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Solution Photocalorimeters

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There exists a wide range of photocalorimetric techniques adapted to different experimental situations and goals. The present article concentrates on instruments used for investigations of solutions and suspensions conducted at ambient temperature range. Basic principles are introduced and different models of photocalorimetric assemblies are discussed. Reported pratical designs are summarized and their properties are compared. The need for use of chemical test and calibration processes is discussed and examplified.

1. Introduction

Investigations of photochemical reactions are important in different areas of pure and applied chemistry and in biology. Many experimental techniques have been employed including different kinds of calorimetry and related methods.

In a photocalorimetric experiment, a sample ("the photolyte") is activated by light energy. A photochemical reaction or chain of reactions (which may include a luminescence step) will take place and the heat quantity evolved is measured. This heat quantity is then compared with the one obtained in a blank experiment conducted under the same conditions using a photoinert reference. Such direct recording of photochemical processes provide sensitive and accurate methods for their thermodynamic characterization and in some cases also kinetic information may be obtained. Photocalorimetric investigations span over wide areas and very different calorimetric techniques have been employed. In the present brief discussion, we have chosen to concentrate on phtocalorimeters designed for measurements of solutions and suspensions under essentially isothermal conditions in the ambient temperature range. Macrocalorimetric as well as microcalorimetric systems will be discussed. Typical application areas include work on organometallic compounds and transition metal complexes[1)-6)], mainly undertaken to obtain data for the characterization of bond energies. Studies of well-designed organic chemical reactions like isomerization[7),8)], and polymerization[9)] also have been reported. Luminescence yields have been measured[10)-12)] and in biology different kinds of photocalorimeters have been used to study the chemistry of vision. Work at ambient temperature in this field has included the use of a typical solution microcalorimeter[13),14)] as well as a novel calorimetric technique where a piezoelectric film (PVDF) was used as sensor for fast temperature changes[15),16)]. In addition to enthalpy changes, this latter method can give kinetic results on the level of 10^{-3}s. Surprisingly, little attention has been given to photosynthesis processes.

Photocalorimeters which will not be discussed in this article include instruments specifically designed for low temperature studies[17),18)], for investigations of thin films[18),19)] and DSC instruments to which light can be supplied[20)-24)]. This latter type of instrument, sometimes called DPC (Differential

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Photo Calorimeter) is commercially available from several manufacturers and has found important use in the characterization of technically important processes in solid materials like the polymerization of UV curable materials.

2. Basic principles

During a photocalorimetric experiment, a certain amount of radiant energy, E_P, is supplied to the calorimeter where part of it will be transformed to heat, Q, which is measured. In some cases, part of the incident light energy, E_r, is reflected. If the vessel and its content are transparent, part of the light energy, E_t, will be transmitted through the vessel to the surroundings. Likewise, if luminescence takes place and the system is transparent, radiant energy of this kind, E_l, will be lost to the surroundings. The enthalpy change for a photochemical process taking place in the calorimeter, Δ_pH, is thus:

$$\Delta_pH = E_P - Q - E_r - E_t - E_l \qquad (1)$$

In order to determine Δ_pH, it is usually necessary to evaluate E_P in a reference experiment where no photochemical process takes place. In analogy with Eqn(1), the energy balance in the reference experiment can be written as

$$0 = E_P - Q' - E_r' - E_t' - E_l' \qquad (2)$$

where Q' is the heat quanity measured in that experiment and E_r', E_t', and E_l' are the energy contributions due to reflection, transmittance, and luminescence, respectively. Usually, the reflection terms in Eqns (1) and (2) are small and, furthemore, nealy identical. When nontransparent calorimetric vessels are used, the two last terms in Eqns (1) and (2) will be zero. Under these conditions, Eqns (1) and (2) will lead to the simple expression

$$\Delta_pH = Q' - Q \qquad (3)$$

For the ideal case, where all light energy is transformed to heat in a reference experiment, Eqn (2) will lead to

$$E_P = Q' \qquad (4)$$

When luminescence reactions are studied, the calorimetric vessel obviously must be transparent and special experimental arrangemants are made in order to evaluate the E_l term, see references 10, 11 and below. Likewise, it might be suitable to measure the transmitted light energy[12),25)].

The molar enthalpy change in the photochemical process, Δ_PH_m, is

$$\Delta_PH_m = \Delta_PH/n \qquad (5a)$$

or, under conditions where Eqn (3) will hold

$$\Delta_PH_m = (Q' - Q)/n \qquad (5b)$$

where n is the amount of substance reacted in the photochemical process.

