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Book Review

Advances in Photochemistry. Volume 21.
edited by D.C. Neckers, D.H. Volman and G. von Bünau, 309 pp, ISBN 0471143324, Wiley Interscience, New York, $75.00.

It is always a pleasure to welcome a new volume of *Advances in Photochemistry*, an important series which has explored the frontiers of photochemistry for 33 years. This volume starts with a long review of 371 references by Bortolus and Monti from Bologna on the photochemistry of cyclodextrin (CD) cavities. The emphasis is on providing a comprehensive literature survey of the vast and complex field of photophysical and photochemical processes in CD cavities. The field is intrinsically complex for two main reasons: (1) the nature of the CD environment cannot be described in terms of the polarity and viscosity, because these properties depend critically on the probe itself; (2) the CD systems are subjected to multiple complexation, with different microenvironments being experienced by the same probe. In general, fluorescence is enhanced for CD-complexed fluorophores due to the protection from external quenchers, notably oxygen, and to the decrease in freedom of some of the molecular motions. In some cases, such protection has allowed the observation of phosphorescence in solution. These changes in luminescence can be explored to investigate the properties of the microenvironment of the photoexcited guests. The authors also provide examples of a decrease in emission in CD systems. For example, acridone and 2-acetylnaphthalene emit in polar and/or H-bonding solvents, but are non-emitting in polar media; the addition of β-CD causes a decrease in the emission of acridine solutions. Attention is directed to intramolecular excimer or exciplex formation, which can be favoured in the presence of CDs, depending on the dimensions of the cavity, and interesting examples are discussed. The acid–base equilibria of ground and excited states can also be affected by CDs for both intermolecular and intramolecular proton transfer. The CD can be functionalized with various types of chromophore which can be used on both the primary and secondary hydroxyl rim, e.g. to induce stereoselectivity and regioselectivity in some photochemical reactions. Compared with homogeneous isotropic solvents, CDs are microvessels capable of modifying the reactivity and improving the efficiency and selectivity of a variety of unimolecular and bimolecular reactions. In solution, this results from the effect of the cavity alone; in solids, the effect of the rigid environment surrounding the guest also plays an important role. For example, in phenylalkylketones, the formation of type II products is increased by α- or β-CD both in solution and in solid complexes, and cyclization is favoured over elimination. The authors reveal, in a clear manner, the importance of this field, which has developed due to the inspiration of chemists from biological examples of acceptor sites, and which requires a deeper understanding of the role of cavity interactions in photochemical transformations.

Synthetic asymmetric photochemistry of unsaturated and conjugated enones and esters is of preparative value in the field of organic synthesis. Most of these reactions induce the creation of new asymmetric centres in products which may be obtained either enantioselectively or diastereoselectively. The second review article by Jean-Pierre Pete from Reims concentrates on two general methods: (1) asymmetric transformation in the ground state of unstable intermediates produced in a photochemical step, the diastereoisomeric phototransformation of chiral molecules; (2) asymmetric photoreactions carried out in a chiral medium, a method particularly interesting because the chiral inductor is not destroyed during the reaction. The article pays due note to the tremendous progress achieved in this field during the past 10 years, although progress in the mechanistic interpretation and in the development of interactions between the inductor and the polar intermediates would be most welcome. Conjugated enones and acid derivatives allow a great variety of photoreactions of preparative interest, some of which can lead to the creation of up to six asymmetric centres. Over 40 preparative schemes are reviewed, including a brief mention of the asymmetric photoreactions in the solid state. This field is becoming potentially very fertile and the author succeeds in conveying this message to the community of organic photochemists.

The final chapter is a timely review of the current state of knowledge on electronic spectroscopy, ab initio surfaces and the primary photochemistry of a number of prototypical small hydride molecules: H_2O, H_2S, CH_3OH, CH_3SH, NH_3, PH_3, CH_3NH_2, CH_4, SiH_4, HCN, C_2H_2 and some isotopomers. New data have been obtained for these molecules using a recently developed technique of H-atom photofragment translational spectroscopy. In some cases, such data have been in the form of a refinement and quantitative improvement in detail of what was already known, but in others (notably the photolysis of CH_4 in the Lyman-α wavelength) the technique, which is briefly introduced in its concepts and potentialities, yields important corrections to existing knowl-

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edge. In particular, strong emphasis has been placed on the product branching ratios, energy and angular momentum disposals, product recoil velocities and rotational alignments. Some of the molecular dissociation processes described are relevant to the chemistry of planetary atmospheres, chemical laser systems, combustion processes and chemical vapour deposition methods. Interesting features are reported, e.g. the energy disposal of OH fragments on photolysis of jet-cooled H_2O molecules at 121.6 nm; the rotational energy associated with the most-populated level is in excess of 33 000 cm^{-1} (rotational quantum number of $N''=46$). The qualitative rationale for these very high levels of rotational excitation in the ground state of OH and OD products is the existence of a marked angular anisotropy of the potential energy surface of the corresponding electronic state, which will cause a rapid opening of the HOH bond angle during the O–H bond fission process. However, the precise details of the way in which a photoexcited water molecule in the $\tilde{B}$ state dissociates to ground state products are only now becoming clear through atom photofragment translational spectroscopy. Most rotationally excited ground state OH or OD species arise as a result of a $\tilde{B} \rightarrow \tilde{X}$ transfer via the conical intersection linking these two surfaces. A similar pattern is found with regard to the $H–NH_2$ dissociation coordinate. The conical intersection linking the $\tilde{A}$ and $\tilde{X}$ state surfaces massively amplifies any out-of-plane bending motion in the photodissociation parent molecule. This is an article that conveys the enthusiasm of the authors, Ashfold, Mordaunt and Wilson from Bristol, for the impact of a new spectroscopic technique on the old and complex branches of spectroscopy and photochemistry of small molecules in the far and vacuum UV.

I enjoyed reading this new volume of *Advances in Photochemistry* for the stimulus of the wide-ranging and fascinating underlying science and the cross-disciplinary exploration conveyed by the book.

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