KINETICS IN A CONTINUOUSLY STIRRED PHOTOCHEMICAL TANK REACTOR[†]

F. GREGOIRE, D. LAVABRE and J. C. MICHEAU

Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique, Equipe de Recherche associée au CNRS 264, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cédex (France)

M. GIMENEZ

Service de Chimie-Physique II, Université Libre de Bruxelles, CP 231 Campus Plaine, boulevard du Triomphe, B-1050 Brussels (Belgium)

J. P. LAPLANTE

Department of Chemistry and Chemical Engineering, Royal Military College, Kingston, Ontario (Canada)

(Received September 9, 1984)

Summary

The réacteur photochimique agité continu (REPAC) is a new semi-automatic apparatus for photochemical measurements. From the kinetic analysis of steady state regimes, this open system allows the determination of the quantum yields, the thermal return rate constants and the spectra of photoproducts. Moreover, the kinetic analysis of transient regimes affords further information on the mechanism of the photochemical process. The possibilities of the REPAC are shown using various photochromic compounds. Theoretical analysis of the kinetic rate equations in the REPAC shows that quite unusual behaviour, such as unstable steady states or photochemical oscillations, can be exhibited. Non-linear photochemical reaction schemes are likely to show such behaviour.

1. Introduction

The determination of the quantum yields, the kinetic rate constants and the UV−visible spectra of slow transient products are ever present problems in photochemistry.

In this paper, we report our initial experiments on a semi-automatic apparatus in which all the above parameters can be determined simultaneously. We have built a continuously stirred photochemical reactor (réacteur

---

[†]Paper presented at a Workshop on Self-organization in Photochemical Systems, Xth IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 22 - 27, 1984.

photochimique agité continu (REPAC)) (Fig. 1). The REPAC provides a means of simulating the behaviour of open systems that are mainly found in natural or industrial processes.
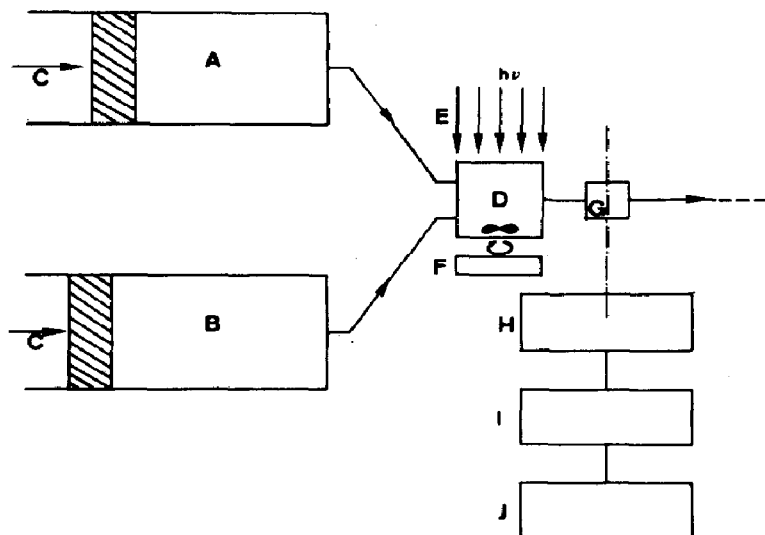

Fig. 1. Schematic experimental set-up of the REPAC system: A, reactant; B, solvent; C, linear pumps; D, reactor; E, fibre optic irradiator; F, variable-speed magnetic stirrer; G, microcell; H, UV—visible spectrophotometer; I, personal computer; J, recorder—printer plotter.

The first part of this paper is devoted to the kinetic analysis of steady regimes. When the external constraints (the flow of reactants, the photon flux etc.) are changed a transient regime appears, leading to another steady state. In the second part of this paper the kinetic properties of the transient regimes will be analysed. Furthermore, some theoretical considerations on non-linear behaviour will be discussed in the third part.

