A. N. LAZAREV, T. F. TENISHEVA, V. P. DAVYDOVA

1964

SovietRxiv

Fig. 1. Infrared spectra of compounds $XO(CH_3)_2SiOSi(CH_3)_2OX$ (samples: polycrystalline powders, suspended in Vaseline oil)

Figure 1: Fig. 1. Infrared spectra of compounds $XO(CH_3)_2SiOSi(CH_3)_2OX$ (samples: polycrystalline powders, suspended in Vaseline oil)

Abstract

Full Text

A. N. LAZAREV, T. F. TENISHEVA, V. P. DAVYDOVA

ON THE MUTUAL INFLUENCE OF BONDS OF THE Si–O^- AND Si–O(Si) TYPES

(Presented by Academician N. V. Belov, 25 IV 1964)

From considerations concerning the participation of $d\pi$—$p\pi$ interactions in the formation of silicon-oxygen bonds there follows the already discussed increase in the bond order R'_3Si—O(R) as the electropositivity of R and the electronegativity of R' increase. Similarly, with increasing electronegativity of R', the order of the Si—O—Si bonds in systems R_3SiOSiR'_3 increases.

Fig. 1. Infrared spectra of compounds $XO(CH_3)_2SiOSi(CH_3)_2OX$ (samples: polycrystalline powders, suspended in Vaseline oil)

For most complex anions in silicates, the presence of Si—O(Si) and Si—O^-(M)$^+$ bonds at the same Si atom is characteristic. Analysis of the results of X-ray structural ([1]) and spectroscopic ([2,3]) studies of silicates with Si_2O_7 anions, the simplest among those containing bonds of both types, led to the assumption of a "competitive" character of the mutual influence of these bonds: a decrease in the order of the Si—O^- bonds with an increase in the share of covalent character in the interaction of the "terminal" oxygen atoms with cations is accompanied by an increase in the order of the Si—O—Si bonds, manifested in an increase of the SiOSi angle and a decrease in bond lengths.

The aim of the present work was to investigate the mutual influence of the "terminal" and "bridging" Si—O bonds on model objects–compounds of the type $XO(CH_3)_2SiOSi(CH_3)_2OX$, where $X = H, Li, Na, K$. (The assignment of frequencies in the IR spectrum was facilitated by the availability of data on spectra of the compounds $X(CH_3)_2SiOSi(CH_3)_2X$ with $X = H, OH, Cl, C_6H_5, CH_3$ ([4,5]).)

The IR spectra of the compounds studied are shown in Fig. 1, and Table 1 gives the frequencies of the absorption maxima and their interpretation.

Fig. 2. Scheme of changes in the frequencies of the stretching vibrations Si–O upon going from $HO(CH_3)_2SiOSi(CH_3)_2OH$ to $KO(CH_3)_2SiOSi(CH_3)_2OK$

Figure 2: Fig. 2. Scheme of changes in the frequencies of the stretching vibrations Si–O upon going from $HO(CH_3)_2SiOSi(CH_3)_2OH$ to $KO(CH_3)_2SiOSi(CH_3)_2OK$

Let us begin consideration of the changes in the spectrum of $XO(CH_3)_2SiOSi(CH_3)_2OX$ on going from $X = H$ to $X = Li, Na, K$ with the most significant and readily interpretable shifts of the Si—O frequencies upon replacing H by K. These shifts (see the upper part of Fig. 2) apparently indicate that, along with an increase in the dynamic bond coefficient Si—O(H, K), there occurs a decrease in the bond coefficient Si—O(Si), causing a lowering of the frequencies ν_{as} and ν_sSiOSi. At the same time, evidently, the SiOSi angle also decreases, whereas, as is known, the frequency ν_{as}SiOSi should fall sharply under the action of both factors, while the change in ν_sSiOSi proves insignificant (since a decrease in ∠SiOSi leads to an increase in this frequency).

