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FORMATION AND REACTIONS OF AZIDE RADICALS

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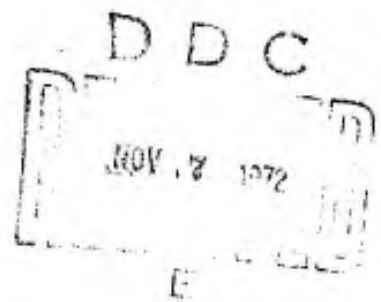
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FORMATION and REACTIONS OF AZIDE RADICALS

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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  $2000\text{\AA}$  was discharged in  $\sim 12\mu\text{sec}$ .

The pulse radiolysis apparatus used has also been described (10). Single pulses of electrons of  $\sim 2.3$  MeV energy and  $\sim 30$  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  $\sim 25$  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  $\sim 280$  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

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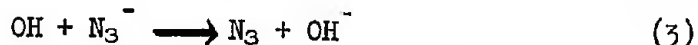
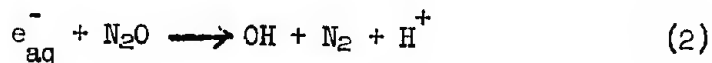
transitions as indicated by the absorption spectrum of  $N_3^-$  ions (14): an  $n, \pi^*$  ( ${}^1\Delta_u - B_2$ ) internally excited state below a charge-transfer-to-solvent (CTTS) state. The photolysis at 2537Å of  $N_3^-$  in aqueous solution is governed by the  $n, \pi^*$  state. Photoionization appears to occur only at wavelengths below  $\sim 230$  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  $\lambda_{max} \sim 710$  nm.



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

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:



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  $\lambda_{max} \sim 272$ nm, 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  $\sim 269$ nm 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

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

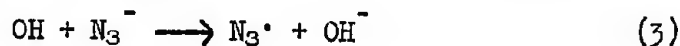
The azide ion has a relatively low reactivity with solvated electrons. However, under appropriate conditions it is possible that the  $N_3^{2-}$  radical anion could be produced



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:



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  $\lambda_{\text{max}} = 278\text{nm}$  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  $N_3^{\cdot}$  was determined (12) to be  $\epsilon_{278} = 2.3 \times 10^3 \text{M}^{-1}\text{cm}^{-1}$ .

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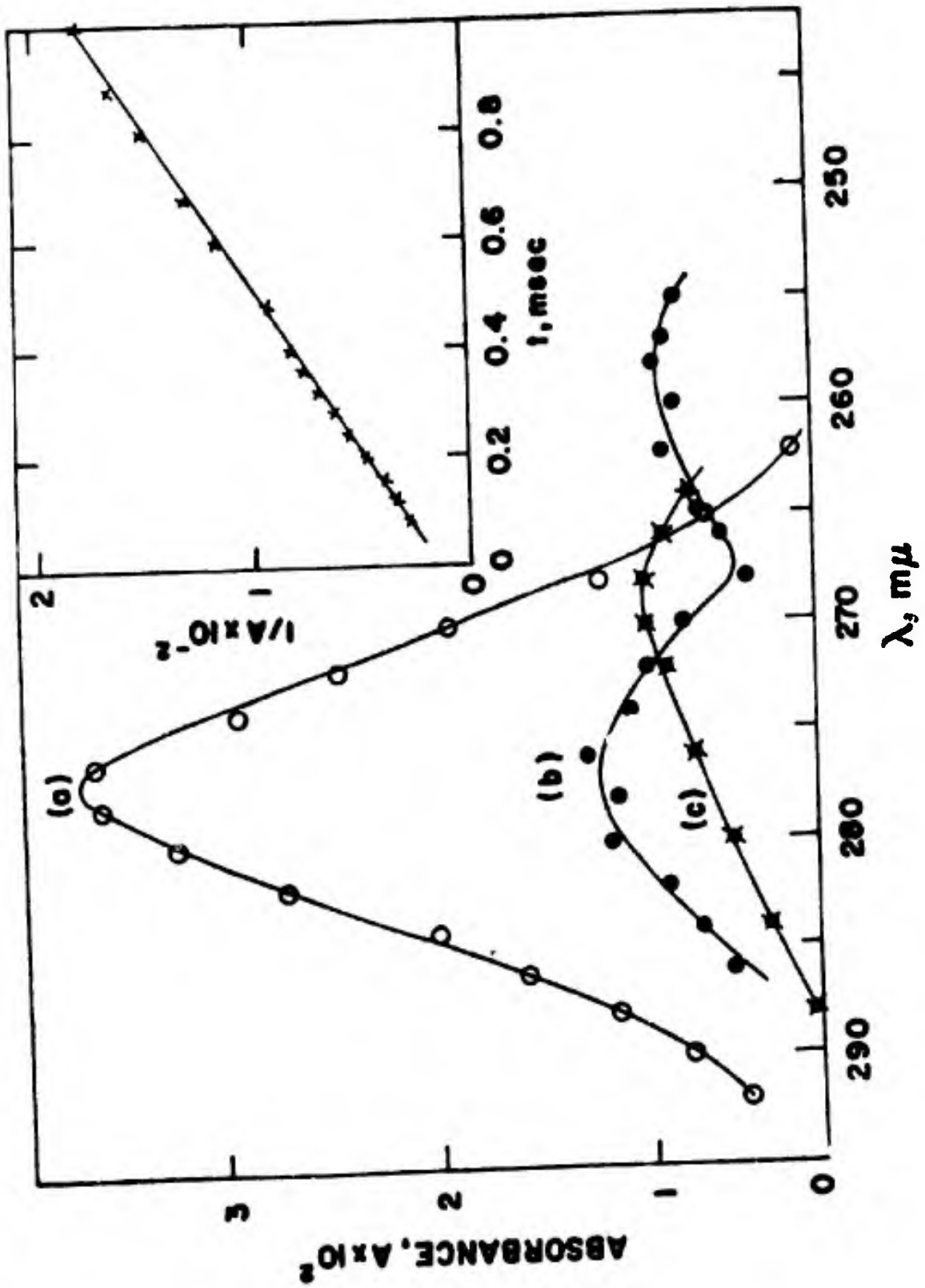