2. Results and discussion

Before presenting experimental results we briefly outline some classical kinetic calculations for a simple photochromic reaction in an open system. Most photochromic reactions are consistent with the following reaction scheme [1 - 3]:

$$A \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} B$$
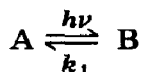
Let us suppose that the REPAC is only fed with a solution of the reactant A at a concentration $[A]_0$. The rate equation for $[A]$ is

$$\frac{d[A]}{dt} = \frac{d}{v}([A]_0 - [A]) + k_1[B] - \phi_A I_0 \epsilon_A(\lambda_i) l_r [A] F(\lambda_i) \tag{1}$$

where $(d/v)[A]_0$ and $(d/v)[A]$ represent the input flow and the output flow respectively of reactant A, d is the flow rate of the solution and v is the volume of the reactor. $k_1[B]$ is the rate of the thermal reverse reaction of photoisomer B to A. The following conservation law is always obeyed:

$$[B] = [A]_0 - [A] \tag{2}$$

ϕ_A is the quantum yield of the photoisomerization reaction. I_0 is the incident photon flux and $F(\lambda_i) = (1 - 10^{-OD(\lambda_i)})/OD(\lambda_i)$ is a correcting factor that takes into account the absorption of monochromatic incident light along the optical path l_r. $OD(\lambda_i) = \{\epsilon_A(\lambda_i)[A] + \epsilon_B(\lambda_i)[B]\}l_r$ and $\epsilon_A(\lambda_i)$ and $\epsilon_B(\lambda_i)$ are the respective extinction coefficients of A and B at the wavelength λ_i of irradiation. ϕ_A, $\epsilon_B(\lambda)$ and k_1 can be determined directly by monitoring the stationary concentration of A for various incremental values of I_0 and d. From a combination of the steady state equation $d[A]/dt = 0$ with eqn. (2) it follows that

$$\left(\frac{d}{v} + k_1\right)([A]_0 - [A]) - \phi_A I_0 \epsilon_A(\lambda_i) l_r [A] F(\lambda_i) = 0 \tag{3}$$

The REPAC is monitored by UV–visible spectrometry. The optical density of the reacting medium is

$$OD(\lambda) = \{\epsilon_A(\lambda)[A] + \epsilon_B(\lambda)[B]\}l_d \tag{4}$$

where l_d is the optical length of the cell. The change in the optical density during the photochemical process is

$$\Delta OD(\lambda) = OD(\lambda)_{initial} - OD(\lambda)$$
$$= [\epsilon_A(\lambda)[A]_0 - \{\epsilon_A(\lambda)[A] + \epsilon_B(\lambda)[B]\}]l_d \tag{5}$$

Combining eqns. (2) and (5) gives

$$\Delta OD(\lambda) = l_d \Delta\epsilon(\lambda)([A]_0 - [A]) \tag{6}$$

where $\Delta\epsilon(\lambda) = \epsilon_A(\lambda) - \epsilon_B(\lambda)$.

A linear relationship between $1/\Delta OD(\lambda)$ and $1/I_0 F(\lambda_i)$ is obtained by combining eqns. (3) and (6):

$$\frac{1}{\Delta OD(\lambda)} = \frac{(d/v) + k_1}{\phi_A \epsilon_A(\lambda_i) l_r [A]_0 l_d \Delta\epsilon(\lambda)} \frac{1}{I_0 F(\lambda_i)} + \frac{1}{[A]_0 l_d \Delta\epsilon(\lambda)}$$

$$= \frac{s}{I_0 F(\lambda_i)} + j \tag{7}$$

The value of $\Delta\epsilon(\lambda)$ is derived from the value of the intercept j:

$$\Delta\epsilon(\lambda) = \frac{1}{[A]_0 l_d j} \tag{8}$$

Then

$$\epsilon_B(\lambda) = \epsilon_A(\lambda) - \Delta\epsilon(\lambda)$$

The ratio

$$\frac{s}{j} = \frac{(d/v) + k_1}{\phi_A \epsilon_A(\lambda_i) l_r} \tag{9}$$

includes k_1 and ϕ_A. If k_1 is already known, then ϕ_A can be calculated. Otherwise, if the flow rate d is varied, ϕ_A and k_1 can both be determined together

