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Heterogeneous Catalysis in Solution

Part 27.†—Reaction between Titanium(III) and Triiodide Ions Catalysed by Platinum

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The rate of the reaction between titanium(III) chloride and triiodide ions in an acid chloride medium has been studied in the absence and presence of a rotating platinum disk. At low concentrations of triiodide the catalytic rate at platinum was found to be first order in I_3^-, zero order with respect to Ti^{III} and H^+, and proportional to the square root of the rotation speed of the disk. These results pointed to diffusion-controlled catalysis, as did the low activation energy of 19 kJ mol^{-1} as compared with 40 kJ mol^{-1} for the uncatalysed reaction.

All these findings are consistent with an electrochemical interpretation of the catalytic mechanism, as was shown by the current–potential curves determined for the two reactants at the same reduced platinum surface. Provided that the voltammograms for Ti^{III} had been carried out in the presence of the same concentration of KI as in the reaction mixtures, the rates and mixture potentials determined electrochemically agreed well with the catalytic rates and potentials measured experimentally. The fact that quite different results were obtained when no KI was present in the $TiCl_3$ solution provides further confirmation for the modified form of the additivity principle.

The redox reaction

$$2Ti^{III} + I_3^- \rightarrow 2Ti^{IV} + 3I^- \qquad (I)$$

in aqueous hydrochloric acid is a slow process whose kinetics have been studied by several workers.[1,2] An unusual feature of this reaction is that it can be homogeneously catalysed by certain quinones, phenazines and quinoxalines[3,4] in concentrations as low as 10^{-7} to 10^{-5} mol l^{-1}. The mechanism appears to depend on the catalyst[4] and one case has been investigated in detail.[5] Reaction (I) has also been found to be catalysed heterogeneously by metallic platinum.[6] This was explained by an electrochemical mechanism whereby the electron passed from Ti^{III} to the iodine *via* the noble metal. The present study aims to test this mechanism quantitatively.

Theory

As in the case of several other metal-catalysed redox reactions,[7,8] the electrochemical mechanism can be tested by combining electrochemical and kinetic studies. The principle is illustrated in Fig. 1 where anodic currents are taken as positive and cathodic currents as negative. Curve (*a*) depicts the increase in current when a solution of Ti^{III} is oxidised electrochemically at a given platinum surface while curve (*b*) shows the variation of current with potential when a solution of iodine in KI solution is reduced electrochemically. When both Ti^{III} and iodine are present together in the solution, the two curves can be added algebraically provided they have been obtained in circumstances which correspond to those in the mixture.[7,9] The platinum surface thus takes up a mixed or mixture potential E_{mix} at which the anodic current I_{mix} on curve (*a*) exactly balances the cathodic current $|I_{mix}|$ on curve (*b*). By Faraday's law, the mixture current is directly proportional to the rate of the reaction between Ti^{III} and iodine on the platinum surface, as given by eqn. 1

$$v_{mix} = I_{mix}/nFA \qquad (1)$$

where n is the number of electrons cancelled out in the overall reaction equation [*i.e.* $n = 2$ for eqn. (I)], F is the Faraday constant and A is the surface area of the platinum. If v_{mix}, derived from purely electrochemical experiments with the separate reactants, agrees with the catalytic rate v_{cat} from kinetic measurements of the reaction mixture, and if E_{mix} obtained electrochemically also agrees with the potential E_{cat} taken up by the platinum catalyst during the reaction, then the catalysis has clearly proceeded by a purely electrochemical mechanism.

In order to control the hydrodynamic conditions, it is useful to present the platinum surface in the form of a large horizontal disk set in an inert trumpet-shaped former which rotates about a vertical axis.[10] The thickness, δ, of the Nernst diffusion layer at the surface is then given by the Levich

