ESR Spectra of Bis(acetylacetonato)oxovanadium(IV) and Related Chelates in Molten *o*-Terphenyl and Some Other Organic Compounds

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All the patterns from the isotropic ESR spectrum to the anisotropic one of bis(acetylacetonato)oxovanadium(IV) and related chelates are recorded by employing molten *o*-terphenyl as a solvent and by changing the temperature above and below the melting point. The results are qualitatively explained in terms of the anisotropic molecular motion and are considered to be evidence for the presence of clusters in the melt. Similar observations are made with some derivatives of 2,4,6-trinitrodiphenylamine, but only partially with *m*-terphenyl and the 3′-methoxy and 3′-ethoxy derivatives of 2,4-dinitrodiphenylamine. The implications of the results concerning the structure of the melts are discussed.

The ESR spectra of oxovanadium(IV) chelates are known to be substantially modified by the medium.1) The isotropic spectra obtainable in liquid solutions consist of eight hyperfine lines arising from the nuclear spin $I=7/2$ of vanadium 51. On the other hand, each of the randomly oriented paramagnetic species immobilized in glasses separately contributes eight transitions to the spectrum; therefore, a superposition of the spectra associated with each orientation, weighted in proportion to the probability of finding the chelate molecules at that particular orientation, may be observed. In several liquid solutions, the appearance of an anisotropic molecular reorientation has been suggested in order to explain a marked deviation from the isotropic spectra.2) If the viscosity of a solvent varies by many orders of magnitude upon a change in the temperature, one may observe all the patterns from the isotropic spectrum to the entirely anisotropic one. Knowledge of such spectral patterns is expected to be useful in studies of motional behavior in general, not only of liquids but also of solids, since the reorientation of the chelate molecule manifests the motion of the solvent or host molecules. In order to standardize the pattern, we initiated our work with an examination of the ESR spectra of three oxovanadium(IV) chelates dissolved in molten *o*-terphenyl, the viscosity of which has been reported in detail by Ubbelohde and his collaborators and also by Greet and Turnbull.3–5) Then, attempts were made to study the motional behavior in melts of some derivatives of 2,4-dinitro- and 2,4,6-trinitrodiphenylamines.

Experimental

The bis(acetylacetonato)oxovanadium(IV), hereafter abbreviated VO(acac)$_2$, was commercially obtained. The bis(benzoylacetonato)oxovanadium(IV), VO(bza)$_2$, and bis(dibenzoylmethanato)oxovanadium(IV), VO(dbm)$_2$, were prepared following the procedures reported by Selbin *et al.*6) The terphenyls were freed from polar impurities by chromatography on a column of activated alumina, using petroleum ether as the elutrient; they were then recrystallized from the same solvent. The melting points of the *o*- and *m*-terphenyls agreed well with the literature values of 55.5 and 87 °C.3) The derivatives of the 2,4-dinitro- and 2,4,6-trinitro-diphenylamines were obtained by the condensation of appropriate derivatives of aniline with 2,4-dinitro- and 2,4,6-trinitrochlorobenzenes respectively. The concentrations of the paramagnetic probe dissolved in the organic melts were in the order of 10^{-3} M. As our work is not concerned with the linewidth, the solutions were not degassed. The spectra were recorded on a JEOL model JES-ME-3X spectrometer with 100 kHz modulation in the range from room temperature to 160 °C. The magnetic-field scan was calibrated with Mn^{2+}-doped MgO powder (86.9 G).

Results and Discussion

The oxovanadium chelates employed here are known to have approximately axial hyperfine and g tensors.7–9) Their components parallel and perpendicular to the V=O bond direction will be denoted by $A_{\parallel}$ and $A_{\perp}$,10)

