Detection of an oscillation stage during the photolysis of toluene solutions of spiropiperidinebenzopyran by oscillations of the quality factor of the cavity resonator

G. F. Novikov,[a]* *M. N. Koval'chuk,*[a] *N. A. Tikhonina,*[a] *R. Guglielmetti,*[b] *A. Samat,*[b] *and M. V. Alfimov*[a]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b]*Groupe de Chimie Organique et Bioorganique, URA CNRS,*
1320 Marseille, France.
Fax: 10 (339)126 9304

Photolysis of toluene solutions of spiropiperidinebenzopyran exhibits an intermediate fast oscillation stage detected by asynchronous (relative to the initial laser pulse irradiation at 337 nm) changes in the quality factor of the 3-cm band cavity resonator containing a sample.

Key words: photomerocyanines, spirochromes; chemical reaction, mechanism, kinetics; photochemistry.

The photolysis of solutions of spirochromes resulting in their coloring has been studied several times; however, the detailed mechanism of this process remains unclear. In particular, it is assumed[1] that the formation of stereoisomers, which determine the color of solutions during photolysis, involves an unknown intermediate product, for example, an open form of the initial spirochrome (*Open*). According to the data of different authors[1] (see also works cited therein), the *Open* form can react with water present in a solvent to form a new structure, Sel^+.

It can be assumed that the Sel^+ form reacts with the OH^- counterion to form a fragment with an increased dipole moment. The purpose of this work is to detect $Sel^+ \cdot OH^-$ dipoles during photolysis of compounds of this class. It has been expected that procedures based on registering photoinduced changes in the microwave absorption of a resonator containing a sample would be efficient. It is known that these methods are equally efficient for studying dipolar relaxation both in solutions and in microdispersed systems.

This approach was used for studying the photolysis of toluene solutions of spiropiperidinebenzopyran (PIP). The preliminary results of these studies are given in the previous publication (Ref. 2).

Experimental

Experimental procedure. Two procedures were used for detecting photoinduced changes in a sample: (1) a pulse procedure for detecting the photoresponse of the microwave absorption;[3] (2) quasisteady-state measurements of the quality factor of the loaded resonator in the 3-cm range. The first procedure is based on the use of a scheme for registering the microwave power (P) reflected from a resonator with a sample. Photoinduced changes in a sample were followed by the photoresponse $\Delta P(t)$ (where t is time). The procedure for analyzing the dependence of ΔP on the frequency of the microwave generator made it possible to detect both the change in the quality factor ($Q_L(t)$) of the loaded resonator and its resonance frequency ($f_0(t)$) and to thus separate components of the photoresponse $\Delta P_Q(t)$ and $\Delta P_{f_0}(t)$ (see Ref. 4).

An R2-65 scanning meter of VSWR and attenuations was used for steady-state measurements of the Q_L value. Changes in the quality factor of the resonator were detected 1 min after ceasing irradiation of a sample. An accuracy of measuring the absolute value of the quality factor by this method was not high; in addition, the Q_L value depends strongly of the volume of the sample and its position in the resonator. Therefore, only relative measurements of Q_L at the fixed position of the sample in the resonator were carried out. To increase the accuracy, the Q_L value was calculated as the mean value of several measurements (in the typical case of three measurements, the mean square error was ±2 %).

An LGI-505 nitrogen laser (pulse duration was 8 to 10 ns, $\lambda = 337$ nm, the maximum intensity was $9.5\ (\pm 3) \cdot 10^{14}$ photon cm^{-2} $pulse^{-1}$, the diameter of the irradiated spot was 0.4 cm) was used for excitation of the photoresponse. To increase the stability of the light intensity in a pulse, a periodic regime of the laser work was used (the frequency of pulses was 10 to 20 Hz), and the necessary number of pulses was yielded by an electromechanical shutter. Light pulses incident on the sample were counted by a frequency meter. The absolute light intensity was measured by a thermocouple.