FIGURE I

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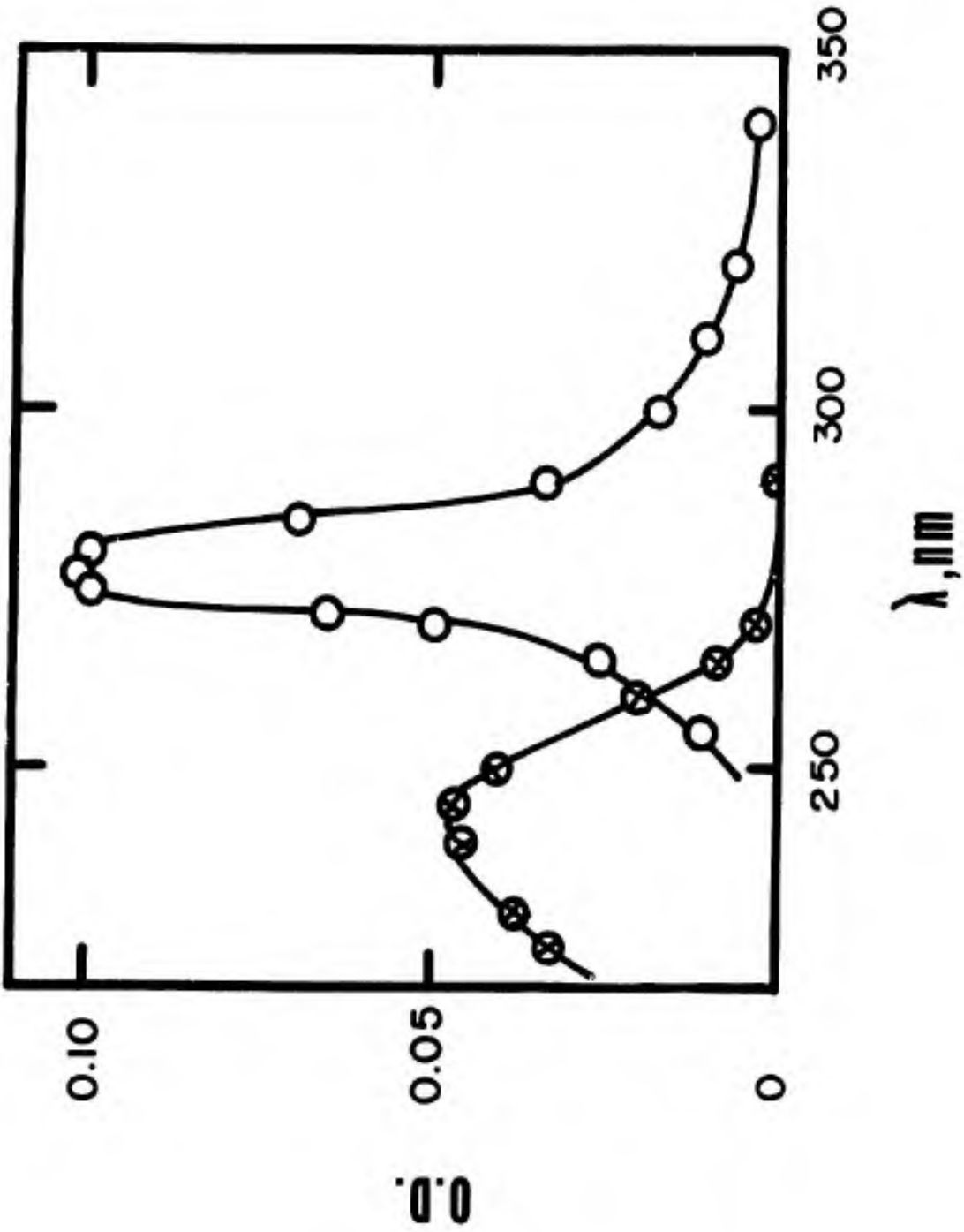


FIGURE II

## 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  $N_3^-$  radicals.



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.



