Intermediates Produced from the One-Electron Oxidation of Hydrazine. Evidence for the Formation and Decay of Tetrazane and Triazene

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Abstract: The nature of the intermediates produced from the one-electron oxidation of hydrazine by hydroxyl radicals has been studied using the technique of pulse radiolysis. The reactivity of hydrazine toward attack by OH radicals was found to be dependent on the state of protonation of the molecule: $k(\mathrm{OH} + \mathrm{N_2H_5^+}) = 1.0 \times 10^9\ M^{-1}\ \mathrm{sec^{-1}}$ and $k(\mathrm{OH} + \mathrm{N_2H_4}) = 1.4 \times 10^{10}\ M^{-1}\ \mathrm{sec^{-1}}$. This reaction produces at pH 9.0 an intermediate which is assigned to the hydrazyl radical $\cdot\mathrm{N_2H_3}$, with an absorption maximum at 230 nm (ϵ_{230} $3.5 \times 10^3\ M^{-1}\ \mathrm{cm^{-1}}$) and a second-order decay $2k = 2.4 \times 10^9\ M^{-1}\ \mathrm{sec^{-1}}$. In neutral and acidic solutions the transient absorption changes and is suggested to result from the acid-base equilibrium of the radical, $\mathrm{p}K(\cdot\mathrm{N_2H_4^+} \rightleftharpoons \cdot\mathrm{N_2H_3} + \mathrm{H^+}) = 7.1 \pm 0.1$. The second-order decay of the hydrazyl radical is postulated to form tetrazane, N_4H_6. A first-order formation of an intermediate with $\lambda_{\max}$ 225 nm (ϵ_{225} $2.8 \times 10^3\ M^{-1}\ \mathrm{cm^{-1}}$) and $k = 8.5 \times 10^2\ \mathrm{sec^{-1}}$ at pH 9.2 is assigned to triazene, N_3H_3. Triazene and ammonia are produced from the unimolecular decomposition of tetrazane. The rate of formation of triazene is pH dependent, and the results suggest the presence of single- and double-protonated forms of tetrazane. From the change in the absorption spectrum of triazene a $\mathrm{p}K\ (\mathrm{N_3H_4^+} \rightleftharpoons \mathrm{N_3H_3} + \mathrm{H^+}) = 7.0 \pm 0.2$ was found. Triazene decays by first-order kinetics, presumably to produce ammonia and nitrogen as required from the stoichiometry of the measured products. The decay rate is markedly dependent upon pH indicating, in part, a more rapid dissociation of the protonated form $N_3H_4^+$. Similar results have been observed for 1,1- and 1,2-dimethylhydrazine. The reactivity of hydrated electrons with hydrazine and various methyl-substituted derivatives was found to be strongly dependent on *both* the state of protonation of the molecule and the acid strength of the hydrazines.

Hydrazine is isoelectronic with hydroxylamine and hydrogen peroxide and shares with them a number of properties. It can be both oxidized and reduced, but N_2H_4 is the most powerful reducing agent of the three and H_2O_2 the most active oxidizing agent. One-electron oxidation of hydrazine (*e.g.*, by one-electron transfer agents Fe^{3+}, Cu^{2+}) converts hydrazine into ammonia and nitrogen, while two-electron transfer agents (*e.g.*, ClO_3^-, IO_3^-, H_2O_2) produce hydrazoic acid as well as NH_3 and N_2.[2]

Higginson[3] and Cahn and Powell[4] investigated the products, kinetics, and mechanism of the reaction between hydrazine and Fe^{3+} ions in acid solution. The mechanism proposed for the one-electron oxidation of $N_2H_5^+$ was based on the formation of the hydrazyl radical, $\cdot N_2H_3$, as the primary intermediate. The products NH_3 and N_2 were postulated to occur *via* the formation and decay of tetrazane, N_4H_6, and/or diimide N_2H_2. No direct evidence for the existence of the intermediates $\cdot N_2H_3$, N_4H_6, N_2H_2, or N_3H_3 in solution is presently available. The $\cdot N_2H_4^+$ radical cation[5] has been observed in aqueous solution (esr spectrum, produced in a flow solution containing Ce^{4+}, $N_2H_5^+$, H_2SO_4), as well as the protonated diimide $N_2H_3^+$.[6]

In gas-phase experiments, Foner and Hudson[7] prepared by thermal or electrodeless discharge decomposition of hydrazine the intermediates $\cdot N_2H_3$, N_2H_2, N_3H_3, and N_4H_4, which were identified by their mass spectrum. A yellow compound believed to be N_4H_6 was prepared[8] by pyrolysis of hydrazine and trapped at 77°K. The $\cdot N_2H_3$ radical has been reported[9] in the flash phtoolysis of hydrazine vapor. The vacuum uv photochemistry of gaseous N_2H_4 has also been investigated.[10]

The radiation chemistry of aqueous solutions of hydrazine has been studied.[11–13] Hydrogen, nitrogen, and ammonia have been determined as the major products of the reaction of OH radicals and e_{aq}^- with N_2H_4. These results will be discussed below.

