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FORMATION AND REACTIONS OF AZIDE RADICALS

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FORMATION and REACTIONS OF AZIDE RADICALS

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Perhaps the best known property of the solid inorganic azides is their ability to explode and detonate. This decomposition can be brought about in a variety of ways, for example, by heat, light, shock, friction and ionizing radiations. In the case of the heavy metal azides, the reaction can be highly exothermic and this energy may be used to detonate secondary explosive materials. The stability of different solid azides, however, can vary over wide limits. Potassium azide, for instance, may be described as a relatively stable compound, but silver, copper and lead azides decompose readily. Extensive studies have been made of the physical properties of azides to determine the role of the lattice disorder and the electronic energy levels on the explosive characteristics of a series of inorganic azides (for reviews see references (1) and (2)).

The azide radical has been postulated as an intermediate in the decomposition of the ionic azides (1) - (3). Such decomposition has been followed by measuring the rate of nitrogen gas evolved as a function of time. The N_3 radical has not, however, been directly observed in thermal, photolytic or radiolytic decomposition of solid inorganic azides at 293° or 77°K, using spectroscopic and ESR techniques for observation. It has recently been suggested (4) that N_3 is probably thermodynamically rather than kinetically unstable. Other radicals have been detected: N_2^-(5)-(8), N_4^- (5)-(6), N_3^{2-} (8) and N atoms (4), see also references cited therein.

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This paper reports the formation and detection of the azide radical in condensed phase. The N_3 radical was produced photochemically and radiolytically using the fast reaction techniques of flash photolysis and pulse radiolysis. The spectroscopic properties and reaction kinetics of the azide radical were followed.

EXPERIMENTAL

The flash photolysis apparatus used has been described previously (9). About 2000 joules of light of wavelength greater than 2000Å was discharged in ~ 12μsec.

The pulse radiolysis apparatus used has also been described (10). Single pulses of electrons of ~ 2.3 MeV energy and ~ 30 nsec duration were used. Kinetic spectroscopy measurements were greatly improved as a result of boosting the monitoring light source (450 watt Xenon lamp) to increase the light output by a factor of ~ 25 times. In addition, a double monochromator (two high intensity Bausch and Lomb monochromators placed in series) was also used to increase wavelength resolution and decrease scattered light, particularly below ~ 280 nm.

Twice recrystallized sodium azide was used, and solutions were prepared in triply-distilled water. Further experimental details can be found in refs. (11) and (12).

RESULTS and DISCUSSION

PHOTOLYTIC DECOMPOSITION

The photochemistry of ionic azide in aqueous solution shows a dependence upon the wavelength used for optical excitation (13). This corresponds to the two types of electronic transitions as indicated by the absorption spectrum of N_3^- ions (14): an n,π^* ($^1\Delta_u$-B_2) internally excited state below a charge-transfer-to-solvent (CTTS) state. The photolysis at 2537Å of N_3^- in aqueous solution is governed by the n,π^* state. Photoionization appears to occur only at wavelengths below ~ 230 nm, where N_3^- undergoes the CTTS type of excitation

Flash photolysis study of N_3^- in aqueous solutions has shown (11) that excitation within the CTTS band yields solvated electrons. The characteristic transient optical spectrum of the solvated electron, e^-_{aq}, has been observed (11), with λ_{max} ~ 710 nm.

$$N_3^- \longrightarrow e^-_{aq} + N_3\cdot \qquad (1)$$

$$\lambda < 230 \text{ nm}$$

Concomitant with the formation of e^-_{aq} was another transient species with an absorption maximum at 277 nm (11), see Fig. 1. The 277 nm band was observed in both the presence or absence of oxygen in solution. In N_2O saturated solutions its yield was doubled, due to the following reactions taking place:

