

510. *The Infrared Spectra of Some Metal Alkoxides, Trialkylsilyloxides, and Related Silanols.*

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Measurements of the infrared spectra of a number of group IV and group V metal alkoxides, trialkylsilyloxides, and related silanols have been recorded. The silicon-oxygen, carbon-oxygen, and metal-oxygen stretching frequencies have been assigned and the relative magnitude of the frequencies discussed.

THE metal trialkylsilyloxides and alkoxides, $M(OSiR_1R_2R_3)_n$ and $M(OR)_n$, are polymeric in some cases.^{1,2} The present work has the object of seeking more evidence concerning the nature of the polymers and of determining the characteristic vibrational frequencies of the M-O-Si and M-O-C systems. Data from heats and entropies of vaporisation³ suggest that the dative bonds from oxygen to metal are relatively weak, with bond strengths of the order of 10 kcal. It may therefore be difficult to confirm the presence of these weak bonds. Additional infrared absorption bands occur in some, but not all, of the polymeric compounds.

Results and Discussion

The infrared spectra of the trialkylsilyloxides and alkoxides, and of related silanols and alcohols were measured in carbon disulphide (Tables 1-5).

1. *The M-O-Si System.*—By comparing the spectra of the trialkylsilyloxides and the parent silanols it can be seen that the M-O-Si system has two characteristic frequencies, an intense band about 900 cm^{-1} and a second, much weaker, band in the 500-600 cm^{-1}

TABLE 1. *Infrared spectra (cm^{-1}) of metal trialkylsilyloxides.*

Ti[O-SiMe ₂ Pr] ₄ :	1252vs, 1064w, 998w, 916vs, 880s, 832s, 808s, 776s, 685w, 608vw, 518m
Zr[O-SiMe ₂ Pr] ₄ :	1251vs, 999m, 971m, 916vs, 884s, 831s, 808w, 774s, 680w, 594w, 515w
Ti[O-SiMe ₂ Pr ⁿ] ₄ :	1251vs, 1066w, 997w, 917vs, 833s, 804m, 770m, 699w, 521m
Ta[O-SiMe ₂ Et] ₅ :	1250vs, 1156vw, 1066w, 997m, 909vs, 880w, 831m, 806m, 776s, 685s, 595m
Ta[O-SiMeEt ₂] ₅ :	1250vs, 1240sh, 1010s, 905vs, 797s, 778sh, 755s, 685m, 667sh, 606sh, 592m
Zr[O-SiEt ₃] ₄ :	1251sh, 1242s, 1017m, 1006m, 966w, 914vs, 941s, 728sh
Al[O-SiEt ₃] ₃ :	1244s, 1064vs, 1015m, 971w, 810vs, 763w, 741s, 728sh, 638m, 585m, 549w
Ti[O-SiEt ₂ Me] ₄ :	1251s, 1235m, 1016w, 1005w, 915vs, 787s, 756s, 746s, 690w, 673m, 510m
Zr[O-SiEt ₂ Me] ₄ :	1252s, 1236s, 1011m, 1002m, 964m, 912vs, 833m, 799s, 752m, 743m, 683w, 601w, 521m
Nb[O-SiEtMe ₂] ₅ :	1250vs, 1010m, 957m, 889vs, 839m, 810m, 787s, 752sh, 699m, 617m, 575m
Ti[O-SiMe ₃] ₄ :	1251vs, 1060w, 1015w, 918vs, 845s, 752s, 685w, 517m, 503w
Zr[O-SiMe ₃] ₄ :	1251vs, 996w, 971w, 916vs, 839s, 752w, 684w, 521m
Ti[O-SiEtMe ₂] ₄ :	1251vs, 1241sh, 1058w, 1015w, 960sh, 915vs, 837s, 816s, 784s, 753w, 699m, 629w, 515m
Zr[O-SiEtMe ₂] ₄ :	1250vs, 1003m, 959m, 913vs, 835s, 781s, 690w
Hf[O-SiEtMe ₂] ₄ :	1251vs, 1042w, 1014s, 986w, 953sh, 932vs, 837s, 785s, 697m

