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Study of Charge Transfer Complexes: The Hexamethylphosphorothioic Triamide–Iodine Complex

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Introduction

Since the pioneering works of Mulliken charge transfer complexes do not cease to stimulate the interest of researchers for their theoretical implications. Also lately[1–2] some pyridine and quinoline derivatives have been investigated and a correlation was found between lgK and the shift of the wavelength of the absorption.

In a previous paper[3] by two of us we have described a spectrophotometric and conductometric study on a charge transfer complex between iodine and hexamethylphosphotriamide (HMPT) which corresponds to the chemical formula $[(CH_3)_2N]_3PO$. Recently[4] the hexamethylphosphorothioic triamide (SHMPT) was identified as a very interesting solvent which acts as a powerful soft cation solvator in terms of Pearson[5] classification. This compound has the same chemical structure as HMPT with the oxygen atom replaced by S. Because of the lower ionization potential of bounded S atom in comparison with oxygen one should expect a greater ability to form complexes with acceptors. We have therefore investigated the complex I_2–SHMPT in order to point out analogies and differences with the oxygen homologous complex.

Experimental

All reagents were pure grade. SHMPT was synthetized from dimethylamine, PCl_3 and S according to Vetter and Noth[6]. Iodine was three times sublimed and its purity checked by titration. Solvent was n-heptane R.S. Carlo Erba (spectrophotometric grade). Spectrophotometric measurements were performed with an Optica CF4 NI spectrophotometer employing cell thickness ranging from 1 to 0.01 cm.

All the solutions were prepared in dry-box and measurements performed in N_2 atmosphere; temperature was maintained constant at ±0.02°C by water circulation.

Results and Discussion

The visible spectrum of iodine in the presence of SHMPT is shown in Figure 1. The well known peak at 520 nm which characterizes the I_2 in noncomplexing solvents is shifted toward the violet at the same wavelength as in the presence of HMPT (445 nm).

Further a strong maximum appears at 310 nm. This maximum is referred to as the well known charge transfer band. Since the free iodine and SHMPT absorption are negligible at the wavelengths of the two maxima, both the maxima can be exploited in order to calculate the equilibrium constant of the complex SHMPT–I_2 according to the relationship[6]

$$F = \frac{lC_{I_2}[\mathrm{SHMPT}]}{A-A_0} = \frac{1}{(\varepsilon_1-\varepsilon_0)K} + \frac{[\mathrm{SHMPT}]}{\varepsilon_1-\varepsilon_0}$$

where C_{I_2} is the total iodine concentration, A the absorbance, $A_0 = \varepsilon_0 l C_{I_2}$, ε_1 and ε_0 the molar absorptions of the complex and of I_2 and [SHMPT] the equilibrium concentration of SHMPT. Since [SHMPT] is in turn a function of K and of the total concentration of I_2 and SHMPT, a non-linear best fitting procedure can be employed in order to determine the parameters K and ε_1. Alternatively [SHMPT] can be firstly assumed as the analytical concentration and the real value can be obtained by iteration. The concentration range studied was 5×10^{-4}–7.5×10^{-1} for SHMPT and 2×10^{-4}–4×10^{-3} for I_2. In Table I the thermodynamic and spectrophotometric quantities of the complex are shown. ΔH values were obtained from the plot of lnK *vs.* 1/T (see Figure 2). As one can see from Figure 1 and Table I the SHMPT–I_2 complex has the same blue shift as the HMPT/I_2 one. This fact is not in agreement with the general trend of a greater shift for the stronger complexes. However, according to Mulliken the blue shift is directly correlated to an exchange repulsion between the σ_u electrons of the donors and the partner molecule. This is not quite so closely correlated with the equilibrium constant or the heat of formation. In particular the greater "softness" of the S lone pairs (and conceivably the availability of *d* orbitals) can reduce the exchange repulsion

