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CHARGE TRANSFER COMPLEXES BETWEEN IODINE AND TRANS-DIPYRIDYLETHYLENES

G. Giacometti, U. Mazzucato and S. Parolini
Institute of Physical Chemistry, University of Padova

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In parallel to a kinetic study on the photochemical and catalytic cis-trans isomerization reaction of 1,2-dipyridylethylenes (DPE's) (1), we observed formation of charge transfer (CT) complexes between the ethylenic derivatives and the iodine used sometimes as a catalyst. These molecular complexes are interesting "per se" (2), furthermore they may play a role in the process of catalytic conversion.

We then started a more detailed examination of the behaviour of five available trans DPE's.

The results obtained from the spectrophotometric study of the stability constants of J_2-DPE's in three different solvents are given here together with some observations on the temperature effect.

The DPE's were obtained from Raschig GmbH and conveniently purified by crystallization from cyclohexane or methanol before use.

The visible absorption spectra of the complexes (perturbed iodine bands) exhibit their maxima in the range 385-405 mμ. The figure shows an example of the complexation equilibria with the isosbestic point between the two bands of free and complexed iodine.

The stoichiometry of the complexes formed in solution was determined by the Job method (3), using the 400 mμ band due to the complexed iodine, and found to be 1:1 within the error limits

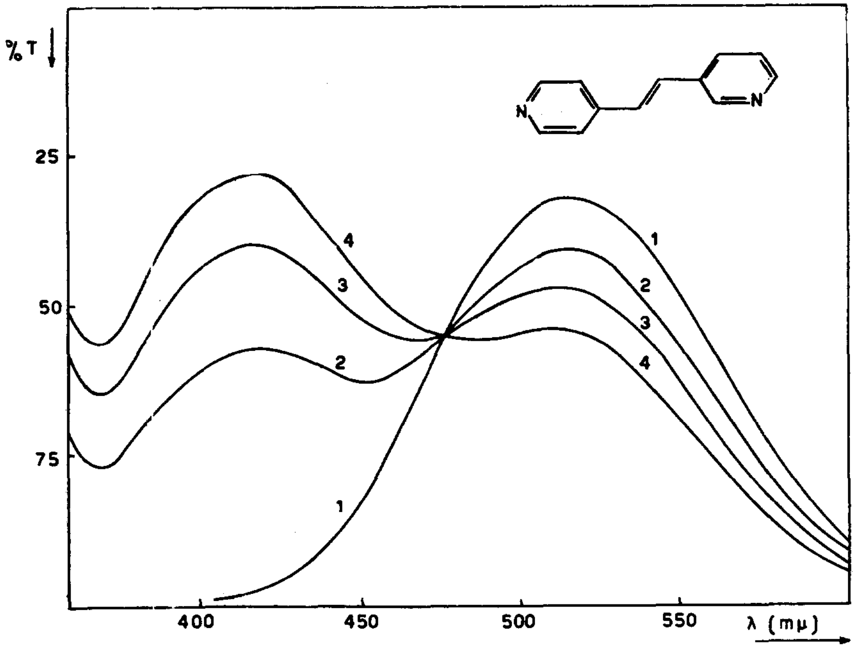

FIG. 1 - Spectra showing the formation equilibria of the complex between iodine and trans 1-(3-pyridyl),2-(4-pyridyl)-ethylene (3,4'-DPE) in dichloromethane. Spectrum 1 refers to the absorption of free iodine; spectra 2,3,4,5 show the band due to the complexed iodine at increasing DPE concentration.

(longer cells and dilute solutions have been used for the less soluble 4,4' complex). Crystalline solids isolated by precipitation from benzenic solutions did not conform to this result. In fact the elementar analysis indicate a DPE $-(J_2)_2$ composition for the 4,4' isomer, while the results for 2,2' and others isomers are less reproducible and give a variable iodine content. This is probably understood assuming that the solid and soluted complex have different stoichiometry or that even in solution two or more types of complexes are formed. Moreover it should be noted that it is difficult to obtain a pure solid complex, which also has a noticeable tendency to decompose evolving iodine.

In any case the formation constants given in the table refer to 1:1 complexes, as found essentially present in solution. They were determined spectrophotometrically at 25°C by Unicam SP. 500 single beam and Optica CF 4 double beam instruments, equipped with thermostatic arrangements; the measurements have been made at a fixed acceptor concentration and different amounts of DPE on the 520 mμ free iodine band and in some cases on the 400 mμ complexed iodine band, using the Benesi-Hildebrand plot (4). In a few experiments also a variable iodine concentration has been used.

The K_{CT} in the table are mean values of 6-10 experimental data obtained in almost two experiments at different wavelengths and concentrations. The reproducibility resulted not so good, mainly in the case of the higher stability constants, where a slight dependence on concentration has been noted; and this is probably due to the reason noted above.

TABLE

Stability Constants K_{CT} (mole^{-1} litre) for the Equilibria of Charge Transfer Complexes between Iodine and Dipyridylethylenes.

Solvent / Compound	Benzene	Chloroform	Dichloromethane
2,2'	32	18	22
2,3'	81.5	66	105
2,4'	120	122	165
3,4'	124	123	234

We tried to carry out investigations in n-hexane, which is an inert solvent suitable for the study of these complexes, but we succeeded only with the 2,3' compound (Job experiment, 1:1 ; $K_{CT} = 192 \pm 9$ at 25°C), as in the other cases the complex solubility is too small.

The five isomers have then been studied in benzene, chloroform and dichloromethane; the latter resulted the more convenient both from the point of view of the absence of interaction with iodine and the reproducibility.

The measurements in benzene, made at equal iodine concentration for all the isomers, allow to state a relative scale of equilibrium constants, even if the values include the equilibrium between iodine and the solvent.

The following order results in the three solvents for the formation constants:

$$K_{CT}(2,2') < K_{CT}(2,3') < K_{CT}(2,4') \leq K_{CT}(3,4')$$

The only value for 4,4' isomer, in dichloromethane, resulted 209 M^{-1}.

It is evident that steric hindrance is much important in the complex formation; that is, the mesomeric situation, which is important f.i., in the protonation processes of pyridine-derivatives (5), is in the present case much less influencing the equilibrium than the proximity of the vinylpyridyl group to the second nitrogen atom.

The steric requirements are stronger in the 2,2' complex with a similar behaviour to that found for 2-styrylpyridine and 2-methylpyridine (6). In this respect it should be much interesting to examine the corresponding cis isomer whose preparation for the photochemical research is in progress but has met several difficulties so far. The corresponding 2,2'-pyridyl examined for comparison purposes do not show CT bands at the same conditions: the complexation equilibrium, if any, is in this case shifted towards the reagents.

If it were possible to avoid precipitation and to study these equilibria at higher acceptor concentration, one could expect to find the formation of 1:2 complexes, as for the solid 4,4' compound, also in the solutions of the other isomers.

If the present results are compared with those of pyridine in chloroform (K_{CT} = 44 at about 28°C) (7), one notes a general increase in complex formation (with the only exception of the crowded 2,2' complex), as can be expected also from the increased availability of reaction centers for the iodine molecule.

The temperature effect on the equilibrium has been investigated in some favorable cases and resulted negative, the ΔH of formation being of the order of -7 Kcal (it seems to increase in the order $2,3' < 2,4' < 3,4'$ indicating a noticeable entropic effect on the equilibrium). The rather large values for the formation enthalpy are in favour of the n-σ character of these complexes.

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