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Electron Spin Resonance Studies of Cation Radicals Produced

during Oxidation of Methylhydrazines

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The radical cations of methylhydrazine (MH) and 1,1-dimethylhydrazine (DMH) were generated by reaction with cerium(IV) in sulfuric acid solutions in a fast-flow mixing chamber. The electron spin resonance (esr) spectra of these were recorded and experimental nitrogen and proton coupling constants were determined by simulation of the spectra. Under some conditions, oxidation of DMH led to the radical cation of tetramethyl-2-tetrazene. A brief discussion of molecular orbital calculations for these molecules and implications of this study to reaction mechanisms for the oxidation of the hydrazines is also given.

Extensive studies have been made on the mechanisms of the chemical and electrochemical oxidation of hydrazine and methyl-substituted hydrazines.[1-8] The mechanisms of the oxidations and the number of electrons transferred in the initial step, one or two, are very dependent upon the nature of the substituents on the hydrazine, the reaction conditions, and the oxidant. Adams and Thomas[9] and Falle[10] observed the cation radical of hydrazine, $N_2H_4^+$, formed by reaction of hydrazine and cerium(IV) in a 1 M H_2SO_4 medium in a rapid-flow system, by esr spectroscopy. This work provided unambiguous evidence for the existence of short-lived radical cation intermediates in the oxidation of hydrazine, itself. Observation of $N_2H_4^+$ by esr in the solid state has also been reported.[11,12] This study was undertaken to investigate whether radical cations of methylhydrazines could be formed under similar conditions and to provide information about the nature and stability of these radical ions. Flow-system studies of both methylhydrazine (MH) and 1,1-dimethylhydrazine (DMH) were carried out.
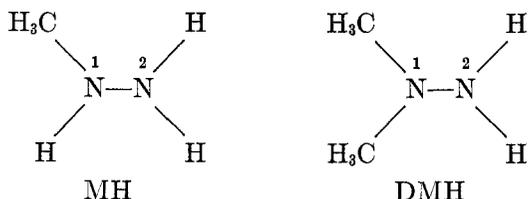
Results

Methylhydrazine. When MH was oxidized by flowing together a 0.1 M solution of ceric ammonium sulfate and a 0.2 M solution of MH, both 1 M in sulfuric acid, in a rapid-flow mixing chamber directly below the esr cell (essentially the same conditions and methods of Adams and Thomas),[9] only a very weak esr signal was observed. The spectrum consisted of several broad lines and had a total span greater than 100 G; the poor signal level and resolution prevented further identifi-

cation of the radical. Upon stopping the flow, this small signal disappeared and no further signal appeared. There is one complication in the application of stopped-flow systems to the study of hydrazines. Upon oxidation of the hydrazines nitrogen gas is vigorously evolved. Ordinarily the rapid-flow rate causes the bubbles to form outside of the esr cavity. However, when the flow is stopped, the bubbles form in the cavity pushing out the solution. This causes a decrease in signal because of the decrease in sample volume and especially detuning of the spectrometer because of the change of dielectric constant. However, there probably are no subsequent radicals formed upon decomposition of the initial radical species in concentrations high enough to be observed. A more intense spectrum was obtained upon decreasing the H_2SO_4 concentration. The spectrum in Figure 1a was obtained with 0.2 M solution of MH and a 0.2 M solution of cerium(IV) which was also 0.5 M in H_2SO_4. A better spectrum (Figure 1b) resulted from using a 0.44 M MH solution, and a 0.18 M cerium(IV) solution in 0.5 M H_2SO_4 with

(1) H. Wheland, "Die Hydrazine," Verlag F. Enke, Ed., Stuttgart, 1913.

(2) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," Wiley, New York, N. Y., 1951.

(3) C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., 1966.

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(8) M. Michlmayr and D. T. Sawyer, *J. Electroanal. Chem.*, **23**, 375 (1969).

(9) J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **39**, 1904 (1963).