$$e^-_{aq} + N_2O \longrightarrow OH + N_2 + H^+ \qquad (2)$$

$$OH + N_3^- \longrightarrow N_3 + OH^- \qquad (3)$$

where $k_2 = 6 \times 10^9 M^{-1}sec^{-1}$ and $k_3 = 1.2 \times 10^{10} M^{-1}sec^{-1}$ (12). Furthermore, both the 277nm and 710nm bands were not produced by light of $\lambda > 230$nm (11), using appropriate cut-off filters. It is concluded (11) that the 277nm band is due to the N_3 radical in its $^2\pi_g$ ground state (see more below). This is the first evidence for the formation of N_3 radicals in condensed phase. This spectrum is in agreement with a gas phase spectrum with λ_{max} ~ 272nm, which was tentatively suggested (15) to be due to N_3. The N_3 radical was found to decay by second-order kinetics (see insert in Fig. 1). On optical excitation of N_3^- in aqueous solution with light of $\lambda > 230$nm, an ill-defined absorption peaking at ~ 269nm was observed (Fig. 1, curve (c)). The latter shows a first-order decay with $k = 750$ sec^{-1}, and its intensity was not affected by N_2O. The 269nm transient is most probably

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produced from the n, π^* ($^1\Delta_u$-B_2) state of N_3^-, but is not likely to be the NH radical since the later radical absorbs at ~ 336nm in the gas phase (16).

The azide ion has a relatively low reactivity with solvated electrons. However, under appropriate conditions it is possible that the N_3^{2-} radical anion could be produced

$$N_3^- + e^-_{aq} \longrightarrow N_3^{2-} \qquad (4)$$

The reactivity of N_3^- with hydrogen atoms, however is almost diffusion-controlled, leading presumably to N_2 and NH^- (or NH_2) radicals.

RADIOLYTIC DECOMPOSITION

Ionic azides undergo a one-electron oxidation mechanism in aqueous solution. The hydroxyl radical produced in the radiolysis of water has been used as the one-electron oxidant, and the reaction followed using the technique of pulse radiolysis and kinetic absorption spectroscopy:

$$OH + N_3^- \longrightarrow N_3\cdot + OH^- \qquad (3)$$

The initial transient absorption spectrum produced from the reaction of OH radicals with 1 mM NaN_3 in N_2O-saturated aqueous solution at pH 9.2 is shown in Fig. 2. This band has a λ_{max} = 278nm and is identical to the spectrum obtained in the flash photolysis of N_3^- in its CTTS band (Fig. 1).

Based on the known yield of OH radicals, the extinction coefficient of N_3 was determined (12) to be $\epsilon_{278} = 2.3 \times 10^3 M^{-1} cm^{-1}$.