$$\frac{s}{j} = \frac{d}{\phi_A \epsilon_A(\lambda_i) l_r v} + \frac{k_1}{\phi_A \epsilon_A(\lambda_i) l_r}$$

$$= \sigma d + \gamma \tag{10}$$

giving

$$k_1 = \frac{\gamma}{\sigma v}$$

and

$$\phi_A = \frac{1}{\sigma v \epsilon_A(\lambda_i) l_r}$$

A preliminary test was carried out on the reaction of mercury dithizonate in xylene [3] (Fig. 2). The orange starting complex was irradiated at 400 ± 60 nm and its residual concentration was monitored at 482 nm. As $\epsilon_A(482) \gg \epsilon_B(482)$ the photochemical isomerization leads to a large reduction $\Delta OD(482)$ in the monitored optical density (Fig. 3). Several incremental values of the photon flux were used and the results are shown in Table 1. When $1/\Delta OD(482)$ is plotted against $1/I_0 F(\lambda_i)$ a straight line is obtained (Fig. 4). Similar calculations can be performed at any monitoring wavelength using a computer.

It can be demonstrated that the curves joining two different steady states are approximately exponential. The starting point of the calculation is the rate equation of A (see eqn. (1)). Since analytical integration is not always possible, a convenient approximation is to assume that the factor $F(\lambda_i)$ is almost constant during the transient phase. Under these conditions the
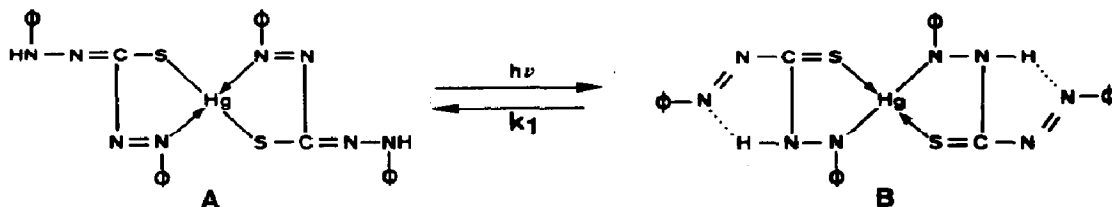

Fig. 2. Photothermal equilibrium of mercury dithizonate: A, orange form ($\lambda_{max} = 482$ nm; $\epsilon_{max} = 38\,000$); B, blue form ($\lambda_{max} = 605$ nm).
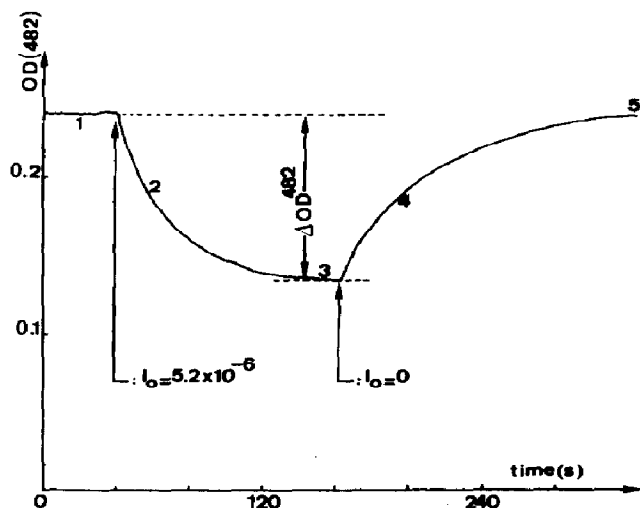
Fig. 3. Evolution of the optical density monitored at 482 nm during the irradiation of a solution of mercury dithizonate in xylene ($[A]_0 = 4.25 \times 10^{-5}$ M in the REPAC; $d = 1.35 \times 10^{-5}$ l s^{-1}; $v = 1.15 \times 10^{-3}$ l): 1, $I_0 = 0$; 2, transient regime; 3, steady regime ($I_0 = 5.2 \times 10^{-6}$ mol l^{-1} s^{-1}); 4, transient regime; 5, steady regime ($I_0 = 0$).