(10) H. R. Falle, *Can. J. Chem.*, **46**, 1703 (1968).

(11) J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.*, **1965**, 6504.

(12) J. K. S. Wan, J. R. Morton, and H. J. Bernstein, *Can. J. Chem.*, **44**, 1957 (1966).

←H |———— 10 g. ————|

Figure 1. Esr spectra of methylhydrazine cation radical. (a) Top: experimental spectrum; the sweeping field is increasing from right to left. (b) Middle: experimental spectrum showing outer portion more clearly. (c) Bottom: calculated spectrum using constants given in Table I.

the flow rate of the MH solution somewhat larger than that of the cerium(IV) solution.

The spectrum can be interpreted as the cation radical, MH^+. The best simulation of the spectrum, based on the coupling constants in Table I, is shown in Figure 1c. The deviations between the simulation and the experimental spectrum arise from some nonlinearity of the magnetic field sweep and the fact that the spectrum arises from a large set of coupling constants of low multiplicity of about the same magnitude. This produces a spectrum with a central portion having a large number of lines of similar intensity, where any small changes in the coupling constants cause major changes in the appearance of the spectrum. The assigned coupling constants are those which give the best fit to the outer portion of the spectrum.

1,1-Dimethylhydrazine. When an aqueous solution of 0.23 M DMH was oxidized in a flow system by an aqueous solution of 0.15 M ceric ammonium sulfate–0.2 M H_2SO_4 solution, a new fairly strong signal was observed. A typical spectrum is seen in Figure 2a. More intense signals were obtained when the DMH flow rate was greater than that of the cerium(IV) solution. Adams and Thomas[9] and Falle[10] also employed hydrazine to ceric ion ratios of 2:1 in the generation of hydrazine cation radical, however, at H_2SO_4 concentrations at least five times as high. Upon halting the flow of reactants, the above signal disappeared and no further signals were observed.

This spectrum can be interpreted as the DMH cation radical. A comparison of a computer-simulated spectrum, based on the coupling constants and line width in Table I, and an experimental spectrum is given in Figure 2.

Different results are obtained at higher H_2SO_4 concentrations. No signal was observed during flow when 0.1 M cerium(IV) and 0.2 M DMH in 1 M H_2SO_4 were employed. Upon stopping the flow, a fairly stable signal appeared within 1 min. This signal was very similar to that reported by Tolles, *et al.*,[13] for tetramethyl-2-tetrazene (TMT) cation radical produced in acetone by electrochemical oxidation or by reaction with tetranitromethane. The coupling constants found here in

$$CH_3 \diagdown   CH_3$$
$$\overset{1}{\diagdown}\overset{2}{}\overset{3}{}\overset{4}{\diagup}$$
$$N—N=N—N$$
$$CH_3 \diagup \diagdown CH_3$$

TMT

the aqueous solution (Table I) are slightly different than those found in acetone. This results in a spectrum in aqueous solution with fewer lines; the observed line width in aqueous solution is narrower, however. To give further evidence that the observed spectrum was that of TMT^+, an authentic sample of TMT in 1 M H_2SO_4 was prepared and electrolytically oxidized at a platinum electrode inside the esr cell. A spectrum identical with that obtained in the flow experiments resulted.

The nature of the reaction leading to the TMT cation radical was investigated in a semiquantitative study of the effects of the concentrations of DMH, cerium-(IV), and acid on the resulting spectra. The solutions were mixed outside the spectrometer and after a known

(13) W. M. Tolles, D. W. Moore, and W. E. Thun, *J. Amer. Chem. Soc.*, **88**, 3476 (1966).

