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INTRAMOLECULAR COORDINATION IN METHYL(AROYLOXYMETHYL)FLUOROSILANES

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Summary

The IR spectra of solutions of methyl(aroyloxymethyl)fluorosilanes, C_6H_5-$COOCH_2Si(CH_3)F_2$ (I), 4-$CH_3C_6H_4COOCH_2Si(CH_3)F_2$ (II), C_6H_5-$COOCH_2Si(CH_3)_2F$ (III) in 11 solvents in the temperature range 223–363 K, and in the gaseous state have been studied. The molecules of the above compounds display an intramolecular coordination between silicon and oxygen of the carbonyl group. Unlike (aroyloxymethyl)trifluorosilanes [1], there exists the equilibrium between the molecules with and without Si ← O bonds in the solutions of I–III. The proportion of intramolecularly coordinated molecules is greater in solvents of low polarity. This is determined not by enthalpy (ΔH) values of the Si ← O bond, but a change in the entropy (ΔS) of the system upon coordination. The coordinate Si ← O bond becomes stronger with increasing number of fluorine atoms in the molecule. A strong dependence of the spectroscopic parameters characterizing the intramolecular coordination on the dielectric constant and the solvent refractive index has been established.

Introduction

The formation by tetrahalosilanes and alkylhalosilanes of complexes with organic bases (B) containing electron-donating atoms of nitrogen, oxygen, phosphorus and sulfer is discussed in several reviews [2–4]. The strength of the coordinate Si ← B bond is controlled by the electron-withdrawing substitutents on the silicon atom and their steric factors. The ability of silicon for intramolecular coordination is best studied in silatrane molecules [5,6]. However, the Si ← N bond energy is evaluated by using only indirect data. We have determined the enthalpy of intramolecular

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Si ← O= coordination for (aroyloxymethyl)trifluorosilanes (AFS) [1]. Much attention has recently been paid to the effect of electron-withdrawing atoms in the axial position to the pentacoordinate silicon atom on the strength of the intramolecular coordination bond [7,8].

An important aspect in the chemistry of coordinate compounds of silicon is their interaction with solvent. No systematic study of intramolecular silicon complexes has been conducted in this field until now. Earlier, we have investigated the effect of solvents on the state of the Si ← N bond in silatrane molecules by ^{29}Si NMR and IR spectroscopy [9,10]. The analysis of ν(Si–H) values in the IR spectra of 1-hydrosilatrane solutions shows that an increase in the solvent polarity strengthens the Si ← N bond whereas the polarizability interaction of silatrane molecules with the solvent is less important. The change in stretching frequencies in the IR spectra of AFS with the change of their aggregate state and upon dissolution indicates a considerable influence of the medium on the coordinate Si ← O bond strength [1]. For the above compounds the $\nu(C{=}O) = f(\varepsilon)$ function is poorly approximated by a linear relationship.

We have studied the influence of the number of fluorine atoms attached to silicon in molecule of methyl(aroyloxymethyl)fluorosilanes, $C_6H_5COOH_2Si(CH_3)F_2$ (I), $4\text{-}CH_3C_6H_4COOCH_2Si(CH_3)F_2$ (II) and $C_6H_5COOCH_2Si(CH_3)_2F$ (III), on the intramolecular coordination ability of the silicon atom. In addition, the nature of the interaction between compounds I–III and the medium has been examined from the spectra of the above compounds in the gaseous state and in solutions in 11 solvents of various polarities. Benzoyloxymethyltrifluorosilane, $C_6H_5COOCH_2SiF_3$ (IV), with characterized intramolecular Si ← O coordination [1], and benzoyloxymethyltriethoxysilane, $C_6H_5COOCH_2Si(OC_2H_5)_3$ (V), containing a tetrahedral silicon atom, have been studied in a similar way.

