TABLE I

EQUILIBRIUM CONSTANT DATA AT 211–271°

($K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$)

T, °K	$10^2(P_{ClF_5}/P_{ClF_3})$	P_{F_2}, atm	10^2K_p, atm^{-1}
484	27.9	3.27	8.52
486	26.8	3.43	7.80
493	25.5	3.44	7.40
497	24.8	3.52	7.06
516	11.1	3.58	3.10
518	9.28	3.60	2.58
542	5.01	3.71	1.35
544	3.99	3.84	1.04

AgCl windows and the halocarbon wax. Most of the errors were systematic and probably affected ClF_3 and ClF_5 values similarly. Since K_p is proportional to the ratio P_{ClF_5}/P_{ClF_3}, systematic inaccuracies in the infrared analysis tend to cancel. Moreover, thermodynamic functions derived from these data involved the logarithm of this ratio and thus are insensitive to errors in the infrared analysis. The data were fitted to the van't Hoff equation, $\ln K_p = 9175/T - 21.30$, by the method of least squares and are plotted in Figure 1. By expressing the equation in the form $\ln K_p = -(\Delta H_r/RT) + (\Delta S_r/R)$, the enthalpy and entropy of reaction in the temperature range near 240° were obtained: $\Delta H_r = -18.2 \pm 0.9$ kcal and $\Delta S_r = -42.3 \pm 1.8$ eu. Although the data were fitted to an equation with a standard deviation of 5%, the straight-line fit should not be interpreted as a measure of the accuracy of the data. Using $\Delta H_{f\,500}(ClF_3(g)) = -37.8$ kcal/mole from the JANAF tables, the authors calculate $\Delta H_{f\,500}(ClF_5(g)) = -56.0$ kcal/mole.

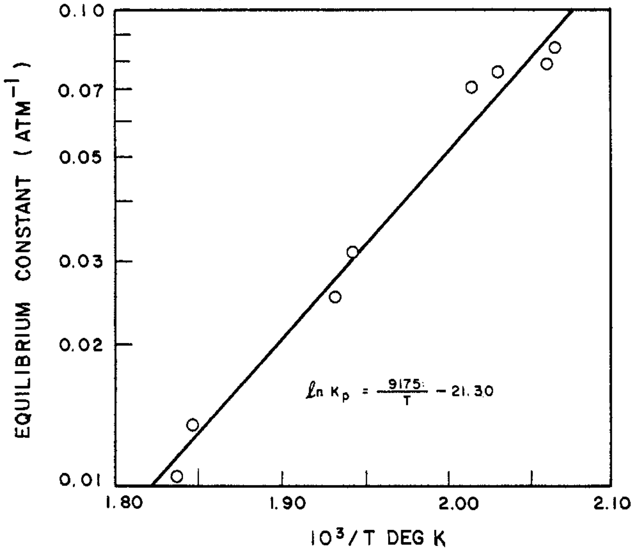

Figure 1.—Equilibrium constant as a function of temperature ($K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$).

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CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY,
LOS ALAMOS, NEW MEXICO 87544

An Interpretation of the Proton Hyperfine Splitting in the Electron Paramagnetic Resonance Spectrum of Vanadyl-Doped Zinc Tutton Salt[1]

BY W. BURTON LEWIS

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Ordinarily the proton hyperfine splitting in hydrated ions of the iron group transition metals is too small to be resolved in epr spectra and contributes only to line broadening. Borcherts and Kikuchi,[2] however, report the resolution of a five-line superhyperfine structure superimposed on the normal eight V^{51} hyperfine components of the $VO(H_2O)_5^{2+}$ epr spectrum present as a 0.5% impurity in single crystals of the Tutton salt $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$. They confirmed that protons are the source of the splitting by examining crystals grown from D_2O solution. A crystal grown from ordinary water gave a 5-gauss superhyperfine splitting only when the static magnetic field H was directed parallel to one of the four V–O bonds to water molecules in a plane perpendicular to the shortest V–O bond (1.67 A). With the field along other directions, the superhyperfine structure disappeared. In particular, the maximum slope line width of a V^{51} hyperfine component for H parallel to the short V–O bond was 8–10 gauss, and for H bisecting the angle between two V–O bonds to adjacent water molecules in the plane perpendicular to the short V–O bond the line width was about 20 gauss. The line widths for a crystal grown from D_2O on the other hand were reduced by a factor of three.