Preferably, n is determined by analysis, but may be calculated if the overall quantum yield at the actual wavelength, ϕ_λ, is known. ϕ_λ is defined by

$$\phi_\lambda = n/N \qquad (6)$$

where N is the total amount of photons supplied to the reaction system:

$$N = E_P/L(hc/\lambda) \qquad (7a)$$

or, when Eqn (4) is an acceptable approximation:

$$N = Q'/L(hc/\lambda) \qquad (7b)$$

L is Avogrado's number, h Planck's constant, c the speed of light and λ the (average) wavelength of the light. Combination of Eqns (5b), (6), and (7b) will lead to

$$\Delta_PH_m = (1 - Q/Q')(L \cdot hc/\lambda) \cdot 1/\phi_\lambda \qquad (8)$$

and

$$\phi_\lambda = n \cdot L \cdot h \cdot c/\lambda \cdot Q' \qquad (9)$$

when eqn (8) is used to calculate Δ_PH_m, it is important that the photocalorimetric experiment and the experiment where ϕ_λ is determined are run under closely similar conditions. If ϕ_λ is not dependent on the wavelength it may be advantageous to determine Δ_PH_m using light of longest possible wavelength. Minimum energy will then be used to induce the process and $(1-Q/Q')$ will be determined with the highest precision. For cases where ϕ_λ is very low, it is not possible to determine precisely low values for Δ_PH_m by this method.

3. Basic calorimetric principles and techniques

The design of photocalorimetric systems described in the literature varies a great deal even when limited to the rather narrow scope of the present review. As in other fields of chemical calorimetry, two main calorimetric principles have been employed: the adiabatic and the heat conduction (heat flow) principle.

In an ideal adiabatic calorimeter there is no net heat exchange between the calorimetric vessel and the surroundings. The determined heat quantity is directly proportional to the measured temperature change, ΔT. The proportionality constant is in the ideal case equal to the heat capacity of the vessel and its content, C.

$$Q = C \cdot \Delta T \tag{10}$$

Reaction vessels in semi-adiabatic (quasi-adiabatic, isoperibol) calorimeters have some heat exchange with the surroundings which must be corrected for. Adiabatic type solution photocalorimeters reported in the literature are in all cases of this type.

In ideal heat conduction calorimeters heat released is quantitatively transferred from the reaction vessel to a heat sink, usually a metal block. Normally, the heat flow, dQ/dt, is recorded by placing a "thermopile wall" between the vessel and the heat sink,

$$dQ/dt = \varepsilon \cdot U \tag{11}$$

where U is the thermopile potential. Integration leads to

$$Q = \varepsilon \int U dt \tag{12}$$

where the proportionality constant ε (the calibration constant) in the ideal case is the ratio between the thermal conductance of the thermopile, G, and the Seebeck coefficient for the thermopile material, e

$$\varepsilon = G/e \tag{13}$$

Thermopiles in heat conduction instruments are usually of the semiconduction type, *i.e.* thermocouple plates manufactured mainly for use as Peltier effect coolers.

The difference between a macrocalorimeter and a microcalorimeter is not well defined and terminology used in the literature is sometimes confusing. Here we use the micro-prefix for calorimeters with a sensitivity in the order of 1 μW or better. The amount of reactant used in short experiments is typically about 1 μmol or less and the reaction vessels often have a volume of a few cm^3. However, it is not uncommon that microcalorimetric vessels have volumes in the order of 25-100 cm^3. The amount of reactant used with a macrocalorimeter is typically in the order of 1 mmol and vessel volumes are usually in the range of 25-200 cm^3.

Solution microcalorimeters are in most cases designed as twin instruments whereas macrocalorimeters normally use single vessels. Twin heat conduction calorimeters are well suited for short as well as for long reaction periods (days) whereas the heat exchange corrections needed for the semi-adiabatic instruments make them less suitable for precise measurements during longer reaction periods than about 20 min. A disadvantage with heat conduction calorimeters is their large time constants and thus the need for correction of their potential-time curves before accurate kinetic information is obtained. Such corrections can be made by on-line computer treatment of the potential-time curves[26].

4. Photocalorimetric assemblies

The light source in photocalorimetric assemblies consists of tungsten filament lamps, mercury lamps, mercury-xenon arc lamps or lasers. So far, lasers do not seem to have been used as light source in solution photocalorimetry. In most cases, a monochromator or a filter is used and light of a rather narrow band path is supplied to the calorimetric vessel, *e.g.* 15 nm. Electrical power supplied to the lamps is in most cases in the range of 100-1000 W, but only a very small fraction (about 10^{-4}–10^{-6}) of this power will reach the calorimetric vessels. The optical systems often include heat filters and lenses.