Let us explain what has been said with the aid of the five-atom model OSi′OSi′O. Replacement of the group Si$(CH_3)_2$ by one "atom" Si′ with a certain effective mass will,

probably introduces approximately the same error for all compounds $XO(CH_3)_2SiOSi(CH_3)_2OX$. Neglect of the interaction of the $O - X$ vibrations with the $Si - O$ vibrations may be justified by the very high frequencies of OX for $X = H$ and the very low ones for $X = K$. The scheme of the model considered

Fig. 2. Scheme of changes in the frequencies of the stretching vibrations $Si—O$ upon going from $HO(CH_3)_2SiOSi(CH_3)_2OH$ to $KO(CH_3)_2SiOSi(CH_3)_2OK$ (rows 1,2–experimental data; for the first of the compounds the frequencies for the solution spectrum are given (4); rows 3,4–calculated results)

is given in Fig. 3. The matrices of the kinematic interaction for the planar vibrations of this model (symmetry C_{2v}) have the following form:

Q	$\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \cos\alpha$	
q	$\varepsilon_2 \cos\varphi$	$\varepsilon_2 + \varepsilon_3$
γ	$-\varepsilon_2\sigma_2 \sin\varphi - (\varepsilon_1\sigma_1/\sin\varphi)\,[\cos(\alpha-\varphi) + \cos\varphi\cos\alpha]$	$-\varepsilon_2\sigma_1 \sin\varphi \quad \varepsilon_2(\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2\cos\varphi$ $+\varepsilon_1\sigma_1^2 - \left(\varepsilon_1\sigma_1^2/\sin^2\varphi\right)[\cos(2\varphi-\alpha) + 2\cos\varphi\cos($

Q	$\varepsilon_1 + \varepsilon_2 + \varepsilon_1 \cos\alpha$	
q	$\varepsilon_2 \cos\varphi$	$\varepsilon_2 + \varepsilon_3$
δ	$-\sqrt{2}\,\varepsilon_2\sigma_1 \sin\alpha$	$(\sqrt{2}\varepsilon_2\sigma_1/\sin\varphi)\,[\cos(\alpha-\varphi)+\cos\varphi\cos\alpha]$
γ	$-\varepsilon_2\sigma_2 \sin\varphi + (\varepsilon_1\sigma_1/\sin\varphi)\,[\cos(\alpha-\varphi)+\cos\varphi\cos\alpha]$	$-\varepsilon_2\sigma_1 \sin\varphi$

$+\left(\varepsilon_1\sigma_1^2\right.$

Here

$$\varepsilon_1 = \frac{1}{m_O}, \qquad \varepsilon_2 = \frac{1}{m_{Si}}, \qquad \varepsilon_3 = \frac{1}{m_{O^-}}, \qquad \sigma_1 = \frac{1}{r_{Si-O(Si)}}, \qquad \sigma_2 = \frac{1}{r_{Si-O^-}}.$$

The coordinates Q, q, δ, and γ correspond to changes in the distances $Si-O(Si)$, $Si-O^-$, and the angles $SiOSi$ and $OSiO^-$. In the numerical calculations the following were adopted:

$$r_{Si-O(Si)} = 1.63\ \text{Å}, \qquad r_{Si-O^-} = 1.58\ \text{Å}, \qquad \varphi = 109°28', \qquad m_O = 16, \qquad m_{O^-} = 17, \qquad m_{Si} = 35^*.$$

Since there are no data on the frequencies of deformation vibrations, and the model itself is a rough approximation owing to the neglect of vibrations of the $Si(CH_3)_2$ groups, we shall confine ourselves to considering four stretching vibrations. As is seen from Fig. 2, their frequencies agree well with the experimental data for $HO(CH_3)_2SiOSi(CH_3)_2OH$, with the dynamic coefficients from work (5) for the molecule $(CH_3)_3SiOSi(CH_3)_3$: $K_{Si-O(Si)} = 7.3$, inter-

* The use of other values of m_{Si} somewhat changes the absolute values of the dynamic coefficients, but their changes in going from $H \to K$ remain the same.

