Heterogeneous Catalysis in Solution. Part 19.[1] The Effect on Oxidation–Reduction Reactions of Certain Sparingly Soluble Salts and Other Solids

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The addition of various semiconducting solids (silicon and metal sulphides) and of two ionically conducting solids [copper(I) and thallium(I) iodides] appeared either to catalyse or inhibit the rate of iodine formation by the reactions $[Fe(CN)_6]^{3-} + I^-$ and $Fe^{3+} + I^-$ in aqueous solution. The curious effect of CuI on the latter reaction was investigated in more detail. Adsorption experiments demonstrated that $[Fe(CN)_6]^{3-}$ and I_3^- chemically attacked these solids. Their chemical instability in the presence of the oxidants or the reaction mixtures was confirmed by thermodynamic calculations and the observed kinetic effects could then be explained. Only silica and silver(I) iodide did not affect the rates of the reactions; adsorption tests and thermodynamic calculations showed that these two solids were stable under the experimental conditions. The catalytic effect produced by a solid is therefore genuine only if kinetic and/or thermodynamic evidence has established its chemical stability in the reaction mixture.

In earlier papers[1-4] we tested the catalytic effect of various solids on the two redox reactions (1) and (2) in

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

$$2Fe^{III} + 3I^- \longrightarrow 2Fe^{II} + I_3^- \qquad (2)$$

aqueous potassium nitrate solutions. Electron-conducting solids such as the platinum metals[2,4] and carbon[1] were found to be good catalysts whereas electron insulators like $Ba[SO_4]$ did not change the rate of reaction. The present paper deals with the effect on the same reactions of some semiconducting and ionically conducting solids.

Several examples of semiconductors catalysing redox reactions have been reported in the literature. The main type of reaction studied has been the reduction of aqueous Ag^+ [equation (3)] in which the silver metal

$$Ag^+ + Red \longrightarrow Ag(s) + Ox \qquad (3)$$

produced acts autocatalytically. James[5] discovered that the initial rate of the Ag^+ + hydroquinone reaction was considerably increased by various metal sols in 1% gelatine with a smaller increase by a Ag_2S sol. Faerman and Voeikova[6] greatly extended these experiments using buffered solutions of the reductants *p*-hydroquinone, *p*-aminophenol, and 1,4-diaminobenzene. At 25 °C they found strong catalysis by 0.5% gelatine-stabilised sols of Cu, Ag, Se, CuS, Ag_2S, PbS, HgS, and (in two cases) V_2O_5. Little or no catalysis was recorded with sols of silver(I) and mercury(I) halides, $Ca[CO_3]$, $Ba[SO_4]$, glass, and anthracene. The authors concluded that reactions of type (3) were catalysed by electronic conductors and not by other compounds. A closer examination of the results suggests that they should be treated with caution. Thus the relative order of the catalysts, with a given reductant, depends upon the way in which the results are presented (*cf.* Figures 1 and 2 in ref. 6*a*). This probably stems from the difficulty of working with autocatalytic processes. Furthermore, the surface states of these gelatine-stabilised colloidal sols are unknown and certainly chemically complex. This is likely to be one reason for the lack of correlation between catalytic efficacy and the narrowness of the energy gap[7] according to which one might have expected the catalytic sequence Cu, Ag > PbS > Ag_2S > Se > CdS, HgS. Yet, although either the copper or the silver sol was always the most potent, the other metal was frequently less effective than some of the sulphides. The experimental sulphide sequence varied from one reductant to another and, for instance, HgS was sometimes a better catalyst than PbS. It is also curious that colloidal anthracene[8] did not affect the rates.

