THE ELECTROCHEMICAL STUDIES ON WATER-SOLUBLE POLYMERIZATION INITIATORS BASED ON THE 9H-THIOXANTH-9-ONE STRUCTURE

This paper reports polarographic studies on a group of five water-soluble initiators of polymerization, the derivatives of 9H-thioxanth-9-one. Their reduction on the mercury cathode is a two-electron process, and it leads to the corresponding derivatives of 9H-thioxanthen-9-ol.

The respective photoinitiators substituted by the methyl group in position 1 exhibit only single waves whereas the others exhibit two waves. The appearance of the second wave is attributed to formation of a hydrate by the studied 9H-thioxanth-9-ones. The analysis of changes in the limiting diffusion current for aqueous solutions of those compounds as a function of pH enable us to explain the effect of methylation and ionic substituent on the acid-base equilibria occurring there.

INTRODUCTION

Recently, several types of ketones have acquired some importance as photoinitiators for the unsaturated hydrocarbon polymerization [1]. The application of some ionized derivatives of benzophenone or benzil, absorbing the UV light between 200 and 350 nm, has been reported for grafting water-soluble vinylic monomers on to cellulose or wool [2]. However, in spite of their reactivity, these photoinitiators are active only then when they

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are irradiated at 365 nm or below in the UV spectral range, therefore their use in many technical applications which requires the illumination in the blue and of the visible spectrum is impossible. In order to overcome somehow these drawbacks, several research groups had synthesized some 9H-thioxanth-9-one derivatives which used in conjunction with activators, were reported to be particularly suitable for curing some coating formulations between 350 and 450 nm.

These compounds carry a single cationic solubilizing group as it is shown below for five derivatives of 9H-thioxanth-9-one studied by us.

\[
R_1, R_2, R_3, R_4 = A \text{ or } B \text{ or } C \\
A = \text{O-CH}_2\text{-CH-CH}_2\text{N}^+\text{(CH}_3\text{)}_3\text{Cl}^-; \ B = \text{CH}_3; \ C = \text{H}
\]

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>(R_1)</th>
<th>(R_2)</th>
<th>(R_3)</th>
<th>(R_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>A</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>A</td>
<td>C</td>
<td>B</td>
</tr>
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<td>C</td>
<td>A</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>C</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>A</td>
</tr>
</tbody>
</table>

Used in this work symbols (1) - (5) indicate respectively: (1) - 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethylammonium-1-propanium chloride,
(2) - 2-hydroxy-3-(1,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethylammonium-1-propanium chloride,
(3) - 2-hydroxy-3-(9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethylammonium-1-propanium chloride,
(4) - 2-hydroxy-3-(1-methyl-9-oxo-9H-thioxanthen-4-yloxy)-N,N,N-trimethylammonium-1-propanium chloride,
(5) - 2-hydroxy-3-(9-oxo-9H-thioxanthen-4-yloxy)-N,N,N-trimethylammonium-1-propanium chloride.

Loufinot at al. [3] have reported that introduction of the ionic substituent into the 9H-thioxanth-9-one skeleton leads to very high rates of polymerization. Further substitution by the methyl groups into available positions of the benzene ring carrying already the ionic substituent results in profound changes in the reactivity. The performance of compounds (2) and (4) which carry a methyl in position 1, and which are apt to undergo the keto-enol tautomerism in their excited states, does not seem to be diminished by such an intermolecular deactivating process.

Loufinot at al. [3] have also compared the rates of polymerization ($R_p$) of acrylamide in aqueous solutions, in the presence of thioxanthones (1), (3), (4), (5).

It seems to be quite interesting that $R_p$ displays its highest value for compounds (4) and (5), is much lower for compound (1), and is lowest for compound (3). Additionally, 2-hydroxy-3-(1,3,4-trimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethylammonium-1-propanium chloride which is similar to compound (2) studied by us, demonstrates the highest activity as photoinitiator, in comparison with the other compounds mentioned. Unfortunately, the effect of substitution by the methyl groups and the ionic substituent was not explained in full. Additionally, all the five studied photoinitiators (1)-(5) exhibit the loss of activity in acidic and neutral media. No definite reason was given as to account for this effect. Therefore, the aim of the present study is to explain the acid - base equilibria occurring in aqueous solutions of 9H-thioxanth-9-ones studied within the possibly full range of pH. We have hoped that scrutiny of such the equilibria would enable us to explain the above mentioned structural effects.
EXPERIMENTAL

All studied compounds (1)-(5) were manufactured by International Bio-Synthetics in the United Kingdom.

Polarography was carried out for 0.001 M aqueous solutions of five the title photoinitators. A sample for the measurement was always prepared by dilution of 1 cm$^3$ of 0.025 M solution of 9H-thioxanth-9-one studied by addition of the Britten buffer up to the volume of 25 cm$^3$ (pH was varied from 2 to 10). A polarograph PPW-1 was made by Elpan in Poland, and the three-electrode system consisting of: a saturated calomel electrode, a dropping mercury electrode and a compensation electrode formed by the "bottom" mercury were used 0.1 M KCl was used as a supporting electrolyte. IR spectra were recorded using an IR photospectrometer of the Specord 71 IR type.

