I. G. Arzamanova, E. N. Gur’ yanova

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Abstract

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I. G. Arzamanova, E. N. Gur' yanova

HEATS OF FORMATION, DIPOLE MOMENTS, AND ULTRAVIOLET SPECTRA OF MOLECULAR COMPOUNDS OF IODINE WITH ORGANIC SULFIDES

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In accordance with existing concepts, intermolecular bonds in donor–acceptor complexes are formed as a result of charge transfer from the donor molecule to the acceptor molecule. It is believed that in complexes of the $n\sigma$ type the bond is formed with the participation of an unshared pair of valence electrons of a heteroatom (O, S, N, etc.) of one molecule and a vacant orbital of the other. Consequently, the principal factor determining the properties of intermolecular bonds in compounds of the indicated type is charge transfer. To verify the correctness of this concept, it is very important to study the relationships among the various parameters of molecular compounds, and first of all between the dipole moment, the heat of formation, and the energy corresponding to the maximum of the absorption band of the complex. There is a large amount of data in the literature on the UV spectra of donor–acceptor complexes. However, the dipole moments of intermolecular bonds, whose magnitudes are most directly related to charge transfer, have practically not been investigated. In the present work, using as an example the complex-formation reactions of iodine with organic sulfides,

$$\mathrm{J_2 + R_2S \rightleftarrows J_2 \cdot R_2S},$$

an attempt has been made to establish the character of the relationship between the indicated parameters, their values having been determined by independent experimental methods.

Table 1

Heats of formation and dipole moments of iodine complexes with sulfides

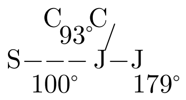
No.	Name of sulfide	$-\Delta H$, kcal/g-mol	μ	$\Delta\mu$
1	Thiophane	10.0	5.49	4.22
2	Dicyclohexyl sulfide	10.5	5.44	4.28
3	Dipropyl sulfide	8.1	4.90	3.65

No.	Name of sulfide	$-\Delta H$, kcal/g-mol	μ	$\Delta\mu$
4	Dibutyl sulfide	8.2	5.14	3.90
5	Dioctyl sulfide	7.4	5.07	3.80
6	Di-sec-heptyl sulfide	8.1	4.90	3.67
7	Di-sec-octyl sulfide	7.4	4.72	3.42
8	Dibenzyl sulfide	4.8	3.78	2.51
9	Diallyl sulfide	4.6	3.64	2.34
10	Diphenyl sulfide	0.3	1.99*	0.43
11	Thiophene	0.4	0.42*	0

* The dipole moments of the sulfides measured in the presence of iodine are given.

The dipole moments of the complexes studied were determined by us earlier (1); the heat effects of the reactions, as well as the ultraviolet spectra of the complexes, were measured in the present work (Table 1).

The heats of formation were determined either by the method of spectrometric titration (2) (Nos. 4-6, 8, Table 1), or by the direct method of calorimetric titration (Nos. 1-3, 7, 9-11, Table 1), developed in our laboratory. The values of $\Delta\mu$ were obtained from the experimental values of μ according to the rule of vector additivity. In the calculation it was taken into account that the molecule of the complex has the following configuration (3):



The dipole moments of the sulfides are $1.5 \div 1.6\,\mathrm{D}$.

The results of investigation of the infrared spectra (4) indicate that the iodine molecule in the complex has a dipole moment, which appears as a result of a disturbance of the symmetry of the electron cloud. We have approximately taken the value of this dipole moment to be $0.5D$. Taking this correction into account leads to a corresponding decrease in the value of the dipole moment of the donor-acceptor bond.

Fig. 1. Dependence of the dipole moment of the intermolecular bond $\Delta\mu$ (effective charge e_{eff}) on the energy parameters ΔH, $\Delta H/h\nu$ of the complexes $R_2S \cdot J_2$, where R_2S is thiophane (1), dicyclohexyl sulfide (2), dipropyl sulfide (3), dibutyl sulfide (4), dioctyl sulfide (5), di-*sec*-heptyl sulfide (6), di-*sec*-octyl sulfide (7), dibenzyl sulfide (8), diallyl sulfide (9), diphenyl sulfide (10), thiophene (11).

Figure 1: Fig. 1. Dependence of the dipole moment of the intermolecular bond $\Delta\mu$ (effective charge e_{eff}) on the energy parameters ΔH, $\Delta H/h\nu$ of the complexes $R_2S{\cdot}J_2$, where R_2S is thiophane (1), dicyclohexyl sulfide (2), dipropyl sulfide (3), dibutyl sulfide (4), dioctyl sulfide (5), di-*sec*-heptyl sulfide (6), di-*sec*-octyl sulfide (7), dibenzyl sulfide (8), diallyl sulfide (9), diphenyl sulfide (10), thiophene (11).

From the data of Table 1 it is seen that the structure of the molecules of organic sulfides has a very substantial influence on the properties of the complexes.

Fig. 1. Dependence of the dipole moment of the intermolecular bond $\Delta\mu$ (effective charge e_{eff}) on the energy parameters ΔH, $\Delta H/h\nu$ of the complexes $R_2S \cdot J_2$, where R_2S is thiophane *(1)*, dicyclohexyl sulfide *(2)*, dipropyl sulfide *(3)*, dibutyl sulfide *(4)*, dioctyl sulfide *(5)*, di-*sec*-heptyl sulfide *(6)*, di-*sec*-octyl sulfide *(7)*, dibenzyl sulfide *(8)*, diallyl sulfide *(9)*, diphenyl sulfide *(10)*, thiophene *(11)*.