Two main methods are used to enter the light

beam into the calorimetric vessel: through a "window" made by glass or quartz or by use of light guides (fibers, fiber bundles or solid rods) made from glass, quartz or plastic. Light guides can often be introduced into existing or slightly modified calorimetric vessels, whereas the window technique normally is used with specially designed phtocalorimetric vessels. Preferably, light guides should dip into the solutions in order to minimize reflections. This may cause problems if plastic fibers or rods are used which are incompatible with most organic solvents. The problem exists also with glass and quartz guides which usually are coated with a thin layer of plastic ("cladding") and with fiber bundles where the ends usually are glued together with epoxy. Deposition of products from photochemical processes on windows and on the end surfaces of light guides may sometimes cause problems.

Optical fibers are flexible which can be of great advantage from the point of view of instrument design and use. However, it should be recognized that the transmittance of light through a flexible guide may change significantly if the position of the cable relative to that of the light source is changed. In accurate work it is therefore important that light guides are given well-defined and fixed positions during the measurements.

For the group of photocalorimeters discussed here, one may distinguish between five different types of experimental assemblies, model I - V,shown in Fig. 1. Macrocalorimeters are usually arranged according to model I, making use of a quartz window in the calorimetric vessel. Reference and reaction experiments are conducted separately using the same vessel charged with different solutions. It is then necessary that the light source and other parts of the system are extremely stable. In some cases, a second calorimeter (or some other light meter) is positioned in series with the photochemical calorimeter for measurements of fluorescence or directly transmitted light, model II. Model III employs a split beam technique where the two light beams are directed to each of the vessels in a twin calorimeter. One of the vessels is charged with the photolyte and in the other, the reference vessel, all light energy is transformed into heat. If the differential calorimetric signal is recorded and in case the system forms a perfect twin, also in respect to the light beams and to their passage between the beam splitter and the calorimetric vessels, the quantity Q' - Q (Eqn(3)) will be obtained directly. As will be discussed later, there may be practical difficulties in reaching the required high degree of twinning. A technique where reaction and reference vessels are illuminated separately (model IV) can therefore be advantageous. But as long as only the differential calorimetric signal is recorded, it will not be possible to derive values for ϕ_λ(Eqn9). In model V one part of a split beam is used to illuminate the sample in the photochemical calorimeter, C_P The other light beam is used as a reference and its power is measured by a separate calorimeter, C_R. Both these calorimeters can be of the twin type (Vb). In calibration experiments, the calorimeters are charged with photo-inert solutions and radiant energy is transformed to heat in both instruments, $Q^\circ(C_P)$ and $Q^\circ(C_R)$, respectively. Alternatively, instead of using a reference calorimeter, some other technique for measurement of radient energy can be used, *e.g.* a photodiod. If energy terms, due to reflexion, transmittance, or luminescence, are proportional to the incident light energy (or can be neglected), the ratio between the two measured heat quantities is an instrument constant for a given wavelength or light composition, c_λ, which does not depend on fluctuations in the incident radiant power.

$$c_\lambda = Q^\circ(C_P)/Q^\circ(C_R) \qquad (14)$$

With an instrument system according to model V, it is thus possible to continuously measure the radiant power supplied to the photochemical system or corresponding light energy during a certain period of time even if there are significant fluctuations in the radiant power from the lamp:

$$E_P = c_\lambda \cdot Q(C_R) \qquad (15)$$

5. Solution photocalorimeters

A brief review

In this section the design and the properties of

some solution (suspension) photocalorimeters will be reviewed. The focus will be on instruments which are judged to be of current interest.