RESULTS AND DISCUSSION

We have previously found [4] that the coulometric reduction of compound (1) in its aqueous solution at the mercury electrode was a two-electron process occuring according to the mechanism given below:
Fig. 1. Changes in the limiting diffusion current, \( i_1 \), and the half-peak reduction potential, \( E_1 \) (attributed to the ketone reduction), and the corresponding values, \( i_2 \), \( E_2 \) (attributed to the hydrate reduction) drawn as a function of pH for \( 1 \cdot 10^{-3} \) M aqueous solutions of compound (1) buffered by the Britten-Robinson buffers, obtained from polarographic reduction of (1) in the three-electrode system.

Also the analysis of the slope of \( \log \frac{i_d - i}{i} \) drawn as a function of the electrode potential for all the polarographic waves recorded for the five 9H-thioxanth-9-ones studied indicates a two-electron mechanism for this reduction. Therefore, we have assumed that the reduction of all the 9H-thioxanth-9-ones studied by us leads to the corresponding derivatives of 9H-thioxanthene-9-ol. Additionally, the half-peak reduction potentials for all the compounds studied drawn as a function of pH shows a linear growth with the increase of pH (see Fig. 1-5). However the diagrams of changes in the limiting diffusion current - \( i_d \) drawn as a function of pH are entirely different for all the photoinitiators studied. Those substituted in position 1 (i.e. compounds (2)}
Fig 2. Changes in the limiting diffusion current, \( i \), and half-peak reduction potential, \( E_{1/2} \), drawn as a function of pH for 1 \( \cdot \) 10\(^{-3} \) M aqueous solution of compound (2) buffered by the Britten-Robinson buffers, obtained from polarographic reduction of (2) in the three-electrode system and (4) - see Tab. 1) exhibit a single-wave for each value of pH. The measured values of \( i_d \) for compounds (2) and (4) decrease gradually with the increase of pH. Only for acidic solutions, i.e. below pH = 3, a deviation from linearity of \( i_d \) is observed (see Fig. 2 and 4). This effect is presumably due to protonation
of the ketone. The remaining three photoinitiators reveal a series of two-electron waves close to each other. The appearance of such two separate waves is attributed to a coexistence of two different forms of the studied salt in the aqueous solutions (i.e. ketone and its hydrate) according to the equilibrium given below, where:

\[
\begin{align*}
R_1 &= R_2 = H \text{ or } CH_3 \\
&\quad Cl^- + H_2O(H^+) \quad \text{Cl}^-
\end{align*}
\]

The formation of the analogous hydrate has previously been described for l-methyl-4-piperidone hydrochloride [5]. The first wave for which the limiting diffusion current was denoted as \(i_d\) was attributed to the reduction of ketone, whereas the second one with the limiting diffusion current \(i_{d_2}\) - to the reduction of its hydrate. Additionally, the IR spectra of samples of compounds (1), (3) and (5) recrystallized from strongly acidic aqueous solutions have shown a weakening the absorption band at ca. 1670 cm\(^{-1}\), which is characteristic of the C = O double bond stretching frequency, and a considerable growth of the absorption band at 3400 cm\(^{-1}\) characteristic of the OH stretching frequency. Contrariwise, compounds (2) and (4) have not shown the analogous behaviour.

Compound (1) reveals two close polarographic waves. \(I_{d_1}\) for the first wave attributed to ketone nearly does not depend on
pH (see Fig. 1), whereas $i_{d_2}$ of the second wave decreases quickly with the increase of pH. It reaches a constant value for pH equal to clearly ca 7.

**Fig. 3.** Changes in the limiting diffusion current, $i_1$, and half-peak reduction potential, $E_1$ (attributed to the ketone reduction) and the corresponding values, $i_2$, $E_2$ (attributed to the hydrate reduction) drawn as a function of pH for $1 \cdot 10^{-3}$ M aqueous solution of compound (3), buffered by the Britten-Robinson buffers, obtained from polarographic reduction of (3) in the three-electrode system.
Fig. 4. Changes in the limiting diffusion current, $i$, and half-peak reduction potential, $E_{1/2}$, drawn as a function of pH for $1 \cdot 10^{-3}$ M aqueous solutions of compound (4), buffered by the Britten-Robinson buffers, obtained from polarographic reduction of (4) in the three-electrode system.

This value of pH would correspond to a minimum hydrate concentration in the solution, and as it is known from literature [3], at this pH compound (1) reveals the highest activity as the photoinitiator. Also polarography of compound (3) reveals a set of two waves (Fig. 3). Neither $i_{d1}$ nor $i_{d2}$ display (any) considerable changes for pH below 7. However, for pH above 7 only a single wave could be observed. Within this region of pH, the
Fig. 5. Changes in the limiting diffusion current, $i_1$, and half-peak reduction potential, $E_1$ (attributed to the ketone reduction), and the corresponding values, $i_2 E_2$ (attributed to the hydrate reduction) drawn as a function of pH for $1 \cdot 10^{-3}$ M aqueous solutions compounds (5), buffered by the Britten-Robinson buffers, obtained from polarographic reduction of (5) in the three-electrode system.
limiting diffusion current being now a sum of \( i_{d1} + i_{d2} \), gradually increases with the increase of pH. Presumably, also the \( \text{OH}^- \) ions would catalyse here formation of the hydrates. Finally, the most unique set of polarographic waves was observed for compound (5) (Fig. 5). For pH above 5, the second wave disappears. This indicates that concentration of the hydrate would be very low here, therefore the activity of the photoinitiator studied is higher as compared with that in acidic solutions.

REFERENCES