The explanation of a five-line proton hyperfine structure with relative intensities in the ratio 1:4:6:4:1 and a splitting of 5 gauss is not immediately obvious. The coordination number of the VO^{2+} ion is normally five or six including the oxygen ion, and one expects therefore a minimum of four water molecules to be coordinated to this ion. Using the structural analysis of Montgomery and Lingafelter[3] for $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$, it can be shown that the dipolar fields arising from the various spin configurations possible with the eight nearest protons yield a spectrum with many components but bunched into 13 distinct groups (for H in the direction of the observed splitting). The separation between groups of lines is 2 gauss and the total spread of the spectrum is 17 gauss. Adding a fifth water molecule at the position opposite the vanadyl oxygen ion would only increase the complexity and spread of this spectrum. While it appears that no reliable estimate has been made of the proton iso-

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) R. H. Borcherts and C. Kikuchi, *J. Chem. Phys.*, **40**, 2270 (1964).

(3) H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **17**, 1295, 1478 (1964).

tropic hyperfine coupling constant of the $VO(H_2O)_5^{2+}$ ion, an order of magnitude of 1 gauss can be predicted for V^{4+} on the basis of the Luz and Shulman model for proton hyperfine coupling in hydrated ions of the transition metals.[4] In this model spin transfer to the protons occurs *via* π-type antibonding orbitals formed from d_{xy}, d_{xz}, or d_{yz} orbitals of the metal ion and certain H_2O molecular orbitals. It is evident that both dipolar and isotropic hyperfine fields at the V^{4+} site due to protons in $VO(H_2O)_5^{2+}$ are of the proper magnitude to contribute significantly to the total hyperfine field, and we wish to show that the observed splitting into five components is just the result one expects if both fields are combined.

The total hyperfine field associated with a particular configuration of proton spins is given by the relation

$$H_{\text{shfs}} = \sum_i A_i m_i \qquad (1)$$

where the summation is over all of the protons, or eight if we neglect for the moment a possible fifth water molecule. Here m_i is the proton spin state $\pm{}^1/_2$ and A_i is the sum of dipolar and isotropic hyperfine terms A_d and A_s, respectively. The value of A_d is readily calculated from the equation[5]

$$A_d = (2\mu/r^3)(3\cos^2\alpha - 1) \qquad (2)$$

where $\mu = \gamma I\hbar$, α is the angle between the applied magnetic field and the direction of the proton from the V^{51} nucleus, and r is the proton distance. Since there are 81 nonequivalent spin arrangements possible with eight protons whose point group symmetry is C_i, the complete proton hyperfine spectrum will consist of 81 lines. When H is parallel to the bond $V–O_9$ (the direction in which superhyperfine structure was resolved),[6] one obtains from eq 1 and 2 the line spectra shown in Figure 1 for three trial values of A_s: 1.42, 2.10, and 2.70 gauss. For clarity those lines lying very close together have been combined, so that only 25 lines are needed to represent the spectrum for this crystal orientation. The observed splitting of 5.4 gauss, redetermined by taking the average of the proton splitting in seven of the V^{51} hyperfine peaks in the original spectrum,[7] is seen to correspond to $A_s = 2.6 \pm 0.2$ gauss if we regard the 1.1 gauss splitting within each group of five lines as being unresolvable. Furthermore, the calculated intensity ratios for the five groups of lines is 1:4:6:4:1 as observed. While Montgomery and Lingafelter[3] have determined a set of proton coordinates in the nickel Tutton salt by a least-squares method, they concede that the results are not accurate and we have therefore assumed above that the protons lie one-third of the distance along the lines connecting water oxygen atoms to the nearest two sulfate oxygen atoms. Grimes, *et al.*,[8] have confirmed that these positions are in accord with the inter-proton vectors obtained by Chidambaram from nmr measurements.[9] Spectra calculated from the former coordinates are also less well resolved than those in Figure 1 and fit at a slightly higher value of A_s.

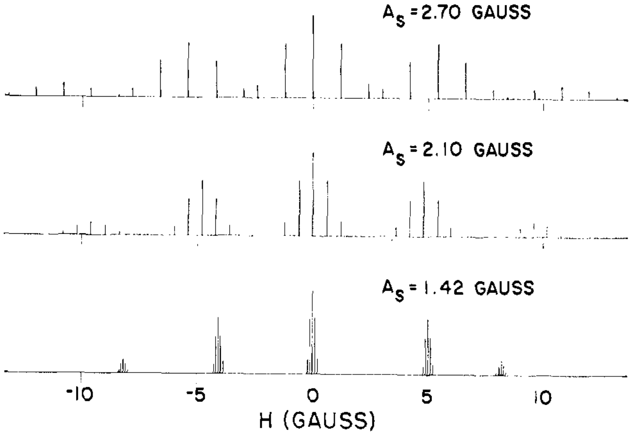

Figure 1.—Calculated proton hyperfine structure for $VO(H_2O)_6^{2+}$ in $(NH_4)_2Zn(SO_4)_2\cdot6H_2O$ with H parallel to $V–O_9$.

With H along the bond $V–O_7$ (the short V–O bond), the calculated spectrum shown in Figure 2 is relatively narrow over-all and no resolution is expected. Although wider than those in Figure 2, the observed spectrum for this crystal orientation is nevertheless unresolved and more narrow than for other orientations.

