Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Grant No. AT (04-3) 767-8.

[21] Arthur Amos Noyes Research Instructor of Chemistry, 1969–1970.

[22] Alfred P. Sloan Foundation Fellow, 1968–1970.

* Address correspondence to this author.

David Holtz,*[21] J. L. Beauchamp,[22] Shelia D. Woodgate
Contribution No. 4157
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

Received August 5, 1970

Absorption Spectra and Kinetics of the Intermediate Produced from the Decay of Azide Radicals

Sir:

Azide ions in aqueous solution undergo a one-electron oxidation mechanism on reaction with hydroxyl radicals

$$N_3^- + OH \longrightarrow N_3\cdot + OH^- \qquad (1)$$

This reaction has been studied by generating OH radicals in the pulse radiolysis of aqueous solutions, in the presence of 1 atm of nitrous oxide to convert >98% of e_{aq}^- to OH radicals. Single pulses of 2.3-MeV electrons and 30-nsec duration were used; all experimental details have been described.[1] Figure 1 shows the transient absorption spectrum obtained immediately after the pulse—this band has a λ_{max} at 278 nm, and is assigned to the $N_3\cdot$ radical. An identical spectrum has recently been obtained,[2] and similarly identified, in the flash photolysis of N_3^- ions in its CTTS band

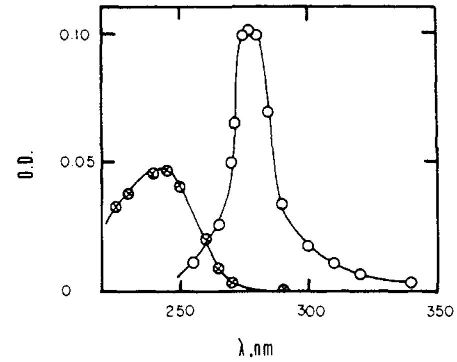


Figure 1. Transient absorption spectra produced from the reaction of OH radicals with 1 m*M* N_3^- ions in aqueous solution at pH 9.2. OD measured at 0.1 μsec (○) and 10 μsec (⊗) after a 30-nsec single pulse of electrons, total dose 4 krads. Identical spectra observed in the presence of 0.1 *M* NaCl and in 10 m *M* NaN_3.

$$N_3^-\cdot H_2O \xrightarrow{h\nu} N_3\cdot + e_{aq}^-$$

Based on G(OH) = 5.6, the extinction coefficient of $N_3\cdot$ is found to be ϵ_{278} 2.3 × 10^3 M^{-1} cm^{-1}. The azide radical decays by a second-order process with $2k$ = 9 ± 1 × 10^9 M^{-1} sec^{-1}, in excellent agreement with the value 9.2 × 10^9 M^{-1} sec^{-1} obtained from flash photolysis work.[2] The rate constant $k(OH + N_3^-)$ = 1.2 × 10^{10} M^{-1} sec^{-1} was obtained, based on kinetic competition with the benzoate ion, and taking[3] k(OH + PhCOO$^-$) = 6 × 10^9 M^{-1} sec^{-1}.

Azides resemble halides and in many respects react like pseudohalides. They do not, however, appear to produce N_6^- radicals

$$N_3\cdot + N_3^- \rightleftharpoons N_6\cdot^-$$

similar to $Cl_2\cdot^-$, $Br_2\cdot^-$, and $I_2\cdot^-$ radicals. The absorption maximum, the decay rate, and the extinction coefficient of the 278-nm band were found to be independent of $[N_3^-]$ in the range 0.4–10 m*M*. The decay kinetics at 280 nm were found to be independent of the ionic strength of the solution (up to 0.2 *M* Na_2SO_4), indicating the absence of a charge on the radical. Finally, in the presence of 0.1 *M* Cl^- ions the $N_3\cdot$ band was unchanged, suggesting the absence of the complex $N_3\cdot + Cl^- \rightleftharpoons N_3Cl\cdot^-$.

Concomitant with the second-order decay of the $N_3\cdot$ radical is the formation of another intermediate with λ_{max} at 242 nm; see Figure 1. This new species X is produced by a second-order process with $2k$ = 6.2 × 10^6 ϵ_{242} M^{-1} sec^{-1}

$$2N_3\cdot \longrightarrow X \qquad (2)$$

Assuming this mechanism, ϵ_{242} is 2.1 × 10^3 M^{-1} cm^{-1}, and the rate of formation of X is $2k$ = 1.3 × 10^{10} M^{-1} sec^{-1}, in good agreement with the rate of decay of $N_3\cdot$ radicals at 278 nm.

