

# INTERACTIONS BETWEEN KETONES AND AMINES IN PHOTOINITIATING SYSTEMS USED FOR RADICAL POLYMERIZATION

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## ABSTRACT

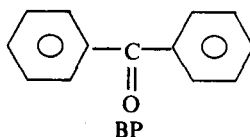
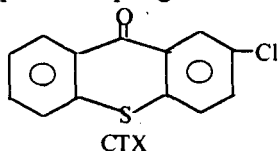
Time resolved laser spectroscopy and GC/MS were used to investigate the primary processes and the side reactions occurring in benzophenone and chlorothioxanthone/amine systems used as photoinitiators of radical polymerization. The discrepancy observed between the experimental data and the expected behaviour is accounted for by detrimental chemical reaction involving the ketone triplet state, the ketyl radical and the amine-derived radical.

## INTRODUCTION

The development of photopolymerizable surface coating technologies<sup>[1]</sup> has led to basic studies aiming at a better understanding of the processes involved. For the last decade, excited state processes have been investigated through laser spectroscopy<sup>[2][3]</sup> and their efficiency checked with the practical reactivity of the photoinitiators<sup>[4]</sup>. It is known that these outstanding initiators of radical photopolymerization, work through cleavage or electron transfer, while the overall mechanism involved is also clearly understood as far as photo-cleavable initiators are concerned, the problem is much more complicated in the case of the other system (scheme 1) which, in addition to the well established electron and proton transfer process, exhibits a lot of side-reactions. The present paper affords a further insight into the nature of these reactions.

## EXPERIMENTAL

The thioxanthone derivative CTX used in this work was kindly donated by Ward Blenkinsop & Co. and used as received without any further purification. Benzophenone (BP), the amines (MDEA, TEA, DBA) and the stable radical 2, 2, 6, 6, -tetramethyl piperidyl nitroxide were purchased from Aldrich. All solvents used were of spectroscopic grade.



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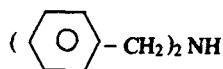
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TEA



MDEA



DBA

UV-visible absorption spectra were recorded with a Beckman UV-visible spectrophotometer, and the GC/MS analysis was performed in a quadrupole Mass spectrometer (Nermag/Sider) with a computer station. The chromatography employed a 20 m silica capillary column. The temperature of the sample inlet port was 150 °C. The light source used in this work was a medium pressure Hg lamp (HPK 125W) with a pyrex filter. Irradiations were conducted for 10 minutes or 4 hours.

The laser spectroscopy device<sup>[5]</sup> and the measurement of the rate of polymerization of methylmethacrylate (MMA) in solution<sup>[6]</sup> have been described elsewhere.

## RESULTS AND DISCUSSION

### 1. Excited state processes

Rate constants of electron transfer,  $k_e$ , between the ketone triplet and the amine (AH) and of monomer (MMA) quenching,  $k_q$ , of the carbonyl triplet are shown in Table 1. They were calculated by plotting the lifetime  $\tau_T$  of the triplet state (generated through the excitation of the solution by a 3 ns light pulse emitted by the YAG/Nd laser at  $\lambda = 353$  nm) against the quencher concentration:

$$\frac{1}{\tau_T} = \frac{1}{\tau_T^0} + k_e[\text{AH}] \quad ; \quad \frac{1}{\tau_T} = \frac{1}{\tau_T^0} + k_q[\text{MMA}]$$

### 2. Rate of polymerization $R_p$

The modification of  $R_p$  vs. the amine concentration was determined for the different couples ketone/ amines. According to the processes involved in the excited states (scheme 1), the law of polymerization should be:

