Chemistry of Rhenium Alkyls. Part II.[1] Electron Spin Resonance and Electronic Absorption Spectra of Tetramethyloxo- and Oxotetrakis-(trimethylsilylmethyl)-rhenium(VI) †

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E.s.r. (*X* and *Q* band) and electronic absorption spectra of tetramethyloxorhenium(VI) and oxotetrakis(trimethylsilylmethyl)rhenium(VI) are reported. From these data, molecular-orbital coefficients for the compounds have been calculated.

IN the previous paper [1] we described the preparation of paramagnetic, d^1, alkyls of rhenium(VI) of formula $ReOR_4$ (R = Me and CH_2SiMe_3). The electron spin resonance and electronic absorption spectra are now reported and discussed.

RESULTS

E.S.R. Spectra.—Tetramethyloxorhenium(VI). A red benzene solution of $ReOMe_4$, prepared under strictly anaerobic conditions, gave a single broad line (ΔH = 70 mT, $g_{iso.} \approx 2{\cdot}04$) at 293 K. At 98 K the same solution yielded a well resolved spectrum showing more than two sets of six rhenium hyperfine lines with unequal spacing. On raising the temperature of the frozen solution this spectrum gradually decayed, giving place to an axially symmetric spectrum devoid of hyperfine structure and characterized by $g_{\parallel} \approx 2{\cdot}25$ and $g_{\perp} \approx 1{\cdot}94$. A similar but different spectrum was observed at 98 K in solutions to which a small amount of air had been admitted. However, on allowing such aerated solutions to remain at room temperature for *ca.* 2 min and refreezing, the original, well resolved but now slightly depleted, signal was obtained; it had the same temperature variation. Evidently oxidation to a diamagnetic species occurs as was found in separate experiments on a larger scale, the new paramagnetic species being intermediate as discussed later.

The spectra can be interpreted in terms of a square-based-pyramidal structure containing one rhenium atom having $S = \frac{1}{2}$. The loss of hyperfine structure at room temperature is typical of a fast spin–lattice relaxation probably through a relatively low-lying excited state. The spectra at intermediate temperatures are those predicted for slow rotational diffusion of a spin-doublet species.[2] This behaviour was also found in compounds of the type CrR_4 (R = CH_2SiMe_3 and CH_2CMe_3) which gave e.s.r. spectra typical of spin-triplet species which were rotating slowly.[3]

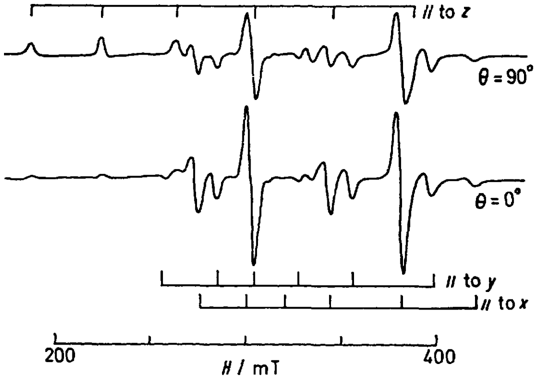
Oxotetrakis(trimethylsilylmethyl)rhenium(VI). Blue solutions of the compound in frozen benzene or n-hexane at 98 K at *X* band were almost identical to those of $ReOMe_4$, though less well resolved. There was no appreciable change on raising the temperature suggesting the absence of molecular motion; the spectra simply became weaker but could still be observed, with a six-line hyperfine structure, at room temperature.

