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Technical Note

Elliptical photochemical reactor for preparative and quantitative studies in the liquid phase

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(Received June 15, 1973)

Although the development of light sources for photochemistry has made great progress during the last decade it is still difficult and time consuming to examine photochemical reactions whose quantum yields are lower than 10^{-2}–10^{-3}. Since we were facing the problem of studying the photochemical behaviour of compounds whose decomposition quantum yields were estimated to be as low as 10^{-7} we have developed a photochemical reactor in which high light intensities can be achieved.

Description

A principal part of the apparatus consists of a stainless-steel elliptocylindrical vessel (Fig. 1) with a xenon type 1500 W light source (Xe-1500 Haereus Hanau) positioned in one focus, the sample containing cell being placed in the second
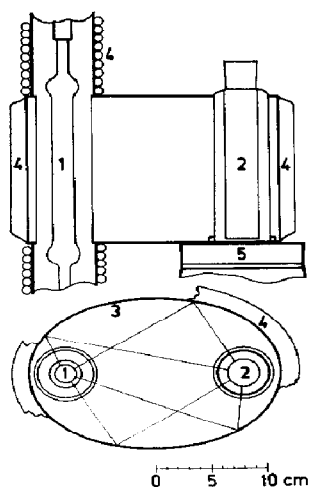

Fig. 1. Elliptical reactor; 1, source; 2, reaction cell; 3, elliptocylindrical vessel; 4, cooling jacket; 5, electromagnetic stirrer.

focus. As a considerable amount of light and heat energy is concentrated in a relatively small space numerous measures had to be taken to ensure efficient cooling both of the source and the cell.

The source is cooled by a stream of filtered air supplied by an air-blower with the output of 200 m³/h. The temperature of the air at the outlet is 180°C. The lamp is housed in a quartz tube fixed inside the reactor. The elliptical vessel is jacketed and cooled by the running water as well as metal tubes where the lamp terminals are fixed. The whole arrangement is controlled by relay pressure contacts included both in air and water circuits. Any failure in air and water supply disconnects the relay and switches off the lamp. The apparatus can thus be left on for several hundreds of hours and requires minimum supervision.

The electric current supply for the lamp (22.5 A) can be regulated by a Variac built into a supply unit. The lamp ignition was effected by a commercial ZX 6001 Siemens ignition unit.
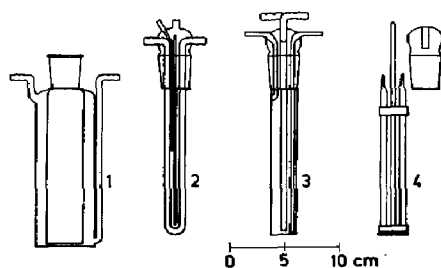

Fig. 2. Reaction cell. 1, jacketed reaction vessel; 2, adaptor for work in 40 ml volume; 3, cold finger; 4, merry-go-round modification.

The jacketed reaction cell (o.d. 50 mm) was made of Sial glass (Fig. 2). The cell can be used for various purposes according to the type of experiment. In most cases a central adaptor (2) is used fitted with a U-tube for cooling, a capillary tube through which any selected gas may enter the cell, and a thin-wall tube holding a thermocouple for continuous temperature measurement during the experiment. A copper–constantan thermocouple was used for this purpose. The reference junction was immersed into a thermostat, the temperature of which was maintained at 25°C. The thermocouple was placed in the thin-wall tube filled with MgO powder. This enabled the actual temperature of the liquid to be measured inside the reaction vessel, the radiant energy being reflected by MgO. When the cooling liquid, maintained at 25°C, circulated through the cooling jacket and through the U-tube connected in series, then the stationary temperature of the reactor contents was observed to be 35–38°C depending on the reaction medium used. In an extreme case of strong absorption (solution of I_2 in CCl_4, 0.5 g/100 ml) this value increased up to 42°C. Samples can be taken by a hypodermic syringe through a rubber septum over the top of the adaptor. The volume of the photolyzed liquid is, in this arrangement, 90 ml.

In special cases a cold finger (3) (o.d. 25 mm) can be used so that the layer of liquid irradiated is only 2.5 mm thick. The volume of the reactor is then 40 ml. Even in this case the reaction mixture can be saturated with gas during the exposure.

In both cases the cell contents can be magnetically stirred using an electromagnetic stirrer placed under the bottom of the reactor.

Another modification converts the reactor into a merry-go-round apparatus. For this purpose, a Teflon holder (4) is placed into the cell. A glass-coated iron bar is fixed to the bottom of the holder thus enabling rotation of the whole device upon switching on the stirrer. Eight thin-wall glass sealed tubes filled with the liquid being photolyzed or with an actinometer solution can be placed into the holder. In this arrangement the cell is filled with spectral grade ethyl alcohol.

