

*Photosensitisation and Photocatalysis using Inorganic and Organometallic Compounds*

K. Kalyanasundaram and M. Grätzel (eds.), Kluwer Academic Publishers, Dordrecht, 1993, xvi + 465 pages (including full combined subject index). UK £136  
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*Charge Transfer Photochemistry of Coordination Compounds*

O. Horvath and K.L. Stevenson, VCH, Weinheim, 1993, xx + 380 pages (including separate compound and subject indexes). DM238.00  
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Undergraduate textbooks usually leave students with the strong impression that only d-d transitions matter. Few pay serious attention to charge-transfer spectra. The connection between the spectra and photochemistry is brought out even more rarely. A glance at either of these books should highlight the wealth of remarkable photochemistry that ensues on irradiating into these transitions.

The book on photosensitisation and photocatalysis aims for a thorough treatment with chapters both on principles and practice. An outstanding opening chapter by Balzani and Maestri tackles intermolecular energy and electron transfer – it is material of this type which needs to find its way to advanced text books. Unfortunately, this fine start is not sustained. The chapter introducing photocatalysis by Hennig *et al.* sets out the confusing history of the term before trying to disentangle itself from its own web. The principles of charge-transfer excitation are introduced by Vogler and Kunkely, complete with metal-metal and ligand-ligand charge-transfer as well as the more familiar types. However, their treatment is too qualitative. By avoiding electronic states and the bonding properties of the orbitals, they draw unwarranted conclusions about the extent of charge redistribution. Moreover their coverage of the literature is sometimes distinctly sketchy (*e.g.* on  $\text{Ni}(\text{CO})_4$ ). There are several chapters which include a major organometallic component. Ziessel tackles photocatalysis of  $\text{CO}_2$  reduction and the water-gas shift reaction including a fine account of his work with  $\text{Cp}^*\text{Ir}$  complexes. He leaves metal carbonyls to Ford *et al.* who tackle various catalytic processes initiated by photolysis. Their treatment of hydrogenation of norbornadiene by metal hexacarbonyls includes the recent experiments implicating dihydrogen complexes as intermediates. However, I was disappointed to find no reference to Seitz and Wrigton's crucial paper, (*Angew. Chem., Int. Ed. Engl.*, 27 (1988) 289) in the section on hydrosilation. Koelle's chapter on photocatalytic transformations of organic substrates

concentrates on photoreactions with simple metal-salts. Crabtree takes the reader through "Photocatalysis in C-H activation", including hydrogen abstraction by  $[\text{Pt}_2(\text{POP})_4]^{4-}$ . He argues a convincing case that two reactive sites (*i.e.* effectively a 14-electron intermediate) are required for catalytic C-H activation. The final chapter by Bockman and Kochi on electron donor-acceptor interactions proved one of the most exciting. They develop both the principles and examples of donor-acceptor interactions (*e.g.*  $\text{Cp}_2\text{MoH}_2 \cdot \text{fumaritrile}$  or  $\text{Cp}_2\text{Co}^+ \cdot \text{Mn}(\text{CO})_5^-$ ). They demonstrate the widespread occurrence of donor-acceptor charge-transfer even among 18-electron complexes and show how photolysis into the charge-transfer band leads to electron transfer. Such transfer is reversed thermally unless the resultant radical intermediates are captured rapidly or decompose. Kalyanasundaram and Grätzel have edited a useful volume, but they could have transformed it into a lasting text had they provided proper cross-references between chapters so the reader has a logical framework. For instance carbonylation may be traced via the index to Koelle's and to Ford's chapters, but is treated most thoroughly by Crabtree (no index entry). None of the authors cross-reference one another! A little editorial work on chapters by non-native speakers of English could have done wonders for the comprehensibility.

The Horvath-Stevenson book opens with three chapters on photochemical principles which take the reader no further than standard texts and certainly cannot prepare the reader for primary literature. They take a very different view of charge-transfer transactions from Vogler and Kunkely giving great prominence to charge-transfer to solvent (CTTS) bands. The remaining 320 pages provide an illustrated catalogue of charge-transfer photochemistry, metal by metal, including main group and transition elements. Great prominence is given to photochemistry in aqueous solution and I had to search hard to find a metal-carbon bond other than to cyanide. Even cobalt corrins seem to have been excised, though one or two of their mimics avoid the scalpel. Coverage of the literature, both Western and Russian is reasonably complete to 1990 with some 1991 papers added as supplementary material.

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