Proof of an Electron-transfer Mechanism by which Metals can Catalyse Oxidation–Reduction Reactions

By M. SPIRO* and P. W. GRIFFIN

(*Department of Chemistry, Imperial College of Science and Technology, London, S.W.7*)

MANY redox reactions in solution are catalysed by metals.[1] Several workers[2] have postulated that such catalysis proceeds *via* electron transfer through the metal phase; we report the first quantitative confirmation of this hypothesis.

The reaction employed was

$$2Fe(CN)_6^{3-} + 3I^- \rightarrow 2Fe(CN)_6^{4-} + I_3^- \qquad (1)$$

catalysed by platinum. If the electron-transfer mechanism is correct, then in the steady state the rate at which ferricyanide ions accept electrons from the platinum equals the rate at which iodide ions donate electrons to it. Each rate, too, equals the rate of heterogeneous catalysis. From the electrochemical point of view, the cathodic current of the ferricyanide–ferrocyanide couple at the metal surface must equal the anodic current of the tri-iodide–iodide couple at the potential—the "mixture potential"—which the metal takes up in the reaction mixture. An experimental test can therefore be made by (i) measuring the rate of heterogeneous catalysis and at the same time the potential adopted by the catalyst during the run, and (ii) determining the current–voltage curves of the two couples individually at the same metal surface. To achieve uniformity of conditions we used a large rotating disc of platinum metal: the hydrodynamic theory of such a system is well established,[3] the practical conditions necessary for large discs to meet the theoretical requirements are now known,[4] and it is relatively easy to condition the surface reproducibly before each experiment.

A platinum sheet (3·8 cm. diam.) was brazed on to a trumpet-shaped stainless steel former, and the latter was insulated from the solution by two coatings of Araldite Clear Lacquer. The platinum surface was preconditioned in M-$HClO_4$ at 0° by being cathodized for 45 min. at +0·140 v and then anodized for 10 min. at +1·400 v. All potentials quoted are with respect to a saturated calomel electrode at 0°. The rate of reaction (1) was determined spectrophotometrically at 350 nm. where I_3^- absorbs strongly. All experiments were carried out at 0° because the contribution of the homogeneous reaction to the overall rate is then relatively small.

The following figures are typical. In a 300 ml. reaction mixture M in KNO_3, 1 mM in $K_3Fe(CN)_6$, and 50 mM in I^-, the homogeneous rate of tri-iodide production was $0{\cdot}5_1 \times 10^{-9}$ mole $l.^{-1}$ $sec.^{-1}$. With the platinum disc immersed and spinning at 200 rev./min., the overall rate was $6{\cdot}7_8 \times 10^{-9}$ mole $l.^{-1}$ $sec.^{-1}$. The heterogeneous contribution, therefore, was $6{\cdot}2_7 \times 10^{-9}$ mole $l.^{-1}$ $sec.^{-1}$, or $6{\cdot}2_3 \times 10^{-9}$ after a small sampling correction. In the catalysed run, the mean concentrations of ferrocyanide and tri-iodide were 14·6 μM and 7·3 μM, respectively. The potential of the platinum disc was $0{\cdot}293_1$v (*versus* S.C.E. at 0°) at the beginning of the run, and $0{\cdot}293_5$v at the end.

Current–voltage curves for the individual couples were then measured by use of the same rotating disc. After allowance for the effect of the residual current, it was found that the cathodic current of a mM-ferricyanide + 14·6μM-ferrocyanide couple in M-KNO_3 equalled the anodic current of a 50 mM-iodide + 7·3 μM-tri-iodide couple in M-KNO_3 at a potential of $0{\cdot}295_5$ v. The corrected currents, which were fairly insensitive to the ferrocyanide and tri-iodide concentrations, respectively, were both 354 μA. By Faraday's law, this is equivalent to the production of tri-iodide at the rate of $6{\cdot}1_1 \times 10^{-9}$ mole $l.^{-1}$ $sec.^{-1}$ in the 300 ml. solution used.

The two independent determinations of both potential and rate are in close agreement. The potential of the disc during catalysis is only 2 mv less than that deduced from the current–voltage curves of the separate couples, and the electrochemically measured rate of electron transfer at the mixture potential agrees to within 2% with the kinetically determined rate of heterogeneous catalysis. Only one basic assumption—the additivity of current–voltage curves—has been made, and this is generally accepted.[5] Within the limitations of its validity and of the experimental errors, the above experiments and others like them prove that platinum metal catalyses reaction (1) by allowing the transfer of electrons through the metal and not by some other mechanism such as direct electron transfer between adjacently adsorbed reactant ions. If this path is a general one, the rates of heterogeneous catalysis by metals of this and other redox reactions can be predicted from electrochemical experiments alone. A similar mechanism is likely to apply to redox reactions catalysed by semiconductors, and indeed the possibility that enzymic oxidoreductions proceed *via* electron transfer through the enzyme was envisaged some years ago.[6]

We thank International Nickel Ltd. for a research grant to P. W. G. and for the loan of the platinum.

(*Received, January 8th,* 1969; *Com.* 026.)

[1] M. Spiro and A. B. Ravnö, *J. Chem. Soc.*, 1965, 78.

[2] R. J. Prestwood and A. C. Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137; C. S. Garner, *J. Phys. Chem.*, 1952, **56**, 857; G. M. Waind, *Chem. and Ind.*, 1955, 1388; C. Baughan, *Discuss. Faraday Soc.*, 1960, **29**, 135; M. Spiro, *J. Chem. Soc.*, 1960, 3678.

[3] V. G. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, Englewood Cliffs, N.J., 1962; A. C. Riddiford, *Adv. Electrochem. Electrochem. Eng.*, 1966, **4**, 47.

[4] R. R. M. Johnston and M. Spiro, unpublished work.

[5] C. Wagner and W. Traud, *Z. Elektrochem.*, 1938, **44**, 391; K. J. Vetter, "Electrochemical Kinetics: Theoretical and Experimental Aspects", Academic Press, New York, 1967, ch. 5.

[6] S. J Leach, *Adv. Enzymol.*, 1954, **15**, 1.