Detection of an Oscillation Stage during the Photolysis of Spiropiperidine–Benzopyran Solutions in Toluene

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Photolysis of spiropiperidine–benzopyran solutions in toluene by impulse laser irradiation has an intermediate fast oscillation stage detected by changes in the quality factor of a 3 cm cavity resonator containing the sample; these changes are asynchronous relative to irradiation.

The photolysis of solutions of spirochromes which results in their colouring has been repeatedly studied. However, the detailed mechanism of the process has not been elucidated. In particular, it has been assumed[1] that the formation of stereoisomers responsible for solution colouring during photolysis involves an unknown intermediate product, for example, some open form of the original spirochrome, below referred to as “Open”. According to data from various authors (see ref. 1 and references cited therein), the “Open” form can interact with water present in the solvent giving a new form, “Sel$^+$”.

It could be assumed[2] that “Sel$^+$” might compose a fragment with an increased dipole moment with OH^- as the counterion. The purpose of the present study is to detect the formation of (even short-lived) dipoles “Sel$^+$–OH$^-$” during the photolysis of compounds of this class. The pulse method of detecting the photoresponse of microwave absorption, which is suitable for studying solutions, crystals and micro-dispersive systems, was supposed to be effective in this case. However, the results obtained in the present work turned out to be unexpected.

Two methods were used for detecting the processes occurring in the sample exposed to light: i, the impulse method of recording the microwave frequency (MWF) absorption photoresponse in the 3 cm region, and ii, quasi-stationary measurement of the quality factor of a loaded cavity resonator (the Q-factor), Q_L, in the same region.

The impulse method for the measurement of microwave frequency absorption has been described in ref. 3. We applied the scheme with the recording of MWF power P reflected from the resonator containing the sample. Changes in the samples caused by light were monitored by the photoresponse $P(t)$ (where t is the time). The method of analysing the dependence of P on the frequency of the MWF generator allowed us to record both the changes in $Q_L(t)$ of the loaded resonator and the variation of its resonance frequency, $f_0(t)$, and, thus, to separate the components of the photoresponse $P_Q(t)$ and $P_{f_0}(t)$.[4]

A “Panoramic analyser of KSVNs and attenuations” R2-65 was used for steady state measurements of Q_L. The technique made it possible to measure the Q-factor of the resonator 1 min after illumination of the sample was stopped. The relative error of Q_L measurements did not exceed 3%.

A LGI-505 laser (pulse duration 8 ns, wavelength $\lambda = 337$ nm, maximum “intensity” $7.5(\pm 3) \times 10^{14}$ phot cm^{-2} imp^{-1}, diameter of the illuminated spot 0.4 cm) was used to generate the photoresponse. To stabilize the light pulse intensities the periodic mode of laser operation was used. The required number of pulses was provided by an electromechanical shutter. A frequency meter was used for counting the light pulses affecting the sample. The absolute light intensity was measured by a thermocouple.

The samples, namely, 10^{-3}–10^{-5} M solutions of spiropiperidine–benzopyran[†] (PIP) in toluene, were poured in quartz ampoules and placed into the resonator. The sample volume was $\simeq 8 \times 10^{-2}$ cm^3.

When such a solution of PIP was affected by a sufficient number of laser pulses it underwent a marked colouring, in agreement with the results in ref. 1. On the other hand, many attempts at selecting conditions suitable for observing the photoresponse (method 1) of microwave absorption by the PIP solution in toluene to the action of laser pulses (*i.e.*, changes in solution concentration, light intensity and frequency of the microwave generator) have been made. However, the expected pulse signal could not be detected.

Therefore, an attempt was made to detect changes in the Q-factor of the resonator due to accumulation of stable photolysis products (method 2). The Q-factor varied under exposure to light. Fig. 1 shows the dependence of the Q-factor of the resonator on the number of photons during UV light pulse irradiation of a 10^{-4} M solution of spiropiperidine–benzopyran in toluene. The hollow circles in Fig. 1 correspond to a sample when exposed to light and the solid circles to that when the light is cut off. Every experimental point is averaged from three measurements. Here the light intensity is 7.5×10^{14} phot cm^{-2} imp^{-1}. As seen from Fig. 1, the Q-factor dependence is neither monotonous nor synchronous with laser pulses. The action of the first light pulses decreases the Q-factor, and the following ones increase it almost to the initial value. Oscillations are not observed when the laser