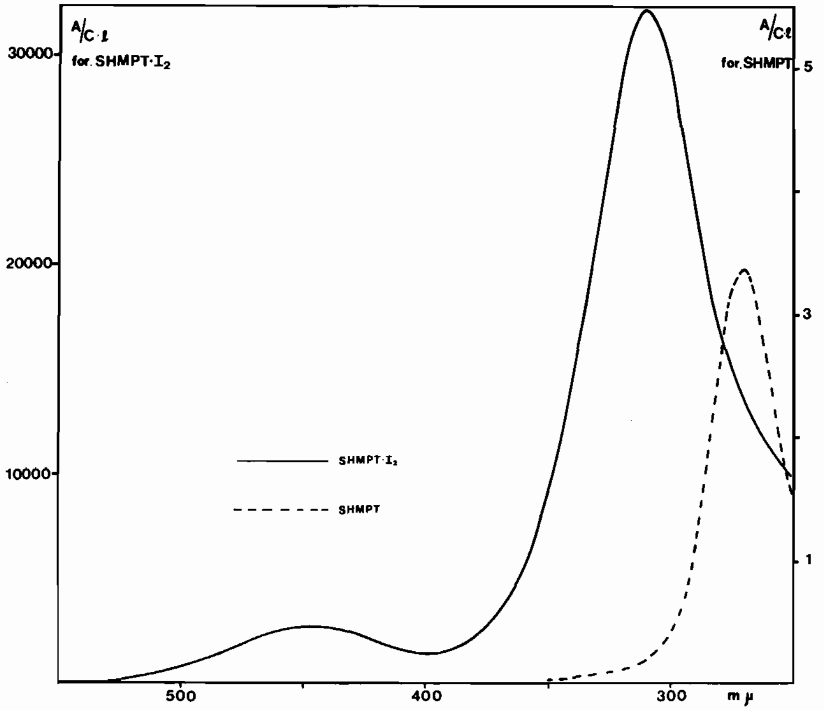

Figure 1. Continuous line: absorption spectrum of I_2 in the presence of SHMPT in n-heptane (ordinate on the left). $C_{I_2} = 3.05 \times 10^{-4} M$; $C_{SHMPT} = 5 \times 10^{-2} M$.

TABLE I. Equilibrium and Spectral Data.[a]

Donor	T °K	K l/mol	ΔH Kcal/mol	Charge Transfer Band λ_{max} nm	ε_{max}	$\Delta\nu_{1/2}$ cm^{-1}	f	μ_D Debyes	Perturbed Iodine Band λ_{max} nm	ε_{max} nm	$\Delta\nu_{1/2}$ cm^{-1}	f	μ_D Debyes
SHMPT	293	1030±10											
	298	829±8			31700	6420	0.879	7.61		2175	4060	0.038	1.90
			−8.1±0.2	310±1					445±1				
	303	652±6											
	313	430±5											
HMPT	298	284±6	−7.3	222	6500	5200	0.146	2.62	445±1	1100	4100	0.019	1.36

[a] Standard errors have been calculated according to W. J. Youden, "Statistical Methods for Chemistry", Wiley, 1951, ch. 5.

between the σ_u electrons of iodine and the electrons of the ligand and this can compensate the closest approach of the partners in the normal state.

In Table I are also summed up the spectral features of the iodine complex with HMPT and SHMPT. Oscillator strength (f) and matrix element of the transition dipole moment μ_D are calculated by the relationships[7]

$$f = 2302.6 \frac{c^2 m_e}{e^2 N_0 \pi} \varepsilon_{max} \Delta\bar{\nu}_{1/2} = 4.319 \times 10^{-9} \varepsilon_{max} \Delta\bar{\nu}_{1/2}$$

$$\mu_D = \sqrt{\frac{2302.6 c 3 h \lambda_{max} \varepsilon_{max} \Delta\bar{\nu}_{1/2}}{N_0 8 \pi^3}} = 0.0958 \sqrt{\varepsilon_{max} \Delta\bar{\nu}_{1/2} \lambda_{max}}$$

where c is the light velocity (cm sec^{-1}), e the charge of the electron (u.e.u.), m_e his mass, N_0 the Avogadro number, h the Plank constant (erg sec), ε_{max} (lmol^{-1} cm^{-1}) the molar absorptivity, $\Delta\bar{\nu}_{1/2}$ (cm^{-1}) the half-width of the band and λ_{max} (cm) the wavelength of the maximum. ε_{max}, f and μ_D values are greater for

