

Review

HYDROGEN AS A PSEUDO-METAL *

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I. Introduction

In the research we have carried out on the organic chemistry of the Main-Group metals we have been faced on a number of occasions with a post hoc recognition of the close parallel that often exists between the behaviour of a metal and of hydrogen in the same molecular structure. If we had appreciated this analogy earlier, it would have saved us a lot of unnecessary work, and we would have achieved the same results some years earlier than we did.

The invitation to contribute an essay to commemorate, on his sixtieth birthday, Professor Mehrotra's many chemical achievements, gives me an opportunity to draw attention to some aspects of this analogy. I hope that it may be helpful to others working in the field, and enable them to avoid the delays which occurred in our work.

II. The autoxidation of organometallic compounds

One of the most obvious properties of many of the organic derivatives of the non-transition metals of Groups I, II, III, and V, is their tendency to react, sometimes with inflammation, with aerobic oxygen. By 1957, we [1] and

* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

others [2,3] had shown that, if the reactions were carried out under controlled conditions in an inert solvent, they involved the insertion of an intact O_2 unit into the carbon-metal bond, and during the next few years, the resulting organoperoxymetallic compounds were characterised from metals such as magnesium, zinc, cadmium, boron, and aluminium (eq. 1) [4].



The formal analogy with the autoxidation of a hydrocarbon (eq. 2) was apparent, but we failed to recognise that the parallel is much deeper than the mere stoichiometry, and extends to include the mechanism:



It was well known at that time that hydrocarbon autoxidation involves a radical chain mechanism with the propagation steps shown in eq. 3 and 4.



A diagnostic test for this mechanism was the inhibition of the reaction by an antioxidant such as a phenol which operates by interrupting the chain sequence. We added these antioxidants to the organometallic systems, but they had no effect.

Alkylperoxyl radicals had also been detected by ESR spectroscopy during the autoxidation of hydrocarbons, but our attempts to do the same during the autoxidation of organometals was unsuccessful. It was concluded therefore that organometallic autoxidation was a heterolytic, not a homolytic, process, and involved the coordination of oxygen and the 1,3-nucleophilic migration of the alkyl group from the metal to oxygen (eq. 5) [5-7]



As knowledge of organometallic oxidation developed during the next decade, this picture grew less and less convincing, but it was difficult to devise an experiment to distinguish between the possible involvement of radicals in the formation of the peroxide ROOM, and the unquestioned involvement of radicals in its decomposition.

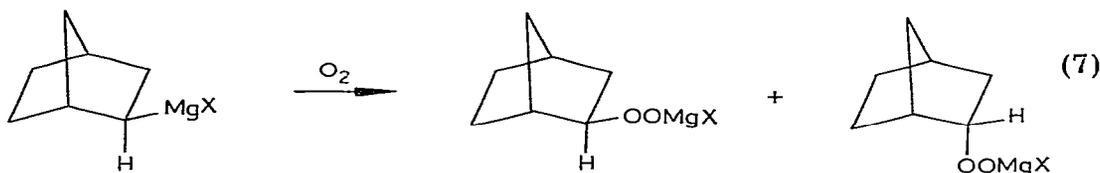
In 1965, however, Mattesen reported the optical resolution of 1-phenylethaneboronic acid [8]. Whereas intramolecular migration of an optically asymmetric group by eq. 5 should retain the asymmetry, the formation of an intermediate alkyl radical should give a racemic product.

Optically active 1-phenylethaneboronic acid was therefore subjected to autoxidation, and gave racemic 1-phenylethyl hydroperoxide (eq. 6) [9].



Equally significantly, we found that the reaction could be inhibited, not by the conventional phenolic inhibitors, but by the more powerful inhibitors which had by then been developed, particularly the stable phenoxyl radical galvinoxyl [9].

Norborn-2-yl derivatives of boron [10] and of magnesium [11] similarly lost their structural integrity during autoxidation, (e.g. eq. 7), and it was shown that the autoxidation of all the organometallic compounds which had been established previously could similarly be inhibited by galvinoxyl.



The organometallic compounds therefore do, after all, undergo autoxidation by the same mechanism as hydrocarbons. The mechanism is written out fully in eq. 8—11, where M can be either hydrogen or a main-group metal; R_i is the rate of initiation and k_p and k_t are the rate constants of one of the propagation steps, and the termination step, respectively.

Initiation



Propagation



Termination



This leads to the kinetic expression (eq. 12), from which values of k_p , the rate constant for the bimolecular homolytic substitution by the alkylperoxyl radical at hydrogen or at a metal can be abstracted [12].

$$-d[\text{O}_2]/dt = k_p [\text{MR}] R_i^{1/2} / (2k_t)^{1/2} \quad (12)$$

Some values for k_p when M is hydrogen or boron are listed in Table 1, and k_p for the trialkylboranes is seen to be very much greater than for hydrocarbons. The early attempts to inhibit the autoxidations of the organometallics had failed simply because the phenols which were used were not reactive enough to compete with the boranes for reaction with the ROO^\cdot radical.

