PHOTOCHEMISTRY IN INDUSTRIAL SYNTHESIS

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(Received December 13, 1983)

1. Introduction

Since about 540 types of preparative organic photoreactions are known [1], the interest of industrial photochemists has shifted from light-induced chain reactions to photoreactions with quantum yields φ of less than or equal to unity, which may be economically feasible if they are able to shorten conventional syntheses considerably or if the products are of unusual structure and/or of high economic value. In the following survey the corresponding knowledge, equipment and problems which always accompany the scaling up of a photoreaction are summarized.

2. Light sources

High pressure discharges up to a power input of 100 kW are available as light sources for photochemical production processes. Figure 1 shows that the radiant flux from mercury high pressure lamps expressed as a percentage of the power input increases with increasing electrical power input and remains nearly constant between 10 and 60 kW [2]. Here, the total output of photochemically utilizable light (200 - 600 nm) averages 44.2%. The insertion of a cut-off filter such as boron silicate glass decreases the light output (300 - 600 nm) to 19.6%, whereas single mercury lines are emitted with an efficiency as low as 5.3% for 366 nm and 3.3% and 4.2% for 313 nm and 254 nm respectively. In addition the scope of polychromatic light sources may be limited by the halfwidths of the absorption bands of the irradiated compounds. Therefore, efforts have been made to shift the maximum emission of the lamps to spectral regions favourable for photochemical syntheses. This can be achieved by doping mercury high pressure lamps with other metals: antimony offers light in the range 270 - 300 nm where undoped mercury lamps emit poorly and TlI creates a very strong line at 536 nm [2]. A disadvantage of doping is the decrease in the lifetime which for undoped mercury high pressure lamps corresponds to 1500 - 6000 h, depending on the operating conditions [2]. Nevertheless, the development of high intensity light sources for industrial photochemistry is directed towards higher monochromaticity. For this reason, the appearance of a new source of intense and nearly monochromatic radiation at
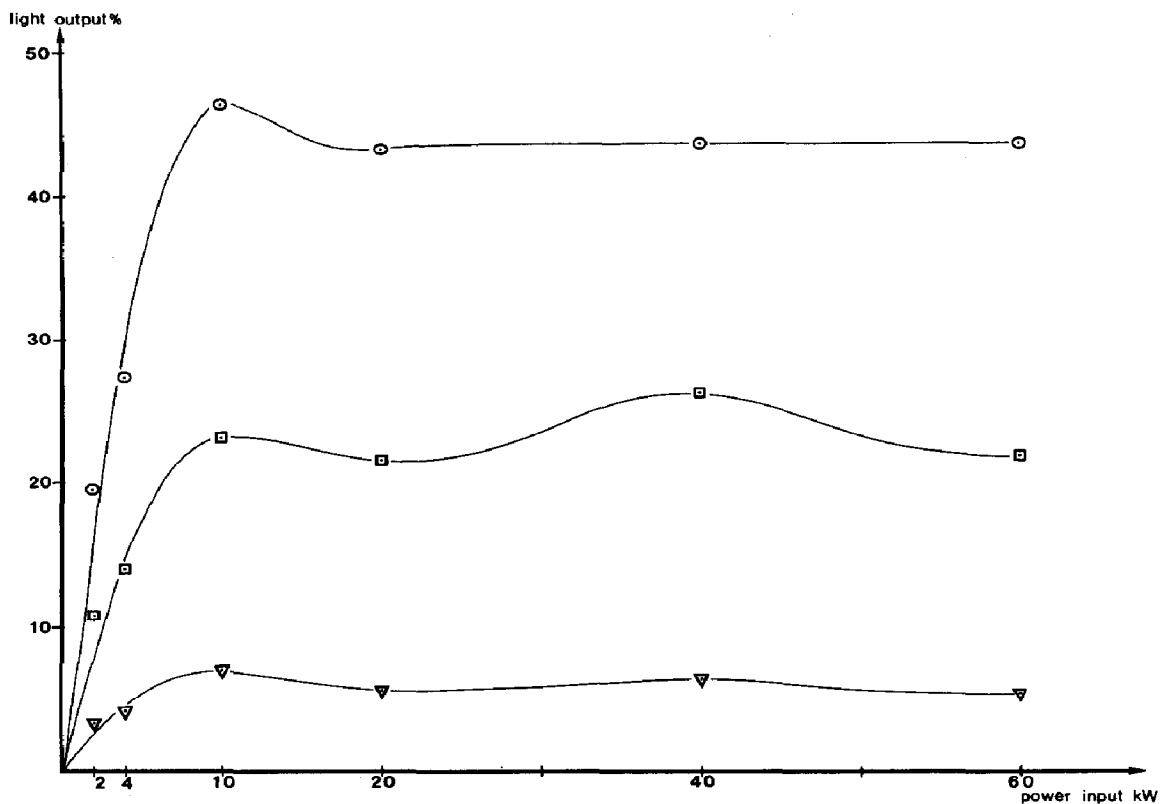
Fig. 1. Light output of mercury high pressure lamps as a percentage of the electrical power input: ⊙, λ = 200 - 600 nm; ⊡, λ > 300 nm; ▽, λ = 366 nm. (From ref. 2.)