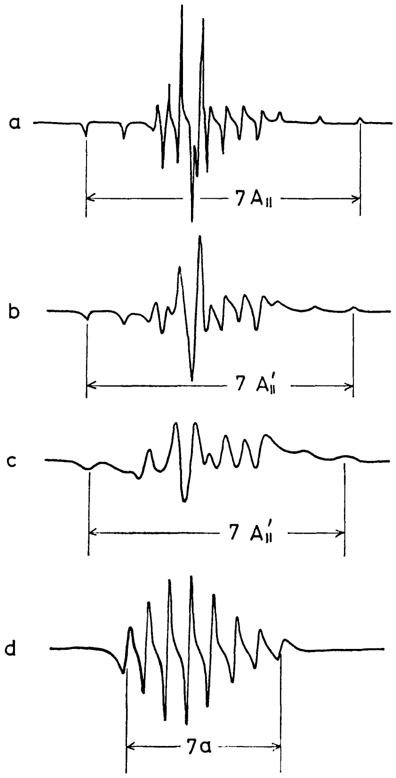

Fig. 1. ESR spectra of bis(acetylacetonato)oxovanadium(IV) in molten *o*-terphenyl at 24 °C (a), 40 °C (b), 50 °C (c), and 100 °C (d).

and by $g_{\parallel}$ and $g_{\perp}$, respectively. However, the rather small anisotropy in the latter will be ignored for the sake of simplicity in the following discussion. Some representative spectra of $VO(acac)_2$ in molten *o*-terphenyl observed at four different temperatures are presented in Fig. 1. At room temperature the supercooled melt exhibits an ESR spectrum typical of glasses. Here, the $VO(acac)_2$ molecules may be supposed to be randomly and rigidly oriented in the space. Although the central portion is complicated by an overlap of the parallel and perpendicular resonance lines, the $M_I = \pm 7/2$ and $\pm 5/2$ parallel resonance lines are well resolved. The values of $7A_{\parallel}$ are given by the distance between the outermost lines corresponding to the $M_I = \pm 7/2$. Thus, $A_{\parallel}$ is estimated to be 189 G.

The spectrum recorded at 40 °C is shown in Fig. 1b. The main feature of the room-temperature spectrum is still noticeable; however, each line has become much broader, and the distance between the outermost lines is markedly diminished, $7A'_{\parallel}$. Although it is not easy to observe, the perpendicular resonance spectrum is expected to be expanded; that is, $A'_{\perp} > A_{\perp}$. These are the spectral characteristics exhibited by a paramagnetic probe undergoing slow motion.[11] The spectrum taken at 50 °C indicates increased molecular motion (see Fig. 1c). If the probe molecules are tumbling rapidly, both $A'_{\parallel}$ and $A'_{\perp}$ are reduced to a, the isotropic hyperfine constant. As is shown in Fig. 1d, the isotropic eight-line pattern normally expected under such conditions is observed at 100 °C. The coupling constant is 107 G; therefore, $A_{\perp}$ may be estimated to be 66 G by the $(A_{\parallel} + 2A_{\perp}) = 3a$ relation. The former value can be well compared with that of 108 G observed in a benzene solution by Stoklosa and Wasson.[9] Some years ago, Luckhurst and Ockwell examined the ESR spectrum of $VO(acac)_2$ in molten *o*-terphenyl.[12] Their measurements were apparently carried out at too high temperatures for the drastic change to be observed.

When the temperature is not high enough to observe the isotropic spectrum, the motion of the present probe molecule may be supposed to be anisotropic. If this motion is rapid, the parameter

$$S = (3\langle \cos^2 \theta \rangle - 1)/2 \tag{1}$$

is known to be equal to

$$(A'_{\parallel} - A'_{\perp})/(A_{\parallel} - A_{\perp}) \text{ or } (A'_{\parallel} - a)/(A_{\parallel} - a), \tag{2}$$

where the θ angle is that between the V=O bond direction and the magnetic field, and where the average is temporal.[13] Upon a further lowering of the temperature, the anisotropic molecular motion may become so slow in the time scale of ESR spectroscopy that the average must be considered to be spatial. Nevertheless, for the sake of convenience, we will continue to employ the $(A'_{\parallel} - a)/(A_{\parallel} - a)$ ratio, denoted by S, as a measure of molecular motion throughout the temperature range examined. As a matter of fact, the S value can be estimated by means of the above equation only in the range from 1.00 (as the rigid limit) to about 0.55. Beyond the latter value, it is not possible to locate the outermost lines. Therefore, the rapid anisotropic molecular motion model may be not valid at all in the observable temperature range.

