Application of Oscillographic Polarography in Photochemistry (I) Pyrimidines

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The oscillopolarographic behaviour of aqueous solutions of a number of pyrimidines have been studied after the ultraviolet irradiation at 2.537 Å. The oscillopolarographic results were compared with spectrophotometric data, published by other authors.

The majority of results from the branch of photochemistry of biologically important substances e. g. nucleic acids, proteins and their compounds had been derived from the post-irradiational changes of their ultraviolet absorption spectra [1, 2].

In the following communication some possibilities are quoted for the application of alternating current oscillographic polarography in the photochemistry of a number of pyrimidines [3—6].

Experimental

Materials and Methods

The compounds studied were: uracil, 5-hydroxymethyluracil, dihydrouracil, uridine, thymine, cytosine, isocytosine, 5-hydroxymethylcytosine and orotic acid. The electrolytes used for the oscillopolarographic analyses were: sodium hydroxide, sulphuric acid and amonium formate in molar concentrations. In our experiments 0.001 M aqueous solutions of investigated compounds were used. Solutions were irradiated by low pressure mercury lamp Philips TUV, 30 W, with the emission maximum at 2.537 Å, mostly at a distance of 5 cm.

For our studies a Polaroscope P 524 (Křižík, Praha) was used, with a mercury dropping electrode and the usual polarographic cells. The oscillograms were registered photographically [7].

Results

The changes passing in the solutions of investigated compounds under the influence of UV irradiation were manifested oscillopolarographically by the progressive decrease of the originally visible indentations up to their disappearance. Some of the reaction products that arose, formed their own additional oscillopolarographic indentations. In this way, it was possible to follow both qualitatively and quantitatively the time course of some photochemical reactions [3].

After the UV irradiation of uracil solution (Fig. 1*a*) a number of new cathodic indentations appeared on the oscillogram in a sodium hydroxide medium (Fig. 1*b*, indentations *I*, *II*, *III*).

The oscillopolarographic indentations corresponding with *II* and *III* (Fig. 1*b*) produced by UV irradiated uracil, resulted also after the UV irradiation of uridine, cytosine and isocytosine solutions.

After the UV irradiation of thymine (Fig. 2*a*), 5-hydroxymethyluracil, dihydrouracil, 5-hydroxymethylcytosine and orotic acid solutions, the indentations *II* and *III*, in the middle part of the oscillogram were never observed (Fig. 2*b*).

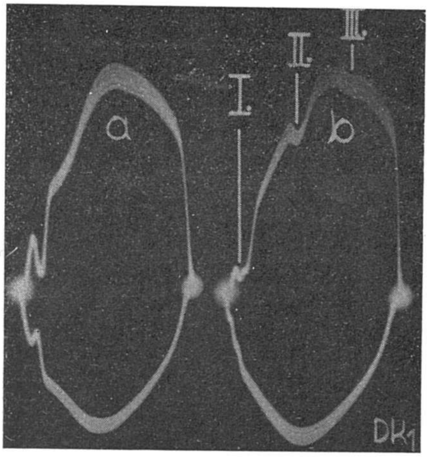


Fig. 1. $dE/dt = f(E)$ curves of 10^{-3} M uracil in 1 M-NaOH.
a) before the UV irradiation; *b*) after 4 hours of UV irradiation.

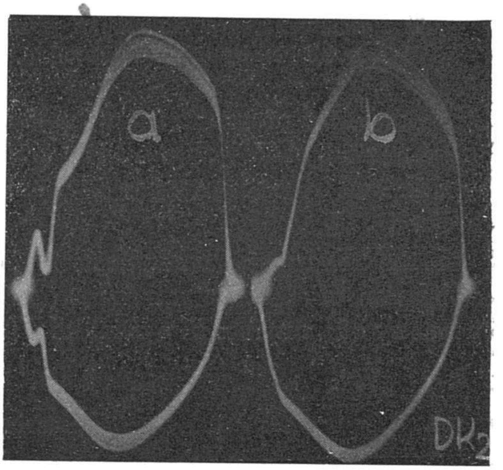
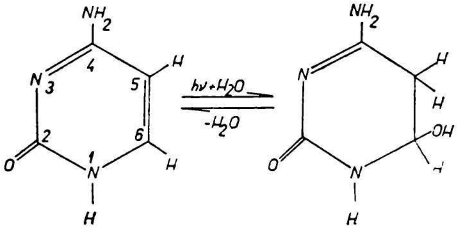


Fig. 2. $dE/dt = f(E)$ curves of 10^{-3} M thymine in 1 M-NaOH.
a) before the UV irradiation; *b*) after 8 hours of UV irradiation.

