plausible to assume $K_2 \approx K_3$ and, thus, $K_3 \approx 140$ and $\approx 65\ M^{-1}$ at -38 and $-3°$, respectively. Hence, the mono complex, $N\cdot^-,Na^+,THF$ forms only 1.5% of all the pairs at $-3°$ and 0.7% at $-38°$, when [THF] = 1 *M*. Its proportion increases to about 15 and 7%, respectively, at the above-mentioned temperatures when [THF] = 0.1 *M*.

The presence of $N\cdot^-,Na^+,THF$ is reflected by the esr data presented in Figure 6. It is plausible to expect a_{Na} to be slightly larger for $N\cdot^-,Na^+,THF$ than for $N\cdot^-,Na^+,2THF$. Hence, the trends shown in Figure 6 become rationalized (note the increase of the observed a_{Na} at higher temperatures and with *decreasing* concentration of THF). Nevertheless, the relatively high values of a_{Na} even at $-90°$ indicate that both complexes, $N\cdot^-,Na^+,THF$ and $N\cdot^-,Na^+,2THF$, are virtually tight pairs at the investigated concentrations of THF. However, as shown by Hirota,[3,4] at still higher concentrations of THF loose pairs (presumably $N\cdot^-,Na^+,4THF$) are formed at sufficiently low temperatures ($a_{Na} \sim 0.2$ G).

Our results indicate that the process

$$N\cdot^-,Na^+\ (\text{in DEE}) + 2THF \rightleftarrows N\cdot^-,Na^+,2THF\ (\text{in DEE})$$

is exothermic to an extent of 4 kcal/mol but the respective $\Delta S \sim 0$. (We should consider "corrected" ΔS's which take into account the fact that THF (or DME in the THP + DME system) molecules are with drawn from 1 *M* solution, while the released DEE (or THP) molecules return to about 10 *M* solution. The corrected ΔS's are larger by about 4.6 eu than the one quoted above.) The interaction of THF molecules with $N\cdot^-,Na^+$ is therefore stronger than that with DEE, and in the formation of the $N\cdot^-,Na^+,2THF$ complex two of the DEE molecules were replaced by two THF molecules. The low value of ΔS is again indicative of the formation of tight pairs, because the formation of the loose pair leads to a negative and absolutely large ΔS. Hence, the thermodynamic results confirm the esr observations.

Finally, the behavior of $N\cdot^-,K^+$ ion pairs calls for some comments. It seems that the interaction of $N\cdot^-,K^+$ with DEE or even THF is weak. It is significant that in spite of the lower ionization potential and heat of sublimation of potassium, when compared with sodium, the relevant ΔH_1 is about 0. Also, the addition of THF led to hardly any increase in $N\cdot^-,K^+$ concentration and again the system was not affected by temperature variation. The low a_K value observed by Hirota and by ourselves is not diagnostic of loose ion pairs; it reflects the much weaker magnetic moment of the ^{39}K nucleus. In view of the weak interaction of $N\cdot^-,K^+$ with the solvent, it may not be justified to treat the ion pairs surrounded by a solvation shell of different composition as distinct thermodynamic species.

Acknowledgment. We wish to thank Drs. Michael Fisher and K. Saito for their help in carrying out this investigation. We acknowledge also the financial help of the National Science Foundation and of the Petroleum Research Fund, administered by the American Chemical Society.

Electron Paramagnetic Resonance Investigation of Transition Metal Complexes. XV. Complexes of Vanadyl Chloride with Tertiary Phosphines[1]

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Abstract: A family of vanadyl–phosphine complexes $VOCl_2\cdot 2(PR_3)$, with varying bulkiness of the substituents R, have been investigated. The epr spectra show increasing line width with increasing molecular volume. The line-width variation can be described by using an equation derived by Kivelson, *et al.*, assuming that the only essential variable is the equivalent spherical hydrodynamic radius of the compounds. Structural information was obtained favoring a trigonal-bipyramidal *vs.* a square-pyramidal arrangement.

