

A Specialist Periodical Report

Photochemistry

Volume 11

A Review of the Literature published between
July 1978 and June 1979



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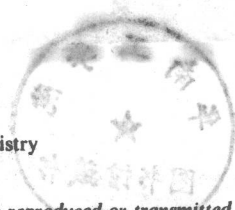
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Introduction and Review of the Year

This year I regret that we must start with an apology for the unduly late appearance of 'Photochemistry'. It would be tedious to go into all the special reasons for this delay, but readers may be assured that both the Royal Society of Chemistry and the Reporters have taken active steps to reduce substantially the interval between the end of the review period and the publication date of future Volumes. Indeed, as I write this Introduction to Volume 11, the production of Volume 12 is already making good progress.

It is more pleasant to be able to welcome Drs. Coyle and Hancock to the team of Reporters. This is perhaps an appropriate time to draw attention to the fact that of the small team of Reporters for Volume 1, only Dr. Horspool now remains with us. I would like to express my personal appreciation of his extremely consistent and authoritative support throughout the production of these eleven Volumes. Long may he continue.

Readers may like to be reminded that Theoretical Aspects and Developments in Instrumentation and Techniques are now covered in alternate years on a biennial basis: this year we have a two-year review of the former by Dr. Devonshire. It should also be noted that the short Chapter on Main Group Elements has had to be carried over to Volume 12 where it will form part of a two-year review: coverage should revert to a one-year basis in subsequent Volumes. As usual, the following Review of the Year refers to what are considered to be some of the more significant developments in the various fields of photochemistry during the period covered by this Volume.

Starting with the more theoretical side of the subject, we draw attention to a generator co-ordinate method (G.C.M.) which has been developed and applied as a theoretical approach to the calculation of molecular spectra that avoids the Born-Oppenheimer separation (Lathouwers *et al.*). An important paper by Bair and Goddard on the iron-sulphur protein, rubredoxin, is probably the most comprehensive *ab initio* study of a transition-metal complex yet to appear. Metz *et al.* have presented a notable new theoretical treatment of two-photon absorption. A strongly allowed two-photon transition has been observed in *trans*-stilbene and tentatively assigned to the 'phantom' singlet state, which has previously been postulated to provide the major pathway for *cis-trans* photoisomerization of stilbene (Stachelek *et al.*). Birks has presented a valuable classification of 'horizontal radiationless transitions' in stilbene and polyenes. Atkinson and Parmenter have presented the results of a highly refined study of the $S_0 \rightarrow S_1$ band of benzene vapour in which they have succeeded in assigning over 90% of the intensity: see also Parmenter and Tang. A quite successful *ab initio* calculation of excited states of pyrazine by Petke *et al.* suggests that approaches using floating spherical Gaussian orbitals (FSGO) may have potential for 'large molecule' calculations. A quantum mechanical theory of *E*-type delayed fluorescence has

been developed by Van der Wers *et al.*, and interesting work on the very low quantum yield and very short-lived anti-Kasha fluorescence of aromatic hydrocarbons has been described by Liu and Topp. Attention is drawn to a number of important papers on superfluorescence (Mollow, Zardecki, and Baribeau, *inter alia*).

Michl has published three important papers on the magnetic circular dichroism of annulenes.

On the inorganic side of the subject, Stevens and Krauss have calculated that excimer-type emission from Mg_2 might be usefully employed in tunable lasers.

The interesting species $Mo(CO)_5Kr$ appears to be formed on irradiation of $Mo(CO)_6$ in krypton matrices. The Mo-Kr bond energy may be *ca.* 23 kJ mol^{-1} (Veillard, Kochanski, and co-workers). Chatt *et al.* have described a remarkable photoalkylation of co-ordinated N_2 in a tungsten complex by alkyl halides:



where $dppe = Ph_2PCH_2CH_2PPh_2$ (*cf.* George, Busby, and Iske). Rest, Salisbury, *et al.* have succeeded in recording luminescence spectra, probably fluorescence, for $Cr(CO)_6$ and other carbonyls at 12 K.

Rather surprisingly, *cis-trans* isomerization of stilbene has been found to be photosensitized by certain palladium and porphyrin complexes with a quantum yield greater than 1: adiabatic photodissociations are postulated to occur (Mercer, Smith, and Whitten).