The xenon lamp emits strong infra-red radiation which must be filtered out. A 1% solution of $CuSO_4$ in 0.1 N H_2SO_4 proved to be suitable for this purpose[1]. Moreover, it is often necessary to use cut-off band filters. Since multijacketing of the cell would be impracticable we employed the liquid filter also as a cooling medium. An imperative requirement is, however, to maintain constant optical properties of the circulating liquid filter over the long run. The use of various pumping systems containing rotating glass or metal parts proved to be unsatisfactory because of the fine powder formed by abrasion; this caused an increasing turbidity of the circulating liquid. The problem was satisfactorily solved by using an all-glass air-lift pump of our own design. The function of the pump is evident from Fig. 3.

Vacuum (water-pump) is applied at the point (3). Upon opening the stopcock (8) air is sucked through a cotton wool plug into the bottom reservoir (1).
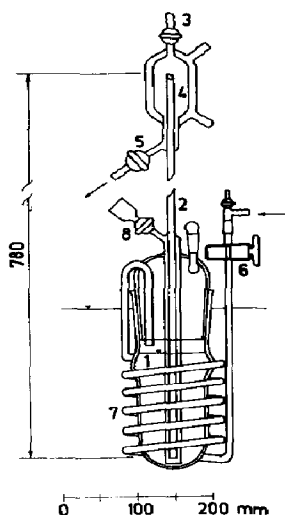

Fig. 3. Air-lift pump; 1, bottom reservoir; 2, pumping tube; 3, vacuum attachment; 4, upper vessel; 5, 6, inlet and outlet stopcocks; 7, cooling coil; 8, air inlet.

The average density of the liquid in the pumping tube (2) is thus lowered as a consequence of the formation of air bubbles. The aerated liquid then ascends through the tube (2) filling the upper vessel (4). Here the bubbles are removed and the liquid flows freely through stopcock (5) into the jacket of a lower positioned reaction cell. The liquid enters the bottom reservoir again through stopcock (6) and a cooling coil. The bottom reservoir is immersed in a constant temperature bath whose temperature is maintained at 25°C. The upper vessel (4) is jacketed and thermostated by circulating water from the constant temperature bath. The water pump is included in this circuit so that a constant vacuum ensuring a regular function of the whole apparatus is maintained.

The experimental arrangement permits working under different atmospheres (O_2, Ar). The gases are dried by passage through molecular sieve 4A columns; argon is further purified by removing traces of oxygen on a copper catalyst (Kontakt BTS, BASF). The gases used for experiments can also be saturated by solvent vapour before entering the cell by passing them through a glass bubbling device filled with the solvent being used and maintained at the same temperature as the reaction vessel.

Calculation of light intensity of the source

High pressure xenon lamps emit a continuous spectrum closely resembling that of the sun[2]. To be able to use our reactor for quantitative experiments we attempted to determine absolute values of the light intensity inside the glass reaction vessel as a function of wavelength.

The relative spectral distribution of the source used was reported by the manufacturer*. Let us introduce a factor β which allows the conversion of these values into absolute ones:

$$\beta = \frac{I_0^{Xe}(\lambda)}{I_0^{Xe}_{rel}(\lambda)} \tag{1}$$

where

$I_0^{Xe}_{rel}(\lambda)$ = relative intensity of the Xe source given in arbitrary dimensionless units as a function of wavelength λ,

$I_0^{Xe}(\lambda)$ = absolute intensity of the Xe source as a function of λ (einstein cm^{-2} s^{-1}),

β = factor independent of λ (einstein cm^{-2} s^{-1}).

The actual intensity I_0 inside the reaction vessel as a function of λ is expressed in the form:

$$I_0(\lambda) = I_0^{Xe}(\lambda) \, R(\lambda) \, T_g(\lambda) \, T_t(\lambda) \tag{2}$$

Using eqn. (1) we obtain

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* Quarzlampen GmbH, Hanau; which also advised us on the Xenotest.

$$I_0 (\lambda) = I_0{}^{Xe}{}_{rel}(\lambda) \; \beta \; R \; (\lambda) \; T_g \; (\lambda) \; T_f \; (\lambda) \tag{3}$$

$R(\lambda)$, $T_g(\lambda)$ and $T_f(\lambda)$ being dimensionless functions of λ with the values within interval $<0,1>$, the physical meaning being reflectancy of the elliptocylindrical vessel walls, transmittance of reaction cell material and transmittance of optical filter solution, respectively.

