

CHEMISTRY

Nuclear Hyperfine Interactions in Diatomic Molecules and the Ground State of VO

THE identification of the ground states of the diatomic oxides of the transition metals presents interesting experimental¹ and theoretical² problems, and the VO molecule is one example. Analogy with TaO suggests³ that the lowest state should be $\sigma^2\delta^2\ ^2\Delta$, but theoretical calculations⁴ indicate that it is $\sigma\delta^2\ ^4\Sigma^-$. This is supported by unpublished observations of P. H. Kasai and W. Weltner of the electron spin resonance spectrum of matrix isolated VO. A rotational analysis⁵ of several bands of the green system ($\nu_{00} = 17,419\text{ cm}^{-1}$) led to values of the internuclear distances in the two states, but the transition was not identified: it was suggested that it might be spin-forbidden.

We now report preliminary results of the rotational analysis of bands of the green and red^{6,7} ($\nu_{00}, F_4 = 12,707\text{ cm}^{-1}$) systems. We have found that both systems may be observed in absorption at $t \sim 1,650^\circ\text{C}$ in a carbon tube furnace with short paths: both systems are therefore most probably allowed. The bands of the green system consist of the four branches analysed correctly by Lagerqvist and Selin⁵ as *R* and *P* branches and, in addition, four broad line branches, two *R* and two *P*. The lines of these branches are about 0.4 cm^{-1} wide, and the widths are independent of *N*, at least for $15 \leq N \leq 70$. The energy levels in all states are determined by an integral quantum number *N* rather than half integral *J*, so that the transition is $^4\Sigma^-$ (case *b*)– $^4\Sigma^-$ (case *b*), with four *R* and four *P* branches.

Analysis of the red system is incomplete, but parts of the two shortest wavelength components of the 1–0 and 0–0 bands have been analysed. These bands show many branches, broad and sharp, and the upper state energy levels are determined by a half integral quantum number *J*. Thus the upper state is a case *a* state. Lower state combination differences are found in excellent agreement with those observed in the green bands. In the shortest wavelength components of the 0–0 and 1–0 bands, six sharp branches have been analysed which may be assigned as the $TR_{43}, SR_{43}, SQ_{42}, RQ_{43}, RP_{42}$, and QP_{43} branches in $^4\Pi_{5/2}-X^4\Sigma^-$.

Line widths in the green bands are unaffected by the many upper state perturbations: this fact, together with the observation of broad lines in the red system, suggests that the cause of the broadening, or unresolved splitting, is to be sought in the behaviour of two of the four components of the $^4\Sigma^-$ ground state. Analysis of the red bands shows that the F_2'' ($J = N + \frac{1}{2}$) and F_3'' ($J = N - \frac{1}{2}$) components are sharp and it is therefore the F_1'' ($J = N + \frac{3}{2}$) and F_4'' ($J = N - \frac{3}{2}$) components which are broadened, by a factor of about three.

The theoretical calculations⁴ suggest that the σ electron in the $\sigma\delta^2$ ground configuration is predominantly $4s\sigma$ on V. The splitting of the levels may be understood on the basis of a magnetic hyperfine interaction of this electron with the ^{51}V nucleus of spin $\frac{7}{2}$ and magnetic moment 5.14 nm. The δ electrons will not contribute significantly to the hyperfine energy which may be written⁸

$$W_{hfs} \approx b \bar{I} \cdot \bar{S},$$

with

$$b = \frac{2}{I} \frac{\mu_0 \mu_I}{I} \left[\frac{8\pi}{3} \psi^2(0) - \frac{3 \cos^2 \theta - 1}{2r^3} \right]_{av} :$$

for a near spherical distribution of charge, only the term in $\psi^2(0)$ will be important. If the magnetic interaction is weak compared with the coupling of the other angular

momenta the overall coupling will be $b_{\beta J}$ and the hyperfine energy will be given by

$$W_{hfs} = \frac{b}{3} \frac{[J(J+1) - N(N+1) + S(S+1)]}{2J(J+1)} \bar{I} \cdot \bar{J}$$

where

$$\bar{I} \cdot \bar{J} = \frac{1}{2} [F(F+1) - J(J+1) - I(I+1)].$$

If this hyperfine splitting is not resolved, the line width will be given by $(W_{F_{\max}} - W_{F_{\min}})$, where $F_{\max} = J + I$ and $F_{\min} = J - I$, as in BiO (ref. 9). This leads to calculated widths of lines originating from F_1'' and F_4'' which are about three times those arising from F_2'' and F_3'' for $N \gtrsim 15$ when the widths become constant, in good agreement with the observed spectrum.

We conclude that the ground state of VO is $\sigma\delta^2\ ^4\Sigma^-$, and that this state provides a further example of a situation in which nuclear hyperfine splittings contribute significantly to the appearance of the optical spectra¹⁰.

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Electron Spin Resonance Study of Nitroxide Radicals from Diethylhydroxylamine, Dioctylhydroxylamine and N-Hydroxypyrrolidine

WE present here the results of an electron spin resonance investigation of the free radicals formed from diethylhydroxylamine, dioctylhydroxylamine and *N*-hydroxypyrrolidine. Dioctylhydroxylamine was prepared by the method of Harris and Olecott¹. Diethylhydroxylamine was obtained from Pennsalt Chemicals (85 per cent and 100 per cent) and from K and K Laboratories (85 per cent). *N*-Hydroxypyrrolidine was prepared by the method Wolfenstein² used for *N*-hydroxypiperidine and by the method described by Blout³.

Purity of compounds was determined by thin-layer chromatography using solvent systems of acetone, methanol and acetone: methanol 1:1 (v/v). The K and K diethylhydroxylamine (85 per cent) gave three spots and the 100 per cent material gave two spots. *N*-Hydroxypyrrolidine also gave two spots. As a result of these tests, the samples were purified as oxalate derivatives and the hydroxylamine was recovered by treatment with liquid ammonia. When standard solutions of the purified materials were spotted immediately after release from the oxalate salt, each gave only a single spot.

The tertiary butylhydroperoxide used to oxidize the hydroxylamines was a product of K and K Laboratories. The molar ratios of hydroperoxide to hydroxylamine were 1:1 or 2:1. Spectra were obtained with a Varian E-3 EPR spectrometer.