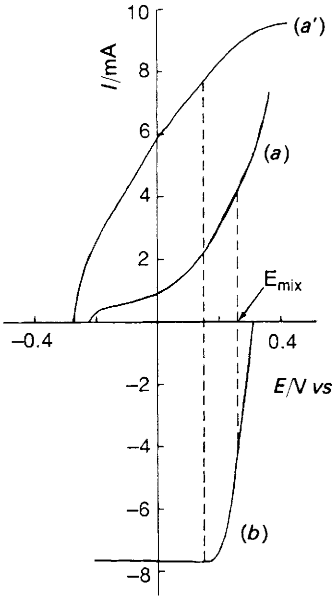

Fig. 1 Voltammograms at 10 mV s^{-1} with the reduced platinum disk rotating at 9 Hz for the oxidation of (*a*′) 23.7 mmol l^{-1} $TiCl_3$ and (*a*) 23.7 mmol l^{-1} $TiCl_3$ in 0.1 mol l^{-1} KI, and (*b*) for the reduction of 0.630 mmol l^{-1} I_3^- in 0.1 mol l^{-1} KI. All solutions were at 25 °C and also contained 0.1 mol l^{-1} HCl and 0.8 mol l^{-1} KCl.

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equation[11]

$$\delta = 0.643D^{1/3}\nu^{1/6}f^{-1/2} \qquad (2)$$

where D is the diffusion coefficient of the diffusing species, ν is the kinematic viscosity of the solution and f is the rotation speed in Hz. Diffusion-controlled currents and diffusion-controlled catalytic rates vary inversely with δ and are therefore directly proportional to the square root of the rotation speed.

Experimental

All solutions were made up with Milli-RO and Milli-Q deionised water (Millipore). The titanium(III) chloride was a BDH product, low in iron, which also contained *ca.* 0.049 g $ZnCl_2$ per ml. The Ti^{III} concentration was determined by standardizing with pure iron.[12] All other reagents were BDH AnalaR.

The geometrical area of the platinum disk was 12.19 cm^2. A saturated potassium chloride calomel electrode (SCE) was used as the reference electrode and a large platinum foil as the counter electrode. Before each experiment the platinum surface was polished with a suspension of 0.3 μm alumina in water, washed, and electrochemically cleaned by cycling it at 50 mV s^{-1} between -0.2 and $+1.7$ V *vs.* SCE in nitrogen-saturated 0.5 mol l^{-1} sulfuric acid while it was rotated at 9 Hz, until reproducible voltammograms were obtained. For the preparation of a reduced surface, the potential was disconnected at 0.2 V and the electrode preconditioned at 0.2 V for 20 s, 1.7 V for 20 s and finally 0.2 V for 600 s. The disk was then thoroughly washed and stored in a desiccator.

All the experiments were carried out in a thermostat bath, usually at 25.0 ± 0.1 °C. Electrochemical experiments were carried out in a three-compartment cell[7] and the catalysed runs in a similar two-compartment cell.[8] The background electrolyte was normally a mixture of 0.1 mol l^{-1} HCl (to reduce the extent of Ti^{III} hydrolysis), 0.1 mol l^{-1} KI (to keep the iodine complexed as I_3^-) and 0.8 mol l^{-1} KCl (to maintain a high and constant ionic strength). In the kinetic runs the background electrolyte and reactant solutions were thermally equilibrated before being mixed. In the catalysed runs the disk was allowed to attain the bath temperature by being spun for 15 min in the thermostatted background solution before the reactants were added.

Nitrogen was passed through the solutions beforehand and the experiments were carried out under a nitrogen atmosphere.

The reaction was followed by removing samples (0.5 or 1 ml) at regular intervals and diluting them with 10 ml of 0.1 mol l^{-1} KI solution. The absorbance A of the triiodide ions was then measured at the band maximum wavelength of 352 nm on a Perkin–Elmer Lambda 2 spectrophotometer. The applicability of Beer's law was confirmed. In the catalysed runs the potential adopted by the platinum disk was recorded each time *vs.* the SCE reference.

Results and Discussion

Homogeneous Kinetics

For both the homogeneous and the catalysed reactions, plots of ln A *vs.* time were normally linear for 30–60 min. The slopes, obtained by least-squares fitting, gave the first-order (with respect to I_3^-) rate constants, k. At a constant initial I_3^- concentration of 0.202 mmol l^{-1}, k was found to be proportional to the initial concentration of $TiCl_3$ over the range 8 to 47 mmol l^{-1}. However, when the initial $TiCl_3$ concentration was fixed at 23.7 mmol l^{-1}, k declined gently as the initial concentration of triiodide increased from 0.1 to 0.6 mmol l^{-1}. All these results could be fitted, with an average deviation of less than 5%, by the equation