A major problem not considered by these authors is chemical interaction between the reacting solutions and the catalysts. Other researchers have indicated that this can be an important factor. It arises, for example, in the much studied flotation of galena (PbS) in the presence of alkyl xanthate ($ROCS_2^-$) and oxygen. One role of the oxygen is to oxidise alkyl xanthate to dixanthogen, catalysed by the electronically conducting PbS.[9] Further study has shown[10] that the oxygen first attacks the PbS surface to form sulphur, thiosulphate, and sulphate, and it is on this modified surface that the adsorption, exchange, and oxidation of xanthate takes place which renders the particles sufficiently hydrophobic for flotation.[11] Interaction with the catalyst was also found to occur[12] in the reduction of $[Co(NH_3)_5Br]^{2+}$ to Co^{II} brought about by suspensions of HgS, for at extended times small amounts of sulphate ion were detected in the solution. It will be shown below that this kind of chemical interaction with supposed catalysts is a more general phenomenon.

RESULTS AND DISCUSSION

The Effects of Silicon and Silica.—Figure 1 shows that the rate of formation of iodine by reaction (1) was unaffected by silica but increased in the presence of silicon. In the case of reaction (2), silica was again without influence on the rate although large amounts (1 g per 100 cm^3 solution) of silicon retarded the reaction. To test whether there was any chemical interaction with the silicon a number of adsorption experiments was carried out. Spectra of the filtered solutions (50 cm^3) were taken at various times after addition of the solid (0.25 g). No change was observed with a 5×10^{-2} mol dm^{-3} $K_3[Fe(CN)_6]$ solution on adding silicon, but the spectrum of a 5×10^{-4} mol dm^{-3} solution showed 2% removal of $[Fe(CN)_6]^{3-}$ and formation of a stoicheiometric amount of $[Fe(CN)_6]^{4-}$. It is evident that $[Fe(CN)_6]^{3-}$ had oxidised the silicon. Had only adsorption taken place, $[Fe(CN)_6]^{3-}$ would have been removed without the accompanying formation of $[Fe(CN)_6]^{4-}$ (as was found with charcoal).[1] Silica had no effect on the spectrum of either the concentrated or dilute $[Fe(CN)_6]^{3-}$ solution. Further evidence was provided by similar experiments with solutions (50 cm^3) 5×10^{-5} mol dm^{-3} in iodine (I_3^-) and 0.05 mol dm^{-3} in KI. Addition of silicon (0.2 g) removed 10% of the iodine after 5 min and 45% after 3 h. This strongly suggests a slow chemical attack by I_3^- on the silicon surface, for the adsorption process itself is normally rapid. Nothing but slight adsorption of I_3^- was observed with silica.

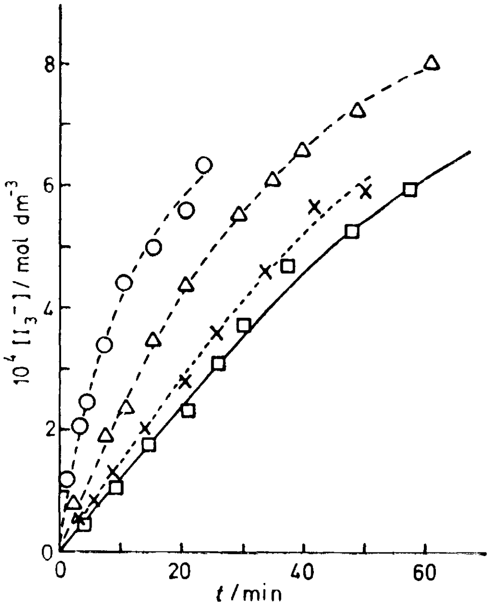

FIGURE 1 Rates of the $[Fe(CN)_6]^{3-}$ (0.05 mol dm^{-3}) + I^- (0.05 mol dm^{-3}) reaction in 2.5 mol dm^{-3} $K[NO_3]$ at 22.5 ± 1 °C in 100-cm^3 solution, in the presence of: no added solid (——); 0.5 g silica (□); 0.5 g silicon (△); 0.5 g thallium(I) iodide (×); 0.5 g copper(I) iodide (○)