In this work, the fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry has been used to produce and observe the intermediates formed in the one-electron oxidation of hydrazine in aqueous solution. The hydroxyl radical, produced from the radiolysis of water, has been used as the one-electron oxidizing agent.

Experimental Section

Experimental details of the pulse radiolysis set-up used have been described.[14] Single pulse of 2.3 MeV electrons and ~30-nsec

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(2) For a general review, see, *e.g.*, F. Bottomley, *Quart. Rev., Chem. Soc.*, **24**, 617 (1970); L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," Wiley, New York, N. Y., 1951.

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Table I. Rate Constants for Reaction of OH Radicals and e_{aq}^- with Hydrazines in Aqueous Solution

Solute	pK^a	$k(e_{aq}^- + S)$, M^{-1} sec$^{-1\,b}$	$k(OH + S)$, M^{-1} sec$^{-1\,b}$
H_2NNH_2	8.07	2.2×10^8 (pH 6.0)	1.0×10^9 (pH 6.0)
		2.3×10^6 (pH 10.5)	1.4×10^{10} (pH 10.0)
CH_3HNNH_2	7.87	1.4×10^9 (pH 5.5)	
		6.5×10^6 (pH 12.0)	
$CH_3HNNHCH_3$	7.52	2.3×10^9 (pH 5.6)	7.2×10^8 (pH 3.5)
		6.1×10^6 (pH 12.4)	1.4×10^{10} (pH 10.1)
$(CH_3)_2NNH_2$	7.21	5.8×10^9 (pH 5.6)	8.1×10^8 (pH 3.5)
		2.4×10^7 (pH 12.0)	1.6×10^{10} (pH 9.7)
$(CH_3)_2NNHCH_3$	6.56	1.3×10^{10} (pH 5.4)	
		$\sim 10^8$ (pH 10.4)	

[a] From ref 16. [b] Rate constant values to ±15%. The $k(OH + S)$ rate determined *vs.* KCNS, taking $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}. The pH values at which determinations were made are given in parentheses.

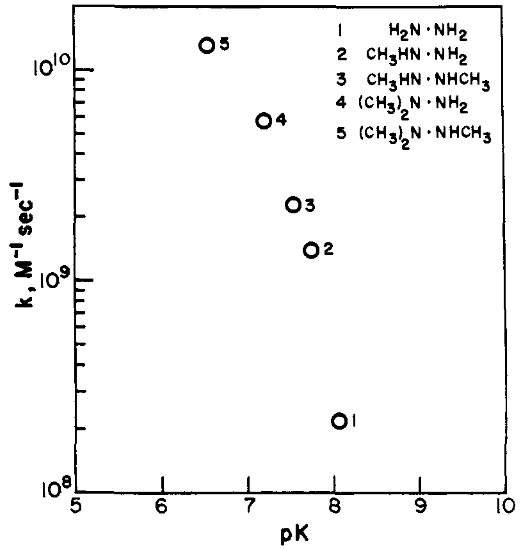

Figure 1. Plot of the rate constant for the reaction of e_{aq}^- with protonated hydrazines *vs.* the pK of the hydrazines.

duration were provided by the Febetron 705 machine (Field Emission Corp.). A 450-W xenon lamp was pulsed for ~1.5 msec to increase the light output by a factor of ~20–25. A double monochromator reduced the scattered light in the wavelength region below 280 nm.

The water used was purified by triple distillation, radiolysis, and photolysis. Reagent grade hydrazine sulfate was supplied by Baker and Adamson; 1,1-dimethylhydrazine by Matheson Coleman and Bell; 1,2-dimethylhydrazine by Aldrich; methylhydrazine sulfate by Eastman. Trimethylhydrazine was prepared in the laboratory.

Perchloric acid, borate, phosphates, and potassium hydroxide were used as buffers. Absorbances were measured at ~0.1 μsec after the electron pulse. Extinction coefficients were derived taking $G(e_{aq}^-) = G(OH) = 2.8$.

