

**Table II.** Redox Potentials vs. SCE

Compd	Oxidation <sup>a,b</sup>		Reduction <sup>b,c</sup>	
	$E_{1/2}^{\uparrow}$	$E_{1/2}^{\downarrow}$	$E_{1/2}^{\uparrow}$	$E_{1/2}^{\downarrow}$
<b>8</b>	0.54	0.77	-1.29	-1.77
Chlorophyll a	0.61	0.84	-1.14	-1.61

<sup>a</sup> In CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN. <sup>b</sup> 0.1 M tetra-*n*-butylammonium perchlorate supporting electrolyte. <sup>c</sup> In DMF.

Although optical spectroscopy of the singlet manifold at ambient temperatures reveals virtually no electronic interaction between the macrocycles, an examination of the doublet states as evidenced by the redox properties of **8** indicates quite the opposite. Cyclophane **8** undergoes photooxidation when irradiated with 650-nm light in the presence of electron acceptors, e.g., iodine, quinones, etc., and chemical oxidation by Zn TPP<sup>+</sup>,<sup>20</sup> to yield a cation radical possessing a Gaussian EPR signal with 6.44-G line width. Based on the treatment of Norris et al.,<sup>21</sup> the narrowing of this line width relative to the 9-G line width of monomeric chlorophyll a indicates that spin is shared *equally* by the two macrocycles analogous to special pair chlorophyll a *in vivo*.

Since the structure of **8** is not affected by polar solvents as is that of the singly linked chlorophyll dimers, we were able to determine the redox potentials of **8** by ac voltammetry (Table II). Cyclophane **8** undergoes reversible one-electron oxidation 70 mV more easily than chlorophyll a. This result is consistent with the delocalization of unpaired electron density over both macrocycles in the cation radical of **8**. Characteristically, chlorophyll special pairs *in vivo* are more readily oxidized than bulk chlorophyll in the organism.<sup>1</sup> The reversible one-electron reduction of **8** is more difficult than that of chlorophyll a by 150 mV. The possibility exists that the unpaired electron may be localized on one macrocycle in the radical anion of **8**. Electron spin resonance experiments have been initiated to clarify this point.

The only evidence that photoreaction center chlorophyll in both purple photosynthetic bacteria and in green plants consists of a *pair* of chlorophyll molecules is derived from magnetic resonance experiments. The line width of the EPR signal produced upon photooxidation of reaction centers is exchange narrowed relative to that exhibited by the corresponding monomeric chlorophyll cation radical *in vitro*.<sup>21</sup> Moreover, ENDOR experiments have shown that the proton hyperfine splittings of the species responsible for the EPR signal *in vivo* are one-half the magnitude of the splittings observed *in vitro*.<sup>21</sup> All known reaction center chlorophylls possess a long wavelength optical transition which is red shifted relative both to that of bulk antenna chlorophyll in the organism and to that of the corresponding monomeric chlorophyll *in vitro*.<sup>1</sup>

The results of this study support our earlier proposal<sup>2</sup> that special pair geometries exist which adequately account for both the redox and spin delocalization properties of chlorophyll special pairs *in vivo*, yet do not give rise to unusually red-shifted optical spectra. Thus, we have shown that the optical spectra exhibited by chlorophyll special pairs *in vivo* need not be exclusively an intrinsic property of the pair itself but may be influenced strongly both by the presence of additional chromophores and by important chlorophyll-protein interactions.

**Acknowledgment.** This work was performed under the auspices of the Division of Basic Energy Sciences of the Department of Energy. We thank Dr. M. H. Studier for obtaining the mass spectrum of **7** and Dr. J. R. Norris for stimulating discussions of this problem.

