Heterogeneous Catalysis in Solution. Part 18.[1] The Catalysis by Carbons of Oxidation–Reduction Reactions

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A mechanism of electron-transfer-through-the-solid is proposed to account for the widespread catalysis by carbons of redox reactions in solution. Charcoal catalysis of the aqueous reaction between Fe^{3+} and I^- ions was predicted, found, and studied kinetically. The activation energy of the heterogeneous process was only 24 kJ mol^{-1} compared with 100 kJ mol^{-1} for the homogeneous reaction. The $[Fe(CN)_6]^{3-}$ + I^- reaction in water was found to be catalysed by carbons as well as by several phthalocyanines. Neither reaction was catalysed by solids such as SiO_2 or $Ba[SO_4]$ which do not conduct electronically.

CARBONS are cheap and potent catalysts for several kinds of solution reaction, yet until recently few efforts had been made to study these catalyses quantitatively. Kinetic information is now available on the way in which carbons catalyse certain substitution [2] and racemisation [3,4] reactions, and in this paper we focus attention on the ability of charcoal to accelerate oxidation–reduction reactions of the type shown in equation (1).

$$\mathrm{Ox_2 + Red_1 \longrightarrow Red_2 + Ox_1} \qquad (1)$$

RESULTS AND DISCUSSION

Analysis of Literature Results.—The scattered literature reports of carbon catalysis of redox reactions are collected in Table 1. Reactions were not included if there was any doubt as to the products formed or if it was not clear whether the addition of the carbon actually speeded up the reaction.

We shall first discuss whether the observations in Table 1 are consistent with the same electrochemical mechanism which so successfully explained the catalysis of redox reactions by platinum [5] and other noble metals.[6] This mechanism postulated that in the presence of couples (2) and (3) the metal automatically adopts a mixture (mixed) potential. At this potential Ox_2 is reduced to Red_2 at the surface at the same rate as Red_1 is oxidised to Ox_1. It is immaterial whether the rate-determining step in either case is diffusion or the surface electron transfer.[1] The equal rates of (2) and (3) at the surface must be identical to that at which electrons are transferred from Red_1 to Ox_2 through the metal: this is therefore the rate at which the metal catalyses reaction (1) by the electrochemical mechanism. Spiro and Griffin [7] have confirmed these predictions for one system by a combination of kinetic and electrochemical experiments. For this mechanism to be applicable to carbon catalysis, three criteria must be satisfied. First, the carbon must adsorb the reactants. This condition is very likely to be fulfilled in all cases since charcoals not only possess high specific areas but are also extensively employed to remove solutes from solutions by adsorption. The second criterion, that the catalyst be a good electronic conductor, is clearly met by graphite and charcoals of various sorts. The final criterion is that the rates at the carbon surface of the electrode processes (2) and (3) be reasonably fast. This will be so if both couples 1 and 2 are electrochemically reversible (*i.e.* exhibit a high exchange-current density i_0 exceeding 0.01 A m^{-2}) at the carbon surface or, should one or even both couples be electrochemically irreversible, if the difference in their Nernst potentials is sufficiently large.[5] An adequate overpotential for each couple is then available at the mixture potential set up at the charcoal, and the resultant current densities (rates) of processes (2) and (3) will be high enough to produce catalysis. We must now test whether the expectations of this third criterion of the electron-transfer-through-the-solid mechanism fit the experimental data in Table 1.

$$\mathrm{Ox_2} + ne^- \longrightarrow \mathrm{Red_2} \qquad (2)$$

$$\mathrm{Red_1} \longrightarrow \mathrm{Ox_1} + ne^- \qquad (3)$$

Electrochemical data for common couples are moderately plentiful for platinum surfaces but less so for carbon ones [8] (Table 2). The situation is complicated by the fact that many different forms of carbon electrode have been employed (*e.g.*, glassy carbon, graphite, and carbon pastes with various pasting liquids) and the exchange-current density of a given couple may vary by a factor of 10—100 when one kind of carbon electrode is substituted for another or when the electrode is pre-treated differently. Even so, the semi-quantitative compilation in Table 2 is meaningful for present purposes. Inspection shows, moreover, that there is a fair correlation between electrochemical reversibilities on platinum and on carbon electrodes. This point has already been made in several electrode kinetic studies in the literature [9,10] in connection with some couples listed in Table 2 as well as with others not listed (*e.g.*, Ce^{IV}–Ce^{III} and MnO_4^-–MnO_4^{2-}); in general, platinum is a better electrode catalyst than carbon but not invariably so. Thus it seems a reasonable working hypothesis to assume that the electrochemical reversibilities of couples not yet studied at carbon electrodes would be similar to the reversibilities which these couples exhibit at platinum electrodes.