Results

The primary species produced in the radiation chemistry of water and aqueous solutions are the OH radicals, hydrated electrons, and H atoms

$$H_2O \rightsquigarrow OH\ (2.8),\ e_{aq}^-\ (2.8),\ H\ (0.55),\ H_2\ (0.45),\ H_2O_2\ (0.71)$$

where the numbers in parentheses are the G values, *i.e.*, the yields produced per 100 eV of energy absorbed by the water. One-electron oxidation reactions initiated by OH radicals can be studied in the absence of e_{aq}^-, by converting the latter into OH radicals in presence of N_2O (1 atm, $\sim 2.5 \times 10^{-2}$ M)

$$e_{aq}^- + N_2O \longrightarrow OH + N_2 + OH^- \qquad (1)$$

where $k_1 = 5.6 \times 10^9$ M^{-1} sec^{-1}.[15]

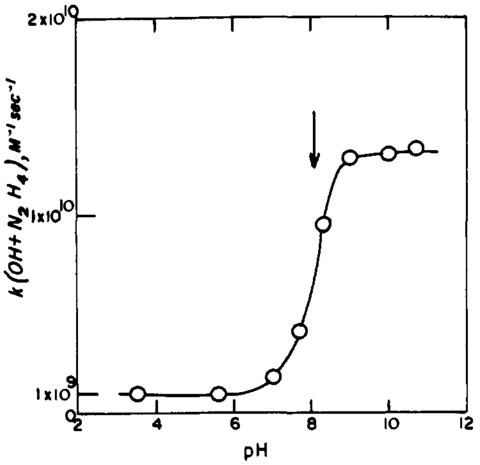

Figure 2. Dependence upon pH of the rate constant for the reaction of OH radicals with hydrazine. Absolute rate derived using the thiocyanate method, taking $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}.

In order to establish complete conversion of e_{aq}^- to OH radicals, *via* reaction 1, in solutions containing hydrazines, the absolute rates of reaction e_{aq}^- with hydrazine and various methyl-substituted hydrazines were determined. This was done by observing the pseudo-first-order decay of e_{aq}^- at 700 nm in the presence of various known concentrations of the hydrazines. These rates were determined for the protonated and unprotonated hydrazines, based on the known[16] pK values for these molecules. The results are presented in Table I and are plotted as a function of the pK value of the various hydrazines in Figure 1. A very marked dependence on both the state of protonation *and* the pK value of the hydrazines was observed. These results will be discussed below.

The rates of reaction of OH radicals with hydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine were determined relative to KCNS, taking $k(OH + CNS^-) = 1.1 \times 10^{10}$ M^{-1} sec^{-1}. Figure 2 shows the pH dependence of the rates of k(OH + hydrazine). This "titration curve" gives a pK = 8.1 ± 0.1 for hydrazine, in excellent agreement with the literature value[16] of 8.07. Table I gives these rates for the three hydrazines. No significant difference was observed between the hydrazines for the rates of reaction with OH radicals. A factor of 10–20 was, however, found between the re-

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Table II. Absorption Maxima, Extinction Coefficients, Decay Rates, and Dissociation Constants of the Intermediates Produced from the One-Electron Oxidation of Hydrazines by OH Radicals, in Aqueous Solutions

System	pH	Suggested intermediate	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	$2k$, M^{-1} sec^{-1}	pK Solute	pK Intermediate
Hydrazine	2.0	$\dot{N}_2H_4^+$	<225	1.5×10^3 [a]	6.0×10^8	8.07	7.1 ± 0.1
	9.2	N_2H_3	230	3.5×10^3	2.4×10^9		
	13.4	$\dot{N}_2H_3$	230	3.5×10^3	2.6×10^9		
	3.7	$N_3H_4^+$	<220	1.4×10^3 [b]	c		7.0 ± 0.2
	9.2	N_2H_3	225	2.8×10^3	c		
1,1-Dimethyl-hydrazine	9.8	d	245	3.9×10^3	6.0×10^8 [e]	7.21	7.9 ± 0.1

[a] At 225 nm. [b] At 220 nm. [c] See Table III. [d] Mixture of $\dot{C}H_3(CH_2)NNH_2$ and $(CH_3)_2N\dot{N}H$ radicals. [e] Measured at 300 nm.