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

TABLE 2. *Infrared spectra (cm^{-1}) of metal alkoxides.*

Ti(OEt) ₄ :	1269w, 1136s, 1101s, 1064s, 1042sh, 916s, 885w, 787w, 625-500s
Ta(OEt) ₅ :	1279w, 1163sh, 1149sh, 1117vs, 1072vs, 1030s, 917s, 880s, 556sbr
Nb(OEt) ₅ :	1270w, 1136sh, 1107s, 1063s, 1029sh, 911s, 877w, 835w, 800w, 571sbr
Ti[O-CEt ₂ Me] ₄ :	1294w, 1218w, 1195w, 1163m, 1144s, 1062m, 1939s, 1011s, 993s, 948m, 903m, 883w, 811w, 780w, 751w, 737w, 615m, 576w
Zr[O-CEt ₂ Me] ₄ :	1292w, 1220w, 1190w, 1163m, 1150s, 1063s, 1039s, 1010s, 991s, 943s, 903s, 883w, 808w, 775w, 755w, 730w, 619w, 559w, 586m, 521m
Hf[O-CMe ₂] ₄ :	1248sh, 1229sh, 1190s, 1138w, 1015s, 990s, 909sh, 904s, 896sh, 786sh, 781m, 567s, 526m
Ti[O-CHMe ₂] ₄ :	1163sh, 1126vs, 1005vs, 962sh, 855vs, 826sh, 619vs, 526w
Zr[O-CHMe ₂] ₄ :	1174vs, 1143vs, 1011vs, 962s, 952w, 943s, 847s, 820s, 559vs, 548s
Al[O-CHMe ₂] ₃ :	1185s, 1174s, 1138s, 1124s, 1036s, 951s, 861m, 835s, 699m, 678s, 610m, 566s, 535m
Ta[O-CHMe ₂] ₅ :	1163s, 1130vs, 1001vs, 951sh, 928vw, 848m, 813w, 683w, 540s
Zr[O-CMe ₃] ₄ :	1235m, 1203s, 1190s, 1065w, 1035sh, 1026sh, 1010sh, 997s, 986sh, 908m, 787w, 781w, 557m, 540m

¹ Bradley and Thomas, *J.*, 1959, 3404.

² Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027.

³ Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

TABLE 3. Infrared spectra of trialkylsilanols.

Me ₃ Si·OH: 1252vs, 990s, 966m, 881vs, 842vs, 775sh, 754s, 687w
EtMe ₂ Si·OH: 1251vs, 1010s, 960s, 855vs, 837s, 784s, 697m
Et ₂ MeSi·OH: 1240s, 1008m, 962m, 847vs, 799s, 766s, 749m, 739sh, 685m, 671w
Pr ⁿ Me ₂ Si·OH: 1252vs, 1003m, 976m, 885s, 855vs, 830s, 775s, 680m, 669w
Et ₃ Si·OH: 1244s, 1018s, 1007sh, 982s, 966s, 835vs, 813sh, 736s

TABLE 4. Metal-oxygen and oxygen-silicon stretching frequencies.

Compound	<i>n</i> *	Si-O	M-O	Compound	<i>n</i> *	Si-O	M-O
Ti[O·SiMe ₃] ₄	1·2	918	517	Zr[O·SiEt ₂ Me] ₄	1·0	912	521
Ti[O·SiEtMe ₂] ₄	1·0	915	515	Zr[O·SiEt ₃] ₄	1·0	914	—
Ti[O·SiPr ⁿ Me ₂] ₄	1·0	916	518	Hf[O·SiEtMe ₂] ₄	1·0	932	—
Ti[O·SiPr ⁿ Me ₂] ₄	1·0	917	521	Al[O·SiEt ₃] ₃	2·0	1,064,	638, 585,
Ti[O·SiEt ₂ Me] ₄	1·0	915	510			810	549
Zr[O·SiMe ₃] ₄	2·0	916	521	Nb[O·SiEtMe ₂] ₅	1·0	889	619, 575
Zr[O·SiEtMe ₂] ₄	1·0	913	521	Ta[O·SiEtMe ₂] ₅	1·0	909	595
Zr[O·SiPr ⁿ Me ₂] ₄	1·0	916	515	Ta[O·SiEt ₂ Me] ₅	1·0	905	606, 592

* *n* = Degree of polymerisation.