The use of photochemical procedures to provide useful catalysts continues to be exploited. Thus, Sanner *et al.* have produced useful olefin isomerization catalysts by irradiation of iron-carbonyl complexes of PPh_2 groups pendant on a polymer chain. This interesting approach merits further study. Hydroformylation catalysts have been prepared by irradiation of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in the presence of poly(vinylpyridine) (Gray, Gupta, and Rembaum in a U.S. Patent). The photolysis of $Fe(CO)_3$ derivatives of substituted 1,3-dienes in acetic acid is reported to provide a useful procedure for regioselective 1,4-hydrogenation of the diene (Franck-Neumann *et al.*). The olefin metathesis reaction (*e.g.*, $2RCH=CHMe \rightarrow RCH=CHR + MeCH=CHMe$) is catalysed by pre-irradiated $W(CO)_6-CCl_4$ mixtures, and shows high stereoselectivity, especially for *trans* olefins (Garnier, Krausz, and Dubais). Nagasawa *et al.* used $TiCl_4$ in place of CCl_4 , but the catalytic intermediate appears to be of a different type. The photopolymerization of isobutene in the presence of $TiCl_4$ has previously been assumed to involve charge-transfer excitation to give the alkene radical-cation, but Diem and Kennedy have now proposed that it is induced by traces of HCl derived from chlorine atoms produced by photolysis of $TiCl_4$.

Halocarbons are reported to be dehalogenated by irradiation in ethanol solution in the presence of ferrocene or ferric chloride (Wilputte-Steinert).

Watts and Bergeron have described the first case of photochemical proton tautomerism in a transition-metal complex.

Donohue has provided the first example of a photoreaction resulting from intrashell *f-s* transitions. The redox photochemistry of excited states of transition-metal complexes is proving much more complex and extensive than was once believed. The superoxide ion has been demonstrated by Srinivasan *et al.* to be

produced from molecular oxygen in irradiated solutions of Rose Bengal and $[\text{Ru}(\text{bipy})_3]^{2+}$.

Uranyl ion photochemistry and photophysics are currently particularly active areas of research. Attention is drawn to two important papers in the field by Marcantonatos, Afonichev *et al.* and Murayama and Sato have found that *trans*- β -hydroxyperoxides are formed stereoselectively by irradiation of alkenes in the presence of uranyl acetate. This type of process seems likely to have wider applications.

Several useful emission studies of the CH radical have appeared (Suzuki and Kuchitsu; Cvetanovic *et al.*, Filseth *et al.*). Unexplained discrepancies exist between different findings for the 1A_1 - 3B_1 splitting in CH_2 (Feldman *et al.*, Lengel and Zaire, in contrast with Zittel *et al.*). Despite extensive work, some uncertainty remains about the first-order rate constant for disappearance of T_1 benzene. In an interesting study by Dunbar, Kim, and Olah, the C_8H_8^+ ions formed from styrene, cyclo-octatetraene, and barrelene and trapped in an ion cyclotron resonance cavity were found not to rearrange over a time scale of several seconds: the species from styrene and barrelene at least appears to preserve the structure of the neutral molecules. In contrast, corresponding C_8H_9^+ species all adopted the styryl ion configuration.

Attention is drawn to two contrasting studies of acetylene photolysis, one using low- and the other high-intensity radiation (Lauser and Bass, and McDonald *et al.*, respectively).

An interesting difference between CH_2O and $\text{C}^2\text{H}_2\text{O}$ has been discovered in that at 'zero pressure', radiationless decay of the former predominates, whereas the fluorescence quantum yield of the latter is close to unity (Weisshaar *et al.*, Shibuya and Lee). Several theoretical studies of S_1 CH_2O have appeared (Kemper and co-workers *inter alia*), but many detailed aspects of the photophysical and photodissociation behaviour of CH_2O remain to be clarified.

The proposed use of hexafluoroacetone as an actinometer at 147 nm (Powell and Sethi) needs to be reconsidered in the light of work by Perkins *et al.* Interpretation of the photodissociation of ketene continues to prove controversial, particularly in relation to the role, if any, of singlet carbene (see *e.g.*, Carr, Hase). Flicker *et al.* have identified a previously undetected triplet state of thiophosgene at 3.1 eV: the observation should greatly assist understanding of the photochemical behaviour of this small molecule.