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Received October 26, 1977

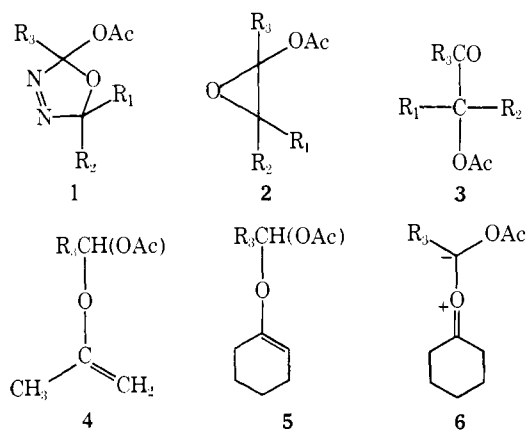
## Thermolysis of 2-Acetoxy- $\Delta^3$ -1,3,4-oxadiazolines. Evidence for Stepwise Homolysis of Cyclic Diazenes

Sir:

Mechanisms of thermal, homolytic decomposition of diazenes (azo compounds) continue to be of interest.<sup>1</sup> Various probes, including activation parameters,<sup>2-4,7,8</sup> stereochemistry,<sup>2,4,8,9</sup> isotope, and other substituent effects on rates,<sup>3,8,10</sup> and dependence of rates on viscosity<sup>11</sup> have been applied in attempts to distinguish between concerted and stepwise loss of nitrogen. The mechanistic pattern that has emerged is that symmetrical diazenes, with few exceptions,<sup>12,13</sup> adopt the concerted pathway and that unsymmetrical diazenes are more prone to homolysis by the stepwise mechanism.<sup>2,9-11,13,14</sup> More detailed structure-mechanism correlations for thermolysis of azo compounds must await further results, including the effects of heteroatom substituents. We now report studies of oxadiazolines **1d-j** which indicates that they undergo stepwise thermolysis through 1,5-diradical intermediates.

Thermolysis of oxadiazolines (**1a-c**) in solution had been reported<sup>15</sup> to yield acetoxyoxiranes (**2a-c**), which, in turn, decomposed to acetoxy ketones (**3a-c**). Compound **1c** had also been decomposed in the presence of olefinic dipolarophiles<sup>16</sup> which trapped an intermediate, probably the carbonyl ylide **6a**, by 1,3 cycloaddition.<sup>16</sup> Acetoxyoxirane **2c** was formed as a by-product.<sup>16</sup>

To our surprise, the analogues (**1f, 1h**)<sup>17,18</sup> gave thermolysis products unrelated to **2** and **3**. In benzene, at 79 °C, decomposition of **1h** is first order ( $k = 1.25 \times 10^{-5} \text{ s}^{-1}$ ) and the products are **4b** (87%) and small amounts of acetaldehyde, acetone, acetic acid, acetic anhydride, 1,1-diacetoxyethane,



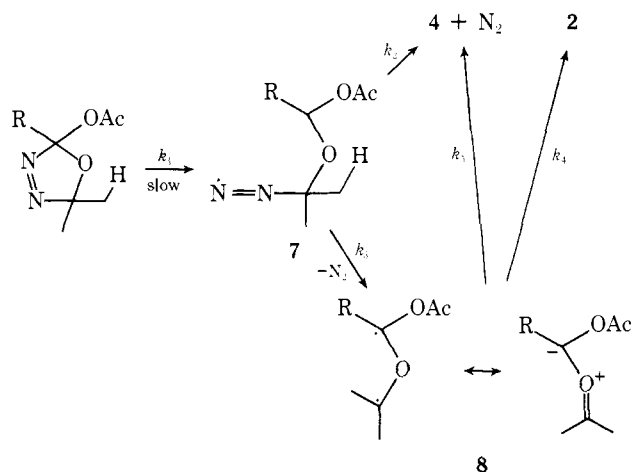
1, 2, 3: a,  $R_1 = R_2 = R_3 = C_6H_5$ ; b,  $R_1 = CH_3$ ,  $R_2 = R_3 = C_6H_5$ ; c,  $R_1, R_2 = (CH_2)_5$ ,  $R_3 = C_6H_5$ ; d,  $R_1, R_2 = (CH_2)_3$ ,  $R_3 = CH_3$ ; e,  $R_1, R_2 = (CH_2)_4$ ,  $R_3 = CH_3$ ; f,  $R_1, R_2 = (CH_2)_5$ ,  $R_3 = CH_3$ ; g,  $R_1, R_2 = (CH_2)_7$ ,  $R_3 = CH_3$ ; h,  $R_1 = R_2 = R_3 = CH_3$ ; i,  $R_1 = R_2 = CH_3$ ,  $R_3 = C_6H_5$ ; j,  $R_1 = R_2 = CD_3$ ,  $R_3 = CH_3$   
4, 5, 6: a,  $R_3 = C_6H_5$ ; b,  $R_3 = CH_3$