The parameters given in Table 1 were derived with the aid of (*a*) the *Q*-band spectrum of $ReO(CH_2SiMe_3)_4$, and (*b*) spectra of partially oriented $ReOMe_4$ and $ReO(CH_2SiMe_3)_4$ in the frozen nematic phase of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline. The Figure shows an enhancement of the perpendicular features of the spectrum at θ = 0° which corresponds to the magnetic field perpendicular to the symmetry axis of the molecule. Likewise the parallel features are enhanced when the frozen solution is rotated to θ = 90°. On warming in the liquid-crystal solvent, the e.s.r. spectra of both compounds retained the rigid-solution appearance and weakened normally until they were lost in the noise. The parameters and the line analysis of the Figure were derived using computer programs MNES and ESRS.[4]

TABLE 1

E.s.r. parameters (energies in cm^{-1}) for the oxorhenium(VI) compounds

	$ReOMe_4$	$ReO(CH_2SiMe_3)_4$
g_x	1·958	1·951
g_y	1·936	1·941
g_z	2·252	2·218
A_x	−0·0330	−0·0355
A_y	−0·0187	−0·0191
A_z	−0·0422	−0·0416
Q_{axial}	0·0045	0·0039
$Q_{rhombic}$	0·0018	0·0021
γ_7	0·539	0·537
α_4	0·672	0·675
α_2	0·768	0·766



E.s.r. spectra of $ReOMe_4$ in liquid crystal. θ Is the angle of rotation of the sample tube from the orientation in which the solution was frozen and θ = 90° corresponds to the magnetic field along the C_{4v} axis of symmetry. Line analysis was derived by using computer programs MNES and ESRS

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† No reprints available.

[1] Part I, K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.

[2] J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.*, 1971, **75**, 3385.

[3] W. Mowat, A. J. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533; W. Mowat, A. J. Shortland, N. J. Hill, and G. Wilkinson, *ibid.*, 1973, 770.

[4] ESRS is a development of the program described by R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294; MNES is a least-squares procedure which uses ESRS. Both programs were written in their present form by R. D. Dowsing, Department of Computer Science, University College of Swansea, Swansea SA2 8PP.

Calculation of the Molecular-orbital Coefficients of ReOMe$_4$ *and* ReO(CH$_2$SiMe$_3$)$_4$.—We assume a square-pyramidal geometry with the oxygen at the apex and rhenium in the plane of the carbon atom,[5] although, as we will see later, the rhenium atom probably lies above the basal plane. The e.s.r. parameters clearly indicate a symmetry slightly lower than axial but we base our present analysis on the C_{4v} symmetry that has previously been assumed for oxo-compounds of vanadium,[5] and chromium, molybdenum, and tungsten.[6] Our aim is to show that the very high g values ($g_{\parallel}$ or g_z in particular) and other Hamiltonian parameters may be accommodated within this model.

If we take the z axis along the Re=O bond and the x and y axes along the Re–C bonds, then molecular orbitals (m.o.s) for ReOMe$_4$, using the notation of Marov *et al.*[6] but allowing for the absence of π-bonding to carbon, are as in equations (1)—(5). The ground state is B_2 and corresponds to

$$4b_1 = \alpha_4 d_{x^2-y^2} - [\alpha_4'(-\sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^3 - \sigma_y{}^4)/2] \quad (1)$$

$$7e = \gamma_7 d_{xz,yz} - \gamma_7''\pi_{x,y}{}^5 \quad (2)$$

$$b_2 = d_{xy}$$

$$2e = \gamma_2 d_{xz,yz} + \gamma_2''\pi_{x,y}{}^5 \quad (4)$$

$$2b_1 = \alpha_2 d_{x^2-y^2} + [\alpha_2'(-\sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^3 + \sigma_y{}^4)/2] \quad (5)$$

