ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 6, pp. 1098–1100. © Pleiades Publishing, Ltd., 2012.
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Nature of “Chlorine Effect” in the ^{17}O NMR Spectra of Sulfur Compounds XSO_2Y

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Received April 18, 2011

Abstract—Nature of “chlorine effect” in the ^{17}O NMR spectra of compounds XSO_2Y associated with the exclusive influence of chlorine on the position of the signal of terminal oxygen is considered. The effect is found to be determined by the electron population of sulfur 3*d* orbitals, which reaches maximum in the case of X, Y = Cl.

DOI: 10.1134/S1070363212060096

In this paper we investigate the nature of the “chlorine effect” in the ^{17}O NMR spectra of sulfonic compounds XSO_2Y (X, Y = F, Cl, Me, OMe). The study of these spectra showed that among various substituents, the chlorine exerts unusual influence on the position of the signal of terminal oxygen ^{17}O: in this case the largest deshielding occurs of the oxygen nucleus [1]. This phenomenon is called “chlorine effect” [1–3]. A similar effect was also observed in the ^{17}O NMR spectra of some oxygen compounds of phosphorus [2]. It was shown that in these compounds the “chlorine effect” is associated with the electron population of the phosphorus 3*d*-AO due to the $3d_P$–$2p_O$ interaction [4]. This fact suggests that the P^+–O^- bond is partially of a double-bond character The π-bonding between S and O in the sulfones, based on the $3d_S$–$2p_O$ interaction, is considered as an important feature of the S^+–O^- bond in sulfone as well [5–8].

In general, it is assumed that the shielding of the second row elements is determined mainly by the local paramagnetic component $(\sigma^p)'$ which is calculated on the basis of the well-known Karplus–Pople equation for a nucleus A:

$$\sigma^p_A = \text{const}\Delta E^{-1} \langle r^{-3}\rangle_{2p}\Sigma Q_{AB}, \quad (1)$$

where ΣQ_{AB} are the elements of the bond order–charge density matrix, ΔE^{-1} is the reciprocal of the average electronic excitation energy of the molecule, $\langle r^{-3}\rangle$ is the average value of reciprocal cube of the radius of 2*p*-AO.

The term ΔE^{-1} may be responsible for the “chlorine effect” because the forbidden transitions in the UV region of *n*–π* type are magnetically active and can cause significant downfield shift of the oxygen signal. However, the related absorption bands in the UV spectra of the XSO_2Cl molecules have not been detected [1]. Authors of several studies assumed that a decrease in electron density on the oxygen atom in the structurally similar compounds caused a decrease in shielding of this atom [9]. “Chlorine effect” has also been explained by the interaction of the oxygen lone pair with antibonding $\sigma^*_{S\text{–}Cl}$ orbital, which leads to the downfield chemical shift of ^{17}O as a consequence of reducing the charge on the oxygen, contributing mainly to the $\langle r^{-3}\rangle_{2pO}$ term. This model of “chloride effect” suggests that the electron distribution in $\sigma^*_{S\text{–}Cl}$ bond is mainly localized on the chlorine atom [3]. However, this conclusion is not confirmed by the data of ^{35}Cl NQR spectroscopy of compounds XSO_2Cl, according to which the effect of the substituent X on the chlorine atom is transferred by almost purely inductive way. Thus, the frequency of chlorine (ν, MHz) for compounds XSO_2Cl varies as follows [10]:

X	Me	MeO	PhO	CCl_3	Cl	F
ν	33.23	35.65	35.66	36.29	37.72	39.35

The dependence of the chlorine frequency on the Taft–Hammett inductive parameter σ_I is well described by a linear equation $\nu = f(\sigma_I)$ + const, any extreme values of frequencies for X = Cl are not observed. According to the Townes–Dailey model, the increase in the frequency of chlorine in this series of compounds is assigned to the decrease in electronic charge on the chlorine [10].

The “chlorine effect” cannot be a consequence of the conformational preferences of sulfone molecules containing chlorine. It is known that conformations of all $MeSO_2Y$ compounds with Y = Me, F, or Cl are the same [3].

It was shown in [11] that the atoms Si, P, S in molecules may include the bound states of electrons in the 3*d*-AO when the positive charge on such atom belongs to a certain range of charges, that is, the charge is between a lower and an upper limits of the charge. Earlier [12] it was assumed that the $3d_S$-AO can be populated when the positive charge of the S atom exceeds certain critical positive charge. The existence of the limits of the charges means that the population of AO is zero when the charge is close to the upper or the lower limit, but within the range of charges, apparently in the mid-range, the population reaches maximum. Depending on the magnitude of the positive charge of an atom P or S in this series of compounds, the electron population of 3*d*-AO of these atoms grows, passes through a maximum, and then falls. Since in this series of structurally similar compounds the positive charge of P or S depends on electronegativity (χ) of substituents X or Y, and χ_{Cl} is approximately in the middle of the Pauling electronegativity scale, the electron population of 3*d*-AO should be near the maximum, that defines the nature of the “chloride effect”. However, in the case of compounds XSO_2Y the dependence of δ_O on χ_X, χ_Y or $\chi_X + \chi_Y$ is very complicated [3]. Therefore, we consider below a dependence of δ_O on the magnitude of the positive charge on sulfur.