Results

The IR spectra of solutions of compound IV show that one of the criteria of Si ← O bonding is stretching frequency values of coordinated groups [1]. The stretching vibration of the carbonyl group, ν(C=O), in spectra of I–III is a doublet with maxima at 1650–1690 and 1720–1730 cm^{-1} (Table 1). The high-frequency doublet component is undoubtedly associated with the uncoordinated C=O group

TABLE 1

THE VALUES OF ν(C=O), ν_{as}(C–O–C) and ν(Si–F) FOR COMPOUNDS IN CS_2 AT 298 K (cm^{-1})

Compound	ν(C=O)	ν_{as}(C–O–C)	ν(Si–F)
I $C_6H_5\text{-}COO\text{-}CH_2\text{-}Si(CH_3)F_2$	1729	1307, 1315	933, 837, 770
	1683	1342	911, 800, 759
II $4\text{-}CH_3\text{-}C_6H_4\text{-}COO\text{-}CH_2\text{-}Si(CH_3)F_2$	1725	1305, 1317	900, 840, 800
	1673	1342	890, 790, 740
III $C_6H_5\text{-}COO\text{-}CH_2\text{-}Si(CH_3)_2F$	1724	1297, 1311	900, 875, 806
	1697	1327	897, 837, 750
IV $C_6H_5\text{-}COO\text{-}CH_2\text{-}SiF_3$	1657	1358	962, 869, 808
V $C_6H_5\text{-}COO\text{-}CH_2\text{-}Si(OC_2H_5)_3$	1723	1296, 1308	–

[1]. The possible conformational inhomogeneity of compounds I–III cannot give rise to the doublet. This follows from the spectrum of compound $C_6H_5COOCH_2Si(OC_4H_9)_2CH_3$ (VI) where the $\nu(C{=}O)$ band appears as a singlet. The above compound was considered as a conformationally inhomogenous model without intramolecular coordination. The absence of concentration dependence of the doublet component intensities indicates that the low-frequency maximum is not due to the formation of intermolecular $Si \leftarrow O$ bond associates. It is possible, therefore, that the low-frequency $\nu(C{=}O)$ band in the spectra of compounds I–III results from the intramolecular silicon–carbonyl oxygen coordination. This is also evidenced by the greater half-width of this band as compared with the high-frequency one ($b_{1/2} = 15$–20 and 10–15 cm^{-1}, respectively). A similar difference in the band half-width values was observed in the spectra of compounds IV and V, displaying single $\nu(C{=}O)$ bands assigned to coordinated and free C=O groups, respectively. For the same reason, the intense antisymmetric stretching vibration bands, $\nu_{as}(C\text{–}O\text{–}C)$, at 1320–1340 cm^{-1} were attributed to the molecules with an intramolecular $Si \leftarrow O$ bond, and the bands at 1300–1310 cm^{-1} to the uncoordinated molecules. Strong mixing of natural coordinates in normal vibrations $\nu(Si\text{–}F)$, and out-of-plane deformations, $\rho_{\text{II}}(CH_3)$, for the $Si(CH_3)F_2$ and $Si(CH_3)_2F$ groups [11] in I–III hinders the assignment of the absorption bands in the 700–900 cm^{-1} range to vibration types.

The temperature change in solutions of I–III in non-polar solvents (n-$C_{10}H_{22}$, CCl_4, CS_2) leads to an intensity redistribution in the $\nu(C{=}O)$, $\nu_{as}(C\text{–}O\text{–}C)$ and $\nu(Si\text{–}F)$ vibration regions (Fig. 1). The decrease in the low-frequency band intensity, $\nu(C{=}O)$, with increasing temperature seems to be due to the $Si \leftarrow O$ bond, resulting in a predominance of the less stable form without coordination. The bands in the $\nu_{as}(C\text{–}O\text{–}C)$ region assigned to both the molecular forms respond to the temperature change in the same way. This dependence of the band intensity in the 700–900 cm^{-1} region on the temperature allows one to assign the $Si(CH_3)F_2$ and $Si(CH_3)_2F$ vibrations to the states with and without $Si \leftarrow O$ intramolecular coordination. The