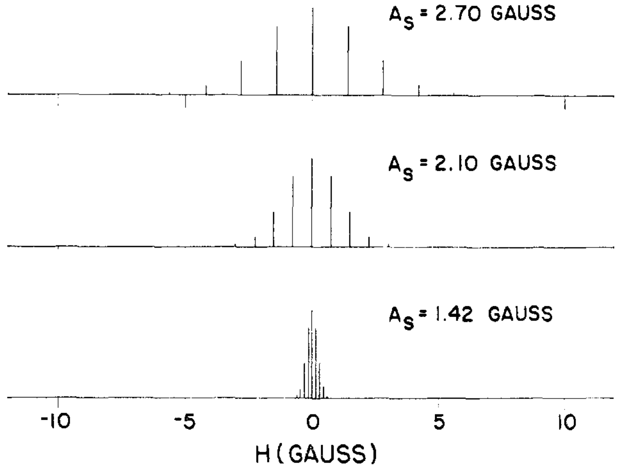

Figure 2.—Calculated proton hyperfine structure for $VO(H_2O)_5^{2+}$ in $(NH_4)_2Zn(SO_4)_2\cdot6H_2O$ with H parallel to $V–O_7$.

A broader unresolved spectrum (20 gauss) is observed when H bisects the angle between $V–O_8$ and $V–O_9$. The spectra calculated for this orientation are shown in Figure 3, and again the number of lines has been reduced by combining those close together. Here also there is a smooth intensity distribution across the spectrum for $A_s = 2.6$ gauss and no resolution would be expected.

Recently McCain and Myers[10] have estimated the residual epr line width of VO^{2+} in aqueous solution by correcting for tumbling line broadening. They find that this residual line width increases only slowly with temperature, whereas the Kivelson theory of spin-

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(4) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(5) G. E. Pake, *ibid.*, **16**, 327 (1948).

(6) We follow the oxygen atom numbering system used in ref 2 and 3.

(7) A better reproduction of the original spectrum which appears in ref 2 is given by Borcherts, *et al.*, in the final report Mich-04275-2-F, Part II, Jan 1963, in Figure 8, p 21.

(8) N. W. Grimes, H. F. Kay, and M. W. Webb, *Acta Cryst.*, **16**, 823 (1963).

(9) R. Chidambaram, *J. Chem. Phys.*, **38**, 210 (1963).

(10) D. C. McCain and R. J. Myers, *J. Phys. Chem.*, **71**, 192 (1967).

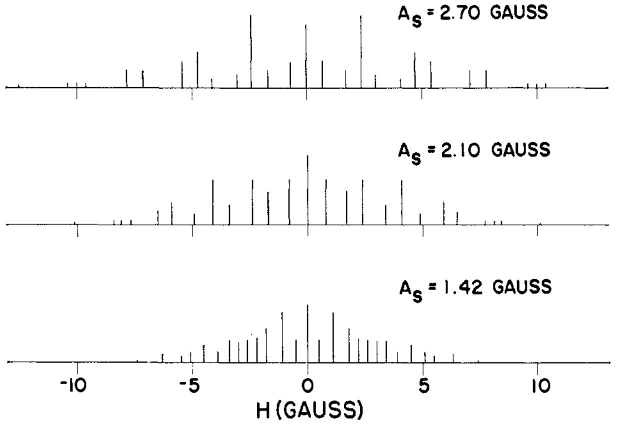

Figure 3.—Calculated proton hyperfine structure for $VO(H_2O)_5^{2+}$ in $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ with H parallel to bisector of V–O_8 and V–O_9.

rotational relaxation[11] predicts that the residual width from this source should vary as T/η. The spin-rotational line width for $VO(H_2O)_5^{2+}$ given by the Kivelson theory is 1.8 gauss at 30° for $\tau_c = 2.5 \times 10^{-11}$ sec. McCain and Myers' residual width at 9070 Mc is 5.1 gauss. The greater observed residual width, particularly the temperature independent part of that width, is very likely due to isotropic proton hyperfine broadening, the dipolar part being averaged to zero by tumbling. By reconstructing the nine-line proton hyperfine spectrum, assuming each to have Lorentzian shape with a width of 9.4 gauss, it is found that the resulting line width is 12.7 gauss for A_s = 2.2 gauss, in fair agree ment with the above interpretation of proton hyperfine splitting in vanadyl-doped $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$.