Recently[1] we reported briefly on the epr spectrum observed in the reaction solution if $VOCl_2$ is solubilized in toluene by an excess of tertiary phosphine. The signal (see Figure 1a) shows the interaction of the unpaired electron of V^{IV} with the ^{51}V nucleus (nuclear spin $I = {}^7/_2$). Each of the eight vanadium lines is further split into a 1:2:1 triplet. This hyperfine structure can be attributed unambiguously to two equivalent phosphorus nuclei, since the corresponding complex with arsine (^{75}As, $I = {}^3/_2$) has a spectrum in which the triplets are replaced by septets (thus excluding hydrogen).[2] The epr signal was thus ascribed to the complex $VOCl_2\cdot 2(C_2H_5)_3P$. From the signal intensity it could be estimated that essentially all vanadium was present in the signal giving form.

The present paper deals with a family of similar complexes which only differ by the substituents at the phosphorus in the phosphine ligands. The epr spectra of these complexes show marked differences in line width

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(1) Part XIV: G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **82**, 955 (1970); *Angew. Chem. Int. Ed. Engl.*, **9**, 957 (1970).

(2) (a) G. Henrici-Olivé and S. Olivé, *Chem. Commun.*, 596 (1969). (b) The arsine spectrum was first observed with a VCl_3 solution.[2a] Experiments with $VOCl_2$ suggest that the reported signal is due to $VOCl_2\cdot 2AsR_3$.

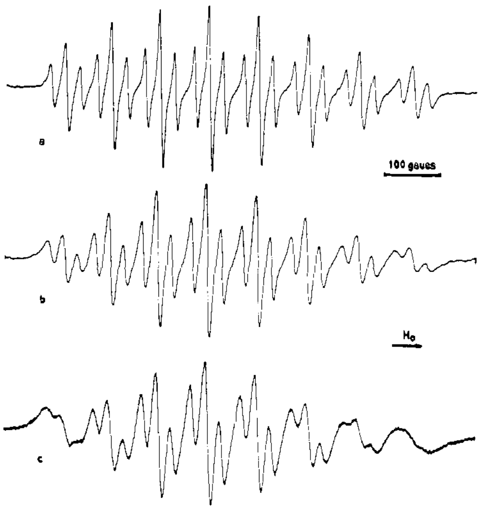

Figure 1. Epr signals of the complexes of $VOCl_2$ with phosphines, in toluene, temperature 20°: (a) triethylphosphine, (b) tri-*n*-propylphosphine, (c) diphenylethylphosphine.

which can be analyzed in terms of the theory of Kivelson, *et al.*[3,4]

Spectra

In Figure 1 the epr solution spectra of three complexes of $VOCl_2$ with different phosphines [triethylphosphine (a), tri-*n*-propylphosphine (b), and diphenylethylphosphine (c)] are represented. Three further complexes have been investigated, namely those with dimethylphenylphosphine (spectrum intermediate to a and b), tri-*n*-butylphosphine (intermediate to b and c), and triphenylphosphine (lines somewhat broader than c, but superimposed by another, weaker signal, and therefore less reliable).

The *g* factor as well as the vanadium and phosphorus hyperfine coupling constants are, within the error limits of the present determination, independent of the phosphine ligand; namely, $g_0 = 1.981 \pm 0.001$, $a_{V,0} = 250 \pm 2$ MHz, and $a_{P,0} = 71 \pm 2$ MHz (second-order corrections have been applied).

The solid-state spectrum of the compound $VOCl_2 \cdot 2(C_2H_5)_3P$ has been obtained in 2-methyltetrahydrofuran at −140°. The signal (see Figure 2) seems to be characteristic for a compound with axial symmetry. The hyperfine lines corresponding to the symmetry axis parallel to the magnetic field ($A_z \equiv A_{\parallel}$) are relatively well resolved and easily discerned. The rather crowded central part of the spectrum is best analyzed in terms of $A_x = A_y \equiv A_{\perp}$, as shown in the stick diagram below the spectrum in Figure 2. The first strong signals of either side of the spectrum, which clearly do not belong to the set of parallel features, have been taken as the $m_I = \pm {}^7/_2$ lines of the perpendicular spectrum (large arrows in Figure 2). From there $A_{V_{\perp}}$ and $g_{\perp}$ are easily obtained. The hyperfine coupling constant $A_{P_{\perp}}$ is best determined in those regions of the spectrum which are not crowded by parallel features (small arrows). The perpendicular data are necessarily somewhat less accurate than the parallel ones.