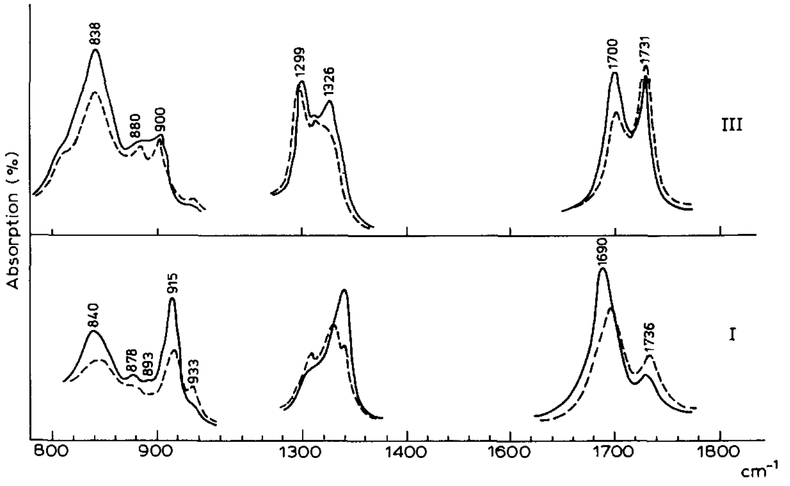

Fig. 1. The $\nu(C{=}O)$, $\nu_{as}(C\text{–}O\text{–}C)$ and $\nu(Si\text{–}F)$ values in the spectra of solutions of compounds I–III in n-$C_{10}H_{22}$. solid line $T = 283$ K; dotted line $T = 363$ K.

bands at 759, 800, 911 cm^{-1} and 750, 837, 897 cm^{-1} are assigned to the coordinated forms of I and III, respectively, whereas the bands at 770, 837, 933 cm^{-1} and 806, 875, 900 cm^{-1} to the forms without intramolecular coordination. The lower stretching vibrations, ν(Si–F) in pentacoordinate silicon compounds as compared with ν(Si–F) in tetravalent silicon compounds may be explained in terms of some weakening of the Si–F bonds with extending the coordination number of the silicon atom.

An increase in the solvent polarity decreases ν(C=O), ν(Si–F) and increases ν_{as}(C–O–C) values for the coordinated compounds I–III (Fig. 2). The shift value, $\Delta\nu$, of these bands is smaller than that of the corresponding bands of compound IV. The band position of these vibrations of uncoordinated molecules I–III are insignificantly affected by the increase in the solvent polarity. The ν(C=O) and ν_{as}(C–O–C)