Uranyl oxalate actinometry[3] was employed to measure light intensity. The solution (0.01 M $UO_2SO_4.3H_2O$ and 0.1 N $H_2C_2O_4.2H_2O$ in water) was exposed for 15–300 s, and the remaining oxalic acid was then titrated with 0.05 N $KMnO_4$. The temperature of the actinometric solution during the exposure was continuously followed, the mean temperature of the experiment calculated and the results corrected by a temperature factor[3] ($1.030/10°$) to $25°C$.

The number of moles of actinometer converted into products at a certain wavelength can be expressed as follows:

$$\Delta n(\lambda) = I_0(\lambda) \; S \; t \; \Phi(\lambda) \; [1 - T_a(\lambda)] \tag{4}$$

where $\Delta n(\lambda)$ = the number of moles of actinometer converted into products at certain wavelength (mol),

$\Phi(\lambda)$ = quantum yield of chemical actinometer decomposition as a function of λ,

$T_a(\lambda)$ = transmittance of the actinometer solution at the pathlength corresponding to dimensions of the reaction vessel (jacket thickness),

S = internal effective area of the reactor (cm^2),

t = time of exposure (s).

If a dimensionless function is defined as:

$$f(\lambda) = I_0{}^{Xe}{}_{rel}(\lambda) \; R(\lambda) \; T_g(\lambda) \; T_f(\lambda) \; \Phi(\lambda) \; [1 - T_a(\lambda)] \tag{5}$$

then by combining eqns. (3), (4), (5) we obtain:

$$\Delta n(\lambda) = S \; t \; \beta \; f(\lambda) \tag{6}$$

The value of $f(\lambda)$ can be calculated for various wavelengths from known data. Integration gives:

$$\int_{\lambda_1}^{\lambda_2} \Delta n(\lambda) d\lambda = S \; t \; \beta \int_{\lambda_1}^{\lambda_2} f(\lambda) d\lambda \tag{7}$$

The value of the right-hand side of the expression was obtained by numerical integration from 290 to 500 nm in 5 nm steps using the data shown in Fig. 4.

Let us define:

$$\int_{\lambda_1}^{\lambda_2} \Delta n(\lambda) d\lambda = \Delta N \tag{8}$$

where ΔN in the overall number of moles of actinometer converted into products found by titration after the exposure t (mol) and
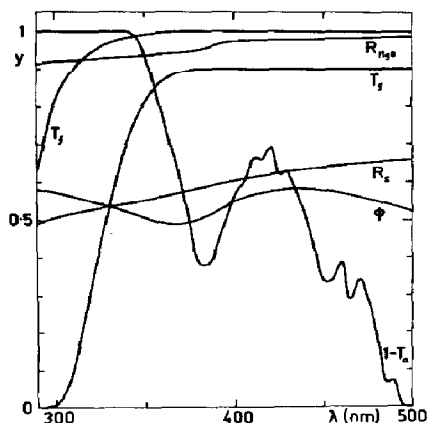
Fig. 4. Parameters for calculation of $f(\lambda)$ according to eqn. (5). R_{MgO}, reflectancy of MgO surface[4]; R_s, reflectancy of stainless steel (V-IId-Stahl type)[5]; Φ, quantum yield of decomposition of uranyl oxalate actinometer; T_g, transmittance of walls of the reaction cell made of Sial glass, T_f, transmittance of the filter solution (1% solution of $CuSO_4$ in 0.1 N H_2SO_4) thickness 1 cm (jacket thickness); $1-T_a$, fraction of light absorbed in the reaction cell by the actinometer solution.

$$\int_{\lambda_1}^{\lambda_2} f(\lambda)d\lambda = F \tag{9}$$

Inserting eqns. (8) and (9) into eqn. (7) the value of β is finally obtained:

$$\beta = \frac{\Delta N}{StF} \tag{10}$$

Using the factor β the absolute intensities of the source as a function of λ can be calculated according to eqn. (1). From eqn. (3) the actual light intensity inside the reaction vessel can also be calculated as a function of λ.

In our experiments we used two types of finish of the reflecting surface inside the elliptocylindrical vessel. In the first case the surface was highly polished stainless steel. It functioned as a mirror reflecting the light from one focus (source) into the second focus (reaction cell) (Fig. 1). In the second case the surface was coated by a layer of MgO produced by ignition of metallic magnesium in an oxygen atmosphere. This time the light impinging the MgO surface is diffusively reflected in all directions with the efficiency approaching 100%[4].

In both cases, however, the value of β which is a constant for given source should be identical.

From calculated values of F and from actinometry measurements evaluated by the least square method the values of β for both types of surface were found to be:
$$\beta = (3.47 \pm 0.26) \times 10^{-10} \text{ einstein cm}^{-2} \text{ s}^{-1} \text{ (MgO)}$$
$$\beta = (3.28 \pm 0.11) \times 10^{-10} \text{ einstein cm}^{-2} \text{ s}^{-1} \text{ (stainless steel)}$$
The values are thus identical within experimental error.