Table I: Esr Data for the Hydrazine and Tetrazene Cation Radicals

Position	No. of equiv nucleii	Nucleus	Experimental coupling constant, a, G	Calcd residues,[a] G		a_H/a_N	a_{Me}/a_N
				Hückel	MacLachlan		
			Hydrazine Cation [Ce(IV) H$_2$O][b]				
1	2	N	11.5	−0.66	−0.63		
1	4	H	11.0	−0.97	−0.51	0.96	
			Methylhydrazine Cation [Ce(IV) H$_2$O][c]				
1	3	H(Me)	15.0	−0.17	14.40		1.09
1	1	N	13.8				
1	1	H	12.5	0.21	−0.65	0.90	
2	1	N	10.7	0.68	−0.05		
2	1	H	9.1⎫	−1.62[d]	2.02	⎰0.85	
2	1	H	8.9⎭			⎱0.80	
Line width			0.3				
			1,1-Dimethylhydrazine Cation [Ce(IV) H$_2$O][c]				
1	1	N	16.05	−0.02	0.89		
1	6	H(Me)	14.39	−0.22	8.91		0.90
2	1	N	9.69	0.66	−0.62		
2	2	H	6.91	−2.83	3.71	0.71	
Line width			0.26				
			Tetramethylhydrazine Cation (electrochemical oxid/MeCN)[e] (tetramethyl-2-tetrazine, MeI H$_2$O)[f]				
1	2	N	13.41[e] 13.5[f]	0.52	0.43		
1	12	H(Me)	12.69 12.7	0.58	3.59		0.94
			Tetramethyl-2-tetrazene Cation [DMH, Ce(IV)/H$_2$O][c] (tetranitromethane, TMT/acetone, −30°)[g]				
1	6	H(Me)	11.52[c] 11.72[g]⎫	1.91[d]	1.55		1.05
1	6	H(Me)	10.40 10.45⎭				0.95
1	2	N	10.96 10.93	0.77	0.04		
2	2	N	1.20 1.07	−0.88	0.15		
Line width			0.26 0.39				

[a] The residues contain the results of the correlation of calculated spin density with experimental coupling constants. Residue = $a_{experimental} - a_{calculated}$. The regression analysis yields the spin polarization parameters which are listed below with the standard deviation of the parameter given in parenthesis. Huckel, S^N = 36.70 (1.87), Q_{NH}^N = −6.19 (0.72), Q_{NC}^N = −3.28 (0.80), Q_{NE}^N = −13.98 (0.92), $Q_{NN'}^N$ (= $-Q_{N'N}^N$) = 8.97 (2.57), Q_{CN}^N = 10.25 (2.00), Q_{NH}^H = 23.93 (0.92), Q_Y = 347.98 (7.54), ($a_{NMe}^H = Q_Y \rho_Y$ and NMe = N-X-Y); MacLachlan, S^N = 38.63 (1.77), Q_{NH}^N = −7.19 (0.69), Q_{CN}^N = −6.16 (0.66), Q_{NE}^N = −13.98 (0.92), $Q_{NN'}^N$ = 7.76 (1.83), Q_{CN}^N = 13.11 (1.71), Q_{NH}^H = 23.02 (0.97), Q_Y = 397.17 (67.18), (λ = 1.2 used in MacLachlan calculations). [b] From ref 9, 10. [c] This work. [d] The average of the experimental couplings for these positions were used in the correlation. [e] From S. F. Nelson, *J. Amer. Chem. Soc.*, **88**, 1930 (1966). [f] From W. H. Bruning, C. J. Michejda, and D. Romans, *Chem. Commun.*, 11 (1967); *J. Amer. Chem. Soc.*, **91**, 3859 (1969). [g] From ref 13.

time placed in the spectrometer; their spectra were then recorded as a function of time. The time required for the signal to reach maximum intensity depended strongly on the acid strength, concentration of the reactants, and even the speed of mixing. In all of the external mixing experiments, the maximum intensity was reached in the 1–2 min necessary to mix the solutions and place an aliquot in the spectrometer. The most intense signal was found to result from a molar ratio of cerium(IV) to DMH of 1.0:2.0. The intensity also varied with the acid strength with molar ratios of cerium(IV) to DMH to acid in the range of 1.0:2.0: 8.0 to 1.0:2.0:16.0 giving essentially equivalent and optimum results; the signal intensity decreased when the ratio of reactants departed in either direction from this range. The absolute concentrations were also important. The optimum concentration of cerium(IV) was 0.080 M with those of the other reactants being in the proper ratio. The speed of mixing also affected the results. A quick complete mixing of the reactants gave the best results. Dropwise addition of the oxidant to the other components resulted in almost no signal.