$$-\mathrm{d}[I_3^-]/\mathrm{d}t = (9.6 \times 10^{-3})[I_3^-][TiCl_3] + (7.1 \times 10^{-7}) \times [TiCl_3] \qquad (3)$$

where the square brackets refer to concentrations in mol l^{-1} and the time t is in s. The first term on the right-hand side was always the larger one under our conditions. The rate of reaction fell almost inversely on raising the HCl concentration, which suggests that $TiOH^{2+}$ is the main reactant even though only *ca.* 5% of the Ti^{III} is present in this form in the medium employed.[13] There was a lesser fall on increasing the concentration of KI. The activation energy between 9.8 and 25.0 °C for the reaction between 0.202 mmol l^{-1} I_3^- and 23.7 mmol l^{-1} Ti^{III} was found to be 40 kJ mol^{-1}.

Johnson and Winstein[2] obtained a similar rate law which they interpreted as indicating rate-determining reactions between $TiOH^{2+}$ and both I_3^- and I_2. For the same background conditions of 0.1 mol l^{-1} HCl, 0.1 mol l^{-1} KI and 0.8 mol l^{-1} KCl and also at 25 °C, their kinetic equation was of the same form as eqn. 3 but with different rate constants, namely

$$-\mathrm{d}[I_3^-]/\mathrm{d}t = 0.103[I_3^-][Ti^{III}] + (1.92 \times 10^{-5})[Ti^{III}] \qquad (4)$$

This difference may be attributed to the presence of $ZnCl_2$ in the BDH $TiCl_3$ solution employed. Experiments with concentrations of I_3^- and Ti^{III} similar to those used in ref. 2, but to which additional amounts of zinc chloride had been added, led to lower rates, as Fig. 2 shows. As the curve rises steeply at low $ZnCl_2$ concentrations, a much higher rate of reaction would be expected for the zinc chloride-free solutions employed by Johnson and Winstein.

Catalysed Kinetics

Reaction (I) was always faster in the presence of the spinning platinum disk, consistent with heterogeneous catalysis by platinum. In order to evaluate the catalytic component in these 'heterogeneous' experiments, their rates and those of the corresponding homogeneous runs were expressed in terms of the number of moles of triiodide reacting per second, (v'), by the equation

$$v' = kV[I_3^-] \qquad (5)$$

where V is the volume of the solution (normally 354 ml) and $[I_3^-]$ is the initial concentration. The areal catalytic rate at

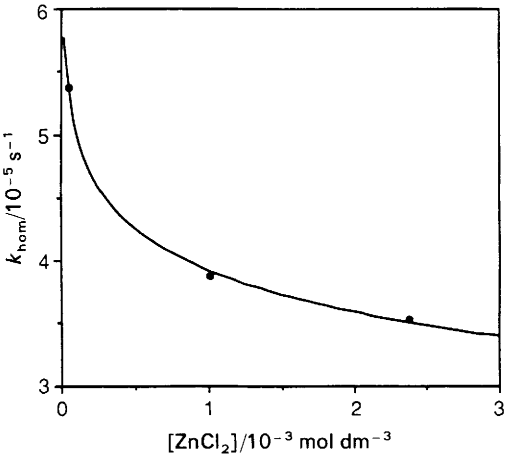

Fig. 2 Homogeneous first-order rate constant k_{hom} *vs.* concentration of zinc chloride, for a reaction mixture containing 8.3 mmol l^{-1} $TiCl_3$, 2.52 mmol l^{-1} I_3^-, 0.11 mol l^{-1} KI, 0.1 mol l^{-1} HCl and 0.82 mol l^{-1} KCl at 25 °C

the surface of the platinum [in (mol I_3^-) m^{-2} s^{-1}] was then given by

$$v_{cat} = (v'_{het} - v'_{hom})/A \qquad (6)$$

Expressing the catalytic rate in this way involves no preconceptions about the kinetic form of the catalytic reaction. It should be borne in mind, however, that v_{cat} depends on the difference between two rates of comparable magnitude and is therefore uncertain by *ca.* ±10%.