one electron in a pure d_{xy} orbital there being no m.o. formation since there are no non-bonding orbitals on the carbon atom available for in-plane π-bonding to the metal. For the same reason, the e orbitals do not include the usual out-of-plane bonding from the ligands. Earlier workers proposed that additional contributions to g shifts, which arise from (*i*), spin–orbit interaction with the ligands, and (*ii*), excited charge-transfer states, oppose the contributions from the normally considered spin–orbit interaction with the metal, and account for the anomalous g values in which $g_{\parallel} > g_{\perp}$ and possibly $g_{\parallel} > 2{\cdot}0023$. Marov *et al.*[6] calculated such effects for a number of MoOX$_4$Y complexes (X = F, Cl, Br, I, *O*-donor, or *S*-donor; Y was undefined) and we summarize their findings in the following statements. Spin–orbit interaction with the ligands in the basal plane is not an important mechanism for raising $g_{\parallel}$ when light atoms such as fluorine or oxygen are considered. The positive contribution to $g_{\parallel}$ from the excited state $2B_1$ formed by charge transfer from $2b_1$ to b_2, though important, was less in these complexes than the normal negative contribution from mixing $4B_1$ into the ground state B_2. The negative contribution to $g_{\perp}$ from mixing of $7E$ into B_2 dominated the other positive contributions, once again the shift being smaller for light elements.

In extrapolating these expectations to ReOMe$_4$, for which the metal charge and orbital size will also both be high, we anticipate $g_{\perp} < 2{\cdot}0023$ (due to $7E$) and, since we can safely ignore the contribution of spin-orbit coupling with such light atoms as carbon in the ligands, the strong positive $g_{\parallel}$ shift which we observe must come from an unusually increased admixture of the charge-transfer state $2B_1$. In order to relate the e.s.r. parameters with the optical data and m.o. coefficients we proceed in the usual way [6,7] assuming an orthonormal set of molecular orbitals [equations (6)—(10)]. In seeking a solution to these equations, several

$$g_{\parallel} - g_e = \Delta g_{\parallel} = -\frac{8\alpha_4\lambda}{\Delta E(4B_1)}(\alpha_4 - \alpha_4'S_{B_1}) + \frac{8\alpha_2\lambda}{\Delta E(2B_1)}(\alpha_2 + \alpha_2'S_{B_1}) \quad (6)$$

$$g_{\perp} - g_e = \Delta g_{\perp} = -\frac{2\gamma_7\lambda}{\Delta E(7E)}(\gamma_7 - \gamma_7''S_E) \quad (7)$$

$$A_{\parallel} = P\left[-\kappa - \frac{4}{7} - \frac{8\alpha_4{}^2\lambda}{\Delta E(4B_1)} + \frac{8\alpha_2{}^2\lambda}{\Delta E(2B_1)} - \frac{6}{7}\frac{\gamma_7{}^2\lambda}{\Delta E(7E)}\right] \quad (8)$$

$$A_{\perp} = P\left[-\kappa + \frac{2}{7} - \frac{11}{7}\frac{\gamma_7{}^2\lambda}{\Delta E(7E)}\right] \quad (9)$$

$$P = g_e g_N \beta_e \beta_N \langle r^{-3}\rangle \quad (10)$$

of the parameters must first be estimated. We used the values of 0·2 and 0·16 for S_{B_1} and S_E the group-overlap integrals. These values were used by Marov *et al.*[6] for a series of oxomolybdenum compounds of this geometry. Their use here is supported by the facts that, relative to Mo$^{\text{V}}$, these integrals are expected to be larger for the heavier atom but smaller because of the higher (formal) oxidation state Re$^{\text{VI}}$. The value of P was found to be 0·0506 cm^{-1} using the value of 12·6 a.u. for $\langle r^{-3}\rangle$ as estimated by McMillan and Halpern [8] for ReOCl$_4$.* Following De Armond *et al.*[9] we used the empirical relation $\lambda = CP$ to estimate the rhenium(VI) spin–orbit coupling constant λ; C was calculated from published values of λ [10] and P [11] for rhenium(IV) in K$_2$[PtCl$_6$]. Our calculated value of λ for Re$^{\text{VI}}$ is 4 820 cm^{-1}; such a high value is anticipated for a high oxidation state of a third-row transition ion. However a 20% reduction in P and λ to 0·0405 cm^{-1} and 3 856 cm^{-1} respectively was thought appropriate to allow for the expected increased covalence in the alkyls. From this value of P and $\frac{1}{3}(A_{\parallel} + 2A_{\perp})$, allowing for second-order effects of g shift, κ was calculated to be 0·83. The ΔE values were taken from the electronic spectrum, as assigned in Table 2. Equation (7) in an iterative procedure with the normalization condition gave the values of γ_7 and γ_7''. The solution for the other coefficients also required an