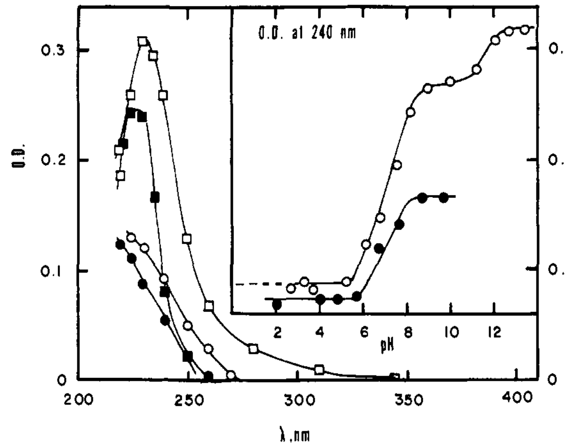

Figure 3. Absorption spectra of intermediates produced by the reaction of OH radicals with hydrazine (20 mmol) in the presence of N_2O (1 atm). Absorbances measured at ~0.1 μsec after a 30-nsec pulse (at pH 9.2, □; and pH 3.7, ○), at 50 μsec (at pH 3.7, ●) and at 10 msec (at pH 9.2, ■). Insert: OD_{240} *vs.* pH (read at 0.1 μsec, ○), and OD_{237} *vs.* pH (read at 10 msec, ●). Total dose ~8.0 krads/pulse.

activity of the protonated and unprotonated forms of the hydrazines. These results attest to the electrophilic nature of the OH radicals. Identical observations were recently found for the dependence of the rates of reaction of OH radicals upon the state of protonation of hydroxylamines[17] and aliphatic amines.[18] In all these cases the OH radicals react much more slowly with the protonated forms.

The intermediates produced in the one-electron oxidation of hydrazine by OH radicals were observed on pulse radiolysis of aqueous solutions of 20 m*M* hydrazine in the presence of N_2O (1 atm). At pH 9.2, an initial transient optical absorption with λ_{max} 230 nm was observed; see Figure 3. This intermediate is produced from the reaction of OH radicals with hydrazine and is assigned to the hydrazyl radical $\cdot N_2H_3$.

$$OH + N_2H_4 \longrightarrow \cdot N_2H_3 + H_2O \qquad (2)$$

This is the first observation of this radical in solution. Its extinction coefficient is ϵ_{230} 3.5×10^3 M^{-1} cm^{-1} and it decays by second-order kinetics with $2k = 2.4 \times 10^9$ M^{-1} sec^{-1}. From these results, one cannot distinguish between an H-atom abstraction as compared to an electron-transfer reaction for the reaction of OH radicals with hydrazine, *viz.*, reactions 2 and 3.

$$OH + N_2H_4 \longrightarrow \cdot N_2H_4^+ + OH^- \qquad (3)$$

In acidic solutions at pH 3.7, a much weaker transient absorption is observed (Figure 3) immediately after the electron pulse, with a maximum below 225 nm. Since the absorption of this intermediate was considerably different from that observed at pH 9.2, the change with pH in the absorbance of this intermediate was monitored at 240 nm. The insert in Figure 3 shows the results obtained in the pH range 2.5–13.4. The first large step in the curve is attributed to the acid–base equilibrium of the hydrazyl radical

$$\cdot N_2H_4^+ \rightleftharpoons \cdot N_2H_3 + H^+ \qquad (4)$$

with a $pK = 7.1 \pm 0.1$. The second small step shows an increase of ~10% and is probably a result of the conversion of H atoms (produced from the radiolysis of water) into OH radicals *via* reactions 5 and 1 with

$$H + OH^- \longrightarrow e_{aq}^- \qquad (5)$$

$k_5 \sim 2 \times 10^7$ M^{-1} sec^{-1}. This increase corresponds to $G(H) \simeq {}^1/_{10}[G(e_{aq}^-) + G(OH)]$.

Based on these observations, the intermediate formed at pH 3.7 is assigned to the $\cdot N_2H_4^+$ radical, its extinction coefficient $\epsilon_{225} = 1.5 \times 10^3$ M^{-1} cm^{-1}, and it decays by a second-order process with $2k = 6.0 \times 10^8$ M^{-1} sec^{-1}. The lower decay rate of this transient is in agreement with the effect of charge on the reaction rate. The $\cdot N_2H_4^+$ radical has been shown[5] to have a planar structure with all hydrogens and both nitrogens equivalent.

Subsequent to the decay of the hydrazyl radicals, and at times which are dependent on the pH of the solution, the formation of a new transient absorption was observed (see Figure 3). The rate of formation of this intermediate does not correspond to the rate of decay of the hydrazyl radicals. There appears to be a gap in time between the decay of the initial transient (the hydrazyl radical) and the appearance of this new transient absorption. Furthermore, while hydrazyl radicals decay by second-order kinetics, the *formation* of this new intermediate follows first-order kinetics; see Tables II and III. The new transient absorption is therefore postulated to be produced from the unimolecular decomposition of an intermediate which does not absorb in this wavelength region.