the interaction of Si—O(Si) bonds with one another, $H = -0.72$, and the interaction of Si—O^- and Si—O(Si) bonds, $h = 0.22 \cdot 10^6$ cm^{-2}; in this calculation it was assumed that $K_{Si-O^-} = 9.0 \cdot 10^6$ cm^{-2} and $\angle\alpha = 145°$.* The best agreement is obtained for the high-frequency vibration $\nu_{as}SiOSi(B_1)$, while the other frequencies turn out to be somewhat underestimated, which is connected with the neglect of angular dynamic coefficients. It is not difficult to show that changes in the frequencies $\nu SiOSi$ and νSiO^-, like those observed in the transition $HO(CH_3)_2SiOSi(CH_3)_2OH \to KO(CH_3)_2SiOSi(CH_3)_2OK$, cannot be obtained by changing only the dynamic coefficients, and require a simultaneous change in the SiOSi angle. The results of such a variation (at constant H and h) are given in the lower part of Fig. 2. These calculated data do not make it possible to obtain reliable values of the absolute magnitudes of the parameters of the

Fig. 3. Five-atom model $O^-SiOSiO^-$, used for the calculation

Figure 3: Fig. 3. Five-atom model $O^-SiOSiO^-$, used for the calculation

molecules under consideration, but they clearly indicate that replacement of H by K leads, along with an increase in the dynamic coefficient of the Si—O^- bond, to a simultaneous and comparable (by 6-9%) decrease in the coefficient of the Si—O(Si) bond and, correspondingly, to a decrease of the SiOSi angle by 8-10°.

Fig. 3. Five-atom model $O^-SiOSiO^-$, used for the calculation

These quantities directly characterize the redistribution of $d\pi - p\pi$ interactions in the Si—O^- and Si—O(Si) bonds, all the more since the dynamic coefficients depend only slightly on the ionic part of the interatomic interaction. It may be assumed that strengthening of the $(p \to d)\pi$ interaction in the Si—O^- bond, caused by an increase in the electron density on the O atom, lowers the effective positive charge of the Si d-orbitals and thereby decreases the order of the Si—O(Si) bond.

It is appropriate to note that, when considering bond orders and the geometric structure of Si_2O_7 groups, together with the influence—discussed here—of substituents at the "terminal" O atoms (or cations), it is also necessary to take into account the magnitude of the charge on the "bridging" O atom. Only from the considerations set forth above is it difficult to explain why in $(RO)_3SiOSi(OR)_3$ molecules the ∠SiOSi, for covalent R—O(Si) bonds, is much smaller than 180° (although here too an increase in the electronegativity of R leads to an increase in ∠SiOSi ([2])), whereas in Si_2O_7 ions of pyrosilicates the ∠SiOSi reaches 180° with still a comparatively small degree of covalency of the bonds $M^+ \ldots O^-(Si)$. In the latter case, probably, the O atoms in the Si—O—Si bond acquire a larger negative charge because of the cations, which ensures the formation of stronger $(p \to d)\pi$-bonds in the Si—O—Si bridge.

Similar to those described, but smaller in magnitude, shifts of the SiOSi frequencies are observed for $X = \mathrm{Li}, \mathrm{Na}$. Conversely, the increase in the νSiO^- frequencies turns out to be appreciably larger, which is probably connected with the smaller mass of the X atom than in the case $X = K$ (this influence cannot be taken into account in the model considered above). Of considerable interest is the strong splitting, observed in the case $X = Li$, of ν_{as}SiOSi, which cannot be explained by "intramolecular" effects and should be attributed to a strong resonance interaction of the vibrations of the groups $O^-(CH_3)_2SiOSi(CH_3)_2O^{-**}$ through the "bridges" $O \ldots Li \ldots O$. The spectrum of $NaO(CH_3)_2SiOSi(CH_3)_2ONa$ apparently contains a considerable number of impurity bands (probably siloxanes).

Experimental part

Potassium tetramethyldisiloxanediolate was obtained by cleavage of octamethylcyclotetrasiloxane (OMCTS) with caustic potassium in toluene (without addition of homo-

* The ratio $K_{\mathrm{Si-O(H)}}/K_{\mathrm{Si-O(Si)}} = 1.23$ is quite plausible ([3]), as is the value of α (obtained by Kriegsman ([4]) for a triatomic model). We recall that in $H_3SiOSiH_3$, according to electron-diffraction data, $\angle SiOSi = 144^\circ$, while in $(CH_3)_3SiOSi(CH_3)_3$ it is probably close to 135-140°.