TABLE 2

Electronic absorption spectra (cm^{-1}, in n-hexane) of the oxorhenium(VI) compounds

Assignment	ReOMe$_4$ (red)	ReO(CH$_2$SiMe$_3$)$_4$ (blue)
$B_2 \rightarrow 2E$	35 090	50 000
$B_2 \rightarrow 7E$	29 285 *	28 500 *
$B_2 \rightarrow 4B_2$	21 740	19 600
$B_2 \rightarrow 2B_1$	17 700	16 600

* Appears as a double shoulder and might incorporate the $B_2 \rightarrow A_1$ transition.

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* 1 a.u. ≈ 5·29 × 10^{-11} m.

[5] H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363.

[6] I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1396, and refs. therein.

[7] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31, 35; D. Kivelson and R. Neiman, *ibid.*, 1961, **35**, 149.

[8] J. A. McMillan and T. Halpern, *J. Chem. Phys.*, 1971, **55**, 33.

[9] K. De Armond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 1019.

[10] J. C. Eisenstein, *J. Chem. Phys.*, 1961, **34**, 1628.

[11] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

iterative procedure. Starting with an approximate value for α_4, the remaining three coefficients were calculated using equation (8) and the normalization conditions. These were sufficient data for a new value of α_4 from the orthogonality condition; the process was repeated until convergence was satisfactory.

Electronic Spectra.—$ReOMe_4$ *and* $ReO(CH_2SiMe_3)_4$. n-Hexane or light-petroleum solutions of these compounds are strongly coloured when freshly prepared. The bright blue solution of $ReO(CH_2SiMe_3)_4$ retains its colour indefinitely even in the presence of air. However, the red $ReOMe_4$ solution when allowed to stand at room temperature under nitrogen slowly becomes yellow over a period of *ca*. 3 d. Visible and u.v. spectra of these compounds (Table 2) are characterized by an intense asymmetric band above *ca*. 35 000 cm^{-1} having two or three shoulders to lower energy, and a strong symmetric band in the visible region. On standing, all the bands of $ReOMe_4$ become weaker but the band at 21 740 cm^{-1} initially increases and then, together with the weak shoulders, decays more rapidly than the rest of the spectrum, under nitrogen or after the introduction of oxygen. The spectrum of the final yellow solution consists of the highest (broadened) and lowest-energy peaks only.

The tentative assignments (Table 2) were based on the assumptions (*i*), that the highest and lowest bands are charge transfer in nature as indicated by their high intensities, and (*ii*), that since the Re=O π-bond is very strong, the $2e$ orbital probably lies below $2b_1$ so the lowest charge-transfer band could be $B_1 \rightarrow 2B_1$. Kon and Sharpless [12] used this argument in assigning the first charge-transfer band in $[MOX_5]^{2-}$ (X = Cl or Br; M = Mo or W) to the transition $B_2 \rightarrow 2B_1$. We have done the same, and in the discussion give other reasons for believing the $2b_1$ orbital to be unusually high in these complexes which contain rhenium–carbon σ-bonds. This assignment of $B_2 \rightarrow 2B_1$ to low energy is compatible with the large positive $g_{\parallel}$ shift which is observed; likewise the assignment of $B_2 \rightarrow 2E$ to high energy is compatible with the absence of a positive $g_{\perp}$ shift in these compounds. We also note that each of the lowest two bands increases by *ca*. 10% on changing from Me to CH_2SiMe_3 and, since the bonding and antibonding orbitals of b_1 symmetry would be affected approximately equally by such a change, we assign the second-lowest transition to $B_2 \rightarrow 4B_1$.

