

Charge-Transfer Complexes Between *p*-Toluidine and Iodine in Solution: A Spectrophotometric and Voltammetric Study

Giancarlo Beggiato^{a,*}, Giuseppe Casalbore^a,
Giancarlo Marconi^a, and Marina Mastragostino^b

^a Istituto di Fotochimica e Radiazioni d'Alta Energia, Consiglio Nazionale delle Ricerche (C.N.R.), I-40126 Bologna, Italy

^b Istituto Chimico "G. Ciamician", Università degli Studi di Bologna, I-40126 Bologna, Italy

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The charge-transfer interaction between an aromatic amine (*p*-toluidine) and a halogen (iodine) is investigated in different solvents. The effects of the solvent dielectric constant, of the ionic strength and of the light absorbed on the transformation of the intermediate "outer" complex into a polar "inner" structure are studied. An overall reaction mechanism is suggested.

(*Keywords:* Charge-transfer complexes; Photoconversion "outer" complex → "inner" complex)

Spektralphotometrische und elektrochemische Untersuchung über Charge-Transfer-Komplexe zwischen p-Toluidin und Jod in verschiedenen Lösungsmitteln

Es wird die Charge-Transfer-Wechselwirkung zwischen einem aromatischen Amin (*p*-Toluidin) und einem Halogen (Jod) in verschiedenen Lösungsmitteln untersucht. Es wird der Einfluß der Dielektrizitätskonstante, der Ionenstärke und der Wellenlänge des absorbierten Lichtes auf die Umwandlung eines Zwischenkomplexes (als "outer"-Komplex bezeichnet) zu einer polaren "inner"-Komplexstruktur studiert. Es wird eine Hypothese über den gesamten Reaktionsmechanismus erstellt.

Introduction

Since many years the structure and the properties of charge-transfer complexes (CTC) are being investigated by a large number of scientists with the aim of understanding their role in the mechanisms of chemical

processes. After the pioneering researches of *Mulliken*¹⁻³ and *Benesi* and *Hildebrand*^{4,5}, much work has been done in this field, largely referenced in books and reviews⁶⁻¹¹.

The formation of "inner" ion-pair complexes from non-ionic "outer" complexes was deeply studied since the early 50's by *Mulliken*¹²⁻¹⁴. The environmental action on the kinetics of this process was also investigated and the stabilizing effect of polar solvents on ionic "inner" complexes observed¹²⁻¹⁴.

In the present work the conversion from "outer" to "inner" complex is examined for the system: *p*-toluidine (as a donor) + iodine (as an acceptor), in solvents of different polarity grade.

In this case, another important factor responsible for this transformation is the light, which can induce a photochemical process parallel and sometimes prevailing on the thermal one.

Since the transformation of the "outer" into the "inner" complex results in the production of ionic species from covalent molecules, we made use of voltammetric techniques, because they appeared particularly suitable to characterize the species involved in the reaction.

Experimental

Materials

p-Toluidine (Carlo Erba, RPE grade) was purified by sublimation under reduced pressure at 40 °C. Iodine (resublimed, Carlo Erba, RP-ACS grade) was used without further purification. Tetrabutylammonium perchlorate (*TBAP*), a Fluka "purum" grade product, was crystallized from methanol, to be used as a support electrolyte for voltammetric experiments. Methylene chloride (E. Merck, "pro analysi" grade) was shaken with a slightly basic NaOH aqueous solution in a separatory funnel; the organic layer was removed, washed several times with distilled water and stored overnight on fresh calcium chloride; then it was refluxed over phosphorus pentoxide, distilled from the pentoxide in a nitrogen atmosphere and stored in a brown glass bottle just before the use. Other solvents, as *n*-Hexane and *n*-Heptane (Carlo Erba, RS grade), were used as supplied by the manufacturer, without any distillation.

Apparatus and Methods

Spectral changes were followed with double-beam spectrophotometers Perkin-Elmer model 555 and model 124 and Varian Cary model 219.

For kinetics at fixed wavelength a single-beam spectrophotometer Perkin-Elmer model 139 was used, the cell holder being thermostated at 20 ± 0.1 °C. The irradiations were performed with an Osram Xenon XBO 900 W lamp, whose light was filtered by an R-UV 337-14 Balzers interference filter.

