

# Photochemistry and photoinitiator properties of novel 1-chloro-substituted thioxanthenes.

## III: Preliminary study of the photoacid generation

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### Abstract

The dehalogenation of a selected number of 1-chloro-4-acyloxy/oxy derivatives of thioxanthone have been studied by a spectrophotometric method, developed using the sodium salt of tetrabromophenol blue as the acid probe. The method has allowed the *in situ* monitoring of the photoacid generation by absorption spectroscopy. This has consequently led to the evaluation of absolute quantum yields of acid generation through steady state photolysis, and the investigation of the derivatives as potential photoacid generators, able to initiate cationic polymerisation of cyclohexene oxide. © 1997 Elsevier Science S.A.

**Keywords:** Photoacid generation; Thioxanthone; Cationic

### 1. Introduction

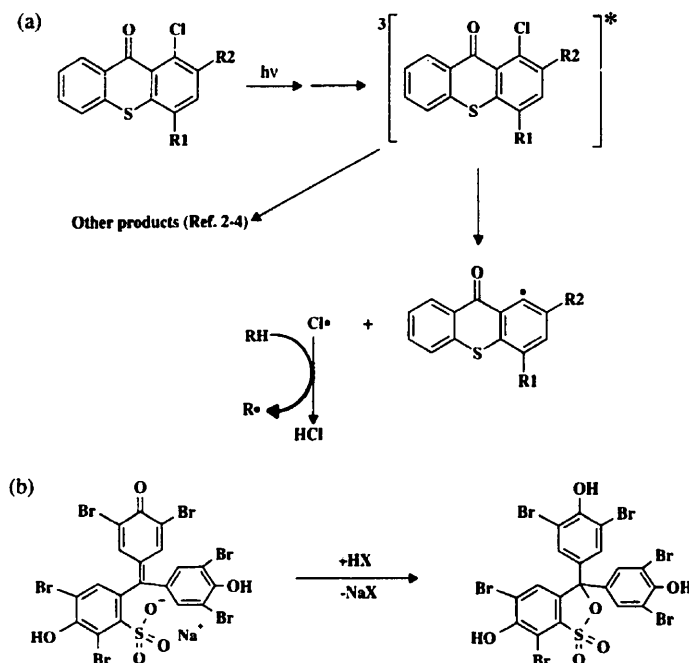
The use of photoinitiators in the fields of photoresists and etching is becoming very important with the development of many systems where acid generation plays a central role. Of particular interest is the photoacid generation from organic molecules to catalyse polymerisation or deprotection reactions applied in the microlithography industry [1]. In this respect, the 1-chloro-4-acyloxy/oxy substituted derivatives of thioxanthone have the potential to act as photoacid generators. Our recent studies [2–4] on these derivatives of thioxanthone have established their photophysical and photochemical properties in terms of their photopolymerisation activity. The primary view that radicals are produced by hydrogen atom abstraction from hydrogen donors has been accepted and is believed to be the main pathway in the initiation mechanism of polymerisation. However, in addition to the above reaction, the process of dehalogenation through C<sub>Ar</sub>-X homolytic photocleavage which produces chlorine

radicals, and in turn, undergoes hydrogen atom abstraction to produce Brønsted acids may also be considered (Scheme 1a). Hence, the acid generated may then initiate the cationic polymerisation of monomers.

In this paper, we describe a spectrophotometric method developed for studying the -HX acid formation to evaluate the dehalogenation process taking place *in situ* under steady-state photolysis of various derivatives of 1-chlorothioxanthone. The absolute quantum yields of acid generation have been evaluated by photolysing methanolic solutions of the thioxanthone derivatives in the presence of the sodium salt of tetrabromophenol blue (TBPB) as an indicator [5]. The acid generated, through photolysis of the C-Cl bond and subsequent hydrogen atom abstraction, reacts with the TBPB (Scheme 1b) causing a decrease in the absorption band of the probe at 615 nm. We present here the results of the changes in absorbance observed over various irradiation times and the subsequent absolute quantum yield values for the photoacid generation. In addition, a preliminary study for their efficiency as cationic initiators has been investigated for the selected derivatives of thioxanthone using cyclohexene oxide (CHO) as the monomer.

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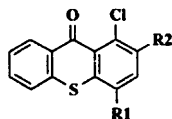


Scheme 1.

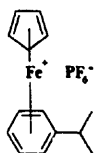
## 2. Experimental

### 2.1. Materials

Methanol and cyclohexene oxide were obtained from Aldrich Chemical, UK and were of Analar or HPLC grade. The sodium salt of tetrabromophenol blue (TBPB) from Aldrich Chemical was used as received. The compounds, (I) 1-chloro-4-*n*-propoxythioxanthone (melting pt. = 91–93°C), (II) 1-chloro-2-methyl-4-*n*-propoxythioxanthone (melting pt. = 116–117°C), (III) 1-chloro-4-benzyloxythioxanthone (melting pt. = 139–140°C), and (IV) 1-chloro-4-acetyloxythioxanthone (melting pt. = 141–142°C) were supplied by Great Lakes Fine Chemicals, Widnes, UK and used as received. Their corresponding structures are shown below. Irgacure 261 (Irg 261) was used as a reference to compare the activity of the initiators above and was supplied by Ciba Additives, Cheshire, UK.