There has been interest in the use of the 1S state of atomic sulphur as an energy-storage level for high-power lasers, and the successful use of this state in a laser has now been demonstrated using COS as a source (Powell, Prosnitz, and Schleicher). NF is also considered to be an attractive energy-storage molecule for laser development, and the *b* state has been generated by Herbelin *et al.*

Attention is drawn to important studies of HCN, ^2HCN , and the CN radical (Simons, MacPherson, and Ashfold: *cf.* Knudtson and Berry, *inter alia*). Chlorine isotope separation has been achieved *via* isotopically selected $A \leftarrow X$ excitation in ICl (Stukey and Marinero, Dams and Lieser).

It is relevant to stratospheric photochemistry that the quantum yields for chlorine atom formation at *ca.* 200 nm from CCl_4 , CFCl_3 , and CF_2Cl_2 are close to unity (Hauteclouque, Rebbert).

The analytical determination of sodium and possibly other elements by flame photometry seems likely to be rendered even more sensitive by the use of laser-induced fluorescence, a technique shown to be able to recognize a signal due to a flux of only 10 atoms per second (Strickler and Rudolph, Freed; but see also Balykin *et al.*, Muller, Schofield, and Steinberg).

A further matter of relevance in atmospheric photochemistry is that remeasurements of the rate constant for the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$, an important process relevant to the maintenance of ozone concentrations, have shown that this is some ten times greater than previously believed (Howard and Evenson, Thrush). Ozone loss *via* freons and other chlorine-containing species may therefore be more serious than has previously been expected, since the reaction $\text{HO} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ is evidently a major source of the chlorine atoms that destroy ozone. Note also that the rate constant for the reaction $\text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ has also been reported to be higher than previously supposed (Ravishankara *et al.*, Chang and Kaufman).

Low-pressure irradiation of $\text{U}(\text{OMe})_6$ by a CO_2 laser gives a ^{235}U enrichment factor per pass ten times greater than that in a gaseous diffusion cell (Miller *et al.*).

Garcia and Keehn have claimed that sensitized decompositions can be induced by CO_2 -laser radiation more specifically than by conventional ultraviolet or thermal procedures; they exemplify this by the case of bicycloheptadiene dissociation sensitized by SiF_4 , which gives cyclopentadiene and acetylene in an extremely clean process.

Strong interest continues in i.r. laser-induced multiple-photon dissociation (MPD): the question whether there is any non-statistical distribution of vibrational energy in the excited molecules has been prominent.

The foregoing examples have been concerned with gas-phase process, but laser photochemistry and applications of fluorescence-based methods in analytical chemistry, especially in the detection of pollutants, drugs, and metabolites, are major growth areas in liquid-phase photochemistry. The selective absorption of fluorescing dyes in biological systems is providing the basis of a valuable structural probe.

Scharf and Naaman have criticized treatments of electronic relaxation by radiationless transition, and suggest that the present omission of higher-order vibronic and spin-orbital vibronic factors is unjustified, and that this may be responsible for poor agreement between experimentally determined and theoretically calculated transition rates (*cf.* Muthukumar and Rice). Khalil and Kasha have described an interesting variant of the Evans method for perturbing singlet-triplet transitions by molecular oxygen. They have for example been able to observe $S_0 \rightarrow T_2$ absorption in benzene. Turro *et al.* have shown that rigid deoxygenation permits the observation of phosphorescence from many organic molecules in fluid solution at room temperature. Phosphorescence can also be enhanced in micelles. The striking enhancement of phosphorescence in an absorbed species produced by adding sugars, which Niday and Saybold have reported, may have applications both in and beyond the analytical field.

It may be a general phenomenon that the radiationless $T_1 \rightarrow S_0$ decay rate increases as the T_1-T_2 and T_1-T_3 energy separations diminish (Basara *et al.*, from

studies with phenanthrolines). Pragst and Ziebeg have described an electrochemical procedure for generating triplet species.

