

Book reviews

Theoretical Aspects of Homogeneous Catalysis, P.W.N.M. van Leeuwen, K. Morokuma and J.H. van Lenthe (Eds.), Kluwer Academic Publishers, Dordrecht, 1995, pp. 217, Dfl. 170, US\$ 109, UK£ 70, ISBN 0792331079

As a preparative inorganic and organometallic chemist I have a considerable suspicion of theoretical chemists. They have yet to prove to me that they can really predict what compounds are likely to be stable much more effectively than I can by counting electrons, and when it comes to calculating reaction pathways my scepticism knows few bounds. However, with the availability of powerful cheap computers and programs, everyone can allow the imagination to flourish in such areas, and it is absolutely necessary to try to understand what the theoretical chemists are trying to tell us, and without being overwhelmed by Hamiltonians and related beasts from the jungles of theory. I approached this small volume with some trepidation and considerable hope.

The first short chapter is a very useful introduction to programs and methodology, with an appropriate reading list. Chapter 2 (P.E.M. Siegbahn and M.R.A. Blomberg) then discusses oxidative addition reactions. This does not really address those reactions of direct interest to preparative chemists, but rather model systems such as bare metal atoms, in the hope that generalisations will be possible and that patterns will emerge. The substrates include H_2 , CH_4 and C_2H_6 . The discussion then moves on to reactions of unsaturated hydrocarbons, to additions of ammonia and water, and to reactions involving metal cations. The general conclusions are that alkane C–C bonds are more difficult to activate than a corresponding C–H bond and that H–H bond activation is easier still. By and large, alkenes are easier to activate. Some inferences are made concerning metal-ion environments likely to favour activation. There is actually a considerable literature on the reactions of metal atoms and ions in oxidative additions, and this chapter relates directly to such work, and rather less to more classical reactions.

The next chapter (N. Koga and K. Morokuma) concerns alkene migratory insertions and C–C bond formation. This is relatively short and deals with material and compounds more familiar to practical chemists, discussing computed energies of transition states and frontier orbitals. The same authors discuss carbonyl insertions in the next chapter, and in the same way. The conclusions to both these chapters are useful but not startling. There follows a chapter devoted to Density Functional calculations on 2_s-2_p addition processes. These are related to reactions such as olefin metathesis. The calculations apparently are in general, but not total, agreement with experiment.

The two ultimate chapters are rather more specific. A. Dedieu reviews Wacker reactions, and concludes that not all the steps are understood theoretically and that the results are still only quantitative. Finally, R. Zwaans, J.H. van Lenthe and D.H.W. den Boer describe possible intermediates in ethene epoxidation catalysed by manganese(III)-chloro-porphyrin, a name which shows some disregard for IUPAC nomenclature recommendations. The Hartree-Fock calculations suggest that the epoxidations occur on the porphyrin, with the role of the manganese being essentially ancillary. This is a useful conclusion, but not necessarily very novel.

In summary, this is an interesting book, and well worth reading. If it confirms to some degree the prejudice of an older chemist such as myself, it also is valuable as an account of the state of current accessible computational art, and an indication that the day when computational methods will be of more direct use to the synthetic chemist is now not so distant.

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