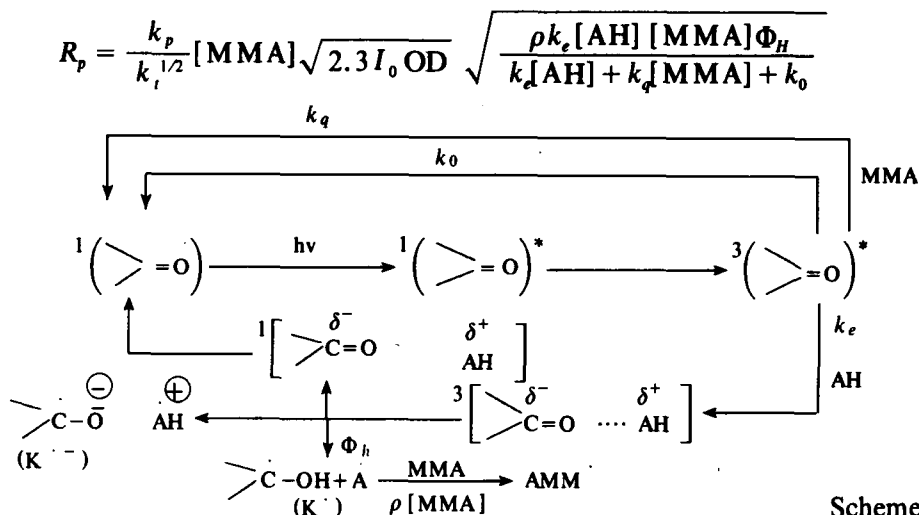


**Table 1** Rate constants of electron transfer ( $k_e$ ) and monomer quenching ( $k_q$ ) –  $b/a$  ratio : see text

| Ketone | $10^{-7} k_q$<br>( $M^{-1}s^{-1}$ ) | amine | $10^{-9} k_e$<br>( $M^{-1}s^{-1}$ ) | $10^2 (b/a)_{theo}$ | $10^2 (b/a)_{exp}$ |
|--------|-------------------------------------|-------|-------------------------------------|---------------------|--------------------|
| BP     | 6.5                                 | MDEA  | 1.3                                 | 36                  | 10                 |
|        |                                     | TEA   | 2.5                                 | 19                  | 13                 |
|        |                                     | DBA   | 2.3                                 | 25                  | 10                 |
| CTX    | 0.2                                 | MDEA  | 3                                   | 0.6                 | 9                  |
|        |                                     | TEA   | 2.5                                 | 0.6                 | 3.3                |
|        |                                     | DBA   | 1                                   | 1.6                 | 1.5                |

where  $k_p$ ,  $k_t^{1/2}$  are the propagation and termination rate constants,  $I_0$  the incident light intensity,  $OD$  the optical density at  $\lambda = 366$  nm,  $\rho$  a parameter related to the efficiency of the chemical reaction between the double bond of the monomer and the initiating radical.

The expression is linearized :

$$\frac{[AH]}{R_p^2} = \frac{1}{\rho \Phi_H} [a [AH] + b]$$

$$\text{with : } \frac{b}{a} = \frac{k_0 + k_q [MMA]}{k_e} \sim \frac{k_q}{k_e} [MMA]$$

It would appear that the experimental data could be checked with such a plot (Figure 1), but the "experimental"  $b/a$  values determined do not fit in any case the "theoretical"  $b/a$  values calculated from the laser spectroscopy data (Table 1). In the most adverse cases, the curve  $R_p = f([AH])$  grows more slowly than in the theoretical model (Figure 1).

This discrepancy was observed for the first time, as the agreement was generally good in our previous experiments with photoinitiators exhibiting an  $\alpha$ -cleavage process<sup>[7]</sup> but arises also in aryl sulfide<sup>[8]</sup>. In the present case, this reflects the inadequacy of the model proposed in scheme 1, and suggests that other sideprocesses occur, e.g. ketyl radical anion,  $K^{\cdot -}$ , formation (which is dependent on the basicity of the amine); the termination reaction of the growing macromolecular chain by  $K^{\cdot -}$  and  $K^{\cdot -}$ ; light absorbing transient (LAT) generation<sup>[16, 17]</sup> adduct formation (as suggested in [9]) between the ketone triplet and the amine radical (thus consuming both excited transient states ( $T_1$ ) and potentially useful initiating radicals,  $A^{\cdot}$ ).

### 3. GC/MS analysis

The analysis of the photolysis products by GC/MS was mainly performed in two specific systems : BP/TEA and CTX/MDEA, in order to shed some light on these

side-reactions, which could open new research prospects with regard to the overall mechanism.