Consider first the three reactions between two reversible couples (nos. 1, 3, and 5 in Table 1). According to the literature, reactions 1 and 5 are catalysed by carbons but not reaction 3.[11] This surprising result prompted us to undertake further experiments on the $Fe^{III} + I^-$ reaction and, as shown below, positive catalysis by graphite and by charcoal was clearly established. All the reactions in Table 1 between reversible couples are therefore catalysed by carbons. Next, the reactions between one reversible couple and one that is irreversible (nos. 2, 4, 6, 7, 9, 10, 11, and 12). According to the electrochemical mechanism,[5] catalysis should then be observed whenever the formal Nernst potentials of the reacting couples are sufficiently far apart (usually several tenths of a volt). The positive catalysis of reactions 7, 9, 10, 11, and 12 is thereby readily explained. The catalysis of reaction 2 is probably produced by the metallic mercury: at mercury electrodes both the Fe^{III}–Fe^{II} and Hg^{I}–Hg^{0} couples are highly reversible.[12] In reaction 4, complexing by chloride ions will decrease the formal potential of the Fe^{III}–Fe^{II} couple and bring it closer to that of the hydrogen couple; slight catalysis is therefore just what would have been expected. The catalysis of reaction 6 by one type of charcoal can be understood by recalling that it was carried out in plain water where the formal potential of the SO_4^{2-}–SO_3^{2-} couple is below the standard potential. However, the potential difference is not so large that it could cope with a form of carbon on which the reversibilities were less, as appears to have been the case with the wood charcoal employed. That $S_2O_6^{2-}$ might have been produced also [13] tallies qualitatively with electrochemical oxidation experiments on sulphite solutions [14] where some dimerisation took place at both metal and carbon anodes. Finally, we come to reactions between two irreversible

TABLE 1

Catalytic effect of carbons on various aqueous oxidation–reduction reactions

Reaction	Medium	θ_c/°C	Form of carbon	Catalysis	Ref.
1 $Tl^{III} + Tl^{I} \longrightarrow Tl^{I} + Tl^{III}$	Perchlorate solutions	25	Graphite	Positive	*a*
2 $Hg^{I} + Fe^{II} \longrightarrow Hg + Fe^{III}$	Perchlorate solutions		Active carbons	Positive [b]	*c*
3 $2Fe^{III} + 3I^- \longrightarrow 2Fe^{II} + I_3^-$			Charcoal	None	11
	1 mol dm^{-3} K[NO$_3$]	22	Charcoal	Positive	This work
			Graphite	Positive	This work
4 $2Fe^{III} + H_2 \longrightarrow 2Fe^{II} + 2H^+$	HCl solution	18—21	Graphite	Slight	*d*
			Activated carbon	Slight	*d*
5 $2[Fe(CN)_6]^{3-} + 3I^- \longrightarrow 2[Fe(CN)_6]^{4-} + I_3^-$			Charcoal	Positive	11
			Graphite	Positive	19
	2.5 mol dm^{-3} K[NO$_3$]	23	Charcoal	Positive	This work
			Graphite	Positive	This work
6 $2[Fe(CN)_6]^{3-} + SO_3^{2-} + H_2O \longrightarrow 2[Fe(CN)_6]^{4-} + SO_4^{2-} + 2H^+$			Wood charcoal	None	13
			Animal charcoal [e]	Positive	13
7 $2[Co(en)_3]^{3+} + 12H^+ + 3I^- \longrightarrow 2Co^{II} + 6H_2en^{2+} + I_3^-$		40	Carbon black	Positive	*f*
8 $2HIO_3 + 5(CO_2H)_2 \longrightarrow I_2 + 10CO_2 + 6H_2O$			Wood charcoal	Positive	*g*
			Sugar charcoal	Positive	*g*
9 $\frac{1}{2}O_2 + 2H^+ + 2Fe^{II} \longrightarrow H_2O + 2Fe^{III}$	0.05—3 mol dm^{-3} H$_2$SO$_4$	30	Coconut charcoal	Positive	*h*
	0.1—4 mol dm^{-3} HCl	1—55	Sugar charcoal	Positive	*i*
	0.1—10 mol dm^{-3} H$_2$SO$_4$	Room	Various charcoals	Positive	*j*
10 $\frac{1}{2}O_2 + p\text{-}C_6H_4(OH)_2 \longrightarrow H_2O + p\text{-}C_6H_4O_2$		18?	Sugar charcoal	Positive	*k*
		Room	Animal charcoal	Positive	*l*
		25	Various carbons	Positive	*m*
11 $\frac{1}{2}O_2 + 2H^+ + 2[Fe(CN)_6]^{4-} \longrightarrow H_2O + 2[Fe(CN)_6]^{3-}$	Water	18?	Sugar charcoal	Positive	*k*
12 $\frac{1}{2}O_2 + 2H^+ + Sn^{II} \longrightarrow H_2O + Sn^{IV}$	0.8 mol dm^{-3} HCl	25	Sugar carbon	Positive	*n*
13 $O_2 + N_2H_4 \longrightarrow 2H_2O + N_2$			Activated carbon	Positive	*o*
14 $\frac{1}{2}O_2 + HCO_2H \longrightarrow H_2O + CO_2$			Various carbons	Positive	*o*
15 $\frac{1}{2}O_2 + (CO_2H)_2 \longrightarrow H_2O + 2CO_2$		30—50	Various charcoals	Positive	*p*
16 $O_2 + CH_2(CO_2H)_2 \longrightarrow HO_2C{\cdot}CHO + CO_2 + H_2O$		40	Sugar charcoal	Positive	*p*
17 $xO_2 + RCO_2H$ (R = H, Me, *etc.*) $\longrightarrow yCO_2 + zH_2O$		40	Sugar charcoal	None	*p*
18 $H_2O_2 + HCHO \longrightarrow H_2O + HCO_2H$			Sugar charcoal	Positive	*q*
19 $H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2$		25	Various carbons	Positive	*o*

