Charge-Transfer Complexes Between p-Toluidine and Iodine in Solution: A Kinetic Study

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The kinetics of charge-transfer interaction between p-toluidine and iodine in methylene chloride was investigated in depth. The *thermal* process of formation of the *"inner"* complex was found to proceed to an equilibrium. The *photochemical* process follows a different reaction coordinate, going through the formation of an exciplex between the excited *"outer"* complex and the amine ground state. In both cases the same ionic complex ($Am_2I^+ I_3^-$, where Am stands for p-toluidine) was detected as the final product.

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

Kinetische Untersuchung der Charge-Transfer-Komplexe zwischen p-Toluidin und Jod

Die Kinetik der Charge-Transfer-Wechselwirkung zwischen p-Toluidin und Jod in Methylenchlorid wurde ausführlich untersucht. Der *thermische* Prozeß, der zur Bildung des „inner"-Komplexes führt, geht bis zu einem Gleichgewicht. Der *photochemische* Prozeß folgt einer unterschiedlichen Reaktionskoordinate und verläuft über die Bildung eines Exziplexes zwischen dem angeregten „outer"-Komplex und dem Amin im Grundzustand. In beiden Fällen wurde derselbe ionische Komplex ($Am_2I^+ I_3^-$, wobei Am für p-Toluidin steht) als Endprodukt festgestellt.

Introduction

In a previous work[1] the interaction between iodine and p-toluidine was studied in solvents of different dielectric constants.

The practically immediate build up of an *"outer"* charge-transfer complex between halogen and amine, with $\lambda_{max} = 340$ nm, was observed. This absorption band, quite stable in non-polar solvents in the dark, shifted towards longer wavelengths and increased in polar solvents and in high ionic strength media. This process was highly accelerated by irradiating the system with light of 340 nm.

From these findings, there was assumed a reaction mechanism involving the *"outer"* complex → *"inner"* complex conversion.

The aim of the present work was to define step by step this mechanism, both for the "dark" and the photochemical process, and to confirm the stoichiometry of the involved complexes under different experimental conditions.

Experimental

p-Toluidine *(Am)* was a Carlo Erba RPE grade product, purified by sublimation under reduced pressure at 40 °C. Iodine (resublimed, Carlo Erba RP-ACS grade product) was used as supplied by the manufacturer without any further treatment. Methylene chloride (E. Merck, "pro analysi" grade), purified by distillation over phosphorus pentoxide, was stored under nitrogen atmosphere in a brown glass bottle, carefully shielded from the light. In the same way, also the test solutions were protected from light and oxygen. The ferrioxalate actinometer used for the calibration of the irradiation source was prepared according to the method suggested by *Parker* and *Hatchard*[2]. Potassium oxalate, ferric chloride, 1,10-phenanthroline monohydrate, and sodium acetate for buffer solution were all E. Merck "pro analysi" products; sulphuric acid was a Carlo Erba Normex product.

Spectrophotometric measurements were carried out with a Perkin Elmer model 555 double beam instrument.

Analyses of the end products were done with a Carlo Erba model Fractovap gas chromatograph equipped with a flame ionization detector and a Dani 1 m Carbowax 20 M column (inner diameter = 2 mm, working temperature = 165 °C); carrier gas was nitrogen at $p = 1.6$ kg cm^{-2}.

The irradiation source was an Osram Xenon XBO 150 W lamp, whose light was filtered by an R-UV 337-14 Balzers interference filter; the incident radiation intensity at 337 nm was of $4.38 \cdot 10^{-7}$ einstein l^{-1} s^{-1}.

Results and Discussion

The spectrum of the system Iodine/*p*-Toluidine in methylene chloride points undoubtedly to the formation of an *"outer"* charge-transfer complex whose thermodynamic and kinetic parameters were already described[1]. This process, the evidence for which comes from the growth of a new absorption band with $\lambda_{max} = 340$ nm, is relatively rapid, especially if compared with the subsequent *"outer"* complex → *"inner"* complex conversion. In effect, working in complete darkness, a "plateau" value for the absorbance at 340 nm was attained a few seconds after the mixing of

the iodine and p-toluidine solutions (this time was about 50 s, with $[I_2]$ $= 5 \cdot 10^{-4} M$ and $[p$-toluidine$] = 6 \cdot 10^{-3}$ M, at room temperature); afterwards a very slow process, many days long, leading to the formation of a new band centered at 360–363 nm, was observed.

