

## PROSPECTS FOR SOLAR SYNTHESIS I: A NEW METHOD FOR SINGLET OXYGEN REACTIONS USING NATURAL SUNLIGHT<sup>†</sup>

J. E. GUILLET, J. SHERREN, H. M. GHARAPETIAN<sup>‡</sup> and W. K. MacINNIS<sup>§</sup>

*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1 (Canada)*

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### Summary

A new method is reported for carrying out organic photochemical reactions using sunlight as the photon source, which is both inexpensive and easily scaled up for commercial synthesis. In this procedure, the organic reagent is absorbed in transparent beads of cross-linked ethylene-(vinyl acetate) copolymer. These beads float readily on water and can be exposed to natural sunlight on the surface of a small pond or pool. After exposure, the beads are collected, washed with water and dried in air. The products and unreacted starting material are removed by selective extraction with suitable solvent mixtures, after which the beads can be recycled through the process. A number of classical photochemical reactions have been studied in these systems, including photoisomerizations, the Norrish type II reaction in various ketones and the addition of singlet oxygen to olefinic double bonds. In the present work the rates of addition of singlet oxygen to squalene were measured. Rose Bengal was used as the sensitizer. The resulting allylic hydroperoxide was estimated by the triphenylphosphine method. Conversions of up to 10% were obtained after 4 days' exposure to sunlight. The results of singlet oxygen additions were compared with those for the type II reaction of aromatic ketones.

### 1. Introduction

The study of organic photochemistry has provided a variety of interesting synthetic routes to novel organic compounds and intermediates. Unfortunately, the high cost of using electrically driven lamps to provide the necessary photon energy has made photochemical steps impractical

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<sup>‡</sup>Present address: Connaught Research Institute, 1755 Steeles Avenue West, Willowdale, Ontario M2R 3T4, Canada.

<sup>§</sup>Present address: EcoPlastics Ltd., 518 Gordon Baker Road, Willowdale, Ontario M2H 3B4, Canada.

in most commercial applications. A new method of carrying out organic photochemical reactions using sunlight as the photon source, which is both inexpensive and easily scaled up for commercial synthesis, is reported in this paper.

### 1.1. The Sun as a photochemical light source

The Sun is an excellent source of photon energy for stimulating the synthesis of organic compounds. The obvious success of plant photosynthesis and the myriad of biochemical reactions which flow from it need no further documentation. The problem, from a chemist's point of view, is that sunlight is less intense than light from electrically driven lamps, and thus is not easily introduced into a conventional chemical reactor. The lack of success in commercial applications of solar photochemistry has much more to do with failures in reactor design, rather than problems of photochemistry. If, for example, the reactor were a thin flat plate 100 m<sup>2</sup> (1 hectare in area), the amount of solar photons available at most terrestrial locations would be quite astonishing [1].

Seasonal variations in intensity do occur, because of both latitude and cloud cover, but even in northern latitudes a substantial flux of photons is available (Table 1). The daily average energy flux ranges from about 110 W m<sup>-2</sup> in southern Sweden to about 300 W m<sup>-2</sup> in arid equatorial zones, averaged over both night and day. The energy input on an area of 1 hectare ranges from 26 400 to 72 000 kW h day<sup>-1</sup>.

Figure 1 shows the distribution of solar photons at the Earth's surface for air mass 1 (AM 1), *i.e.* with the Sun directly overhead at sea-level. This distribution changes slightly with air mass and latitude, but to a reasonable approximation can be considered to be relatively independent of geographic location.

Using the data in Fig. 1 the photon flux available over different wavelength ranges can be calculated. These are summarized in Table 2. The theoretical production of a 1 hectare solar chemical reactor can be estimated from these data, assuming that the product has a molecular weight of 400 and a quantum yield of unity. These data are shown in Table 3. Even for

TABLE 1  
Solar power input<sup>a</sup>

	Daily average (24 h) (W m <sup>-2</sup> )	Energy per hectare per day (kW h)	Value <sup>b</sup> per day (U.S. \$)	Value per annum (U.S. \$)
Equatorial desert (southern Egypt)	≈ 300	72000	3600	1300000
Southern Sweden	≈ 110	26400	1320	482000

<sup>a</sup>Standard solar intensity, 1000 W m<sup>-2</sup> = 100 mW cm<sup>-2</sup>.

