Journal of Organometallic Chemistry, 60 (1973) C17–C18
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The electron donor properties of ferrocene. The oxidation of ferrocene by carboxylic acids

M. CASTAGNOLA, B. FLORIS, G. ILLUMINATI and G. ORTAGGI

Department of Chemistry and Centro C.N.R. dei Meccanismi di Reazione, University of Rome, 00185 Rome (Italy)

(Received August 8th, 1973)

SUMMARY

Carboxylic acids are reduced by ferrocenes to aldehydes, the rate of reaction increases with the electron-donating ability of the ferrocene and with the acid strength of the acid, a Brönsted-type free-energy correlation being observed.

Ferrocene is known to be oxidized to the ferricenium cation by common oxidizing agents[1]. A recent report of the reduction of enones by ferrocene and HCl or H_2SO_4 [2] prompts us to present some results of a detailed study of the reduction of carboxylic acids to aldehydes by ferrocenes[*].

When ferrocene was added at room temperature to a benzene solution containing 3 molar proportions of trichloroacetic acid, ferricenium trichloroacetate precipitated almost quantitatively as violet crystals. The salt was isolated as $(C_{10}H_{10}Fe)^+CCl_3CO_2^- \cdot CCl_3CO_2H$, and identified by means of elemental analysis (Found: C, 32.84; H, 2.43. Calcd.: C, 32.83; H, 2.17%), electronic spectrum (absorption maxima, log ϵ 4.08 and 2.55 at 250 and 617 nm, respectively), and magnetic moment (2.55 BM at 296 K)[**]. The CCl_3CO_2H was quantitatively titrated against a standardized solution of NaOH.

The reduction of trichloroacetic acid was monitored by the potentiometric titration of aliquots of a solution of ferrocene ($5.4 \times 10^{-2} M$) and CCl_3CO_2H ($0.383 M$) in benzene at 40 °C. The end of the reaction was checked spectrophotometrically; at this point the solution was $0.306 M$ in acid and the molar ratio of the oxidized ferrocene to the trichloro-

---

[*] These results were presented in part at the Meeting on the Mechanisms of Inorganic Substitution Reactions, London, 30 March–3 April 1969 and at the Meeting on Stability and Reactivity of the Coordination Compounds, Bressanone (Padua) 1–4 September 1971.

[**] See ref. 1 for comparison with the data for ferricenium salts.

acetic acid used up was 1.43, *i.e.*, near to 3/2. By the Karl Fisher method, water was found to be formed in the ratio of one mole per two moles of ferrocene. Trichloroacetaldehyde was identified as its 2,4-dinitrophenylhydrazone derivative (m.p. 129 °C; lit. 131 °C [3]).

All the above data are consistent with the following stoichiometric equation (Cp = cyclopentadienyl ring)

$$2Cp_2Fe + 3RCO_2H \rightarrow 2(Cp_2Fe^+, RCO_2^-) + RCHO + H_2O$$

It is noteworthy that the oxidation of ferrocene was found to be quite negligible in 0.26 *M* and 3*M* HCl—benzene solutions. The result implies that there is no direct electron transfer between ferrocene and the acid which would lead to hydrogen gas; although this could be predicted on the basis of the redox potentials[4], the possibility of gas evolution was examined carefully and ruled out experimentally.

The kinetics of the reaction were studied by spectroscopic methods and were found to be dependent on the strengths of the acids used. While complex kinetics were observed in the CCl_3CO_2H—benzene system, linear first-order plots were obtained in neat CF_3CO_2H ($k = 1.1 \times 10^{-3}$ sec^{-1} at 25 °C). In neat acetic acid the rate is negligible.

With the more powerful electron donor permethylferrocene, the oxidation rates were much higher than with the parent compound. The oxidation in CF_3CO_2H is complete in a few minutes, while in CH_3CO_2H the observed rate constant is 6.7×10^{-4} sec^{-1} at room temperature. The oxidation of permethylferrocene occurs easily in benzene in the presence of several carboxylic acids RCO_2H (R = CF_3, CCl_3, $CHCl_2$, CH_2Cl), and obeys to a linear free-energy relationship between the Brönsted type and the dissociation constants of the acids ($\alpha = 0.75$).

The results indicate that the electron donor properties of ferrocenes as well as the acid strength of the oxidizing agent are both important factors in the reaction. The dependence of the rates on acid strength suggests that some interaction between the ferrocene and the acid occurs prior to the reduction step; the latter may then proceed by a radical type mechanism. Since metal protonation requires reagents of markedly high proton-donor ability[5], the interaction between the ferrocene and the acid probably does not involve the iron atom, and is probably the same as that observed under similar protic conditions by spectroscopic methods[6].

REFERENCES

1 M. Rosenblum, *Chemistry of the Iron Group Metallocenes, Part 1*, Interscience, New York, 1965, Chapter 3; see also T.E. Bitterwolf and A.C. Ling, *J. Organometal. Chem.*, 40 (1972) C29.
2 K. Yamakawa and M. Moroe, *J. Organometal. Chem.*, 50 (1973) C43.
3 *Handbook of Tables for Organic Compound Identification*, 3rd Edition, The Chemical Rubber Co, 1967, p. 145.
4 Ref. 1. p. 50
5 T.J. Curphey, J.O. Santer, M. Rosenblum and J.H. Richards, *J. Amer. Chem. Soc.*, 82 (1960) 5249.
6 B. Floris, G. Illuminati and G. Ortaggi, *Tetrahedron Lett.*, (1972) 269.