The thermodynamic formation constant (K_1) and the extinction coefficient (ε) for the *"outer"* charge-transfer complex were measured in methylene chloride, keeping the sample in the dark, by using the *Benesi-Hildebrand*[3,4] and *Rose-Drago*[5,6] plots. The values obtained in this solvent $(K_1^{20} = 5 \pm 2 \, \mathrm{mol}^{-1} \mathrm{l}; \varepsilon_{340} = 20\,000 \pm 1\,000 \, \mathrm{mol}^{-1} \mathrm{l} \, \mathrm{cm}^{-1})$ are very similar to those measured in n-hexane[1], where the *"outer"* complex is more stable.
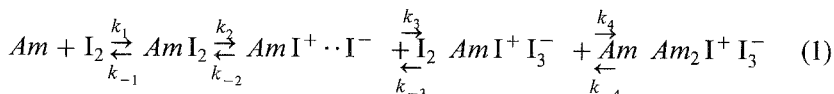
As already shown[1], the slow *"outer"* complex $\rightarrow$ *"inner"* complex conversion was found to be strongly accelerated by 340 nm light.

In the present study, the "dark" and the "photochemical" kinetics were investigated thoroughly and the results are shown and discussed in the sections below.

The "Dark" Process

The thermal process of formation of the *"inner"* charge-transfer complex was followed spectrophotometrically on the basis of the growth of the absorption at 360 – 363 nm. The experimental optical density values at these wavelengths were corrected for the contribution of the 340 nm band tail, due to the residual *"outer"* complex absorption. The plot of A_{360} vs. time, for a solution kept in the dark under pure nitrogen atmosphere at room temperature for about two months ($[I_2] = 2 \cdot 10^{-4} M$; $[p$-toluidine$]$ $= 5 \cdot 10^{-3} M$), shows an asymptotic trend towards a "plateau" absorbance value, which suggests the attainment of an equilibrium concentration of the *"inner"* complex. This assumption is also supported by the fact that even in the proximity of the "plateau" for the 360 nm band a not negligible absorption at 506 nm due to free iodine was detected.

In order to evaluate the kinetic parameters for the various steps of the overall mechanism derived from that previously suggested for the photoinduced process[1]:

$$Am + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Am\,I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Am\,I^+ \cdots I^- \underset{k_{-3}}{\overset{k_3}{\underset{+I_2}{\rightleftarrows}}} Am\,I^+\,I_3^- \underset{k_{-4}}{\overset{k_4}{\underset{+Am}{\rightleftarrows}}} Am_2 I^+\,I_3^- \quad (1)$$

Some simplifying conditions were necessarily assumed:

a) The *"outer"* complex equilibrium $(K_1 = k_1/k_{-1})$ is extremely rapid in comparison with the subsequent *"inner"* complex equilibrium $(K_2 = k_2/k_{-2})$; consequently, the *"outer"* complex can be considered always in equilibrium with the donor and the acceptor. This assumption seems to be largely acceptable if the different times to reach the first

"plateau" at 340 nm (about 50 seconds) and the second one at 360–363 nm (more than 50 days) are compared.

b) The thermodynamic constant $K_3 = k_3/k_{-3}$ for the equilibrium:

$Am\,I^+ \cdots I^- + I_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Am\,I^+\,I_3^-$, is very large and this equilibrium is reached much more rapidly than that between the *"outer"* complex and $Am\,I^+\cdots I^-$. This is highly probable if the thermodynamic constant for the rapid equilibrium: $I_2 + I^- \rightleftharpoons I_3^-$ in methylene chloride is considered: $([I_3^-]/[I_2]\,[I^-]) \simeq 10^9\,mol^{-1}l$ at $0\,°C^7$. This value can be assumed to be not too different from that at 20 °C, because the reaction enthalpy is small in this temperature range ($\Delta H° = 4.51\,kcal\,mol^{-1}$ in water[8]).

