

currently in progress to determine if the esr signal observed is that of the parent anion  $(Me_4Si_3)^-$ .

**Acknowledgment.** This work was sponsored by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF Grant No. AF-AFOSR-69-1772.

\* Address correspondence to this author.

Andris Indriksons, Robert West\*

Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706

Received July 10, 1970

## Deuteron Nuclear Magnetic Resonance Spectra of Some Paramagnetic Transition Metal Acetylacetonates

Sir:

Isotropic nmr shifts have proven to be extremely useful for investigating a number of solution properties of paramagnetic transition metal complexes, such as bonding, kinetics and thermodynamics of stereochemical equilibria, and isomerism.<sup>1,2</sup> Unfortunately, well-resolved spectra are realized for only a limited number of metal ions, since a rapid electron spin relaxation time,  $\tau_s$ , is required. In 1965, Eaton<sup>3</sup> measured pmr line widths of a series of transition metal acetylacetonate complexes in an effort to determine which ions have sufficiently short  $\tau_s$ 's for useful pmr studies. The best resolution was found for acetylacetonates of V(III), Mn(III), and Ru(III). Well-resolved spectra have been observed for certain complexes of other ions, notably Ni(II), Co(II), and Cr(II).<sup>1,2</sup> It appears that  $\tau_s$  is a function of ligand-field strength and symmetry.

Recently Reuben and Fiat<sup>4</sup> pointed out that deuteron nmr (dmr) signals in a paramagnetic environment should be narrower than pmr signals under the same conditions by a factor of  $\gamma_H^2/\gamma_D^2 = 42.5$ , where  $\gamma_H$  and  $\gamma_D$  are the magnetogyric ratios of the proton and deuteron. Since chemical shift differences in hertz are smaller for dmr by a factor of  $\gamma_H/\gamma_D = 6.5$ , the overall resolution of the dmr spectrum should be better by a factor of 6.5.<sup>5</sup> The only dmr studies of paramagnetic systems reported thus far have involved solutions of metal ions in deuterium oxide.<sup>6</sup>

We have examined dmr spectra of six deuterium-substituted, paramagnetic acetylacetonate complexes in order to compare the resolution of dmr and pmr for discrete molecular species. Pmr spectra of the corresponding protonated complexes were also recorded in order to make line-width comparisons under the same

conditions. Proton and deuteron spectra were run at 100 and 15.3 MHz, respectively, using a Varian HA-100 instrument. Deuterium-substituted acetylacetonate was prepared by refluxing acetylacetonate in  $D_2O$  with a small amount of  $Na_2CO_3$ . The complexes were prepared by methods described in the literature.<sup>7</sup> Chemical shift values in parts per million of the isotropically shifted resonances are in agreement with those reported by Eaton<sup>3</sup> and are the same for the pmr and dmr spectra of a given complex, since isotropic shifts are independent of the nuclear magnetogyric ratio.<sup>8</sup> The line widths measured in hertz at half maximum amplitude are given in Table I.

Table I. Comparison of Pmr and Dmr Line Widths<sup>a,b</sup>

Complex	Pmr	Dmr	Ratio A/B
	line width, A, c Hz	line width, B, c Hz	
V(acac) <sub>3</sub>	46	2.6 <sup>d</sup>	~18
Cr(acac) <sub>3</sub>	1400	35	40
Mo(acac) <sub>3</sub>	310	18 <sup>d</sup>	~17
Mn(acac) <sub>3</sub>	96	10	~10
Fe(acac) <sub>3</sub>	920	36	26
Ru(acac) <sub>3</sub>	35	3.9	~9

<sup>a</sup> In  $CDCl_3$  solution at 30°. <sup>b</sup> Error estimates are in the range 3–10%. <sup>c</sup> Data refer to the methyl resonance. <sup>d</sup> Value obtained from one component of multiplet (see text).

The methyl dmr resonance of the deuterated V(III) complex surprisingly appeared as a multiplet of three signals with separations of the order of 8–10 Hz. The ligand used to prepare this complex was deuterated only to an extent of ~80%. Thus pmr of the same sample was feasible and showed an identical multiplet with separations of ~55 Hz. The complex was prepared again using ligand >90% deuterated. Dmr and pmr of this sample showed a dominant peak accompanied by a small satellite at higher field.<sup>9</sup> Multiple dmr signals were also found for the Mo(III) complex. It appears that chemical shift differences are so magnified by the isotropic shift effect that complexes differing only in the extent of deuterium substitution are distinguishable. The phenomenon will be further investigated.