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Concomitant with the second-order decay of the  $N_3$  radical is the formation of another intermediate with  $\lambda_{\max}$  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  $2k = 6.2 \times 10^6 \epsilon_{242} M^{-1} \text{sec}^{-1}$



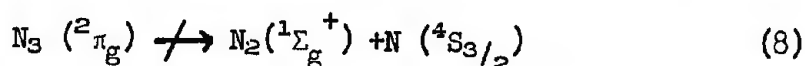
Assuming this mechanism,  $\epsilon_{242} = 2.1 \times 10^3 M^{-1} \text{cm}^{-1}$  and the rate of formation of X becomes  $2k = 1.3 \times 10^{10} M^{-1} \text{sec}^{-1}$ . This is in good agreement with the rate of decay of  $N_3$  radicals at 278nm, supporting reaction 6.

The intermediate X was found to decay by a first-order process, with  $k = 3.6 \times 10^3 \text{sec}^{-1}$ . The yield of nitrogen gas produced was determined and found (12) to be stoichiometrically 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

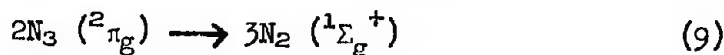


Reaction 7 is a unimolecular process and indeed the decay of X is also a first-order reaction.

The decomposition of the  $N_3$  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:



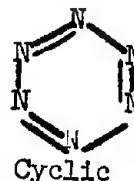
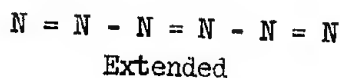
with  $\Delta H = 7.5 \pm 3$  kcal/mole. On the other hand dissociation of  $N_3$  into an excited state  $N(^2D)$  is allowed, but this requires 62 kcal/mole (1). Therefore the unimolecular decomposition of  $N_3$  is probably not important at normal temperatures. The reaction between two azide radicals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



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

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The following can be said in support of a cyclic structure, similar to that of the benzene ring:

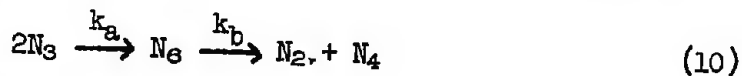
(a) The nitrogen atom is isoelectronic with the  $-\text{CH}-$  radical, and this endows it with similar physical properties of molecular symmetry and structure;

(b) The absorption maximum of  $\text{N}_6$  is close to the first absorption band of benzene,  $\lambda_{\text{max}} \sim 255\text{nm}$  and  $\epsilon_{255} \sim 200 \text{ M}^{-1}\text{cm}^{-1}$ .

(c) The electrolysis of aqueous solutions of  $^{14}\text{N}^{15}\text{N}^{14}\text{N}$  gave (18) no  $^{15}\text{N}_2$  but  $^{14}\text{N}_2$  plus  $2^{14}\text{N}^{15}\text{N}$ .

The initial structure of  $\text{N}_6$  could also be extended, similar to that of 1,3,5-hexatriene  $\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH} = \text{CH}_2$  which has absorption maxima at 251, 244, 241 and 234nm, and  $\epsilon \sim 6000 \text{ M}^{-1}\text{cm}^{-1}$  (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  $\text{N}_6$  structure.

Alternatively, it could be argued that the decay of  $\text{N}_3$  could give rise to



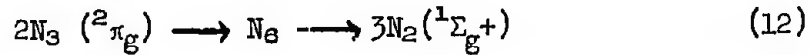
if the intermediate X is  $\text{N}_4$ , the kinetics require that  $k_b \gg k_a$ . However, the isotopic distribution of nitrogen in the electrolysis experiments (18) cannot differentiate between reactions 10 and 11



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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



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  $N_3$  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  $CuN_3$ .

Acknowledgment: This work was carried out in collaboration with Dr. M. Simic and Dr. A. Treinin.

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LEGEND TO FIGURES

- Fig. 1. Transient absorption spectra produced by flash photolysis of  $\text{NaN}_3$  at pH 9.4 in oxygen-free aqueous solutions. Curves (a) and (b):  $10^{-4}$   $\text{NaN}_3$  read at 120  $\mu\text{sec}$  and 400  $\mu\text{sec}$ , respectively, after start of flash. Curve (c)  $2 \times 10^{-3}\text{M}$   $\text{NaN}_3$ , with 1% acetic acid cut-off filter, read at 250  $\mu\text{sec}$  after the flash. Insert: Second-order decay plot of  $\text{N}_3$  radical at 280nm.
- Fig. 2. Transient absorption spectra produced by pulse radiolysis of 1 mM  $\text{NaN}_3$  in aqueous solution at pH 9.2. Absorbances measured at 0.1  $\mu\text{sec}$  (O,  $\text{N}_3$  radical) and 10.0  $\mu\text{sec}$  (⊗,  $\text{N}_3$  intermediate) after a 30 nsec single pulse of electrons.

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