** This resonance may be another cause of the increase in the νSiO^- frequencies.

Table 1

Frequencies of vibrations and their assignment

Assignment of frequencies	X = H, Raman spectrum (cryst.) ([4])	X = H, IR spectrum ($p \to p$ in CCl_4) ([4])	X = H, IR spectrum (cryst.)	X = Li* IR spectra (cryst.)	X = Na IR spectra (cryst.)	X = K IR spectra (cryst.)
$\delta_s CH_3$	1255	1261	1257 v.s.1180 w.1114 w.	1249 v.s.1200 v.w.1150 v.w.	1263**1255 v.s.1206 v.w.1168 w.1122 w.1066**	1249 v.s.
ν_{as}SiOSi		1073	1049—1037 v.s.	1055 } v.s.1022 } v.s.	1010—1000 v.s.	998 v.s.
νSiO(X)	920	910	905 v.s.	980 v.s.	963 sh.	941 s.
ν'SiO(X)		902	878 s.	939 sh.	940 sh.	925 m.
$\rho CH_3(CO_3^{--}?)$					880 w.	880 m.
ρCH_3		857	863 s.853 w.	855 m.	852 m.	848 m.
ρCH_3		812	812 v.s.	806 v.s.	840**799 v.s.	802 v.s.
ν_{as}CSiS	791	791	789 v.s.	789 v.s.	781 v.s.	780 v.s.
ν'_{as}CSiC?	752	745	750 v.w.730 v.w.	725 w.	768**722 v.s.	733 v.w.
ν_sCSiC	699	698	680?	694?	703 w.685?	696 v.w.
ν'_sCSiC	660	655	652 m.	645 sh.	655 m.643**600 v.w.	646 v.s.590 sh.
ν_sSiOSi	558	555	555 m.	{565?{537?	551 w.517**	539 w.

* In the spectrum there is a band near 3720 cm^{-1} and a broad absorption region 600-500 cm^{-1} (apparently masking the ν_sSiOSi bands).
** Impurity?

···of homogenizing additives in the form of water or alcohol) in a flask with a water-separating device of the Dean-Stark trap type. Yield 83%.

Found, %: K 32.3; 32.0; 33.8
Calculated, %: K 32.3

Sodium tetramethyldisiloxanediolate, obtained in an analogous manner in 50% yield, contained a larger amount of impurities and was therefore also prepared by the known method ([6]) in an alcoholic-aqueous solution, but it also proved to be impure.

Cleavage of OMTS with lithium hydroxide proved unsuccessful. In the reaction of tetramethyldisiloxane-1,3-diol, prepared according to Hyde ([7]), with metallic lithium in absolute ethyl ether under a stream of nitrogen, it was possible to obtain lithium tetramethyldisiloxanediolate (yield 40%). The product contained 13.8% lithium (calculated 7.79%); the presence of lithium hydroxide is confirmed spectroscopically.

Institute of Chemistry of Silicates named after I. V. Grebenshchikov
Academy of Sciences of the USSR

Received
20 IV 1964

CITED LITERATURE

1. D. W. J. Cruickshank, J. Chem. Soc., **1961**, 5486.
2. A. N. Lazarev, Izv. AN SSSR, ser. khim., **1964**, 235.
3. A. N. Lazarev, T. F. Tenisheva, Izv. AN SSSR, OKhN, **1961**, 964.
4. H. Kriegsmann, Z. anorg. u. allgem. Chem., **299**, 78 (1959).
5. D. W. Scott et al., J. Phys. Chem., **65**, 1320 (1961).
6. M. V. Sobolevskii, L. A. Chistyakova et al., *Plasticheskie massy*, No. 10, 17 (1962).
7. J. F. Hyde, J. Am. Chem. Soc., **75**, 2166 (1953).

Note: Figure translations are in progress. See original paper for figures.