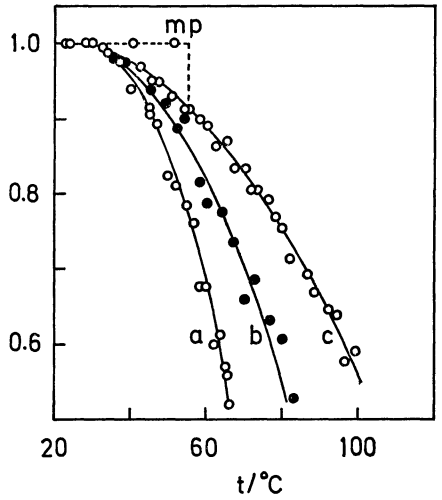

Fig. 2. Temperature dependence of the parameter S for $VO(acac)_2$ (a), $VO(bza)_2$ (b), and $VO(dbm)_2$ (c) in *o*-terphenyl. The horizontal line is for $VO(dbm)_2$ in solidified *o*-terphenyl.

The variation in S with the temperature for $VO(acac)_2$ is plotted in Fig. 2, along with those for $VO(bza)_2$ and $VO(dbm)_2$. At the melting point of pure *o*-terphenyl, the values of S are 0.77 for $VO(acac)_2$, 0.87 for $VO(bza)_2$, and 0.91 for $VO(dbm)_2$. Thus, the larger the chelate molecule, the more difficult the motion round two axes lying in the flat plane of the molecule appears to be. In order to achieve the same value of S, say 0.80, *o*-terphenyl must be heated to 73 °C in the case of $VO(dbm)_2$ compared with 53 °C in the case of $VO(acac)_2$. The agreement in S does not mean that the motional behavior of one chelate is the same as that of the other, since the mode of the molecular motion expressed as a function of θ depends upon the size and shape of the chelate molecule.

As the melting point is approached, molten *o*-terphenyl is known to show a marked departure from the linearity in the plot of the logarithm of the viscosity against $1/T$. On the basis of this departure, the formation of interlocked clusters in molten *o*-terphenyl near and below the melting point has been postulated by Ubbelohde and his collaborators.[3,4] According to them, clusters of a few molecules exist from temperatures of about 195 down to 70 °C. At the latter temperature the volume fraction of the cluster is estimated to be about 0.3. As the motion of the chelate molecule is largely governed by the volume of the solvent to be displaced by it, interlocking to this extent is enough to affect the ESR spectra of $VO(bza)_2$ and $VO(dbm)_2$ markedly. Between 70 °C and the melting point, clusters of a higher order appear to be formed in appreciable concentrations. In this temperature range, the rotation of even the smallest chelate molecule, $VO(acac)_2$, is clearly restricted. When the temperature is lowered still further, the clustering mechanism becomes more complex, eventually leading to the ESR spectra of the immobilized chelate molecule.

Upon a rise in the temperature, the viscosity, η, of the medium and also the kinetic energy of the probe molecule change. The two changes certainly contribute to the decrease in the parameter, S. Therefore, the

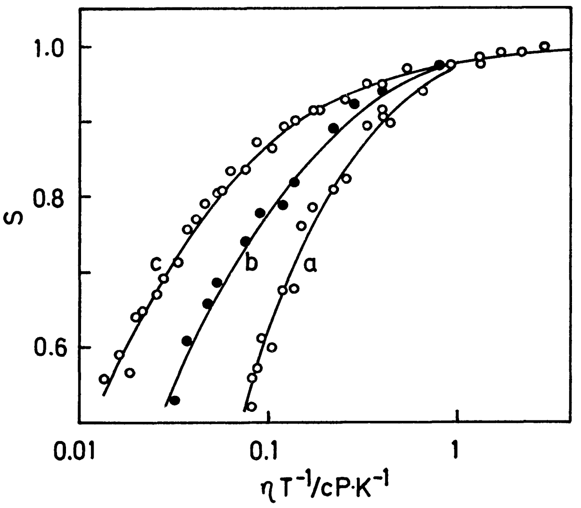

Fig. 3. Variation of the parameter S with η/T for VO(acac)$_2$ (a), VO(bza)$_2$ (b), and VO(dbm)$_2$ (c) in *o*-terphenyl.