<sup>b</sup>Value at 5 ¢ (kW h)<sup>-1</sup>.

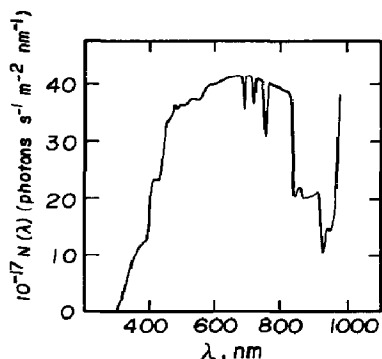


Fig. 1. AM 1 solar radiation: spectral photonic flux density.

TABLE 2

Distribution of solar energy

Wavelength range (nm)	Percentage of total	Solar power input at noon (kW hectare <sup>-1</sup> )	$E_{\min}$ (kcal mol <sup>-1</sup> )
UV < 300	1.2	120	95.5
UV 300 - 350	3.4	340	81.8
UV 350 - 400	4.4	440	71.5
Visible 400 - 700	39.8	3980	40.9
Near IR 700 - 1000	22.1	2210	28.7
IR > 1000	29.1	2910	< 28.7

TABLE 3

Theoretical production of a 1 hectare solar plant

Wavelength range (nm)	Solar power input at noon (kW hectare <sup>-1</sup> )	Photon energy (einsteins (kW h) <sup>-1</sup> )	Theoretical yield <sup>a</sup> (t day <sup>-1</sup> )
< 300	120	9.02	3.5
300 - 350	340	10.5	11.4
350 - 400	440	12.0	16.9
400 - 700	3980	21.0	267
700 - 1000	2210	30.0	212
> 1000	2910	> 30	279

<sup>a</sup>Assumes product molecular weight of 400; average solar input, 300 W m<sup>-2</sup>; quantum yield, 1.0.

short wavelength UV ( $\lambda < 300$  nm) theoretical yields of several tons per day are predicted, while compounds synthesized with visible light ( $\lambda = 400 - 700$  nm) might yield as much as several hundred tons per day. Of course, no practical process is likely to achieve such yields because of inefficiencies due to absorption and reflection losses, as well as side reactions and other

chemical causes for reduced efficiency. Thermodynamic and other contributions to the inefficiency of solar processes are the subject of an authoritative review by Bolton [2]. Nevertheless, the potential is obvious, if a suitable reactor design could be achieved.

### 1.2. Principles of reactor design

Clearly, the most successful reactor design is that of the leaf of a green plant. Since photons are strongly absorbed by thin layers of organic pigments, leaves are relatively thin flat membranes containing mechanical devices to assure access to the reagents (namely  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) and removal and/or storage of the products ( $(\text{CH}_2\text{O})_n$  and  $\text{O}_2$ ). They also contain photon harvesting devices (antenna chlorophyll) which absorb photons and transfer the photon energy to the active sites where the photochemistry actually takes place. In parallel work in our laboratories we have shown how to construct polymeric molecules which mimic this essential feature of plant photosynthesis [3].

The leaf structure of most green plants is highly redundant, in that the leaf area of the plant is much greater than the area of ground which surrounds it. However, one plant that is highly efficient in this regard is the aquatic plant *Lemna minor* (often known as duckweed). It consists of small clusters of circular leaves, 2 - 3 mm in diameter, which float on water. Collections of these plants will completely cover an undisturbed water surface with a nearly continuous green membrane only fractions of a millimetre thick. The plant is such an efficient solar collector that its chemistry cannot match the pace of the absorption of solar photons from direct sunlight and it tends to grow only in areas of diffuse light. It is this plant which gave us the key to a design for an inexpensive solar chemical reactor.