More than 50 years ago, Daniels and coworkers reported the design of a photocalorimeter with features that still are of interest[25]. The instrument (model II, Fig.1) can be characterized as a single vessel heat conduction microcalorimeter. A copper-constantan thermopile was used as sensor for the heat flow. The cylindrical reaction vessel was made from quartz, volume about 3 cm^3. Light from a 500 W projection lamp was introduced through the front wall of the quartz cylinder. Immediately behind the rear end wall of the cylinder, a second thermopile was positioned and used for measurements of transmitted light. The instrument was used, for example, for the determination of quantum efficiency of photosynthesis of algae. During the following 30 years, there appears to be no significant report of any photocalorimeter for

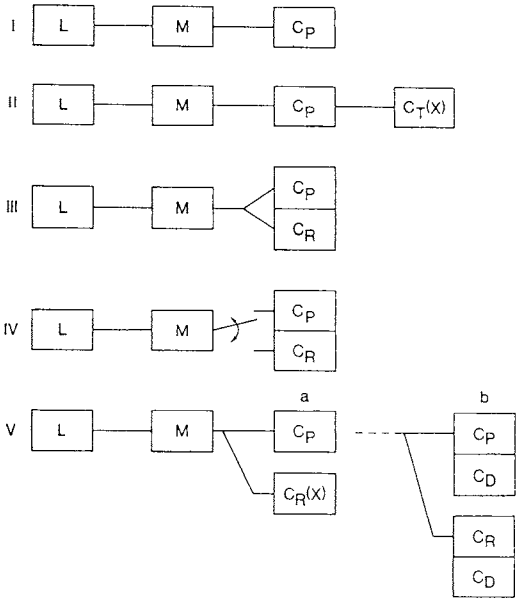

Fig.1 Solution photocalorimetric assemblies, *cf* the text. L, Light source; M, monochromator, lenses, filters; C_P, photocalorimeter; C_T, photoinert calorimeter for transmitted light; C_R, photoinert reference calorimeter; X, non-calorimetric device for measurement of radient energy.

studies of solutions or suspensions but in the late sixties, Seybold *et al*[10] measured the fluorescence quantum yield of organic dyes by use of an unusual type of semi-adiabatic double calorimeter (model II, Fig.1). One of the calorimetric vessels was charged with the fluorescent solution and the other vessel, used for measurement of the transmitted light, was charged with a black solution. The fluorescence quantum yield, ϕ_f, was calculated from Eqn (16),

$$\phi_f = \lambda_f/\lambda_a[(K_b - K_f)/(K_b - K_s)] \quad (16)$$

where λ_f and λ_a are the average values of the wavelength of the fluorescent and absorbed light, respectively. K_b is the initial heating rate of a nonfluorescent compound with the same optical density, at a given wavelength, as the fluorescent sample. K_f and K_s are the initial heating rates of the fluorescent sample and the solvent, respectively. Matching solutions were prepared using results of calorimetric measurements. For details of experimental and correction procedures, see reference 10.

In the late seventies, Olmsted and co-workers[11),12)] studied fluorescence quantum yields by use of small volume Dewar vessel calorimeters. Light from a 75 W medium pressure Hg lamp was passed through a lens and a filter to the Dewar vessel which had a square cross section with inner dimension 1 cm. The vessel was made from Pyrex but was fitted with quartz windows for passage of the light beam. Thermistors were used as temperature sensors. The fluorescence experiments were conducted similar to those reported by Seybold *et al.*[10] but the solutions with matched absorbancies were prepared by a spectrophotometric technique.

In another report[27], Olmsted describes a similar instrument designed for photon flux measurements. This simple instrument consisted of a cylindrical Dewar vessel, inner diameter 3 cm, equipped with a quartz window, a magnetic stirrer, a calibration heater, and a thermistor used as temperature sensor. The vessel was charged with a solution of tetraphenylcyclopentadienone in toluene, which is highly absorbing throughout the visible and UV-spectrum.

At about the same time, Adamson *et al.*[1]

reported the design of a photocalorimetric assembly using a semi-adiabatic calorimeter, Fig.2, related to the Olmsted instruments and like them a typical representative of model I (Fig.1). A glass reaction vessel, volume estimated to about 50 cm^3, was equipped with thermistor, calibration heater and a magnetic stirrer bar. The vessel was enclosed by a double-wall container thermostatted by water flow from a separate thermostatted bath. The space around the reaction vessel could be evacuated. The vessel and the double-wall container were fitted with quartz windows for the incident light beam. This instrument, developed at the University of Regensburg, Germany, was used in measurements of photolysis of trans-azobenzene, metal oxalate complexes and metal carbonyl compounds. Adamson and coworkers at University of Southern California, Los Angeles, subsequently used a slightly modifed version of this instrument[2] in their further investigations of other systems[3),4),6),8)]. The Regensburg instrument was further developed by Wachter and Winkler. A first version was described in great detail in Winkler's thesis and was used in measurements on several metal carbonyl complexes[5]. The final (unpublished) design by Wachter (deceased 1991) is shown in Fig.3. The lamp house contained a 1000 W Hg/Xe arc lamp fitted with an elliptical reflector giving a collector efficiency of about 60%. At a wavelength of 366 nm, the output of the monochromator was about 180 mW for a band pass of 20 nm. Part of the monochromator output was reflected by a quartz plate and the light flux measured by a silicon photodiode, *cf* X in model V, Fig.1. Light transmitted through the quartz plate was passed through quartz windows to the interior of an 180 cm^3 reaction vessel made from Pyrex. It was