Potassium bromate was also used as an oxidant. The most pronounced difference between it and cerium-(IV) was the time necessary for the appearance of the TMT⁺ radical. In contrast to the cerium(IV) case, in which less than 2 min was required for the radical to appear, as long as 15 min was required when bromate was used. This induction period was a function of the acid concentration. With solutions 0.20 M in DMH and 0.10 M in KBrO$_3$, 2 min was required for a solution 0.6 M in acid and 13 min for a solution 0.3 M in acid.
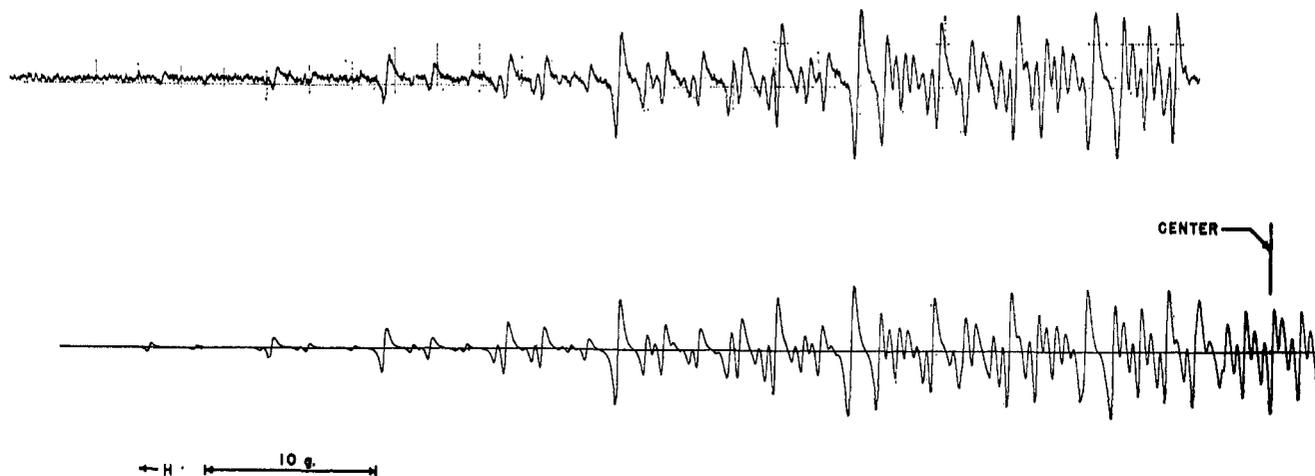
Figure 2. Esr spectrum of dimethylhydrazine cation radical. (a) Top: experimental spectrum; the sweeping field is increasing from right to left. (b) Bottom: experimental spectrum showing outer portion more clearly.

Discussion

Coupling Constants and Molecular Orbital Calculations. Radicals containing nitrogens with substituent protons or methyl groups are frequently compared with respect to the ratio of the proton coupling constant, a_H, to that of the nitrogen to which it is attached, a_N, $R_H = a_H/a_N$ or the ratio of the methyl proton coupling constant, a_{Me}, to a_N, $R_{Me} = a_{Me}/a_N$.[14-16] These ratios range from 0.6 to 2.0 and are frequently close to 1 for molecules such as those reported here, although these ratios can be very sensitive to steric effects, as found, for example, in the cation radical of tetrakis(dimethyl-amino)ethylene.[14] The ratios in the cation radicals of MH and DMH are shown in Table I and are in the expected range of values; a tabulation of R_H and R_{Me} for 25 related compounds is given elsewhere.[17] The ratio R_H (0.71) for DMH cation radical is somewhat lower than that expected from similar compounds.