TABLE 1

Variation in $\Delta OD(482)$ as a function of the incident photon flux I_0

I_0	OD(400)	$F(400)$	$\Delta OD(482)$	$1/\Delta OD(482)$	$1/F(400)I_0$
5.2×10^{-6}	0.24	1.77	0.105	9.5	1.09×10^5
1.4×10^{-5}	0.22	1.81	0.155	6.5	3.95×10^4
1.7×10^{-5}	0.20	1.85	0.170	5.9	3.18×10^4
2.6×10^{-5}	0.17	1.91	0.189	5.3	2.02×10^4
6.9×10^{-5}	0.16	1.93	0.200	5	7.52×10^3
1.2×10^{-4}	0.15	1.95	0.211	4.7	4.28×10^3
2.2×10^{-4}	0.14	1.97	0.215	4.7	2.31×10^3

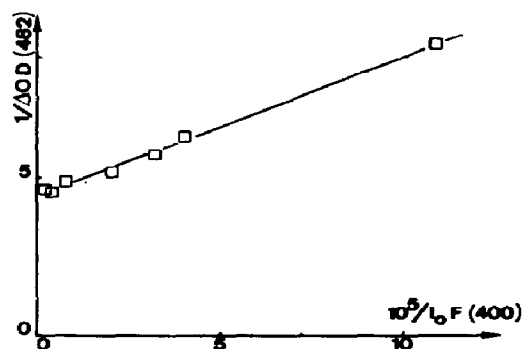The experimental conditions are the same as those in Fig. 3.

Fig. 4. Plot of $1/\Delta OD(482)$ vs. $10^5/I_0 F(400)$. From the intercept $j = 4.42$, $\Delta\epsilon(482) = 35\,000$; then $\epsilon_B(482) = 38\,000 - 35\,000 = 3000$. From the slope $s = 4.7 \times 10^{-5}$ mol l^{-1} s^{-1} a value of the quantum yield ϕ_A of photoisomerization of 0.3 ± 0.05 can be estimated by using $k_1 = (8.7 \pm 1.5) \times 10^{-3}$ s^{-1}.

observed rate constant k_{obs} is given by

$$k_{obs} = \frac{d}{v} + k_1 + \phi_A I_0 \epsilon_A(\lambda_i) l_r F(\lambda_i)$$ (11)

As k_1 and d/v are known, ϕ_A can be determined (Table 2). In spite of some lack of accuracy which can be attributed to the approximations we made and to manual data analysis, ϕ_A was found to be of the same order of magnitude as the value obtained by steady state analysis ($\phi_A \approx 0.3 \pm 0.1$).

In order to illustrate the interest of the transient phase, another photochromic system was studied in the REPAC. According to White and Sonnenberg [4] the 2,4,5-triphenylimidazyl radical system exhibits three main species with two photothermal equilibria (Fig. 5). Analysis of the transient regime shows that the monitored species D is involved in a more complicated kinetics reaction scheme. When the intensity of the photon flux is increased, an unusual transient regime appears, exhibiting an overshoot (Fig. 6).

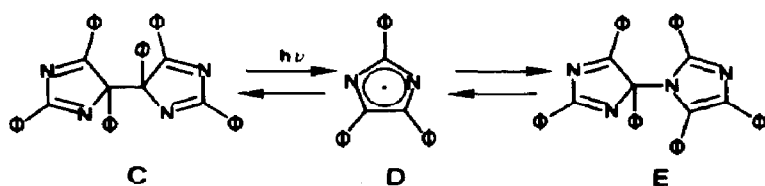This phenomenon can be interpreted by considering a scheme involving three species:

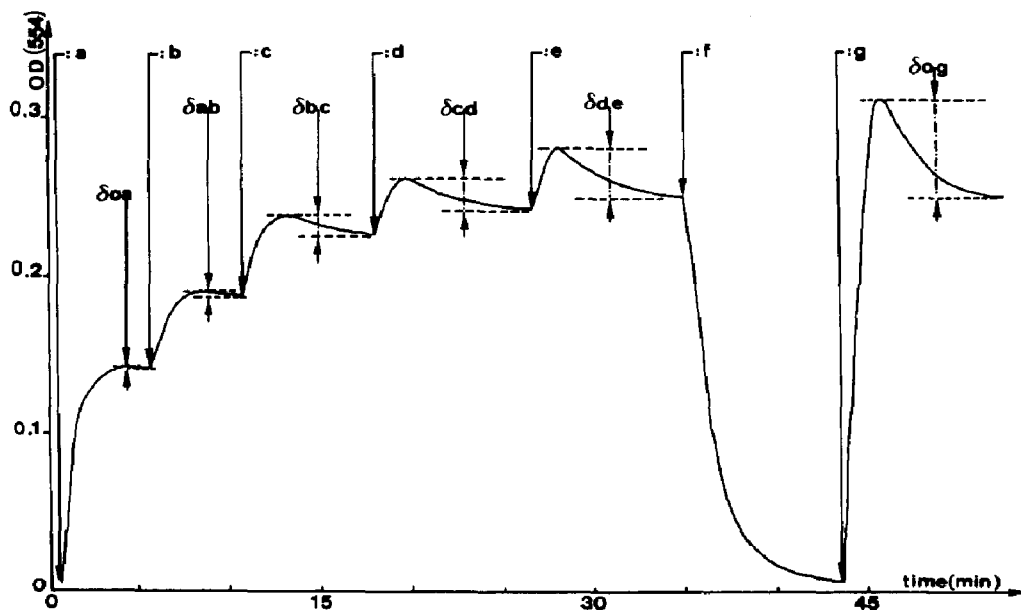Fig. 5. Photothermal equilibria of 2,4,5-triphenylimidazyl radical dimer (D, violet form; $\nu_{max} = 554$ nm).


Fig. 6. Transient regime exhibiting overshoots δOD during the irradiation of the 2,4,5-triphenylimidazyl radical system in the REPAC ([C]$_0$ = 6.2 × 10^{-3} M (CCl$_4$); d = 3.9 × 10^{-6} l s^{-1}; λ(monitoring) = 554 nm).

TABLE 2

Kinetics analysis of some transient regimes obtained by varying the incident photon flux I_0

Run	Imposed photon flux I_0	Initial photon flux	τ_{obs} (s)	k_{obs} (s^{-1})	$\phi_A I_0 \epsilon_A(400) l_r F(400)$	OD(400)	$F(400)$	ϕ_A [a]
1	1.7×10^{-5}	0	15 ± 5	$(5 \pm 2) \times 10^{-2}$	$(3.7 \pm 2) \times 10^{-2}$	0.2	1.85	0.25 ± 0.1
2	2.6×10^{-5}	1.7×10^{-5}	14 ± 2	$(5 \pm 1) \times 10^{-2}$	$(3.6 \pm 1) \times 10^{-2}$	0.17	1.91	0.15 ± 0.1
3	5.2×10^{-5}	3.5×10^{-6}	23 ± 5	$(3 \pm 1) \times 10^{-2}$	$(1.5 \pm 1) \times 10^{-2}$	0.24	1.77	0.4 ± 0.2
4	1.4×10^{-5}	5.2×10^{-6}	16 ± 3	$(4.5 \pm 1) \times 10^{-2}$	$(3 \pm 1) \times 10^{-2}$	0.22	1.81	0.25 ± 0.1

$d/v + k_1 = (1.5 \pm 0.2) \times 10^{-2}$ s^{-1}.