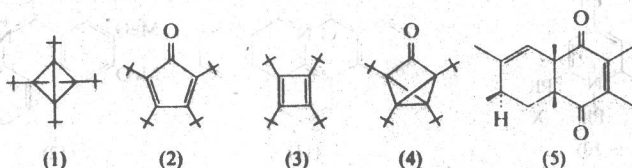
Hirajama and Phillips have observed exciplex emission in the vapour phase, and Brillante *et al.* have for the first time been able to demonstrate vibronic details in a charge-transfer spectrum. The exciplex emission which Leismann *et al.* have observed from benzene and certain alkenes is believed to proceed from complexes of dipole-dipole rather than charge-transfer type. The formation of charge-transfer complexes in triplet systems is becoming a well established phenomenon (see Inoue and Hida, Loutfy, Dogra, and Yip, *inter alia*). From studies of the irradiation of benzene and alkylbenzenes in glasses at 77 K, Nazarov *et al.* have shown that hexatrienes derive from the T_1 state, whereas higher triplet states give radicals. The symmetries of the S_1 and S_2 states of triphenylene have been reassigned by Merle *et al.*

Goto and Nakamura have made the interesting observation that β -indolyldioxetan decomposes thermally to produce *ultraviolet* chemiluminescence ($\lambda_{\max} = 320$ nm) with considerable efficiency.

We come now to developments in the less physically oriented areas of organic photochemistry.

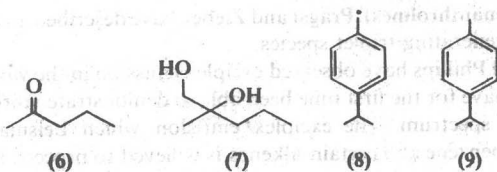
Since acetic acid is normally fairly photostable under conditions conventionally employed, the observation by Kraentler and Bard that irradiation in the presence of platinized n-type TiO_2 brings about clean cleavage to methane and carbon dioxide merits extension to other systems. Ishigawa *et al.* have reported an interesting dependence on ionization-potential differences in certain crossed photodimerizations of ethylenes to give cyclobutanes. Effects of this type have previously been described by Bryce-Smith, Gilbert, and their co-workers for photoaddition of ethylenes to benzenes. Ors and Srinivasan have described an interesting extension of their previous synthesis of macrocycles based on cinnamate-type photodimerization: cyclic polyesters containing up to 36 ring members have been obtained by this method in quite good yields.

One of the most outstanding developments during the year has been the synthesis by Maier *et al.* of tetra-*t*-butyltetrahedrane (1) by irradiation of the corresponding cyclopentadienone (2) at -100°C in ether. The cyclobutadiene (3) is remarkably stable and is probably an intermediate. On the other hand, irradiation of (2) in argon at 20°C gives the ketone (4).



Attention is drawn to a particularly interesting study of temperature-dependent effects in the photochemistry of citral (Barany *et al.*), and some notable work on the phase-dependent photochemistry of the diene-dione (5) by Scheffer *et al.*

Kittel *et al.* have described an interesting method for the determination of intersystem-crossing efficiencies in aromatic compounds, which is based on a shift of the tautomeric equilibrium in ethyl acetoacetate towards the keto form.



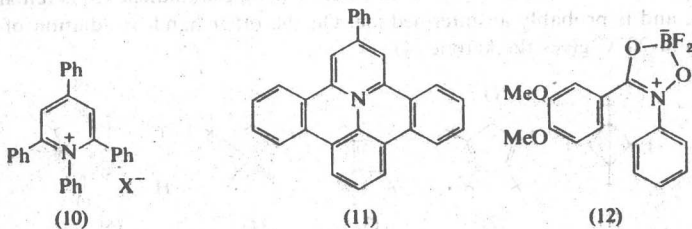
An X-ray diffraction study has shown that the previously assigned structure for the photodimer of chalcone is erroneous (Caccamese *et al.*). Oppolzer and Godel have devised a simple photochemical entry into the longifolene skeleton.

Sato *et al.* have shown that ketones may be converted into 'mixed' pinacols in good yields by irradiation in methanol in the presence of TiCl_4 [e.g., (6) \rightarrow (7)].