variation in S with η/T shown in Fig. 3 may be more useful than the variation in S with t (or T) shown in Fig. 2. The viscosity values of the molten *o*-terphenyl required for the plots were calculated by means of the equation of Greet and Turnbull applicable to the range from -16 to 250 °C.[5] The η/T ratio appears in the well-known equation relating the viscosity of a medium to the Debye correlation time, τ

$$\tau = 4\pi r^3\eta/3kT, \qquad (3)$$

where r is the radius of the probe molecule rotating in the medium. As r may not be constant in the slow-motion model, the plots in Fig. 3 may be different from the variation in S with τ.

Now, let us comment on the observation made by Stoklosa *et al.*[2] Their spectra of VO(bza)$_2$ in quinoline and 2-methylbenzoxazole measured at room temperature are well approximated by our spectra in *o*-terphenyl at 80 °C (S=0.61) and 83 °C (S=0.53) respectively. The spectral pattern is so sensitive to the temperature that one can easily differentiate such a small change. The viscosities of quinoline and 2-methylbenzoxazole have been reported by them to be 2.314 and 3.403 cP at 25 °C. The corresponding values of η/T, 0.0078 and 0.011 cP K^{-1}, are markedly smaller than the values of *o*-terphenyl at the above-mentioned temperatures, as can readily be seen by Fig. 3. Therefore, it is apparent that viscosity alone cannot account for the deviations from the isotropic ESR spectra observed by Stoklosa *et al.* It must be added that, in this temperature range, the viscosities calculated by means of the equation of Greet and Turnbull are larger than those of Andrews and Ubbelohde. Fortunately, the choice does not affect the present conclusion. When the size of the probe molecule is larger, the viscosity effect becomes more dominant in the determination of the ESR spectrum. The spectrum of VO(dbm)$_2$ recorded in 2-methylbenzoxazole can well be compared with that observed in *o*-terphenyl at 92 °C (S=0.65), the η/T value being 0.022 cP K^{-1} (Greet and Turnbull) or 0.015 cP K^{-1} (Andrews and Ubbelohde). The latter value agrees almost entirely with the observed one.

When *o*-terphenyl solidifies, VO(acac)$_2$ and VO(bza)$_2$ exhibit single broad absorptions, indicating the segregation of the chelates, but VO(dbm)$_2$ remains dissolved. Although the spectrum of the last-mentioned substance consists of rather broad lines, the pattern is similar to that shown in Fig. 1a. No temperature dependence was observed up to the melting point, as is indicated by the horizontal line in Fig. 2. In sharp contrast to this, VO(dbm)$_2$ has been found to move slowly in some solid charge-transfer complexes. The results of these measurements will be the subject of forthcoming papers.

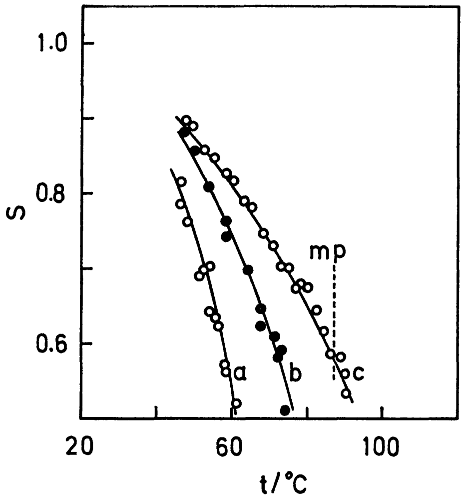

Fig. 4. Temperature dependence of the parameter S for VO(acac)$_2$ (a), VO(bza)$_2$ (b), and VO(dbm)$_2$ (c) in *m*-terphenyl.

