5 x $10^{-5}M$ dyes), N_2O (1atm) at pH 5.5, 0 and pH 9.2, [radical]~10μM. See Table 1 for listing of donors used].

The acid k_{12}-base equilibrium for the $(CH_3)_2{}^{\bullet}NH^+$ radical has been found by ESR[6] to be between 6.5 and 7.5.

The solution contained 1.0M t-butyl alcohol, used to scavenge[8] the $^{\bullet}OH$ radicals,$10^{-3}M$ CH_3NHOH and $10^{-3}M$ of the electron donor compounds (2-2.5 x $10^{-5}M$ used for dyes). Experiments were carried out in argon (1atm) at pH 5.0 and 9.0. The concentrations [R$^{\bullet}$]~10μM and [DH]=$10^{-3}M$ were used for the generation and one-electron reduction of the $CH_3{}^{\bullet}NH_2^+$ and $CH_3{}^{\bullet}NH$ radicals. The results obtained are presented in Fig.4.

A kinetic potential E_k^{01} value of +0.06V was obtained for the $CH_3{}^{\bullet}NH_2^+/CH_3NH_2$ couple, and an E_k^{01} value of -0.05V for the $CH_3{}^{\bullet}NH$ /CH_3NH_2 couple (see Table 2).The methylamino radicals were "titrated" using p-hydroquinone (E_0^1=+0.28V) as the electron donor. The results are shown in Fig. 3(b). From this titration curve, a pK_a =7.2 ± 0.2 was obtained for equilibrium (14).

The hydrazyl radicals $^{\bullet}N_2H_4^+$ and $^{\bullet}N_2H_3$

The reaction of hydoxyl radicals with hydrazine was shown[7] to lead to the formation of hydrazyl radicals:

$$^{\bullet}OH + N_2H_5^+ \rightarrow {}^{\bullet}N_2H_4^+ + H_2O \quad (15)$$

$$^{\bullet}OH + N_2H_4 \rightarrow {}^{\bullet}N_2H_4^+ + OH^- \quad (16)$$

with[8] k_{15}=1.0 x 10^9 $M^{-1}sec^{-1}$ and k_{16}=1.4 x 10^{10} $M^{-1}sec^{-1}$. The pK_a of $N_2H_5^+$ is 8.07 and that of the radical was found[7] to be 7.1 ± 0.1.

$$^{\bullet}N_2H_4^+ \leftrightarrow {}^{\bullet}N_2H_3 + H^+ \quad (17)$$

pK_a~7.1 ± 0.1

Experiments were carried out in the presence of N_2O (1atm) to convert e^-_{aq} into $^{\bullet}OH$ radicals. A concentration of about 5 x $10^{-4}M$ concentrations of the electron donors was used in studying these radicals, under conditions such that all the $^{\bullet}OH$ radicals reacted with hydrazine. The results obtained are shown in Fig.5. It can be noted that the maximum efficiency of electron transfer to these radicals is only ~75%, whereas a value close to 100% has been observed for the other radicals studied. This difference is experimentally significant and would appear to indicate that ~25% of the $^{\bullet}OH$ radicals react with hydrazine to produce

radicals other than the ones suggested[8] by reactions (15) and (16).

From Fig.5, kinetic potential values E_k^{01} of +0.34V and +0.20V for the $^{\bullet}N_2H_4^+/N_2H_4$ and $^{\bullet}N_2H_3/N_2H_4$ couples, respectively, have been calculated (see Table 2).

The hydroxyamino and methoxyamino radicals

These radicals were produced[5] by reaction of $^{\bullet}OH$ radicals with hydroxylamine (pK_a=6.0) and O-methylhydroxylamine (pK_a=4.6) at pH 8.0 in N_2O-saturated aqueous solutions:

$$^{\bullet}OH + NH_2OH \rightarrow {}^{\bullet}NHOH + H_2O \quad (18)$$

$$^{\bullet}N^+H_2OH \leftrightarrow {}^{\bullet}NHOH + H^+ \quad (19)$$

$$pK_a \sim 4.2 \pm 0.1$$

$$^{\bullet}OH + NH_2OCH_3 \rightarrow {}^{\bullet}NHOCH_3 + H_2O \quad (20)$$

$$^{\bullet}N^+H_2OCH_3 \leftrightarrow {}^{\bullet}NHOCH_3 + H^+ \quad (21)$$

$$pK_a \sim 2.9 \pm 0.1$$

with[7] k_{18}=9.5 x 10^9 $M^{-1}sec^{-1}$ and k_{20}=1.4 x 10^{10} $M^{-1}sec^{-1}$. Only the base forms of these radicals were examined, since experimental conditions could not be properly adjusted to generate and reduce the acid forms of these radicals.