- I: R1 = OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, R2 = H  
 II: R1 = OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, R2 = CH<sub>3</sub>  
 III: R1 = OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R2 = H  
 IV: R1 = OCOCH<sub>3</sub>, R2 = H



IRGACURE 261

### 2.2. Quantum yield of acid generation

Quantum yields of acid generation ( $\phi_{\text{acid}}$ ) of the selected thioxanthone derivatives (Compounds I–IV), in the presence of TBPB, were determined in methanol at equivalent concentrations of  $1.85 \times 10^{-5} \text{ mol dm}^{-3}$  for both the indicator and the photoinitiator. Samples were irradiated at a wavelength of 365 nm, the wavelength at which the photostability of TBPB had been previously ensured. Wavelength selection was provided by a Philips high pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostated at 30°C and the solutions were nitrogen saturated ( $\ll 5 \text{ ppm O}_2$ ). The absorbed light intensity was measured using an International Light Model 700 radiometer previously calibrated by the Aberchrome 540 actinometer [5] and was used to relate the digital display of the radiometer to an absolute value for the amount of incident light per unit of time. The reaction between TBPB and the generated HCl was monitored by the reduction in absorbance at the wavelength maximum of the indicator (615 nm), for various irradiation times.

### 2.3. Cationic polymerisation

Cyclohexene oxide was distilled from CaH<sub>2</sub>, under nitrogen, and used fresh for polymerisation. The polymerisation mixture was composed of equivalent concentrations ( $3.87 \times 10^{-3} \text{ mol dm}^{-3}$ ) of monomer and photoinitiator. The initiator was dissolved directly with the monomer and deaerated with whitespot nitrogen ( $\ll 5 \text{ ppm O}_2$ ) before

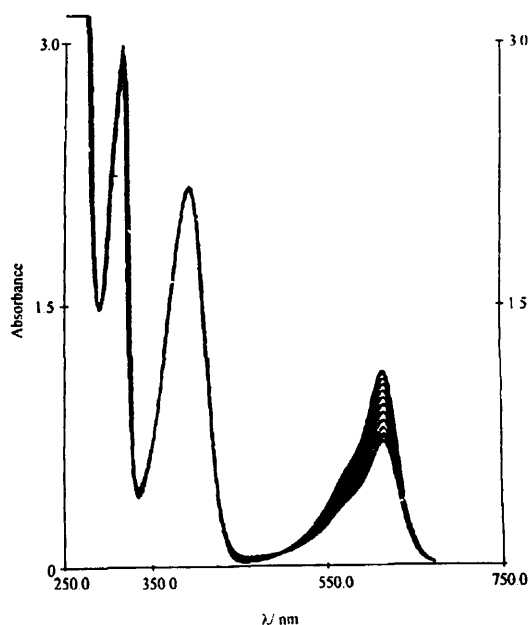


Fig. 1. The photoacid: TBPB complexation, monitored by UV-VIS. Absorption spectroscopy for 1-chloro-2-methyl-4-*n*-propoxythioxanthone (II) in methanol with TBPB ( $1.85 \times 10^{-5}$  M) at different irradiation times.

irradiating with a high pressure Hg lamp (400 W, Honle UV, Birmingham, UK) for various times. After the allocated, specific irradiation time, the samples were kept in the dark for 30 min to allow any 'dark reaction' to take place [7]. The subsequent polymerised material was precipitated from methanol, collected and dried. The final weight of the polymerised material was noted for the various samples, irradiated at different times.

### 3. Results and discussion

The dehalogenation of the derivatives of thioxanthone, in the presence of methanol, has been monitored spectrophotometrically utilising TBPB as an acid probe. The reaction is between one mole of dye to one mole of photo-generated acid (Scheme 1b). The progress of acid generation may thus be monitored through the observed decrease in the absorption maximum at 615 nm for TBPB, with irradiation time as shown in Fig. 1. The extent to which dehalogenation occurs is shown in Fig. 2, for each of the thioxanthone derivatives. From the slope, the absolute quantum yields of acid generation were calculated (Table 1). The results indicate that II showed the highest quantum yield of acid generation while IV exhibited the lowest yield. The dehalogenation activity follows the order: Compounds II > I > III >> IV and may be related to the corresponding substituents attached to the thioxanthone nucleus. In the case of Compound II, which shows the highest quantum yield, the result is most likely to be due to the presence of the methyl group in the two-position, which would act as an electron donor and, in turn, aid in the dehalogenation process. In comparison, Compound I is the next highest acid generator, a finding which is in agreement with the photopolymerisation results [2,3]. The lower dehalogenation activity of 1-chloro-4-benzyloxythioxanthone (III), compared to Compounds I and II, is likely to be due to the presence of the phenyl group. The electron donation of the bridge methylene group in the 4-position is likely to be shared between the thioxanthone nucleus and the delocalisation over the phenyl group. This would have some influence on the transition state, leading to the aryl radical product. Compound IV, showed the least dehalogenating activity and is possibly due to the presence of the acetyloxy substituent which is a poor electron donor. Hence, delocalisation of electrons over