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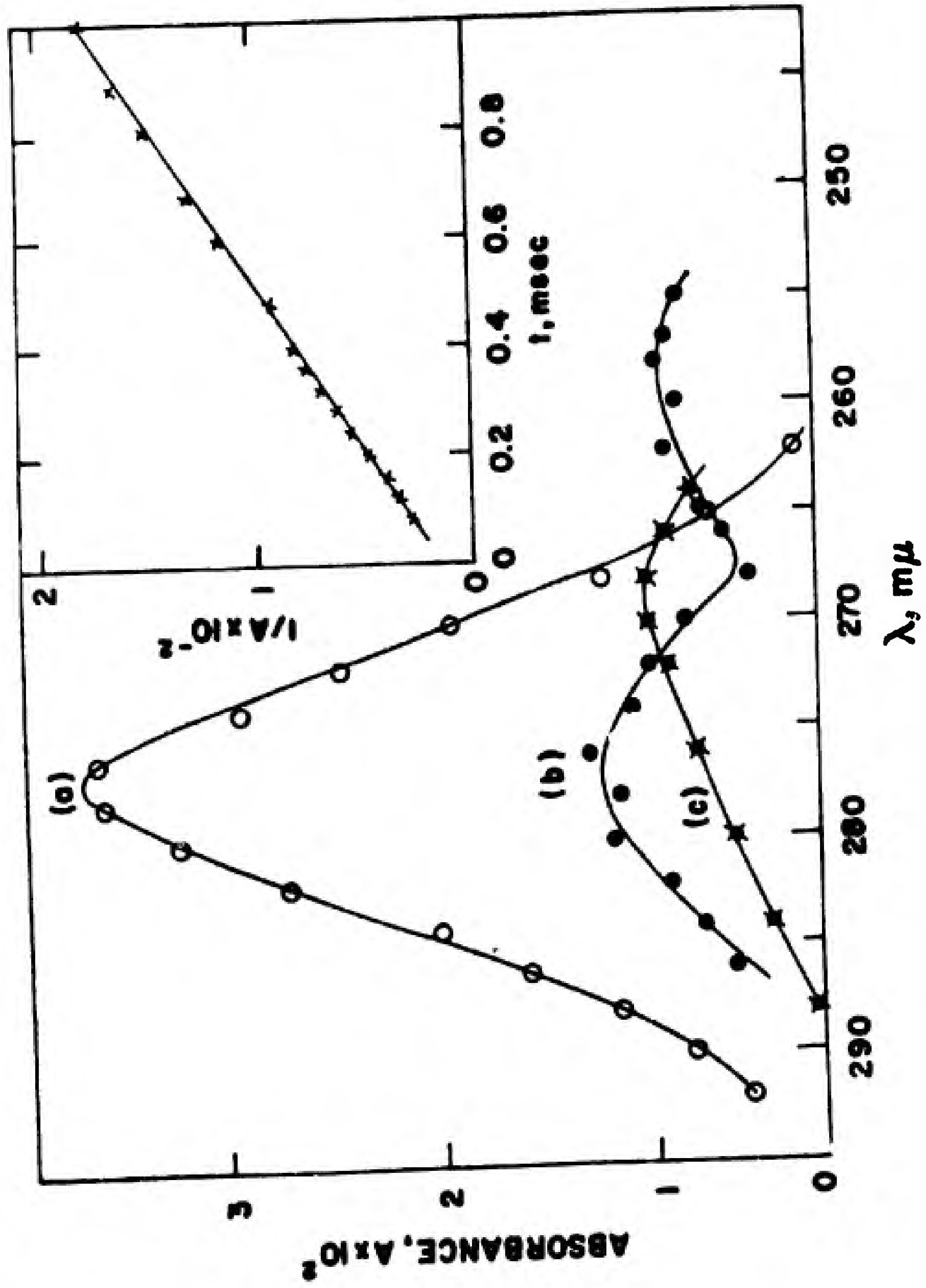
ABSORBANCE, A×10²
0
1
2
3
λ, mμ
250
260
270
280
290
(a)
(b)
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1/A ×10⁻²
0
1
2
t, msec
0
0.2
0.4
0.6
0.8

