Stability of N_2O^- in Cyclohexane

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Summary Pulse-radiolysis studies show that N_2O^- formed in cyclohexane solution can transfer an electron rapidly to galvinoxyl (GAL), a property shared by the anions of O_2, SF_6, CO_2, and CH_3NO_2 but not by those of I_2, CCl_4, and $C_2(CN)_4$; N_2O^- is estimated to have a lifetime in cyclohexane not less than 20 μs.

Nitrous oxide is a powerful electron scavenger. Mass-spectrometric studies show that the appearance potential of the O^- ion is too small to be measured[1] and hence ΔE^0 for the dissociative electron capture process is $\simeq 0$. However, the experiments of Holtslander and Freeman[2] suggest that N_2O^- can have a lifetime of 10^{-4} to 10^{-3} s in the gas phase and the question arises as to whether N_2O^- can persist in liquids sufficiently long to be of chemical significance. In protic media the evidence[3] suggests that, if it is formed, N_2O^- rapidly decomposes to form N_2 and the oxidising species O^- but in cyclohexane the dependence of $G(N_2)$ on $[N_2O]$ in γ-irradiated solution of N_2O has been interpreted by Warman *et al.*[4] as indicating that N_2O^- formed in reaction (1) can persist to react with another molecule of N_2O according to equation (2).

$$N_2O + e^- \longrightarrow N_2O^- \qquad (1)$$

$$N_2O^- + N_2O \longrightarrow N_2 + N_2O_2^- \qquad (2)$$

In addition, Mishra and Symons[5] have recently presented e.s.r. spectroscopic evidence which suggests that N_2O^- is stable at 77 K in a carbon disulphide matrix.

It appears that if N_2O^- exists, its absorption spectrum does not permit its detection by existing pulse-radiolysis techniques. However, by using a second solute that has a higher electron affinity than N_2O and forms an anion with a characteristic intense absorption spectrum it should be possible to detect formation of the anion by electron transfer from N_2O^-. Capellos and Allen[6] have shown that the stable free-radical galvinoxyl (GAL) is also a powerful electron scavenger, forming the anion, GAL^-, with a strong optical absorption (λ_{max} 580 nm) which can be used to measure the yield of free electrons and we now report data which show that GAL can rapidly extract an electron from N_2O^-.

Solutions of GAL in cyclohexane either deaerated by several freeze–pump–thaw cycles, great care being taken to remove any carbon dioxide, or saturated with N_2O, SF_6, O_2, or CO_2, were irradiated with 25, 200, or 600 ns pulses of 3 MeV electrons and the formation of GAL^-, which was identified by its absorption spectrum,[6] was followed at 580 nm using methods already described.[7]

For carefully deaerated 5×10^{-5}M-solutions of GAL in cyclohexane at a dose per pulse <300 rad $[GAL^-]$ increased in a pseudo-first-order manner over about three half-lives with $t_{\frac{1}{2}} = 2\,\mu$s, indicating the occurrence of reaction (3) in which the electrons are uniformly distributed in space and

$$e^- + GAL \longrightarrow GAL^- \qquad (3)$$

$k_3 \simeq 7 \times 10^9 M^{-1}s^{-1}$. At high doses per pulse some electrons react with positive ions formed in the primary act and the growth of $[GAL^-]$ deviates from the first-order law.

Iodine is known to be an efficient electron scavenger in cyclohexane and the observation that $10^{-3}M$-I_2 completely prevented the formation of GAL^- was expected. A similar effect was observed in solutions containing the electron scavengers $CCl_4(10^{-1}M)$ and $C_2(CN)_4$ $(10^{-3}M)$. In marked contrast the maximum yield of GAL^- from 10^{-5} to 10^{-4}M-solutions of GAL was unaffected by the presence of N_2O even when $[N_2O] = 10^4$ [GAL] *i.e.* when virtually all the electrons are expected to be scavenged by N_2O. These observations clearly prove (a) that reaction (4) is occurring and (b) that the electron affinity of GAL is less than those of I_2 (1·6—2·4 eV),[8] CCl_4(2·12 eV),[8] and $C_2(CN)_4$ (2·88 eV),[8] and greater than that of N_2O ($\simeq$0·1 eV)[4]. From the