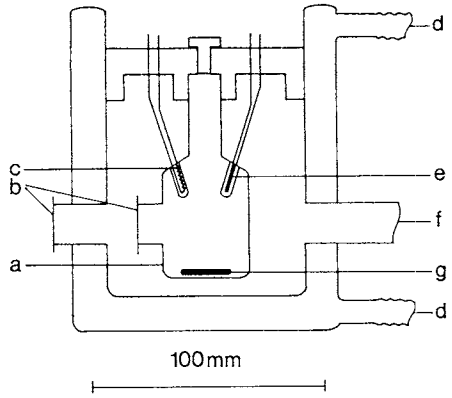

Fig.2 A semiadiabatic photocalorimeter (Adamson *et al.*[1]). a, glass reaction vessel; b, quartz window; c, calibration heater; d, to thermostatted bath; e, thermistor; f, to vaccuum pump; g, stirrer bar.

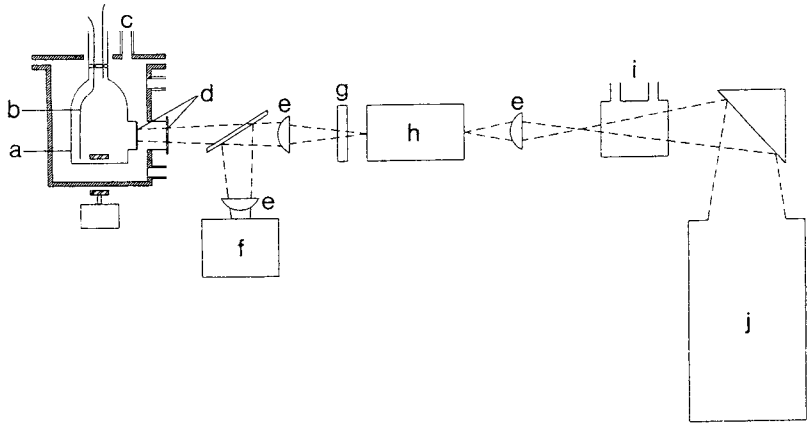

Fig.3 Photocalorimeter according to Wachter (unpublished). a, glass reaction vessel fitted with magnetic stirrer and thermistor (not shown) and calibration heater (not shown); b, teflon titration tube; d, quartz window; e, quartz lens; f, photodiode detector; g, shutter; h, monochromator; i, heat filter; j, lamp house.

positioned in a double-walled brass can through which thermostatted water was circulated. The space between the brass can and the vessel was evacuated. The vessel content was stirred magnetically and a thermistor was used as temperature sensor. Reagents could be added through a Teflon tube and the calorimeter allowed work under inert atmosphere. Temperature changes could be measured with an estimated accuracy of $\pm 5 \cdot 10^{-4}$ K corresponding to an error in enthalpy measurements of about 0.5 mJ allowing precise measurements on the millimolar scale.

In all the calorimeters described so far, light was introduced to the calorimetric vessel through a window made from glass or quartz. The use of optical light guides can sometimes be more attractive but as they in practice usually have a rather small aperture, the method is most common with microcalorimeters.

Although not a photocalorimeter in the sense this term is used here, the work by Mc Ilvane and Langerman[28] should be mentioned in this context. These workers used a semi-adiabatic titration calorimeter (Tronac 450) fitted with 7 mm quartz fibre bundle in their calorimetric measurements of luminescent bacteria. Light generated by the microorganisms was transmitted by the light guide to a photomultiplier. Langerman[29] has also described the use of a Tronac 550 isothermal calorimeter (a thermoelectric heat pump calorimeter) fitted with fiber optics for the simultaneous measurement of heat evolution and light production.