Quartz tubes with samples, toluene solutions of spiropiperidinebenzopyran ($[PIP] = 5 \cdot 10^{-3}$ to 10^{-5} mol L^{-1}), were placed into the resonator, the volume of a sample being $\sim 8 \cdot 10^{-2}$ cm^3.

Experimental results. The action of a sufficient number of laser pulses ($>10^3$) resulted in noticeable coloring of a toluene

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1720—1724, September, 1995.

solution of PIP, which corresponds to the data obtained previously.[1] At the same time, despite multiple attempts, we failed to choose conditions (by changing the concentration of the solution, the light intensity, and the frequency of the microwave generator) for observation of the photoresponse of the microwave absorption (procedure 1). Therefore, we used procedure 2 for detecting changes in the quality factor of the resonator due to accumulation of stable products of photolysis. It was found that the quality factor of the resonator changed upon irradiation. First light pulses always decreased Q_L, next pulses increased it almost to the initial values, and then the quality factor decreased again and then increased gradually, decreasing the amplitude of the changes. When the laser beam was shielded, the changes in Q_L were very slow (with a characteristic time of ~10^3—10^4 s) or were not detected at all, and oscillations of Q_L were regenerated when irradiation was continued. Thus, the changes in the quality factor presented on a real time scale and detected in ~10^2 s after irradiation seemed chaotic and had no systematic character.

The results of measurements become more definite, if the experimental data are presented not in the real time scale, but as a function of the quality factor of the resonator on the total light energy (dose) absorbed by a sample. To demonstrate the effect of light irradiation, Figs. 1—4 show not only experimental values of the quality factor of the resonator for the irradiated sample (light points), but also control values of Q_L obtained with conditions under which measurements are continued but the light beam is specially shielded (dark points), *i.e.,* the arbitrary number of photons that could fall on the sample at the open shutter is plotted on the abscissa. Each experimental point in Figs. 1—4 is the mean value of three measurements, and the mean square measurement error is shown by vertical intersepts.

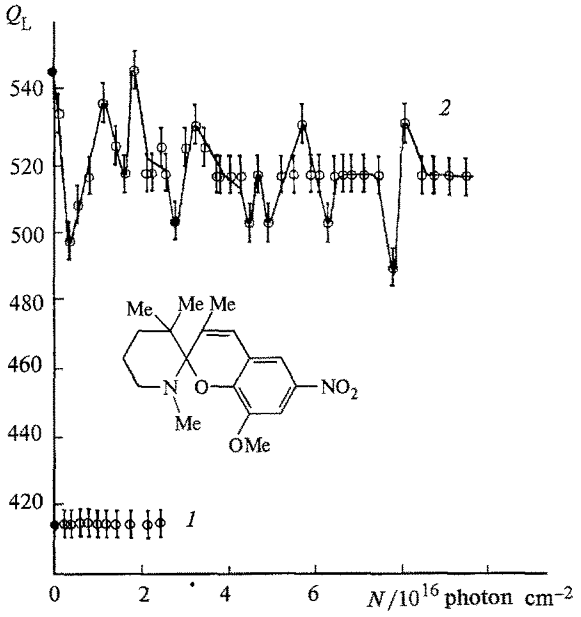

Fig. 1. Dependence of the quality factor of the loaded resonator on the number of photons during pulse irradiation of pure toluene (*1*) and a toluene solution of PIP ($C = 2 \cdot 10^{-5}$ mol L^{-1}) (*2*). The wavelength of the laser $\lambda = 337$ nm, the light intensity is $9.5 \cdot 10^{14}$ photon cm^{-2} pulse^{-1}. Here and in Figs. 2—4: dark circles indicate the situation when the light is switched off, and light circles show the case when the sample is irradiated.