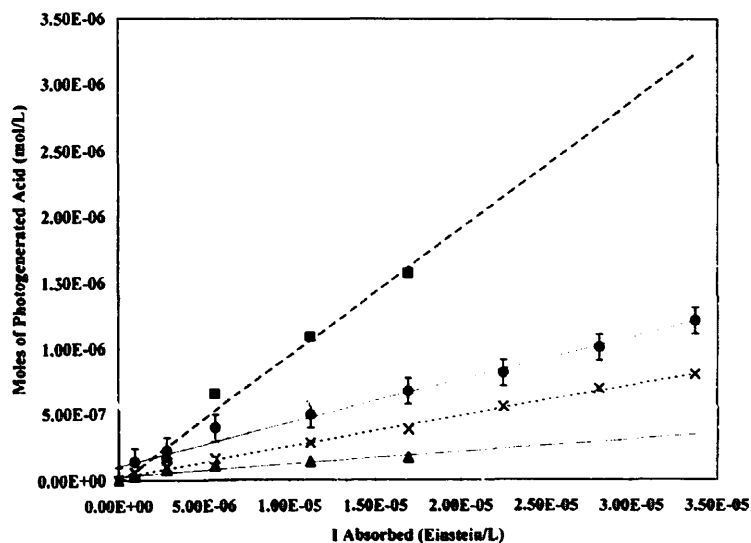


Fig. 2. Moles of photogenerated acid versus intensity ( $I$ ) observed at 365 nm irradiation for: (●) 1-chloro-4-*n*-propoxythioxanthone (I); (■) 1-chloro-2-methyl-4-*n*-propoxythioxanthone (II); (×) 1-chloro-4-benzyloxythioxanthone (III); and (Δ) 1-chloro-4-acetyloxythioxanthone (IV).

Table 1  
Quantum yield of acid generation for the selected derivatives of thioxanthone

Thioxanthone derivative	Absolute $\phi_{acid}$
<b>I</b>	0.036
<b>II</b>	0.237
<b>III</b>	0.023
<b>IV</b>	<0.003

Table 2  
Weight increases of the polymerised material against irradiation time for derivatives of thioxanthone. Irgacure 261 was used as a reference and under equivalent conditions the amount of polymer produced was 3.11 g

Irradiation time (h)	Weight of polymerised material (mg)			
	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>
0.5	120.0	50.3	154.3	131.4
1.0	319.8	122.3	288.6	124.1
6.0	887.5	241.8	317.6	121.1

the thioxanthone ring is limited as well as the subsequent dehalogenation of the chlorine atom. The dehalogenation results are in line with our previous photopolymerisation studies [2,3] which showed, under UV irradiation, a similar trend as above.

Since the selected thioxanthone derivatives showed the generation of acid upon steady-state photolysis, a study was undertaken to investigate the activity of these compounds as cationic photoinitiators in the presence of cyclohexene oxide. A commercially available cationic initiator, Irgacure 261, was used as a reference to compare the activity of the other derivatives of thioxanthone. Table 2, summarises the increases in the observed weight of the polymerised material obtained upon increasing the irradiation time.

The observed weight increases for the polymerisation of CHO, are in line with the dehalogenation results, with the exception of compound **II** which showed much higher generation of acid. Compounds **I–III** show a steady increase in weight of the polymerised material with increase in irradiation time as seen in Table 2. The data correlate well with the results listed in Table 1 for the acid generation by photolysis. However compound **IV**, shows a slight decrease in weight of the polymerised material with increasing irradiation time. This is indicated by the low quantum yield of acid generation established from the results above. In the case of compounds **I** and **III**, the final weight of polymerised material is higher than that for compound **II**. The overall concentration of photoacid generated in compound **II** is much higher than for any of the other derivatives and, consequently, competing reac-

tions such as substitution to other parts of the ring may have an important role. This is reflected in the lower final weight of the polymerised material observed.

#### 4. Conclusion

The steady state photolysis study of the derivatives of 1-chlorothioxanthone has shown that apart from hydrogen-atom abstraction, a dehalogenation process also takes place during photolysis. The *in situ* spectrophotometric method of detecting the photoacid generated in the presence of the sodium salt of tetrabromophenol blue (TBPB), has shown the extent of the dehalogenation process for each of the selected derivatives. The overall study shows that the 1-chloro-4-cxy derivatives are more effective at dehalogenation than are the 1-chloro-4-acyloxy derivatives of thioxanthone. This is reflected by the results of the quantum yield of acid generation as well as by the increases in weight of the polymerised material, obtained by photoinitiated, cationic polymerisation of cyclohexene oxide.

The study shows that such derivatives of thioxanthone have the potential to generate acid under irradiation and have the advantage of their high absorptivity in the near UV to visible region. This may have a dual role in the initiation of polymerisation where both radical and cationic initiation may take place. Further study in this area is in progress and will form the basis of future communication.

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