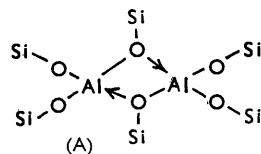
TABLE 5. Infrared spectra of alcohols.

EtOH: 1081s, 1050s, 876s, 802w
Me ₂ CH·OH: 1153s, 1125s, 1070s (C-O stretch), 946s, 813m
Me ₃ C·OH: 1234sh, 1205s, 1140s (C-O stretch), 911s, 750m
Et ₂ CMe·OH: 1176sh, 1161s, 1133s (C-O stretch), 1055m, 1034sh, 997sh, 973s, 905s, 883sh, 797w, 784w, 772w, 707w

region. The characteristic frequencies for the trialkylsilyloxides are summarised in Table 4. The exceptional data for the aluminium compound will be considered later in this section. It has been suggested⁴ that the 900 cm.⁻¹ band is an Si-O stretching mode, and in view of its high intensity and the shift in passing to the corresponding silanol, this seems to be correct. We suggest that the band around 500 cm.⁻¹ is an M-O stretching mode, by comparison with results for the dichromate ion,⁵ where the Cr-O-Cr symmetric and antisymmetric stretches are taken to be 560 cm.⁻¹ and 770 cm.⁻¹, respectively. Also, in hexamethyldisiloxane the symmetric and antisymmetric stretches in the Si-O-Si skeleton are assigned to 522 cm.⁻¹ and 1055 cm.⁻¹.^{6a} Kriegsmann and Licht^{6b} measured both the Raman and infrared spectra of Ti[O·SiMe₃]₄ and the latter is in good agreement with the present results. Their assignments of the absorption bands at 500 cm.⁻¹ and 900 cm.⁻¹ agree with ours, although they also tentatively assign several weaker bands to Ti-O and Si-O stretching modes.

The size of the alkyl groups attached to the silicon atom does not affect the frequencies, and even changing the metal has only a small effect on the Si-O stretching frequency. Comparison of quadrivalent and quinquivalent metals suggests that the Si-O stretching vibrations are essentially independent of each other, because in all cases only one band is observed. In the titanium and zirconium compounds only one Si-O stretching vibration should be infrared-active if the M-O-Si groups are linear and the molecule is tetrahedral (the alkyl groups being ignored). However, in the niobium and tantalum compounds with five silyloxy-groups there should be at least two infrared-active Si-O stretching vibrations whatever the geometry of the molecule, if the various Si-O groups interact.

This is an important point when the spectrum of the aluminium compound is considered because it shows two bands which are both assigned to Si-O stretches on the basis of their high intensity and absence from the parent silanol. This compound is dimeric⁷ and can be tentatively formulated as A (alkyl groups being omitted). It is suggested that the 1064 cm.⁻¹ band

⁴ Zeitler and Brown, *J. Phys. Chem.*, 1957, **61**, 1174.⁵ Stammreich, Bassi, Sala, and Siebert, *Spectrochim. Acta*, 1958, **13**, 192.⁶ (a) Kriegsmann, *Z. Elektrochem.*, 1957, **61**, 1088; (b) Kriegsmann and Licht, *Z. Elektrochem.*, 1958, **62**, 1163.⁷ Thomas, Ph.D. Thesis, London, 1959.

corresponds to stretching vibrations of the terminal Si-O groups, while the band at 810 cm^{-1} represents stretching vibrations of the bridging Si-O groups.

The compound $\text{Zr}[\text{O}\cdot\text{SiMe}_3]_4$ is also apparently dimeric¹ although it would be expected to be a mixture of monomer and trimer.⁸ In either case it should show a second band corresponding to the bridging Si-O group, but no extra band could be found. The $\text{O}\rightarrow\text{Zr}$ bond may be appreciably weaker than the $\text{O}\rightarrow\text{Al}$ bond and thus lead to a much smaller shift in the Si-O frequency, perhaps only broadening the existing band instead of appearing as a second.

The absence of a band around 520 cm^{-1} in $\text{Zr}[\text{O}\cdot\text{SiEt}_3]_4$ is also difficult to understand, unless it has become much weaker or moved to just below 500 cm^{-1} .