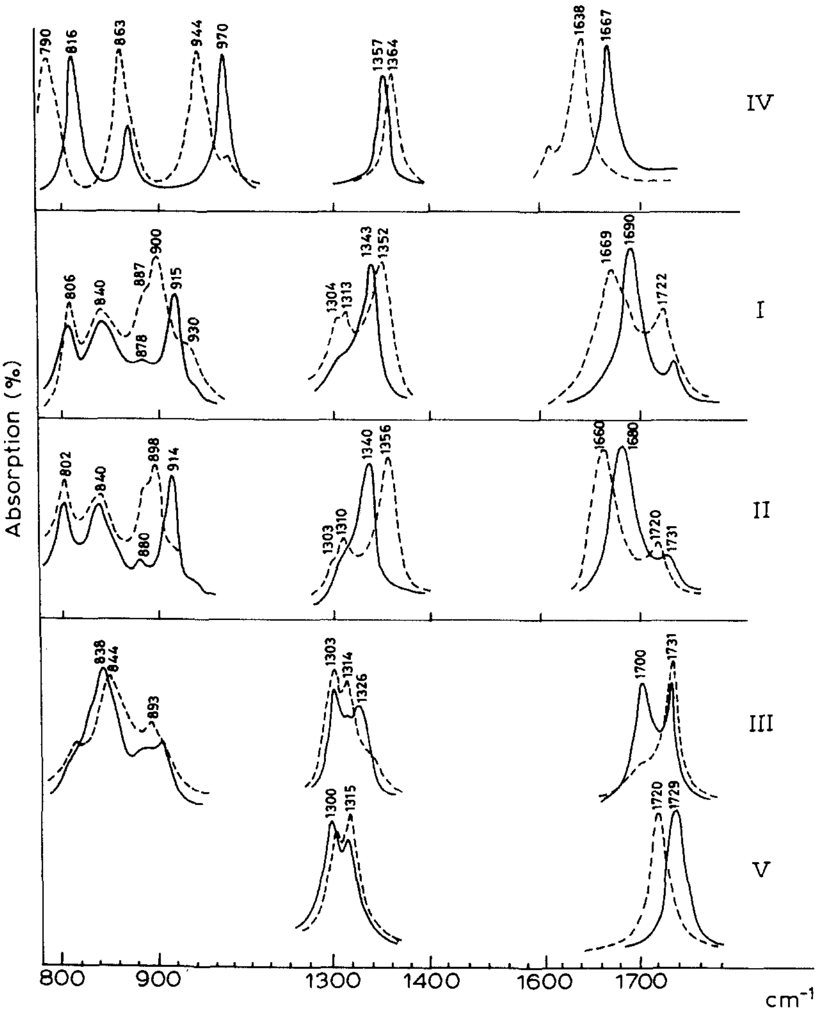

Fig. 2. The ν(C=O), ν_{as}(C–O–C), ν(Si–F) values in the spectra of compounds I–V at 289 K. solid line in n-$C_{10}H_{22}$; dotted line in CH_3CN.

doublet intensity ratio in the spectra of compounds I–III is strongly dependent on the medium polarity (ε) (Fig. 2).

Discussion

The high sensitivity of stretching vibrations of the groups involved in coordination to the medium change [1] is considered by us as strong evidence for pentacoordinate silicon in compounds I–III. The dependence of the measured ν(C=O) values on a function of the dielectric constant (ε) and the refraction index (n) of the medium can be expressed by the Buckingham equation:

$$\nu = A + B\frac{\varepsilon - 1}{2\varepsilon + 1} + C\frac{n^2 - 1}{2n^2 + 1}$$

The parameters A, B and C, the partial correlation coefficients, r_{ij}, and the multiple correlation coefficient, R, were evaluated for $\nu(\mathrm{C{=}O}) = \mathrm{f}\ (\varepsilon, n)$ of the two components of double bands arising from compounds I, III and single bands from compounds IV and V in eleven organic solvents (Table 2). The equations $y = \varepsilon - 1/2\varepsilon + 1$ and $z = n^2 - 1/2n^2 + 1$ are linearly independent, i.e. $r_{yz} = 0.6$. The parameters A in eqs. 1–6 are coincident with the ν(C=O) values measured for compounds I, III, IV and V in the gaseous state. Introduction of the solvent polarizability parameter, $C(n^2 - 1)/2n^2 + 1$, in the regression equation significantly increases the correlation coefficient R.

Equation 6 for the ν(C=O) band of compound V with a free carbonyl group and eqs. 3 and 5 for the high-frequency ν(C=O) doublet components of compounds I and III differ in only parameters A. The contributions from the solvent polarization $B\ (\varepsilon - 1)/2\varepsilon + 1$ and the polarizability interactions are approximately equal in this case. The role of the polarization interaction with respect to the polarizability increases for the low-frequency components of the ν(C=O) doublet of compounds I and III (eqs. 2, 4); this is caused by the increase in the dipole moments of intramolecularly coordinated molecules. An increase in the number of fluorine atoms (n) in the $\mathrm{Si(CH_3)_{3-n}F_n}$ group increases the relative value of the polarization interaction (with $n = 1 \rightarrow 2 \rightarrow 3$, $B = 48 \rightarrow 62 \rightarrow 99$). In general, the $\nu(\mathrm{C{=}O}) = \mathrm{f}(\varepsilon, n)$ relationship differs for the compounds studied from that for 1-hydrosilatranes in