Schaarschmidt and Lamprecht[30] have described two different calorimetric vessels, volume 100 cm^3, equipped with light guides. The vessels, used with a Calvet microcalorimeter (Setaram) were designed for studies of living yeast cells. One of the vessels, fitted with a stirrer and a thick quartz light guide, diameter 10 mm, was used for studies of the sensitivity of yeast cells to UV radiation. The other vessel, also stirred, has two thin light guides (diameter 1 mm) which were bent to a distance of 5mm. This vessel was not designed for use as a photocalorimetric vessel but rather for the simultaneous determination of the heat production and the optical density, and thus the concentration of cell suspensions. One of the light guides was illuminated, the light passed through the 5 mm gap in the cell suspension and through the other light guide bringing the light path to a photomultiplier.

Cooper and Converse[13] equipped an LKB batch microcalorimeter (a rotating twin thermopile heat conduction calorimeter[31] with optical fiber bundles for their study of the photochemistry of rhodopsin. The instrument assembly, shown schematically in Fig.4, is represented by model IV (Fig.1). The optical system consisted of a stabilized 200 W Hg-Xe arc lamp, a monochromator, and glass fiber bundles. The entrance faces of the light guides, at the exit of the monochromator, were mounted on a movable platform so that either vessel (the photochemical vessel or the reference vessel) could be illuminated. The optical fibers were introduced into the two gold vessels through vapour tight silicon rubber collars on the loading ports. The ends of the fiber bundles were imbedded in clear epoxy and positioned just below the surface of the reference solutions. During an experiment the two vessels were illuminated for identical length of time.

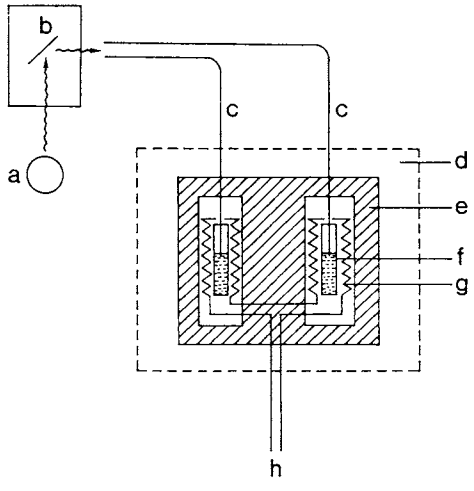

Fig.4 An LKB batch twin microcalorimeter transformed to a photocalorimeter (Cooper and Converse[13], cf Fig.1, model IV.
a, light source; b, monochromator; c, optical fiber bundle; d, thermostatted air bath; e, heat sink; f, reaction vessel; g, thermocouple plate; h, differential potential signal from the thermopiles.

Frequent checks were made with inert solutions in both vessels in order to make small compensations for the deviations from a perfect twin system. The energy fluxes to the vessel were in the range 10-300 μW depending on the wavelength.

Teixeira and Wadsö[32] recently described a photocalorimetric system using two twin calorimeters of the thermopile conduction type (LKB/Thermo-Metric microcalorimetric system[33]. The experimental assembly, shown in Fig.5, is represented by model Vb (Fig.1). Six optical cables of the plastic, single-fiber type, diameter 1 mm, guided light from the exit slit of a monochromator to the two photocalorimetric vessels of the two twin calorimeters. One of them, the photocalorimetric reaction vessel in calorimeter P, was a stirred titration-perfusion vessel[34]. The other calorimeter, R, serving as a photoinert reference, used a simple light absorption vessel. For each of the two twin calorimeters (equipped with simple reference "vessels" consisting of steel rods), the differential signal was recorded.

The photochemical reaction vessel, Fig.5e, is shown in some detail in Fig.6. The sample

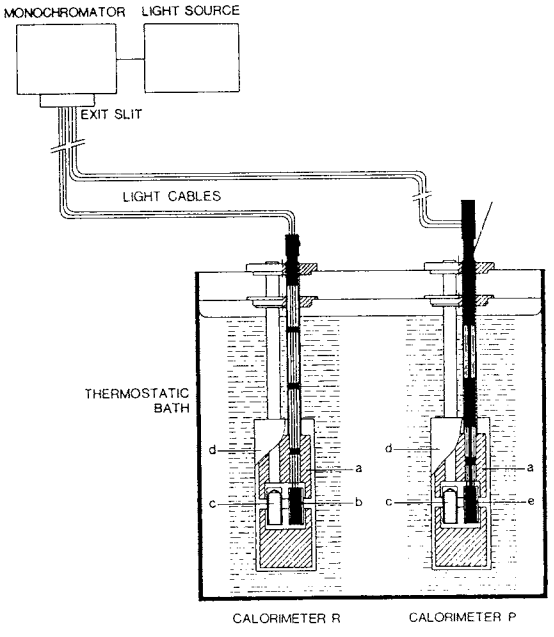

Fig.5 Simplified picture of a photocalorimetric system based on two twin ThermoMetric microcalorimeters (Teixeira and Wadsö[32], cf Fig.1, model IV b). The two twin calorimeters (R,P) are immersed in a thermostatted bath. Calorimeter P is used as a photochemical calorimeter and calorimeter R serves as a photoinert reference.
a, heat sink; b, photoinert light absorption vessel; c, calorimetric reference "vessel"; d, steel can; e, photochemical reaction vessel. The thermopiles are not shown.