Since the *"inner"* complexes are similar to ionic compounds[9-12] and therefore the spectral and voltammetric behaviour of the free and complexed I_3^- ion in methylene chloride is practically indistinguishable[1], the equilibrium constants calculated for free ions may be taken as well for the corresponding *"inner"* complexes. From the assumption above the steady-state approximation can be applied to the short living species $Am\,I^+\cdots I^-$. Consequently, the term $k_{-2}[Am\,I^+\cdots I^-]$ in the kinetic treatment below can be considered practically constant during the whole course of the reaction[13].

c) The last equilibrium $Am\,I^+\,I_3^- + Am \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Am_2\,I^+\,I_3^-$ does not influence the molar extinction coefficient and λ_{max} of the I_3^- absorption band in the *"inner"* complex[1].

With these assumptions, the kinetic treatment can be done as follows:

$$d\,[I_3^-]/dt = k_3\,[I_2]\,[Am\,I^+\cdots I^-] - k_{-3}[Am\,I^+\cdots I_3^-] \qquad (2)$$

$$\begin{aligned} d\,[Am\,I^+\cdots I^-]/dt = &\ k_2\,[Am\,I_2] - k_{-2}[Am\,I^+\cdots I^-] \\ &- k_3\,[I_2]\,[Am\,I^+\cdots I^-] + \\ + k_{-3}&[Am\,I^+\cdots I_3^-] = 0 \text{ (steady state approx.)} \end{aligned} \qquad (3)$$

whence:

$$d\,[I_3^-]/dt = k_2\,[Am\,I_2] - k_{-2}[Am\,I^+\cdots I^-] \qquad (4)$$

When the *whole* system ist at equilibrium (index e):

$$(d\,[I_3^-]/dt)_e = k_2\,[Am\,I_2]_e - k_{-2}[Am\,I^+\cdots I^-]_e = 0$$
$$\text{i.e.} \qquad k_{-2}[Am\,I^+\cdots I^-]_e = k_2\,[Am\,I_2]_e \qquad (5)$$

For the condition (b), it seems reasonable to assume:

$$[Am\,I^+\cdots I^-] = [Am\,I^+\cdots I^-]_e \qquad (6)$$

whence, equation (4) can be written as:

$$d\,[I_3^-]/dt = k_2\,[Am\,I_2] - k_2\,[Am\,I_2]_e \qquad (7)$$

Bearing in mind that the *"outer"* complex equilibrium (K_1) is always operative and that $[I_2] = [I_2]_0 - 2[I_3^-]$, where $[I_2]_0$ is the initial concentration of iodine, the equation (7) becomes:

$$d[I_3^-]/dt = k_2 K_1 [I_2][Am] - k_2 K_1 [I_2]_e[Am]_e$$
$$= k_2 K_1 [Am]([I_2]_0 - 2[I_3^-]) - k_2 K_1 [I_2]_e[Am]_e \qquad (8)$$

If the initial concentration of amine, $[Am]_0$, is in large excess with respect to that of iodine, i.e. $[Am]_0 \gg [I_2]_0$, it can be assumed unchanged during the course of the process and equation (8) becomes:

$$d[I_3^-]/dt = k_2 K_1 [Am]([I_2]_0 - 2[I_3^-]) - k_2 K_1 [I_2]_e[Am] \qquad (9)$$

whose integration gives:

$$t = -(1/2 k_2 K_1 [Am]) \ln\{([I_2]_0 - [I_2]_e)/2 - [I_3^-]\}$$
$$+ (1/2 k_2 K_1 [Am]) \ln\{([I_2]_0 - [I_2]_e)/2\}$$
$$= -(1/2 k_2 K_1 [Am]) \ln\{[I_3^-]_e - [I_3^-]\} + (1/2 k_2 K_1 [Am]) \ln[I_3^-]_e \quad (10)$$

which can be written as:

$$\ln\{[I_3^-]_e - [I_3^-]\} = \ln[I_3^-]_e - 2 k_2 K_1 [Am] t \qquad (11)$$

The concentration of I_3^- was calculated from spectrophotometric measurements at 360 nm, the molar extinction coefficient $\varepsilon_{I_3^-}$ was found to be $30\,000\ mol^{-1} 1 cm^{-1}$ in this solvent[1].