Somewhat similar results and intermediates have been observed from the one-electron oxidation of 1,1-dimethylhydrazine (Figure 4) and 1,2-dimethylhydrazine (Figure 5) by OH radicals in aqueous solutions. In this case, the transient absorption bands might be due to more than one intermediate since H-atom abstrac-

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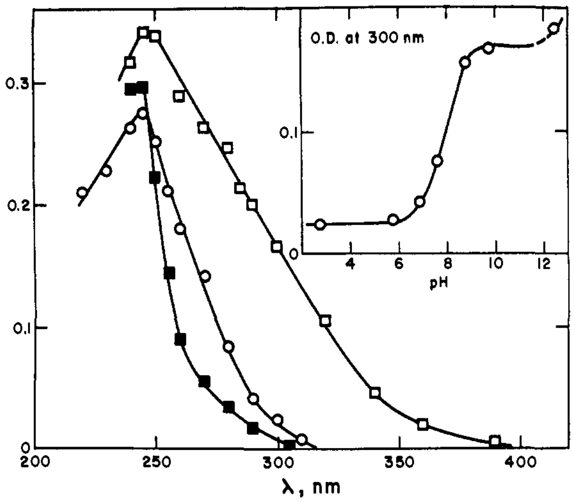

Figure 4. Absorption spectra of intermediates produced by the reaction of OH radicals with 20 mmol of 1,1-dimethylhydrazine in the presence of N_2O (1 atm). Absorbances measured at ~0.1 μsec (pH 9.8, ⊡; and pH 2.8, ⊙) and at 100 μsec (pH 9.8, ■) after the 30-nsec pulse, Insert: OD_{300} *vs.* pH, read at ~0.1 μsec. Total dose ~8.0 krads/pulse.

Table III. First-Order Rates of Formation and Decay of Triazene, N_3H_3, as a Function of pH, in Aqueous Solutions of Hydrazine (N_2O saturated)[a]

pH	Rate of formation, k, sec^{-1}, of triazene[b]	Rate of decay, k, sec^{-1}, of triazene
2.0		1.3×10^2
2.8		2.1×10^2
3.7		1.7×10^2
4.8		1.0×10^2
5.5		7.3×10^1
6.6		3.5
8.0	8.7×10^3	1.3×10^{-1}
9.2	8.5×10^2	3.6×10^{-2}
10.0	1.5×10^2	1.3×10^{-1}
10.8	3.0×10^1	7.6×10^{-1}
11.3	1.4×10^1	2.0

[a] Wavelength monitored 240 nm. [b] Rates of formation of N_3H_3 from the decay of tetrazane, N_4H_6. Hence, rates also correspond to the first-order decay of N_4H_6 in aqueous solution.

tion by OH radicals might occur at more than one site, *e.g.*

$$CH_3NH\overset{+}{N}H_2CH_3 \longrightarrow CH_3\overset{\cdot+}{N}NH_2CH_3 + H_2O \qquad (6a)$$

$$CH_3NH\overset{+}{N}H_2CH_3 \longrightarrow \dot{C}H_2NH\overset{+}{N}H_2CH_3 + H_2O \qquad (6b)$$

The extinction coefficients and decay kinetics of the intermediates observed are given in Table II.

Discussion

The primary intermediate produced from the one-electron oxidation of hydrazine by OH radicals is the hydrazyl radical. From the observed transient optical absorption spectrum of this radical (see Figure 3 and Table II), it was possible to distinguish between the protonated and unprotonated forms, $\cdot N_2H_4^+$ and $\cdot N_2H_3$, and to determine the dissociation constant of this radical as $pK(\cdot N_2H_4^+ \rightleftharpoons \cdot N_2H_3 + H^+) = 7.1 \pm 0.1$. This value is about one unit lower than the pK of hydrazine itself.

The bimolecular decay of hydrazyl radicals is postulated to yield the dimer, tetrazane, N_4H_6.