Hückel molecular orbital (HMO) calculations were attempted for these molecules as a confirmation of the spectral assignments and to find a set of parameters useful in treating molecules of this type. The hydrazine cation radicals were assumed to be planar with the nitrogens sp² hybridized.[9,12] Both nitrogens of 2,2-diphenyl-1-picrylhydrazyl (DPPH) have been shown to be trigonal in the crystalline state, although steric effects prevent coplanarity of the entire molecule.[18] The following procedure was adopted for the HMO calculations and the calculation of the coupling constants. A set of reasonable HMO parameters was adopted; these are given in Table II with references to their sources. The parameters were used to perform HMO and McLachlan calculations for 27 radical ions, including those of hydrazines, amines, anilines, *p*-phenylenediamines, and N-methylated azines.[17] The resultant spin densities were then correlated against the experimental coupling constants using the appropriate spin polarization equations by means of multiple re-

gression[19] analysis using the spin-polarization parameters (Q_{NH}^N, Q_{NC}^N, etc.) as adjustable coefficients. The spin-polarization parameters giving the best least-squares fit are given in the footnotes to Table I. These polarization parameters show varying degrees of agreements with those suggested in other studies.[15,19,20]

The value of Q_Y which relates the nitrogen-methyl proton splitting a_{Me}^H to the spin density on the pseudo-p orbitals formed from the methyl proton s orbitals, ρ_Y, by the relationship $a_{NMe} = Q_Y\rho_Y$ has been found to be

Table II: HMO Parameters for Spin Density Calculations

h_A	A	k_{AB}	AB	Radicals	Ref
1.3	N	0.95	CN	NH_2R, R=N, C	a
1.2	N	0.85	CN	NHMeR, NMe₂R, NR₂Me, R=N, C, Me	a
0.75	N	0.95	CN	NR₂E, R=N, C, H	b
		1.0	NN	All	c
−0.10	X	0.70	NX	N-Me = N-X-Y	a
−0.50	Y	2.50	XY	N-Me = N-X-Y	a
2.01	N	1.62	NO	Nitro groups	d
1.5	O	1.04	CN	Nitro groups	d

a P. D. Sullivan and J. R. Bolton, *J. Mag. Res.*, 1, 356 (1969). *b* A. Carrington and J. dos Santos-Viega, *Mol. Phys.*, 5, 21 (1962). *c* E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 39, 1635 (1963). *d* P. T. Cottrell and P. H. Rieger, *Mol. Phys.*, 12, 149 (1967).

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(15) B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, 41, 1455 (1964).
(16) P. Smith and W. M. Fox, *Can. J. Chem.*, 47, 2227 (1969).
(17) T. V. Atkinson, Ph.D. Dissertation, The University of Texas at Austin, Austin, Texas, 1970.
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(20) C. L. Talcott and R. J. Myers, *Mol. Phys.*, 12, 549 (1967).

348 (using HMO calculations) or 397 (using the Mc-Lachlan calculation). Normally a value of about 169 would be expected.[15] The exceptionally high value obtained in this case may be due to the use of the molecular orbital parameters for the methyl group shown in Table I, which were originally intended for the toluene anion rather than for an N-methyl group. In addition, the neglect of the spin density on the methyl carbon may also add some contribution to this exceptionally high term. An alternative expression for the methyl group may be given by $a_{NMe} = Q_{NMe}^H \rho_N$, where ρ_N is the spin density in the nitrogen π orbital. In this case, Q_{NMe}^H has been found to be 25.5 ± 0.5 for Mc-Lachlan calculations and 33.8 ± 1.2 for HMO calculations, which compare favorably with similar parameters obtained for the carbon–methyl group.