The reliability of the equation (11) was verified experimentally for a solution of iodine ($[I_2] = 2.00 \cdot 10^{-4}\,M$) and *p*-toluidine ($[p\text{-toluidine}]$ $= 5.00 \cdot 10^{-3}\,M$), kept in the dark under nitrogen atmosphere.

The best linearization of the equation (11) was obtained for K_1 $= 7\,mol^{-1} 1$, $\varepsilon_{340} = 20\,000$ and $[I_3^-]_e = 3.71 \cdot 10^{-5}\,M$, corresponding to an equilibrium absorbance $A_{360} = 1.114$ (for $\varepsilon_{360} = 30\,000$ and optical path $= 10\,mm$). These values are in very good agreement with the experimental data: $K_1 = 5 \pm 2\,mol^{-1} 1$ (from *Benesi-Hildebrand* plots) and $A_{360}^\infty = 1.2$, the "plateau" absorbance, extrapolated from the absorbance vs. time plot (Fig. 1 — Fig. 2).

From the slope, k_2 was calculated to be $8.3 \cdot 10^{-6}\,s^{-1}$.

It is to be pointed out that the equilibrium *"outer"* complex $\rightleftharpoons$ *"inner"* complex is not completely shifted to the right, as it was otherwise observed in high ionic strength media[1]. This fact strongly supports the hypothesis that a high polar solvent stabilizes the ionic structure of the *"inner"* complex.

The last equilibrium of the overall mechanism (1) was investigated by spectrophotometry and gas chromatography. The addition of a second amine molecule to the halocation, already observed in voltammetric-spectrophotometric experiments[1], was confirmed. In fact, a system formed by $5.05 \cdot 10^{-3}\,M$ iodine and $5.10 \cdot 10^{-3}\,M$ *p*-toluidine yielded, 30 hours after mixing, $7.33 \cdot 10^{-4}\,M\,I_3^-$, while the *p*-toluidine concentration
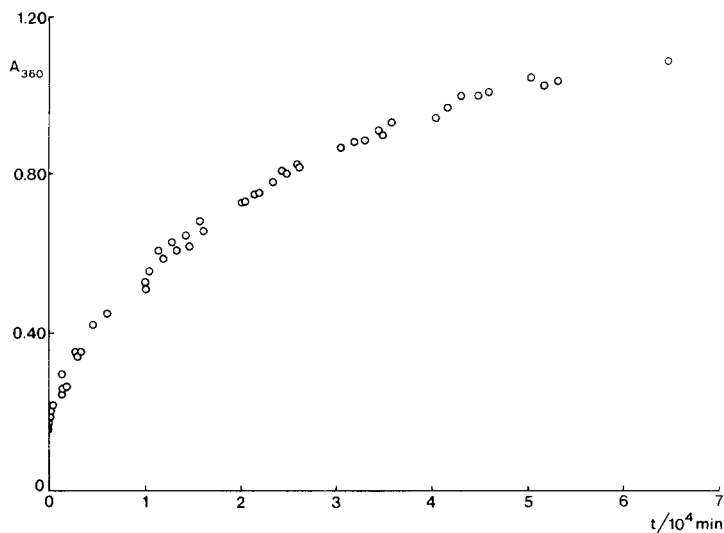
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Fig. 1. Plot of absorbance at 360 nm vs. time for the system iodine/*p*-toluidine in methylene chloride in the dark. Concentrations: $[I_2]_0 = 2.0 \cdot 10^{-4}\,M$; $[p\text{-toluidine}]_0 = 5.0 \cdot 10^{-3}\,M$
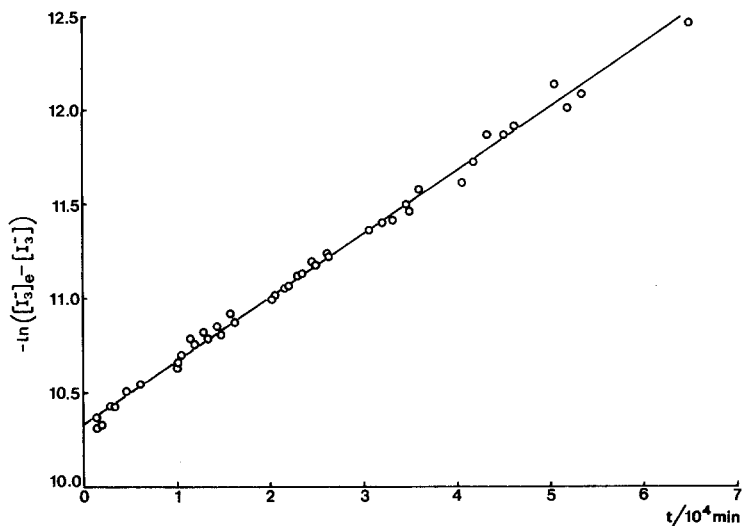