For voltammetric measurements an AMEL Electrochemolab instrument was used, with a platinum working microelectrode and a reference saturated

calomel electrode (SCE). These experiments were carried out in a thermostated quartz cell, from which time by time small portions of the solution were taken for spectrophotometric analysis.

Results and Discussion

When iodine and *p*-toluidine are dissolved in methylene chloride, a new absorption band with maximum wavelength at 340 nm is observed. An absorption increase is observed also at 293 nm, where, unfortunately, also the free *p*-toluidine absorbs. If the sample is not kept in the

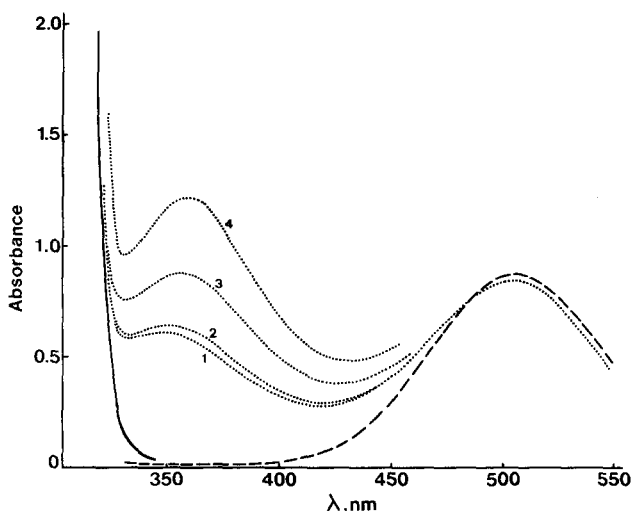


Fig. 1. Spectra of the system iodine/*p*-toluidine in methylene chloride at different times after mixing ($T = 20^\circ\text{C}$). Solid line (—): [*p*-toluidine] = $5 \cdot 10^{-3} M$; dashed line (---): [iodine] = $5 \cdot 10^{-4} M$; dotted line (...): spectra of iodine ($[\text{I}_2]_0 = 5 \cdot 10^{-4} M$) + *p*-toluidine ($[\text{p-toluidine}]_0 = 5 \cdot 10^{-3} M$), recorded: 1 10 min, 2 100 min, 3 6 h, 4 24 h after mixing

dark, the 340 nm band evolves towards 360 nm and its intensity increases (Fig. 1). In the dark, these modifications, however not negligible, are much slower.

From theoretical considerations¹⁵, the 340 nm band was assigned to a Mulliken's "outer" charge-transfer complex between amine and iodine. The light induced red shift towards 360 nm could be interpreted as a result of the conversion from "outer" to "inner" polar complex.

Indeed, in other similar systems¹⁶⁻¹⁹ the appearance of absorption peaks at 363 nm and 293 nm was attributed to the formation of a charge-transfer complex between amine and halogen having an ionized

structure like $RNH_2I^+ \cdots I_3^-$, taking into account that the spectrum of I_3^- in ethylene dichloride shows two absorption maxima at 362 nm ($\epsilon = 25\,000 \text{ mol}^{-1} \text{ cm}^{-1}$) and 292 nm ($\epsilon = 45\,800 \text{ mol}^{-1} \text{ cm}^{-1}$)¹⁷. This complex should originate from an early intermediate "outer" complex $RNH_2 \cdots I_2$, which should be responsible for the absorption at 340 nm, as suggested before.