The data are summarized in Table I, together with those obtained from the solution spectrum of the same complex. The data are self-consistent, as shown by the relatively close agreement between measured values of $g_{\perp}$, $a_{V_{\perp}}$, and $a_{P_{\perp}}$ with those calculated according to

$$g_0 = (g_{\parallel} + 2g_{\perp})/3 \qquad a_0 = (A_{\parallel} + 2A_{\perp})/3 \tag{1}$$

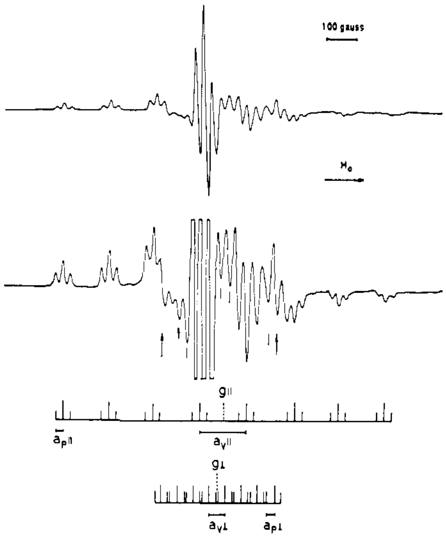

Figure 2. Epr spectrum of the complex $VOCl_2 \cdot 2(C_2H_5)_3P$ in a rigid glass (2-methyltetrahydrofuran at −140°). For the significance of the arrows in the enlarged, lower spectrum, see text.

The solid-state spectra of the other complexes are not as well resolved and do not allow the determination of all parameters. From the distance and position of the parallel features for $m_I = \pm {}^7/_2$ it was, however, estimated that $A_{V_{\parallel}}$ and $g_{\parallel}$ are the same for all complexes under investigation, to within the limits of the data. It was therefore assumed that the *g* tensor and the vanadium hyperfine tensor are, to a first approximation, the same for all six compounds.

Table I. Magnetic Parameters of the Complex $VOCl_2 \cdot 2(C_2H_6)_3P$ (Corrected to Second Order)

Parameter	Measured	Calculated (eq 1)
g_0	1.981	
$g_{\parallel}$	1.974	
$g_{\perp}$	1.980	1.984
$a_{V,0}$, MHz	250	
$A_{V_{\parallel}}$, MHz	440	
$A_{V_{\perp}}$, MHz	154	155
$a_{P,0}$, MHz	72	
$A_{P_{\parallel}}$, MHz	79	
$A_{P_{\perp}}$, MHz	70–80	73

Analysis and Discussion of the Line Width

Figure 1 shows pronounced differences in line width for the various complexes. Given the close similarity of the magnetic parameters (*g* and *A* tensors) within the different compounds, it is tempting to relate the line-width variation to the increasing molecular volume, making use of the theory for the line width of paramagnetic species with anisotropic *g* tensors and hyperfine tensors advanced by Kivelson, *et al.*[3,4] According to

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(3) R. Wilson and D. Kivelson, *J. Chem. Phys.*, 44, 154, 4440, 4445 (1966).