2. *The M-O-C System.*—The isopropyl group has⁹ characteristic frequencies at 1170, 1150, 950, 920, and 850–750 cm^{-1} . Data for the isopropoxide (Table 2) show the presence of an additional strong band in the 1000 cm^{-1} region and one or more bands around 550–700 cm^{-1} . In aluminium isopropoxide the isopropyl bands at 1170 cm^{-1} and 1150 cm^{-1} are both split into doublets, probably by intramolecular coupling. Our results are in good agreement with those of previous examinations of metal isopropoxides.^{4,10} Kreigsmann and Licht^{6b} have given assignments for a series of titanium alkoxides, and Guertin *et al.*¹¹ suggest that bands at 1000 cm^{-1} in aluminium alkoxides are due to Al-O stretching modes. We consider that these bands are predominantly C-O stretching modes of the Al-O-C groups and that the Al-O stretching modes occur at lower frequencies, not covered by the investigations of Guertin *et al.* A comparison of the metal alkoxides with the corresponding alcohols (Table 5) permits the tentative assignments shown in Table 6. Most of

TABLE 6. *Metal-oxygen and carbon-oxygen stretching frequencies.*

Compound	<i>n</i> *	C-O	M-O
$\text{Ti}[\text{O}\cdot\text{CHMe}_2]_4$	1.4	1005	619
$\text{Zr}[\text{O}\cdot\text{CHMe}_2]_4$	3.0	1011	559, 548
$\text{Al}[\text{O}\cdot\text{CHMe}_2]_3$	3 to 4	1036	699, 678, 610, 566, 535
$\text{Ta}[\text{O}\cdot\text{CHMe}_2]_5$	1.0	1001	540
$\text{Zr}[\text{O}\cdot\text{CMe}_3]_4$	1.0	997	557, 540
$\text{Hf}[\text{O}\cdot\text{CMe}_3]_4$	1.0	990	567, 526
$\text{Ti}[\text{O}\cdot\text{CEt}_2\cdot\text{Me}]_4$	1.0	1011	615, 576
$\text{Zr}[\text{O}\cdot\text{CEt}_2\cdot\text{Me}]_4$	1.0	1010	586, 559, 521
$\text{Ti}(\text{OEt})_4$	3.0	1064, 1042	625, 500
$\text{Ta}(\text{OEt})_5$	2.0	1072, 1030	556
$\text{Nb}(\text{OEt})_5$	2.0	1063, 1029	571

* *n* = Degree of polymerisation.

the comparisons are obvious but the difficulty in assigning the C-O frequency in alcohols has been discussed by Bellamy,¹² and assignments for the ethoxides must be considered tentative.

The most definite evidence for the assignment of the two C-O stretching modes was obtained from experiments on the hydrolysis of the ethoxides with limited amounts of water.¹³ The band at 1030 cm^{-1} disappears after a relatively small proportion of hydrolysis has taken place but the rest of the spectrum is unaltered. This suggests that the 1030 cm^{-1} band is associated with bridging ethoxide groups which are removed by hydrolysis, while the 1060 cm^{-1} band is associated with terminal ethoxide groups which are not hydrolysed until later.

The M-O stretching region of the aluminium isopropoxide spectrum provides more evidence for intermolecular bonding through oxygen atoms. In monomeric aluminium

⁸ Bradley, *Nature*, 1958, **182**, 1211.

⁹ Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

¹⁰ Bell, Heisler, Tannenbaum, and Goldenson, *Analyt. Chem.*, 1953, **25**, 1720.

¹¹ Guertin, Wiberley, Bauer, and Goldenson, *J. Phys. Chem.*, 1956, **60**, 1018.

¹² Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen. London, 1958.

¹³ Holloway, Ph.D. Thesis, London, 1959.

isopropoxide there could be a maximum of only three Al-O stretching vibrations, whatever the stereochemistry of the molecule. Actually five bands are observed in this region and the presence of bridging oxygen atoms seems to be the most reasonable explanation. Unfortunately, only one C-O stretching frequency has been definitely identified whereas at least two would be expected. This may arise from the difficulty in assigning frequencies in this part of the spectrum, and the two bands tentatively assigned to coupling of the isopropyl skeletal vibrations may in fact be C-O stretching vibrations.