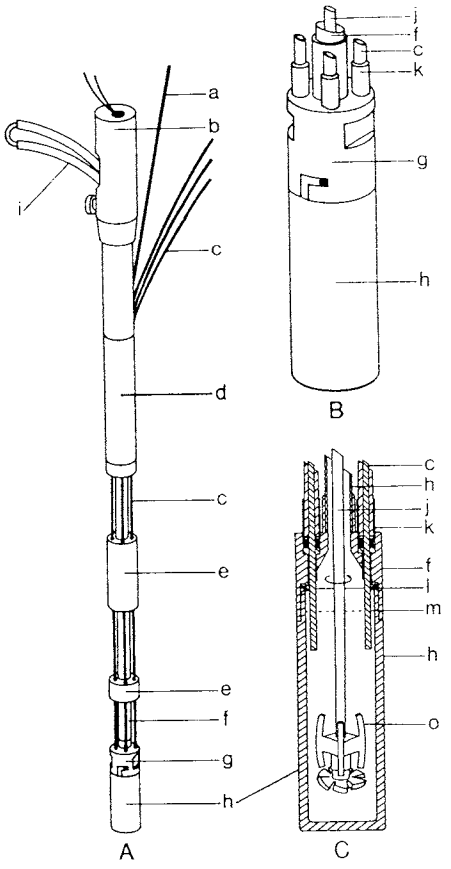

Fig.6 A, the photochemical vessel (in calorimeter P, Fig.5). B, details of the sample container and the lid. C, section through the sample compartment and the lid, a, titration tube; b, stirring motor; c, optical cable; d, plastic tube; e, heat exchangers (brass bolts); f, steel tube; g, lid; h, sample compartment; i, teflon tubes (used in perfusion experiments); j, stirrer shaft; k, steel sleeves imbedding the optical cable; l, teflon ring; m, liquid surface; o, stirrer.

container, h, volume 3 cm^3, was made from acid proof steel with its inside coated with Teflon. The light source was a 100 W tungsten lamp. At the wavelength 436 nm and a band pass of 13 nm, the radiant power in each of the optical cables was about 20 μW. In separate experiments the photochemical vessel was charged with a photoinert solution and light was thus quantitatively transformed to heat in both calorimeters leading to a value for c_λ, Eqn(14). The radiant energy supplied to the photochemical vessel during the main experiment could then be calculated, Eqn (15). With this calorimetric arrangement, it is thus not necessary that the radiant power is constant provided that the value for c_λ, does not change. However, it is important that variations in the radiant power have the same relative influence on the two beams. Movement of the optical fibers might affect the c_λ value. Subsequently Teixeira and coworkers[7] used the same kind of twin microcalorimeter and phtochemical reaction vessel in the arrangement illustrated by model III (Fig.1), *i.e.*, two identical light beams were introduced to a photochemical reaction vessel and to an inert reference vessel, respectively, which formed twin vessels of one calorimeter. The arrangement is less expensive than that with two separate (twin) calorimeters shown in Fig.5, but it is a limitation that the quantum yield cannot be determined. Further, it may in practice be difficult to adjust the light beams to the same power. With the beam split device used by Cooper and Converse[13] (model IV, Fig.1), this difficulty is avoided provided that the loss of radiant power in the cables to reaction and reference calorimeters, respectively, is the same.

A few comments

Microcalorimetric techniques have been much developed during recent years and are now becoming increasingly used in solution thermochemistry and in biology[35]. For example, they are essential for work with expensive, hazardous or slightly soluble substances. For biochemical processes substances are not only expensive but the molar concentrations used are nearly always in a range for which microcalorimetry is required. Further, for some processes, including many photochemical reactions, it is important to keep the concentration of the reactants low in order to minimize unwanted side reactions. It is felt that both the adiabatic and the heat conduction principle may be applied successfully on the microcalorimetric level. However, true microcalorimeters used in solution photocalorimetry have so far always been of the heat conduction type. Commercially available solution microcalorimeters are easy to convert to photo-calorimeters by use of light guides. These instruments are as a rule also well suited for measurements of rather large thermal powers or heat quantities, well in the range typical for macro-calorimeters. However, adiabatic type calorimeters designed for work on the macro scale can hardly be used as microcalorimeters.