(4) R. W. Atkins and D. Kivelson, *ibid.*, 44, 169 (1966).

these authors, the line width T_2^{-1} (radians sec^{-1}) is given by

$$T_2^{-1} = (\alpha'' + \alpha') + \beta m + \gamma m^2 + \delta m^3 \qquad (2)$$

where m is the z component of the nuclear spin. The parameters α', β, γ, and δ are consequences of the anisotropy of the g and A tensors. For the special case of axial symmetry, they are given by[3,5]

$$\alpha' = \frac{b^2}{40} I(I + 1)(3 + 7u)\tau_R + \left(\frac{\Delta g}{g}\omega\right)^2 \frac{1}{45}(4 + 3u)\tau_R - \frac{b^2a}{40\omega}I(I + 1)5uf\tau_R - \frac{\Delta g}{g}\frac{ba}{30}I(I + 1)(1 + u)\tau_R \qquad (3)$$

$$\beta = \frac{\omega}{15g}b\Delta g(4 + 3u)\tau_R - \frac{b^2a}{20\omega}I(I + 1) \times (1 + u + 7uf)\tau_R - \frac{b^2}{40}\frac{a}{\omega}(3 + 2u)\tau_R - \frac{\omega a}{45}\left(\frac{\Delta g}{g}\right)^2(8 + 6u + 6uf)\tau_R \qquad (4)$$

$$\gamma = \frac{b^2}{40}(5 - u)\tau_R - \frac{ab\Delta g}{30g}(7 + 5u + 12uf)\tau_R + \frac{b^2a}{40\omega}5uf\tau_R \qquad (5)$$

$$\delta = \frac{b^2a}{20}(1 + u + uf)\tau_R \qquad (6)$$

where I = nuclear spin ($I = {}^7\!/_2$ for ^{51}V), ω = microwave frequency = 5.8×10^{10} radians sec^{-1}, $u = 1/(1 + \omega^2\tau_R^2)$, $f = u\omega^2\tau_R^2$, $a = a_{V,0}$, $b = 2(A_{\parallel} - A_{\perp})/3$, and $\Delta g = g_{\parallel} - g_{\perp}$. In eq 3–6, τ_R represents the rotational relaxation time

$$\tau_R = 4\pi r^3\eta/3kT \qquad (7)$$

where r is the equivalent spherical hydrodynamic radius of the compound.

The parameter α'', on the other hand, arises from spin rotational relaxation[4,6] and is given by

$$\alpha'' = \frac{(\Delta g_{\parallel}{}^2 + 2\Delta g_{\perp}{}^2)kT}{12\pi r^3\eta} \qquad (8)$$

with $\Delta g_{\parallel} = g_{\parallel} - 2.0023$ and $\Delta g_{\perp} = g_{\perp} - 2.0023$.

The determination of the line width T_2^{-1} from the experimental spectra has been accomplished by comparison with computer-simulated spectra, assuming Lorentzian line shape. These data are given in Table II as T_2^{-1}(exptl).

The numerical values of $\alpha = (\alpha'' + \alpha')$, β, γ, and δ can then be determined by fitting the experimental line-width data to eq 2 by the least-squares method. The results, converted to radians per second, are given in Table III (first four lines). The recalculation of T_2^{-1} with these values is included in Table II. As already observed by Kivelson, *et al.*,[3] the fit is less satisfactory if the cubic term in eq 2 is omitted.

Table II. Line-Width Data, MHz

m	T_2^{-1}(exptl)	T_2^{-1}(calcd)	T_2^{-1}(exptl)	T_2^{-1}(calcd)
	$VOCl_2 \cdot 2(C_2H_5)_3P$		$VOCl_2 \cdot 2(CH_3)_2P(C_6H_5)$	
−7/2	21.0	20.9	25.3	25.4
−5/2	17.2	17.5	20.0	20.0
−3/2	15.6	15.6	17.3	17.1
−1/2	15.2	15.1	16.0	16.3
+1/2	16.0	16.0	17.8	17.5
+3/2	18.3	18.3	20.0	20.3
+5/2	21.7	21.8	24.7	24.6
+7/2	26.6	26.6	30.0	30.0
	$VOCl_2 \cdot 2(n\text{-}C_3H_7)_3P$		$VOCl_2 \cdot 2(n\text{-}C_4H_9)_3P$	
−7/2	45.0	43.1	55	56.1
−5/2	31.0	31.6	44	41.5
−3/2	24.5	25.3	33	33.7
−1/2	23.0	23.6	31	31.8
+1/2	26.0	26.1	34	35.2
+3/2	32.0	32.2	44	43.4
+5/2	40.0	41.4	57	55.5
+7/2	55.0	53.0	70	70.5
	$VOCl_2 \cdot 2(C_2H_5)P(C_6H_5)_2$		$VOCl_2 \cdot 2(C_6H_5)_3P$	
−7/2		80.0		87.1
−5/2	55	54.8		64.3
−3/2	42	41.9	52	51.9
−1/2	38	38.3	48	48.5
+1/2	43	42.3	53	52.9
+3/2	50	51.8	64	64.1
+5/2	66	65.2		80.6
+7/2		80.3		101.4