III. Other S_H2 reactions at metal centres

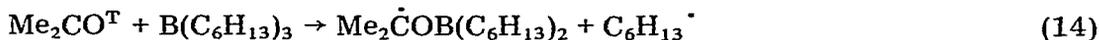
Once the analogy between hydrogen and metals as centres for S_H2 reactions was recognised, the extension of this principle to a number of new organo-

TABLE 1

RATE CONSTANTS FOR BIMOLECULAR HOMOLYTIC ALKYLPEROXYDEALKYLATION AT BORON AND HYDROGEN AT 30° C

| Compound | k_p (l mol ⁻¹ s ⁻¹) |
|-------------------------------------|--|
| Bu ₃ B | 2 × 10 ⁶ |
| Bu ^s ₃ B | 8 × 10 ⁴ |
| (PhCH ₂) ₃ B | 5 × 10 ⁶ |
| (BuBO) ₃ | 1 × 10 ³ |
| (Bu ^s BO) ₃ | 5 × 10 ⁴ |
| (Bu ^t BO) ₃ | 3 × 10 ⁴ |
| (PhCH ₂ BO) ₃ | 1 × 10 ⁶ |
| Bu-H | 1 × 10 ² |
| Bu ^s -H | 3 × 10 ⁴ |
| Bu ^t -H | 3 × 10 ³ |
| PhCH ₂ -H | 1 × 10 ² |

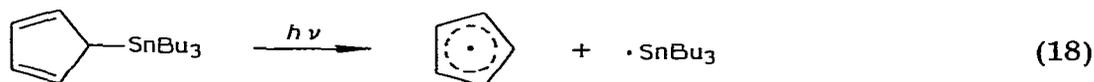
metallic reactions was obvious. The following equations (13–17) illustrate some of the processes which were established, usually with the help of the technique of ESR spectroscopy [15]. In each of the examples, the corresponding reaction is known to occur at hydrogen. This work could have been carried out ten years earlier if we had appreciated then the mechanistic implications of the autoxidation of the organometallics.



IV. Unimolecular C–H and C–M homolysis

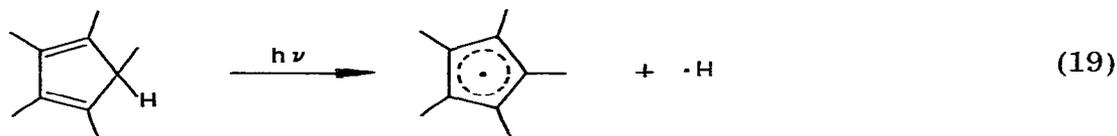
In one case we were able to exploit the analogy in the reverse direction, and establish a new reaction of a hydrocarbon on the model of a known organometallic reaction.

The cyclopentadienyl derivatives of a variety of Main-Group metals [e.g. Li, Na, Hg, Sn^{II}, Sn^{IV}, Pb^{IV}] are photolysed by ultraviolet light to give the cyclopentadienyl and metal radicals (e.g. eq. 18) [16].



An important factor here is the resonance stabilisation of the cyclopentadienyl radical. The pentamethylcyclopentadienylmetallic compounds are even more sensitive, perhaps because of an extra hyperconjugative contribution, and it seemed possible that this photosensitivity might extend even to the hydro-

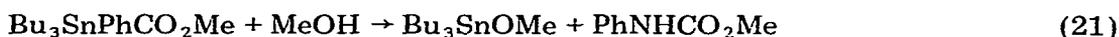
carbon [17]. This indeed proved to be true: the pentaalkylcyclopentadienes give off a stream of hydrogen when they are irradiated with ultraviolet light, as the result of the unimolecular homolysis shown in eq. 19. Such photosensitivity is unprecedented in a hydrocarbon.



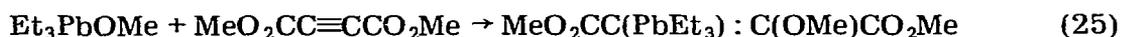
V. Heterolytic reactions of M—O and M—N bonds

The principle of modulating the nucleophilic reactivity of an alcohol by converting it into a metallic derivative was implicit in Williamson's synthesis, in the middle of the last century, of diethyl ether from sodium ethoxide and ethyl iodide. The wide variety of metal alkoxides now available makes possible the "fine tuning" of the reactivity, leading to protection or activation of the parent protic alcohol.

The reaction of alcohols and their organotin derivatives with organic isocyanates provides a good example [18]. Tributyltin methoxide reacts, much faster than methanol, with phenyl isocyanate to give the *N*-tributylstannyl carbamate (eq. 20). This is rapidly solvolysed by methanol to give methyl phenylcarbamate and regenerate the tributyltin methoxide (eq. 21). A trace of tributyltin methoxide will therefore catalyse the addition of an alcohol to an isocyanate (eq. 22) and use is made of this in the commercial production of polyurethanes.



This principle holds widely throughout organic chemistry: protic alcohols and metal alkoxides, or water and metallic oxides, or protic amines and metal amides show parallel reactions, and the hydrogen can be regarded as behaving as a pseudo-metal. Some examples of the reactions of the metallic derivatives are given in eq. 23–25.



VI. Conclusion

I have referred here only to those organometallic examples of the hydrogen—metal analogy in which we have been directly involved, and I have not attempted to analyse the factors underlying the phenomenon. It is in fact of general importance throughout chemistry, and was established in the organic field (e.g. in the Williamson synthesis referred to above), the physical field (e.g. in protic and Lewis acids), and the inorganic field (e.g. in hydrogen bonding and coordination) long before it was recognised in organometallic chemistry. I suggest it is a very useful principle to bear in mind when considering organometallic reactivity.

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