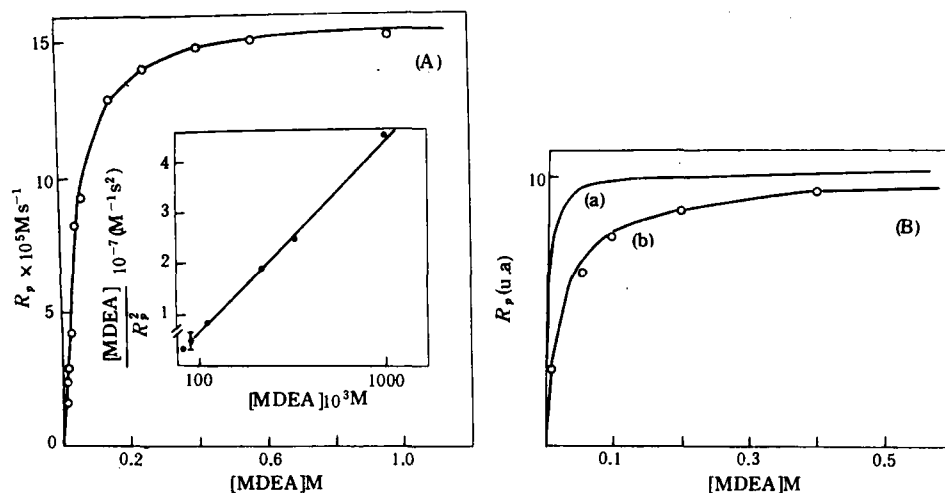


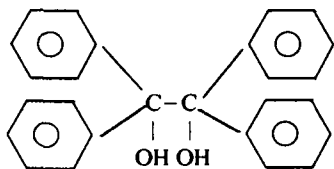
Fig. 1 (A) Rate of polymerization vs  $[\text{MDEA}]$  (B) Dependence of  $R_p$  on  $[\text{MDEA}]$  (a) Calculated and (b) experimental

The radical trapping technique<sup>[10, 11]</sup>, which provided useful information on the mechanism of photochemical reactions, particularly by allowing identification of any intermediate radicals involved, attracted more attention. As it is known that the sterically hindered piperidyl nitroxyl radical acts as a very efficient stabilizer for polyolefins. It can be used as a radical scavenger to bring a radical chain reaction as a stop by recombination with an active radical. The hindered piperidyl nitroxide, which is a stable radical, cannot abstract hydrogen from hydrogen-donating hydrocarbon compounds<sup>[12-13]</sup>, but can react with active carbon radicals to form alkyloxyl amines. Accordingly, inspection of the recombination products arising from the photoreaction may help in discriminating between active and inactive radicals.

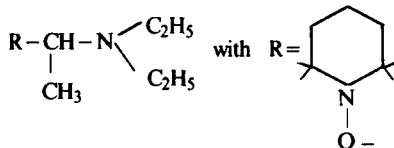
All experiments in this part were carried out in solution.

#### A-BP/TEA system:

The most interesting products obtained from the mass spectra of BP/TEA/R are listed below:

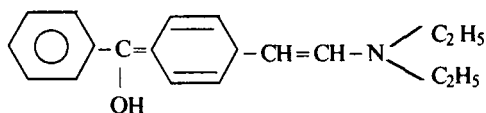


1



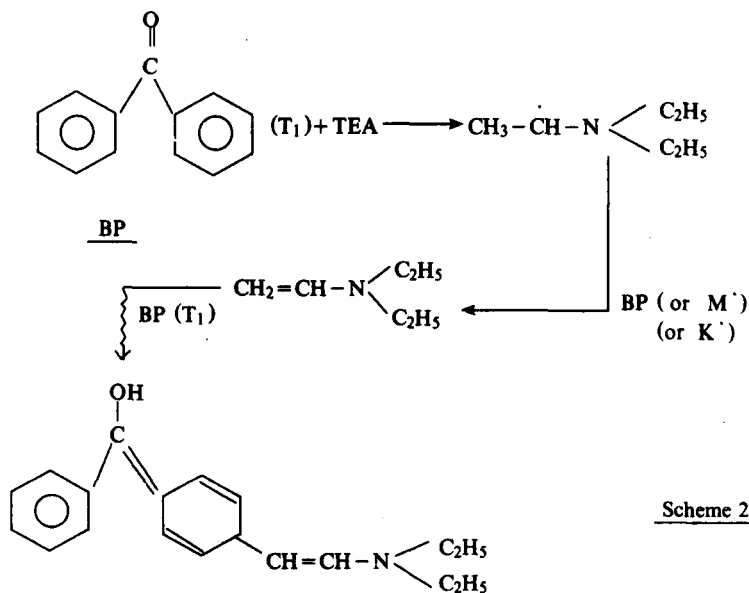
2

It can be shown that the expected TEA radical may be trapped by  $\text{R}^\bullet$  to form an adduct with the mass number 256. This demonstrates that the TEA radical generated



3

in these photoreaction is an active radical. On the contrary, no trace of the recombination product of ketyl and  $R^\cdot$  was discovered and, therefore, the ketyl radical is inactive. The mass spectrum displays a trace of benzopinacol **1**, generated by the dimerization of a photoreduction product of BP. In addition, it is worth noting that a large amount of a species **3** with the mass number 279 is found in the mass spectrum. It can probably be assigned to an adduct between the amine radical and the triplet state of benzophenone. This product had been taken into account by other investigators a few years ago<sup>[9]</sup>. The mechanism may be outlined as follows (scheme 2):



Scheme 2

The generation of LAT in BP is well-known<sup>[16,17]</sup> (it has been observed both in solutions and in films) and will not be inquired into once again: the apparent overall optical density of the sample is enhanced and the fraction of light absorbed by BP decreases<sup>[14]</sup>. Further reactions involving the photochemistry of LATs may play a role, e.g. the photolysis of LATs or the quenching of the ketone triplet state by LATs<sup>[15]</sup>.

**B – CTX/MDEA system:**

a) LATs in CTX

In Figure 2a, the UV – visible absorption spectra of CTX/MDEA dissolved in methanol (purged by bubbling  $N_2$  for ten minutes), irradiated by 366 nm at different time intervals, were recorded. It is apparent that the characteristic absorption peak of CTX at 380 nm disappeared almost completely after irradiating for only a few

minutes. Meanwhile, a new absorption centered at 320 nm was generated. Simultaneously, an isosbestic point near 330 nm was clearly observed. It follows, therefrom, that the new absorption band generated upon irradiation, is closely connected with the disappearance of CTX.

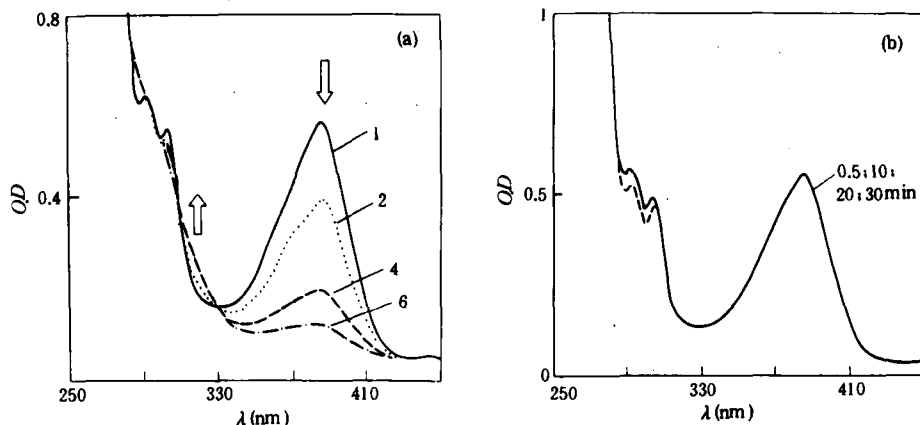
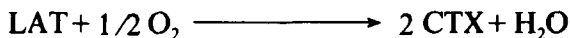


Fig.2 (a) UV-visible absorption spectra of a CTX/MDEA solution in methanol irradiated by a 366 nm light under N<sub>2</sub> at different time intervals. 1) before irradiation 2) 2 mins. 4) 4 mins. 6) 6mins. (b) UV-visible spectra of CTX/MeOH irradiated by a 366 nm light in N<sub>2</sub> at different time intervals.