DISCUSSION

There have been several e.s.r. and optical studies on square-pyramidal complexes with a d^1 configuration and detailed discussions are available.[13] Usually mixing in of states in which the unpaired electron has been promoted depresses both $g_{\parallel}$ and $g_{\perp}$ below 2·0023, but examples of anomalous g values have required one or both of two effects for their explanation. These are (*i*), mixing in of charge-transfer states in which a bonding electron is promoted up to pair with the unpaired electron, and (*ii*), when the covalence is high, inclusion of spin–orbit interaction between the unpaired electron and the ligand atoms. The $g_{\parallel}$ values we report for $ReOMe_4$ are the highest on record for this geometry, apart from the value of $g_{\parallel} = 2{\cdot}274$ for $[MoOI_4]^-$ reported by Marov *et al.*[6] However, in this anion, most of the positive g shift comes from reason (*ii*) above, because the heavy iodide ligand has a very high spin–orbit coupling constant.* Such a mechanism must be relatively unimportant for the two molecules we report on here, primarily because carbon has a very small spin–orbit coupling constant. This means that reason (*i*) is the important one in our case and for a positive $g_{\parallel}$ shift the state which is mixing in is $2B_1$ resulting from excitation from $2b_1$ to b_2. At the same time we anticipate that the normal mechanism for lowering $g_{\parallel}$ might be reduced. Inspection of equations (6)—(9) shows that both these effects will occur if there is a mechanism for raising both the $2b_1$ and $4b_1$ orbitals relative to b_2.

There are special features of the methyl group which cause $2b_1$ and $4b_1$ to be raised relative to b_2 more in this compound than in the compounds previously studied where the ligands were oxygen donors, sulphur donors, or halides. (*a*) The combination of ligand σ-orbitals which has the same symmetry as the rhenium $d_{x^2-y^2}$ orbital, and consequently the $2b_1$ bonding and $4b_1$ antibonding orbitals which result from m.o. formation, lies relatively high in energy for two reasons: first, the $2s$ and $2p$ atomic orbitals of carbon relative to those of say oxygen or fluorine are high in energy because of the low effective nuclear charge; secondly, these atomic orbitals are raised in energy on reorganization as sp^3 hybrid orbitals before bonding between the methyl group and the metal. (*b*) Previous treatments have included in-plane π-bonding between the ligands and the b_2 (d_{xy}) orbital. This has had the effect of raising the energy of the b_2 orbital, which houses the unpaired electron, to an antibonding $b_2{}^*$ orbital. Such π-bonding cannot take place in $ReOMe_4$ because there are no lone-pair electrons on the carbon atom and its absence in this compound means that b_2 must be relatively low. (*c*) There are precedents for expecting the rhenium atom to rest above the base plane.[14-16] We have, as yet, no direct structural evidence that this occurs in this molecule, but if it is so $2b_1$ would again be raised, but $4b_1$ would be lowered, relative to b_2. Thus we can see good reasons to account for the strong positive contribution to the $g_{\parallel}$ shift and a possible reduction in negative contribution to the $g_{\parallel}$ shift. The detailed calculations have resulted in the m.o. coefficients in Table 1 using the optical assignments in Table 2. Considering the nature of the compounds, it is not surprising to see values of α_4 and α_2 which deviate considerably from one; they indicate strong covalent bonding between rhenium and carbon.

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* *Note added in proof*. Ali H. Al-Nowali and Andrew L. Porte, *J.C.S. Dalton*, 1975, 50 have recently described the electronic structures of $ReOCl_4$ and $[ReOCl_4R]$ (R = NCMe, $OPCl_3$, and Cl^-.) In all of these the ground state is b_2 and the fact that $g_{\parallel} > g_{\perp}$ again is shown to be due to spin-orbit coupling on the halide ligands.

[12] H. Kon and N. E. Sharpless, *J. Phys. Chem.*, 1966, **70**, 105.

