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Book Review

Advances in Photochemistry, Vol. 11, edited by J. N. Pitts, Jr., G. S. Hammond and K. Gollnick; Associate Editor, D. Grosjean; published by John Wiley and Sons, New York, 1979; 538 + xii pp.; price £22.00.

Ever since the first volume of this series appeared in 1963, the editors have presented a selection of articles of great variety and interest. Volume 11 continues the tradition and the six reviews cover a wide range of fascinating photochemistry.

The book starts with a review by G. A. Delzenne of organic photochemical imaging systems. The economic disadvantages of silver-based processes, the need for dry processing, and the requirement for direct access to recorded information have all acted as stimuli to research on photographic systems based on organic reactions. Delzenne considers first the relative sensitivity of silver halide and non-silver photographic systems. He then examines a number of potentially useful organic processes, including photoinitiation of polymerization, photochromism, photofluorescence and various free-radical imaging systems. Photofluorescence, which depends on photochemical generation of stable fluorescent products from non-fluorescent precursors, is perhaps the most novel of the techniques. It is capable of high sensitivity, although it still falls four orders of magnitude short of the fastest silver halide processes. However, in comparison, diazofilm with thermal development is another four orders of magnitude slower.

D. Belluš provides the second article, on physical quenchers of singlet molecular oxygen. The article is almost entirely concerned with the $^1\Delta_g$ species, which is the first excited state of O_2, and is a review of the compounds known to quench $O_2(^1\Delta_g)$ in liquid and solid phases. Attention is given to structure–activity correlations, and to critical evaluation of existing data. After considering the general kinetic features of physical quenching, Belluš goes on to the various classes of quencher: carotenoids, amines, other nitrogen-containing compounds including proteins, phenols, 1,4-quinone methides, sulphides, metal chelates, inorganic anions, and some dyes and polymers. Specially designed quenchers might be needed to protect systems against the action of singlet oxygen, but it is evident that the structure requirements for efficient quenching are still only vaguely known. However, there appears to be a general rule that efficient antioxidants are also efficient quenchers of singlet oxygen.

Luminescence measurements have recently been used to study several phenomena in natural and synthetic polymers. S. W. Beavan, J. S. Hargreaves and D. Phillips give a very useful review of photoluminescence methods in

polymer science. Apart from the fundamental interest in the photoemission phenomena, as for example interchromophoric interactions or the luminescence of small molecules in polymeric environments, there are a number of applications. Luminescence studies of probe molecules permit evaluation of polymer properties such as the ordering of chains or phase transitions. Polymer photo-oxidation has also been studied by luminescence techniques, and luminescence spectroscopy further provides a method for the identification of polymeric materials. Each of these topics is discussed by the authors, and the chapter starts with a survey of the background theory and of the available experimental techniques for spectrofluorimetry and lifetime determinations.

Over the past ten years important new results have been obtained on the photochemistry of vitamin D, its isomers, and the related simple dienes and trienes. H. J. C. Jacobs and E. Havinga present a chapter on the photochemistry of vitamin D and its isomers and of simple trienes, in which they give a survey of the recent experimental findings and indicate developments in the rationalization of the observations. One area where much progress has been made is concerned with the "over-irradiation" products of irreversible reactions, which predominate in mixtures obtained from long-term irradiations. Ten sections of the review give the experimental results, and the authors suggest that the major photoreactions and products can be identified. However, rationalization of the phenomena has been dealt with only fragmentarily and the authors go on to discuss mechanistic considerations. Some of the pathways are novel, and it is clear that the factors determining the route from excited reactants to photoproducts will have to be elucidated.

Kinetics and mechanisms of the reactions of the hydroxyl radical with organic compounds in the gas phase is the subject of the next chapter in the volume; it is written by R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr. Thermal kinetics is not an obvious subject for inclusion in a work on photochemistry. It is true that some of the techniques used for the study of OH depend on photochemical processes: flash photolysis generation, resonance fluorescence detection, modulation phase shift, and relative photolytic rate measurements all involve light in one way or another. However, the main justification for inclusion of the chapter lies in the application of the data to various areas of atmospheric photochemistry. It has become clear that OH is one of the most important intermediates in photochemical smog formation. Hydroxyl radicals also play a key role in the catalytic cycles determining the ozone content of both the natural and the polluted stratosphere. Furthermore, OH may provide a significant route for *loss* of potential anthropogenic pollutants. The main part of the chapter is entitled "Rate, mechanism and product data obtained" and, for each of nine classes of compound, the relevance of the results to atmospheric (photo)-chemistry is assessed. An interesting concluding section gives a comparison of OH reactivity with that of oxygen, hydrogen and sulphur atoms. The tables of data compilations are a most valuable part of the chapter.

The final article in the book is entitled "What's new in excimers? ". Excimer formation and behaviour in ordered systems can be used as an indicator of structure and, of course, much importance attaches to excimer states in UV lasers. V. Yakhot, M. D. Cohen and Z. Ludmer emphasize that excimer formation is a widespread phenomenon and that excimers are intermediates in some photoreactions. The authors start their theoretical approach, which is a harmonic approximation, by pointing out that the binding of the excimer pair is so strong that the molecules "forget" about their individual environments in the ground state. That is, the excimer environment is to be regarded only as a heat bath. The treatment continues by looking at excimer–exciton migration in crystals, and at the relationship between crystal structure and the temperature dependence of excimer emission bands. Excimer emission from flexible molecules, and excimers as intermediates in photodimerization reactions, are the two concluding topics.

The volume, as a whole, contains a nicely balanced range of subjects. Naturally the styles and approaches of the several chapters are different, but in general the writing is lucid. The book is produced from typewriter copy and the text is not right justified. Diagrams are clear, although again the style and lettering varies from one article to another. There are a few spelling errors, which it would be best to attribute to uncorrected typing mistakes, but the number is small and not irritating. The book is a worthy successor to the previous ten volumes.

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