[a] G. M. Waind, *Discuss. Faraday Soc.*, 1960, **29**, 135. [b] The interpretation of this result is complicated by the formation of metallic mercury which would be expected to catalyse the reaction. [c] P. A. Herrlin, *Nord. Kemikermøde*, 1939, **5**, 194 (*Chem. Abs.*, 1944, **38**, 2872). [d] V. V. Lyul'ka, *Izvest. Kiev Politekh. Inst.*, 1960, **29**, 86 (*Chem. Abs.*, 1961, **55**, 20576). [e] The catalytic process may also produce significant amounts of dithionate (ref. 13). [f] R. J. Mureinik and M. Spiro, *J.C.S. Dalton*, 1974, 2486. [g] E. Millon, *Ann. Chim. Phys.*, 1845, **13**, 29; G. Lemoine, *Compt. rend.*, 1921, **173**, 7. [h] A. B. Lamb and L. W. Elder, jun., *J. Amer. Chem. Soc.*, 1931, **53**, 137. [i] A. M. Posner, *Trans. Faraday Soc.*, 1953, **49**, 389. [j] G. Thomas and T. R. Ingraham, *Unit Process Hydromet.* 1965, **1**, 67. [k] A. King, *J. Chem. Soc.*, 1936, 1688. [l] M. Matsui, *Mem. Col. Sci. Eng. Kyoto*, 1909, **1**, 386 (*Chem. Abs.*, 1909, **3**, 2698). [m] P. F. Bente and J. H. Walton, *J. Phys. Chem.*, 1943, **47**, 133, 329. [n] E. C. Larsen and J. H. Walton, *J. Phys. Chem.*, 1940, **44**, 70. [o] G. Brinkmann, *Kolloid-Z.*, 1951, **123**, 116. [p] E. K. Rideal and W. M. Wright, *J. Chem. Soc.*, 1925, **127**, 1347; 1926, 1813, 3182. [q] A. S. Loevenhart and J. H. Kastle, *Amer. Chem. J.*, 1903, **29**, 397.

couples (reactions 8 and 13—19 in Table 1). A much larger difference between the formal potentials of the two reacting couples, of the order of 1 V, is here required before catalysis can occur by the heterogeneous electron-transfer mechanism. This accounts satisfactorily for the catalysis reported for reactions 8, 13, 14, 15, 18, and 19; for reaction 17 the potential difference available appears to have been insufficient for the charcoal employed although it was adequate for other carbons (see reaction 14), and for one of the couples in reaction 16 there is a complete lack of electrochemical information. It may be added that absence of catalysis is rarely reported. In summary, then, and bearing in mind the assumptions made, the catalytic data in Table 1 are consistent with the mechanism of electron transfer through carbon.

