Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Metallocene basicity
II*. Reaction of the ferrocenonium cation with O_2 and SO_2

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(Received January 20th, 1972; by publisher May 23rd, 1972)

In a series of publications Wasserman *et al.*[1-3] claimed the preparation of a series of stable ferrocenium "adducts" involving various postulated radical counter ions of the form $(HA)^-$. This claim of stable radical acid anions caused considerable consternation in this group, and others, since it appeared to violate presently known chemical behavior[4]. In addition, evidence from titrations of trichloroacetic acid adduct with base[5], and comparison of the IR spectra from the Wasserman compounds with those of ferrocenium trichloroacetate prepared by standard techniques (silver oxidation)[6], gave little or no support to the presence of any species $(HA)^-$ and seemed to indicate that these adducts were simply solvated ferrocenium salts.

In a recent paper by Prins and Kortbeek[7], strong evidence is presented against Wasserman's interpretation of room temperature ESR spectra of the uniquely prepared adduct series[3]. Since Wasserman's preparative technique utilized oxygen-saturated acids, Prins and Kortbeek[7] have speculated that the reaction might best be formulated in terms of oxidation by oxygen as shown in reaction (1).

$$4Cp_2Fe + 4H^+ + O_2 \longrightarrow 4\,Cp_2Fe^+ + 2H_2O \qquad (1)$$

We have performed a tensiometric titration of ferrocene in trifluoroacetic acid with O_2 at room temperature and pressure, and, as shown in Fig. 1a, have confirmed the stoichiometry implied by reaction (1)***. A secondary reaction of O_2 with ferrocenium

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***It should be pointed out that the observation made by Wasserman of continued reaction under degassed conditions could be attributed to a photolytic induced process involving an irreversible charge transfer complex between ferrocene and the halogenated solvent[18,19]. We find that degassed samples of ferrocene in halogenated acids, and more significantly in their anhydrides, are very sensitive to UV light, and that trichloroacetic acid for example, leads to Cl^- formation as evidenced by precipitation with $AgNO_3$.

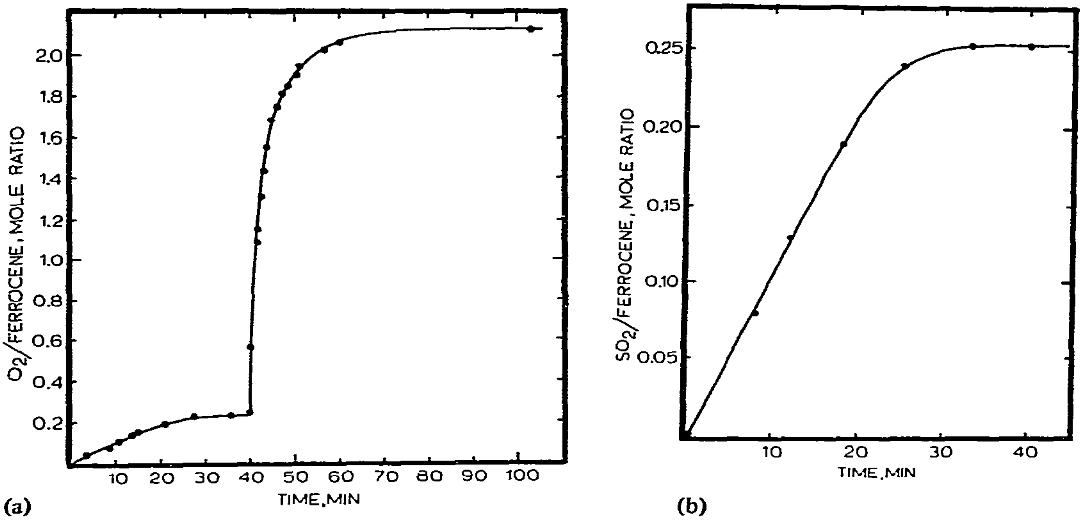

Fig. 1. Tensiometric Titration of Ferrocene in Trifluoroacetic Acid with (a) O_2 and (b) SO_2 at room temperature and pressure.

occurs after the initial reaction is complete, and is indicated by a rapid change from the dark blue ferrocenium ion solution to an orange suspension of Fe^{III} salts. The decomposition appears to be radical-induced as there is no evidence of O_2 uptake by a trifluoroacetic acid solution of ferrocenium trichloroacetate. No further effort was made to elucidate the nature of this reaction.