Fig. 2. Plot of the function $-\ln([I_3^-]_e - [I_3^-])$ vs. time for the system iodine/*p*-toluidine in methylene chloride. Concentrations: $[I_2]_0 = 2.0 \cdot 10^{-4}\,M$; $[p\text{-toluidine}]_0 = 5.0 \cdot 10^{-3}\,M$. $A_{360}^\infty = 1.2$ (extrapolated limiting absorbance, from Fig. 1). $[I_3^-]_e = 3.71 \cdot 10^{-5}\,M$ (I_3^- concentration at equilibrium)
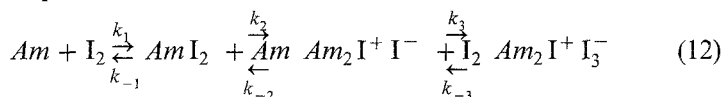
decreased to $3.3 \cdot 10^{-3} \, M$. This means that for the consumption of two p-toluidine moles about one I_3^- mole had been produced. Since at this stage of the process the "*outer*" complex was found negligible with respect to the "*inner*" one and iodotoluidines were not detected, it can be inferred that almost the whole amount of the p-toluidine consumed was converted into the "*inner*" complex. Accordingly, the "*inner*" complex formula was confirmed to be $Am_2 I^+ \cdots I_3^-$. The not large difference of the experimental ratio [(moles of Am consumed) : (moles of I_3^- produced)] from the value $(2:1)$ is probably due to the approximation of the molar extinction coefficient of I_3^- ($\varepsilon_{360} = 30\,000 \pm 3\,000 \, \mathrm{mol}^{-1} \mathrm{cm}^{-1}$ ¹) and other minor analytical causes.

The addition of the second amine molecule to the complex was considered subsequent to the "*inner*" complex formation, for these reasons:

1. The composition of the "*outer*" complex was found to be 1 : 1 with respect to I_2 and p-toluidine.

2. The "*outer*" complex would not be considerably stabilized by a further p-toluidine molecule; moreover, the energy barrier between "*outer*" and "*inner*" complex would not be sensibly lowered (see below).

3. The mechanism shown in the scheme (12), whose rate determining step is the reaction of the "*outer*" complex $Am\,I_2$ with Am to give the "*inner*" complex, was also considered.

$$Am + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Am\,I_2 \underset{k_{-2}}{\overset{k_2}{\underset{\longleftarrow}{\overset{\longrightarrow}{+Am}}}} Am_2 I^+ I^- \underset{k_{-3}}{\overset{k_3}{\underset{\longleftarrow}{\overset{\longrightarrow}{+I_2}}}} Am_2 I^+ I_3^- \qquad (12)$$