The Solomon-Bloembergen expressions for the longitudinal and transverse relaxation times of nuclei in a paramagnetic molecule contain a number of variables, including the electron-nuclear distance, the electron relaxation time, the electron Larmor frequency, the tumbling time of the molecule, and the square of the nuclear magnetogyric ratio,  $\gamma_N$ .<sup>10</sup> Upon replacing a proton by a deuteron in a given molecule, the only

(1) (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (c) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

(2) (a) L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 1855 (1970); (b) G. N. La Mar and E. O. Sherman, *ibid.*, **92**, 2691 (1970); (c) G. N. La Mar, *ibid.*, **92**, 1806 (1970); (d) G. N. La Mar and G. R. Van Hecke, *ibid.*, **92**, 3021 (1970); (e) R. E. De Simone and R. S. Drago, *ibid.*, **92**, 2343 (1970), and references cited in these papers.

(3) D. R. Eaton, *ibid.*, **87**, 3097 (1965).

(4) J. Reuben and D. Fiat, *ibid.*, **91**, 1242 (1969).

(5) This factor does not take into account the lower signal-to-noise ratio and quadrupolar broadening for dmr. Quadrupolar broadening is expected to be masked by the more efficient magnetic dipole relaxation mechanism in a paramagnetic environment.<sup>8a</sup>

(6) (a) G. Laukien and F. Noack, *Z. Phys.*, **159**, 311 (1960); (b) P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

(7) V(acac)<sub>3</sub>, G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970); Cr(acac)<sub>3</sub>, W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957); Mo(acac)<sub>3</sub>, M. L. Larson and F. W. Moore, *ibid.*, **8**, 153 (1964); Mn(acac)<sub>3</sub>, R. G. Charles, *ibid.*, **7**, 183 (1963); Fe(acac)<sub>3</sub>, A. Hantzsch and C. H. Desch, *Justus Liebigs Ann. Chem.*, **323**, 1 (1902); Ru(acac)<sub>3</sub>, G. A. Barbieri, *Atti Accad. Lincei Rend.*, **23**, 334 (1914).

(8) The contact contribution to the isotropic shift is given<sup>1</sup> as  $(\Delta H/H_0)_i = -A_i(\gamma_e/\gamma_N)(g\beta S(S+1)/3kT)$ . Since the coupling constant  $A_i$  is proportional to  $\gamma_N$ ,  $\Delta H/H_0$  is independent of  $\gamma_N$ . The expression for the dipolar contribution does not contain  $\gamma_N$ .<sup>1a</sup>

(9) Since this communication was submitted we have prepared 100%-deuterated ligand. A single methyl resonance is observed for the V(III) complex of this ligand.

(10) For a discussion of these equations, see R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *J. Chem. Phys.*, **30**, 950 (1959).

variable changed is  $\gamma_N$ . Thus the pmr/dmr line-width ratio is expected to be close to the value of  $\sim 42$  predicted by theory. It is apparent from the table that this ratio is not always realized. In order to test for the effects of changes in concentration and possible saturation, pmr and dmr spectra of the Mn(III) complex were measured on samples ranging from 0.08 to 0.40 M and at several radiofrequency power levels. The resulting line widths agree within about 10%. Deviations from the theoretical line-width ratio were found earlier for solutions of paramagnetic metal ions in H<sub>2</sub>O and D<sub>2</sub>O.<sup>6</sup> These results imply that other factors, presently undetermined, affect the relaxation times of nuclei in paramagnetic environments.

Although the pmr/dmr ratios in Table I are not generally in agreement with theory, the present results do indicate a gain in resolution upon replacing protons by deuterons in paramagnetic molecules. We hope this will allow extension of isotropic shift studies to metal ions having relatively long  $\tau_s$ . The improvement in resolution is most noticeable for Cr(acac)<sub>3</sub>; both the CH<sub>3</sub> and C-H resonances are clearly seen in the dmr spectrum. The C-H signal is not apparent in the pmr spectrum. Another advantage of dmr over pmr for paramagnetic systems is that selective deuteration allows unambiguous signal assignments and avoids interference from resonances of nuclei at other sites (not deuterated). Furthermore, spectra are less likely to be complicated by spin-spin coupling, since  $J_{DD} < J_{DH} < J_{HH}$ .

\* To whom correspondence should be addressed.

Ann Johnson, Grover W. Everett, Jr.\*

Department of Chemistry, University of Kansas  
Lawrence, Kansas 66044

Received August 1, 1970

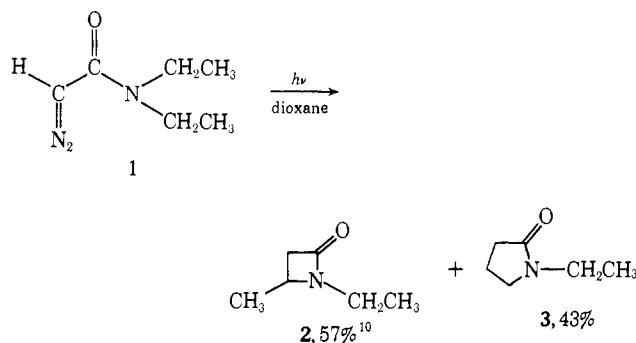
## Conformational and Solvent Effects on Carbene Reactions<sup>1</sup>