Since ferrocene and its compounds are generally regarded as being stable to atmospheric oxygen, it is necessary to postulate a reaction mechanism that will explain the observed oxidation. All of the reactions discussed by Wasserman involve strong acids, and since ferrocene is known to undergo protonation at the metal[8,9★], we are led to conclude that it is the protonated ferrocene, ferrocenonium ion, which is involved in the oxidation. This conclusion is supported by the following: (1) Oxidation of ferrocene in $BF_3 \cdot H_2O$ solution is very rapid when the solution is exposed to air, and ferrocene is almost completely protonated in this media. (2) Rates of oxidation reported by Wasserman[1] depend on the acid K_a values in O_2 saturated solutions. Obviously the position of the equilibrium in the protonation process will depend directly on K_a, thus the steady state concentration of ferrocenonium ion and the reaction rate will be dependent upon this parameter. It should be noted, that the steady state concentration of ferrocenonium ions may be quite small in these acids, accounting in part for the

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[★] In a recent communication, Illuminati *et al.*[20] have reported a UV study of ferrocene in trichloroacetic acid/benzene solutions (analogous to the Wasserman conditions) which, they claim, suggests that in milder acids than $BF_3 \cdot H_2O$, protonation occurs on the ring and not on the metal. We feel that the data, as presented, is insufficient to support any unique interpretation, but because of a lack of experimental detail in the communication and assurances[21] that further evidence for this position is forthcoming, we must reserve detailed comment for a later time.

failure to observe this species by NMR[8]. (3) Analogous dicyclopentadienylmetal hydrides Cp_2ReH and Cp_2MoH_2 are readily oxidized in air[10]. (4) Rosenblum[11,12] reports that the ferrocenonium salt $(Cp_2FeH)^+(AlCl_4)^-$ has a greenish hue which is attributable to ferrocenium contamination. We have experimentally confirmed that both the ferrocenonium and 1,1′-dimethylferrocenonium salts of $AlCl_4^-$ yield easily to oxidation when in contact with atmospheric O_2, the appearance of the blue ferrocenium ion being confined initially to the surface layer of the solid in contact with air. (The isolated oxidized salt had the analysis: C, 29.91; H, 3.96; Cl, 32.40; Fe, 14.09. $C_{20}H_{20}Al_2Cl_8Fe_2 \cdot H_2O$ calcd.: C, 32.97; H, 3.30; Cl, 38.90; Fe, 15.22%.)

In conjunction with the investigation of the behavior of ferrocene in the presence of acids to O_2, we have also reexamined the anomalous reaction of ferrocene with SO_2 in acid solutions. Weinmayr[13] reported in 1955 that ferrocene was oxidized to ferrocenium when heated to 100° with SO_2 in HF, but that no reaction occurred with SO_2 in acetic acid. We observed very rapid oxidation when ferrocene was treated with CF_3SO_3H in liquid SO_2 at room temperature. Tensiometric titration of ferrocene in trifluoroacetic acid under an atmosphere of SO_2, as shown in Fig. 1b, and qualitative observation of the presence of sulfur in the spent reaction mixture, indicated that reaction (2) was occurring:

$$4Cp_2Fe + SO_2 + 4H^+ \longrightarrow Cp_2Fe^+ + 2H_2O + S \qquad (2)$$

Since ferrocene was found to be quite stable to oxidation in liquid SO_2 at room temperature for periods exceeding two months, it appears that it must be the protonated form which is suffering facile oxidation.

As a proposed model for the observed reactions of $(Cp_2FeH)^+$ with O_2 and SO_2 we wish to draw attention to the following: Both SO_2 and O_2 can be regarded as Lewis acids interacting with the lone pair orbitals of the metal. In the well documented cases of compounds $CpFe(CO)_2R$[14], the requisite metal orbitals are exposed to attack, whereas in the neutral ferrocene molecule they are shielded by the cyclopentadienyl rings. However, in ferrocenonium cations, the protonation step leads to tilting of the ring systems[9], thus exposing the metal orbitals to attack by O_2 and SO_2. It might then be envisioned that oxidation proceeds via insertion of O_2 and SO_2 into the Fe–H bond, followed by loss of the unstable radical species $H\dot{O}_2$ or $H\dot{S}O_2$ respectively, and formation of the relatively stable Cp_2Fe^+ cation. The radical species released are not stable at room temperature and it has not proven possible to trap them by scavenger techniques to support this proposed mechanism. While there have been no confirmed reports of analogous insertions of SO_2 into Fe–H bonds of $CpFe(CO)_2H$, this molecule is very unstable to oxidation[15] in the manner of ferrocenonium cations. In addition, it appears very likely that a reaction identical to those discussed above would account for the gradual formation of paramagnetic material which Lillya and Sahatjian[16,17] have noted in their recent paper on the protonation of tricarbonyl(arene)chromium compounds in FSO_3H/SO_2 solution. It is possible that this proposed mode of reaction may supply an answer to several other reported reactions of ferrocene, providing a generalized view of mechanistic facets to metallocene chemistry in acidic media.