Only the sum of α'' and α' can be determined by this method, whereas the parameters β, γ, and δ are obtained separately and can be used to calculate the equivalent spherical radii of the compounds, making use of eq 4–7. All necessary magnetic data are known (see Table I) and are assumed to be the same for the six compounds; T/η for toluene at 20° has been given by Kivelson, *et al.*,[3] as 5×10^4 °K/P.

The negative coefficient δ of the cubic term in eq 2 is relatively small and shows a certain scatter (see Table III); it has therefore been discarded for the determination of the radii.

The values of r best fitting eq 4 and 5 are given as $r(\beta)$ and $r(\gamma)$, respectively, in Table III. They show a reasonable agreement for every complex, thus giving credence to the assumption that the radius r is the only, or at least the most prominent, cause for the line-width variation.

The parameters α'' and α', the first being proportional to r^{-3}, the second increasing with increasing r^3, can be separated within the framework of the theory of Kivelson, *et al.*, calculating α'' from eq 8. The averaged radii, $\bar{r}(\beta,\gamma)$, have been used for this calculation. Substracting then α'' from α, one also obtains α'. The data are included in Table III. With eq 6 and 7, a third, independent value of the radius, $r(\alpha')$, can be calculated. The agreement with the data obtained formerly is fairly good (compare lines 9 and 10 in Table III).

On the whole, the spectra are in good agreement with Kivelson's theory, the difference of line widths being, at least predominantly, due to variations of the molecular volume. The absolute values of the radii of the compounds are reasonable and in a meaningful relationship to one another and to the value of 3.28 Å found by Kivelson[3] for vanadylacetylacetonate, VO(acac)$_2$.

It should perhaps be noted that the Kivelson theory presupposes isotropic motion of the molecule in the solution. It has been pointed out recently by Luck-

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(5) G. R. Luckhurst and J. N. Ockwell, *Mol. Phys.*, 16, 165 (1969).
(6) P. S. Hubbard, *Phys. Rev.*, 131, 1155 (1963).

Table III. Calculated Parameters[a] and Radii r (Å) for the Six $VOCl_2$–Phosphine Complexes

Parameter	$(C_2H_5)_3P$	$(CH_3)_2P(C_6H_5)$	$(C_3H_7)_3P$	$(C_4H_9)_3P$	$(C_2H_5)P(C_6H_5)_2$	$(C_6H_5)_3P$
$\alpha \times 10^{-6}$	96.4	104.5	153.0	206.0	248.0	310.0
$\beta \times 10^{-6}$	5.8	7.4	15.8	22.0	25.1	28.3
$\gamma \times 10^{-6}$	4.3	5.6	12.1	15.7	20.6	22.8
$\delta \times 10^{-6}$	−0.059	−0.26	−0.56	−0.71	−1.95	−1.26
$\alpha'' \times 10^{-6}$	7.1	5.2	2.2	1.6	1.3	1.2
$\alpha' \times 10^{-6}$	89.3	99.3	150.8	204.4	246.7	308.8
$r(\beta)$	3.7	4.25	5.8	6.6	6.85	7.1
$r(\gamma)$	3.5	3.75	4.8	5.3	5.75	5.9
$\bar{r}(\beta,\gamma)$	3.6	4.0	5.3	5.95	6.3	6.5
$r(\alpha')$	3.95	4.25	5.1	5.7	6.2	6.7

[a] α $(=\alpha'' + \alpha')$; β, γ, and δ (radians sec^{-1}).