The intermediate X decays by a first-order process to give nitrogen

$$X \longrightarrow 3N_2 \qquad (3)$$

with k_3 = 3.6 × 10^3 sec^{-1}, *i.e.*, $\tau_{1/2}$ of ~200 μsec. In support of reactions 2 and 3, the yield of N_2 in this system was determined, since in earlier work[4] complicated factors involving the reaction of e_{aq}^- were not eliminated. ^{60}Co γ irradiation of 10^{-2} *M* NaN_3, pH 8.5, saturated with N_2O gave a $G(N_2)$ = 11.0 ± 0.4, $G(H_2)$ = 0.33, and $G(O_2)$ = 0.37. Assuming G(OH) = $G(e_{aq}^-)$ = 2.8, G(H) = 0.6, $G(H_2)$ = 0.45, and $G(H_2O_2)$ = 0.72, a $G(N_2)$ = 11.8 ± 0.4 can be expected, based on reactions 1–3. The formation of O_2 and the slightly lower yield of N_2 observed could be due to

$$H + N_3^- \longrightarrow N_2 + NH^- \text{ (or } NH_2) \qquad (4)$$

$$NH^- + H_2O_2 \longrightarrow NH_3 + O_2^- \qquad (5)$$

$$O_2^- + O_2 \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^- \qquad (6)$$

$$N_3\cdot + H_2O_2 \longrightarrow \text{products} \qquad (7)$$

where k_7 = 7.3 × 10^9 M^{-1} sec^{-1} (ref 5). Under the above experimental conditions, the reaction of $N_3\cdot$ with H_2O_2 plays only a minor part.

It is interesting to speculate on the nature and structure of the intermediate X. The azide ion[6] is linear and symmetrical, and since removal of an electron from the nonbonding orbital is expected to have almost no effect on the bond lengths, vibration frequencies, and force constants, $N_3\cdot$ can be said to resemble closely N_3^-. Dimerization of N_3 is not forbidden by spin-conservation rules and, thermochemically, is highly

---

[1] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 73, 3794 (1969); E. Hayon, *J. Chem. Phys.*, **51**, 4881 (1969).

[2] A. Treinin and E. Hayon, *ibid.*, **50**, 538 (1969).

[3] P. Neta and L. M. Dorfman, *Advan. Chem. Ser.*, **No. 81**, 222 (1968). The CNS^- method could not be used since $(CNS)_2^-$ undergoes a fast reaction with N_3^- ions.

[4] P. Kelly and M. Smith, *J. Chem. Soc.*, 1479, 1487 (1961).

[5] J. Halpern and J. Rabani, *J. Amer. Chem. Soc.*, **88**, 699 (1966).

[6] See review by P. Gray, *Quart. Rev., Chem. Soc.*, **17**, 441 (1963).

favorable,[6] with $\Delta H = -210 \pm 6$ kcal/mol for the overall reaction $2N_3 \rightarrow 3N_2$. Indeed this could account, in part, for the explosion and detonation decomposition of azide crystals. It is tentatively suggested that the nature of the intermediate X is N_6. The structure of N_6 could be either extended or cyclic. The following points could be used in support of a cyclic structure, similar to that of the benzene ring: (a) the nitrogen atom is isoelectronic with the -CH- radical, and this endows it with similar physical properties of molecular symmetry and structure; (b) the absorption maximum of N_6 is close to the first absorption band of benzene[7] (λ_{max} ~255 nm and ϵ ~200 M^{-1} cm^{-1}); (c) the electrolysis of aqueous solutions of $^{14}N^{15}N^{14}N$ gave[8] no $^{15}N_2$ but $^{14}N_2 + 2\,^{14}N^{15}N$. An extended structure for N_6 could be related to 1,3,5-hexatriene, which has absorption maxima[9] at 251, 244, 241, and 234 nm and ϵ ~6000 M^{-1} cm^{-1}. It is interesting to note that the gas-phase photolysis[9] of 1,3,5-hexatriene produces benzene and other cyclic products. The exothermicity of reaction 3 could induce the cyclization of the intermediate N_6.

Alternatively, the decay of $N_3\cdot$ could give rise to

$$2N_3 \xrightarrow{k_a} N_6 \xrightarrow{k_b} N_2 + N_4$$

If the intermediate X is N_4, the kinetics require that $k_b \gg k_a$. Further work is in progress to elucidate the nature and structure of the 242-nm absorption band.

Acknowledgment. Discussions with Dr. A. Treinin, and also with Dr. G. Herzberg, were most stimulating. The gas analysis was carried out at the University of Newcastle-upon-Tyne, and we thank Drs. G. Scholes and P. Kelly and Mr. E. Hart for making available their general facilities.