When heterogeneous runs were carried out with the same initial concentrations of reactants as for the homogeneous runs, the catalytic kinetics were quite different. Thus, with $[I_3^-] = 0.202$ mmol l^{-1}, v_{cat} was found to be completely independent of the Ti^{III} concentration over the range 8–47 mmol l^{-1}. However, when the initial concentration of $TiCl_3$ was kept constant at 23.7 mmol l^{-1}, v_{cat} increased linearly with $[I_3^-]$ according to the equation

$$v_{cat}/\text{mol m}^{-2}\ \text{s}^{-1} = (2.92 \times 10^{-6}) + (3.17 \times 10^{-2})[I_3^-] \qquad (7)$$

The catalysed reaction was therefore first order in I_3^- and zero order in Ti^{III}. Unlike the homogeneous reaction rate, v_{cat} was independent of the hydrogen ion concentration when it was varied from 0.05 to 0.2 mol l^{-1}. However, it decreased from 1.83×10^{-5} to 1.02×10^{-5} mol m^{-2} s^{-1} when the KI concentration was raised from 0.1 to 0.2 mol l^{-1} and stayed at the lower value for KI concentrations of 0.3 and 0.5 mol l^{-1} (the ionic strength being kept constant by appropriately lowering the amount of KCl).

As shown in Fig. 3, v_{cat} increased proportionately with the square root of the rotation speed. This is a clear indication of diffusion control, a conclusion supported by the low activation energy of $19._4$ kJ mol^{-1} obtained between 0.202 mmol l^{-1} I_3^- and 23.7 mmol dm^{-3} Ti^{III} over the range 9.8–25 °C. It follows that the first-order (with respect to I_3^-) catalytic rate constant is given by the equation[14]

$$k_{cat} = k_{het} - k_{hom} = \frac{v_{cat}A}{V[I_3^-]} = \frac{DA}{V\delta} \qquad (8)$$

where D is the tracer diffusion coefficient of I_3^- in the medium employed. Combination with eqn. 2 leads to

$$v_{cat} = 1.555D^{2/3}\nu^{-1/6}f^{1/2}[I_3^-] \qquad (9)$$

Taking the viscosity of the supporting electrolyte medium at 25 °C as 0.8888×10^{-3} kg m^{-1} s^{-1} [15] and its density as 1.0493 g ml^{-1} [16] gives $\nu = 0.8470 \times 10^{-6}$ m^2 s^{-1}. The resulting value of D from the lower plot of Fig. 3 is 1.02×10^{-9} m^2 s^{-1}. Allowance for the correction term[17,18] $[1 + 0.298(D/\nu)^{1/3} + 0.145(D/\nu)^{2/3}]$ gives $D = 1.07 \times 10^{-9}$ m^2 s^{-1}. This is in reasonable agreement with the value of 1.13×10^{-9} m^2 s^{-1} obtained by Newson and Riddiford,[19] also in the presence of 0.1 mol l^{-1} KI.

In most heterogeneous runs the catalyst potential E_{cat} rose in the early stages and then declined. In other cases, E_{cat} initially stayed constant before decreasing while, with higher I_3^- concentrations, E_{cat} decreased throughout the experiments. The initial values of E_{cat} fell as the $TiCl_3$ concentration increased and rose as the I_3^- concentration increased. These findings are explained in the next section.

Electrochemical Experiments

If the catalytic mechanism is an electrochemical one, the catalytic rates and potentials should be predictable from electrochemical experiments with the two reactants. Voltammograms were therefore determined for appropriate solutions of $TiCl_3$ and I_3^- in the normal supporting electrolyte medium. Two examples are depicted in Fig. 1. Here the mixture potential, E_{mix} obtained from curve (*a*) for 23.7 mmol l^{-1} Ti^{III} and curve (*b*) for 0.630 mmol l^{-1} I_3^- was 274 mV *vs.* SCE while the initial potential E_{cat} measured in the catalysed reaction mixture was 280 mV. Furthermore, the rate v_{mix} calculated from the mixture current of 4.26 mA in Fig. 1 by means of eqn. 1 was 1.81×10^{-5} mol m^{-2} s^{-1} while the measured catalytic rate v_{cat} evaluated from eqn. 6 was 1.83×10^{-5} mol m^{-2} s^{-1}. This good agreement for both the potential and the rate would be difficult to explain by any catalytic mechanism other than an electrochemical one in which the electrons are transferred from the Ti^{III} reductant to the I_3^- oxidant through the platinum catalyst.