Hydrogen-atom extraction from hydrocarbons such as *p*-cymene by a photo-excited ketone can have certain superimposed polar characteristics when the latter is a strong electron-acceptor such as PhCOCF_3 : this favours the formation of the primary radical (8) rather than the tertiary radical (9). A charge-transfer complex may be involved (Wagner and Puchalski). Breslow has continued his interesting study of hydrogen extraction by excited benzophenone from long-chain alkyl groups as a means of studying conformations, and has used the technique to study structure in spherical micelles and lamellar systems: the former show much greater disorder. Wong has demonstrated that in the photoreduction of quinones, either hydrogen atom- or electron-transfer to the quinone can occur, depending on the conditions. Thus the former occurs predominantly in alcohol whereas the latter predominates in alcoholic triethylamine (*cf.* Levy and Cohen).

Sekiguchi *et al.* report that carbonyl oxides $\text{R}_2\text{C}=\overset{+}{\text{O}}-\text{O}^-$ formed as intermediates in the photoreaction of diazoalkanes with singlet oxygen can act as very efficient oxygen-transfer agents.

The double oxidative photocyclization of the pyridinium salt (10) to (11) reported by Katritzky *et al.* is an unusual example of a familiar type of reaction. In the related photocyclization of benzanilides, the poor yield normally resulting from

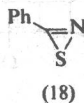
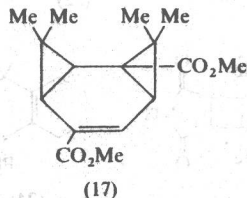
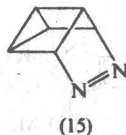
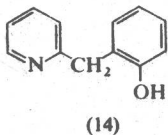
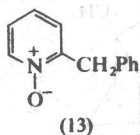


unfavourable geometry have been greatly improved by the ingenious use of a boron complex (12) to fix the 'enol' form in a *cis* configuration: the corresponding phenanthridine is formed after removal of the protecting group (Prabhakar *et al.*).

Bellamy and Streith have observed an interesting and apparently specific catalytic effect of Cu^{2+} in the photoisomerization of pyridine *N*-oxides to the corresponding 2-formylpyrroles: the corresponding formation of oxaziridines is

inhibited by boron trifluoride, and oxygen transfer occurs instead, as in the conversion of (13) into (14) (Sammes *et al.*).

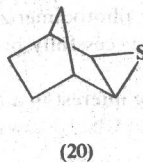
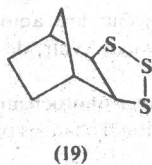
The presence of a cationic surfactant surprisingly increased by some 20-fold the quantum yield for the photodenitrosation of 4-nitrophenylnitromethane to 4-nitrobenzaldehyde (Yamada *et al.*). This example should stimulate a search for other examples of the phenomenon. Attention is drawn to a particularly interesting study of the photochemistry of 6- β -nitroso-oxy-5 α -cholestan-3- β -yl acetate by Barton and his co-workers.



Mirbach *et al.* have made the notable observation that the rate constants for photoelimination of molecular nitrogen from cyclic azoalkanes correlate with the lowest ionization potential of the azoalkane. Various interesting examples of this type of reaction have been described this year, notably the photoconversion of the bridged azoalkane (15) into a mixture of Dewar-benzene, benzvalene, prismane, and benzene at room temperature: at -78°C nitrogen is retained, giving largely the monocyclic isomer (16) (Turro and Ramamurthy). Attention is also drawn to the formation of bis- σ -homobenzenes, *e.g.*, (17), by photoelimination of nitrogen from a cyclic azoalkane precursor (Fühlhuber *et al.*).

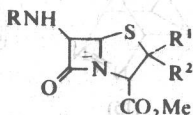
Phenylthiazirine (18) has been obtained by Holm *et al.* as a stable species in a poly(vinyl chloride) matrix at *ca.* 15 K by photoelimination of nitrogen from the corresponding thiazirazole.

Inoue *et al.* have reported that elemental sulphur photoadds to norbornene in CS_2 in a novel way, giving a mixture of (19) and (20). Maki and Sako have described an important new photochemical route to penam derivatives (21) *via* S-S bond homolysis.

