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Photoelectron spectra and CTC-tetracyanoethylene spectra of hexaethyldisilthiane and bis(triethylsilylalkyl) sulfides

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Abstract

Photoelectron spectra of organosilicon sulfides $[R_3Si(CH_2)_n]_2S$ ($R = C_2H_5$, $n = 0$–3) and their CTC spectra with tetracyanoethylene have been studied. The anomalously low J_1 value for bis(triethylsilylmethyl) sulfide ($n = 1$) as well as the ν_{tc}/J_1 relationship for this sulfide with π-donors, indicate delocalization of the lone electron pair orbital of the sulfur atom in the sulfide onto the neighbour CH_2–$Si\lessgtr$ fragment.

Introduction

Diorganyl sulfides normally are oxidized without any significant anomalies to form the corresponding diorganyl sulfoxides or sulfones depending upon the reaction conditions [1].

Previously, we have shown with vinyl(trialkylsilylalkyl) sulfides that the presence of a trialkylsilyl group in their molecule makes the oxidation reaction occur in an unusual manner. Thus, vinyl(trialkylsilylmethyl) sulfides are completely decomposed under the action of oxidants [2]. The oxidation of bis(triethylsilylalkyl) sulfides $[R_3Si(CH_2)_n]_2S$ ($R = C_2H_5$; $n = 1$–3) with hydrogen and t-butyl peroxides also proceeds abnormally. An attempt to synthesize bis(triethylsilylmethyl) sulfoxide in this way has led to cleavage of the Si–C and S–C bonds in the starting sulfide to form the following adducts: hexaalkyldisiloxane, bis(triethylsilylmethyl) disulfide, methyl(triethylsilylmethyl) disulfide and triethylsilylmethyl(formyl) sulfone.

This anomalous reactivity of organosilicon sulfides with a geminal arrangement of Si and S atoms, in particular, that of bis(triethylsilylmethyl) sulfide, is likely to be due to their peculiar orbital structure or charge distribution in their molecule.

Results and discussion

In the photoelectron spectra of diorganyl sulfides the first absorption band is caused by displacement of the sulfur LEP electron out of the orbital [3]. In analysis

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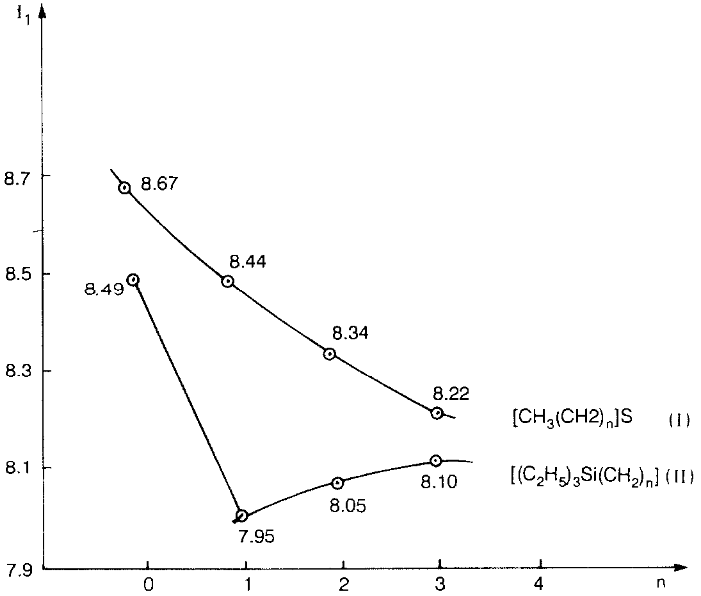

Fig. 1. The dependence of the first ionization potential upon the number of methylene groups for alkyl sulfides (I) and organosilicon sulfides (II). The curve for I was constructed using the data of Ref. 3.

of the orbital structure of organosilicon sulfides having the general formula $R_3Si(CH_2)SR'$ account should be taken of possible interference of the sulfur LEP orbitals with those of Si–C bond σ-MOs of appropriate symmetry [4].