$$N_2O^- + GAL \longrightarrow N_2O + GAL^- \qquad (4)$$

first-order growth (see Figure) of $[GAL^-]$ in N_2O saturated solutions subjected to doses less than 500 rad we calculate $k_4 = (1{\cdot}0 \pm 0{\cdot}2) \times 10^{10}M^{-1}s^{-1}$ and since for solutions containing 10^{-5}M-GAL this growth continues for more than 20 μs, N_2O^- must be stable for at least this period in cyclohexane.

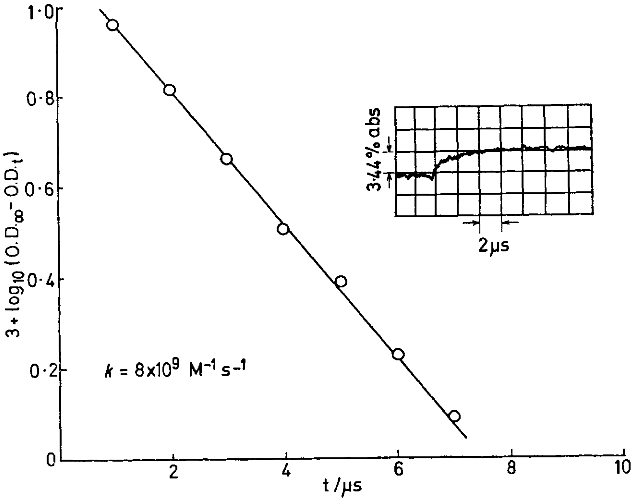

Figure. *Growth of* GAL^- *in* N_2O*-saturated cyclohexane solution.* $[GAL] = 5 \times 10^{-5}M$, λ = 580 nm, *pulse length* = 0·2 μs, *dose* $\simeq$ 300 rads.

At doses > 500 rad/pulse the growth of $[GAL^-]$ deviates from first-order in a manner attributed to the concurrent reaction (5) where CH^+ is a cyclohexane cation and P

$$N_2O^- + CH^+ \longrightarrow N_2 + P \qquad (5)$$

denotes oxidation products of cyclohexane. k_5 was estimated to be $(2{\cdot}3 \pm 0{\cdot}8) \times 10^{12}M^{-1}s^{-1}$ by observing the growth of $[GAL^-]$ in solutions containing $10^{-5}M < [GAL] < 10^{-4}M$ subjected to doses/pulse up to 4 k rad. The data were treated by the method of least-square refinements with numerical integration of the rate equations and making corrections for the decay of GAL^- in reaction (6).

$$GAL^- + CH^+ \rightarrow \text{Product} \qquad (6)$$

From the decay of GAL^- after its formation in reaction (4) had become negligible, k_6 was found to be $(6{\cdot}5 \pm 0{\cdot}5) \times 10^{11}M^{-1}s^{-1}$.

Data obtained for solutions of GAL containing other solutes show that GAL can abstract electrons from O_2^-, SF_6^-, and CO_2^- ($k \simeq 2 \times 10^{10}M^{-1}s^{-1}$) and $CH_3NO_2^-$ ($k \simeq 8 \times 10^{9}M^{-1}s^{-1}$). The reported values of the electron affinities of O_2, SF_6, and CO_2 are $(0{\cdot}43 \pm 0{\cdot}02)$,[8] $(1{\cdot}49 \pm 0{\cdot}21)$[8] and *ca.* 3·8 eV,[8] respectively. The fact that CO_2^- can transfer its charge to GAL whereas I_2, CCl_4, and $C_2(CN)_4$ cannot suggests that the reported value of the electron affinity of CO_2 is much too large.

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