When a non-polar solvent, like *n*-hexane or *n*-heptane, is used, the

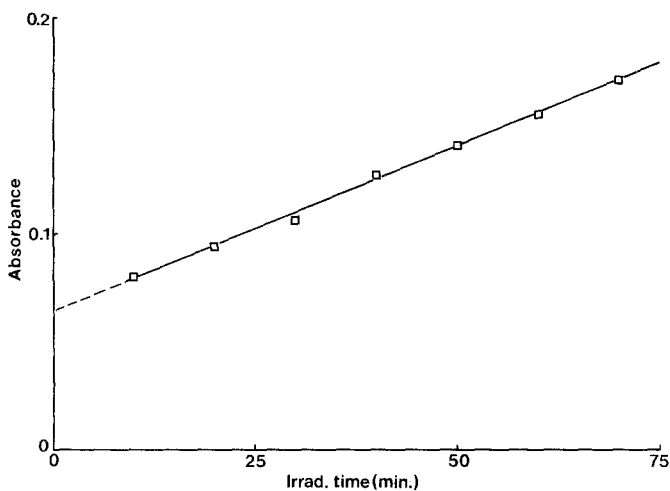


Fig. 2. Plot of absorbance at 363 nm versus irradiation time for the system iodine/*p*-toluidine in methylene chloride. Concentrations: $[I_2]_0 = 1 \cdot 10^{-3} M$; $[p\text{-toluidine}]_0 = 1 \cdot 10^{-3} M$. Irradiation source: Osram Xenon XBO 900 W lamp, filtered by a Balzers R-UV 337-14 interference filter

340 nm band is quite stable in the dark and the spectral changes induced by the light, as described above, are in this case very slow.

When the system iodine/*p*-toluidine in methylene chloride is irradiated with light of 335-340 nm, the optical density at 363 nm rises up linearly with the irradiation time, with a behaviour equal to that already qualitatively observed in the experiments carried out in the sunlight, following a zero-order kinetics (Fig. 2).

Besides the intrinsic polarity of the solvent, as it was remarked above, also the ionic strength of the medium strongly influences the build up of the "inner" ionic complex. This fact was clearly observed when, for electrochemical purposes, a highly polar electrolyte, like *TBAP*, was added to the system. In these experiments an absorption

band with λ_{\max} at 363 nm was observed from the beginning; an individual band at 340 nm was practically undetectable.

On the contrary, when non-polar solvents, like *n*-hexane, were used, the "outer" complex $RNH_2 \cdots I_2$ was stabilized and its thermodynamic stability constant could be calculated. The stoichiometric composition of the "outer" complex (amine:iodine = 1:1) was also determined in *n*-hexane from spectrophotometric measurements at 340 nm, utilizing the *Job* continuous variations method²⁰.

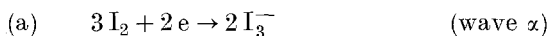
The extinction coefficient at 340 nm and the formation constant were established by a graphical method, utilizing the *Benesi-Hildebrand*⁵ and *Rose-Drago*^{21, 22} equations. The following values were found:

$$K_{eq}^{20^\circ C} = 4 \pm 1 \text{ l mol}^{-1}; \epsilon_{340} = 20\,000 \pm 1\,000 \text{ mol}^{-1} \text{ cm}^{-1}$$

The interpretation of the spectral changes induced by solvent polarity, by ionic strength and by light of 340 nm as a conversion from an "outer" complex to a polar structure containing the I_3^- ion was strongly supported by parallel spectrophotometric-electrochemical measurements.

The zero-time voltammetric pattern of the system iodine/*p*-toluidine in methylene chloride shows three waves:

Two diffusion controlled reduction waves, associated with the processes:

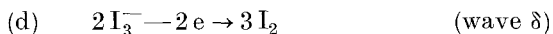


and



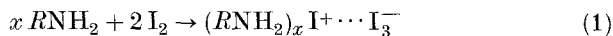
the oxidation wave of the amine (wave γ), whose height was found proportional to the concentration, at least in the experimental concentration range.

This pattern evolves in the time, showing a decrease of the iodine reduction wave (α) and of the amine oxidation wave (γ), while a new anodic wave (δ) appears and increases (Fig. 3 a-c). This last wave was attributed to the process (d) of oxidation of I_3^- to I_2 ²³:



and its evolution is accompanied by an increase of absorption at 293 nm and at 363 nm. Table 1 is exemplifying on this respect.

From the decrease of the iodine wave and the parallel increase of the optical density at 363 nm, the extinction coefficient at this wavelength in methylene chloride was calculated for the following overall stoichiometry:



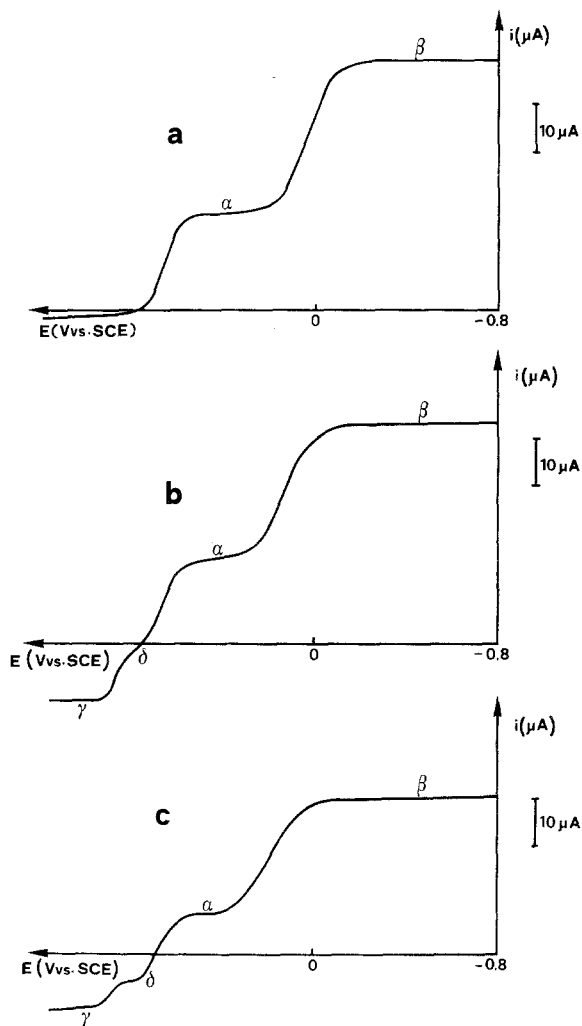


Fig. 3. *a* Voltammetric pattern of iodine ($[I_2] = 1.58 \cdot 10^{-3} M$) in methylene chloride with $0.1 M$ *TBAP*. *b* Voltammetric pattern of the system iodine/*p*-toluidine in methylene chloride ($[I_2]_0 = 1.58 \cdot 10^{-3} M$; $[p\text{-toluidine}]_0 = 1.31 \cdot 10^{-3} M$) with $0.1 M$ *TBAP*, 6 min after mixing. *c* Voltammetric pattern of the same system as in Fig. 3 *b*, 6.5 h after mixing

The value obtained ($\epsilon_{363} = 30\,000 \pm 3\,000 \text{ mol}^{-1} \text{ cm}^{-1}$) is close to those quoted in literature for I_3^- in chlorinated solvents^{17,19}. The stoichiometry (1) is consistent with the height of the waves δ and β measured at the end of the experiments, the diffusion coefficients being assumed $8.1 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for I_2 and $5.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for I_3^- ²³.

ments²³, the zero order of the overall process “outer” complex \rightarrow “inner” complex is in accord with the scheme above if we assume that the additional step (d), required by the experimental stoichiometry of the “inner” complex, does not influence the final spectrophotometric and voltammetric pattern. In fact, the voltammetric and spectrophotometric changes observed can be motivately attributed to a quasi-free ion I_3^- and, therefore, should not practically depend on the cation (AmI^+ or Am_2I^+).

Theoretical Considerations

The results reported and discussed in the previous section can be rationalized in terms of structural changes of the species involved in the process under examination.

The first step of the process can be individuated in the formation of a charge-transfer complex between *p*-toluidine and iodine, with a partial electron delocalization from the highest π molecular orbital of the amine to the lowest unoccupied σ_u^* molecular orbital of iodine.

Calculations made in our institute¹⁵ indicate that the most favorable geometrical situation is that of a molecule of iodine in axial position with respect to the molecular plane of the amine, at a distance of 3.0:3.4 Å from the $-NH_2$ group. At the equilibrium distances, the electronic wave functions for the complex in the ground and excited state can be written respectively as:

$$\Psi_n = a\Psi_0(Am, I_2) + b\Psi_1(Am^+, I_2^-) + \sum_i c_i \Psi_i(Am^{+*}, I_2^-) + \dots \quad (3)$$

$$\Psi_v = a^*\Psi_1(Am^+, I_2^-) + b^*\Psi_0(Am, I_2) + \sum_j d_j \Psi_j(Am^*, I_2) + \dots \quad (4)$$