In the next experiments the frozen solutions of uracil and thymine were irradiated with the UV light and thawed samples were analysed oscillopolarographically again. Neither the cathodic indentation *II*, nor *III* in the middle part of the oscillogram of uracil, appeared under these experimental conditions. Likewise by thymine only, the indication of the indentation *I* (Fig. 1*b*) and decrease of the original indentation near the left marginal point of the oscillogram (Fig. 2*a*) were observed. The complete photochemical regeneration of original indentations has been ascertained oscillopolarographically after 7 minutes of the additional UV irradiation of thawed samples of uracil and thymine at pH 12.

Discussion

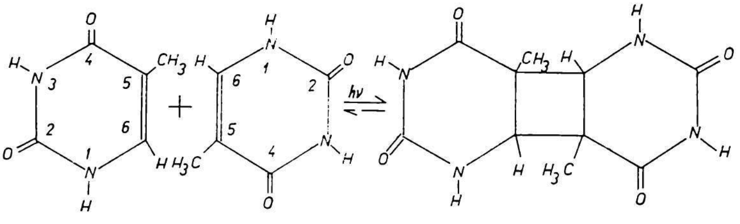
The formation of new cathodic indentations *II* and *III* (Fig. 1*b*) namely in the middle part of the oscillogram of some pyrimidine solutions after the UV irradiation was probably connected with the reactions related to the photochemical hydration of the 5.6 double bond of the pyrimidine ring, according to S. Y. Wang and co-workers [8—10]:



Schema 1. Photochemical hydration of uracil caused by the UV irradiation in aqueous solution.

The pyrimidine compounds possessing 5 or 6 substituents do not yield spectrophotometrically detectable photo-hydration of the 5.6 double bond [11]. The oscillopolarographic results agree well with spectrophotometric findings, because the UV irradiated 5 or 6 substituted pyrimidines produced also no additional cathodic indentations similar to *II* or *III*.

A. Śmietanowska and D. Shugar [12] reported that via the procedure of R. Beukers and W. Berends [13] the reactions occuring during the UV irradiation of frozen solutions of uracil and thymine led both to the formation of dimers of these compounds:



Schema 2. Formation of thymine dimer after the UV irradiation of frozen solution of thymine.

By D. Shugar and J. J. Fox [14] the additional UV irradiation of these dimers at alkaline pH 12 and 13 was found to result in dimer dissociation with a concomitant quantitative regeneration of the alkaline absorption spectra of uracil and thymine.

The oscillopolarographic behaviour of thawed samples of uracil and thymine dimers solutions, irradiated additionally with the UV light at alkaline pH entirely corresponds to the photochemical regeneration of the original monomers [14].

As to electrochemical nature of the indentations resulting after the UV irradiation of uracil and some other pyrimidine derivatives in a sodium hydroxide medium, the so called oscillopolarographic artefacts are presumed according to M. Heyrovský [15].

The alternating current oscillographic polarography means thus a new, speedy and experimentally not very pretentious analytical method in the branch of photochemistry. It may therefore be assumed that it will be possible to extend in this way a knowledge of the course of some photochemical, and probably also radiation-chemical reactions.

The author is indebted to Dr. E. Paleček and Dr. J. Janík from the Biophysical Institute of th Czechoslovak Academy of Sciences in Brno, for some pyrimidine compounds used for this study.

VYUŽITIE OSCILOGRAFICKEJ POLAROGRAFIE VO FOTOCHÉMII (I) PYRIMIDÍNOVÉ DERIVÁTY

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Skúmalo sa oscilopolarografické chovanie vodných roztokov niektorých pyrimidínov pred ožiarením a po ožiarení ultrafialovým žiarením o vlnovej dĺžke 2537 Å. Oscilopolarograficky zistené výsledky sa porovnávali s výsledkami iných autorov, získanými spektrofotometricky v ultrafialovej oblasti.

ПРИМЕНЕНИЕ ОСЦИЛЛОГРАФИЧЕСКОЙ ПОЛЯРОГРАФИИ В ФОТОХИМИИ (I) ПРОИЗВОДНЫЕ ПИРИМИДИНА

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Исследовалось осциллополярографическое поведение водных растворов ряда пиримидиновых составляющих нуклеовых кислот и родственных веществ после облучения ультрафиолетовым светом (2537 Å). Результаты, полученные осциллополярографическим анализом, были сопоставлены с результатами, полученными спектрофотометрическим путем другими авторами.

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