and 2,2-diacetoxypropane.<sup>19-21</sup> Similarly, **1f** afforded **5b** in >95% yield when decomposed in anhydrous benzene in a sealed tube. Attempts to trap a possible carbonyl ylide intermediate **6b** with acrylonitrile gave an adduct analogous to the one reported<sup>16</sup> from decomposition of **1c** in the presence of acrylonitrile. However, the yield was very low (6.5%) even in neat acrylonitrile.

In view of the surprising difference between the thermolysis products from **1f** and **1h** and those reported<sup>15</sup> from **1a-c**, we prepared and thermolyzed **1i**. Its decomposition in benzene, at 41 °C, was first order ( $k_1 = 6.2 \times 10^{-5} s^{-1}$ ) and afforded two major products (TLC, NMR) in approximately equal yields. One of them, **2i**, rearranged at a higher temperature (GC column, 150 °C) to **3i**, as expected.<sup>15</sup> The other major product (~50%) was **4a**.<sup>22,23</sup>

Any mechanism for thermolysis of **1** must be able to accommodate the novel products (**4, 5**) and the effect of substituent changes at C-2 on the rate and on the product distribution. Such a mechanism is depicted in Scheme I. Either rate-determining homolysis of the 2,3 bond to form **7** (Scheme I) or concerted homolysis to form **8** in one step would be expected to show the observed C-2 substituent effect on rate. However, a concerted mechanism does not fit the C-5 substituent effects<sup>24</sup> nor does it readily fit the products, because it would require that **8** ( $R = CH_3$ ) fails to close to acetoxyoxirane but that **8** ( $R = C_6H_5$ ) does ring close. Ample experimental evidence for closure of 1,3 diradicals<sup>25</sup> and the possibility that such closure has no activation energy<sup>26</sup> lead to the

Scheme I



expectation that  $k_4 \gg k_5$ .<sup>27</sup> If **8** had much ylide character it should still ring close,<sup>28</sup> although there is one report of an intramolecular proton-transfer reaction, such as that depicted ( $k_5$ ) in Scheme I.<sup>29</sup>

The stepwise mechanism, through **7**, provides a rationale for all of the observations, for the fate of **7** depends on the ratio of  $k_2/k_3$ . For **7** ( $R = C_6H_5$ ) the abstracting site is benzylic and  $k_2$  should be small relative to its value for **7** ( $R = CH_3$ ). Rate constant  $k_3$ , however, should be insensitive to the substituent  $R$ . Thus, **7** ( $R = C_6H_5$ ) is partitioned between the two pathways, leading to olefin, oxirane, and efficient trapping,<sup>16</sup> as observed. On the other hand, **7** ( $R = CH_3$ ) takes the  $k_2$  route with consequent absence of oxirane and poor yields in trapping experiments.<sup>30</sup> The alternative possibility,  $k_3 \gg k_2$  for all substituents, cannot be ruled out, however, although it would require properties for **8** that are unusual for diradicals and carbonyl ylides, as discussed above.