[13] See, for example, refs 5, 6, 9, and 12, and H. A. Kruska and M. T. Rogers in 'Radical' Ions, eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968, p. 579.

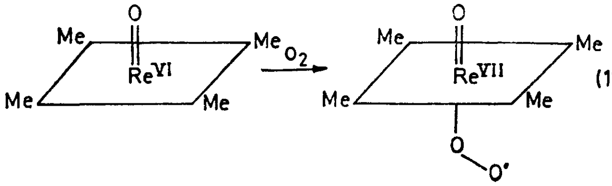
[14] P. W. Frais and C. J. L. Lock, *Canad. J. Chem.*, 1972, **50**, 1811.

[15] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 417.

[16] A. J. Edwards, *J.C.S. Dalton*, 1972, 582.

The very low value of γ_7 is consistent with strong rhenium–oxygen π-bonding as evidenced by the ReO stretching frequencies at 1 016 cm^{-1} in solid alkyls (1 002 cm^{-1} in CS_2 solution).

The bands which disappear from the electronic absorption spectrum when a solution is allowed to stand either with or without the introduction of air are those which, according to our assignment, correspond to exciting an electron from the b_2 orbital d_{xy}. This implies that the d_{xy} electron is missing from the product. The corresponding e.s.r. spectra had $g_{\parallel} = 2{\cdot}00$ and $g_{\perp} < 2{\cdot}00$ and, being devoid of rhenium hyperfine structure, were not unlike that expected for a highly perturbed hyperoxide ion O_2^-. Thus the observations on these reaction products are consistent with the initial reaction (11).



(11)

The structures of several tetrahalide oxides have recently been determined.[17,18] The $ReOCl_4$ crystalline solid consists of square-pyramidal molecules with apical oxygen. The molecular units are weakly associated into dimers and endless chain arrangements through long Re ··· Cl interactions which are *trans* to Re–O bonds. There is no significant lengthening of the Re ··· Cl distance for the chlorine atoms involved in this bridging, and no significant deviations from C_{4v} symmetry for the monomer units.[16]

For the alkyl compounds there is a change of only 14 cm^{-1} in the Re=O stretching wavenumber from the solid to solution. The presence of a broad shoulder at 1 004 cm^{-1} on the 1 016 cm^{-1} band in the solid suggests the possibility of very weak Re–O–Re linkages between the monomers. Further evidence for only weak interaction between the monomers in solid $ReOMe_4$ is provided by the physical characteristics of the compound, such as its low m.p. and high solubility in non-polar solvents, and by the mass spectrum which shows the existence of $ReOMe_4$ as a discrete monomeric molecule in the gas phase. For related molecules such as molybdenum and tungsten tetrafluoride oxides, a square-pyramidal configuration has been assigned on the basis of i.r. measurements.[19] In contrast molybdenum pentachloride,[20] tungsten tetrachloride oxide, and tungsten tetrachloride sulphide have a trigonal-bipyramidal structure in the vapour phase, with the sulphur and oxygen atoms in equatorial positions.[21]

EXPERIMENTAL

The alkyls were prepared as described previously [1] and were handled by vacuum-line techniques or in oxygen-free nitrogen.

E.s.r. spectra were obtained at *X* band (*ca.* 9·2 GHz) using a Varian E 12 spectrometer and at *Q* band using a Varian 36·0 GHz bridge, V4502 console, and a Newport Instruments type F magnet. *N*-(*p*-Methoxybenzylidene)-*p*-butylaniline (Eastman Kodak) was used for liquid-crystal measurements. The sample was warmed to the isotropic phase and allowed to cool to the nematic phase in a magnetic field of 600 mT which was maintained for a further 15 min before the sample tube was rapidly cooled by passage of cold nitrogen.

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[20] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.

[21] M. G. B. Drew and R. Mandyczewsky, *J. Chem. Soc.* (*A*), 1970, 2815.