The results obtained are shown in Fig.6. With these radicals two steps were observed in the percentage efficiency vs. E_m curves were. The overall efficiency for reduction of the radicals is close to 100%. The small steps in the curves are probably due to the formation of radicals other than the ones proposed in reactions (18) and (20). These are tentatively suggested to be $NH_2O^{\bullet}$ and $NH_2O^{\bullet}CH_2$ radicals The E_k^{01} are -0.40V and -0.45V for the $^{\bullet}NHOH/NH_2OH$ and $^{\bullet}NHOCH_3/NH_2OCH_3$ couples, respectively (see Table 2). It is clear that these radicals are relatively poor oxidizing agents.

Rate constants of electron transfer reactions

The one-electron reduction of these inorganic nitrogen radicals by various electron donor compounds was followed by monitoring the formation of $D^{\bullet}$ radicals or disappearance ("bleaching") of the DH compounds at the appropriate wavelengths. The formation and/or bleaching kinetics was found to be pseudo-first order, dependent on the concentration of DH. From these values, the second order rate constants for reaction (3) were determined (Table 3). These rate

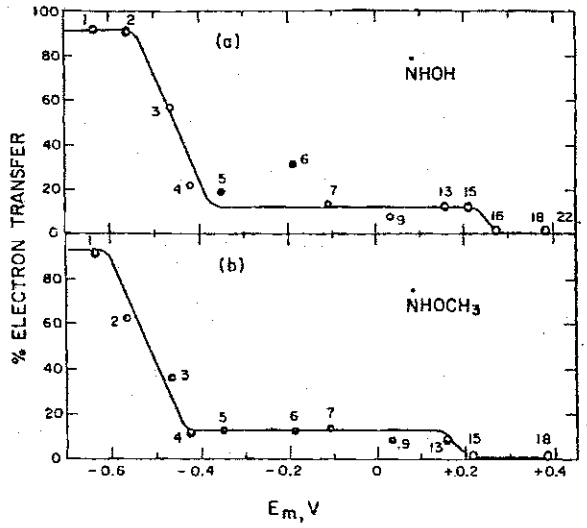


Fig 6- Dependence upon the redox potential of the electron donor compounds of the one-electron reduction of (a) the hydroxyamino $^{\bullet}NHOH$ radical: hydroxylamine, ($10^{-3}M$) DH 2.5 x $10^{-5}M$ (dyes), N_2O (1atm), pH 8.0, [$^{\bullet}NHOH$]~2μM; (b) the methoxy amino $^{\bullet}NHOCH_3$ radical: O-methyl hydroxylamine, ($10^{-3}M$) DH ($10^{-3}M$) (2.5 x 10^{-5}) dyes), N_2O (1atm), pH 8.0, [$^{\bullet}NHOCH_3$]~8μM (~2μM with dyes). See Table 1 for listing of donors used.

constants are the observed rates and have not been corrected for the back reaction.

The reduction of $^{\bullet}N_3$ radicals ($E_k^{01} \geq +0.41$V) was studied in greater detail. With the exception of phenosafranine and safranine T, the observed rates increase with decrease in the redox potential (i.e. more negative) of the DH compounds, qualitatively as expected. Similar trends can be seen for the other radicals. It should be pointed out, however, that the absolute rate values for different radicals are not in quantitative agreement. This difference could be accounted for on the basis of the nature (e.g. inner-sphere vs. outer-sphere) of the electron transfer processes.

Discussion

From the results presented above it is clear that the kinetic potentials for the one-electron reduction of these free radicals are higher (i.e. more positive) for the acid form $R^{\bullet}NH_2^+$ than those for the base form $R^{\bullet}NH$. This means that $R^{\bullet}NH_2^+$ radicals can be more readily reduced (or stronger oxidising agents) than $R^{\bullet}NH$ radicals (Table 2).

It is interesting to note that the E_k^{01} values for $^{\bullet}NH_3^+$ and $CH_3{}^{\bullet}NH_2^+$ radicals are +0.55V and +0.06V, respectively. When R=CH_3 in $R^{\bullet}NH_2^+$

Table 3- Reaction rate constants of some electron transfer processes in aqueous solution at ~22°