[a] ϕ_A is calculated from eqn. (11).

$$C \xrightarrow{h\nu} D \longrightarrow E$$
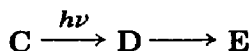
where D is the monitored species. A positive increment in the photon flux induces a large and rapid increase in [D], while pumping and reactions slowly reduce [D] to its steady state value. The larger the increment is, the more distinct the overshoot, its amplitude being proportional to the increment ΔI_0 in the photon flux (Fig. 7). The occurrence of an overshoot during the transient phase demonstrates qualitatively that the kinetics network is not of the simplest type $A \rightleftharpoons B$.
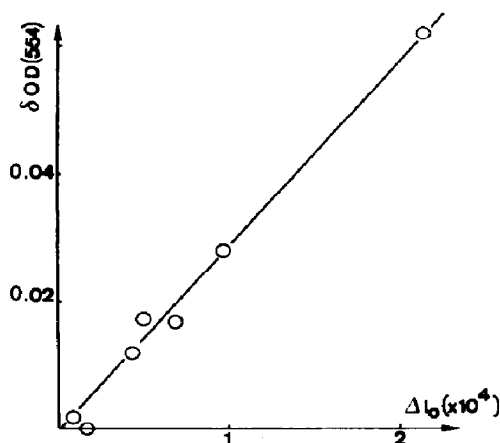

Fig. 7. Amplitude of the overshoot $\delta OD(554)$ *vs.* the positive incremental values ΔI_0 of the photon flux. The experimental conditions are the same as those in Fig. 6.

While simple reaction schemes give rise to quasi-exponential transient regimes, a slightly more complicated system, namely the 2,4,5-triphenyl-imidazyl radical system, exhibits an unusual overshoot. Even more unusual transient behaviour, such as bistability or photochemical oscillations, can be observed in the REPAC using appropriate photochemical systems [5].

A very simplified mathematical analysis can help to clarify the question. Let us consider a hypothetical photochemical reaction generating two transients X and Y through a sufficiently complex kinetics network. The kinetics equations of the combined transient X and Y can be written as

$$\frac{dX}{dt} = f(X, Y)$$

and

$$\frac{dY}{dt} = g(X, Y)$$

where f and g are non-linear functions of X and Y as well as of kinetic parameters related to the reaction network and to the operating conditions of the REPAC.

Since microscopic fluctuations are always present, the effect on the kinetic behaviour of the system of a small perturbation δX and/or δY can be determined by a linear stability analysis of the kinetics reaction scheme; thus

$$\frac{d(X + \delta X)}{dt} = f(X + \delta X; Y + \delta Y)$$

$$= f(X, Y) + \frac{\partial f}{\partial X}\delta X + \frac{\partial f}{\partial Y}\delta Y + \ldots$$

and

$$\frac{d(Y + \delta Y)}{dt} = g(X + \delta X; Y + \delta Y)$$

$$= g(X, Y) + \frac{\partial g}{\partial X}\delta X + \frac{\partial g}{\partial Y}\delta Y + \ldots$$

Since the perturbations δX and δY whose time dependence is to be studied are small, higher order terms can be neglected, leaving the following set of linear differential equations:

$$\frac{d(\delta X)}{dt} = \frac{\partial f}{\partial X}\partial X + \frac{\partial f}{\partial Y}\partial Y$$

$$\frac{d(\delta Y)}{dt} = \frac{\partial g}{\partial X}\delta X + \frac{\partial g}{\partial Y}\delta Y$$

General solutions of these linear equations are given by

$$\delta X = \delta X_0 \exp(\omega t)$$

and

$$\delta Y = \delta Y_0 \exp(\omega t)$$

The argument ω is obtained by replacing δX and δY in the preceding equations. Non-trivial solutions are obtained when the secular determinant is equated with zero:

$$\begin{vmatrix} \omega - \dfrac{\partial f}{\partial X} & - \dfrac{\partial f}{\partial Y} \\ - \dfrac{\partial g}{\partial X} & \omega - \dfrac{\partial g}{\partial Y} \end{vmatrix} = 0$$

The expansion of this determinant yields a quadratic equation in ω. Depending on the mechanism of the photochemical process and on the experimental operating conditions of the REPAC, four distinct types of behaviour can be expected *a priori*.