Sir:

Carbalkoxycarbenes, generated by the photolysis of the parent diazo esters, undergo facile intermolecular C-H insertion and double bond addition reactions in hydrocarbon solvents.<sup>2,3</sup> Curiously, the intramolecular counterparts of these reactions, which would generate lactones, are not realized. For example, the photolytic decomposition of allyl diazoacetate in cyclohexane gives rise to allyl cyclohexylacetate as the sole product.<sup>4</sup> One only starts to see lactone formation when the alkoxy portion of the diazo ester is exceptionally bulky. Photolysis of *tert*-butyl diazoacetate in cyclohexane affords 9.5%  $\gamma,\gamma$ -dimethylbutyrolactone along with 90.5% *tert*-butyl cyclohexylacetate.<sup>5</sup> It would appear that the dominant factor in these reactions is a conformational one,<sup>6</sup> whereby the *O*-alkyl

moiety of the diazo esters never achieves sufficient proximity to the divalent center, except in the bulky *tert*-butyl case, for intramolecular reactions to ensue. If this is indeed the case, we would expect *N,N*-dialkyl diazo amides to undergo principally intramolecular lactam formation upon photolysis, since one alkyl group must lie in close proximity to the divalent center as a consequence of the planar peptide bond. We herein report the results of a study of the photochemistry of *N,N*-diethyldiazoacetamide (**1**) and demonstrate a remarkable solvent effect on its reactions.

*N,N*-Diethyldiazoacetamide (**1**) was prepared by condensing *p*-nitrophenyl diazoacetate with diethylamine in the usual manner.<sup>7</sup> After purification on Woelm activity grade IV alumina, **1** was obtained as a viscous yellow oil which exhibited strong infrared absorption (CHCl<sub>3</sub>) at 4.69 and 6.2  $\mu$  and nmr absorption (CDCl<sub>3</sub>) at  $\tau$  4.9 (s) of relative area 1, 6.7 (q)<sup>8</sup> of relative area 4, and 8.8 (t)<sup>8</sup> of relative area 6. Photolysis<sup>9</sup> of 270 mg of the diazoamide in 15 ml of dry, distilled *p*-dioxane led to the recovery of 205 mg of a light yellow oil after the removal of the dioxane. Vapor phase chromatography of this material on 5 ft  $\times$  1/4 in. 5% Carbowax 20M on Chromosorb W (60-80 mesh) at 150° column temperature showed that two major products had formed accounting for 97% of the total amount. The product



with the longer retention time proved to be 1-ethyl-2-pyrrolidinone (**3**) by comparison with authentic material.<sup>11</sup> The other product proved to be 1-ethyl-4-methyl-2-azetidinone (**2**). This  $\beta$ -lactam exhibited carbonyl absorption in the infrared (CHCl<sub>3</sub>) at 6.28  $\mu$ ,<sup>12</sup> nmr<sup>13</sup> absorption (CDCl<sub>3</sub>) at  $\tau$  6.3 (m) of relative area 1, 6.8 (q) of relative area 2, 7.2 (m) of relative area 1, 7.4 (m) of relative area 1, 8.7 (d) of relative area 3, and 8.9 (t) of relative area 3. The mass spectrum of the colorless oil **2** revealed the expected molecular ion at

(7) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *ibid.*, **90**, 4088 (1968).

(8) The fact that a single methylene quartet and a single methyl triplet are observed probably means that rotation about the peptide bond is rapid at room temperature relative to the nmr time scale in diazoamides.

(9) Photolyses were carried out through Pyrex vessels using G.E. sunlamps with external water cooling. The reactions were run until the diazo stretching absorption (4.69  $\mu$ ) was no longer visible in the infrared spectrum (usually 8-10 hr).

(10) Relative per cent yields were obtained from the vpc trace after suitable corrections for electrical conductivity and statistical factors were made. The absolute overall yield is 94% based on diazo amide.

(11) Infrared and nmr spectra were compared along with vpc retention times.

(12) An amide carbonyl absorption this high is quite indicative of a  $\beta$ -lactam moiety; see L. M. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 214.

(13) The nmr spectrum of the compound was quite similar to analogous  $\beta$ -lactams in K. D. Barrow and M. T. Spotswood, *Tetrahedron Lett.*, 3325 (1965).

(1) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society (No. 1489-G1).

(2) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **78**, 4947 (1956); **83**, 1989 (1961).

(3) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 6.

(4) W. Kirmse and H. Dietrich, *Chem. Ber.*, **98**, 4027 (1965).

(5) W. Kirmse, H. Dietrich, and H. W. Bucking, *Tetrahedron Lett.*, **19**, 1833 (1967).

(6) F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966).