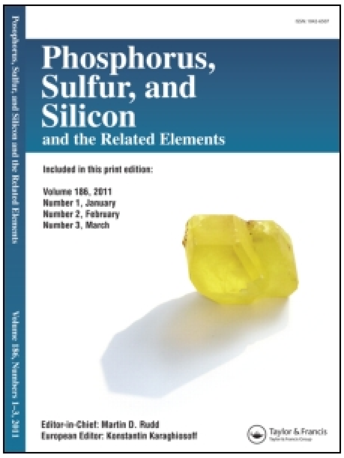

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THE ELECTROCHEMICAL STUDIES ON FIVE WATER-SOLUBLE POLYMERIZATION INITIATORS BASED ON THE THIOXANTHONE STRUCTURE

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THE ELECTROCHEMICAL STUDIES ON FIVE WATER-SOLUBLE POLYMERIZATION INITIATORS BASED ON THE THIOXANTHONE STRUCTURE

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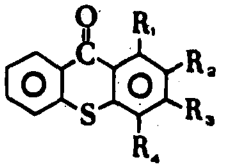
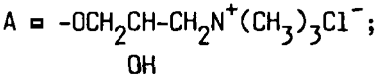
ABSTRACT Polarographic and spectroscopic studies have been carried out on a set of five photoinitiators based on the thioxanthone structure. Analysis of the obtained results enabled to explain the structural effects on the activity of these photoinitiators and acid - base equilibria occuring in their aqueous solutions.

INTRODUCTION

Recently several types of ketons acquired importance as photoinitiators of unsaturated hydrocarbon polymerization[1-2]. These compounds can carry the cationic solubilizing group as it is demonstrated below for five studied by us derivatives of thioxanthone.



R_1, R_2, R_3, R_4 = A or B or C



$$A = -OCH_2\underset{OH}{CH}-CH_2N^+(CH_3)_3Cl^-;$$

$B = CH_3$, $C = H$

Table I. Formulas of the water-soluble TXS

product	R_1	R_2	R_3	R_4
1	C	A	B	B
2	B	A	C	B
3	C	A	C	C
4	B	C	C	A
5	C	C	C	A

Other authors[3] compared the rates of polymerization of acrylamide in aquous solutions in the presence of (1),(2),(3),(4),(5) thioxanthones. Anfortunately the effect of substitution of methyl groups and ionic substituent was not fully explained by them. Therefore the aim of the present study was to explain acid-base equilibria occuring in aqueous solutions of the studied thioxanthones in the full range of pH.

EXPERIMENTAL

All five studied thioxanthones were manufactored by International Bio-Synthetics in United Kingdom. Polarography was carried out for 0.001 M aquous solution of photoinitiators buffered by Britten buffer. A polarograph PPW-I made by Elpan in Poland and the standard three electrode system were used. IR Spectra were recorded using IR spectrometer of type specord 71 IR. ^{1}H.n.m.r. spectra were recorded on a Bruker 400 instrument using CD_3OD solvent and Me_4Si as an internal standard.

RESULTS AND DISCUSSION

The reduction of all studied thioxanthones is a two electron process and it leads to the corresponding to them derivatives of thioxanthone-9-ol. Additionally the half peak reduction potentials for all compounds drawn in the function of pH have shown a linear growth with the increase of pH. However the diagrams of changes of the limiting diffusion current - i_d drawn in the function of pH are entierly different for compounds (1), (3) and (5) in comparison with (2) and (4). Those substituted in position 1 (it means (2) and (4)) exhibit a single wave for each value of pH. Remaining three photoinitiators reveal the series of two closed to each other two electron waves. The appearance of such two separate waves has been attributed to the coexistence in the aqueous solution of two different forms of the studied salt (it means ketone and its hydrate). The formation of the analogous hydrate has been previously described for 1-methyl-4-

-piperidone hydrochloride[4]. Additionally IR spectra of the samples of (1),(3) and (5) crystalised from strongly acidic aqueous solutions have shown weakening of the absorption band at aproximately 1620 cm^{-1} and a considerable growth of the absorption band at 3400 cm^{-1}. 3,4-dimethyl-2-QTX (1) reveals a set of two close to each other polarographic waves. I_d for the first wave attributed to ketone nearly does not change with pH, whereas i_d for the second wave decreases sharply with increase of pH. It reaches a constant value for pH eaual to aprox 7. This value of pH corresponds to the minimum concentration of the hydrate in the solution and to the highest activity of 3,4-dimethyl-2-QTX as a photoinitiator[3]. The analogous behaviour was also exhibited by compounds (3) and (5). Also the comparison of ^1H.n.m.r. spectra of the dried in high temperature sample of 3,4-dimethyl-2-QTX and the sample of the same compound obtained after slow crystallization from water confirmed the coexistence of the hydrate and ketone in the aqueous solution. The first one shows single peaks at 2.37, 2.48 and 7.94 p.p.m. which correspond respectively to the chemical shifts of methyl groups substituted in position 3 and 4 and to the aromatic proton in position 1. Whereas analogous peaks for the second sample are formed by two very close peaks. The quotient of their high is constant and aquals to 2.5:1, which corresponds to the ratio of concentrations of ketone and its hydrate in the studied sample. Finally we were anxious to determine the impact of the sulfoxide group on the formation of hydrates by studied photoinitiators. Again 3,4-dimethyl-2-QTX (1), which is treated by us as the model compound representative for two other thioxanthones (3) and (5), was chosen. Its oxidation to the sulfoxide has been carried out in aqueous solution at platinium electrode at potential 1.25 vs.SCE.

The discussed reaction was a two electron process. IR spectrum of the obtained sulfoxide has shown weakening of the absorption band corresponding to carbon to oxygen double band frequency at aproximately 1670 cm^{-1} and the growth of the absorption band at 3400 cm^{-1} characteristic for OH streching frequency in comparison with 3,4-dimethyl-2-QTX. Presumably the molecule of this sulfoxide occurs in aqueous solution predominately in the form of hydrate. Therefore we assume it should demonstrate much lower activity as the photoinitiator in reactions of polymerization of unsaturated hydrocarbons than the starting thioxanthone.

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