The source electron population of $3d_S$-AO in the considered sulfone derivatives is the terminal oxygen atom, because this atom is the most effective electron donor. Therefore, its ^{17}O chemical shift should be changed as follows: with increasing positive charge on S in this series of structurally similar compounds up to reaching the magnitude of positive charge of sulfur associated with the chlorine in the Cl_2SO_2, the signal of oxygen is shifted downfield (the population of the $3d_S$-AO grows and the charge on the terminal oxygen falls). At further increase of the positive charge on sulfur the situation is changed: the signal of oxygen is shifted upfields (population of $3d_S$-AO falls and the charge on the oxygen grows).

Consider now, how the ^{17}O chemical shift in the series of sulfone derivatives depends on the positive charge on sulfur. The charges on sulfur were determined by *ab initio* quantum-chemical calculations (RHF/MP2/MINI-4//RHF/MP2/MINI-4 [13]) of these molecules. In the calculations, the scale factors of the valence orbitals of all atoms of compounds were optimized with a criterion of minimum energy of the molecule. Optimization was stopped when *E* increment was less than 0.0002 a.u.

The magnitudes of the positive charges of sulfur in the series of compounds (Q_S, a.u.), chemical shifts δ_O and δ_S are given below [3]. Chemical shifts are given in ppm relative to the external CS_2 for sulfur and external H_2O for oxygen, positive values indicate downfield resonance with respect to the references. The experimental error is ±1 ppm.

	Me_2SO_2	$MeSO_2Cl$	Cl_2SO_2	$MeSO_2OMe$	$MeSO_2F$	$MeOSO_2F$	F_2SO_2
Q_S	0.896	1.180	1.196	1.283	1.365	1.523	1.632
δ_O	164	238	296	170	186	148	148
δ_S	320	335	287	335	334	311	297

The data obtained show that the maximum ^{17}O chemical shift corresponds to the compound Cl_2SO_2. The increase in the positive charge magnitude on sulfur in going from Me_2SO_2 to Cl_2SO_2 leads to a downfield shift of the ^{17}O signal, and further increase in the charge shifts the ^{17}O signal upfield. Such a behavior of δ_O can be interpreted as an increase in electron population of the $3d_S$-AO (up to Cl_2SO_2) and its subsequent decrease. The charge on the sulfur in SO_2Cl_2 is in the middle of the range of positive charges on sulfur: 0.896 a.u. (Me_2SO_2) to 1.632 a.u. (F_2SO_2).

The data presented in general agree satisfactorily with the assumptions on the nature of changes in δ (^{17}O). However, the ^{17}O chemical shift of compound $MeSO_2OMe$ is expected to be higher. It is known that in certain classes of compounds the presence of γ-*gauche* methyl group near the oxygen atoms of SO_2 group leads to shielding the oxygen atom by approximately 10 ppm. In this regard, $\delta(^{17}O)$ for the $MeSO_2OMe$ should be adjusted (increased) [14]. The preferred conformation of sulfonic compounds is also a complicated problem.

Note that the trends in the chemical shifts of sulfur and oxygen depending on the charge on sulfur are in general identical with some exceptions. Until the compound Cl_2SO_2, the sulfur signal is shifted downfield when the populations of $3d_S$-AO increases, and after that compound an upfield shift occurs (paramagnetic contribution decreases) with a decrease in the populations of $3d_S$-AO. It is expectable that the ^{33}S chemical shift (285 ppm) of the compound Cl_2SO_2 must be greater than the sulfur chemical shift of the compound $MeSO_2Cl$ (335 ppm). Apparently, small changes in $\delta(^{33}S)$ caused by "chloride effect" may partially result from the compensation due to ΔE and ΣQ_{AB} in the case of Cl_2SO_2 [3]. The ^{33}S chemical shifts of the sulfonic compounds apparently are mainly determined by the paramagnetic contribution to the shielding constants.

It should be noted in conclusion that the change in the shielding of oxygen and sulfur in the studied series of sulfones is basically the same as the shielding of oxygen and phosphorus in the corresponding phosphorus compounds. The ^{31}P resonance of oxygen compounds of tetracoordinated phosphorus is largely determined by the population of the $3d_P$-AO [15]. For example, in the compounds $Cl_{3-n}POF_n$ the increase in the number of fluorine atoms, that is, the increase in the positive charge on phosphorus, results in growing shielding of both oxygen and phosphorus [2, 16]. Apparently, this can be attributed to a common feature of these compounds: the presence of $3d$-AO both in sulfur and phosphorus, whose electron population decreases with increasing positive charge on these atoms leading to a decrease in the paramagnetic component and an increase in the shielding constants of both phosphorus and sulfur.

Thus, the nature of the "chlorine effect" in the sulfones XSO_2Y is apparently determined by the electron population of the sulfur $3d_S$-AO, which is maximal in the case of X, Y = Cl.

In quantum-chemical calculations GAMESS software was used [17].

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