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UV Spectrum of 1,3-Dithiolan-2-one in Cyclohexane

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The effects of hydrogen bonding, dielectric and pH of the medium have been examined on the two absorption bands at λ_{max} 2450 Å (I) and 2150 Å (II) of 1,3 dithiolan-2-one in cyclohexane. Band-I is assigned to pi* ← n and II to pi* ← pi transitions. The anomalous behaviour of the higher oscillator strength of the (pi*, n) band is explained.

UNSATURATED acyclic and cyclic β-keto sulphides undergo charge transfer excited state interaction and perturbation of the (pi*, n) excited state of the carbonyl group[1,2]. Further $3d$ and $4s$ orbitals of sulphur are known to participate and give complex transitions from both Rydberg and σ*←n excitations[3,4]. The excited state reactivity is dependent upon the transition[5] and since we proposed to investigate the photochemistry of 1,3-dithiolan-2-one (DTL-one), the assignment of electronic transitions and a study of the effect of the medium on these transitions were undertaken. The effects of directly linked sulphur atoms to carbonyl group on the electronic transitions of the latter have also been examined.

DTL-one was prepared by oxidizing ethylene trithiocarbonate with (a) mercuric acetate[6] and (b) copper nitrate[7]. The products from both the oxidations were recrystallized from pet. ether (40-60°) and were found to be identical (m.p., UV and IR). The solvents used were of spectrograde quality and the spectra were taken on UV-VIS Specord and Hilger and Watts spectrophotometers.

Polarity of the solvents is helpful in assigning transitions[8,9] and the absorption spectra of DTL-one in various solvents are given in Fig. 1. Bands-I and II undergo red shift with increase in the polarity of the medium suggesting pi*←pi transitions[10]. However, two pi*←pi transitions are not possible and it is difficult to preclude pi*←n transition of carbonyl group[11].

The spectrum in the acidic medium (H_2SO_4 = $9.0 \times 10^{-3}M$), however, showed no change in the spectral characteristics, suggesting that even if pi*←n
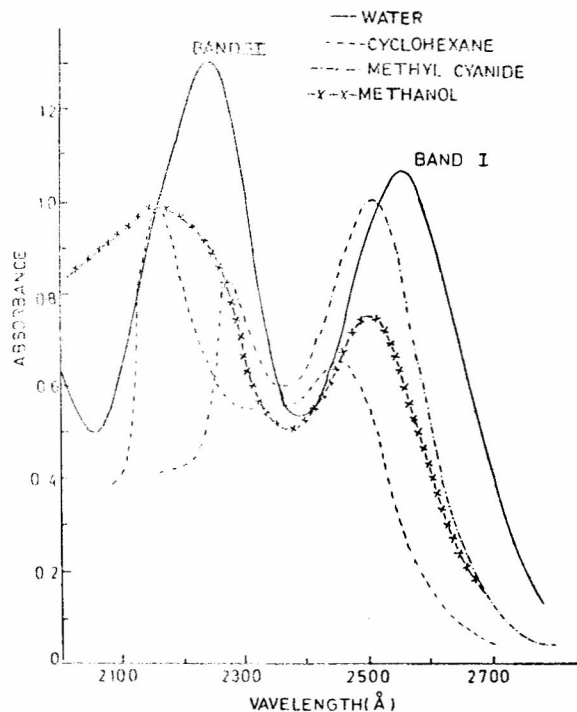
Fig. 1 — Absorption spectra of 1,3-dithiolan-2-one ($3.20 \times 10^{-4}M$) in solvents of different polarities

transition exists, the lone pair on oxygen is not bonding with the protons; otherwise pi*←n transition should have disappeared[12]. This is possible if the electron density on oxygen is appreciably decreased by the two sulphur atoms directly linked to >C=O group. The carbonyl group contains contributions from the resonance structures like

