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Complexation and Reactions of Molecular Iodine with Dimethyl and Diethyl Sulfoxides

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Abstract—The complexation and reactions of molecular iodine with dimethyl sulfoxide and diethyl sulfoxide in the neat sulfoxides and in their mixtrues with water were studied by conductometry, pH-metry, argentometric titration, UV spectroscopy, and GLC analysis. According to the results obtained, molecular iodine initially forms a charge-transfer complex with the sulfoxide, which subsequently undergoes chemical transformations to hydrogen iodide and the corresponding sulfones. A possible reaction mechanism was suggested.

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Molecular interactions in solutions containing dialkyl sulfoxides and iodine were a subject of numerous studies [1–5]. A significant contribution was made by Klaboe [1] who, in particular, spectroscopically proved the formation of 1 : 1 charge-transfer complexes of dimethyl sulfoxide with iodine. Previously we determined the equilibrium constants and thermodynamic characteristics of these complexes [5]. For high concentrations of the components, formation of iodide and triiodide ions was also considered [1–5]. It should be noted that solutions of iodine in dimethyl sulfoxide are used in medicine [6, 7]. The biological significance of diethyl sulfoxide also increased recently [8, 9]. It can be expected that diethyl sulfoxide solutions can also find biomedical applications.

In this study we examined the physicochemical properties of $Me_2SO–I_2$ and $Et_2SO–I_2$ binary systems and of their aqueous solutions by conductometry, argentometric titration, and UV spectroscopy. A possible mechanism of chemical transformations of the complexes was suggested on the basis of these data.

Figure 1 shows the UV spectra of solutions of I_2 in Me_2SO and Et_2SO. The absorption bands of charge-transfer complexes formed in these systems appear in the range 290–370 nm. It should be noted that the band intensities in the spectra of the $Me_2SO–I_2$ system ($[I_2]$ 1×10^{-4} M) did not change during a period of 1 h, whereas in the $Et_2SO–I_2$ system with the same I_2 concentration they appreciably decreased (Fig. 1). The absorption bands of the molecular complexes $Et_2SO–I_2$ are stronger than those of the $Me_2SO–I_2$ complexes. At the same time, the stability constant of the $Et_2SO–I_2$ complex is higher, as shown in [5].

The UV spectra of the ternary systems Et_2SO (Me_2SO)–H_2O–iodine are characterized by two absorption maxima at about 300 and 365 nm. Figures 2a and 2b show that the absorption intensity in both systems decreases during a period of 1 h, with this trend being more pronounced in the Et_2SO-containing solutions (Fig. 2b).

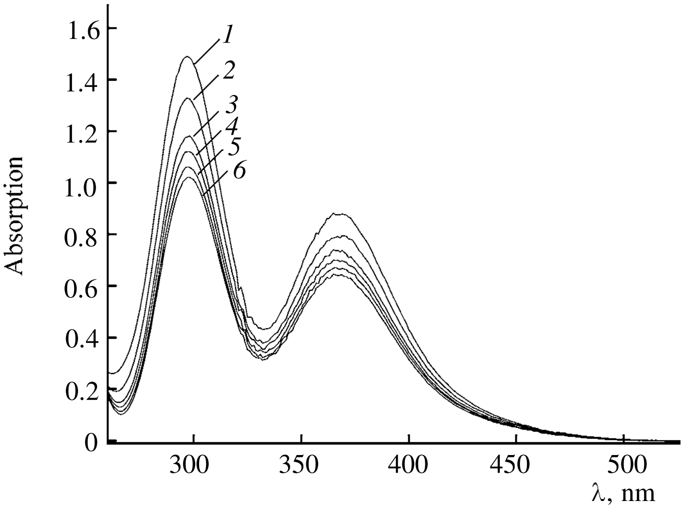

Fig. 1. Evolution with time of the electronic absorption spectrum of the Et_2SO–iodine system. Time, min: (*1*) 5, (*2*) 10, (*3*) 25, (*4*) 35, (*5*) 45, and (*6*) 60 min. $[I_2]$ 1×10^{-4} M; 20°C.