hurst and Ockwell[5] that this supposition is somewhat unrealistic for molecules with axial symmetry. Rotation about the symmetry axis does not contribute to the line width since the spin Hamiltonian is invariant under such rotation. Only rotation about the axes perpendicular to the symmetry axis results in relaxation and is therefore determinant for the line width. Taking this effect of anisotropic motion into account, these authors found that the expression r^3 in eq 7 should be replaced by

$$r^3 = \frac{4(a_3{}^4 - a_1{}^4)}{3[(2a_3{}^2 - a_1{}^2)S - 2a_3]} \tag{9}$$

where $2a_3$ is the length of the symmetry axis of an axially symmetrical ellipsoid representing the molecule and $2a_1$ is the length of the axes perpendicular to the symmetry axis.

For $a_3 < a_1$

$$S = \frac{2}{(a_1{}^2 - a_3{}^2)^{1/2}} \tan^{-1}\left(\frac{(a_1{}^2 - a_3{}^2)^{1/2}}{a_1}\right) \tag{10}$$

and for $a_3 > a_1$[7]

$$S = \frac{2}{(a_3{}^2 - a_1{}^2)^{1/2}} \ln\left(\frac{a_3 + (a_3{}^2 + a_1{}^2)^{1/2}}{a_1}\right) \tag{11}$$

By making use of these relationships it is possible to make an estimate about the molecular structure of the complexes being investigated. Five-coordinate transition metal complexes have commonly either trigonal-bipyramidal or square-pyramidal arrangements. For the compound $VOCl_2 \cdot 2N(CH_3)_3$, the first configuration has been reported with the amine ligands at the apices,[8] whereas $VO(acac)_2$ forms a square pyramid with the oxygen at the apex.[9]

For the complex $VOCl_2 \cdot 2P(C_2H_5)_3$, one can estimate from molecular models[10] values of $a_3 \simeq 6.2$ Å, $a_1 \simeq 2.55$ Å for the trigonal bipyramid with the phosphine ligands at the apices, and $a_3 \simeq 1.95$ Å,[5] $a_1 \simeq 5.1$ Å for the square pyramid. In the first case this leads to a value of 73 Å^3 for the experimental quantity r^3 (eq 9 and 11); in the second case a value of 91 Å^3 is obtained (eq 10 and 11). Comparison with Table III ($\bar{r} \simeq 3.7$ Å, $\bar{r}^3 \simeq 51$ Å^3) would then indicate that the trigonal bipyramid is the more probable configuration for the present complexes.

Experimental Section

All samples were prepared and measured *in vacuo*. A Varian V-4502 spectrometer with 100-kHz field modulation was used for the epr measurements. The characteristic parameters (g factors, hyperfine coupling constants) were obtained by comparison with a standard sample of peroxylamine disulfonate (g = 2.0055, a_N = 13.0 ± 0.1 G = 36.5 ± 0.3 MHz).

The concentration of the samples as well as the modulation amplitude and the rf power were maintained below the level that resulted in influence on the line width.

The line-width data were obtained by comparing each triplet with computer-simulated 1:2:1 triplets of varying line width. Since simulated and experimental spectra have not been measured with the same spectrometer equipment, an internal calibration had to be used, as described in a preceeding paper.[12]

Acknowledgment. Thanks are due to Dr. G. R. Luckhurst, Department of Chemistry, University of Southampton, for helpful criticism, and to Varian A.-G., Zug, for permitting the use of the Spectro System 100 for spectra simulations.

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(7) J. H. Freed, *J. Chem. Phys.*, **41**, 2077 (1964).

(8) J. E. Drake, J. Vekrig, and J. S. Wood, *J. Chem. Soc. A*, 1000 (1968).

(9) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

(10) Dreiding models have been used; the van der Waals radii[11] of the outer atoms (H, Cl, O) have been added to the measured distances. For the bond length V–P a value of 2.5 Å has been used, which is the bond length V–N from ref 8, plus the difference of the covalent radii of P and N.

(11) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(12) G. Henrici-Olivé and S. Olivé, *J. Organometal. Chem.*, **21**, 377 (1970).