The interactions of (=O→Si)-(benzoyloxymethyl)trifluoro- and -(benzoyloxymethyl)methyldifluorosilanes with a solvent

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The IR spectra of solutions of (=O→Si)-(benzoyloxymethyl)trifluorosilane (**1**), -(benzoyloxymethyl)methyldifluorosilane (**2**), and butyl benzoate (**3**) are examined in the region of the ν(C=O) stretching vibrations in 24 solvents. The ability of compounds **1**—**3** to undergo specific intermolecular interactions is evaluated from the dependence of ν(C=O) on the Kamlet—Taft (π*, α, β) parameters, which was obtained for the carbonyl groups involved in the intramolecular coordinate (=O→Si) bond and for free carbonyl groups. The corresponding values of the coefficients in the Kamlet—Taft equations are indicative of a weak ability of pentacoordinate silicon compounds **1** and **2** to undergo acid-base interactions.

Key words: intramolecular coordinate bond; silicon atom; carbonyl group; IR spectroscopy, solvent effect; (benzoyloxymethyl)trifluorosilane, (benzoyloxymethyl)methyldifluorosilane.

The reactivity of draconoids, compounds of pentacoordinate silicon containing an intramolecular coordinate =O→Si bond, has been little studied.[1] Data are available showing that the stability of the Si—F bond of (aroyloxymethyl)trifluorosilanes $RC_6H_4C(=O)OCH_2SiF_3$ toward hydrolysis and alcoholysis is higher than that of the Si—F bonds in organyltrifluorosilanes $RSiF_3$, which contain a tetrahedral silicon atom.[1,2] Alkaline hydrolysis of these compounds is accompanied by an increase in the coordination number of the silicon atom to form the corresponding tetra- and pentafluorosilicates.[2] The reactions of (aroyloxymethyl)trifluorosilanes with mono- and bidentate nitrogen bases (pyridine, triethanolamine, 1,2-bis(dimethylamino)ethane, 2,2′-dipyridyl, and 1,10-phenanthroline) result in the formation of compounds of hexacoordinate silicon[3,4] with =O→Si←N or N→Si←N coordinate bonds. The oxygen atoms of the C(=O)O group and the π-system of the benzene ring in (aroyloxymethyl)trifluorosilanes are potential centers of σ,π-basicity.

We performed a quantitative estimation of the ability of (benzoyloxymethyl)trifluorosilane (**1**) and (benzoyloxymethyl)methyldifluorosilane (**2**) of the general formula $C_6H_5C(=O)OCH_2SiF_n(CH_3)_{3-n}$, $n = 3$ and 2, respectively, to undergo specific interactions with solvents. The empirical dependence of the IR spectroscopic parameters of a dissolved substance on the solvatochromic parameters of a solvent, which is similar to that suggested by Kamlet—Taft,[5] was used.

$$A = C + S\pi^* + a\alpha + b\beta \qquad (1)$$

In our case, A is the frequency of the ν(C=O) stretching vibrations of C=O participating in the O→Si bond and of free carbonyl groups for the series of solvents, C is the statistical value of ν(C=O) in an inert solvent, π*, α, and β are parameters that characterize the bipolarity, acidity, and basicity of a solvent, respectively.[6—8]

The shifts of the frequency of absorption of the noncoordinate carbonyl group as functions of the nature of the medium were studied for compound **2**, which exists in solutions as equilibrium mixtures of cyclic molecules with the intramolecular coordinate =O→Si bonds and acyclic molecules with coordination-free carbonyl groups. The similar empirical dependence $\nu(C=O) = f(\pi^*, \alpha, \beta)$ was used for solutions of butyl benzoate $C_6H_5C(=O)OC_4H_9$ (**3**).

The correlation equations (2)—(5) were obtained for compounds **1**—**3** studied.

$$\mathbf{1}: \nu(C=O)(\text{coord.}) = 1666 - 31\pi^* - 0.2\alpha - 2.9\beta, \quad R = 0.94,\ S_0 = 2.1 \qquad (2)$$

$$\mathbf{2}: \nu(C=O)(\text{coord.}) = 1690 - 23\pi^* + 1.0\alpha + 0.1\beta, \quad R = 0.87,\ S_0 = 2.3 \qquad (3)$$

$$\mathbf{2}: \nu(C=O)(\text{free}) = 1733 - 11\pi^* - 18\alpha - 5.0\beta, \quad R = 0.92,\ S_0 = 2.4 \qquad (4)$$

$$\mathbf{3}: \nu(C=O) = 1726 - 14\pi^* - 23\alpha + 0.2\beta, \quad R = 0.96,\ S_0 = 1.7 \qquad (5)$$