254 nm (216 W ≡ 24.1% of the electrical power input) with a lifetime of more than 3000 h is noteworthy [3]. The fabrication of high intensity light sources indicates that there is a demand for them, although users spread an aura of secrecy over their application to photochemistry in industrial synthesis. This attitude does not promote advancement of photochemical technology.

3. Reactor design

According to the Beer–Lambert law of light absorption, photoreactions are characterized by their spatial inhomogeneity. The light absorption profile is also affected by the following: (1) the dependence of the consumption of the light-absorbing species on the irradiation time; (2) competitive light absorption in multicomponent systems [4]; (3) the use of polychromatic light sources; (4) possible deviations from the Beer–Lambert law, *e.g.* those resulting from economically desirable high concentrations.

These factors have complicated mathematical treatments in the past, but the approximate computer calculations available today facilitate at least in part the scaling up of photochemical processes. Even the simplest case with only one light-absorbing component present during the photoreaction illustrates the problems arising from the spatial inhomogeneity very well.

For a reaction zone defined by an extinction E of unity (90% light absorption) the term $1/\epsilon c$ (cm) derived from the Beer–Lambert law determines its thickness. High extinction coefficients ϵ (l mol^{-1} cm^{-1}) and high concentrations c (mol l^{-1}) of the light-absorbing substance may reduce the thickness of the reaction zone to several micrometres, i.e. to a region where the flow of a turbulent liquid is also kept laminar by adhesive forces from the wall. The result is a decreasing contribution of the macroscopic homogenization processes to the exchange of reactants out of and into the reaction zone. The rate of the photoreaction becomes increasingly more diffusion controlled. Finally, overirradiation products occur as well as light-attenuating films. To overcome these difficulties several methods have been proposed as follows, but few are technically practicable.

(1) The surface of a falling liquid film is irradiated [5].

(2) The reaction zone is transferred from the wall to the faster moving centre of a stream consisting of two synchronously flowing non-miscible liquids of which the light-transmitting liquid is directed towards the incident light [6].

Because laminar flow is required in both these cases, the problems arising when $1/\epsilon c \ll 1$ are solved only to a limited extent.

(3) Turbulences are generated by gas bubbles in irradiation solutions which stream rapidly upwards. This improves the reactant exchange significantly [7].

To produce the gas bubbles a centrifugal pump has been developed, which is able to transport gas–liquid mixtures containing up to 20 vol.% gas [8]. High quantum stream densities (in einsteins per hour per square centimetre) may also render the removal of the irradiation products from the reaction zone and its supply with starting material more difficult. Because the intensity of radiation varies inversely as the square of the distance from the light source, it might be helpful to elongate the distance between the reaction zone and the lamp. However, expansion is not desirable as the space required contributes to the economical evaluation of any industrial process.

The majority of industrial photoreactors are of the immersion lamp type. Products of high economic value (e.g. vitamin D_3) are prepared at a rate of up to about 20 ton year^{-1} in a number of single cylindrical reactors surrounding tube-like lamps. Photochemical mass production in the range of 50 - 120 ton day^{-1} (cyclohexanone oxime for Nylon 6) requires large reaction vessels equipped with many high intensity lamps [9]. In these the arrangement of the lamps depends on the reaction profile of the irradiated solution. The distance between two adjacent lamps should not exceed

twice the thickness of the reaction zone defined above. Removal of the heat is only one problem arising in this type of photoreactor.

The handling of photosensitized reactions is less difficult when there is a constant sensitizer concentration. In this case it is not necessary to take into account the changes in the light absorption profile due to the time-dependent consumption of the light-absorbing species.

4. Materials

Apart from light-transmitting quartz or glass, non-metallic construction materials are preferred because traces of polyvalent metal ions, *e.g.* from stainless steel, may change the direction of a photoreaction considerably. Only contact with extremely corrosive solutions which occur in photonitrosation processes requires expensive titanium vessels [9]. Pumps are another source of possible contamination. Therefore, centrifugal pumps with magnetic coupling are recommended, provided that all the parts in contact with the pumped medium consist of materials with suitable properties.

Most of the known liquid light filters are not stable when combined with high intensity light sources. To satisfy the requirements of industrial photochemistry stable cut-off filter solutions had to be developed [10]. Another important detail is the elimination of UV-attenuating films which in general are not visible. For this purpose an aqueous solution of 10% HF was found to be most effective. In addition the appearance of hazardous electrostatic charges is observed when ethers (*e.g.* 1,4-dioxan, *tert*-butyl methyl ether) circulate as solvents through tubes made from glass or polyfluorinated plastics. Electrostatic charging can be avoided by not earthing the apparatus but using an admixture of hydroxylic solvents, *e.g.* 2% *tert*-butanol, which do not participate in the photoreaction.