Fig. 4 shows that similar good agreement between v_{mix} and v_{cat} was obtained in many other sets of experiments. The concordance found between E_{mix} obtained from the voltammograms and E_{cat} measured in the reaction mixtures is demonstrated in Fig. 5.

It must be emphasized that all the above electrochemical data were based on voltammograms for $TiCl_3$ solutions containing 0.1 mol l^{-1} KI, the same KI concentration as in the reaction mixtures. Quite different voltammetric curves were obtained for solutions of $TiCl_3$ without KI, as curve (*a*′) in Fig. 1 illustrates. This difference arose from the strong adsorption of iodide ions on the reduced platinum surface, a

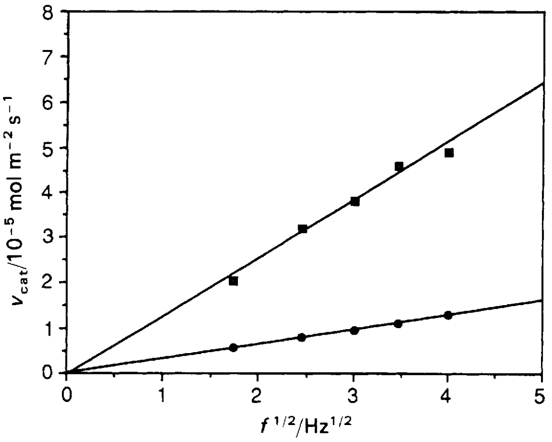

Fig. 3 Catalytic rate at 25 °C *vs.* the square root of the disk rotation speed, for solutions containing 23.7 mmol l^{-1} $TiCl_3$, 0.1 mol l^{-1} KI, 0.1 mol l^{-1} HCl, 0.8 KCl mol l^{-1} and (●) 0.202 mmol l^{-1} triiodide or (■) 4.04 mmol l^{-1} triiodide

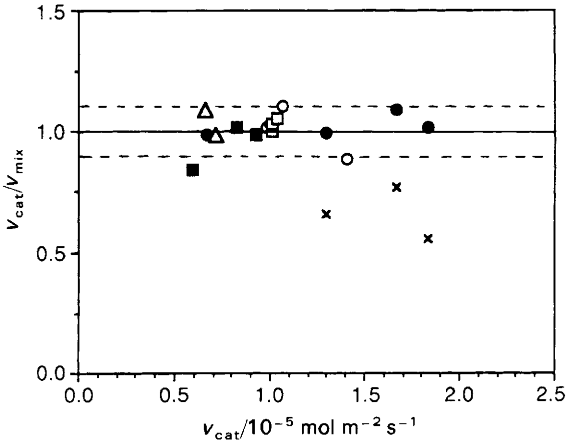

Fig. 4 v_{cat}/v_{mix} *vs.* v_{cat} for experiments in which the following parameters were varied: ○, $TiCl_3$ concentration; ●, I_3^- concentration; □, KI concentration; ■, HCl concentration and △, temperature. The symbols, ×, refer to values of v_{mix} obtained from voltammograms for $TiCl_3$ solutions containing no KI. The dashed lines represent the 10% uncertainty limits.

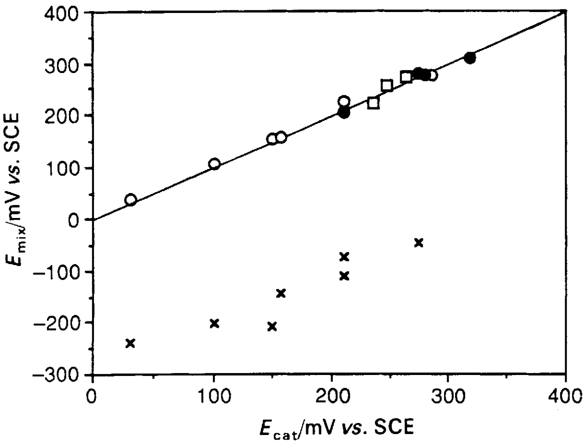

Fig. 5 E_{mix} vs. E_{cat} for experiments in which the following parameters were varied: ○, $TiCl_3$ concentration; ●, I_3^- concentration; □, KI concentration. The symbols × refer to values of E_{mix} obtained from voltammograms for $TiCl_3$ solutions containing no KI. The straight line has a slope of unity.