$$\overset{\delta^+ \ \ \delta^-}{>\text{C}-\text{O}} \quad \text{and} \quad \overset{\delta^- \ \ \delta^+}{>\text{C}-\text{O}}$$
$$\text{(a)} \qquad\qquad \text{(b)}$$
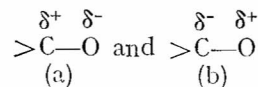
in which the magnitude of charge development and separation depends upon the structure of the molecule[13]. If we consider the carbonyl bonding predominantly via structure (b) in 1,3-dithiolan-2-one, the basic medium should affect the spectral features. This was found to be so in $8.0 \times 10^{-3}M$ aq. KOH wherein band-I was suppressed while band-II remained unchanged. Hence, it is likely that band-I may correspond to pi*←n transition. The spectra were also taken in electron donating solvents like 1,4-dioxane, tetrahydrofuran and ether. In these solvents pi*-orbital is expected to be lowered without affecting the n-orbital much, thereby resulting in decreased energy gap between these states. A red shift of 40 Å was observed in 1,4-dioxane and ether and of 110 Å in tetrahydrofuran (relative to n-hexane). A comparison of the dielectric constants of the media shows that these shifts cannot be assigned to the dielectric effects.

In the polar solvents, there exists the possibility of two distinct effects: (i) bonding with the solvent; and (ii) stability of polar states of the molecule. Hydrogen bonding of the carbonyl compounds in hydroxylic solvents leading to a blue shift is well established[14]. In solvents of higher dielectrics, the dipole-dipole interactions are strong and if the

excited state of a molecule is lowered to a greater extent as compared to the ground state in such solvents, the red shift is understandable. In α-hydroxyketones this kind of red shift has been observed[15]. The spectra in Fig. 1 show that the effect due to stability of polar states dominates in the present system and the red shift increases with the dielectric constant of the medium. A detailed analysis is, however, not possible, since the charge distribution is expected to be affected by even hydrogen bonding and if it leads to increased dipole moment, the expected blue shift due to hydrogen bonding may get cancelled[16]. The contribution of the polar structure is further apparent from the results presented in Table 1. The oscillator strength (f) continuously increases with the dielectric. A linear relationship is observed between the transition energies and the dielectric constant of the medium. With increase in polarity, the separation between the two concerned electronic states decreases. In terms of Franck-Condon principle excitation from a solvated ground state leads not to the energetically most stable solvated conformation of the excited state, but to a conformation geometrically identical to the solvated ground state[17]. Thus in the transition a change in the solvation energy can result leading to decreased separation between the ground and the excited state as observed.

Now band-II can be assigned to pi*←pi transition. It undergoes a red shift with the increase in polarity of the medium; it is of higher energy than pi*←n transition and it is of higher intensity than band-I (as expected[18]) when solute-solvent interactions are minimum.

Another interesting feature is that the (f) value for pi*←n transition is of the order of 10^{-2}, while in normal cases it is of the order of 10^{-3} to 10^{-4}. This could be due to the symmetry of various states being modified by vibrational interactions particularly because of the allowed and forbidden excited states

being close[19]. The pi*←n transition in the present case is only ~15 kcal below pi*←pi transition and the (f) value for band-II is lower than that for band-I in methylcyanide (Table 1). Furthermore, the bands are closer in this solvent which demonstrates the possible contribution of polar states and mixing of states.

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TABLE 1 — ENERGIES AND OSCILLATOR STRENGTH (f) OF ABSORPTION BANDS[a]

Dielectric constant[b]	Band-I		Band-II	
	Energy kcal mole^{-1}	(f)[c] × 10²	Energy kcal mole^{-1}	(f) × 10²
CYCLOHEXANE				
2·02	116·7	2·975	132·9	4·537
METHANOL				
32·63	114·6	4·062	132·6	(d)
METHYL CYANIDE				
36·70	114·0	4·441	125·9	2·511
WATER				
80·00	112·1	6·479	127·6	7·929

(a) Spectra were recorded at 25° ± 2°. (b) Values of the dielectric constants were taken from Handbook of chemistry (Longmans, New York), 1957. (c) Oscillator strengths are calculated from the absorption bands and their widths at half height. (d) Diffused band.

High Temperature Thermal Expansion Studies of Pure UO₂, Gd₂O₃ & of UO₂-1·5 w/o Gd₂O₃ Solid Solution

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Thermal expansions of pure UO₂, Gd₂O₃ (C-type) and UO₂-1·5 w/o Gd₂O₃ solid solution have been measured employing high temperature X-ray diffractometry in the range 298-1700 K in pure helium atmosphere. The results show that the coefficient of linear thermal expansion of pure UO₂ is higher than that of Gd₂O₃ (C-type) or urania-gadolinia solid solution.

URANIUM dioxide (UO₂) has a face-centred cubic structure and is known[1] to form a single phase cubic fluorite type solid solution with Gd₂O₃ up to