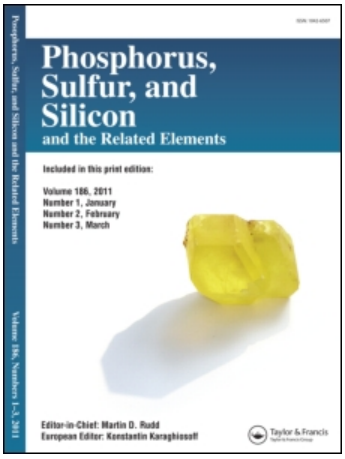

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ELECTRON-DONOR PROPERTIES OF SULFUR COMPOUNDS WITH A FEW DONOR SITES

E. N. Guryanova[a]; L. A. Ganushin[a]; I. P. Romm[a]
[a] Karpov Institute of Physical chemistry, Moscow, USSR

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ELECTRON-DONOR PROPERTIES OF SULFUR COMPOUNDS WITH A FEW DONOR SITES.

E.N.Guryanova, L.A.Ganushin, I.P.Romm

Karpov Institute of Physical chemistry, Moscow, USSR.

The structure and the coordination properties of sulfur compounds such as RS-$(CH_2)_n$-SR,(I), n=1-10 and RS-$(CH_2)_n$COOR' (II), n=1,2 have been investigated by dipole moment, calorimetrie, IR-spectroscopy and cryoscopy methods.

From the point of view of the intermolecular electron-donor-acceptor interaction such compounds have two donor sites: two sulfur atoms in (I) and a sulfur atom and a carbonyl oxygen atom in (II).

This investigation was undertaken firstly to provide information on the electron-donor activity of these centres of bidentate donors as compared to the corresponding monodentate donors, secondly to get a reliable quantitative estimate of how the complexing of one of the centres influenses the properties of the other centres, and, thertly to study the effect of molecular structure on the coordination capabilities of the bidentate donors.

Boron tribromide, aluminium bromide and gallium trichloride were employed as electron acceptors. These compouds form stable and do not practically dissociate in benzene (cyclohexene) solutions complexes with sulfides and esters.

The results of the calorimetric measurments of successive coordination of acceptor molecules with sulfur atoms in (I) and with carbonyl oxygen atom and sulfur atom in (II) have proved the effect of methylene bridge length (n) on the electrondonor properties of the corresponding atoms. From the data obtained it appears that at $n > 3$ the sulfur atoms in (I) are independent. The enthalpies of the addition of the first and the second of acceptor molecules are almost identical and nearly to the heats of complex formation with corresponding monosulfides. When $n \leq 3$ the donor properties of sulfur atoms

are somewhat lower and the complexing of the first atom results in a marked decrease of the donor abilities of the second atom. The smaller (n) the greater the decrease of the donor activity of the second sulfur atom in complex I:I.

Only one of the sulfur atoms of various dialkyl disulfides (n=o) takes part in the formation of the donor-acceptor bond with the above acceptors. The donor activity of the dialkyl-disulfides is significantly lower than that of corresponding monosulfides.

It was discovered that interaction of aryldisulfides with strong acceptors ($AlBr_3$, $GaCl_3$) results in breaking the disulfide bonding and in the formation of complexes with corresponding free RS-radicals. This has been proved by the study of the EPR-spectra.

It has been shown that donor properties of oxygen and sulfur atoms of compounds (II) and their complexes I:I depend not only on the inductive effects of substitutes as it was observed for (I)-compounds, but also on resonance effects. The energy of intramolecular interaction sharply decreased with the increase of the length of a methylen bridge.

The obtained values of the dipole moments make it possible of drow some conclusions pertaining to the structures of (I) and (II) - compounds and their complexes.