TABLE 2

Standard electrode potentials and electrochemical reversibilities in water at 25 °C of the redox couples in Table 1

Couple	$E^\ominus$ [a]/V	On carbon	On platinum [b]
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	1.25	Mod. rev.[c,d]	Rev.
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	0.79	[e]	Rev.
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77	Rev.[d,f]	Rev.
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	0.36	Rev.[d,f-h]	Rev.
$[Co(en)_3]^{3+} + 6H^+ + e^- \rightleftharpoons Co^{2+} + 3H_2en^{2+}$	1.99 [i]		Irrev.
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.15	Mod. rev.[k]	Irrev.
$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	0.00	Mod. irrev.[l]	Rev.
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.54	Rev.[m]	Rev.
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	1.20	Irrev.[m,n]	Mod. rev.
$SO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SO_3^{2-} + H_2O$	−0.10	Irrev.[o]	Irrev.[o]
$S_2O_6^{2-} + 2e^- \rightleftharpoons 2SO_3^{2-}$	0.03	Irrev.[o]	Irrev.[o]
$N_2 + 4H^+ + 4e^- \rightleftharpoons N_2H_4$	−0.34		Irrev.
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23	Irrev.[p,q]	Irrev.
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.77	Irrev.[p]	Irrev.
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.68	[r]	Mod. rev.
$p\text{-}C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons p\text{-}C_6H_4(OH)_2$	0.70	[s]	Rev.
$HCO_2H + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O$	0.06		Irrev.
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	−0.20		Irrev.
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons (CO_2H)_2$	−0.49		Irrev.
$CO_2(g) + HO_2C{\cdot}CHO + 4H^+ + 4e^- \rightleftharpoons CH_2(CO_2H)_2 + H_2O$			Prob. irrev.

[a] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952, or calculated from data therein. [b] Refs. 5, 12, and M. Spiro, *Electrochim. Acta*, 1964, **9**, 1531. [c] S. D. James, *Electrochim. Acta*, 1967, **12**, 939. [d] L. R Sharma and J. Dutt, *Indian J. Chem.*, 1970, **8**, 170. [e] This couple does not seem to have been studied, but the couples Hg^{II}–Hg^{I} (G. Torsi and G. Mamantov, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **32**, 465) and Hg^{II}–Hg^{0} (M. Stulikova, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1973, **48**, 33) have both been reported as irreversible on carbon electrodes. [f] Refs. 9 and 10. [g] J. B. Morris and J. M. Schempf, *Analyt. Chem.*, 1959, **31**, 286. [h] J. Lindquist, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1974, **52**, 37. [i] R. J. Mureinik and M. Spiro, *J.C.S. Dalton*, 1974, 2480. [j] H. Bartelt and H. Skilandat, *J. Electroanalyt. Chem., Interfacial Electrochem.*, 1969, **23**, 407. [k] B. G. Ateya and L. G. Austin, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1974, **51**, 85. [l] M. P. J. Brennan and O. R. Brown, *J. Appl. Electrochem.*, 1972, **2**, 43. [m] H. E. Zittel and F. J. Miller, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1967, **13**, 193. [n] Ref. 10. [o] Ref. 14. [p] R. J. Taylor and A. A. Humffray, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **64**, 63, 85, 95. [q] Oxygen evolution on previously oxidised glassy carbon electrodes appears to be reversible (D. Laser and M. Ariel, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1974, **52**, 291). [r] The rate of this reaction is very pH dependent, being relatively irreversible in acid conditions [p] and reversible in alkaline ones [p] (I. Morcos and E. Yeager *Electrochim. Acta*, 1970, **15**, 953). [s] The quinone–hydroquinone couple behaves irreversibly on some carbon electrodes [g,h] and reversibly on others [h] (S. S. Lord, jun., and L. B. Rogers, *Analyt. Chem.*, 1954, **26**, 284).

$Fe^{III} + I^-$ *Reaction*.—According to the electrochemical mechanism, the reaction between these two reversible couples should be carbon catalysed. Figure 1 amply confirms this prediction for both graphite and a commercial charcoal. Why Waind [11] observed no catalysis by charcoal is difficult to explain. No details were given of the experimental procedure used, but if the charcoal had been separated from the reaction mixture before analysis then much of the iodine formed catalytically would have remained adsorbed on the carbon surface and so been undetected. Alternatively, the type of charcoal tried might have given unusually low exchange currents. Yet Waind did report positive catalysis by charcoal of the ferricyanide + iodide reaction which, one would suppose, had been studied by a similar experimental procedure.

Catalysis by the electron-transfer-through-the-solid mechanism cannot occur in the presence of solids which are insulators or poor electronic conductors, or which exhibit low exchange-current densities for the couples in question. In line with this prediction we found, on the addition to 50 cm³ of reaction mixture of 0.5 g of various powdered solids, no catalysis by SiO_2, TiO_2, or $Ba[SO_4]$, and slight acceleration by anthracene. It could be argued that these solids were ineffective because their surface areas are much less than those of the carbons. However, our earlier experiments with platinum foil and wire, which possessed even lower surface areas, revealed marked catalysis.[5,6] Unexpectedly, some catalysis of the $Fe^{III} + I^-$ reaction was shown by BN (Figure 1). This was not due to a B_2O_3 impurity since B_2O_3 itself slightly retarded the reaction, but the influence of other impurities cannot be ruled out. An alternative explanation is that the catalysis, if genuine, took place by another mechanism such as by the direct electron transfer between neighbouring adsorbed Fe^{3+} and I^- ions. The effect of various other solids on the $Fe^{III} + I^-$ reaction has been examined in the following paper.[15]