Interestingly, it can be seen from the results of GC/MS that the photoproduct includes a large amount of CTX, and the ratio of abundances between CTX and the compounds containing CTX and other species derived from CTX ( $[CTX]/[CTX] + [CTX \text{ derived species}]$ ) approaches 80%. It follows, therefrom, that the CTX consumption remains comparatively low during the process of photoirradiation. Nevertheless, the characteristic absorption peak at 380 nm disappears very quickly even at the beginning of the irradiation. This phenomenon could be explained by the formation of a LAT. Indeed, a similar investigation on benzophenone in cyclohexane<sup>[16][17]</sup> showed that, in absence of oxygen, a para (or ortho) coupling product (usually referred to as a LAT, with a peak located in the  $n\pi^*$  transition region of the UV spectrum) is observed upon irradiation. This product is sensitive to the presence of oxygen.

In the present case, such a phenomenon was also observed (Figure 3). The formed product disappears rapidly when the cell is opened to air. It has been reported<sup>[18]</sup> that the LAT can also be formed in thioxanthone, but the investigators did not provide spectroscopic data. They merely stated that the absorption peak at 380 nm vanishes in the UV spectrum upon irradiation after 13 minutes. It can be seen from our results that, at the beginning of the irradiation of the CTX solution, the LAT yield is high and the ground state CTX obtained from GC/MS is recovered through the reaction between LAT and O<sub>2</sub> as follows:



LAT can be formed by a coupling reaction between the CTX ketyl radical and another ketyl radical, or other derived radicals which are formed in this system. Such a phenomenon does not occur in the CTX/MeOH system, under the same irradiation conditions (Figure 2b). It is well-known that, in absence of an amine, it is

impossible to form efficient ketyl radical. In addition, the intensity of the characteristic absorption of CTX at 380 nm should be kept constant. These experiments demonstrate that the formation of a ketyl radical is the key step for decreasing the intensity of the CTX absorption. Furthermore, the molar absorption coefficient of LAT from CTX is low, perhaps because of the non-coplanarity of the LAT species.

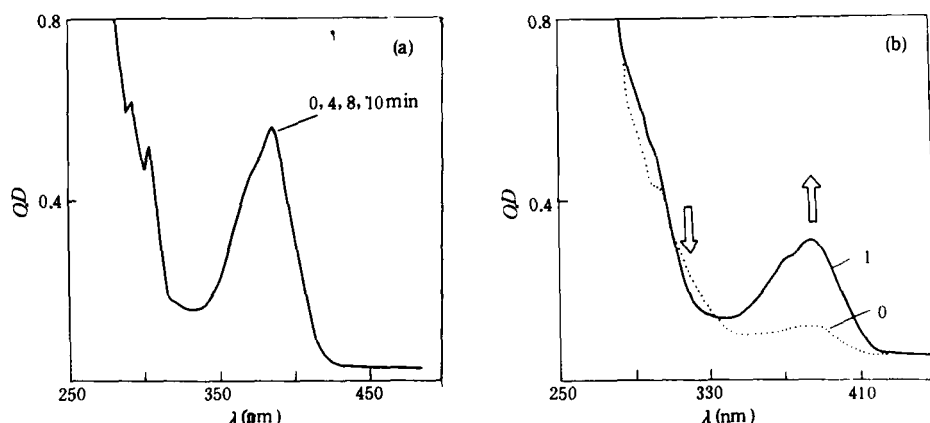
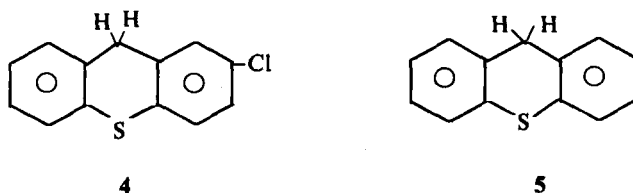


Fig.3 (a) UV-visible absorption spectra of CTX ( $1 \times 10^{-4} M$ ) / MDEA ( $2.5 \times 10^{-2} M$ ) solution in methanol irradiated by 366 nm light in air at different time intervals (0, 4, 8, 10 min., respectively).