We examined a change in the first ionization potential (J_1) of the organosilicon sulfides of the series $[(C_2H_5)_3Si(CH_2)_n]_2S$ where $n = 0$ (I), 1 (II), 2 (III), 3 (IV). In contrast to dialkyl sulfides $[CH_3(CH_2)_n]_2S$ where $n = 0$ (V), 1 (VI), 2 (VII), and 3 (VIII), the first ionization potential, plotted according to the n value of sulfides (I–IV) does not vary monotonically (Fig. 1). The anomalous low J_1 value for bis(triethylsilylmethyl) sulfide ($n = 1$) is not covered by the induction effect transfer of substituents at the sulfur atom thus indicating the existence of interaction between the sulfur LEP orbitals and σ^* (Si–C) orbitals, i.e. partial delocalization of these orbitals onto the neighbour CH_2–Si$\leqslant$ fragment.

The dependence of the charge transfer band energy ($h\nu_{ct}$) in the spectra of π–π DA complexes upon the first potential ionization of donor (J_{1D}) is described by linear equation

$$h\nu_{tc} = aI_{1D} + b \tag{1}$$

where a and b constants differ for n- and π-donors [6].

Thus, when considering aliphatic sulfides the absence of the dependence relationship between the energy of electron removal from HOMO and the energy of charge transfer in the DA complexes provides another criterion for the existence of delocalization of the sulfur LEP in the organosilicon sulfides (I–IV) under investigation. With this aim in view we have studied CTC spectra of compounds I–IV with tetracyanoethylene and compared them with the known literature data for dialkyl sulfides (V–VIII) and alkylaryl sulfides $CH_3SC_6H_5$ (IX), $CH_3SCH_2C_6H_5$ (X), and $CH_3SC_{12}H_9$ (XI).

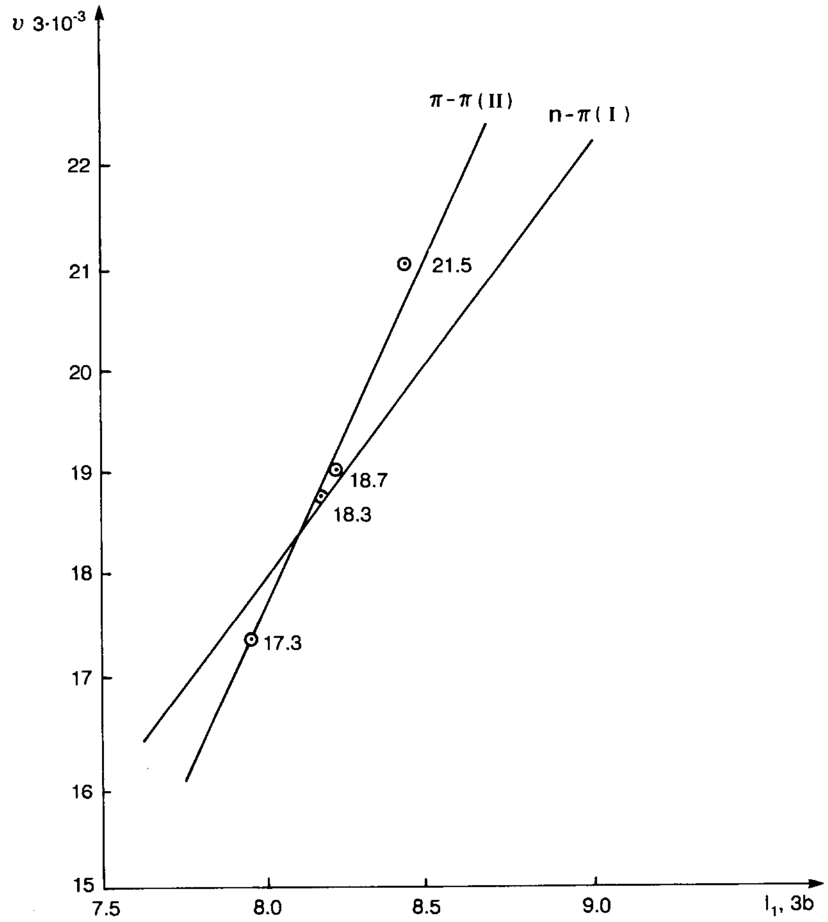

Fig. 2. The dependence of the band position of charge transfer complexes of alkyl sulfides and organosilicon sulfides upon I_1. Dependence I is compiled on the basis of data of Ref. 3, dependence II is based on the data of Ref. 5 and 6.