For a well designed thermopile heat conduction calorimeter the measurement of the integrated heat flow (Eqn 12) is not affected by temperature gradients in the reaction vessel during the reaction. A photochemical (-biological) process can be initiated without mixing of reagents and a static ampoule can therefore in many cases serve as a suitable reaction vessel. Accurate temperature measurements in an adiabatic type of instrument requires that there are no temperature gradients in the reaction vessel. This means that a liquid content must be well stirred which sometimes may create problems, *e.g.* when very visous solutions are investigated or when the viscosity (and thus the heat of friction) will change during a measurement due to a polymerization process. When biological tissues are investigated, the integrating principle of a thermopile heat conduction instrument seems ideal.

6. Test and calibration processes

Practically all chemical or physical processes are accompanied by heat effects which makes reaction calorimeters suitable as general process monitors, in addition to their use as thermodynamic instruments. But it will also make all kinds of calorimeters vulnerable to systematic errors. Such risks tend to be larger the smaller the investigated heat quantities are. Calorimeters are usually calibrated electrically. This is a convenient method which is also very accurate from the point of view

that electrical power or energy can easily be measured with the accuracy needed in any microcalorimetric experiment. However, the comparison between heat released in an electrical calibration experiment sometimes is not very close to that in the chemical or biological processes studied. These facts often seem to be overlooked, not the least when commercial instruments are used. In our opinion, chemical test and calibration processes should be used more frequently, especially in microcalorimetry. Several chemical test and calibration processes suitable for use in aqueous solution microcalorimetry have recently been described[36]. Photo reduction of potassium iron oxalate (Parker's actinometer), frequently used in general photochemistry, has also been employed as a test reaction in solution photocalorimetry: $[Fe(C_2O_4)_3]^{3-} \rightarrow [Fe(C_2O_4)_2]^{2-} + CO_2 + 0.5C_2O_4^{2-}$(0.15M in 0.05 M aqueous H_2SO_4; $\phi \approx 1.0$ at 436 nm) The agreement between results reported for $\Delta_P H_m$ is satisfactory: -54.0 ± 8.0 kJ·mol^{-1} [13]; -53.6 ± 2.9 kJ·mol^{-1} [1]; -52.6 ± 0.8 kJ·mol^{-1} [32]; and -51.2 ± 2.0 kJ·mol^{-1} [7].

One problem with the process is that aqueous H_2SO_4 is used and that Fe^{II} is formed. If stainless steel vessels are employed there might be some corrosion effects at which Fe^{II} also is formed. The calorimetric as well as the analytical values may then be in significant error. Corrosion effects on steel vessels may be avoided by coating the reaction vessel with teflon[32]. Another useful test reaction is the isomerization of trans to cis azobenzene in organic solvents (heptane). Two enthalpy values, which are in good agreement, have been reported: 49.0 ± 5.4 kJ·mol^{-1} (λ = 546nm; ϕ = 0.45)[1] and 48.9 ± 2.3 kJ·mol^{-1} (λ = 436 nm)[7]. These values, coupled with the enthalpies of dissolution in heptane of the two isomers lead to $\Delta_r H_m$ (trans-cis, cr) = 45.2 ± 2.4 kJ·mol^{-1} which is slightly lower than the result obtained by reaction-dissolution calorimetry, 49.1 ± 1.0 kJ·mol^{-1} [7].

7. Conclusions

Photo induced processes are of great importance in pure and applied chemistry, plant biology, and medicine including pharmacology. The area of solution photocalorimetry is well developed with respect to principles, instrumentation, and working procedures. It may be concluded, however, that as yet there are very few scientific groups in the world which are active in this field-despite the fact that it is in many cases feasible, and simple, to convert commercially available microcalorimeters to phtocalorimeters by providing them with optical light guides.

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要　旨

異なる実験的な立場と目標に適合する広範囲の光熱量測定の技術が存在している。この総説は室温付近での利用されている光を通す溶液とサスペンションの研究に利用されている装置について書かれたものである。基礎的な原理は紹介され，異なるモデルの光熱量計部分が議論されている。部分的な設計の報告がまとめられ，それらが比較されている。化学的な試験の利用の必要性と検定の手順が議論され，例示されている。