#### 1.2.1. Solar photochemical reactors

Following the principles discussed previously, two reactor designs have been developed. The key to the concept is that the reagents must be exposed in relatively thin layers to ambient sunlight. Water flotation gives both a self-levelling means of support and a vehicle for transport of the devices. Two designs<sup>†</sup> which have been used consist of (1) thin membranes of a cross-linked amorphous polymer rather similar in dimensions to *Lemna minor* (i.e. 2 - 3 mm in diameter, 0.3 - 1 mm thick) and (2) cross-linked amorphous polymer in the form of beads 2 - 3 mm in diameter. The polymer must, of course, be photochemically inert and capable of reversibly absorbing the reagent and products of the desired photochemical reaction. In the first experiments, an ethylene-(vinyl acetate) (EVA) copolymer (Elvax 150) which had been cross linked with  $\gamma$  radiation was used. After extraction of

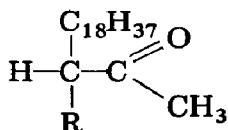
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<sup>†</sup> Patents on these designs have been applied for in most major industrial countries. Experimental quantities of the cross-linked beads are available from EcoPlastics Ltd., 518 Gordon Baker Road, Willowdale, Ontario M2H 3B4, Canada, under the trade name Solaron<sup>®</sup>.

the sol portion, this procedure gives transparent beads or films which will readily absorb up to 50% of their weight of organic substrates in a few minutes. Furthermore, because of their low density, the beads float on water. After exposure to sunlight on a water surface, the beads are placed in a column and selectively extracted with organic solvents to remove the products and unconverted reagent. They can then be loaded with reagent and exposed again. This procedure can be repeated many times. The advantage of the bead or plate reactor is that the thickness of the exposed layer and the concentration of the reagents can be controlled precisely, and the products recovered in a form which seldom requires further purification.

### 1.3. Photochemical reactions

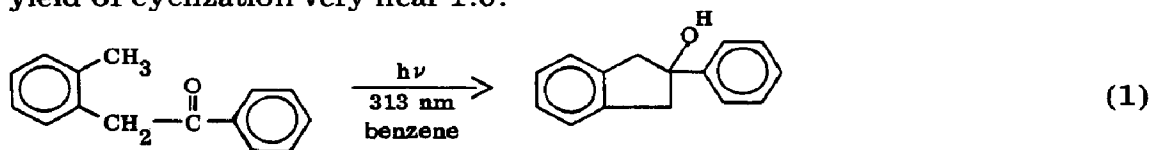
In early studies of the photochemistry of small organic ketones absorbed in polyethylene films Li and Guillet [4] showed that the quantum yields for the Norrish type I and II processes in ketones of the general structure



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were equal to or greater than those where the reactions were carried out in conventional aliphatic solvents such as heptane, namely 0.2 - 0.3. These reactions, however, were not carried out in natural sunlight using the water flotation method. The first experiments with the EVA beads in natural sunlight gave substantial yields of the type II photoproducts from 2-undecanone [5]. This compound has been used as an actinometer in our laboratory and has a  $\phi_{\text{II}}$  of  $0.20 \pm 0.02$ .

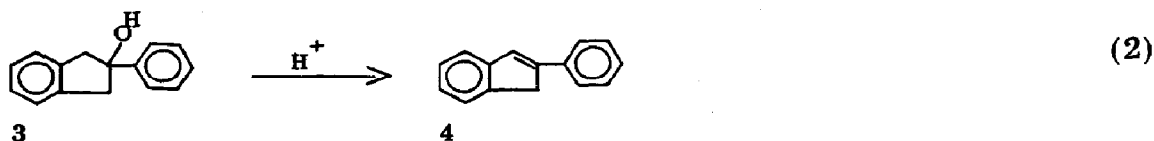
Another model reaction of particular value for evaluation of the efficiency of solar chemical reactors has recently been reported. Meador and Wagner [6] have shown that  $\alpha$ -(*o*-tolyl)acetophenone (2) undergoes a quantitative photocyclization to give 2-phenyl-2-indanol (3) with a quantum yield of cyclization very near 1.0:



2

3

Although the reaction occurs via the triplet state of the ketone, the triplet lifetime is quite short (6 ns). The ketone (2) has a maximum at 313 nm ( $n-\pi^*$  transition) with an extinction coefficient of 109, while the indanol (3) is essentially transparent above 300 nm. The product can easily be separated from 2 since it is an alcohol and appears to be photostable. However, potential problems may exist due to the ease of dehydration of the indanol to give 2-phenylindene (4):

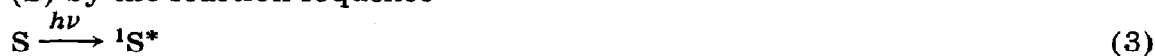


This reaction should be facile because of the extended conjugation found in 4. The reagent and products can be readily determined by gas chromatography. We have synthesized this compound and confirmed its photochemical efficiency. Nearly quantitative conversions to the primary product (3) were obtained after relatively short exposures to a mercury arc lamp. Exposure of the compound absorbed in cross-linked EVA beads gave a 58% conversion to product after 15 min exposure to an OAI 500 W deep-UV photoilluminator.