m-Terphenyl behaves similarly, but less significantly than *o*-terphenyl, in the transport process.[3] In this terphenyl, too, a dramatic change in the ESR spectra could be recorded. The values of S measured with the three chelates are plotted against the temperature in Fig. 4. As the melts could not be cooled low enough for the anisotropic spectra to be observed, the $A_{\parallel}$ values determined in *o*-terphenyl were applied to these systems. The melting point of *m*-terphenyl is higher by about 30 °C than that of *o*-terphenyl; nevertheless, the temperature ranges shown in Fig. 4 are lower than the corresponding ones in Fig. 2. For example, an S value of 0.58 is found at the melting point in the case of VO(dbm)$_2$. If one assumes that the η/T value of *m*-terphenyl at this temperature is equal to that in *o*-terphenyl at S=0.58, the viscosity may be estimated to be 6.2 cP. This is in fair agreement with the value of 5.4 cP calculated by means of the equation of Andrews and Ubbelohde.[3]

The results presented above strongly suggest that extensive molecular interlocking in organic melts may be detected by measurements of the ESR spectra of dissolved oxovanadium chelates. Furthermore, the viscosity of the medium may be estimated by comparing these spectra with the ESR spectra recorded in molten *o*-terphenyl. As we have seen in the cases of VO(bza)$_2$ dissolved in quinoline and 2-methylbenzoxazole, the apparent viscosity obtained by the ESR technique is significantly larger than the actual one if some other interactions between the probe and the medium are conceivable. The present author earlier reported that the melts of some derivatives of 2,4,6-trinitrodiphenylamine are colored more deeply than the crystals and that they are readily supercooled without fading.[14] The presence of a strong molecular entanglement, assisted by the charge-transfer interaction between the electron-donating moiety of a molecule and the accepting moiety of the neighboring molecule, was suggested to account for this phenomenon. As will be described in the following paragraphs, the ESR spectra of dissolved $VO(acac)_2$ revealed that the viscosities at their melting points are as large as the corresponding values of molten *o*-terphenyl. The $A_{\parallel}$ values were found to be essentially the same as that in molten *o*-terphenyl. On the other hand, the *a* values could not be measured because of the rapid decomposition of $VO(acac)_2$ at high temperatures. Therefore, the latter was assumed to be 107 G.

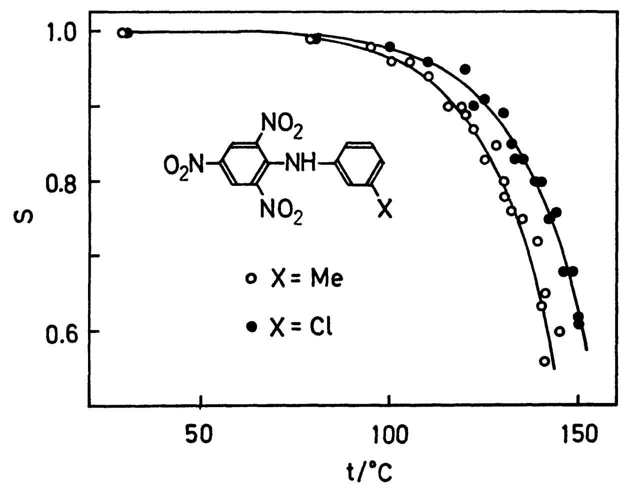

Fig. 5. Temperature dependence of the parameter *S* for $VO(acac)_2$ in 2,4,6-trinitro-3′-methyldiphenylamine (○) and 2,4,6-trinitro-3′-chlorodiphenylamine (●).

In Fig. 5, the results obtained by the use of the 3′-methyl and 3′-chloro derivatives are presented. The melting point of the former compound is 133 °C (130 °C by Busch and Pungs[15]) and that of the latter, 142—143 °C (137—139 °C by Wedekind[16]). The substituents are similar in size, but the bond moments are very different from each other. The higher melting point of the 3′-chloro derivative may be ascribed to the contribution of the large C–Cl bond moment to the intermolecular forces. The curve for the 3′-chloro derivative in Fig. 5 appears to be shifted to a higher temperature than that for the 3′-methyl derivative by just the difference in the melting point. As is shown by the electronic absorption spectra, the intermolecular charge-transfer interaction in melts is more pronounced in the 3′-methyl derivative than in the 3′-chloro derivative. However, its effect on the *S* value could not be detected. The *S* values at the melting points are 0.75 in both cases. The apparent viscosities are 65—67 cP. In these cases, the *S* values vary more gradually with the temperature than that in molten *o*-terphenyl. In other words, the temperature dependence of the viscosity of the diphenylamines is less than that of *o*-terphenyl.