Saturated sulfides of normal and iso structure (Nos. 1-7, Table 1) form rather stable complexes with iodine, for which $\Delta H = -8 \div -10$ kcal/g-mol. These complexes are characterized by large dipole moments, $4.6 \div 5.5D$.

Aromatic and unsaturated sulfides (Nos. 10, 11, Table 1) interact with iodine extremely weakly. The thermal effects of the reactions are very low, $0.3 \div 0.4$ kcal/g-mol. The dipole moments of these sulfides, measured in the presence of iodine, are close to the dipole moments in the pure solvent. Thus, the dipole moment of thiophene in the presence of iodine is 0.42 (literature value 0.54), and the dipole moment of diphenyl sulfide in the presence of iodine is 1.99 (literature value 1.56).

Unsaturated sulfides in which the double bond is in the β- or γ-position with respect to the sulfur atom show an ability to form complexes, but the ΔH and μ of the complexes are lower than in the case of saturated compounds (Nos. 8, 9, Table 1). The heats of formation of the complexes of diallyl sulfide and dibenzyl sulfide are -4.6 and -4.8 kcal/gm, respectively, and the dipole moments are 3.6 and $3.8D$.

The difference in the complex-forming ability of unsaturated sulfides from that of saturated ones is apparently explained by the different degree of interaction of the unshared $3p^2$ pair of electrons of the sulfur atom, responsible for complex formation, with the π-electrons of the unsaturated systems.

The data of Table 1 indicate a parallelism in the changes of ΔH and $\Delta \mu$. This is more clearly seen from Fig. 1(I)—a rectilinear dependence is observed between the indicated quantities. In the series of sulfide complexes with iodine investigated, the length of the intermolecular bond apparently changes little in going from one compound to another. Taking this quantity as constant (^{3}), it is possible, in a first approximation, to calculate the effective charges e_{eff}, the values of which characterize the degree of charge transfer from donor to acceptor. The dependence ΔH—e_{eff} is also given in Fig. 1(II).

The direct proportionality we have found between the heats of formation of the complexes and the dipole moments of intermolecular bonds, or effective charges, is consistent with Mulliken' s theory (^{5,6}).

According to Mulliken, the equation of the wave function describing the ground state of a charge-transfer complex is written in the form

$$\psi_N(DA) = a\psi_0(D, A) + b\psi_1(D^+A^-).$$

Katelaar showed (^{7}) that for compounds whose heat of formation is several kcal/g-mol, the relation between the coefficients a and b, which characterize the degree of charge transfer, and the energy parameters of the complexes is expressed, in a first approximation, as follows: $b^2/a^2 \approx \Delta H/h\nu$. Here $h\nu$ is the energy of the spectral transition corresponding to the maximum of the charge-transfer band; b^2/a^2 is a measure of the polarity of intermolecular bonds.

We recorded the ultraviolet spectra of some of the complexes we investigated. The results are given in Table 2, where the values of λ are given in mμ, and the values of $h\nu$ and ΔH in electron volts.

Table 2

Ultraviolet spectra of iodine complexes with sulfides. Concentrations of solutions: I_2, $2 \div 5 \cdot 10^{-4}$ g-mol/l; R_2S, $2 \div 5 \cdot 10^{-2}$ g-mol/l

No.	Name of sulfide	λ	$h\nu$	ΔH
1	Thiophene	285	4.35	0.017
2	Diallyl sulfide	301	4.11	0.199
3	Diethyl sulfide	303	4.08	0.336*
4	Dipropyl sulfide	305	4.06	0.350
5	Dibutyl sulfide	306	4.04	0.354
6	Thiophane	308	4.01	0.432

* The value of ΔH was taken from the literature (^{8}).

It should be noted that the values of λ found by us for iodine complexes with thiophane and diethyl sulfide agree with the data of Ref. (^{8}).

As can be seen (Table 2), the relative changes in $h\nu$ for the complexes studied are small. The maximum difference does not exceed 10%.

The heats of formation of the complexes change incomparably more sharply: thus, on going from the iodine complex with thiophane (−10.0 kcal/g-mol) to the complex with thiophene (−0.4 kcal/g-mol), ΔH changes by more than a factor of 20.

Consequently, $h\nu$ for this series of compounds is practically constant in comparison with ΔH. Therefore the observed rectilinear dependence between $\Delta\mu$ and ΔH is retained, as is seen in Fig. 1 (III), when passing to the quantities $\Delta\mu$–$\Delta H/h\nu$.

The rectilinear dependence established in the present work between $\Delta\mu$ and $\Delta H/h\nu$ is, to a certain extent, a criterion for the correctness of the concepts of Mulliken' s theory of charge-transfer complexes ([5],[6]).

A comparison of the data of Tables 1 and 2 shows that there is a definite relation between the dipole moments and the energy of the spectral transition corresponding to the charge-transfer band. With an increase in the dipole moment of the complex and, correspondingly, with an increase in ΔH, the value of $h\nu$ decreases. A similar inverse dependence between ΔH and $h\nu$ can be found by comparing data for iodine complexes with benzene derivatives ([9]). However, the value of $h\nu$, as is seen from the data of Table 2, is much less sensitive to changes in ΔH than is $\Delta\mu$.

The totality of the results obtained in this work permits the conclusion that the strength of donor-acceptor bonds in complexes of the donor-acceptor type is determined mainly by the degree of charge transfer. The dipole moment is one of the most direct and sufficiently sensitive characteristics of the degree of charge transfer.

Physicochemical Institute
named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.