It can be seen from Fig. 1 (curve *1*) that the quality factor is constant for the pure solvent, and its changes are not greater than 9 % at [PIP] ≤ $2 \cdot 10^{-5}$ mol L^{-1} (see Fig. 1, curve *2*). When [PIP] > $2 \cdot 10^{-5}$ mol L^{-1} (see Figs. 2—4), the changes in Q_L are ~15 % of the initial value, they are nonmonotonic and asynchronous with laser pulses. A decrease in the light intensity (by weakenening light filters) decreases the amplitude of oscillations (see Fig. 4), but affects weakly their initial periods (~10^{-7} s) expressed as the product of the pulse duration and the number of laser pulses. No oscillations were registered when the light intensity was more than tenfold decreased.

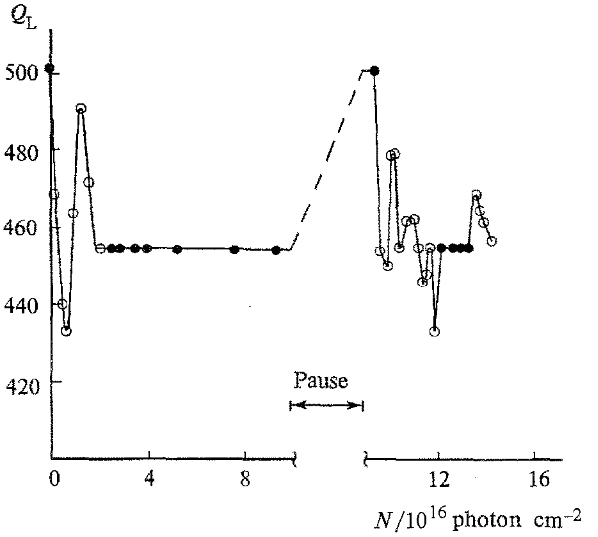

Fig. 2. Dependence of the quality factor of the loaded resonator on the number of photons during pulse irradiation of a toluene solution of PIP ($C = 1 \cdot 10^{-4}$ mol L^{-1}). The light intensity is $7.5 \cdot 10^{14}$ photon cm^{-2} pulse^{-1}. For designations see Fig. 1.

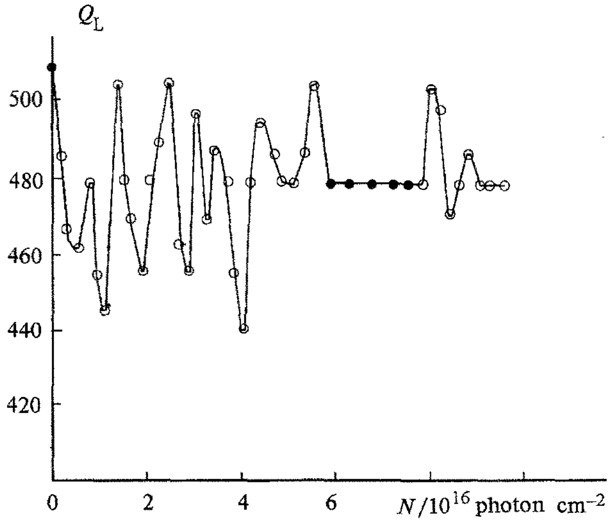

Fig. 3. Dependence of the quality factor of the loaded resonator on the number of photons during pulse irradiation of a toluene solution of PIP ($C = 5 \cdot 10^{-4}$ mol L^{-1}). The light intensity is $9.5 \cdot 10^{14}$ photon cm^{-2} pulse^{-1}. For designations see Fig. 1.