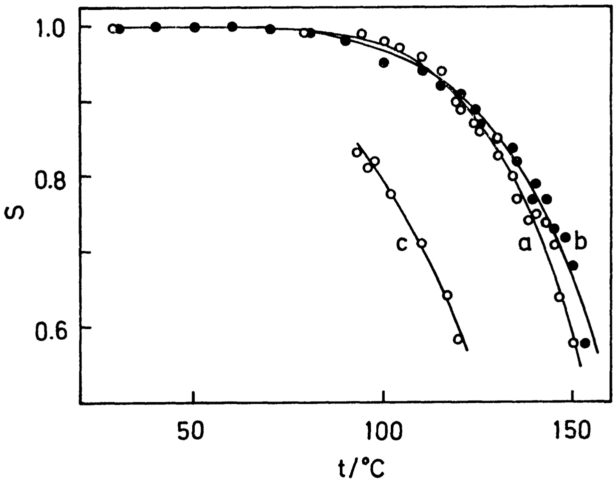

Fig. 6. Temperature dependence of the parameter *S* for $VO(acac)_2$ in 2,4,6-trinitro-2′-methoxydiphenylamine (a), 2,4,6-trinitro-3′-methoxydiphenylamine (b), and 2,4-dinitro-3′-methoxydiphenylamine (c).

The values of *S* displayed by the 2′- and 3′-methoxy derivatives are plotted against the temperature in Fig. 6. The substituent is more strongly electron-donating and more polar than methyl group. These factors favor a strong intermolecular interaction, but the bulkiness opposes it. As a result, the former compound melts at 148 °C (143 °C by James *et al.*[17]) and the latter, at 123—124 °C. Once melted, the 3′-methoxy derivative is slightly more viscous than the 2′-methoxy derivative in most of the examined temperature range. Two curves are nearly superimposed on the curve for the 3′-chloro derivative given in Fig. 5. The *S* value at the melting points are 0.63 and 0.89 respectively. Hence, the viscosities are about 44 and 130 cP. One may conclude that the intermolecular interaction in the 3′-methoxy derivative is drastically intensified upon melting.

Before reporting our attempts with 2,4-dinitro-2′-methoxydiphenylamine, it will be interesting to note other information. In the first place, this compound is known to be dimorphic. The unstable orange-yellow form transforms into the bright red form around 145 °C, and then melts at 165.5 °C.[18] The second outstanding feature of interest is that the melting point is markedly higher than that of 2,4,6-trinitro-2′-methoxydiphenylamine. Moreover, the color of the stable form is deeper than that of the trinitro compound. In contrast to the melt of the latter, the melt of the former compound could not be supercooled. The 3′-methoxy derivative is yellow and melts at 141—142 °C. This temperature, too, is higher than the melting point of the corresponding trinitro compound. Nonetheless, the curve for this compound (shown in Fig. 6) is located about 35 °C lower. Besides, the crystallization takes place around 93 °C. It is clear that no extensive formation of clusters occurs near the melting point of this compound. Thus, the absence of the nitro group at the

6 position increases the stability of the crystalline state, but decreases the cluster-forming potential in the melt. The clusters are some form of structural association into groups different from crystal nuclei; therefore, spontaneous crystallization may be prevented by extensive cluster formation. In addition to the stability of the crystalline state, the difficulty in cluster formation helps to explain why the dinitro compounds show a pronounced tendency to crystallize.

The behavior of the 2′- and 3′-ethoxy derivatives of 2,4-dinitro- and 2,4,6-trinitro-diphenylamines resemble that of the corresponding methoxy derivatives. Because of the presence of the bulky ethoxy group, each curve observed with the trinitro compound is located at a temperature about 10 °C lower than that of the methoxy derivative. The melt of 2,4-dinitro-3′-ethoxydiphenylamine could be supercooled to 85 °C, but that of the 2′-ethoxy derivative could not. The curve obtained with the former compound lies at slightly lower temperatures than that obtained with 2,4-dinitro-3′-methoxydiphenylamine. It is clear that the non-ideal viscosity-against-temperature characteristics displayed by these compounds are sensitive to small changes in the molecular shape.

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