FIGURE I

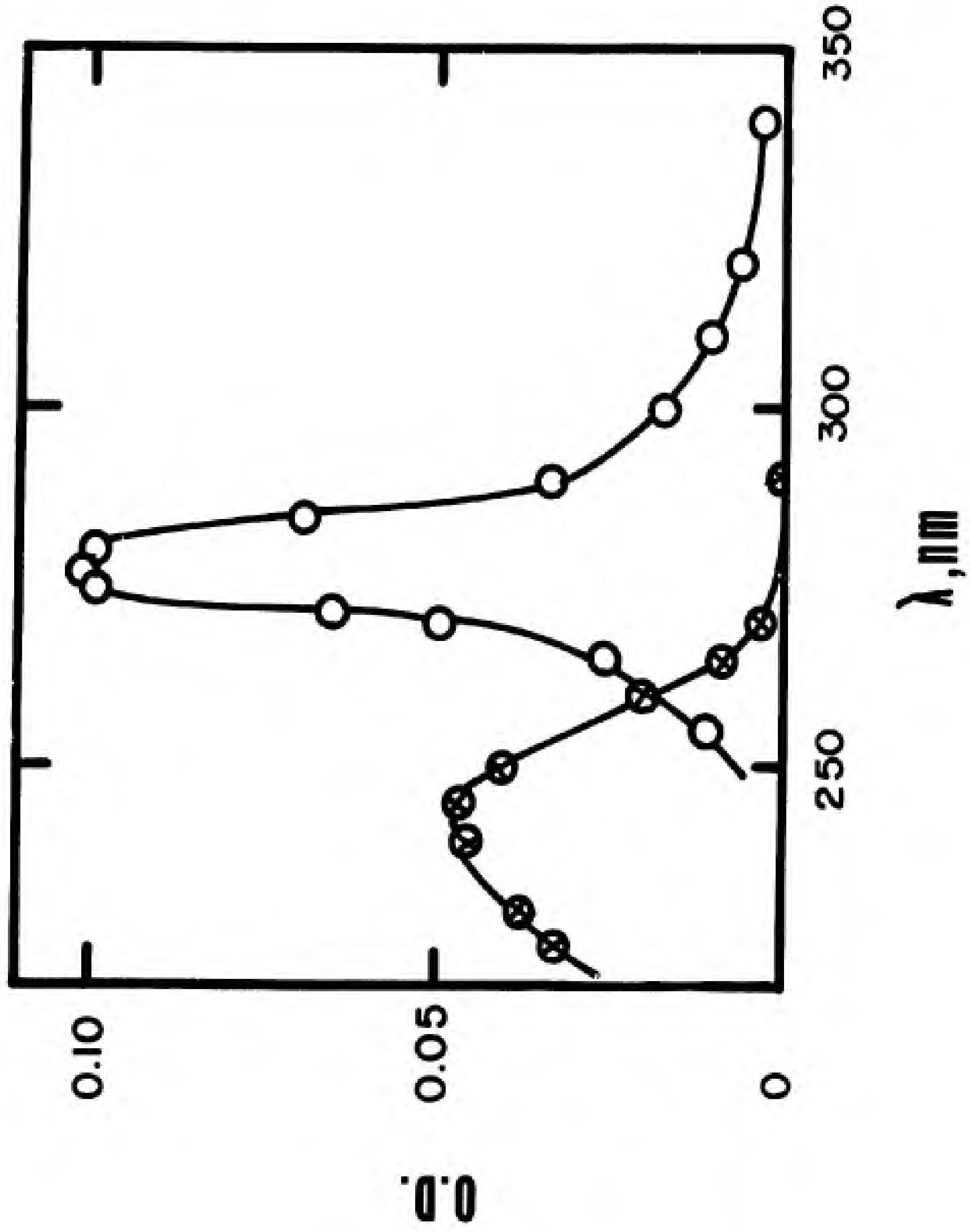


FIGURE II

PROPERTIES OF THE AZIDE RADICAL

The azide ion (2) 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, the N_3 radical can be said to resemble closely N_3^-. The N_3 radical is also isoelectronic with the ion CO_2^+ and is therefore expected to be linear and symmetrical, with an inverted $^2\pi_g$ ground state. This also follows from the calculations of Walsh (17) who showed that triatomic groups with sixteen or less valence electrons will be linear in their ground state.

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

$$N_3 + N_3^- \rightleftharpoons N_6^- \qquad (5)$$

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

The azide radical shows (11) high chemical reactivity. Its apparent yield and decay rate were sensitive to impurities. It was found to react with hydroxylamine, and more slowly with alcohols. These reactions lead to an electron transfer with the regeneration of the N_3^- ion. The $N_3\cdot$ radical does not, however, appear to react with O_2.

Decay Kinetics of the Azide Radical. The azide radical produced under pulse radiolysis conditions decays by a second-order process with $2k = 9.0 \pm 1.0 \times 10^9 M^{-1} sec^{-1}$ (12), in excellent agreement with the value of $9.2 \times 10^9 M^{-1} sec^{-1}$ obtained (11) from flash photolysis work.

Concomitant with the second-order decay of the N_3 radical is the formation of another intermediate with λ_{max} at 242nm, see Fig. 2. The rate of formation of this new species X could be observed. It was produced by a second-order process with $2k = 6.2 \times 10^6 \epsilon_{242}\ M^{-1}sec^{-1}$

$$2N_3 \longrightarrow X \tag{6}$$

Assuming this mechanism, $\epsilon_{242} = 2.1 \times 10^3 M^{-1}cm^{-1}$ and the rate of formation of X becomes $2k = 1.3 \times 10^{10} M^{-1}sec^{-1}$. This is in good agreement with the rate of decay of N_3 radicals at 278nm, supporting reaction 6.

The intermediate X was found to decay by a first-order process, with $k = 3.6 \times 10^3 sec^{-1}$. The yield of nitrogen gas produced was determined and found (12) to be stoicheometrically equivalent to the yield of the initially-formed N_3 radicals. This material balance suggests, therefore, that the intermediate X decays to give nitrogen according to

$$X \longrightarrow 3N_2 \tag{7}$$

Reaction 7 is a unimolecular process and indeed the decay of X is also a first-order reaction.