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The values of the coefficient S, which characterizes bipolar properties of a dissolved substance, are the greatest in Eqs. (2) and (3). They vary in accordance with the enthalpy of the intramolecular coordination of the silicon atom. For example, for the gaseous states of **1** and **2** the values of $-\Delta H$ are 33.0 and 11.7 kJ mol^{-1}, respectively.[9] In Eqs. (4) and (5), the S values for the free C=O group of the molecules of compounds **2** and **3** are considerably lower. This testifies that the classic solvation component plays a more important role in the case of cyclic molecules **1** and **2**, containing a pentacoordinate silicon atom, than in the case of acyclic molecules **2** and butyl benzoate **3**, which have a lower dipole moment.[2]

The coefficients a and b in the Kamlet—Taft equations (2) and (3) for coordinate compounds reflect the acid and base properties, respectively, of the compounds studied. They are small and comparable to the values of the standard deviations S_0. All values of ν(C=O)(coord.) for the solutions of **1** and **2** obey in fact the same dependence ν(C=O)(coord.) = f(π*) [Eqs. (6) and (7)].

$$\mathbf{1}: \nu(\mathrm{C{=}O})(\mathrm{coord.}) = 1665 - 31\pi^*,\ R = 0.97,\ S_0 = 2.3 \quad (6)$$

$$\mathbf{2}: \nu(\mathrm{C{=}O})(\mathrm{coord.}) = 1690 - 22\pi^*,\ R = 0.92,\ S_0 = 2.2 \quad (7)$$

Hence it follows that the ability of pentacoordinate silicon compounds to undergo acid-base interactions is fairly low.

In the narrower terms of universal intramolecular interaction theory, the shifts of the ν(C=O) frequency in the spectra of (aroyloxymethyl)trifluorosilanes and (aroyloxymethyl)methyldifluorosilanes on going from their gaseous states to solutions in organic solvents that are not prone to specific interactions are well described by the Burkingham equation.

$$\nu(\mathrm{C{=}O}) = A + B(\varepsilon - 1)/(2\varepsilon + 1) + C(n^2 - 1)/(2n^2 + 1) \quad (8)$$

Such solvents as alcohols, chloroform, tetrahydrofuran, dioxane, and benzene and its substituted derivatives do not obey the Burkingham correlation equations for ν(C=O) in the spectra of compounds **1** and **2**.

The terms with coefficients B and C in Eq. (8) are related to the energies of the induction-orientation and dispersion intramolecular interactions, respectively.

The low-frequency shift of ν(C=O) as the polar properties of the medium increases is caused by an enhancement of the coordinate =O→Si bond strength and a decrease in the order of the carbonyl group in molecules **1** and **2**. This shift is described by the equations:

Table 1. Absorption frequencies ν(C=O) in the IR spectra of solutions of compounds **1**, **2**, and **3** in different solvents and parameters π*, α, and β of the solvent

Solvent	π*	α	β	ν(C=O)/cm^{-1}			
				1	**2**		**3**
				coord.	coord.	free	
cyclo-C_6H_{12}	0	0	0	1667	1692	1734	1726
n-$C_{10}H_{22}$	0.03	0	0	1667	1689	1733	1726
CCl_4	0.28	0	0	1660	1685	1731	1718
$CHCl_3$	0.58	0.44	0	1645	1673	1715	—
$(C_4H_9)_2O$	0.24	0	0.46	1658	1681	1724	1724
$ClCH_2$—CH_2Cl	0.81	0	0	1641	1673	1723	1711
CH_3CN	0.75	0.19	0.37	1638	1669	1721	1712
$(C_2H_5)_2O$	0.27	0	0.47	1655	1684	1730	1723
CH_2Cl_2	0.82	0.30	0	1642	1671	1720	1710
$C_6H_5OCH_3$	0.73	0	0.22	1642	1673	1726	1714
$C_6H_5NO_2$	1.01	0	0.30	1640	1671	1724	1714
$O(CH_2CH_2)_2O$	0.55	0	0.37	1646	1676	1725	1717
$C_6H_5CH_3$	0.54	0	0.11	1649	1678	1728	1719
$(CH_3)_3COH$	0.41	0.68	1.01	1650	1681	1729, 1710	1723, 1704
C_4H_9OH	0.47	0.79	0.88	1650	1682	1731, 1710	1723, 1701
C_2H_5OH	0.54	0.83	0.77	1648	1679	1727, 1707	1719, 1699
CH_3OH	0.60	0.93	0.62	1645	1677	1728, 1711	1716, 1697
$(CH_3)_2CHOH$	0.47	0.77	0.95	1650	1682	1729, 1710	1723, 1702
C_6H_5Cl	0.71	0	0.07	1643	1675	1726	1717
$(CH_2)_4O$	0.58	0	0.55	1645	1674	1724	—
$(CH_3)_2CO$	0.71	0.10	0.48	1642	1672	—	—
$[(CH_3)_2CH]_2O$	0.27	0	0.47	1657	1685	1733	1723
C_6H_6	0.59	0	0.10	1647	1679	1726	1717
$(CH_3)_2SO$	1.0	0	0.76	1633	1668	1717	1711