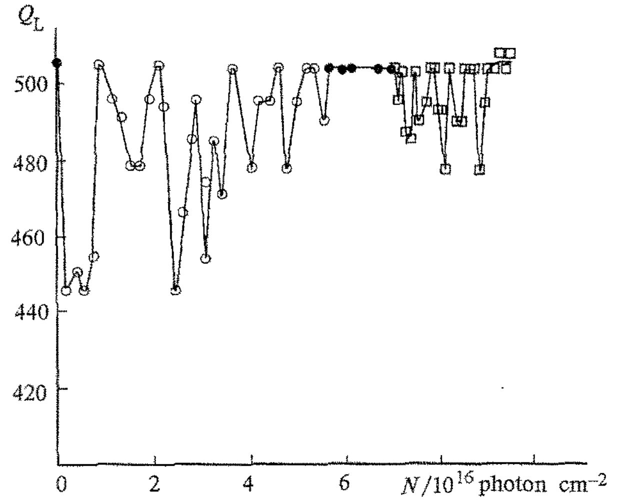

Fig. 4. Dependence of the quality factor of the loaded resonator on the number of photons during pulse irradiation of a toluene solution of PIP ($C = 5 \cdot 10^{-3}$ mol L^{-1}). The light intensity is $9.5 \cdot 10^{14}$ photon cm^{-2} pulse^{-1}. For designations see Fig. 1; light squares designate $I = 0.4I_0$.

Results and Discussion

The observed photoinduced changes (ΔQ_L) in the quality factor of the loaded resonator are not related to possible noise (electromagnetic interferences) from the working laser, because, first, oscillations are not registered when the beam is shielded and, second, they are absent for measurements in a pure solvent and become negligible with prolonged (>10^3 pulses) irradiation. Oscillations cannot be caused by relaxation of the energy stored in the resonator as well, because this process attenuates at least for the time $t \approx 6Q_L/f_0 \approx 3 \cdot 10^{-7}$ s, and the quality factor has been measured considerably later (in ~10^2 s).

It is also difficult to relate the effect observed to the possible thermochemical effect of the laser light.[5] In fact, even if it is assumed that the whole light energy of the pulse is transformed to the heat and this heat is released into the volume in which the light is absorbed (for the maximum PIP concentration used ($5 \cdot 10^{-3}$ mol L^{-1}) for an extinction coefficient (ε) of PIP equal to ~$3.5 \cdot 10^4$ L mol^{-1} cm^{-1} at $\lambda = 337$ nm the absorbing volume $V \approx 0.1 \cdot (5 \cdot 10^{-3} \cdot 2.3 \cdot 3.5 \cdot 10^4)^{-1} = 2.5 \cdot 10^{-4}$ cm^3), and the heating does not exceed the value $\Delta T \approx 7 \cdot 10^{-5}/(2.5 \cdot 10^{-4}) \approx 0.3$ K.

The results of experiments at various concentrations of PIP allow one to assume that the changes in Q_L observed are caused by the formation of products during photolysis, whose dipole moments are higher than those of initial substances. Then the comparison with the data obtained without photolysis (see Figs. 2—4) makes it possible to draw a conclusion that the kinetics of the photolysis of PIP in the real time scale corresponds to the case of multiplicity of stationary states. For the data presented, three of such stationary states can be arbitrarily characterized by the values of relative effect $\Delta Q_L \approx 0$, 7, and 10 %. At the same time, some periodicity of oscillations of Q_L asynchronous to irradiation appears on the dependences on the irradiation dose, which probably indicates the oscillatory character of the photochemical process during irradiation, which is "ceased" when the light is switched off. It is likely that after finishing fast stages some products "live" till the time ($t \approx 10^2$ s) when the quality factor is measured.

It is still difficult to suggest a detailed mechanism of the photochemical process responsible for the oscillations of Q_L observed. At the same time, beginning from the classic works of Belousov and Zhabotinskii (see, *e.g.*, Refs. 6 and 7), which first demonstrated the oscillatory chemical reaction on a real time scale, the processes accompanied by oscillations of concentrations of intermediate products have been studied by many authors.[8] Photochemical reactions were also discussed rather widely,[9] although to a lesser extent than dark reactions (see also works cited in Ref. 9). However, the experimental data presented have several specific features, which can hardly be described in terms of the known photochemical schemes based, as a rule, on participation of excited states in processes. In particular, it is necessary to take into account the role of water[1] that is present in toluene and to observe oscillations during pulse irradiation. Therefore, the known model of the "brusselator"[10] was used as an example for demonstrating the possibility of the appearance of oscillations not on the real time scale, but depending on the dose during pulse irradiation. It turned out that this model can be easily modified for concordance with the results obtained previously,[1] and excited states, which are unambiguously involved in the photochemical process, were not taken into consideration for simplicity.[9]