The chemical interaction observed with silicon is consistent with thermodynamic data.[13] The standard potential of couple (4) at 25 °C is —0.86 V, and at pH 5

$$\mathrm{SiO_2(s) + 4H^+ + 4e^- \rightleftharpoons Si(s) + 2H_2O} \qquad (4)$$

the potential is -1.16 V. All the couples $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ ($E^\ominus = 0.36$ V), I_3^-–I^- ($E^\ominus = 0.54$ V), and Fe^{3+}–Fe^{2+} ($E^\ominus = 0.77$ V) are therefore capable of oxidising the silicon surface to SiO_2. The same conclusion follows from inspecting the Pourbaix E against pH diagram for silicon.[14] This shows that at the experimental pH and at the potentials likely to be imposed by the three couples above, or by their reaction mixtures,[4] the stable phase is SiO_2 and not Si. Silica was therefore without effect on the reaction rates whereas the effect of silicon was complex. Attack on it by a reactant $\{[Fe(CN)_6]^{3-}$ or $Fe^{3+}\}$ would diminish the reactant concentration and so decrease the actual rate of iodine formation, whereas attack by the iodine product would lead to an apparent lowering of the rate. Net inhibition, as found with reaction (2), is therefore readily explained. The net acceleration observed with reaction (1) can be ascribed to a side effect of the silicon oxidation process (4), namely to the simultaneous formation of acid. Hydrogen ions are known to catalyse strongly the $[Fe(CN)_6]^{3-} + I^-$ reaction.[15]

The Effects of Metal Sulphides.—Addition of Ag_2S, CdS, Hg_2S, HgS, Sb_2S_3, and Bi_2S_3 to $[Fe(CN)_6]^{3-} + I^-$ reaction mixtures appeared completely to inhibit the formation of iodine. Addition of PbS led to a slower rate of iodine formation than in the homogeneous mixtures whereas the presence of CuS and MoS_2 considerably increased the rate. The latter results are illustrated in Figure 2. Adsorption experiments, of the type already described, again revealed the existence of chemical interaction. Thus spectrophotometric examination showed that all soluble $[Fe(CN)_6]^{3-}$ had disappeared from 5×10^{-4} mol dm^{-3} solutions (50 cm^3) that had been in contact with CuS or PbS (0.25 g) for 10 min, and that appreciable amounts of $[Fe(CN)_6]^{4-}$ had appeared in its place. With MoS_2 only *ca.* 10% of $[Fe(CN)_6]^{3-}$ was removed and converted to $[Fe(CN)_6]^{4-}$ in 10 min. Addition of MoS_2 to 5×10^{-5} mol dm^{-3} tri-iodide solution removed 20% of the iodine in 5 min and 50% after 3 h. These experiments clearly indicate oxidation of the sulphides in Figure 2, with MoS_2 the least strongly attacked.

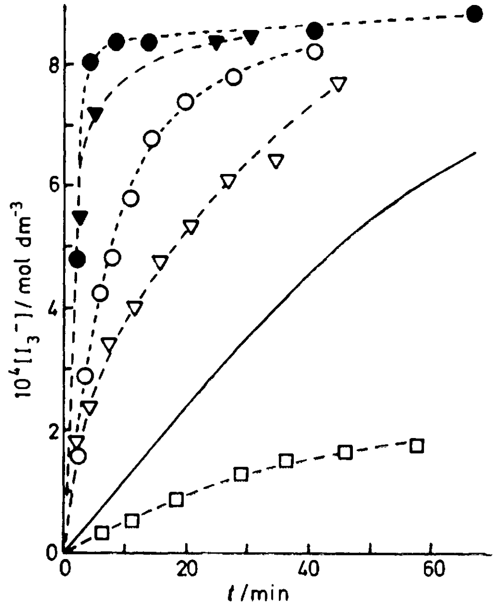

FIGURE 2 Rates of the $[Fe(CN)_6]^{3-}$ (0.05 mol dm^{-3}) + I^- (0.05 mol dm^{-3}) reaction in 2.5 mol dm^{-3} $K[NO_3]$ at *ca.* 21 °C in 100 cm^3 solution, in the presence of: no added solid (——); 0.005 g molybdenum sulphide (○); 0.5 g molybdenum sulphide (●); 0.05 g copper(II) sulphide (▽); 0.5 g copper(II) sulphide (▼); 0.5 g lead sulphide (□)