ACKNOWLEDGMENTS

We wish to thank the Research Corporation for partial support of this work, Professor Harry Gray for some stimulating discussions, Professor A. Schlueter for data on trichloroacetic acid adducts, and Professors D.A. Zatko, K. Gosling, and C.G. Pierpont for helpful suggestions.

REFERENCES

1 M. Aly, R. Bramley, J. Upadhyay, A. Wasserman and P.R. Woolliams, *Chem. Commun.*, (1965) 404.
2 M. Aly, D.V. Banthorpe, R. Bramley, R.E. Cooper, D.W. Jopling, J. Upadhyay, A. Wasserman and P.R. Woolliams, *Monatsch. Chem.*, 98 (1967) 887.
3 A. Horsfield and A. Wasserman, *J. Chem. Soc. (A)*, (1970) 3202.
4 (a) P.B. Ayscough, K. Mach, J.P. Oversby, and A.K. Roy, *Trans. Faraday Soc.*, 67 (1971) 360; (b) P.B. Ayscough and J.P. Oversby, *idem*, 67 (1971) 1365; (c) D. Greatorex and T.J. Kemp, *idem*, 67 (1971) 1576; (d) E.J. Hart, S. Gordon and J.K. Thomas, *J. Phys. Chem.*, 68 (1964) 1271; (e) G.R.A. Johnson and J.L. Redpath, *Trans. Faraday Soc.*, 66 (1970) 861; (f) D.E. Wilson and D.A. Armstrong, *Radiat. Res. Rev.*, 2 (1970) 297.
5 H.B. Gray, D. Hendrickson and A. Schlueter, personal communication, 1971.
6 T.E. Bitterwolf and A. Campbell Ling, Presented in part at the *Combined South-East/South-West Reg. Meet. Amer. Chem. Soc.*, New Orleans, La., December 2–4, 1970.
7 R. Prins and A.G.T.G. Kortbeek, *J. Organometal. Chem.*, 33 (1971) C33.
8 T.J. Curphey, J.O. Santer, M. Rosenblum and J.H. Richards, *J. Amer. Chem. Soc.*, 82 (1960) 5249.
9 T.E. Bitterwolf and A.C. Ling, *J. Organometal. Chem.*, 40 (1972) 197.
10 M.L.H. Green, J.A. McCleverty, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 4954.
11 M. Rosenblum and J.O. Santer, *J. Amer. Chem. Soc.*, 81 (1959) 5517.
12 M. Rosenblum, J.O. Santer and W.G. Howells, *J. Amer. Chem. Soc.*, 85 (1963) 1450; see also I. Pavlik and J. Subrt, *Coll. Czech. Chem. Commun.*, 32 (1967) 76.
13 V. Weinmayer, *J. Amer. Chem. Soc.*, 77 (1955) 3009.
14 A. Wojcicki, *Accounts Chem. Res.*, 4 (1971) 344 and references therein.
15 M.L.H. Green and P.L.I. Nagy, *J. Organometal. Chem.*, 1 (1963) 58.
16 C.P. Lillya and R.A. Sahatjian, *Inorg. Chem.*, 11 (1972) 889.
17 C.P. Lillya, personal communication.
18 J.C.D. Brand and W. Snedden, *Trans. Faraday Soc.*, 53 (1958) 894.
19 A.M. Tarr and D.R. Wiles, *Canad. J. Chem.*, 46 (1968) 2725.
20 G. Illuminati, B. Floris, and G. Ortaggi, *Tetrahedron Lett.*, (1972) 269.
21 G. Illuminati, personal communication.