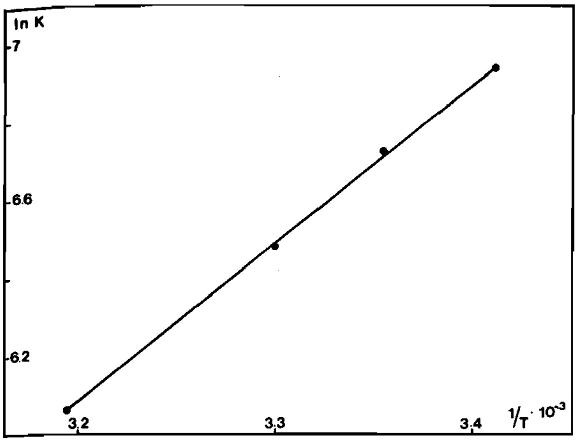

Figure 2. Plot of the lnK values against the reciprocal of temperature.

SHMPT than for HMPT. This fact reflects the greater value of the coefficient b in the ground state $\psi_N = a\psi_0 + b\psi_1$ whose square is a measure of the amount of charge transfer in the ground state ψ_N. ψ_0 and ψ_1 are respectively the wave functions of the no-bond state (A, B) and of the state corresponding to the transfer of one electron from B to A. This is well understandable because of the greater polarizability of S atom.

It is worthy of note that the increase of the equilibrium constant of SHMPT–I_2 complex in comparison with the oxygen analog is much lesser than for other charge transfer complexes of PO and PS grouping[8]. Maybe in our case the lone pairs of N atoms can play some role in increasing the interation in the HMPT–I_2 complex.

The maximum of the charge transfer band is related to the ionization energy of the electrons of the donor by the relationship

$$h\nu = I_D - A + \frac{2\beta^2}{(I_D - A)}$$

Although this equation has a parabolic shape, the curvature is very small and the empirical relationship

$$h\nu = I_D - B$$

where B is a constant characteristic of the acceptor was found to fit very well the experimental points. It is so possible to calculate the difference between the ionization energy of SHMPT and HMPT which amounts to 1.5 ev.

The value of ΔS of the complex is very close to that for HMPT (13.7 e.u.). This fact and the considerations on the symmetry of the isolated molecules, make plausible the hypothesis that the two analogous complexes have the same structure with the iodine molecule partially bound to S or O atom in the plane containing the projection of lone pairs. This model allows to obtain a totally symmetrical singlet state for ψ_1 employing the ground state of ionized donor and acceptor. Moreover this model provides for a good Coulomb attraction energy in $W_1 = \int \psi_1 H \psi_1 d\tau$.

As for a possible ion dissociation in pure donor solutions, conductometric measurements were performed, employing the apparatus described in a previous paper[10]. Specific conductance increases with increasing I_2 concentration. Employing values of λ_0 calculated by the Stokes law it is possible[3] to determine the dissociation degree and therefore the dissociation constant. In the I_2 concentration range 2×10^{-4}–4×10^{-3} a value of the ionization constant of 4×10^{-5} mol/liter was found. This means that in pure SHMPT the complex is fairly dissociated into SHMPT I^+ and I^- ions. The true value of the equilibrium constant can be effectively higher because the presence of a certain amount of I_3^- ions can probably lessen the conductivity value. In effect in concentrated SHMPT solution and in pure SHMPT, a peak at 370 nm masks the peaks at 310 nm and 445 nm. This peak is characteristic of I_3^- in many solvents.

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