Thermodynamic calculations confirm that the reaction mixtures are capable of oxidising the sulphides to sulphate. We therefore require the potential of reaction

(5). Its standard potential $E_5^\ominus$ is obtained by combining equations (6) and (7) to give equation (8). Equation (9) then gives the Nernst potential E_5 at 298 K where[16] $E_7^\ominus = 0.153$ V. We adopt the usual convention[14] that

$$SO_4^{2-} + mM^{\frac{2}{m}+} + 8H^+ + 8e^- \rightleftharpoons M_mS(s) + 4H_2O \quad (5)$$

$$M_mS(s) \rightleftharpoons mM^{\frac{2}{m}+} + S^{2-}; \quad \Delta G_6^\ominus = -RT \ln K_{sol.} \quad (6)$$

$$SO_4^{2-} + 8H^+ + 8e^- \rightleftharpoons S^{2-} + 4H_2O; \quad \Delta G_7^\ominus = -8FE_7^\ominus \quad (7)$$

$$E_5^\ominus = E_7^\ominus - (RT/8F) \ln K_{sol.} \quad (8)$$

$$E_5 = 0.153 - 0.059\,2\text{ pH} + 0.007\,4 \log_{10}([SO_4^{2-}][M^{\frac{2}{m}+}]^m) + 0.007\,4\text{ p}K_{sol.} \quad (9)$$

significant attack on the solid has occurred if the concentrations of the ions formed exceed 1×10^{-6} mol dm^{-3}. At this limit for all soluble species except H^+, no solid $M_m[SO_4]$ will precipitate and the solute should be completely dissociated into ions. We thus obtain, from equation (10), the potential that must be exceeded to cause significant oxidation of the metal sulphide to sulphate ions. The potentials so calculated are listed in the

$$E_{10} = 0.153 - 0.044\,4\,(1 + m) - 0.059\,2\text{ pH} + 0.007\,4\text{ p}K_{sol.} \quad (10)$$

Table. They clearly show that at the experimental pH of 5—6 the $[Fe(CN)_6]^{3-} + I^-$ reaction mixtures as well as the individual $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ and I_3^-–I^- couples (mixture potentials[4] and potentials[13] in the range 0.5—0.7 V) would have been capable of oxidising the surfaces of the metal sulphides to sulphate. E Against pH diagrams for the sulphides[17] lead to the same conclusion. Only for MoS_2 is there some doubt. Its solubility product is unknown, aqueous Mo^{IV} is unstable,[18] and there is evidence[19] that MoS_2 is resistant to attack by all but the strongest oxidising agents. This contrasts strangely with our adsorption experiments. It may be that an inert layer of, say,[14] MoS_3 is formed on the MoS_2 surface, very little reagent being required for this purpose.

Eadington and Prosser,[10] in their careful study of the rate of oxidation of aqueous PbS suspensions by oxygen, found that the formation of sulphate was slow and was preceded by the formation of sulphur and of thiosulphate. It is unlikely that PbS is unique in this respect. We can now discuss the effect of the sulphides on the rate of iodine formation by reaction (1). Attack on a sulphide by $[Fe(CN)_6]^{3-}$, and by I_3^-, will decrease the observed rate. If the surface is partly converted to metal thiosulphate an additional decrease in the iodine concentration will result. These phenomena seem to have predominated for most of the sulphides tested. Only two sulphides exhibited apparent catalysis: MoS_2 and CuS. Oxidation of their surfaces to sulphate and hydrogen ions during the course of the experiments might account for this, since H^+ ions catalyse reaction (1).[15] More specific reasons are provided by the metal constituents. MoS_2 upon oxidation will be converted either to MoO_3 or to aqueous molybdenum oxycations; formation of either product will be accompanied by the catalytically efficacious H^+ ions even if the sulphide ions are only oxidised to sulphur. As for CuS, attack by $[Fe(CN)_6]^{3-}$ releases Cu^{2+} ions which react with the iodide ions present to form extra iodine by equation (11). This reaction will be considered further in the following section.