The wavelength-dependent functions of R, T_g, T_f, Φ and $1-T_a$ are shown in Fig. 4 whereas Fig. 5 depicts functions I_0^{Xe}, I_0 (MgO) and I_0 (stainless steel).
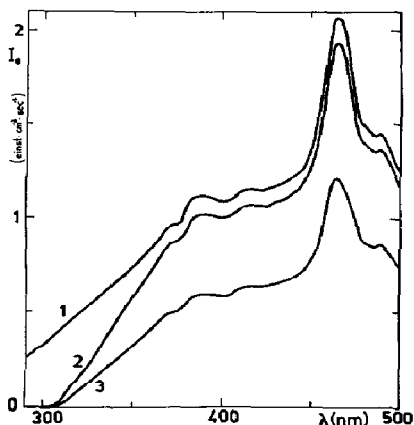
Fig. 5. The dependence of light intensity on the wavelength in absolute units einstein cm^{-2} s^{-1}. 1, I_0^{Xe} the intensity of source placed into a quartz jacket; 2, I_0 (MgO) the intensity inside the reaction cell immediately behind the inner wall; MgO coating of the reflector; 3, the same value as 2 but with the reflector finished in polished stainless steel.

It is seen that the spectral distribution of light entering the reaction vessel remains practically unchanged both for polished stainless steel and MgO coated surface of the elliptocylindrical reflector.

Though the total light reflected is somewhat higher in the case of MgO

coating $\left(\displaystyle\sum_{290\ nm}^{500\ nm} I_0 = 3.76 \times 10^{-7} \text{ einstein } cm^{-2}\ s^{-1} \right)$ than that measured in the

case of the stainless steel surface $\left(\displaystyle\sum_{290\ nm}^{500\ nm} I_0 = 2.27 \times 10^{-7} \text{ einstein } cm^{-2}\ s^{-1} \right)$ the

latter finish is preferred since it is more durable and does not change its optical properties in the long run.

Assuming a total absorption over the whole range of emited wavelengths the limiting attainable absorbed intensity is:

$$I_a^{max} = I_0\ S/V \tag{11}$$

where, in our case, the inner surface of the reaction cell S was 127.2 cm^2 and the volume $V = 90$ cm^3 so that:

$I_a^{max} = 5.32 \times 10^{-4}$ einstein l^{-1} s^{-1} \qquad (MgO)

$I_a^{max} = 3.21 \times 10^{-4}$ einstein l^{-1} s^{-1} \qquad (stainless steel)

Use of reactor for quantitative measurements

Knowledge of absolute values of function $I_0(\lambda)$ enables the use of the reactor for quantitative measurements. Let us consider n absorbing components. The absorbed intensity of an i th component I_a^i (einstein l^{-1} s^{-1}) is expressed by:

$$I_a{}^i(\lambda) = \frac{\varepsilon_i(\lambda)c_i \times 10^3 \times I_0(\lambda)S}{V \sum\limits_{i=1}^{n} \varepsilon_i(\lambda)c_i} \left[1 - 10^{-d \sum\limits_{i=1}^{n} \varepsilon_i(\lambda)c_i} \right] \tag{12}$$

where $\varepsilon_i(\lambda)$ = molar decadic extinction coefficient of the i th component in the solvent used at certain λ (1 mol^{-1} cm^{-1}),

c_i = concentration of the i th component,
d = pathlength (cm),
V = reaction cell volume (cm^3).

The meanings of S and $I_0(\lambda)$ have already been defined.

Integrating eqn. (12) over the range of absorption of the i th component an overall rate of light absorption by the latter can be computed. A Hewlett-Packard 9100 B calculator was used for this purpose, the programme being written for a maximum of 4 absorbing components for the interval of 290–500 nm in 5 nm steps.

The result is obtained directly in einstein l^{-1} s^{-1} units which makes possible a rapid calculation of quantum yields of photochemical transformations.

Examples

Using this apparatus, we photolysed a 0.1 M solution of valerophenone in benzene under an argon atmosphere. The quantum yield of acetophenone formation via the Norrish type II reaction was found to be 0.36 which is in excellent agreement with the literature data[6,7] obtained under similar conditions but with monochromatic light. In our apparatus the conversion of 10% was, in this particular case, achieved during 6 min of exposure.

In another case we attempted to measure the quantum yield of photolysis of hydroxybenzotriazole compounds frequently employed for u.v. stabilization of polymers. The conversion of 10% was achieved in $\sim 8 \times 10^{-5}$ M solution after ~ 100 h so that quantum yields of the order of 10^{-7} could be calculated.

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