The "brusselator" model has been well studied presently. It is known that for some values of parameters in the real time scale it results in the periodic solution, which is a limiting cycle.[11] The modified scheme of reactions was presented in the preliminarily publication (see Ref. 2). If the open form of PIP, *Open*, is related to the *cis*-configuration, this scheme[2] can be simplified by the following way:

$$\text{PIP} \underset{}{\overset{h\nu}{\rightleftharpoons}} cis\text{-PIP} \quad (1)$$

$$cis\text{-PIP} + H_2O \longrightarrow Sel^+ \cdot OH^- \quad (2)$$

$$2\ cis\text{-PIP} + Sel^+ \cdot OH^- \longrightarrow 3\ cis\text{-PIP} + H_2O \quad (3)$$

$$cis\text{-PIP} \overset{h\nu}{\rightleftharpoons} trans\text{-PIP} \quad (4)$$

The following formal scheme corresponds to reactions (1)—(4):

$$Y_1 \xrightarrow{k_1} Y_2 \quad (5)$$

$$Y_2 \xrightarrow{k_1'} Y_1 \qquad (6)$$

$$Y_2 + Y_3 \xrightarrow{k_2} Y_4 \qquad (7)$$

$$2\,Y_2 + Y_4 \xrightarrow{k_3} 3\,Y_2 + Y_3 \qquad (8)$$

$$Y_2 \xrightarrow{k_4} Y_5 \qquad (9)$$

$$Y_5 \xrightarrow{k_4'} Y_2 \qquad (10)$$

Here reactions (5), (6), and (9) with the rate constants k_1, k_1', and k_4 are photoinduced, and reactions (7), (8), and (10) with the rate constants k_2, k_3, and k_4' are dark reactions.

The formal scheme of reactions (5)—(10) corresponds to the system of Eqs. (11)—(15) (for simplicity the light absorption is assumed to be weak).

$$\frac{dY_1}{dt} = -k_1Y_1 + k_1'Y_2 \qquad (11)$$

$$\frac{dY_2}{dt} = k_1Y_1 - k_1'Y_2 - k_2Y_2Y_3 + k_3Y_2^2Y_4 - -k_4Y_2 + k_4'Y_5 \qquad (12)$$

$$\frac{dY_3}{dt} = -k_2Y_2Y_3 + k_3Y_2^2Y_4 \qquad (13)$$

$$\frac{dY_4}{dt} = k_2Y_2Y_3 - k_3Y_2^2Y_4 \qquad (14)$$

$$\frac{dY_5}{dt} = k_4Y_2 - k_4'Y_5 \qquad (15)$$

The complete analysis of solutions of this system of equations is not the purpose of this work: it can be performed using well known methods.[12—15] Let us consider only a qualititative example of the solution, which shows that at certain concentrations of initial compounds and particular values of rate constants reactions (1)—(4) can result in ocsillations of concentrations of initial and intermediate products not only under continuous irradiation (on the real time scale), but under pulse irradiation (on concentration dependences of the dose of the absorbed light) as well.

Figure 5, *a* illustrates the calculation of the time dependences of concentrations of the initial PIP and intermediate photolysis products for continuous irradiation of a solution until an instant of switching off indicated by the point in terms of model (11)—(15). It can be seen that when irradiation is ceased, the concentrations of all components at chosen values of parameters stop changing almost immediately, and oscillations are regenerated when the light is switched on again.

Figure 5, *b* presents the results of the numerical calculation of the dependences of concentrations of the initial PIP and intermediate photolysis products detected in the same time (Δt = 10^{-6} s) after irradiation on the total duration of pulse irradiation. In this case, the time (on the abscissa) corresponds to various instants of switching off the light. Constants k_1' for the light and for the dark reactions were chosen to be equal for simplicity (curve *2'* corresponding to $Y_2(t)$ = 0 is not shown). It can be seen that oscillations of concentrations also appear under pulse irradiation (with one exception for the monotonic increase in the concentration of the *trans*-form).

