

## The Rate and Activation Parameters for the Cleavage of the Metal–Metal Bond of the Anion Radical of a Di-iron Carbonyl Complex

Stephen G. Davies,<sup>\*a</sup> Stephen J. Simpson,<sup>a</sup> and Vernon D. Parker<sup>\*\*b</sup>

<sup>a</sup> *The Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford OX1 3QY, England*

<sup>b</sup> *Laboratory for Organic Chemistry, Norwegian Institute of Technology, N-7034 Trondheim-NTH, Norway*

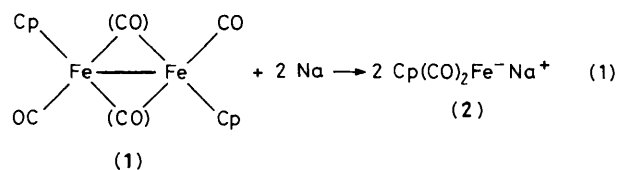
Electron transfer to  $[(C_5H_5)Fe(CO)_2]_2$  gives an anion radical in which the electronic configuration of one Fe no longer conforms to the '18 e' rule and which undergoes cleavage of the metal–metal bond with a rate constant equal to  $1060\text{ s}^{-1}$  at 273 K and an activation energy of  $15.7\text{ kcal mol}^{-1}$  (1 kcal = 4.18 kJ) in acetonitrile.

It is a well recognised fact that electron transfer can play an important role in the reactions of organo-transition metal compounds and can thus be a primary step in homogeneous catalysis.<sup>1</sup> In spite of the importance of such processes little detailed information is available concerning the reactions of ion radicals of this class of compounds.<sup>1</sup>

We report the preliminary results of a detailed investigation of the redox reactions of complex (1) and related substances.

Reaction (1) is observed to take place when complex (1) (Cp = cyclopentadienyl) is exposed to metallic sodium.<sup>2</sup> Although the mechanism of the reaction is not known we considered it likely that either the anion radical resulting from the transfer of 1 e<sup>-</sup> or the dianion from 2e<sup>-</sup> transfer is the species which undergoes cleavage of the metal–metal bond.

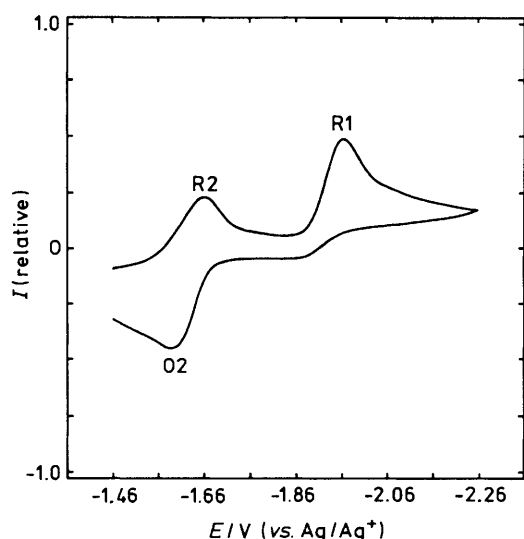
The electron transfer process is illustrated by the steady state voltammogram for the reduction of (1) in acetonitrile at



**Table 1.** Kinetic and activation parameters for the decomposition of  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2^-$  anion radical in acetonitrile.

[Substrate]/mM	0.25	0.50	1.00
$k_{244}/\text{s}^{-1}$	35.9	30.5	35.4 ( $\pm 16\%$ )
$E_a/\text{kcal mol}^{-1}$	—	—	15.7 ( $\pm 0.3$ )
$\Delta S^\ddagger/\text{cal (K mol)}^{-1}$	—	—	11
$k_{273.2}^a/\text{s}^{-1}$	—	—	1060

<sup>a</sup> The rate constant at 273.2 K evaluated from the Arrhenius plot. All experiments were conducted in solvent containing  $\text{Bu}_4\text{NBF}_4$  (0.10 M).

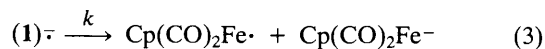


**Figure 1.** Steady state cyclic voltammogram for the reduction of  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2^-$  (1) in acetonitrile at 263 K and  $1.00 \text{ V s}^{-1}$ .

