CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Measurement of Reaction Kinetics Using Chronocoulometry

Purpose

It is well known that electron deficient organometallic complexes are much more labile than their electronically saturated analogues. A recently studied example of this is the 33 electron dinuclear complex $Fe_2(CO)_7(\mu\text{-}PPh_2)$, which is synthesized using chemical or electrochemical oxidation of the 34 electron monoanion (F1). It was shown by cyclic voltammetry that the oxidized complex rapidly reacts with phosphines at room temperature to give the monosubstituted phosphine derivative (the neutral complex does not react under these conditions). A further study was undertaken to measure the rate of the substitution reaction, and to investigate the effect of variation in the steric and electronic properties of the phosphine on this rate.

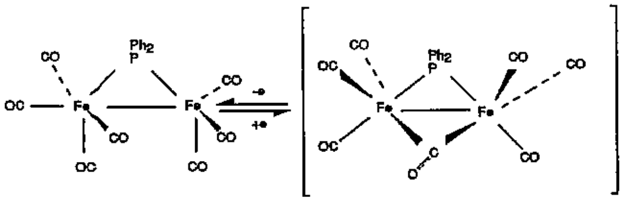

Figure 1. Redox interconversion of $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^n$ (n =0,-1).

Reference

Spectroscopic, Structural, Electrochemical, and Kinetic Studies of Ligand Substitution in the 33e Dinuclear Radical $Fe_2(CO)_7(\mu\text{-}PPh_2)$ and the 34e Analogues $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-$ and $FeCo(CO)_7(\mu\text{-}PPh_2)$, R. T. Baker, J. C. Calabrese, P. J. Krusic, M. J. Therien and W. C. Trogler, J. Am. Chem. Soc. 110 (1988) 8392 - 8412.

Method

Cyclic voltammetry is a powerful technique for the qualitative investigation of the reactions of electrogenerated species in solution. However, the interplay of heterogeneous and homogeneous processes complicates calculation of quantitative data, and other techniques are generally preferred. One such technique is chronocoulometry. In this method, the potential is stepped from a value at which no electrolysis occurs (E_i) to a potential at which the electroactive species is converted to a different oxidation state at the working electrode (E_s). The working electrode is then held at this potential for a time τ, after which the potential is stepped to another value (often the initial potential) at which the electrolyzed species is converted to the original oxidation state (E_f) (F2a). The potentials used are calculated from cyclic voltammetric data and are sufficiently different from the redox potential to cause very rapid electron transfer, which eliminates the effect of slow heterogeneous charge transfer. The current (and hence the charge) for both steps is therefore diffusion controlled. In chronocoulometry, it is the charge for both steps that is measured (F2b). For a simple electron transfer, the charge ratio Q_r/Q_f is 0.586 (i.e. some of the molecules electrolyzed in the first step diffuse away from the working electrode before the second step). However, if the electron transfer is followed by a chemical reaction, there are fewer molecules available for electrolysis in the second step, and the ratio decreases. The magnitude of this decrease depends on τ (i.e. the time available for the chemical reaction); therefore, the rate of this chemical reaction can be calculated by measuring the variation in Q_r/Q_f due to changes in τ.

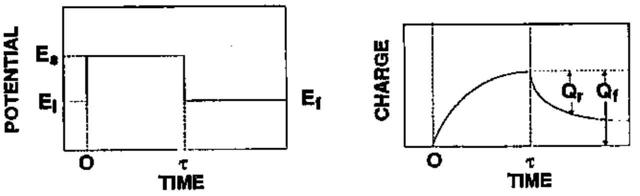

Figure 2. a) Applied potential vs. time plot for chronocoulometry. b) Charge vs. time plot for chronocoulometry.

Results

The chronocoulometry experiment was carried out on a solution containing the monoanion and a phosphine, with oxidation of the monoanion occurring in the first step. In addition to varying τ, the concentration of the phosphine was also varied and a range of phosphines with differing steric and electronic properties was used. Working curves are available (1) that relate Q_r/Q_f to $k_1[P]$ for various values of $k_{-1}/k_1[P]$ (where k_1 and k_{-1} are the rate constants for the forward and reverse chemical reactions respectively, and [P] is the concentration of the phosphine). For this system, Q_r/Q_f tended to zero for moderate P and large τ, which showed that the rate of the reverse reaction was negligible (i.e. the chemical reaction is irreversible). The values of $k_1[P]$ were therefore taken for the working curve for $k_{-1}/k_1[P] = 0$ (F3), and k_1 was calculated. As discussed above, k_1 was several orders of magnitude larger than the rate constant for substitution of the monoanion. Variations in k_1 for different phosphines showed that the substitution reaction is associative. The activation parameters calculated from variable temperature measurements of k_1 were also consistent with an associative mechanism (e.g. the entropy of activation was negative).

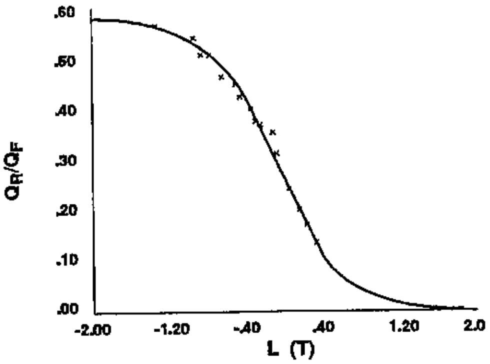

Figure 3. Variation of Qr/Qf with L(T) ($L(T) = \log(k_1[P]\tau)$) for an EC mechanism where the chemical reaction is irreversible.

Additional Reference

1) M. K. Hafney, R. L. Scott, T. H. Ridgway and C. N. Reilly, Anal. Chem. 50 (1978) 116 - 125.