Electron donor (E_0^1, V)[a]	Acceptor Radical	*p*H	*k*(electron transfer)$M^{-1}sec^{-1}$[b]
p-Hydroquinone (+0.280)	$^{\bullet}N_3$	9.2	2.3 x 10^9
Iodide ion (+0.230)	$^{\bullet}N_3$	9.2	3.6 x 10^9
Indigo tetrasulphonate (-0.046)	$^{\bullet}N_3$	9.2	4.0 x 10^9*
Indigo disulphonate (-0.125)	$^{\bullet}N_3$	9.2	4.5 x 10^9*
Phenosafranine (-0.254)	$^{\bullet}N_3$	9.2	1.5 x 10^9*
Safranine T (-0.289)	$^{\bullet}N_3$	9.2	1.5 x 10^9*
Iodide (+0.230)	$^{\bullet}NH_3^+$	5.0	7.8 x 10^8
Safranine T (-0.289)	$^{\bullet}NH_3^+$	5.0	2.4 x 10^9*
p-Hydroquinone (+0.280)	$^{\bullet}NH_2$	8.0	2.5 x 10^8
Safranine T (-0.289)	$^{\bullet}NH_2$	8.0	2.2 x 10^9*
Trimethyl *p*-hydroquinone (+0.109)	$CH_3{}^{\bullet}NH_2^+$	5.0	4.0 x 10^9
Methylene blue (+0.011)	$CH_3{}^{\bullet}NH_2^+$	5.0	5.2 x 10^9*
Trimethyl *p*-hydroquinone (+0.109)	$CH_3{}^{\bullet}NH$	9.0	3.0 x 10^9
Safranine T (-0.289)	$CH_3{}^{\bullet}NH$	9.0	5.0 x 10^9*
Trimethyl *p*-hydroquinone (+0.109)	$^{\bullet}N_2H_4^+$	5.5	1.1 x 10^9
Safranine T (-0.289)	$^{\bullet}N_2H_4^+$	5.5	8.2 x 10^8*
Trimethyl *p*-hydroquinone (+0.109)	$^{\bullet}N_2H_3$	9.2	1.0 x 10^9
Safranine T (-0.289)	$^{\bullet}N_2H_3$	9.2	9.5 x 10^8*

[a]Values at *p*H 7.0 and ~25°C;[b]Astericks indicate that the rates were determined by following the "bleaching" kinetics of the electron donors at the appropriate wavelength.

radicals, the electron donating properties of the methyl group make $CH_3{}^{\bullet}NH_3^+$ more difficult to be reduced, as compared to $^{\bullet}NH_3^+$. The effect of the $-CH_3$ group is apparently smaller for the neutral $^{\bullet}NH_2$ and $CH_3{}^{\bullet}NH$ radicals, as reflected by their E_k^{01} values. Substitution of the $R^{\bullet}NH_2^+$ and $R^{\bullet}NH$ radicals, e.g., when R=NH_2, OH and OCH_3, brings about considerable changes in the kinetic potentials of these radicals (see Table 2). Electron

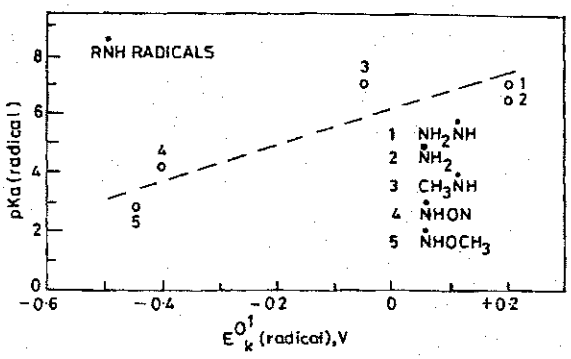


Fig 7- Correlation between the kinetic potentials of $R^{\bullet}NH$ radicals in water and the pK_a of the radicals: (1) R=NH_2, (2) R=H, (3) R=CH_3, (4) R=OH, and (5) R=OCH_3. Data taken from Table 2.

attracting groups make the radical more easily reducible, while electron donating groups show the opposite trend, i.e., such radicals have much more negative E_k^{01} values.Indeed, it would appear that a correlation exists between the kinetic potentials of $R^{\bullet}NH$ radicals and the ionization constants (pK_a) of the same radicals. Figure 7 shows a plot of such a correlation with the values taken from Table 2. A reasonable correlation was observed, indicating that the higher the pK_a of a radical (i.e. the lower the affinity of this radical for a proton), more readily it can be reduced by a large number of electron donor compounds (i.e. the kinetic potential of the radical is high and more positive). A similar correlation can be shown to exist between the E_k^{01} (radical) and the pK_a of the parent compounds.

A knowledge of the kinetic potentials of free radicals is important for explaing or predicting the course of chemical reactions, as well as chemical kinetics. For example, since the E_k^{01} for the $^{\bullet}NH_3^+/NH_3$ couple is +0.55V and that for the $O_2/^{\bullet}O_2^-$ couple[11] is +0.07V it is clear that reaction (22) can be expected to occur.

$$^{\bullet}NH_3^+ + {}^{\bullet}O_2^- \rightarrow NH_3 + {}^{\bullet}O_2 \qquad (22)$$

Reaction (23), however, is expected to be slower

$$^{\bullet}NH_2 + {}^{\bullet}O_2^- \xrightarrow{H_2O} NH_3 + O_2 + OH^- \qquad (23)$$

since the E_k^{01} for the $^{\bullet}NH_2/NH_3$ couple is +0.20V. Similarly, the $^{\bullet}N_3/N_3^-$ couple has an $E_k^{01} \geq +0.41$V and one can expect reaction (24) to take place with high efficiency if there are no other competing reactions

$$^{\bullet}N_3 + {}^{\bullet}O_2^- \rightarrow N_3^- + O_2 \quad (24)$$

On the other hand, the $^{\bullet}$NHOH radical is not likely to be reduced by the $^{\bullet}O_2^-$ radical. Many other reactions with free radicals, oxygen, and electron donor or acceptor compounds can be predicted in this way.

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