$$2Cu^{2+} + 5I^- \rightleftharpoons 2CuI(s) + I_3^- \quad (11)$$

Potentials at which various metal sulphides (M_mS) can be oxidised in aqueous suspension to form metal sulphates (1×10^{-6} mol dm^{-3}) at 298 K

Sulphide	m	p$K_{sol.}$ *	E_{10}/V (pH 0)	E_{10}/V (pH 5)
MoS_2	0.5			
CuS	1	35.1	0.324	0.028
Ag_2S	2	49.1	0.383	0.087
CdS	1	26.1	0.257	−0.039
Hg_2S	1	43.2	0.384	0.088
HgS (red)	1	51.5	0.445	0.149
PbS	1	27.1	0.265	−0.031
Sb_2S_3	0.667	19.5	0.223	−0.073
Bi_2S_3	0.667	32.1	0.317	0.021

* All taken, for consistency, from Waggoner's compilation (ref. 18). The p$K_{sol.}$ values for Sb_2S_3 and Bi_2S_3 are one-third of those of Waggoner's because of the definition employed in equation (5).

The Effects of Metal Iodides.—It can be seen from Figure 1 that the rate of iodine production by reaction (1) is slightly increased by TlI and more significantly increased by CuI; it was not affected by addition of AgI. Reaction (2) was speeded up by small amounts of CuI but there was no appreciable effect by TlI or AgI. Whether this last finding conflicts with the reported catalysis by a mixture of freshly precipitated AgBr and AgI of the reverse reaction between Fe^{II} and iodine[20] can only be decided by reinvestigating this complex system.

The apparent catalysis of reaction (2) by CuI is well known and has actually been applied in analytical chemistry.[21] A more extended study was therefore undertaken with different masses of CuI (w_{CuI}) in the $Fe^{3+} + I^-$ reaction mixtures (50 cm^3). Rohwer[22] had reported that CuI is catalytically effective only up to its solubility limit in the solution and that additional CuI is without influence on the kinetics. Our results were quite different. As illustrated in Figure 3, the initial rate of iodine formation was found to increase proportionately to w_{CuI} well beyond the solubility of CuI in 0.01 mol dm^{-3} KI (*ca.* 0.1 mg in 50 cm^3).[13] However, much larger quantities of CuI, of the order of 0.1—0.5 g per 50 cm^3, appeared strongly to inhibit the reaction! The explanation for this curious phenomenon emerged when the catalysed runs were followed for longer periods. In the presence of CuI, reaction (2) no longer went to completion; the more CuI that was added, the smaller was the extent of reaction (Figure 3). This removal of iodine brought about by CuI is readily accounted for by equation (11). Any changes that shift reaction (11) to the right should then restore the original equilibrium conditions of reaction (2). And indeed, when an excess of KI was added to any of the mixtures that had ceased reacting, the $Fe^{3+} + I^-$ reaction went to completion quite quickly and a fine suspension of CuI became visible at the endpoint. In one experiment, a $Fe^{3+} + I^-$ mixture was allowed to stand with 36 mg CuI for 3 weeks, after which the liquid was pale yellow and only a small speck of solid CuI remained. Addition of either Cu^{2+} or I^- ions increased the iodine colour and generated white crystals of CuI. In the analytical application of copper(I) iodide as a catalyst for reaction (2), the procedure specifies [21] a suspension of *ca.* 5 mg CuI in the solution to be titrated and the use of an excess (*ca.* 0.12 mol dm^{-3}) of KI. Under these conditions reaction (2) should not only be significantly catalysed but also proceed to completion. The above discussion shows that the apparent inhibition by larger amounts of CuI can be attributed to the intervention of reaction (11) and the subsequent large change in the position of equilibrium.