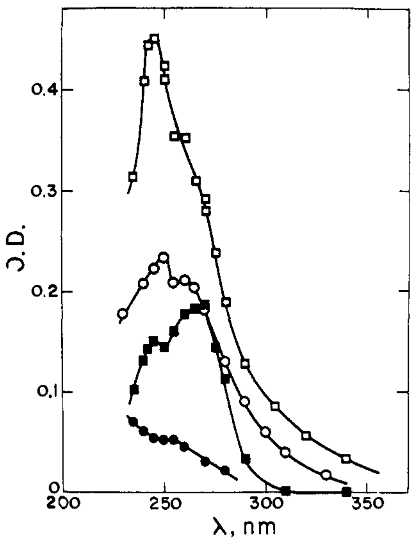

Figure 5. Absorption spectra of intermediates produced by the reaction of OH radicals with 10 mmol of 1,2-dimethylhydrazine in the presence of N_2O (1 atm). Absorbances measured at ~0.1 μsec (pH 10.1, ⊡; and pH 5.0, ⊙) and at 100 μsec (pH 10.1, ■; and pH 5.0, ●) after the 30-nsec pulse. Total dose ~8.0 krads/pulse.

$$2\cdot N_2H_3 \longrightarrow N_4H_6 \qquad (7)$$

$$2\cdot N_2H_4^+ \longrightarrow N_4H_8^{2+} \qquad (8)$$

This short-lived diamagnetic intermediate is a "saturated" molecule and is expected to absorb in the far-uv region, below ~220 nm. Under the present experimental conditions, the absorption of hydrazine and other experimental limitations would not allow one to observe it. Tetrazane, it is interesting to note, is the nitrogen analog of the often-postulated H_2O_4 or O_4^{2-} species.

Alternatively, the bimolecular decay of the hydrazyl radical could lead to a disproportionation with the formation of the diimide.

$$2\cdot N_2H_3 \longrightarrow N_2H_2 + N_2H_4$$

The diimide could then decompose to N_2 and H_2. Based on the stoichiometry[13] for the decomposition of hydrazine (see below) and the absence of an equivalent yield of hydrogen, it would appear that diimide is not produced in the one-electron oxidation of hydrazine.

Tetrazane is unstable in aqueous solution and is suggested to decay unimolecularly to produce an intermediate with an absorption maximum λ_{max} ~225 nm, at pH 9.2, Figure 3. This intermediate is assigned to triazene, N_3H_3, and its protonated forms. It was possible to observe the rate of formation of triazene, and in all cases this rate was found to be first order; see Table III and Figure 6.

Since the rate of decay of tetrazane (as observed from the rate of formation of triazene, Table III and Figure 6) is pH dependent in the range 8–11.5, it is suggested that it is doubly protonated, reactions 9 and 10.

$$N_4H_8^{2+} \rightleftharpoons N_4H_7^+ + H^+ \qquad (9)$$

$$N_4H_7^+ \rightleftharpoons N_4H_6 + H^+ \qquad (10)$$

It can be seen to be similar[19] to ethylenediamine which has pK's of 7.5 and 10.0. The rate of formation of

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[19] We thank Dr. D. Meyerstein for suggesting this comparison.

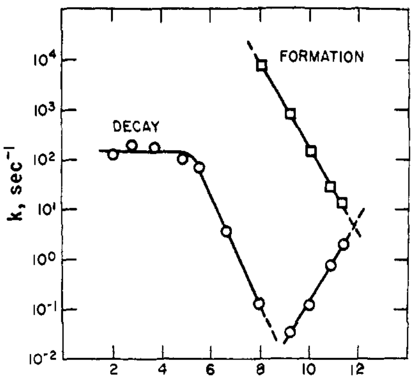

Figure 6. Dependence upon pH of the first-order rates for the formation (⊡, at 240 nm) and decay (⊙, at 240 nm) of triazene, N_3H_3. Triazene is formed from the decay of tetrazane, N_4H_6, which is produced by the reaction of OH radicals with hydrazine (see text).

triazene could not be determined below pH ~8.0, since in neutral and acidic solutions the doubly protonated tetrazane decayed too fast and at 240 nm could not be separated (due to overlap) from the decay of the hydrazyl radical. The two pK_a's of tetrazane could be in the range of 5–11 but are probably between 5 and 9.

The radiation chemistry of aqueous solutions of hydrazine produced[11–13] nitrogen and ammonia as the main products. Belloni and Haissinsky[13] clearly showed that the stoichiometry $2G(N_2) = G(NH_3) = G(-N_2H_4)$. These results indicate, therefore, that each molecule of tetrazane should produce two molecules of NH_3 and one molecule of N_2. The first-order formation of triazene from the decay of tetrazane leads to the formation of the first molecule of NH_3.

$$N_4H_8^{2+} \xrightarrow{H_2O} NH_3 + N_3H_4^+ + H_3O^+ \qquad (11)$$

The pH dependence of k_{11} supports the view that the formation of ammonia involves an intramolecular electron transfer, whose rate will be greater when the terminal amino groups of tetrazane are in their protonated forms. The singly protonated $N_4H_7^+$ decays at a lower rate to give also ammonia and triazene.