By applying the steady state approximation to the intermediate species $Am_2 I^+ \cdots I^-$ and with the same general assumptions as before, the kinetic treatment could be summarized by the following sequence of differential equations:

$$\mathrm{d}\,[I_3^-]/\mathrm{d}t = k_3 [Am\,I^+ \cdots I^-][I_2] - k_{-3}[Am_2 I^+ \cdots I_3^-] \qquad (13)$$

$$= k_2 [Am][Am\,I_2] - k_{-2}[Am_2 I^+ \cdots I^-] \qquad (14)$$

$$= k_2 K_1 [Am]^2 ([I_2] - 2[I_3^-]) - k_2 K_1 [Am]_e^2 [I_2]_e \qquad (15)$$

whose integration leads to equation:

$$\ln\{[I_3^-]_e - [I_3^-]\} = \ln[I_3^-]_e - 2k_2 K_1 [Am]^2 t \qquad (16)$$

A direct test of schemes (1) and (12) can be made by matching equations (11) and (16), which can be written in the general form:

$$\ln\{[I_3^-]_e - [I_3^-]\} = \ln[I_3^-]_e - 2k_2 K_1 [Am]^\alpha t \qquad (17)$$

where $\alpha = 1$ or 2, with respect to whether scheme (1) or (12) is operative.

By plotting the function $-\ln\{[I_3^-]_e - [I_3^-]\}$ vs. time, a straight line would be obtained, whose slope must depend on the first or second power
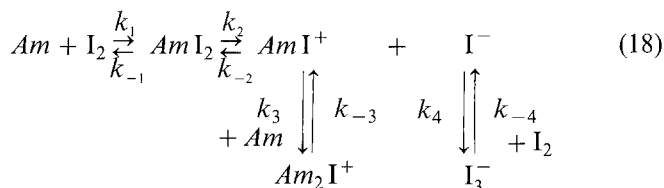
of the amine concentration, according to the respective reaction mechanism.

Experimental data drawn from kinetics carried out with the same $[I_2]$ $(2.00 \cdot 10^{-4} M)$ and different amine concentrations $(5.00 \cdot 10^{-3} \cdots 1.00 \cdot 10^{-2} M)$ fit equation (17) with a satisfactory approximation for a value of $\alpha = 1$.

Therefrom it can be reasonably inferred that scheme (1) represents more properly the reaction mechanism, so meaning that the second molecule of amine must react with the already formed "*inner*" complex.

This conclusion is supported also by the following consideration: while the fast reaction of I_2 with I^- increases the stability of the anionic part of the complex, the addition of one molecule of *p*-toluidine can stabilize the cationic part without modifying sensibly the properties of I_3^-.

Now, since the reaction between the second amine molecule and the "*inner*" cation [reaction (a)] was found to be complete, it is also possible that its rate (not evaluated in this work) be competitive or higher than that of I_3^- formation [reaction (b)]. Should that be the case, a more appropriate kinetic scheme, taking into consideration that both the reactions (a) and (b) are much faster than the "*inner*" complex formation (rate determining step), would be the following:

$$Am + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Am\,I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Am\,I^+ \quad + \quad I^- \tag{18}$$

$$\begin{array}{cc} k_3 \Big\Uparrow k_{-3} & k_4 \Big\Uparrow k_{-4} \\ + Am & + I_2 \\ Am_2\,I^+ & I_3^- \end{array}$$

By applying the steady state approximation to I^- and $Am\,I^+$, a kinetic treatment quite similar to that employed for the mechanism (1) can be used. It is to be noted that the kinetic-thermodynamic parameters therefrom obtained by using the experimental data have the same values as reported before, calculated from scheme (1).

The Photochemical Process

To investigate the photochemical mechanism of the "*outer*" complex → "*inner*" complex conversion, solutions of I_2 and *p*-toluidine in methylene chloride with variable donor and acceptor concentrations were irradiated with light of 337–340 nm.

In all the cases investigated experimentally straight lines with high correlation coefficients were obtained for a plot of A_{360} vs. irradiation time. Only at relatively high donor and/or acceptor concentrations the

correlation coefficients became worse, probably because in these cases the thermal process was not negligible with respect to the photochemical one.