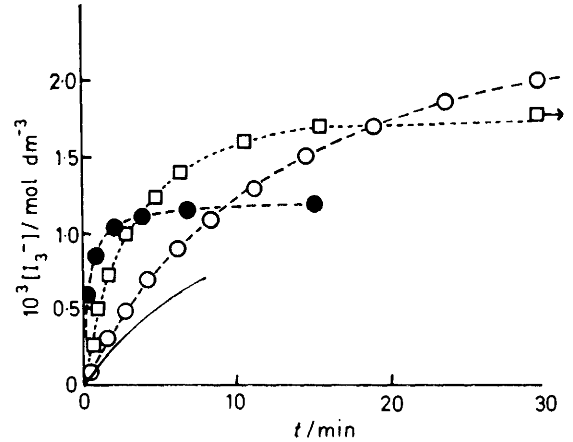

FIGURE 3 Rates of the Fe^{III} (0.005 mol dm^{-3}) + I^- (0.01 mol dm^{-3}) reaction in 1 mol dm^{-3} $K[NO_3]$ at 25 °C in 50 cm^3 solution, in the presence of: no added solid (——); 0.0009 g CuI (○); 0.0183 g CuI (□); 0.0361 g CuI (●)

In adsorption experiments with 5×10^{-4} mol dm^{-3} $K_3[Fe(CN)_6]$ solution, contact with CuI removed all $[Fe(CN)_6]^{3-}$ ions but released less than the stoicheiometric amount of $[Fe(CN)_6]^{4-}$, probably because of the formation of some insoluble copper(II) hexacyanoferrate(II). When CuI (0.25 g) was added to 5×10^{-2} mol dm^{-3} solution (50 cm^3) *ca.* 2% $[Fe(CN)_6]^{3-}$ disappeared in the first 20 min and *ca.* 20% after 18 h. These are clear signs of chemical attack. Visual evidence of such attack was obtained during the rate measurements themselves. Reaction mixture (1) with CuI produced a mustard-coloured suspension followed by a slow transition to a dark red-brown precipitate. Addition of Cu^{2+} to a $[Fe(CN)_6]^{3-}$ solution forms a mustard-coloured suspension, and reaction between Cu^{2+} and $[Fe(CN)_6]^{4-}$ gives a dark brown precipitate. The spectrum of a 5×10^{-4} mol dm^{-3} $[Fe(CN)_6]^{3-}$ solution was not measurably affected by silver iodide. Thallium(I) iodide produced only a slight decrease in absorbance at the $[Fe(CN)_6]^{3-}$ peak of 420 nm but a marked increase at 240 nm where I_3^- absorbs strongly. This points to partial oxidation of iodide ions. By contrast, none of the three solids affected the spectrum of 5×10^{-4} mol dm^{-3} $K_4[Fe(CN)_6]$. In adsorption experiments with a 5×10^{-5} mol dm^{-3} tri-iodide solution, addition of CuI removed 40% iodine in 5 min and 70% in 3 h. Very similar results were found with TlI while AgI removed only a few per cent iodine. Thus I_3^- oxidised CuI and TlI but only adsorbed on AgI.

The stability of the iodides, unlike that of the sulphides, is almost independent of pH in the range of interest. Diagrams of E against pH are therefore less appropriate than ones of E against $\log_{10}[I^-]$. Such a diagram for CuI shows [17] that this substance is thermodynamically stable only over a small triangular area. At the potentials and iodide-ion concentrations existing in our reaction mixtures, CuI would have been dissolved and oxidised. The TlI diagram [17] indicates that oxidation to iodine would have been possible but at a higher potential than for CuI, while the diagram for AgI [17] proves it to be redox stable under all our experimental conditions. Thus these stability diagrams, which illustrate what interactions are thermodynamically possible under various conditions, support the explanations given earlier for the phenomena observed in the kinetic and adsorption experiments.

EXPERIMENTAL

The supporting electrolyte, titrants, and reagents were of AnalaR quality except for iron(III) nitrate (Riedel de Haen in the exploratory runs, B.D.H. lab. reagent in the quantitative ones). The powdered solids were largely B.D.H. reagents.

The experiments exploring the effects of various solids on reactions (1) and (2) were carried out (by T. G.) as described previously,[1] as were the $Fe^{III} + I^-$ runs in the presence of CuI (by J. M. A.). The copper(I) iodide was pre-equilibrated for 3 h in the appropriate KI solution at 25 °C since the rate was less if this was not done.

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