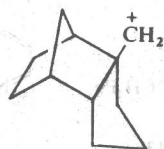


Among a considerable volume of work on azide photodecomposition, carbohydrate chemists may like to note the new procedure for generating an aldehyde function in carbohydrates described by Durette *et al.*, and the conversion of glycosyl azides into the next lower aldose reported by Szarek *et al.*

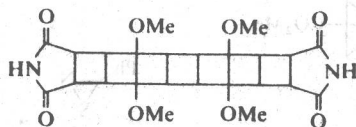
The competitive ionic and radical photochemical behaviour exhibited by alkyl and vinyl halides is now being studied by several groups. Takaishi *et al.* have described a particularly interesting case in which a primary alkyl carbocation (22), formed from the iodide, rearranges in a manner different from that observed in



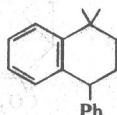
(21)



(22)



(23)



(24)

sulphuric acid. Intramolecular eliminations of HCl, HBr, and HI continue to find wide applications in the synthesis of alkaloids and related species.

Takamuka *et al.* have reported the partial asymmetric synthesis of the chiral *trans*-cyclo-octene by photoisomerization of the *cis* isomer sensitized by chiral aromatic esters.

Several interesting developments have been reported in the year on the synthetic aspects of the photochemistry of benzene rings. Thus Zupan, Sket, and Pahor have observed that benzophenone sensitizes a novel 1,2-addition of cyclohexane to hexafluorobenzene. Shaikhrazieva *et al.* have reported the formation of the remarkable [2 + 2]photoadduct (23) from maleimide and 1,4-dimethoxybenzene. Maroulis and Arnold report that *p*-dicyanobenzene photosensitizes a new mode of photoaddition of isobutene to 1,1-diphenylethylene, giving (24).

Unusual effects of a naphthalene sensitizer and heavy-atom solvents are reported in the photoreaction of benzene with hexafluorobenzene by Bryce-Smith, Gilbert, and Twitchett. Gilbert and Taylor, and Pallmer and Morrison, have reported a number of interesting new intramolecular photoadditions to benzene rings.

There are a growing number of reports that photoreactivity can be considerably increased by adsorption onto various supports such as silica gel. The photo-Fries reaction and the photodimerization of anthracene are among the reactions which have been successfully promoted in this way (Avnir, de Mayo, and Ono; Barthel *et al.*).

There is growing interest in all aspects of polymer photochemistry. Aviram has described a polymer which shows marked dimensional changes on exposure to u.v. radiation.

In the important field of photoinitiated vinyl polymerization, there is increasing recognition of the importance of complexing between the monomer and the initiator (see *e.g.*, Gosh and co-workers). It is evident that many charge-transfer complexes and perhaps exciplexes can themselves act as initiators, and the presence of charged micelles can be important (Tsunooka and Tanaka). Phillips and his co-workers are demonstrating the value of time-resolved fluorescence spectroscopy in studies of the development of excimer and other excited species in polymers.

Chiral cyclobutane dimers, trimers, and oligomers have been prepared for the first time by Addadi and Lahav.

The mechanisms which operate in the photodegradation of polymers continue to attract interest, and some controversy. Work by Allen *et al.* and Guillet has provided further evidence that carbonyl groups rather than hydroperoxides are of main importance in initiating the photo-oxidation of polyolefins and related species, a process which normally leads to chain-scission; but hydroperoxides are the main chain carriers. With poly(vinyl chloride) however, the prior processing history can be an important determinant of the photo-oxidation mechanism (Scott *et al.*, *cf.* Verdu, and Mori *et al.*). The pre-oxidation of cellulose has been found to render it more sensitive to photografting with vinyl monomers (Ogiwara *et al.*). In general, the role of singlet oxygen in the photo-oxidation of polymers still remains to be fully clarified, and major differences of opinion remain, together with some apparent conflicts between experimental results.

2,2,6,6-Tetra-substituted piperidines are showing outstanding promise as multi-functional stabilizers in polymers. They appear to form a nitroxyl radical, which then scavenges radical centres on the polymer; and they also inhibit photolysis of $C=C-C=O$ moieties in the polymer, and prevent photoyellowing of the phenolic antioxidants with which they are usually employed (see Allen and McKellar *inter alia*).