TABLE 2

THE PARAMETERS OF CORRELATION EQUATIONS FOR COMPOUNDS $\mathrm{C_6H_5{-}COO{-}CH_2{-}X}$ [a]

X	Number of eq.	A	B	C	$r_{\nu y}$	$r_{\nu z}$	r_{yz}	R
$\mathrm{SiF_3}$	1	1689	−99	−25	0.986	0.680	0.600	0.990
$\mathrm{Si(CH_3)F_2}$	2	1700	−62	−2	0.981	0.680	0.600	0.984
	3	1746	−35	−33	0.944	0.820	0.600	0.972
$\mathrm{Si(CH_3)_2F}$	4	1715	−48	−19	0.973	0.720	0.600	0.986
	5	1743	−39	−31	0.940	0.760	0.600	0.970
$\mathrm{Si(OC_2H_5)_3}$	6	1740	−39	−32	0.700	0.969	0.600	0.982

[a] $\nu(\mathrm{C{=}O}) = A + By + Cz$; $y = \varepsilon - 1/2\varepsilon + 1$; $z = n^2 - 1/2n^2 + 1$; The $\varepsilon_{298\ \mathrm{K}}$ and $n_{298\ \mathrm{K}}$ values were taken from ref. 13; $S_\mathrm{B} = 4\ \mathrm{cm^{-1}}$; $S_\mathrm{C} = 8\ \mathrm{cm^{-1}}$; $S_\nu^{\mathrm{stat.}} = 1.4\ \mathrm{cm^{-1}}$; $S_\nu^{\mathrm{exp.}} = 1.5\ \mathrm{cm^{-1}}$.

TABLE 3

THE THERMODYNAMIC PARAMETERS ΔH (kJ mol^{-1}) and ΔS (J K^{-1}mol^{-1}) FOR COMPOUNDS X′–C_6H_4–COO–CH_2–X″ AND THE EQUILIBRIUM CONSTANT K AT 298 K

Medium	X′ = H, X″ = SiF_3			X′ = H, X″ = $Si(CH_3)F_2$			X′ = H, X″ = $Si(CH_3)_2F$			X′ = 4-CH_3, X″ = $Si(CH_3)F_2$		
	ΔH	ΔS	K	ΔH	ΔS	K	ΔH	ΔS	K	ΔH	ΔS	K
gas[a]	33.5	63	0.00	11.7	25	0.18	5.4	16	0.72	9.2	19	0.23
$C_{10}H_{22}$				12.6	27	0.16	5.4	19	1.07	9.2	20	0.27
$(C_4H_9)_2O$				12.6	30	0.24	3.8	16	1.41	8.8	21	0.36
CCl_4				12.6	26	0.14						
CH_2ClCH_2Cl				10.5	25	0.30				8.8	20	0.31
CH_3CN				12.6	33	0.32	3.8	27	5.76	8.8	21	0.38

[a] The ΔH and ΔS values for gaseous compounds were determined by L.V. Klyba; $\Delta(\Delta H) = 0.4$ kJ mol^{-1}; $\Delta(\Delta S) = 3$ J K^{-1}mol^{-1}

which the solvent-induced shifts of ν(Si–H) are characterized well by the single-parameter equation containing the f(ε) term only.

The ν(C=O) vibrations in the spectra of I–IV in solution in pyridine are displayed as a single band at 1720–1730 cm^{-1}. This is indicative of Si ← O bond cleavage due to intermolecular silicon–pyridine coordination.

The thermodynamic parameters (ΔH, ΔS) of the intramolecular Si ← O coordination have been obtained for solutions of I–III in media of various polarity (Table 3). The enthalpy value is lower for the monofluoro derivative (III) than for difluoro derivatives (I,II) in the same medium. This is in agreement with the observed decrease in ν(C=O) of the coordinated C=O group and the increase in the parameter B in the corresponding correlation equations when the number of the fluorine atoms increases from 1 to 3.