Charcoal was the best catalyst of the solids tried, and it was therefore decided to carry out quantitative kinetic measurements on the heterogeneous process involved. As in the exploratory experiments, the iodine produced was determined titrimetrically. To ensure that all the iodine, whether in solution or adsorbed on carbon particles, was included, successive 0.1 cm^3 portions of standardised sodium thiosulphate solution were added to the whole reaction mixture. The successive values of $\Delta[I_3^-]/\Delta t$ so obtained were plotted against time t to produce curves concave to the time axis; these were extrapolated to zero time to yield values of $(d[I_3^-]/dt)_0$. Heterogeneous rates were calculated by subtracting the homogeneous contributions from the overall rates. The results at 25 °C are given in Table 3. Several runs were also carried out at 15 °C and 5 °C where the homogeneous contributions were relatively small and the heterogeneous rates consequently more precise.

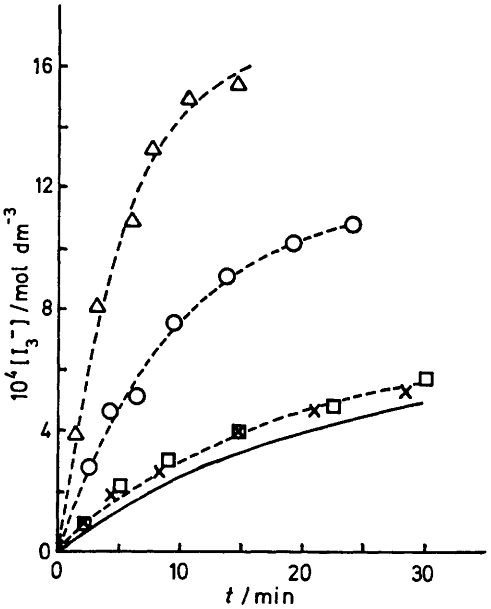

FIGURE 1 Rates of the Fe^{III} (0.005 mol dm^{-3}) + I$^-$ (0.01 mol dm^{-3}) reaction in 1 mol dm^{-3} K[NO$_3$] in 50-cm^3 solution, in the presence of no added solid (——); 0.005 g charcoal (△); 0.005 g graphite (○); 0.25 g boron nitride (Borax) (□); 0.5 g anthracene (×)

The initial homogeneous rates in 1 mol dm^{-3} K[NO$_3$] fit the rate expression (4) where $k_{hom.} = 4.3 \times 10^2$ dm^6

$$(d[I_3^-]/dt)_0 = k_{hom.}[Fe^{III}]_0[I^-]_0^2 \qquad (4)$$

mol^{-2} min^{-1} at 25 °C. The activation energy was found to be 100 ± 4 kJ mol^{-1}. The third-order form of equation (4) has often been reported and discussed [16] but it is difficult to make an exact comparison of the rate constant since a variety of supporting electrolytes has been employed. The result of Fudge and Sykes [16] at 0.6 mol dm^{-3} K[NO$_3$] and 20 °C is 10% higher than ours when due allowance has been made for the change in temperature; this agreement is very fair when the difference in ionic strength is borne in mind.

The initial heterogeneous rates at 25 °C can be represented by equation (5) where, with concentrations in mol

$$(d[I_3^-]/dt)_0 = k_{het.}\, m_{cat.}\, [Fe^{III}]_0^{0.87}[I^-]_0^{0.51} \qquad (5)$$

dm^{-3}, masses of carbon catalyst in g, and time in min, $k_{het.} = 21$. At 5 °C the exponent of the $[I^-]$ term is 0.45. However, because of the experimental errors associated with the results, the values of these exponents are subject to some uncertainty. Different fractional exponents result if allowance is made for the formation of [FeI]$^{2+}$ complex ions.[17] The activation energy corresponding to the initial concentrations $[Fe^{III}]_0 = 0.005$ mol dm^{-3} and $[I^-]_0 = 0.01$ mol dm^{-3} is *ca.* 24 kJ mol^{-1}, considerably lower than that of the homogeneous process.