In view of the possibility that the VO^{2+} ion may be coordinated to five H_2O molecules in this Tutton salt, the spectrum for ten protons with the fifth H_2O molecule in the O_7 position and H parallel to the V–O_9 bond was also calculated, both with and without isotropic hyperfine coupling to the fifth H_2O molecule. The result was a severely broadened spectrum in both cases, which suggests that the fifth H_2O molecule is very likely absent. It is perhaps significant that Palma-Vittorelli, *et al.*,[12] have found that in $VOSO_4 \cdot 5H_2O$ there are only four H_2O molecules coordinated to the VO^{2+} ion, the sixth coordination position being filled by a sulfate oxygen atom.

[11] P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966).

[12] M. B. Palma-Vittorelli, M. U. Palma, and D. Palumbo, *Nuovo Cimento*, **3**, 718 (1956).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Photochemistry of Borazine. Preparation of B-Monoalkoxyborazines[1]

BY M. NADLER AND R. F. PORTER

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Recent studies[2] have shown that B-monohydroxyborazine is a product of the photochemical reaction of gaseous borazine and water vapor. This product was found to be unstable and could not be separated and isolated in macroscopic quantities. However, since it was shown that substitution of OH at a single boron atom could occur photochemically, further work was initiated to test the procedure for preparing monoalkoxyborazines by irradiating gaseous mixtures of borazine and alcohol. In this paper we describe results of the reaction using methanol, ethanol, and 2-propanol as reagents.

Experimental Section

The experimental apparatus has been described.[2] The reaction vessel holding a quartz immersion cell was modified by joining it to an infrared cell through a 2-in. opening of Pyrex. The optical path for the ultraviolet radiation extended from the quartz well into the infrared cell to a total length of about 84 mm. With this arrangement the reaction could be monitored by noting changes in the infrared spectrum with time. It was essential to terminate the reaction when the alcohol was completely consumed to prevent thermal reactions between borazine and alcohol from occurring when the mixture was condensed in the separation steps. The radiation source was a Hanovia medium-pressure Hg lamp, providing intense radiation at about 1850 A. Borazine absorbs strongly between about 1700 and 2000 A.[3] Methanol and ethanol absorb in this region[4] but not as strongly as borazine.

B-Monomethoxyborazine.—Borazine and methanol were added to the reaction vessel to provide initial pressures in the ranges 10–15 mm and 15–20 mm, respectively. A thermal reaction between borazine and methanol produces $B(OCH_3)_3$ and NH_3 in the gas phase. For this reason it was necessary to initiate the irradiation immediately after mixing the reagents. The irradiation time was usually between 20 and 25 min for the disappearance of methanol. The products were pumped through a series of traps at −35, −80, and −196° and hydrogen was removed. Unreacted borazine was recovered from the −80 and −196° traps. The −35° trap contained NH_3 and $B(OCH_3)_3$, identified from their infrared spectra,[5] and a new product which was not observed in the absence of irradiation. Ammonia and $B(OCH_3)_3$ could not readily be distilled from the mixture, since on liquefication they form an adduct[6] that has a volatility close to that of the unknown product. Separation was finally achieved by allowing the NH_3 to react with a small quantity of B_2H_6 to form a nonvolatile adduct and pumping off the $B(OCH_3)_3$ while the mixture was held at −35°. The product recovered from the −35° trap has a vapor pressure of about 6 mm at 25°. The best yield obtained was about 25% based on the amount of borazine reacted. A mass spectrum and infrared spectrum of the compound in the vapor phase are shown in Figures 1a and 2a. The high-mass cutoff in the mass spectrum is consistent with a molecular weight for $B_3N_3H_5OCH_3$. High-mass groupings corresponding to the hypothetical compounds $B_3N_3H_5(OCH_3)_2$ and $B_3N_3H_3(OCH_3)_3$ were not observed. A trace of $B(OCH_3)_3$ in the product was noted by the appearance of a small-ion intensity of $B(OCH_3)_2^+$. The infrared spectrum of the new compound shows frequencies expected for a borazine derivative, the B–H stretch (2520 cm^{-1}), the N–H stretch (3480 cm^{-1}), and ring stretching vibrations at 1490 and 1440 cm^{-1}. The presence of the latter two bands is probably a consequence of a splitting of an E′ ring stretching vibration in borazine by symmetry change due to substitution at one ring position. The strong band at about 1275 cm^{-1} may be assigned to a B–O stretch. Other bands

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency, Cornell University, Ithaca, N. Y.

[2] G. H. Lee, II, and R. F. Porter, *Inorg. Chem.*, **6**, 648 (1967).

[3] H. B. Klevens and G. W. Schaeffer, *J. Chem. Phys.*, **15**, 598 (1947).

[4] A. J. Harrison, B. J. Aderholm, and M. A. Terwilliger, *ibid.*, **30**, 355 (1959).

[5] W. J. Lehman, J. P. Onak, and I. Shapiro, *ibid.*, **30**, 1215 (1959).

[6] D. T. Haworth and L. F. Hohnstedt, *J. Am. Chem. Soc.*, **81**, 842 (1959).