An alternative concerted mechanism, leading directly from **1** to **4** through a transition state with bicyclo[2.2.1] geometry, would be expected to show a substantial primary deuterium kinetic isotope effect. This possibility could be ruled out when it was found that  $k(\mathbf{1h})/k(\mathbf{1j}) = 1.00 \pm 0.05$ .<sup>31</sup> A heterolytic, rate-determining bond scission of **1h** was ruled out on the basis of the solvent effect ( $k_{C_6H_5NO_2} = 0.85 k_{C_6H_6}$ ) which is small and in the wrong direction for a polar mechanism.<sup>32</sup>

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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- (1) For leading references to the literature on mechanisms of decomposition of azo compounds, see ref 2-6. Only selected papers from the bibliographies of ref 2-6 are individually cited here.
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- (12) The exceptional cases are for thermolyses in the gas phase.<sup>8,13</sup>
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- (17) Synthesized by oxidation of the acetyl hydrazones of the appropriate ketones with lead(IV) acetate in methylene chloride.
- (18) Satisfactory analyses and spectra (infrared, <sup>1</sup>H NMR) consistent with the assigned structures were obtained for new compounds except **1d**, **1e**, and **1g** which were not analyzed.
- (19) The minor components were separated by gas chromatography and were identified by infrared and/or NMR spectroscopy. We thank Drs. J. W. Scheeren and S. C. Wicherink, Catholic University, Nijmegen, The Netherlands, for spectral data pertaining to the last two compounds.
- (20) Acetoxyoxirane **2h** and acetoxy ketone **3h** were not detected.
- (21) Yields of the minor products could be suppressed, but not reduced to zero, by carrying out the thermolysis with anhydrous sodium sulfate present, suggesting that the minor products arise, at least in part, from hydrolysis of the sensitive **4b** by adventitious moisture.
- (22) Similarly, oxadiazoline **1c** decomposed in benzene to form two major products one of which was identified as **3c**.<sup>15</sup> The other was not obtained analytically pure, but its vinyl and benzylic <sup>1</sup>H NMR signals analogous to those of **4a** indicate that it must be **5a**.
- (23) The fact that Hoffmann and Luthardt<sup>15</sup> did not report analogues of **4** and **5** may be attributable to ready hydrolysis of such products and to the fact that they did not use GC and NMR. It is interesting to note that a product analogous to **4** and **5** has been reported (G. C. Pitt, *J. Org. Chem.*, **30**, 3242 (1965)) and that its significance was lost because the starting material was not recognized as an oxadiazoline.
- (24) The effect of ring size on thermolysis rates was investigated with **1d-g**. Relative rates (110 °C, C<sub>6</sub>H<sub>6</sub>) follow: **1d** (2), **1e** (4), **1f** (1.0), **1g** (13). These

ring-size effects, which are much smaller than corresponding factors for thermolysis of symmetric *cis*-azo-1-methylcycloalkanes (A. Schulz, N. T. Glac, and C. Rüchardt, *Tetrahedron Lett.*, 845 (1977)) and which do not follow the same trend, suggest that N-4 to C-5 bond breaking is not part of the rate-determining step in thermolysis of **1d-g**. We thank Dr. C. Rüchardt for suggesting the use of ring-size effects to probe for concertedness in oxadiazoline thermolysis.