The general form of equation (5) is that predicted [1] by an electrochemical analysis of the consequences of the electron-transfer-through-the-solid mechanism. The standard potential of the Fe^{III}–Fe^{II} couple is 0.23 V greater than that of the I$_3^-$–I$^-$ couple; in the early stages of the reaction the Nernst potentials differ even more (typically, 0.28 V at 1% formation of product). The current–voltage curves of both couples should therefore lie in the Tafel regions at the mixture potential. Under these conditions the electrochemical theory predicts that the rate of the catalysed reaction should be proportional to a fractional power of the oxidant (Fe^{III}) concentration, a different fractional power of the reductant (I$^-$) concentration, and also be proportional to the area (hence mass) of catalyst. The rate-determining step is thus the electron transfer through the carbon between the adsorbed species, *i.e.* equation (6). It should be emphasized

$$Fe^{3+}_{ads.} + I^-_{ads.} \longrightarrow \text{products} \qquad (6)$$

that in this mechanism it is not necessary for the Fe^{3+} and I$^-$ species to be adsorbed next to each other.

TABLE 3

Rates of the homogeneous and the heterogeneous reactions in aqueous 1 mol dm^{-3} K[NO$_3$] at 25 °C

		$10^4(d[I_3^-]/dt)_0$/mol dm^{-3} min^{-1}		
$10^3[Fe^{III}]_0$/ mol dm^{-3}	$10^3[I^-]_0$/ mol dm^{-3}	Homogeneous	0.0025 g Carbon	0.0107 g Carbon
10	5	1.05 ± 0.05	0.45 ± 0.15	2.15 ± 0.45
7.5	5	0.73 ± 0.05	0.40 ± 0.12	1.57 ± 0.25
5	5	0.51 ± 0.05	0.32 ± 0.10	1.34 ± 0.25
2.5	5	0.23 ± 0.05	0.13 ± 0.05	0.62 ± 0.10
5	10	2.15 ± 0.10	1.25 ± 0.30	1.95 ± 0.30
5	5	0.51 ± 0.05	0.32 ± 0.10	1.34 ± 0.25
5	3.75	0.35 ± 0.02	0.20 ± 0.04	1.65 ± 0.17
5	2.5	0.125 ± 0.005	0.23 ± 0.15	1.28 ± 0.06
5	1.25	0.040 ± 0.005	0.24 ± 0.05	0.90 ± 0.06

It might be argued that the form of equation (5) implies only that the reactant ions adsorb on the charcoal surface according to Freundlich isotherms, with the rate-determining step again being (6). If a Langmuir–Hinshelwood mechanism is envisaged, the adsorbed reactants would then have to sit side by side on the surface. To test this supposition, independent adsorption experiments were carried out at 25 °C. Much larger amounts of carbon (1 g in 75 cm^3 solution) had to be employed than in the kinetic runs in order to produce sufficient adsorption. The iodide results fitted a Freundlich plot well, with an exponent of 0.61. That this differs from the kinetic exponent of 0.51 could then be ascribed either to the experimental uncertainties, or to the fact that the exponent of I$^-$ adsorption would be altered in the kinetic situation by the interaction with adsorbed Fe^{3+}

ions. A still simpler explanation is given by the electrochemical theory according to which there should be no direct relation between the iodide exponents in adsorption and in the kinetics. A similar study of Fe^{III} adsorption was thwarted by a slow and well known[18] side-reaction between Fe^{III} and charcoal to produce Fe^{II}. The rate of this side-reaction was much slower than that of the $Fe^{III} + I^-$ reaction and did not interfere with the kinetic observations which could in fact be followed to within 4% of completion.

$[Fe(CN)_6]^{3-} + I^-$ *Reaction*.—The catalysis of this redox reaction by metals has previously been investigated in this laboratory,[5-7] and its catalysis by both charcoal[11] and graphite[19] has been reported. We wished to confirm these observations and then test the effects of several other solids.

The reaction was again followed by the Harcourt and Esson procedure[20] of adding aliquots of standard thiosulphate solution to the entire reaction mixture. The initial homogeneous rate against $[Fe(CN)_6{}^{3-}]_0[I^-]_0{}^2$ was linear with a rate constant of 0.098 $dm^6 mol^{-2} min^{-1}$ in 2.5 mol dm^{-3} $K[NO_3]$ at 22 °C. This is lower than the value predicted by the activation energy and salt-effect equation published by Majid and Howlett,[19] as was to be anticipated in the light of literature rate curves applicable to high salt concentrations.[21]