The monomeric alkoxides show varying numbers of bands in the M-O stretching region but none of them has more bands than would be expected for a monomer, and the variation may be due to steric effects. With the smaller alkyl groups the four oxygen atoms may be arranged tetrahedrally around the central metal atom and there would be only one infrared-active M-O stretching mode. The larger alkyl groups could lead to steric hindrance which would distort the tetrahedron of oxygen atoms and make several of the M-O stretches infrared-active.

With the exception of the ethoxides the C-O stretching frequency falls from the alcohol to the alkoxide. If double bonding occurs between the metal and oxygen, then a contribution from a structure of the type $C \equiv \overset{+}{O} = \bar{M}$ would tend to drain electrons away from the carbon-oxygen σ -bond and weaken it, with a resultant lowering in the C-O stretching frequency. In the case of the trialkylsilyloxides, a rise in the Si-O stretching frequency occurs when the silanolic hydrogen is replaced by a metal although there is still some uncertainty about the positions of the Si-O stretching frequency in the silanols (see Section 3). Comparison of the M-O stretching frequencies in the two series is of interest. For the titanium and zirconium compounds, the M-O frequency rises from trialkylsilyloxyde to alkoxide. This can be explained since the silicon atom has available d orbitals which compete with the d orbitals of the metal in the formation of $d\pi-p\pi$ bonds with the oxygen atom. The carbon atom in the alkoxide group has no d orbital available so that the oxygen atom can only form π -bonds with the metal, thus leading to a higher bond order for the metal-oxygen bond in the alkoxides than for the corresponding bond in the trialkylsilyloxides. The actual degree of this π -bonding may be relatively small in both cases since the M-O frequencies are much lower than the frequencies observed for M=O systems.¹⁴

3. *The Si-O-H System.*—The data for the silanols (Table 3) enable us tentatively to assign the Si-O stretching frequency in these compounds. It has been suggested¹⁵ that this might occur at either 880—830 cm^{-1} or 1100 cm^{-1} , while Kriegsmann¹⁶ assigns a band at 785 cm^{-1} in trimethylsilanol as the Si-O stretch. Comparison of Tables 1 and 3 shows that the strong band at 910 cm^{-1} in the spectra of the trialkylsilyloxides is absent from those of the silanols which show a new strong band in the 880—830 cm^{-1} region; this new band is assigned to the Si-O stretching vibration in the silanols, and the frequencies are listed in Table 7. The band observed by Kriegsmann at 785 cm^{-1} is present in both the metal trimethylsilyloxides and trimethylsilanol, whereas the 880 cm^{-1} band is present only in the latter.

TABLE 7. *Silicon-oxygen stretching frequencies (cm^{-1}) in silanols.*

$Me_3Si\cdot OH$, 881; $Me_2SiEt\cdot OH$, 855; $Me_2SiPr\cdot OH$, 855; $Et_2SiMe\cdot OH$, 847; $Et_3Si\cdot OH$, 835.

The results suggest that there may be some coupling between the Si-O stretching vibration and the rest of the molecular vibrations, since the frequencies fall with increase in size of the alkyl groups. Alternatively, the effect may arise from a variation in the inductive effects of the alkyl groups. The order of magnitude of the Si-O frequency seems correct by comparison of the Si-O-H system, with frequencies of the order of 850

¹⁴ Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

¹⁵ Richards and Thompson, *J.*, 1949, 124.

¹⁶ Kriegsmann, *Z. anorg. Chem.*, 1958, 294, 113.

and 3600 cm^{-1} , with the Si-O-Si group in hexamethyldisiloxane, which has stretching frequencies at 522 and 1055 cm^{-1} .

EXPERIMENTAL

Compounds were prepared as previously described.^{1,2,3,7}

Infrared spectra were measured in carbon disulphide by use of a Grubb-Parsons G.S. 2A double-beam grating spectrometer. The trialkylsilyloxides and alkoxides were measured as 25% (wt./vol.) solutions in a 0.03-mm. potassium bromide cell. The polymeric compounds were also examined as 1% (wt./vol.) solutions in a 1-mm. cell, but in all cases the spectra were identical with the results obtained in the more concentrated solutions. The silanols and alcohols were examined as 1% (wt./vol.) solutions in a 1-mm. potassium bromide cell. Spectra were recorded over the range 500—1300 cm^{-1} .

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