- (25) See, for example, ref 9, 15, and (a) D. E. McGreer and J. W. McKinley, *Can. J. Chem.*, **49**, 105 (1971); (b) R. Moore, A. Mishra, and R. J. Crawford, *ibid.*, **46**, 3305 (1968).
- (26) For a discussion and references, see E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 5680 (1973).
- (27) An alternate possibility, that **1h** does yield the corresponding acetoxyoxirane **2h** which, however, rearranged to **4b** rather than to the expected **3h**, was eliminated by synthesis of **2h** independently (enol ester plus *m*-chloroperbenzoic acid) and by showing that it is thermally rearranged, in nearly quantitative yield, to **3h**.
- (28) For example, *cis*- and *trans*-stilbene oxides are photochemically interconverted in competition with irreversible formation of deoxybenzoin: G. A. Lee, *J. Org. Chem.*, **41**, 2656 (1976).  $\alpha$ -Cyano-*cis*- and *trans*-stilbene oxides also form carbonyl ylide intermediates reversibly: V. Markowski and R. Huisgen, *J. Chem. Soc., Chem. Commun.*, 439 (1977); R. Huisgen and V. Markowski, *ibid.*, 440 (1977).
- (29) The enol ether was not actually detected, but its intermediacy was postulated in a reasonable mechanism to account for the product that was obtained: I. J. Lev, K. Ishikawa, N. S. Bhacca, and G. W. Griffin, *J. Org. Chem.*, **41**, 2654 (1976).
- (30) A poor yield of product from trapping need not point to a carbonyl ylide intermediate but instead to the interception of some **7**.
- (31) Compound **1j** was at least 95% deuterated, as determined by analysis of the mass spectrum. It gave deuterated **4b**.
- (32) B. K. Bandlish, A. W. Garner, M. L. Hodges, and J. W. Timberlake, *J. Am. Chem. Soc.*, **97**, 5856 (1975).

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Received July 18, 1977

## Electron Spin Resonance of Methoxy Radicals Trapped in Methanol X-Irradiated at 4.2 K

Sir:

Methoxy radicals are one of the most important radical intermediates in organic chemistry, especially in radiation and photochemistry. Nevertheless, the direct ESR observation of trapped  $\text{CH}_3\text{O}\cdot$  has not been successful except for the very recent detection by laser magnetic resonance in the gas phase,<sup>1</sup> which did not give details of the magnetic interaction parameters.

In the present study, we have directly observed the ESR spectra arising from  $\text{CH}_3\text{O}\cdot$  which is trapped in polycrystalline methanol x-irradiated at 4.2 K. The hyperfine coupling constant and the *g* factor have been determined for the first time. The experimental setup is the same as that reported in our previous papers.<sup>2-4</sup> It is believed that the direct evidence for the formation and trapping of  $\text{CH}_3\text{O}\cdot$  in irradiated methanol must be invaluable in radiation chemistry. Its trapping at 4.2 K provides us a further way to study the detailed behavior of this important radical intermediate.

Figure 1 shows the ESR spectrum obtained from polycrystalline  $\text{CH}_3\text{OD}$  x-irradiated and measured at 4.2 K.  $\text{CH}_3\text{OH}$  gave essentially the same spectrum with a slightly broader line width than that from  $\text{CH}_3\text{OD}$ . The signals at around the free spin *g* value indicated by the arrows and the circles in Figure 1 are due to  $\dot{\text{C}}\text{H}_3$  and  $\dot{\text{C}}\text{H}_2\text{OD}$ , respectively. The weak hyperfine structure on the low-field tail arises from  $\text{CH}_3\text{O}\cdot$  which is characterized by its highly positive *g* shift. The overlay spectrum is measured with 10 times higher gain. The hyperfine structure on the  $g_{\text{max}}$  component consists of seven lines which is characteristic of the  $\text{CH}_3$  group undergoing tunneling rotation at low temperature. The stick diagram indicates the splitting of the A and E lines.<sup>5,6</sup> The spacing of the A line, 52 G, corresponds to the hyperfine coupling constant of the methyl protons. The spacing of the E lines (47 G) is slightly smaller

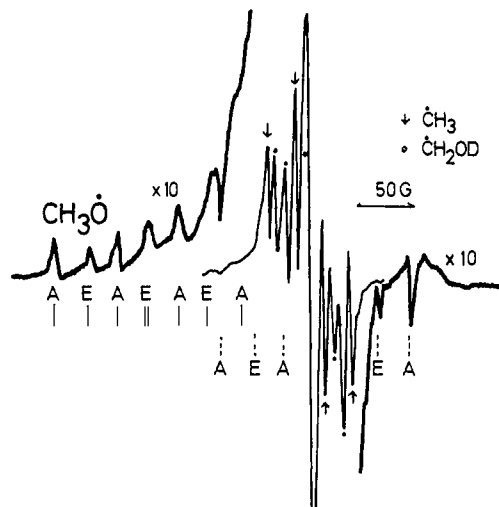


Figure 1. X-band ESR spectra of polycrystalline methanol ( $\text{CH}_3\text{OD}$ ) x-irradiated and measured at 4.2 K. The overlay spectrum is recorded with 10 times higher gain. The other spectrometer conditions are the same: microwave power =  $6 \mu\text{W}$ , field modulation width = 1.5 G.