Figure 2 confirms the predicted strong catalysis by two different forms of commercial charcoal and by graphite. Also in line with theoretical expectations was the observed absence of catalysis by poor electronic conductors: glass[19] and powdered SiO_2 and $Ba[SO_4]$. {Platinum foil of even lower surface area had strongly catalysed the $[Fe(CN)_6]^{3-} + I^-$ reaction.[5-7]} Boron nitride from one source (Borax Ltd.) had no effect on the rate whereas that from B.D.H. produced an increase; this was not due to a B_2O_3 impurity as addition of the oxide did not affect the reaction. Of special interest are the positive catalyses by various phthalocyanines (Figure 3), substances recently found to be good electrode catalysts[22] and therefore likely to enhance the rates of redox reactions. A curious feature was the activity of an impure sample of copper phthalocyanine (I.C.I.) while a purified sample was relatively inactive. Chlorophyll C produced no catalysis. Haemoglobin inhibited the reaction, probably because of a protein impurity which caused frothing and thereby removed reactants and products from the solution. The unusual effects of certain other solids (CuI and metallic sulphides) have been considered elsewhere.[15]

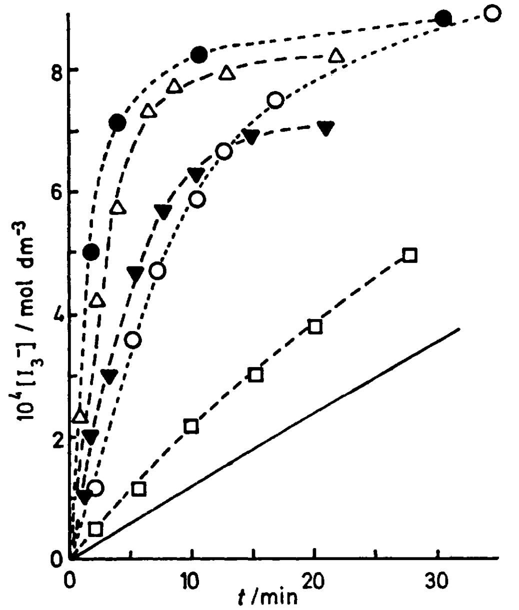

FIGURE 2 Rates of the $[Fe(CN)_6]^{3-}$ (0.05 mol dm^{-3}) + I^- (0.05 mol dm^{-3}) reaction in 2.5 mol dm^{-3} $K[NO_3]$ in 100 cm^3 solution, in the presence of no added solid (——); 0.005 g charcoal (Hopkin and Williams) (△); 0.05 g charcoal (Riedel de Haen) (▼); 0.005 g graphite (○), 0.05 g graphite (●), 0.05 g boron nitride (B.D.H.) (□)

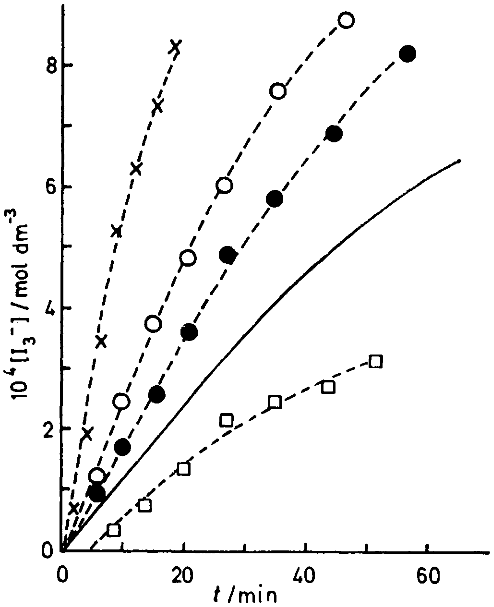

FIGURE 3 Rates of the $[Fe(CN)_6]^{3-}$ (0.05 mol dm^{-3}) + I^- (0.05 mol dm^{-3}) reaction in 2.5 mol dm^{-3} $K[NO_3]$ in 100 cm^3 solution, in the presence of no added solid (——); 0.025 g phthalocyanine (●); 0.025 g magnesium phthalocyanine (○); 0.01 g copper phthalocyanine (I.C.I.) (×); 0.5 g haemoglobin (□)

The kinetic measurements were supplemented by spectrophotometric examination of the adsorption by the solids employed (0.25 g in 50 cm^3 solution) of ferricyanide ions. Dilute solutions (5×10^{-4} mol dm^{-3}) were needed to detect the concentration changes adequately. Charcoal was found to adsorb *ca.* 30% of the $[Fe(CN)_6]^{3-}$ ions whereas the graphite sample removed only 2%, so parallelling their catalytic activities and possibly their effective surface areas. Addition of SiO_2, $Ba[SO_4]$, and BN had no measureable effect on the spectra, nor did these solids affect the spectrum of a 5×10^{-4} mol dm^{-3} ferrocyanide solution. In the case of a 5×10^{-5} mol dm^{-3} tri-iodide-ion solution, the latter group of solids (0.1 g in 25 cm^3 solution) absorbed only 10% of the iodine after 3 h whereas as little as 0.002 g charcoal in 25 cm^3 solution absorbed 90%.