The absorption spectrum of triazene was found to be dependent upon the pH of the solution (see Figure 3). On monitoring this change at 237 nm, a pK = 7.0 ± 0.2 was observed (insert Figure 3) and is attributed to

$$N_3H_4^+ \rightleftharpoons N_3H_3 + H^+ \qquad (12)$$

The decay of triazene was found to follow first-order kinetics at all pH values (Table III and Figure 6). This rate was independent of pH in the range 2–5, with $k_{13b} \sim 2 \times 10^2$ sec^{-1}. In the pH range 5.0 to ~9.0, the rate of decay of triazene decreases considerably. This region closely parallels the pK region of triazene, indicating that the rate of the unimolecular decomposition of triazene is markedly dependent on the state of protonation of N_3H_3.

$$HN{=}N{-}NH_2 \overset{+H^+}{\rightleftharpoons} HN{=}N{-}\overset{+}{N}H_3 \rightleftharpoons$$

$$H_2\overset{+}{N}{=}N{-}NH_2 \overset{-H^+}{\rightleftharpoons} NH_2N{=}NH \qquad (13a)$$

$$N_3H_4^+ + H_2O \longrightarrow N_2 + NH_3 + H_3O^+ \qquad (13b)$$

Such a pH dependence again indicates that an intramolecular electron transfer probably takes place, which is favored when triazene is protonated, *i.e.*, $N_3H_4^+$.

The proposed mechanism and the yields of ammonia and nitrogen produced from the decay of tetrazane are in complete accord with the observed[3,4] isotopic composition of NH_3 and N_2 produced from $^{15}N_2H_4$: 50% of the molecular nitrogen produced had random isotopic composition and 50% had the same isotopic composition as that of the parent hydrazine.

At pH >9.0, the first-order decay of triazene increases again (Figure 6). At this pH triazene is probably present as N_3H_3. The yields of N_2, NH_3, and $-N_2H_4$ have been found[11,13] to decrease in this pH region, and it is not clear as to what is occurring. The increased decay rate of $HN{=}NNH_2$ in alkaline solution might be due to an OH^- ion-catalyzed hydrolysis, regenerating in part hydrazine.

The reported[8] yellow color due to N_4H_6 could not be observed under our experimental conditions. No other transient absorption could be seen in the wavelength region 350–800 nm. The yellow compound could be due to higher polymeric species. Triazene is also expected[20] to be yellow with a low-intensity absorption band.

As mentioned above, the intermediates produced from the one-electron oxidation of $(CH_3)_2NNH_2$ and $CH_3NHNHCH_3$ by OH radicals are somewhat more complex, since attack at more than one site can be expected. It is interesting to note, however, that the pK of the $(CH_3)_2\overset{+}{N}HNH$ radical (Figure 4) is ~ 7.9 ± 0.2, higher than the pK of $(CH_3)_2NNH_2$ = 7.21. Infrared data has shown[21] that the proton is attached to the nitrogen carrying both methyl groups, *i.e.*, $(CH_3)_2\overset{+}{N}HNH_2$.

For 1,1-dimethylhydrazine, the rate of formation of the corresponding triazene $HN{=}NN(CH_3)_2$ from tetramethyltetrazane is $k = 4.4 \times 10^3$ sec^{-1} at pH 9.8 and 9×10^1 sec^{-1} at pH 12.4. These values are higher than for the formation of N_3H_3. Here, instead of NH_3, dimethylamine is expected to be the corresponding product. The decay of $HN{=}NN(CH_3)_2$ also follows first-order kinetics with $k = 2 \times 10^{-2}$ sec^{-1} at pH 9.8 and 5×10^3 sec^{-1} at pH 12.4. These values were monitored at 250 nm.

For 1,2-dimethylhydrazine, the rate of formation of $HN{=}NNHCH_3$ is $k \sim 4 \times 10^2$ sec^{-1} at pH 10.1 and the rate of decay is $k = 7.5 \times 10^{-1}$ sec^{-1} at pH 5.2. These values were monitored at 250 nm.

In the alkyl-substituted hydrazines, beside the formation of substituted tetrazanes, a variety of intermediates and products could be produced from H-atom abstraction at the methyl groups.