(i) When ω is real and negative, all the perturbations decay and the system is termed stable.

(ii) When ω is real and positive, the initial small perturbations are spontaneously amplified and the system is termed unstable.

(iii) When ω is complex with its real part negative, the values of the concentrations oscillate in a damped mode, stabilizing to a stationary value.

(iv) When ω is complex with its real part positive, the values of the concentrations go into sustained oscillations.

To ensure positive or complex roots the kinetics equations must be sufficiently non-linear. Some feedback must therefore be present in real photochemical reactions to lead to such unusual phenomena. These could be found in cases where there is a sensitization by the product, chain reactions, autocatalysis, etc.

3. Conclusion

Kinetic analysis of both steady and transient regimes in the REPAC represents two independent ways of collecting kinetics and spectral data from a photochemical reaction. Experimental results from the photochemical reactions of mercury dithizonate or triphenylimidazyl radical are in agreement with our previous kinetics calculations. The REPAC appears to be a useful tool not only for the study of classical photochemical phenomena (photoreduction, photoisomerization, photochromism, photodimerization etc.) but also for the study of the more complicated processes that occur in natural or industrial photochemical systems [6]. Non-linear behaviour, such as instability or photochemical oscillations, has been predicted on theoretical grounds but experimental evidence is scanty. These results are not of purely academic interest since non-linear behaviour is frequently encountered in photobiology [7].

4. Experimental details

4.1. Products

Mercury dithizonate A and 2,4,5-triphenylimidazyl radical dimer C were synthesized according to previously published methods [3, 4].

4.2. Apparatus

Calibrated flow rates were delivered by linear pumps (Precidor) fitted with Glenco gas–liquid syringes. The photochemical reactor consisted of a Pyrex cylinder (1 cm in outside diameter, 1.5 cm high) stoppered with a Teflon plug and fitted with a miniature variable-speed magnetic stirrer. A Schott KL 1500 fibre optic source with a 150 W quartz–halogen lamp and a BG 37 blue filter was used as the irradiation device. As no chemical actinometer was available, the standardization of the photon flux was performed with an EGG model 150-1 radiometer. The value of the maximum

available photon flux impinging on the reactor was taken as equal to 2.2×10^{-4} mol 1^{-1} s^{-1} regardless of some possible discrepancies due to geometrical requirements [8]. Incremental values of the incident photon flux were obtained within the range from 1.6% to 100% by interposing diaphragms or neutral grid filters. The experimental set-up was tightly enclosed inside a copper block which acted as a thermostat. The solution flowing out of the reactor was immediately monitored in a capillary cuvette (1 mm $\times$ 1 mm $\times$ 1.5 mm) placed in a Beckmann Acta MIV connected to a microcomputer.

Acknowledgment

References

1 R. Guglielmetti, R. Meyer and C. Dupuy, *J. Chem. Educ.*, *50* (1973) 413.
2 H. G. Heller and S. Oliver, *J. Chem. Soc., Perkin Trans. I,* (1981) 197 - 201.
3 L. S. Meriwether, E. C. Breitner and C. L. Sloan, *J. Am. Chem. Soc.*, *87* (1965) 4441 - 4448.
   A. E. Goodwin and H. A. Mottola, *Anal. Chem.*, *55* (1984) 329 - 334.
4 M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, *88* (1966) 3825 - 3829.
5 D. Huber, *Chimia, 37* (1983) 292 - 298.
6 J. C. André, A. Saïd, M. L. Viriot, J. Y. Jezequel and M. Moll, *Proc. 10th IUPAC Symp. on Photochemistry, Interlaken, July 22 - 27, 1984,* Presses Polytechniques Romandes, Lausanne, 1984.
7 L. H. Pratt, *Photochem. Photobiol. Rev., 4* (1979) 59 - 124.
8 D. Balland, R. Guillard and J. C. André, *Polym. Photochem., 4* (1984) 111 - 133.