The value for Q_{NH}^H used in the expression for the nitrogen-proton splittings are -23.9 ± 0.9 for Mc-Lachlan calculations and -23.0 ± 1.0 for HMO calculations. This is significantly lower than that obtained by Barton and Fraenkel, of -34, who based this parameter on a different analysis.[15] They point out, however, that small changes in the molecular orbital parameters will have a significant effect on Q_{NH}^H. In general, Q factors obtained in this work and those obtained in other studies compare satisfactorily within the framework of HMO-type calculations.

Calculated coupling constants for the radicals of interest here based on these parameters are given in Table I. While the values calculated from HMO theory show fair agreement with the experimental values, they cannot be used with confidence to either support or refute the assignments suggested.

Implications to Reaction Mechanisms. The chemical and electrochemical oxidations of alkyl-substituted hydrazines[7,21] have generally only produced evidence for a primary two-electron step. For example, the oxidation of DMH with alkali halates and halogens[20] in acidic solutions was shown to produce the moderately stable 1,1-dimethyldiazenium ion

$$Me_2NNH_3^+ \longrightarrow Me_2N=NH^+ + 2H^+ + 2e \quad (1)$$

In alkaline solutions, this ion deprotonated and coupled to form TMT

$$Me_2N=NH^+ + OH^- \longrightarrow Me_2N=N + H_2O \quad (2)$$

$$2Me_2N=N \longrightarrow Me_2NN=NNMe_2 \quad (3)$$
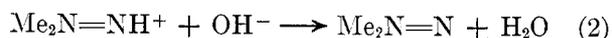
The electrochemical oxidation of DMH in 1 M H_2SO_4 at a platinum electrode also gave unequivocal evidence of an initial two-electron step, followed by a slow decomposition of the diazenium ion and further oxidation. The results here demonstrate that, at least when a one-electron oxidizing agent such as cerium(IV) is employed, the radical cation may be an intermediate in the formation of the diazenium ion and further oxidation products. Moreover, since the DMH cation

radical spectrum can be assigned based on the structure $(CH_3)N-NH_2\cdot^+$, the radical cation formed, even in acid solutions, is not protonated. This indicates that the basicity of DMH cation radical is much smaller than that of the parent DMH. Similarly, the cation radical of TMT is unprotonated in acidic solutions, although the pK_b of the parent TMT is 7.80.[21a] The existence of the cation radical of TMT following oxidation of DMH with a one-electron oxidant suggests alternate paths of TMT from radical intermediates may be possible. The following reactions then can be added to pathways already proposed.

$$Me_2NNH_3^+ \longrightarrow Me_2NNH_2\cdot^+ + H^+ + e \quad (4)$$

$$Me_2NNH_2\cdot^+ \longrightarrow Me_2N=NH^+ + H^+ + e \quad (5)$$

$$2Me_2NNH_2\cdot^+ \longrightarrow Me_2NNH_3^+ + Me_2N=NH^+ \quad (6)$$

$$2Me_2NNH_2\cdot^+ \overset{HH}{\longrightarrow} Me_2NNNNMe_2 + 2H^+ \quad (7)$$

$$\overset{HH}{Me_2NNNNMe_2} \longrightarrow$$

$$Me_2NN=NNMe_2 + 2H^+ + 2e \quad (8)$$

$$Me_2NN=NNMe_2 \longrightarrow Me_2NN=NNMe_2^+ + e \quad (9)$$
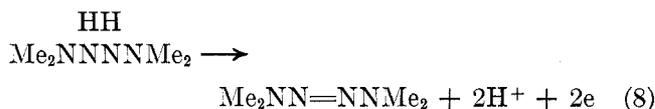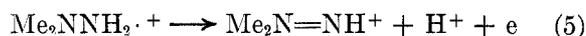
Analogous expressions have been proposed for the oxidation of hydrazine.[1-3] The absence of any evidence of radical cation formation during electrochemical oxidation of the hydrazines in similar solutions, even for experiment durations of about 10 msec, suggests that the electrode acts as a polyelectronic oxidant so that cation radicals formed in the vicinity of the electrode are immediately oxidized further (eq 5). In the flow experiment the ratio of hydrazine to oxidant is such that cation radicals can be formed in the absence of any excess oxidizing agent.