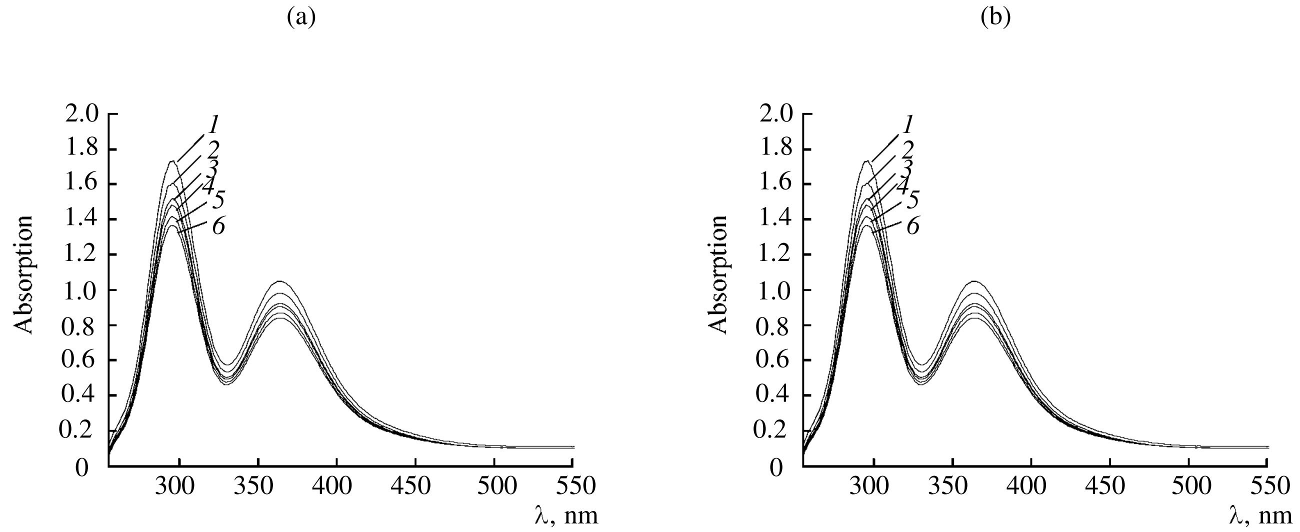

Fig. 2. Evolution with time of the electronic absorption spectra of the systems (a) $Me_2SO–H_2O$–iodine and (b) $Et_2SO–H_2O$–iodine. Time, min: (*1*) 5, (*2*) 10, (*3*) 25, (*4*) 35, (*5*) 45, and (*6*) 60. Composition of the mixed solvent Me_2SO (or Et_2SO) : H_2O = 4 : 1 (volume ratio), $[I_2]$ 1×10^{-4} M, 20°C.

However, in the $Me_2SO–I_2–H_2O$ system, in contrast to the anhydrous system, the gradual decrease in the absorption is also appreciable, and this trend becomes more pronounced with an increase in the water content and temperature. Figure 3 shows the kinetic dependences of the optical density of I_2 solutions in $Me_2SO–H_2O$ at three different temperatures.

The gradual chemical transformations of the molecular complexes sulfoxide–iodine also follow from the conductometric and pH-metric data. The electrical conductivities of the binary systems $Me_2SO–I_2$ and $Et_2SO–I_2$, and also of the corresponding ternary systems with water (at different sulfoxide/water volume ratios) were determined at a constant I_2 concentration of 1.25×10^{-2} M and were compared with the data for the sulfoxide/water binary systems. It should be noted that the conductivity of Et_2SO is considerably higher than that of Me_2SO [10], and the same appeared to be true for the aqueous solutions: The conductivity of the Me_2SO–water system varied in the range from 5 to 6 S m^{-1} depending on the water content, whereas for Et_2SO–water system at the same temperature it was 2–3 times higher. The Et_2SO-based system showed also higher conductivity in the presence of iodine. Whereas in the system $Me_2SO–H_2O–I_2$ the conductivity increased by a factor of less than 10, in the system $Et_2SO–H_2O–I_2$ it increased by a factor of more than 20 (see table). The table also shows that pH of the system tends to decrease in the presence of I_2, which is due to the formation of HI. The formation of the I^- anion was confirmed by argentometric titration. It is interesting that the I^- concentration in the system with Et_2SO is two times higher compared to the system with Me_2SO. Another important feature of the system with Et_2SO is the formation of the triiodide ion: $I^- + I_2 = I_2^-$.