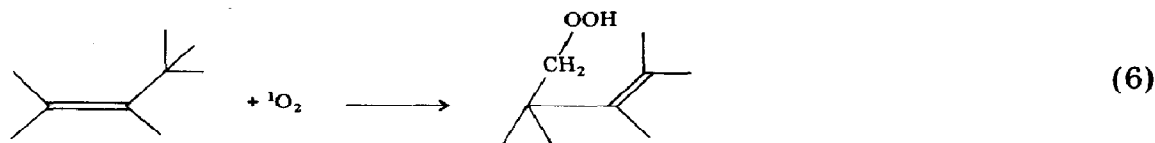
When exposed outdoors on a cloudy weekend in Toronto (December 1983) in the bead reactor system, a conversion of 72% was achieved in 3 days. Because of the high quantum yield and the ease of analysis, this reaction seems to be ideal for testing solar reactor designs and in monitoring near-UV intensity for solar photochemical experiments.

#### 1.4. Singlet oxygen reactions

The relatively high permeability of polyethylene to oxygen makes possible the study of singlet oxygen additions to olefinic substrates. The singlet oxygen is generated within the bead using Rose Bengal as sensitizer (S) by the reaction sequence



In the presence of a suitable olefin, a bimolecular reaction takes place, resulting in the formation of an allylic hydroperoxide, *e.g.*



In our initial experiments we used squalene (a hexamer of isoprene) as the olefin. Because of its high molecular weight (410.7) it has a negligible vapour pressure and can be exposed for extended periods without loss by vaporization. The dye sensitizer and squalene were dissolved in a pentane-pentanol mixture and poured on the beads. After tumbling for 15 - 20 min at 30 °C the solution is completely absorbed by the beads and the solvent is removed by drying under vacuum. The concentration of dye was adjusted so that about 70% of the light was absorbed at the maximum thickness of the bead. The beads were then exposed by floating on water or water-methanol mixtures (to prevent freezing during winter exposures). After

exposure, the squalene was removed by three extractions with isopropanol and the peroxide concentration was determined by the triphenylphosphine method of Stein and Slawson [7].

The rate of singlet oxygen addition to squalene in winter sunlight at Toronto (February - March) is shown in Fig. 2. The reaction appears to slow down at longer times. The conversion depends on the concentration of squalene (Table 4), but the amount of hydroperoxide formed does not. This suggests that the rate is limited by the stationary concentration of singlet oxygen and that higher conversions could be expected if the oxygen concentration were increased or the squalene concentration reduced still further. A reduction in bead size might also be beneficial in improving rates and yields. In any case, as shown in Table 4, conversions of 10% were obtained in 4 days' exposure to winter sunlight, and more rapid rates would be expected in summer exposures.

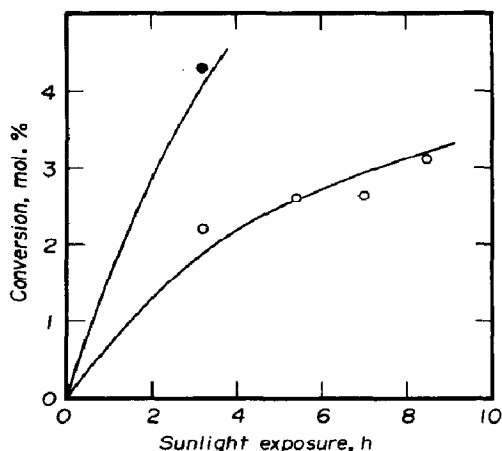


Fig. 2. Rate of hydroperoxide formation: ○, 2.5% loading; ●, 1.2% loading.