The ΔH values for each of compounds I–IV do not depend much on the dielectric constant of the medium, being coincident with those for the gaseous state of these compounds (Table 3). Such a consistency in the ΔH values does not, however, imply that the Si ← O bond strength is unchanged. This is seen from the strong dependence of the ν(C=O) values of coordinated carbonyl groups on the polarization term in the correlation equations 1, 2 and 4. The opposite signs of the change in the ν(C=O) and ν(Si–F) frequencies on one hand and ν_{as}(C–O–C) on the other hand in the intramolecular coordinate bonding indicate the possibility of compensatory effects. As a result, the change in the enthalpy of the molecules is independent of the polarity of the medium.

The intramolecularly coordinated compounds I–III have a dipole moment greater than that of the uncoordinated form of these compounds [1]. Therefore, the relative increase in the ν(C=O) intensity of free carbonyl groups with an increased ε value at constant temperature is quite unexpected in the spectra of compounds I–III (Fig. 2). In our opinion, this effect is due to the increase in the ΔS value with increasing solvent polarity (ε). The equilibrium constant of intramolecular complex formation changes according to the equation

$$K=\frac{N_1}{N_2}=e-\frac{H}{RT}\,e^{-}\,\frac{S}{R}$$

where N_1 and N_2 are the percentages of molecules with free and coordinated carbonyl groups, respectively. The role of the entropy is most important with the lowest values of ΔH. Thus, the increase in the ΔS values from 16 to 27 J $K^{-1}mol^{-1}$ for compound III ($\Delta H = 5.4$ kJ mol^{-1}) in going from the gaseous state to the solution in CH_3CN increases K from 0.72 to 5.76. This corresponds to $N_1 = 40\%$, $N_2 = 60\%$ for the gaseous state, and $N_1 = 84\%$, $N_2 = 16\%$ for solution in CH_3CN. A similar effect is observed for compounds I and II (Table 3). However, higher ΔH values for fluoro derivatives I and II determine lower concentrations of the uncoordinated forms under comparable conditions. It is evident that the $\Delta S = f(\varepsilon)$ dependence is the factor causing the anomalous change in the ν(C=O) doublet ratio in the spectra of compounds I–III.

Experimental

IR spectra of compounds were recorded on a Specord 75 IR spectrophotometer with rock-salt optics. The concentrations of the solutions were about 0.1–0.01 mol

l^{-1}. Measurements were carried out in the temperature range of 223–363 K; the temperature range was kept constant to within ±0.5 K. The spectra of gaseous compounds I–III were taken in gas-tight cells (l = 1–5 cm) in the 400–500 K range at atmospheric pressure.

The synthesis of methyl(aroyloxymethyl)fluorosilanes was described previously [12]. The $\nu(C{=}O) = f(\varepsilon, n)$ dependence was analyzed from the spectra of solutions of compounds I–IV in the following solvents: n-C_5H_{12}, n-C_6H_{14}, n-$C_{10}H_{22}$, CCl_4, CS_2, $(C_4H_9)_2O$, $(C_2H_5)_2O$, C_4H_8O, CH_2Cl_2, CH_3CN, CH_2Cl-CH_2Cl. All the solvents used were purified and dried by standard procedures.

Thermodynamic parameters of intramolecular coordination ($\Delta H, \Delta S$) were estimated from the temperature relationship of the $\nu(C{=}O)$ band intensities of coordinated and uncoordinated carbonyl groups:

$$\ln\frac{D_1}{D_2} = -\frac{\Delta H}{R}\frac{1}{T} + \ln\frac{i_1}{i_2} + \frac{\Delta S}{R}$$

D_1, D_2, i_1 and i_2 are the optical densities and absorption coefficients in band maxima of uncoordinated and coordinated C=O groups, respectively. In spectra of solutions of IV and V in different solvents the i_1 and i_2 values are similar, being in the 500–700 l $mol^{-1}cm^{-1}$ range. This suggests, therefore, that for compounds I–III, which may be considered as intermediates, the i_1/i_2 ratio does not differ much from 1 and, consequently, $\ln i_1/i_2 \approx 0$.

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