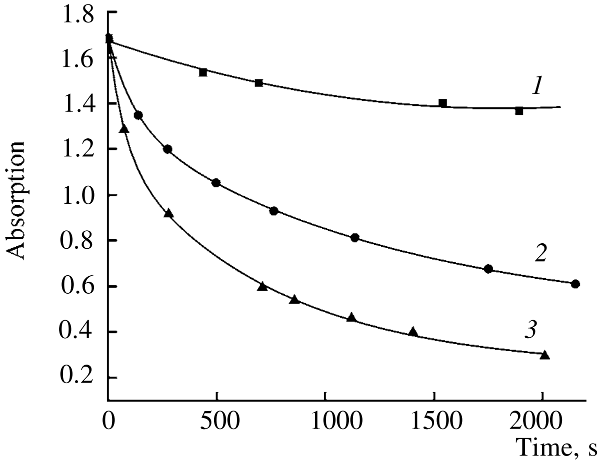

Fig. 3. Kinetic curves of the Me_2SO–water–iodine system at (*1*) 20, (*2*) 40, and (*3*) 60°C. Volume ratio $Me_2SO : H_2O$ = 2 : 1, λ_{max} 295 nm, $[I_2]$ 1×10^{-4} M.

Gas-chromatographic measurements revealed the presence of sulfones (R_2SO_2) in these systems. Based on the data obtained, we suggest the following pathway of chemical transformations of the complexes $R_2SO–I_2$:

$$R_2SO + I_2 + H_2O \longrightarrow R_2SO_2 + 2HI,$$

$$R = CH_3,\ C_2H_5.$$

However, as noted above, an excessive amount of HI is formed in the system with Et_2SO, in contrast to

Conductivity and pH of the systems Me_2SO (Et_2SO)–H_2O and Me_2SO (Et_2SO)–H_2O–I_2 at 20°C[a]

Solvent (volume ratio)	pH	$10^4\chi$, S m^{-1}	Solvent (volume ratio)	pH	$10^4\chi$, S m^{-1}
Me_2SO	10.415	5.93	Me_2SO–I_2	3.664	40.0
$7Me_2SO$–$1H_2O$	7.890	6.25	$7Me_2SO$–$1H_2O$–I_2	3.625	41.5
$5Me_2SO$–$1H_2O$	7.447	6.38	$5Me_2SO$–$1H_2O$–I_2	3.598	47.3
$4Me_2SO$–$1H_2O$	7.605	6.42	$4Me_2SO$–$1H_2O$–I_2	3.574	51.8
Et_2SO	3.632	9.42	Et_2SO–I_2	1.502	207
$7Et_2SO$–$1H_2O$	3.522	10.13	$7Et_2SO$–$1H_2O$–I_2	1.475	220
$5Et_2SO$–$1H_2O$	3.456	11.56	$5Et_2SO$–$1H_2O$–I_2	1.385	265
$4Et_2SO$–$1H_2O$	3.322	12.12	$4Et_2SO$–$1H_2O$–I_2	1.348	281

[a] The conductivities of straight Me_2SO and Et_2SO coincide with those reported in [10].

that with Me_2SO. Therefore, an additional pathway of HI formation is suggested for solutions of iodine in diethyl sulfoxide:

$$(C_2H_5)_2SO + I_2 \longrightarrow CH_2{=}CH{-}S(O){-}CH_2{-}CH_3 + 2HI.$$

A similar reaction (dehydrogenation of the electron donor) was also found in the triethylamine–iodine system; the dehydrogenation products are diethylvinylamine and HI [11].

EXPERIMENTAL

Diethyl sulfoxide was prepared and purified according to [12]. The purity of Et_2SO was 99.8% according to GLC data. Me_2SO was purchased from Sigma. Iodine was purified by sublimation.

Solutions were prepared by adding appropriate amounts of iodine to the sulfoxide or mixed sulfoxide–water solvents.

The UV spectra were measured on a Specord 50 PC spectrophotometer. Cells were 0.1 cm thick. The measurements were performed in the temperature range 20–60°C (±0.3°C) after thermostating for 5 min. A Lauda A100 thermostat supplied with the spectrophotometer was used. The electrical conductivity and pH were measured with a Jenway 4330 pH/conductometer. At least two replicate runs were performed in each case; the standard deviation was 1–2%. Measurements were performed at a constant temperature (20.0±0.3°C) after attainment of the equilibrium.

The products were analyzed on an LKhM-8MD gas–liquid chromatograph using a 1000 × 4-mm column packed with 10% polyethylene glycol + 5% Apiezon on Chromosorb. The column temperature was 145°C, and the temperature of the thermal conductivity detector, 175°C. The carrier gas was He, flow rate 20 ml min^{-1}. Iodide ion was determined by argentometric titration.

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