Reaction of e_{aq}^- with Hydrazines

The hydrated electron has been clearly shown[11,13] to react with $N_2H_5^+$ and produce H_2 in yields equivalent to the yield of $G(e_{aq}^-)$. The mechanism is, however, not clear. The rate of reaction of H atoms with N_2H_4 must be relatively low, $k < 10^6$ M^{-1} sec^{-1} (see Figure 3), but no information is available for the rate of H atoms with $N_2H_5^+$. The following reactions are considered.

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(20) Suggested by a referee.

(21) R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 3151 (1963).

$$e_{aq}^- + N_2H_5^+ \longrightarrow H + N_2H_4 \qquad (14a)$$

$$e_{aq}^- + N_2H_5^+ \longrightarrow H_2 + \cdot N_2H_3 \qquad (14b)$$

$$H + N_2H_5^+ \longrightarrow H_2 + \cdot N_2H_4^+ \qquad (15)$$

The available results cannot distinguish between reactions 14a and 14b, and it should prove interesting to look for a competition for H atoms between reaction 15 and other added H-atom scavengers.

The marked dependence of the rate constant for reaction of e_{aq}^- with methyl-substituted hydrazine derivatives upon the state of protonation of the hydrazines and the dissociation constant are presented in Table I and Figure 1. Quantitatively, the electron affinity of these hydrazines does not correlate with the electron affinity of other inorganic protonic acids (*e.g.*, NH_4^+, $H_2PO_4^-$, $H_2PO_3^-$, NH_3OH^+). Presumably, in order to conform to the Brønsted relation the nature of the interaction (and therefore *primary* intermediates) between the hydrated electron and the inorganic acids must be similar.

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Electronic Spectra, Photochemistry, and Autoxidation Mechanism of the Sulfite–Bisulfite–Pyrosulfite Systems. The SO_2^-, SO_3^-, SO_4^-, and SO_5^- Radicals

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Abstract: The electronic spectrum and the photochemistry of the sulfite–bisulfite–pyrosulfite systems in solution were investigated. The effects of pH, concentration, and environment upon the electronic spectrum were studied, and information was derived on some thermodynamic properties of the system and on the nature of the electronic transitions involved. Above 190 nm only HSO_3^- displays a charge-transfer-to-solvent (CTTS) band, but there is efficient ionization of the SO_3^{2-} ion on excitation within its intramolecular transition. The chain oxidation of sulfite ions in solution can lead to fast removal of oxygen from the system thus permitting the observation of the strong transient absorption of e_{aq}^- in such "air-containing" solutions. A mechanism for the autoxidation is proposed: $SO_3^{2-} + h\nu \rightarrow SO_3^- + e_{aq}^- (+ O_2 \rightarrow O_2^-)$; $SO_3^- + O_2 \rightarrow SO_5^-$; $SO_5^- + SO_3^{2-} \rightarrow SO_4^- + SO_4^{2-}$; $SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^-$, and termination reactions of the radicals. Some of the species may be present in their acidic forms. This mechanism is based on results concerning the radicals SO_3^-, SO_4^-, and SO_5^-. Information on these radicals was obtained from the flash photolysis of SO_3^{2-} and $S_2O_6^{2-}$, and from the pulse radiolysis of SO_3^{2-}, $S_2O_8^{2-}$, and HSO_5^-. No direct evidence is presented for the role of SO_4^- radicals in the chain reaction, but it is inferred from the nature of the inhibition induced by alcohols (SO_3^- and SO_5^- are relatively inert to alcohols) and from the production of O_3^- in alkaline solutions. The photolysis of $S_2O_5^{2-}$ leads to the formation of SO_2^- radicals. The flash photolysis of $S_2O_5^{2-}$ has provided new information on this radical. A survey is presented on some of the properties of the oxyanions and oxyradicals of sulfur. The absorption maxima, extinction coefficients, decay kinetics, and reactivity of the radicals SO_2^-, SO_3^-, SO_4^-, and SO_5^- are included.

The photolysis and oxidation (both thermal and photochemical) of sulfite ions have long been considered to involve electron transfer as a primary process.[2–4] This view was strongly supported by flash photolysis work,[5] which revealed the transient absorption of SO_3^- radicals in the uv region. In parallel, a strong short-lived absorption appeared around 700 nm, which closely resembles that of solvated electrons.[5] However, its appearance in "oxygen-containing" sulfite solutions in both pulse radiolysis and flash photolysis experiments has led to its assignment to an electron adduct.[5,6] It was later suggested by Devonshire and Weiss[7] that the light-induced chain oxidation of sulfite can lead to the fast removal of O_2 from the solution, and that the 700-nm band is indeed due to solvated electrons. This has been verified by our preliminary experiments, which also indicate that e_{aq}^- is rather inert

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