263 K (Figure 1). The cyclic voltammogram was measured at a mercury electrode after about 10 cycles between  $-1.46$  and  $-2.26 \text{ V}$  (vs.  $\text{Ag}/\text{Ag}^+$ ) at a voltage sweep rate of  $1.00 \text{ V s}^{-1}$ . Under these conditions the process corresponds to the reduction of (1) at R1 with a peak potential of  $-1.97 \text{ V}$  and the oxidation of a reaction product [presumably (2)] at O2 with a peak potential equal to  $-1.576 \text{ V}$ . After the first cycle a new reduction peak R2 which is linked to O2 is observed.

By going to either lower temperatures or higher sweep rates the oxidation of the anion radical regenerating (1) can be observed on the reverse scan. This allowed the kinetics of the reaction to be studied by derivative cyclic voltammetry (d.c.v.), a transient technique which has recently been discussed.<sup>3</sup> The data in Table 1 are for measurements carried out at temperatures ranging from 243 to 273 K and voltage sweep rates from  $1.00$  to  $100 \text{ V s}^{-1}$ . The rate constants were evaluated from theoretical data<sup>4</sup> for the  $\text{ECE}_h$  mechanism which consists of reactions (2) to (4) in this case.

The dianion was ruled out as a possible intermediate by the observation that  $I_p/v^{1/2}$ , where  $v$  is the voltage sweep rate, changes by about a factor of 2 as  $v$  is varied to observe the change from complete to no reaction under the time scale of the measurements.<sup>5</sup> Any contribution from electron transfer



reaction (4) to rate control was ruled out by the fact that the observed rate constants were independent of the substrate concentration in contradiction to the expected behaviour for a second order reaction of  $(1)^{\cdot-}$ .<sup>3</sup> Three independent determinations of the rate constant at 244 K with a substrate concentration of 1 mM showed a standard deviation of  $\pm 16\%$ . This error is somewhat greater than is usually encountered using d.c.v. and is likely to be due to some interference by product adsorption on the electrode. Because of this it was necessary to change the mercury surface frequently during the experiments.

The activation parameters for this reaction are of interest. In spite of the fact that the configuration around one Fe atom in the anion radical no longer conforms to the stable situation described by the '18 electron rule' the Arrhenius activation energy ( $E_a$ ) is of considerable magnitude, *i.e.*  $15.7 \text{ kcal mol}^{-1}$ .<sup>†</sup> This implies a reasonably high barrier to the cleavage of the metal-metal bond in the anion radical. As would be expected for rate determining reaction (3) the entropy of activation,  $\Delta S^\ddagger$ , was observed to be positive and equal to about  $11 \text{ cal (K mol)}^{-1}$ . The only data available for comparison deal with the cleavage of arenes from cation radicals of tricarbonylchromium complexes.<sup>6</sup> Activation energies ranging from  $8$ – $18 \text{ kcal mol}^{-1}$  were found but the activation entropies were negative. The reaction having an activation energy of  $16 \text{ kcal mol}^{-1}$ , comparable to that reported here, had a rate constant of only  $0.46 \text{ s}^{-1}$  at  $298 \text{ K}$  which is several orders of magnitude less than we can calculate in this case. In fact the rate constant in this case is greater than  $10^3 \text{ s}^{-1}$  at  $273 \text{ K}$ . Thus, compared, to the other known cases<sup>6</sup> we conclude that the facile reaction (3) is driven by the positive entropy of activation.

It is our general conclusion that the study of the kinetics and mechanisms of electron transfer reactions involving organo-transition metal compounds is feasible and can be expected to provide highly useful information on the reactions of these very important compounds.

Received, 6th December 1983; Com. 1586

## References

- 1 T. J. Meyer, *Prog. Inorg. Chem.*, 1975, **19**, 1; R. E. Dessy, R. Kornmann, S. Smith, and R. Haytor, *J. Am. Chem. Soc.*, 1968, **90**, 2001, and references therein.
- 2 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104; E. O. Fischer and R. Böttcher, *Z. Naturforsch., Teil B*, 1955, **10**, 600.
- 3 V. D. Parker, *Adv. Phys. Org. Chem.*, 1983, **19**, 131.
- 4 E. Ahlberg and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1981, **35**, 117.
- 5 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
- 6 T. Ikeshoji and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1983, **37**, 715.

<sup>†</sup>  $1 \text{ kcal} = 4.18 \text{ kJ}$ .