5. Economic considerations

For the economic evaluation of a large-scale photoreaction a simple consideration of its quantum yield and the electrical cost of running a light source such as that given in ref. 11 is inadequate and other factors have also to be taken into account.

(1) Quantum yields are defined only for specific wavelengths. They are not applicable to polychromatic light sources, especially in combination with broad absorption bands of the irradiated substance, and must be substituted by empirically determined irradiation times.

(2) By assuming that about 10% of the power input is utilized as light approximately the total power input has to be removed as heat. This in-

creases the electrical cost which must therefore be calculated by multiplication of the power input of the lamp by about a factor of 3.

(3) The molecular weight of the photoproduct must also be taken into account as it determines the amount of material produced by photoreactions with the same molar conversion in the same irradiation time, *e.g.* in photonitrosations substitution of cyclohexanone oxime (for Nylon 6) by cyclododecanone oxime (for Nylon 12) produces 1.7 times the amount by weight. An approximate doubling of the molecular weight as in 1,3-dipolar or [2 + 2] cycloadditions or use of starting materials of high molecular weight (steroids for vitamin D_3, aldosterone, cortisone etc.) increases the viability of scaling up a photoreaction.

(4) To avoid side reactions such as dimerizations many photoreactions must be performed in dilute solutions. In these cases the cost resulting from solvent losses and recycling may exceed the electrical cost of running the lamp. This is obvious from the following example. To suppress subsequent photoreactions of the photoproduct, irradiation of a dissolved compound with a concentration of 5 wt.% has to be stopped at 50% consumption. With the assumption that there is no change in molecular weight by the transformation of the starting material into the photoproduct 1 ton of product requires the recycling of 40 ton of solvent.

(5) In addition to the cost of equipment and the cost arising from the limited lifetimes of the light sources it has to be considered that a radiant flux of 1 einstein h^{-1} is equivalent to 130.8 W at 254 nm but only 60.8 W at 546 nm.

The application of photochemistry in industrial synthesis is limited for the above economic reasons. Some photochemically performed industrial processes have already been mentioned, but in general products of high economic value such as hydroxylated vitamin D_3 and derivatives or fragrant chemicals tend to be prepared. For fragrant chemicals photooxidation broadens the scope of photochemistry (rose oxide), although photosensitizers producing singlet oxygen are consumed and have to be added continuously during the reaction. Finally, it should be mentioned that photochemistry in pharmaceutical industries might be a useful tool for the quick manufacture of drugs in quantities of up to 20 - 30 kg for clinical trials.

In contrast with the application of photochemistry to industrial synthesis photochemical destruction of hazardous chemicals such as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) leads to photolytic processes which can also be exploited commercially. It is interesting to note that the photolytic destruction of TCDD was chosen, mainly for reasons of safety, after extensive evaluation of other possible methods [12]. When a 10 kW lamp was used for the photolysis of TCDD in hexane solution the destruction efficiency was 99.94%. Meanwhile, the photochemical dehalogenation to decrease the toxicity of these products has been extended to a large number of chlorinated compounds [13].

6. Future prospects

6.1. Equipment

Lasers meet the requirements for light sources with higher monochromaticity but at present their radiant flux (in einsteins per hour) is in fact as inadequate as their efficiency in the UV region, which is up to 15%. It is expected that more energy-efficient lasers will be designed. Already in 1970 gas dynamic lasers had reached a continuous power output of 60 kW, which can be optionally increased by enlargement of the installation [14]. Further development was undertaken in the U.S.A. and the U.S.S.R. in secret for military purposes only. As these powerful lasers are not available commercially, industrial application of lasers in photochemistry is now restricted to selective separation of molecules at the atomic and/or molecular level, e.g. to the photochemical separation of isotopes.

Lasers as light sources for photochemical syntheses in industry could initiate a drastic change in reactor design. The excellently collimated laser beams could be focused on a high speed jet stream. This technique would facilitate substance transportation out of and into the reaction zone, even at high concentrations of the light-absorbing component, and therefore save considerable amounts of solvent.

6.2. Applications

New perspectives for photochemistry in industrial synthesis are created by the requirement of the public to avoid the pollution of water and air. Many organic syntheses in which compounds of lead, chromium, manganese, mercury, thallium etc. are used as reagents may be substituted by ecologically clean photoreactions. The increasing cost associated with the complete elimination or recycling of these metals enables photoreactions to compete. Further applications of photochemistry in industry do not concern synthesis but destruction of harmful byproducts, chemical warfare material etc. as has been demonstrated for TCDD.

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