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 499.

(8) K. Clusius and H. Schumacher, *Helv. Chim. Acta*, 41, 972 (1958).

(9) Reference 7, p 512.

(10) National Academy of Science–National Research Council Research Associate at Natick.

* Address correspondence to this author.

E. Hayon,* M. Simic[10]
Pioneering Research Laboratory, U. S. Army Natick Laboratories
Natick, Massachusetts 01760

Received August 17, 1970

A Correlation between Negative Charge on Nitrogen and the Reactivity of Aromatic Nitrenes

Sir:

The chemistry of organic nitrenes has received considerable attention in recent years,[1] because of their potential in synthesis. While carbonyl nitrenes[2] and sulfonyl nitrenes[3] insert into CH bonds, add to double bonds, and abstract hydrogen very efficiently from suitable substrates, the aromatic nitrenes appear to be less reactive and their common precursors, aromatic azides and nitroxides, have often been disappointing in preparative applications.

We have recently measured the hydrogen abstraction rates of a few simple aromatic nitrenes in hydrocarbons and alcohols.[4] The rate constants are remarkably low for diradical species (typical values for hydrogen abstraction from ethanol are on the order of 10^2 l. mol^{-1} sec^{-1}). A similar conclusion can be drawn from the high selectivity of hydrogen abstraction by phenylnitrene.[5] Abstraction yields from primary, secondary, and tertiary CH bonds are in the ratio 1 : 10 : 100.

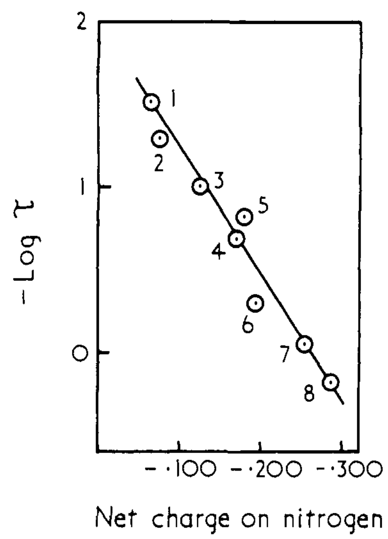
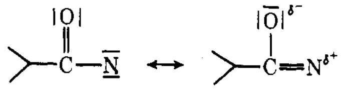


Figure 1. The lifetimes (τ, sec) of some aromatic triplet nitrenes in a polystyrene matrix as a function of the net negative charge on nitrogen: 1, 4-nitrenoacetophenone; 2, 3-nitrenoquinoline; 3, phenylnitrene; 4, dinitrenobiphenyl; 5, mesitylnitrene; 6, 1-nitrenonaphthalene; 7, 1-nitrenoanthracene; 8, 4-*N*-morpholinophenylnitrene.

This low reactivity of an electron-deficient molecular fragment is unexpected. We believe it is due to the negative charge which appears on nitrogen when connected to an aromatic system. To test this hypothesis we have measured the lifetimes of a group of aromatic triplet nitrenes in polystyrene matrices. In the solid medium nitrene recombination and attack upon azide by nitrene are eliminated. The lifetime of the nitrene in the matrix is then a measure of the rate of hydrogen abstraction.[4] It can be seen from Figure 1 that the logarithm of the lifetime correlates quite well with negative charge on nitrogen as calculated by the Hückel molecular orbital method.

Thus, the aromatic nitrenes appear to be in the paradoxical situation of an electron-seeking reagent which is repelled by sites of high electron density. One can now understand why carbonyl nitrenes, sulfonyl nitrenes, and indeed carbenes, are so much more reactive. The carbene function does not attract electrons from the aromatic system; in the carbonyl nitrenes the negative charge is removed from the reaction site to oxygen. The same applies to the sulfonyl nitrene.



$$\text{C(=O)}-\bar{N} \longleftrightarrow \text{C}(-O^{\delta-})=N^{\delta+}$$

---

(1) C. W. Rees and T. L. Gilchrist, "Carbenes, Nitrenes and Arynes," Nelson, London, 1969.

(2) W. Lwowski, *Angew. Chem.*, 79, 922 (1967).

(3) L. Horner and A. Christmann, *Angew. Chem., Int. Ed. Engl.*, 2, 599 (1963).

(4) A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, 64, 3265 (1968).

(5) J. H. Hall, J. W. Hill, and Hu-Chu Tsai, *Tetrahedron Lett.*, 2211 (1965).

* Address correspondence to this author.

A. Reiser,* L. Leyshon
Research Laboratory, Kodak Limited
Wealdstone, Harrow, Middlesex, England

Received September 24, 1970