$$\mathbf{1}\text{: } \nu(\mathrm{C{=}O})(\text{coord.}) = 1688 - 99Y - 25Z, \quad R = 0.99,\ S_0 = 1.1, \tag{9}$$

$$\mathbf{2}\text{: } \nu(\mathrm{C{=}O})(\text{coord.}) = 1700 - 62Y - 2Z, \quad R = 0.98,\ S_0 = 1.4, \tag{10}$$

where $Y = (\varepsilon - 1)/(2\varepsilon + 1)$, $Z = (n^2 - 1)/(2n^2 + 1)$.

The interaction of molecules **1** and **2**, which contain a pentacoordinate silicon atom, with the medium is predominantly induction-orientation (and not dispersion).

The shifts of the frequencies of the absorption of the free carbonyl groups in **2** that occur when the medium is varied in accordance with the parameters indicated above, are also described by the Burkingham equation.

$$\nu(\mathrm{C{=}O})(\text{free}) = 1746 - 35Y - 33Z,\ R = 0.94,\ S_0 = 3.0 \tag{11}$$

The value of the coefficient B is the lowest for the free C=O groups (B = 35) and increases in the case of the coordinate carbonyl groups (B = 62 and 99 for **2** and **1**, respectively), *i.e.*, as the pentacoordination enthalpy increases.

The ν(C=O) line has a doublet structure (Table 1) for the coordination-free carbonyl group in the spectra of alcoholic solutions of compounds **2** and **3** for which the acidity parameter α varies, according to Kamlet—Taft, from 0.67 to 0.98. The anomalously low values of one of the doublet components reflect the ability of the carbonyl groups in molecules **2** and **3** to form hydrogen bonds with proton donors and were used in the Kamlet—Taft correlation equations. The value of coefficient a in Eqs. (4) and (5), which characterizes the basic properties of the C=O groups, becomes rather significant (a = 18 and 23, respectively). The carbonyl groups in molecules **1** and **2** that are involved in the coordinate =O→Si bond cannot be proton acceptors.

References

1. M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2664 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2319 (Engl. Transl.)].
2. M. G. Voronkov and L. I. Gubanova, *Main Group Metal Chem.*, 1987, **10**, 209.
3. Yu. L. Frolov, T. N. Aksamentova, G. A. Gavrilova, N. N. Chipanina, V. B. Modonov, L. I. Gubanova, V. M. D'yakov, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1982, **267**, 646 [*Dokl. Chem.*, 1982, **267** (Engl. Transl.)].
4. M. G. Voronkov, L. I. Gubanova, G. A. Gavrilova, N. N. Chipanina, Yu. L. Frolov, and N. F. Chernov, *Dokl. Akad. Nauk SSSR*, 1987, **292**, 1133 [*Dokl. Chem.*, 1987, **292** (Engl. Transl.)].
5. C. Reichardt, in *Solvent Effects in Organic Chemistry*, Verlag Chemie Weinheim, New York, 1979, 355.
6. M. I. Kamlet, Ch. Dickinson, and R. W. Taft, *J. Chem. Soc., Perkin Trans.*, 1981, P2, 353.
7. M. I. Kamlet, Ch. Dickinson, and R. W. Taft, *Chem. Phys. Letters*, 1981, **77**, 69.
8. M. H. Abraham and P. L. Grellier, *Can. J. Chem.*, 1988, **66**, 2673.
9. Yu. L. Frolov and M. G. Voronkov, *J. Mol. Struct.*, 1990, **217**, 265.

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