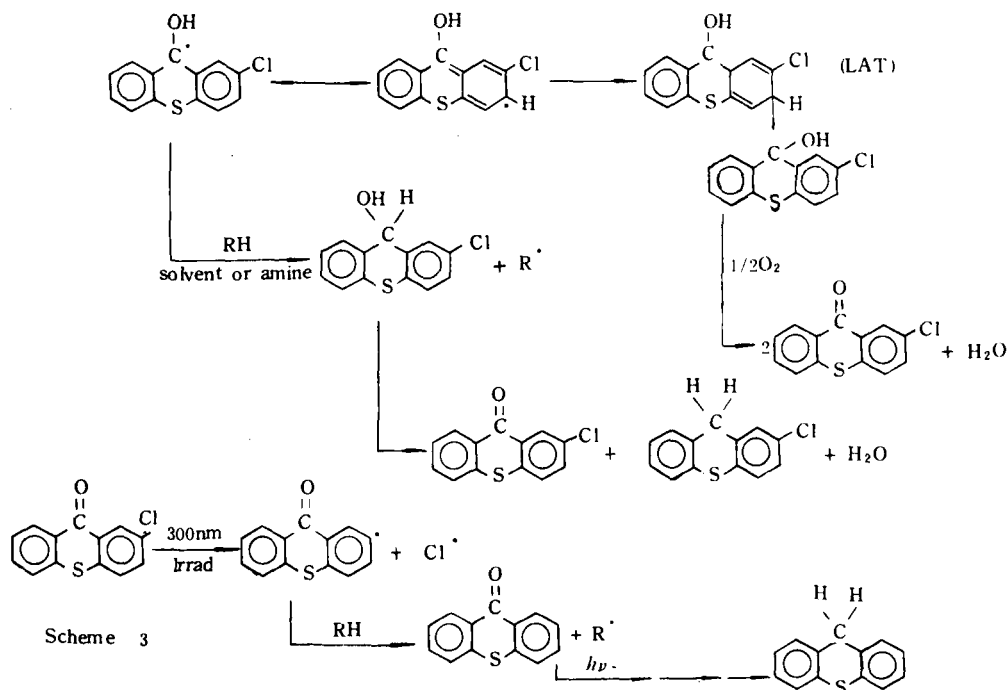
(b) The recovery of the absorption peak at 380 nm for a CTX/MDEA solution in methanol which was irradiated for 10 min. in a  $N_2$  atmosphere. 0: just after the irradiation for 10 min. 1: the same solution after storing 40 min. in the dark, in air.

### b) Photolysis products

From the GC/MS data, it is apparent that various photolysis products (especially chlorothioxanthene 4 and thioxanthene 5) are formed:



According to ref [18], thioxanthene can be generated by disproportionation of thioxanthol in the injection part of the GC apparatus, i. e. this reaction occurs on heating. These investigators also reported that thioxanthone is only a minor product in the pyrolysis of the photoproduct (1.3 % yield). In our results, however, chlorothioxanthene and thioxanthene account for a large percentage of the CTX photoproducts (nearly 10%). Of course, our experiments were not conducted under the same conditions (e.g. the irradiation was performed for a longer time in our experiments). Even if we also discovered chlorothioxanthene and thioxanthene in the direct-inlet mass spectrum at a very low scanning number, the large amount of 4 is mostly accounted for by formation in the subsequent process of light irradiation at room temperature; these results are consistent with data reported twenty years ago on thioxanthone itself; thioxanthene was assumed to be formed by the disproportionation of thioxanthidrol [19].