where the last terms refer to minor contributions of excited configurations of the fragments. The transformation of the “outer” ($a > b$) to the “inner” complex ($b > a$) requires the rearrangement of electrons to give a polarized bond of the type $ArNH_2 \cdots I^+ \cdots I^-$, which eventually is stabilized by the addition of another molecule of I_2 to give the more stable I_3^- ion. Indeed, the formation of tetra-coordinated ammonium ion, which is usually observed as a product of the evolution of strong $n\pi^*$ donor-acceptor systems with iodine¹⁸, in this case seems to require strong cooperation of polar solvent and highly dielectric medium. The whole process can be visualized as in Fig. 4, where a possible situation of potential curves is drawn. From this figure it appears that the overcome of the barrier U , necessary to reach the ionic species of the “inner” complex, can occur both in the ground state (W_n) with the aid of the polarity of the solvent and in the excited state, taking advantage

of the photochemical process along the upper surface (W_v) and eventual passage of the molecule to the ground state in correspondence of the maximum of the barrier. The height of the barrier is related to the ionization of the "outer" complex (prevalently covalent) and can be expressed by the formula:

$$U = e(I_p - E_a) - C - E_{st} - E_{solv} \quad (5)$$

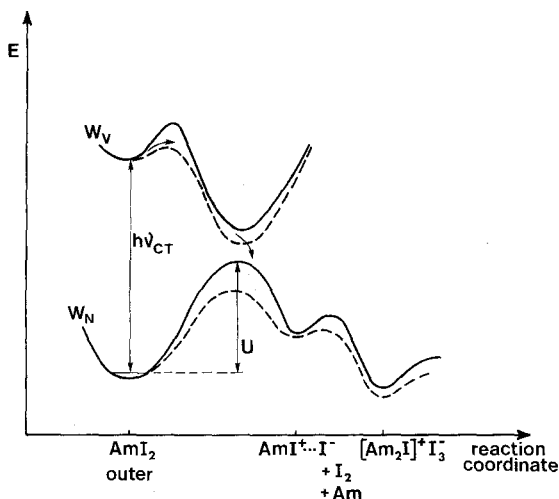


Fig. 4. Possible energy surfaces for the transformation "outer" complex \rightarrow "inner" complex proposed in the reaction scheme (2); dashed line (—) refers to the stabilizing effect of polar solvent

where I_p is the ionization potential of the donor, E_a is the electron affinity of the acceptor and the third term $C = \sum_{ij} \frac{e_i \cdot e_j}{r_{ij}}$, represents the

Coulombic interaction of two fragments with partial charge e_i and e_j at a distance r_{ij} . Here E_{st} represents a stabilization energy due to intramolecular factors like resonance structures for aromatic compounds. Assuming $E_a = 1.7 \text{ eV}$ ²⁴ and calculated values of $I_p = 7.7 \text{ eV}$ and $C = 2.7 \text{ eV}$ (point charge approximation)¹⁵, a barrier of 3.3 eV (76 kcal/mol) would result for a complete separation of charges ($e = 1$). This barrier can be lowered by the delocalization of the positive charge on the *p*-toluidinium ion (E_{st}) and especially by the action of a polar solvent on the partially charged species. Studies on the halogenation of cyclohexene in polar solvents have shown that the effect of highly

dielectric solvents in separating the charges is to lower the barrier from 70 to 30 kcal/mol²⁵.

The intermediate AmI^+I^- , which is probably unstable³, can reach a more favourable energetic situation by the addition of another molecule of iodine to form the well-known stable species I_3^- . A further stabilization of the "inner" product can occur through the cooperative action of two amine molecules on the positive ion I^+ , with a possible delocalization of the positive charge, as suggested by the stoichiometry resulting from the voltammetric measurements.

A more detailed study on the quantum-mechanical description of the "inner" complex as well as of the intermediates of the reaction will be the object of a subsequent paper¹⁵.

Conclusions

The interaction between *p*-toluidine and iodine brings about a charge-transfer complex, whose structure is strongly influenced by the solvent polarity. Moreover, it is to be pointed out that the conversion from "outer" to "inner" complex is made easier not only by running the experiments in more polar solvents, but also by irradiating with light absorbed only by the "outer" complex (340 nm). The importance of the photochemical factor is underlined by the findings that, when 340 nm light is used, the kinetics of the process ("outer" complex \rightarrow "inner" complex) follow a zero order relationship.

This fact, together with the value of the stoichiometric ratio between amine and iodine in the two complexes, can greatly help with the study of the "outer" \rightarrow "inner" reaction coordinate and of the excited states of charge-transfer complexes.

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