The ν_{ct}/I_1 dependence for sulfides (I–IV) as well as for aliphatic and araliphatic sulfides (IX–XI) (Fig. 2) shows that the charge transfer energy in DA-complexes with tetracyanoethylene in organosilicon sulfides I and II is more exactly described by eq. 1 for π-donors, especially when sulfides II are being considered. In contrast to this, organosilicon sulfides III and IV are intermediate between the n- and π-donors.

Thus, in organosilicon sulfides containing a $SiCH_2S$ fragment ($n = 1$) the sulfur LEP orbitals are delocalized on the neighbour σ^* orbital of the Si–C bond. This seems to be main reason for the anomalous behaviour of sulfide II in the oxidation reaction.

The observed partial LEP delocalization of the sulfur atom in hexaethyldisilthiane is likely to be due to interaction of LEP with vacant 3*d*-orbitals of the silicon atom.

Table 1

First ionization potential (I_1) in the photoelectron spectra for bis(triethylsilylalkyl)- and dialkyl sulfides

R	I_1 (eV)	$\nu_{tc}\cdot 10^{-3}$ [a] (cm^{-1})	R	I_1 (eV)	$\nu_{tc}\cdot 10^{-3}$ [a,b] (cm^{-1})
$Si(C_2H_5)_3$	8.49	21.5 ± 0.3	CH_3	8.67	20.4
$CH_2Si(C_2H_5)_3$	7.95	17.3	CH_2CH_3	8.44	19.8
$CH_2CH_2Si(C_2H_5)_3$	8.05	18.3	$CH_2CH_2CH_3$	8.34	19.4
$CH_2CH_2CH_2Si(C_2H_5)_3$	8.10	18.7	$CH_2CH_2CH_3CH_3$	8.22	18.87

[a] Run in CH_2Cl_2. [b] Data of Bock [5].

Experimental

Photoelectron spectra of compounds $[(C_2H_5)_3Si(CH_2)_n]_2S$ ($n = 0$–3) were recorded on an ES-3201 electron spectrometer. The He(I) resonance band (21.21 eV) was used for excitation. The energy scale was calibrated by argon and chlorobenzene first ionization potentials (15.76 and 9.06 eV, respectively). Error in the determination of ionization potentials is ±0.05 eV. CT-complexes were obtained from solutions of organosilicon sulfides $[(C_2H_5)_3Si(CH_2)_n]_2S$ ($n = 0$–3) with TCE in CH_2Cl_2. Measurements were carried out on a Speecord UV–Vis spectrometer in the 3000–13000 cm^{-1} region.

Compounds $[(C_2H_5)_3SiCH_2]_2S$ were prepared by the procedure described in [7]. Compounds $[(C_2H_5)_3Si(CH_2)_2]_2S$ and $[C_2H_5)_3Si(CH_2)_3]_2S$ were prepared by the procedure described in [8].

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References

1 S.D. Barton and W.D. Ollis (Eds.), Sulphur Compounds, Comprehensive Organic Chemistry, Pergamon Press, Oxford, 1979.
2 M.F. Shostakovskii, N.V. Komarov, N.N. Vlasova and G.A. Rinkus, Zh. Obshch. Khim., 36 (1966) 904.
3 H. Bock, G. Wagner and J. Kroner, Chem. Ber., 107 (1974) 68.
4 V.F. Traven, M.I. German, M.Yu. Eismant, Ye.E. Kostyuchenko and B.I. Stepanov, Zh. Obshch. Khim., 527 (1978) 2232.
5 H. Bock, W. Wagner and J. Kroner, Chem. Ber., 105 (1972) 3850.
6 V.F. Traven, R. Uzht, V.F. Donyagina and B.I. Stepanov, Zh. Obshch. Khim., 45 (1974) 824.
7 M.G. Voronkov, F.P. Kletsko, N.N. Vlasova, L.N. Gont and V.I. Kaigorodova, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1849.