TABLE 4

Effect of squalene concentration

Loading (wt.%)	Percentage yield <sup>a</sup>	Peroxide value ( $\times 10^2$ milliequivalents)
2.1	10	0.79
4.4	6.0	0.98
10.0	2.5	0.79

<sup>a</sup>4 days' sunlight exposure.

## 2. Experimental details

The bead reactors were prepared by cross linking a commercially available EVA copolymer (Elvax 150) containing about 20% vinyl acetate.

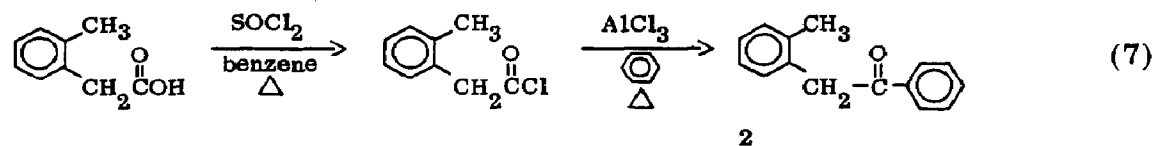
The beads were placed in a glass jar and sealed under nitrogen. They were then exposed in a Gammacell 220 (AECL) to 60 Mrad of  $\gamma$  radiation from  $^{60}\text{Co}$ . Before use, the beads were extracted overnight with diethyl ether, using a Soxhlet extractor, which removes all un-cross-linked polymer (sol fraction). Typically the beads swell in ether to about double their original size. The beads are then dried in air at 35 °C.

The beads are loaded by preparing a dilute solution of the reagents in distilled ether. This is then added to the required amount of beads, which are gently tumbled to assure uniform absorption. After 10 - 30 min the solution is completely absorbed and the solvent can be removed by drying in a stream of warm air or nitrogen. The beads are typically exposed outdoors on a water surface in transparent polystyrene drinking cups or developing trays. After exposure the beads are washed with distilled water, dried briefly and extracted to remove the products. This can be done either using a Soxhlet extraction with ether or with successive additions of the solvent employed for analysis.

In experiments with singlet oxygen addition to squalene the solvent was a 50:50 pentane:*n*-pentanol mixture. Analysis for hydroperoxide was carried out using the colorimetric procedure of Stein and Slawson [7].

### 2.1. Synthesis of $\alpha$ -(*o*-tolyl)acetophenone

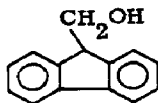
$\alpha$ -(*o*-Tolyl)acetophenone was easily synthesized from *o*-tolylacetic acid:



The acid chloride was not isolated but was used directly in the next step. The product was isolated as white crystals (melting point, 69.5 - 71 °C) (62 - 62.5 °C reported in ref. 8) in a 62% yield. A preparative scale irradiation of the ketone (2) was done under argon using 0.5 g of the compound in 50 ml dry benzene in a Pyrex vessel. A Rayonet reactor equipped with 15 RPR 3000 Å lamps was used and the solution was irradiated for 3 h. Analysis by thin layer chromatography indicated that a quantitative reaction had occurred. This was verified by nuclear magnetic resonance analysis. Some difficulty was encountered in purifying the indanol, presumably due to its tendency to dehydrate (eqn. (2)). However, some white crystals were obtained (melting point, 55 - 57 °C). These were used to calibrate the gas chromatogram. It should be noted that a solution of pure indanol in acetone turned yellow after several days. Gas chromatography analysis indicated that 20% of the indanol had been converted to a compound with shorter retention time (presumably 2-phenylindene (4)).

The flame ionization detector response factors for both  $\alpha$ -(*o*-tolyl)-acetophenone and 2-phenyl-2-indanol were determined using 9-fluorene-methanol (5)





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as the internal standard. A 5 ft  $\times$  2 mm glass column of 5% Carbowax 1540 on chromosorb WHP 80/110 was used at 212 °C. Ethyl acetate was used as a solvent to load the beads and to recover the product.

### 3. Conclusions

We have shown that it is possible to carry out a variety of photochemical reactions in bead or platelet reactors consisting primarily of cross-linked amorphous copolymers of ethylene and vinyl acetate, using sunlight as the photon source. Even in northern latitudes in the winter season, respectable rates of conversion can be attained. The rate of formation of singlet oxygen adducts appears to be limited by the steady state concentration of singlet oxygen.

### Acknowledgments

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