Fig. 3 shows the plot A_{360} vs. time for a constant donor concentration, $[Am] = 1.97 \cdot 10^{-3} M$, and variable iodine concentrations $(1.93 \cdot 10^{-3} \cdots 7.25 \cdot 10^{-5} M)$; Fig. 4 shows the same plot for a constant acceptor concentration, $[I_2] = 1.97 \cdot 10^{-3} M$, and different amine concentrations $(1.91 \cdot 10^{-3} \cdots 9.55 \cdot 10^{-5} M)$. These graphs show that large changes of the
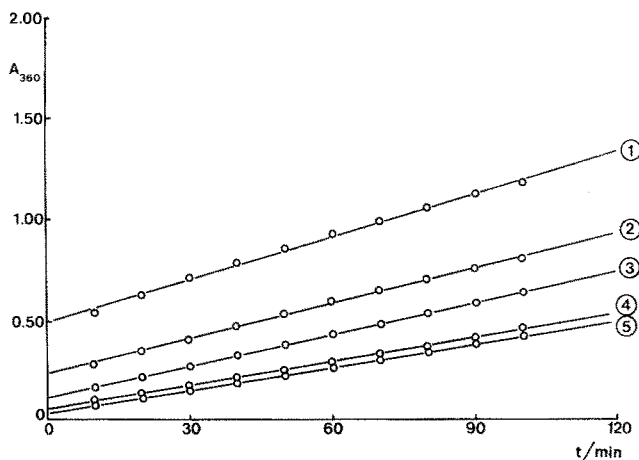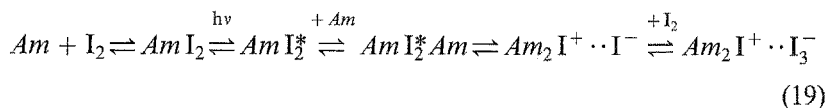

Fig. 3. Plot of absorbance at 360 nm vs. irradiation time for the system iodine/p-toluidine in methylene chloride, for $[p\text{-toluidine}]_0 = 1.97 \cdot 10^{-3} M$ and different iodine concentrations, $[I_2]_0 = 1$ $1.93 \cdot 10^{-3} M$, 2 $9.67 \cdot 10^{-4} M$, 3 $4.83 \cdot 10^{-4} M$, 4 $1.45 \cdot 10^{-4} M$, 5 $7.25 \cdot 10^{-5} M$. Irradiation source: Osram Xenon XBO 150 W lamp, filtered by a Balzers R-UV 337-14 interference filter

iodine concentrations do not cause considerable slope variations; the slope depends more strongly on the amine concentration. The last finding can be explained by an interaction of the excited "*outer*" complex with the amine ground state to give an exciplex involving two molecules of amine and one of I_2. The resulting reaction mechanism can be drawn as follows:

$$Am + I_2 \rightleftharpoons Am\,I_2 \overset{h\nu}{\rightleftharpoons} Am\,I_2^* \overset{+Am}{\rightleftharpoons} Am\,I_2^* Am \rightleftharpoons Am_2\,I^+ \cdots I^- \overset{+I_2}{\rightleftharpoons} Am_2\,I^+ \cdots I_3^-$$

$$(19)$$

It is noteworthy that the photochemical reaction coordinate is not the same as for the "dark" process, although in both cases the same ionic complex was detected as the final product.