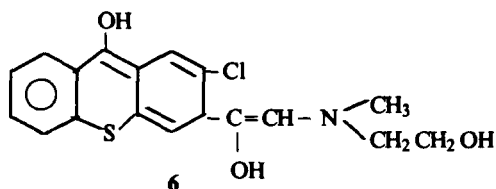


It is worthy of note that, apart from chlorothioxanthene, a large amount of thioxanthene is also formed. It means that the chlorine atom in CTX can be split off during the process of photoirradiation (it behaves like an independent fraction in gas chromatography and is also detected at a low scanning number in the mass spectrum). Another important evidence for this result is that a recombination product between the 2, 2, 6, 6-tetramethylpiperidynitroxide stable radical and the CTX radical formed after the C-Cl bond scission is detected in the mass spectrum. These results show that thioxanthene is formed during the process of photoirradiation (scheme 3).

Different irradiation conditions were used to clear up the dechlorination process of CTX. The results show that when the irradiated wavelength is selected by a filter at  $\lambda = 366$  nm, the yield of dechlorinated CTX exhibits a 5 fold decrease. Thus, the CTX was dechlorinated by photoirradiating at a wavelength below 320 nm, which corresponds to the energy of the C-Cl bond (95 Kcal/mole in chlorobenzene).

Reference can also be made to many amine-derived products, revealing the degree of complexity of such chemical and photochemical side-processes which, unfortunately, prevent any accurate and complete description of the ketone/amine interactions.

An adduct between CTX and an amine-derived product 6 is found with a low yield. A possible structure, in agreement with the MS spectrum, is very similar to the corresponding adduct observed with BP:



Just like in the case of BP, this adduct provides evidence for a detrimental process between  $A^\cdot$ ,  $K^\cdot$  and  $T_1$ , which in turn can seriously affect the quantum yield of the initiating radicals  $A^\cdot$ .

## CONCLUSION

The data reported in the present investigation suggests the following comments, relevant to the processes occurring during the photopolymerization of organic coatings.

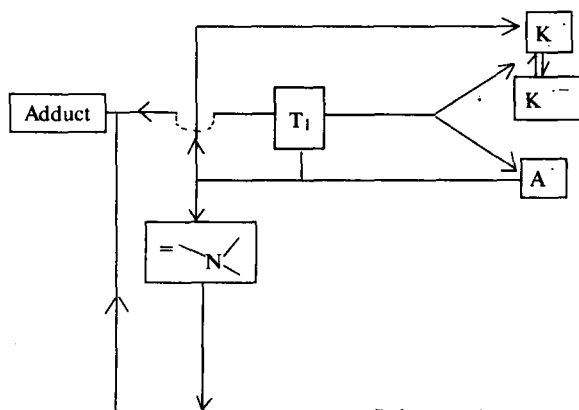
Dechlorination of CTX under polychromatic and high intensity light beams could induce further side processes and, thus, result in a low initiation efficiency.

Molecular oxygen dissolved in thin coating films can be expected to modify completely the photochemistry of CTX, as compared with reactions taking place in a nitrogen atmosphere.

Both the above-mentioned processes, the concentration effects (in CTX and the amine), the light intensity and irradiation wavelength effects, explain why the comparison of data obtained under different experimental procedures is generally difficult and unreliable.

The equilibration process between  $K^\cdot$  and  $K^{\cdot-}$  for various ketones, which is suspected to play a specific role in photopolymerization reactions (both in homogeneous<sup>[20]</sup> and heterogeneous solution<sup>[21]</sup>), should receive much more attention in the future.

The side-reactions detected in BP/TEA, occur in other systems BP/amines and in CTX/amines (although indispensable experimental evidence is only available in the case of CTX/MDEA). In a general way, the following simplified scheme 4 can be proposed tentatively, to explain that increasing the amine concentration in Figure 1 does not necessarily result in the expected corresponding increase of  $R_p$ . This assumption does not rule out the possibility of an enhancement of the termination process of the polymerization reaction by ketyl species, which should be dependent on the amine concentration. In this case, both a slow modification of  $R_p$  vs.  $[AH]$  (at low amine concentration) and a lower plateau value (at high amine concentration) may be expected.



Scheme 4

**Keywords :**

Photoinitiating systems , photopolymerization , Benzophenone/Amine system , Chlorothioxanthone/Amine system , Light absorbing transient (LAT) .

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