Experimental Section

MH and DMH were obtained from Aldrich Chemical Co. and Matheson Coleman and Bell Chemical Co. Ceric ammonium sulfate was obtained from G. F. Smith Chemical Co. All were employed without further purification. TMT was prepared by the method of McBride and Kruse.[21a]

A Varian Associates V-4502 Spectrometer employing 100-kc field modulation was employed. The field sweep was calibrated by using Fremy's salt; the high- and low-field coupling constants were taken as 13.160 $\pm$ 0.008 and 13.101 $\pm$ 0.004. Flow experiments were performed using the V-4549 liquid flow mixing chamber system, comprising a four-jet mixing chamber with a 0.05-ml volume and a flat quartz cell. Solution flow rates of 1 to 10 ml/sec were employed.

(21) (a) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957); (b) W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959); (c) W. R. McBride and W. E. Thun, *Inorg. Chem.*, **5**, 1846 (1966).

The spectra were simulated using the program Breit[17] which simulates spectra having second-order shifts[22] of the line positions. This program is based on the first-order simulation program of Stone and Maki[23] but is extended to include second-order shifts for nuclei of any spin.

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Electron Paramagnetic Resonance Spectroscopic Study of Radical

Cations from Hydrazine, Methylhydrazine, and Dimethylhydrazines[1]

by P. Smith,* R. D. Stevens, and R. A. Kaba

Paul M. Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, North Carolina 27706 (*Received September 28, 1970*)

The substrates hydrazine, methylhydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine have been investigated in turn within an aqueous continuous-flow system at $25 \pm 2°$ using the titanous chloride–hydrogen peroxide radical-generating method. For each hydrazine the electron paramagnetic resonance spectrum of the corresponding monopositive radical ion was the only one observed, *viz.* $[NH_2NH_2] \cdot {}^+$, $[CH_3NHNH_2] \cdot {}^+$, $[(CH_3)_2NNH_2] \cdot {}^+$, $[cis\text{-}CH_3NHNHCH_3] \cdot {}^+$, and $[trans\text{-}CH_3NHNHCH_3] \cdot {}^+$. The hydrogen and nitrogen nuclear hyperfine coupling constants of these radical cations have been determined and discussed in terms of the $\sigma-\pi$ interaction theories of Karplus and Fraenkel and McConnell. Values for several empirically calculated spin-polarization parameters are presented.

Introduction

The reaction between titanous chloride and hydrogen peroxide in dilute aqueous sulfuric acid has been shown to furnish the basis of a useful continuous-flow method for the generation of transient free radicals from reactive substrates for the purpose of electron paramagnetic resonance (epr) spectroscopic observations.[2]

The mechanisms of the reactions which occur with the use of this radical-generating system have attracted recent attention.[3-12] These studies indicate that the basic initial reaction may be adequately represented by the equation

$$Ti(III) + H_2O_2 \longrightarrow Ti(IV) + OH^- + \cdot OH \quad (1)$$

and this is followed by secondary processes such as

$$\cdot OH + SH \longrightarrow H_2O + S \cdot \quad (2)$$

or

$$\cdot OH + SH \longrightarrow \cdot SHOH \quad (3)$$
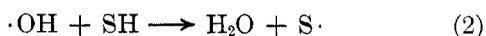
where SH denotes the reactive substrate.

Norman, *et al.*,[13] have shown that with the use of hydrazine as substrate this radical-generating system produces an epr spectrum of nine equally spaced lines with relative intensities close to 1:6:17:30:36:30:

(1) This work was supported by National Science Foundation Grants GP 7534 and GP 17579.

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