It is not surprising that most aspects of photochemistry having potential applications in the utilization and storage of solar energy continue to attract an increasing number of research groups. A number of the approaches are concerned with the redox photochemistry of excited states of transition-metal complexes, and this branch of the subject is proving much more complex and extensive than was once believed.

The complex $[Ru(bipy)_3]^{2+}$ continues to be very popular among workers in this area, largely owing to reports, some tantalizingly difficult to confirm, of its ability to promote the photodissociation of water. Kalyanasundaram *et al.* have observed the evolution of hydrogen from irradiation of an aqueous homogeneous system comprising $[Ru(bipy)_3]^{2+}$, methylviologen as an electron-acceptor, and triethanolamine or cysteine as an electron-donor in the presence of Adams catalyst. Rayson in a U.S. Patent Application has described a cyclic process for the solar photolysis of water whereby Eu^{III} undergoes photo-oxidation, giving hydrogen: a photoexcited ruthenium complex then reduces the oxidized europium reagent. Lehn *et al.* have now published details of their interesting system for photogeneration of hydrogen in systems containing $[Ru(bipy)_3]^{2+}$, $[Rh(bipy)_3]^{2+}$, triethanolamine, and colloidal platinum. Lehn has also described an ingenious complementary oxygen-generating system. These various systems show obvious resemblances one to the other, and to the system using methylviologen described by Moradpour *et al.* in 1978. Porter's

system for the photochemical formation of oxygen from water is somewhat different, and involves the irradiation of Mn^{II} and Mn^{III} tetrapyrridylporphyrin complexes in the presence of quinone as hydrogen-acceptor.

There is growing interest (which the present writer suspects may be misplaced) in the possibility of using anthracene-type photodimers for the storage of solar energy. It is interesting, however, that the geometrical requirements for excimer formation appear to differ from those for dimerization, since excimers are normally considered to be precursors of the dimers (Bergmark *et al.*, Huybrechts *et al.*). Differing estimates have been given of the limiting efficiency for photochemical storage of light energy as chemical energy: Dolton gives 12–13%, whereas Almgren sets the figure at about 20%. Carlsson and Wettermark calculate that systems employing endergonic photoreactions should be able to deliver up to 100 W of heat at $>200^\circ C$ for each square metre of collector area.

Interesting reports have appeared on the photofixation of nitrogen (Dickson and Nozik) and carbon dioxide (Halmann).

The challenge of devising photo-electrochemical systems for the utilization of solar energy is stimulating some of the most original and important work now being carried out in the whole field, and the development of workable and efficient systems appears to be coming closer each year. Schwerzel has presented a novel proposal for a 'tandem' photoelectrolysis plant in which the anodic process would produce hydrogen and the photoanodic process would generate alkanes. Stirn has described a double-junction GaAlAs photovoltaic cell having a power conversion efficiency of 56% at 807.5 nm, the highest yet reported. There is increasing evidence that the photoactivity of $SrTiO_3$ electrodes may depend on the presence of Ti^{III} on the surface (Lo and Somorjai; *cf.* Mavroides). Bolts *et al.* have reported that the surface modification of silicon by 1,1'-ferrocenyldichlorosilane may prove useful in improving the stability of photocells for solar-energy conversion.

The development of efficient photovoltaic cells based on polycrystalline silicon would provide major economic advantages, so it is interesting that Chu *et al.* have now reported such cells having an efficiency of up to 9.5%. Even amorphous silicon cells are beginning to show some promise (Hamakawa *et al.*). Cu_2S/CdS cells having an efficiency of greater than 10% have now been reported by Bhat *et al.*; and indium-doped SnO_2/Si cells based on single-crystal silicon can now slightly exceed that (Feng *et al.*). Godfrey and Green have reported a most promising metal/insulator/semiconductor cell having an efficiency of 17.6%.

Finally, to illustrate the extremely wide range of journals scrutinized by our diligent team of Reporters, I draw attention to a reference quoted by Dr. Coyle from *Stamp Collecting* on the colour change of British postage stamps in light, which is believed to result from dechlorination of a phthalocyanin green pigment:

D. Bryce-Smith

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Introduction and Review of the Year
By D. Bryce-Smith

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