As a whole, the model described by reactions (1)—(4), which involves no excited states,[9] is likely far from reality and serves only as an illustration of the experimental data obtained. However, the numerical calcu-

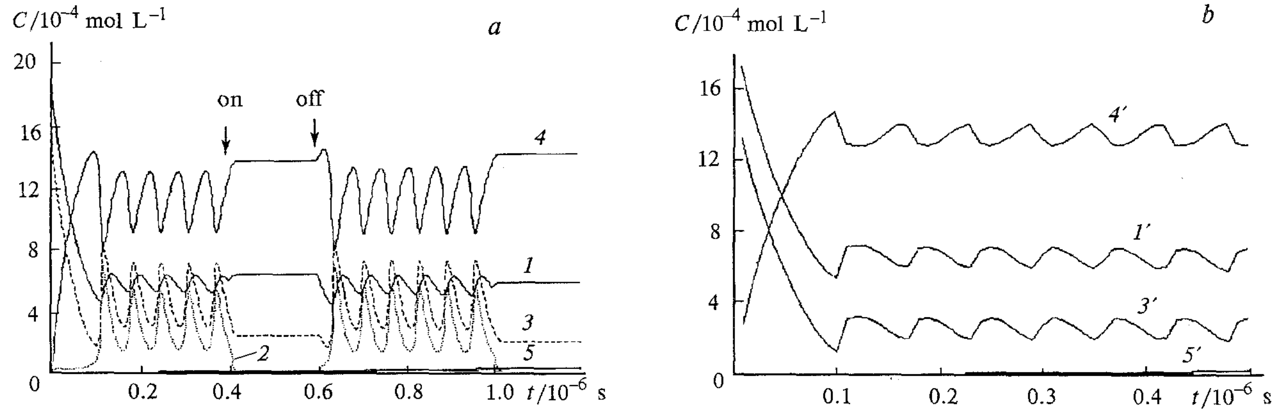

Fig. 5. Numerical calculation of the kinetics for model (11)—(15) during continuous irradiation of a solution till the instant of switching off the light (point) (*a*) and during pulse irradiation (pulse duration is $0.01 \cdot 10^{-6}$ s) (*b*): concentration dependences registered in the same time Δt = 10^{-6} s after irradiation on the total duration of pulse irradiation. Curves: *1* and *1'*, Y_1 ≡ PIP; *2*, Y_2 ≡ *cis*-PIP; *3* and *3'*, Y_3 ≡ H_2O; *4* and *4'*, Y_4 ≡ $Sel^+ \cdot OH^-$; 5 and 5', Y_5 ≡ *trans*-PIP (see the text). Initial concentrations, $Y_i(0)/10^{-4}$ mol L^{-1}: $Y_1(0)$ = 20; $Y_3(0)$ = 16; $Y_2(0)$ = $Y_4(0)$ = $Y_5(0)$ = 0. Rate constants, $k_i/10^{-6}$ s^{-1}: k_1 = 15, k'_1 = 30, k_2 = 100, k_3 = 15, k_4 = 0.1, k'_4 = 0.01.

lation of the kinetics of reactions (1)—(4) for pulse irradiation agrees with the experiment, and the scheme of reactions presented takes into account the results obtained previously[1] (the rate constant k_3 turned out to be somewhat increased, but this can mean that reaction (8) occurs in two stages). It seems important to carry out experiments under continuous irradiation of a solution; however, it is difficult to carry them out at light intensities necessary for exciting oscillations (10^{22} to 10^{23} photon cm^{-2} s^{-1}).

The authors are grateful to B. I. Golovanov and A. V. Koval'chuk for help in experiments and to V. A. Benderskii, E. B. Gordon, and M. F. Budyka for critical remarks and valuable advices during preparation of this publication.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-18031) and the International Science Foundation (Grant NJA 000).

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Received December 29, 1994