Table I.  $\text{CH}_3$  Proton Coupling Constant and *g* Tensor Elements of  $\text{CH}_3\text{O}\cdot$  Trapped in Polycrystalline  $\text{CH}_3\text{OD}$  X-Irradiated and Measured at 4.2 K

	<i>g</i> factor	$a_\beta(\text{CH}_3)$ , G
$g_{\text{max}}$	$2.088 (2.076 \pm 0.014)^a$	52 (52) <sup>b</sup>
$g_{\text{int}}$	$(2.006 \pm 0.001)^a$	
$g_{\text{min}}$	$1.999 (1.998 \pm 0.002)^a$	

<sup>a</sup> The numbers in parentheses are the average values reported for substituted alkoxy radicals.<sup>11</sup> <sup>b</sup> The calculated values from the  $B_0 + B_2 \cos^2 \theta$  rule.<sup>11</sup> See text.

than that of the A lines, suggesting that there is a contribution from the term other than that depending upon  $\cos^2 \theta$ , where  $\theta$  is the conformation angle for  $\beta$ -proton coupling.<sup>6</sup> The two outermost lines of the hyperfine structure on the  $g_{\text{min}}$  component can be seen in the high-field end of the spectrum as shown by the dotted lines. The spacing of the two lines is nearly the same as that of the two outermost lines on the  $g_{\text{max}}$  component. This indicates that the hyperfine coupling is nearly isotropic and is consistent with the assignment to the rotating methyl group. Thus, the  $g_{\text{max}}$  and  $g_{\text{min}}$  values are ascertained to be 2.088 and 1.999, respectively. These results are tabulated in Table I.

The large positive *g* shift is characteristic of the oxygen centered radicals in which the unpaired electron is in the nonbonding oxygen  $p_\pi$  orbital. The  $g_{\text{max}}$  value of 2.088 for  $\text{CH}_3\text{O}\cdot$  is in nearly the same range as that reported by us for the OH radicals trapped in organic crystals.<sup>7,8</sup> The  $\beta$ -proton coupling of 52 G in the rotating methyl group is considerably larger than  $\sim 25$  G in carbon-centered  $\pi$  radicals, but is rather similar to that found in some nitrogen-centered  $\pi$  radicals. For example, nitrogen-centered  $\pi$  radicals  $\text{H}_2\text{N}\dot{\text{C}}\text{H}_2\text{R}$  found by us in irradiated glycine exhibited a large  $\beta$  coupling with  $B_2 = 99$  G in the  $B_2 \cos^2 \theta$  rule.<sup>9</sup> This gives 50 G for the freely rotating methyl group. The oxygen-centered  $\pi$  radical may be rather similar to the nitrogen-centered  $\pi$  radicals.

Since Lee and Box<sup>10</sup> have first observed the substituted alkoxy radical in a single crystal of serine x-irradiated at 4.2 K, a number of other examples of the substituted alkoxy radicals have been found in irradiated nucleosides and nucleotides. Very recently their *g* tensors and  $\beta$ -proton couplings have been well characterized by Bernhard et al.<sup>11</sup> According to their Table III of ref 11, the  $g_{\text{max}}$  and  $g_{\text{min}}$  values are given as  $2.076 \pm 0.014$  and  $1.998 \pm 0.002$ , respectively, in an agreement with those of  $\text{CH}_3\text{O}\cdot$ . They have also summarized the hyperfine