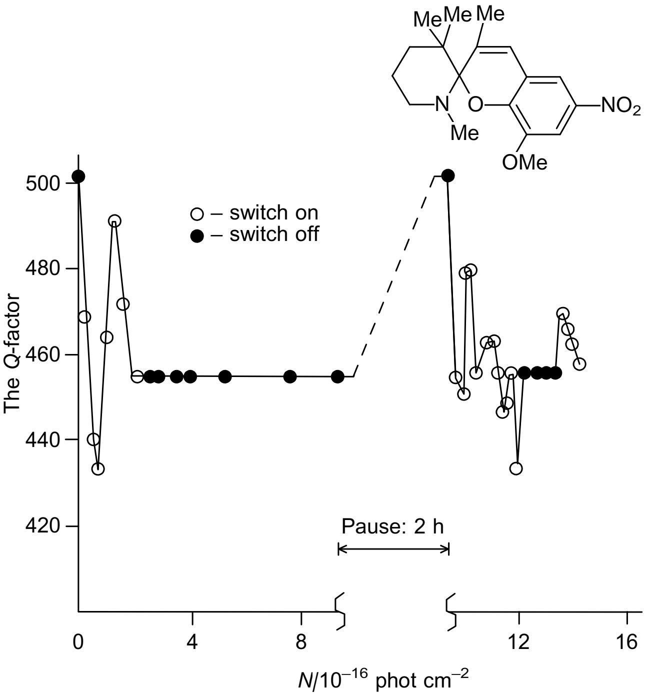

Fig. 1 The dependence of the quality factor of a loaded cavity resonator on the number of photons under impulse irradiation. A 10^{-4} M solution of spiropiperidine–benzopyran in toluene is used as the sample. Laser wavelength $\lambda = 337$ nm, light intensity 7.5×10^{14} phot cm^{-2} imp^{-1}, impulse duration 8–10 ns. Hollow circles: the sample is exposed to light; filled circles: light is cut off; “pause” corresponds to laser switching off.

[†] Spiropiperidine–benzopyran was kindly provided by Professor R. Guglielmetti (Groupe de Chimie Organique et Bioorganique, URA CNRS 1320, France) and Professor A. Samat (Research Department, CNRS, France).

beam is cut off but appear again when irradiation is continued.

Decreasing the light intensity (by attenuating light filters) diminishes the oscillation amplitude but only slightly affects their initial period ($\simeq 0.1$ μs) determined by multiplying the pulse duration by the number of laser pulses. When light intensity is decreased more than tenfold the oscillations are no longer detected.

Obviously, the oscillations observed are not related to a possible noise (electromagnetic induction) from laser operation because, firstly, the oscillations are not detected when the laser beam is cut off and, secondly, no oscillations are recorded in the pure solvent and they become vanishingly small during prolonged irradiation (more than 1000 pulses). The oscillations are also not related to the energy stored in the resonator because this process is attenuated at least during $\simeq 6Q_L/f_0 \simeq 3 \times 10^{-7}$ s but the Q-factor measurements are carried out much later, after $\simeq 10^2$ s.

The results of experiments at various PIP concentrations allow us to assume that the observed oscillations of the Q-factor of the resonator are caused by the formation of photolysis products with higher dipole moments than those of the original samples. Probably, the observed asynchronous oscillations of the Q-factor represent the oscillation nature of the photochemical process. Perhaps, when the fast stages are completed, some products "survive" until the time $\sim 10^2$ s when the Q-factor is measured.

Since the work of Belousov and Zhabotinskii[5,6] oscillating chemical reactions have been studied by many authors.[7–9] Photochemical reactions have also been widely considered but to a smaller extent[10] (see also references to the publications of J. Ross in ref. 10). The known schemes of photochemical oscillating reactions are based on the participation of excited states. We could propose a sequence of reactions providing oscillations in real time for the photolysis of PIP. To do this one can use, for example, the R4 scheme from ref. 10 or schemes of catalytic oscillators from ref. 9 supposing the formation of Spir* and (Spir·Spir*). However, it is unclear which intermediate product in such reactions has a high dipole moment resulting in the decrease in the Q-factor. We must also take into account: i, the influence of H_2O,[1] and ii, the oscillations of the Q-factor during impulse illumination (not in real time but on the dependencies on the dose).

To provide oscillations, one can assume reactions based on the model in refs. 11, 12, Scheme 1.

$$\begin{aligned}
\text{Spir} &\overset{h\nu}{\rightleftharpoons} \text{Open} && (1)\\
\text{Open} + H_2O &\rightarrow \text{Sel}^+ + OH^- && (2)\\
2\text{Open} + \text{Sel}^+ &\rightarrow 3\text{Open} + H^+ && (3)\\
OH^- + H^+ &\rightarrow H_2O && (4)\\
\text{Open} &\rightarrow \textit{cis} && (5)\\
\textit{cis} &\xrightarrow{h\nu} \text{Spir} && (6)\\
\textit{cis} &\xrightarrow{\text{hv}} \textit{trans} && (7)
\end{aligned}$$

Scheme 1

A numerical solution showed that Scheme 1 gives oscillations for both impulse and continuous illumination. However, this scheme is likely to be far from reality and can serve only as an illustration for the available experimental data. Therefore, it would be important to carry out the experiments with continuous illumination. However, it should be noted that at the light intensities required for the excitation of oscillations (10^{22}–10^{23} phot cm^{-2} s^{-1}), it seems difficult to carry out such experiments with continuous illumination of solutions.

A more complete presentation of the results of this study will be given in the next paper.

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