well attested phenomenon.[20,21] It was confirmed in the present work by a cyclic voltammogram taken after immersing the platinum disk in a typical reaction mixture, which showed a large anodic peak at *ca.* 1.3 V which disappeared in the second sweep. If curve (a') rather than curve (a) in Fig. 1 is combined with the I_3^- curve (b), E_{mix} becomes 152 mV, completely different from the E_{cat} value of 280 mV. Moreover, the larger I_{mix} value of 7.72 mA leads to a correspondingly larger v_{mix} of 3.28×10^{-5} mol m^{-2} s^{-1}, some 79% greater than the experimental value of v_{cat}. Similar disagreement in other cases is clearly indicated by the data points marked with crosses in Fig. 4 and Fig. 5. This is further confirmation that the original principle of the additivity of current–potential curves[22] should only be applied in the modified form given by Creeth and Spiro.[9] This states that current–potential curves can be added only if they have been obtained in circumstances which correspond to those of the mixture.

It remains to show how the observed catalytic kinetics follow directly from the electrochemical curves. This is demonstrated in Fig. 6 where all currents have been plotted as positive. The intersections of the I_3^- reduction curves (b_1)–(b_3) with the Ti^{III} oxidation curves (a_1) or (a_2) therefore mark the respective mixture potentials and mixture currents. Inspection of the diagram makes it clear that, for the low I_3^- concentration curves (b_1) and (b_2), the intersections with both (a_1) and (a_2) lie in the limiting-current plateau regions of the I_3^- curves. Thus I_{mix} and v_{mix}, and hence v_{cat}, are independent of the concentration of $TiCl_3$. Since the limiting currents are proportional to $[I_3^-]$, v_{mix} and hence v_{cat} are first order in I_3^-. Moreover, limiting currents vary inversely with the thickness, δ, of the diffusion layer and therefore v_{mix} and v_{cat} are proportional to the square root of the disk rotation speed. On the other hand, when $[I_3^-]$ becomes sufficiently large [curve (b_3)], the intersection mixture point with curve (a_1) in Fig. 6 lies below the limiting-current plateau. It follows that v_{mix} and thus v_{cat} will rise less than proportionately with $[I_3^-]$ at high concentration as can be seen, for example, by comparing the slopes of the two lines in Fig. 3. Inspection of Fig. 6 also makes it easy to understand why E_{mix}, and hence E_{cat}, were found to rise with increasing I_3^- concentration and fall with increasing concentration of Ti^{III}. The electrochemical interpretation of the catalytic mechanism therefore allows us to explain satisfactorily the various aspects of the catalysis by platinum of the reaction between Ti^{III} and I_3^-.

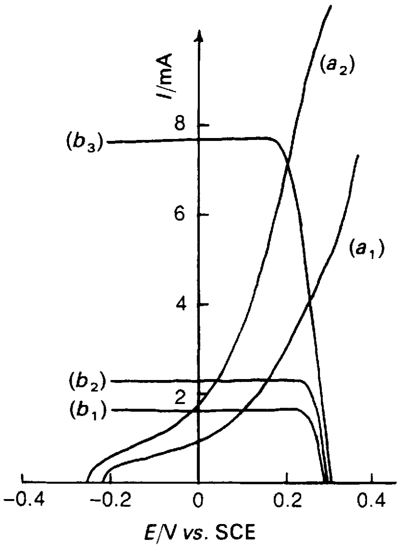

Fig. 6 Voltammograms at 10 mV s^{-1} with the platinum disk rotating at 9 Hz for the oxidation of $TiCl_3$ [(a_1) 23.7 and (a_2) 47.3 mmol l^{-1}] and the reduction of I_3^- [(b_1) 0.135; (b_2) 0.202 and (b_3) 0.630 mmol l^{-1}]. All solutions were at 25 °C and also contained 0.1 mol l^{-1} KI, 0.1 mol l^{-1} HCl and 0.8 mol l^{-1} KCl.

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