This feature can be explained on the basis of a different stabilization of the intermediates by an additional molecule of amine. In fact, referring to the potential energy curves reported in Fig. 4 of Ref.[1], it can be seen that the formation of an exciplex can act on the excited state curve by lowering both the energy of the minimum of the *"outer"* complex and that of the small barrier leading to the partially ionized species.
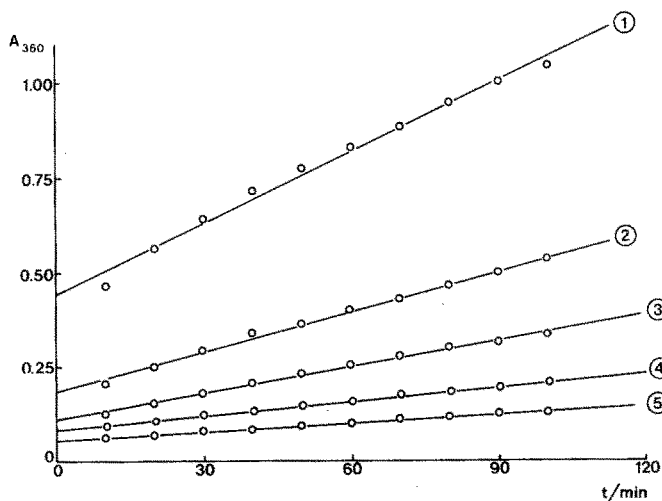

Fig. 4. Plot of absorbance at 360 nm vs. irradiation time for the system iodine/*p*-toluidine in methylene chloride, for $[I_2]_0 = 1.97 \cdot 10^{-3}\,M$ and different *p*-toluidine concentrations, $[Am]_0 = 1 \; 1.91 \cdot 10^{-3}\,M$, $2 \; 7.64 \cdot 10^{-4}\,M$, $3 \; 3.82 \cdot 10^{-4}\,M$, $4 \; 1.91 \cdot 10^{-4}\,M$, $5 \; 9.55 \cdot 10^{-5}\,M$. Irradiation source: Osram Xenon XBO 150 W lamp, filtered by a Balzers R-UV 337-14 interference filter

The configurations responsible for such a lowering of energy are of the type $d\Psi_i(Am_2^*\,I_2) + g\Psi_j(Am_2^+\,I_2^-)$, where the first term represents the exciton contribution and the second one represents the electron transfer contribution. This latter term is expected to be dominant in polar solvents $(g > d)$ because it induces an effective dipole-dipole interaction with the environment. Thus, in the present case, the interaction of the excited *"outer"* complex with the ground state amine results in a lowering of the energy barrier leading to ionic products with an enhancement of the product yield.

For the thermal reaction, however, the contribution of electron transfer terms deriving from a ternary complex formation is negligible, as the ground state of the *"outer"* complex is dominated by the term Ψ_0 $(Am\,I_2)$. However, the complete separation of charges, as found in the final products, requires the greatest delocalization of charges, which can be

realized through the formation of the particularly stable I_3^- ion and a counter part like $(Am_2 I)^+$.

As far as the formation of a triple exciplex of the type $Am_2 I_2^*$ is considered, it is to be remarked that several examples of complexes between two donors and one acceptor with prevalent ionic structure have been detected and reported in the literature[14,15]. A photophysical characterization of such a complex, based on emission measurements, is in progress.

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13 The steady state approximation is congruent with a constant concentration of $Am\,I^+ \cdot \cdot I^-$. This can be easily verified by assuming $k_{-2}[Am\,I^+ \cdot \cdot I^-]$ and $k_{-3}[Am^+ \cdot \cdot I_3^-]$ to small with respect to the other kinetic terms in equation (3) and keeping into account the large excess of the Amine. Therefrom: $[Am\,I^+ \cdot \cdot I^-] \simeq (k_2 K_1/k_3) \cdot [Am] = $ constant. These considerations are not completely valid when the equilibrium is going to be approached. However, we assumed equation (6) valid because a sharp change of $[Am\,I^+ \cdot \cdot I^-]$ in the proximity of the equilibrium should involve strong variations both in the disappearance and in the formation rate of this intermediate species to verify the equilibrium conditions. These changes, however, should require correspondingly high variations both in reagent and product concentrations, in contrast with the situation in the vicinity of the equilibrium, where minimal concentration changes are observed. In any case, a small difference between $[Am\,I^+ \cdot \cdot I^-]$ and $[Am\,I^+ \cdot \cdot I^-]_e$ can be accepted, because it should not involve any change in the kinetic behaviour of the system but only a small uncertainty in the calculation of the kinetic constants.
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15 *Tsujino N., Masuhara H., Mataga N.,* Chem. Phys. Lett. **21**, 301 (1973).