The decomposition of the $N_3\cdot$ radical in the ground state into N_2 and N atom requires activation energy (1), since this simple dissociation is forbidden by the spin conservation rules:

$$N_3\ (^2\pi_g) \not\longrightarrow N_2(^1\Sigma_g^{\ +}) + N\ (^4S_{3/2}) \tag{8}$$

with $\Delta H = 7.5 \pm 3$ kcal/mole. On the other hand dissociation of N_3 into an excited state $N(^2D)$ is allowed, but this requires 62 kcal/mole (1). Therefore the unimolecular decomposition of N_3 is probably not important at normal temperatures. The reaction between two azide radicals is not forbidden by spin conservation rules and, thermochemically, is highly favorable:

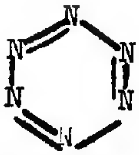
$$2N_3\ (^2\pi_g) \longrightarrow 3N_2\ (^1\Sigma_g^{\ +}) \tag{9}$$

with $\Delta H = -210 \pm 6$ kcal/mole.

It is suggested, therefore, that the nature of the intermediate X is N_6. The structure of N_6 could be either extended or cyclic

$N = N - N = N - N = N$

Extended



Cyclic

The following can be said 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, $\lambda_{max} \sim 255$nm and $\epsilon_{255} \sim 200\ M^{-1}cm^{-1}$.

(c) The electrolysis of aqueous solutions of $^{14}N^{15}N^{14}N$ gave (18) no $^{15}N_2$ but $^{14}N_2$ plus $2^{14}N^{15}N$.

The initial structure of N_6 could also be extended, similar to that of 1,3,5-hexatriene $H_2C = CH - CH = CH - CH = CH_2$ which has absorption maxima at 251, 244, 241 and 234nm, and $\epsilon \sim 6000M^{-1}cm^{-1}$ (19). Optical excitation of hexatriene has been found (19) to produce benzene and other cyclic products. It is possible that the exothermicity of reaction 9 could induce the cyclization of the extended N_6 structure.

Alternatively, it could be argued that the decay of N_3 could give rise to

$$2N_3 \xrightarrow{k_a} N_6 \xrightarrow{k_b} N_2 + N_4 \qquad (10)$$

if the intermediate X is N_4, the kinetics require that $k_b \gg k_a$. However, the isotopic distribution of nitrogen in the electrolysis experiments (18) cannot differentiate between reactions 10 and 11

$$N_6 \longrightarrow 3N_2 \qquad (11)$$

CONCLUSIONS

This work has, for the first time, detected and observed the azide radical in condensed phase, produced by both photolytic and radiolytic reactions. In addition to the spectral absorption properties of N_3, information was obtained on the chemical properties of this radical as well as on the decay kinetics. The highly exothermic reaction

$$2N_3\ (^2\pi_g) \longrightarrow N_6 \longrightarrow 3N_2(^1\Sigma_g+) \qquad (12)$$

with $\Delta H = -210 \pm 6$ kcal/mole is the reaction which is considered (1) important in the decomposition of solid ionic azides. The observation of the short-lived intermediate N_6 provides support for this process.

The role of N_3 in the explosion and detonation decomposition of azide crystals has still to be determined. The electronic energy levels of the heavy metal azides have to be established more clearly in order to relate them with the activation energies for thermal and photochemical decomposition. The total energy required to promote an electron from the full band to the conduction band diminishes, for example, for CuN_3 compared to KN_3 i.e. less energy is required to produce an N_3 radical in CuN_3.

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LEGEND TO FIGURES

Fig. 1. Transient absorption spectra produced by flash photolysis of NaN_3 at pH 9.4 in oxygen-free aqueous solutions. Curves (a) and (b): 10^{-4} NaN_3 read at 120 μsec and 400 μsec, respectively, after start of flash. Curve (c) $2 \times 10^{-3}M$ NaN_3, with 1% acetic acid cut-off filter, read at 250 μsec after the flash. Insert: Second-order decay plot of N_3 radical at 280nm.

Fig. 2. Transient absorption spectra produced by pulse radiolysis of 1 mM NaN_3 in aqueous solution at pH 9.2. Absorbances measured at 0.1 μsec (O, N_3 radical) and 10.0 μsec (⊗, N_6 intermediate) after a 30 nsec single pulse of electrons.

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