EXPERIMENTAL

Materials.—Iron(III) nitrate was supplied by Riedel de Haen; all the other reactants, supporting electrolytes, and titrants were of AnalaR quality. The charcoal was Hopkin and Williams finely divided activated purified charcoal which for the quantitative runs was heated overnight in an oven at 100 °C and cooled for 1 h in a desiccator before use. Riedel de Haen activated powder A.R. charcoal was also used in some ferricyanide + iodide runs. The other powdered solids were largely B.D.H. reagents; one boron nitride sample was supplied by B.D.H., another by Borax Ltd. Samples of purified phthalocyanines and of chlorophyll C were kindly provided by Professor J. A. Elvidge; copper phthalocyanine was also available as an unpurified I.C.I. product. The haemoglobin was B.D.H. Technical.

Methods.—The reaction mixtures in the exploratory $Fe^{III} + I^-$ runs (by T. G.) were 0.005 mol dm^{-3} in $Fe[NO_3]_3$, 0.01 mol dm^{-3} in KI, and 1.0 mol dm^{-3} in $K[NO_3]$ (to keep the ionic strength constant). The innate pH of the mixtures was 2.7, a value which stayed nearly constant throughout. No buffering materials were added since attempts to do so produced precipitates of iron salts. The relatively low acidity in these experiments decreased the homogeneous rate constant.[23] For the quantitative runs (by J. M. A.), AnalaR nitric acid (0.6 cm^3) was added to each $Fe[NO_3]_3$ stock solution (500 cm^3, 0.01 mol dm^{-3}) to prevent hydrolysis, and the reaction mixtures were again 1.0 mol dm^{-3} in $K[NO_3]$.

The exploratory reaction mixtures (50 cm^3) were continuously agitated at 22 ± 1 °C in a Griffin SD-100 mechanical shaker. To allow rapid analysis, the reaction mixture (with the addition of the finely divided solids) was then run from a graduated pipette into a known volume of standardised sodium thiosulphate solution, the endpoint being indicated by the blue colour of a little starch indicator. For the quantitative runs, the reaction mixtures (100 cm^3) in a water thermostat at 25 °C were stirred at 500 revolutions per min by a ring-type glass stirrer. The Harcourt and Esson [20] ' clock method ' was employed here: aliquots (0.1 cm^3) of standardised thiosulphate solution, containing the same concentration of iodide ions as did the reaction mixture, were successively added from a microburette, and the times noted when the colour in the reaction vessel turned blue.

To determine the adsorption isotherm of iodide ions, 1 mol dm^{-3} $K[NO_3]$ solutions (75 cm^3) containing initially 0.002—0.03 mol dm^{-3} KI were shaken with 1 g charcoal at 25 °C for at least 24 h. The samples were centrifuged to separate the charcoal and analysed for iodide by titration with standard $K[IO_3]$ solution. Attempts to measure Fe^{III} adsorption were carried out similarly.

The solute concentrations in the $[Fe(CN)_6]^{3-} + I^-$ experiments (by T. G.) were always 0.05 mol dm^{-3} $K_3[Fe(CN)_6]$, 0.05 mol dm^{-3} KI, and 2.5 mol dm^{-3} $K[NO_3]$; the initial pH was adjusted to 5 by the addition of a small amount of nitric acid. Both homogeneously and heterogeneously catalysed mixtures (100 cm^3) were continuously shaken at 22 ± 1 °C by a Griffin SD-100 shaker. The iodine formed was titrated with freshly prepared 5×10^{-4} mol dm^{-3} sodium thiosulphate solution using a little starch as indicator.

Adsorption experiments connected with this reaction were carried out spectrophotometrically. The solutions used were either 5×10^{-4} mol dm^{-3} $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ in 1 mol dm^{-3} $K[NO_3]$ at pH 5, or 5×10^{-5} mol dm^{-3} iodine (present as I_3^-) in 0.05 mol dm^{-3} KI. The solid material (usually 0.25 g) was placed in a dry 150-cm^3 flask, 50 cm^3 of the appropriate electrolyte solution were added, and the flask shaken at 22 ± 1 °C. Samples, taken at various periods up to a few hours, were filtered through porosity 4 sintered-glass discs before the spectra were determined on a Beckman DB double-beam recording spectrophotometer or a Zeiss PMQII single-beam machine.

A few blank experiments were done to see if any iodine in the kinetic runs had been formed by the oxidation of iodide ions by dissolved or adsorbed oxygen. No iodine could be detected in a solution 0.05 mol dm^{-3} in KI, 2.5 mol dm^{-3} in $K[NO_3]$, and at pH 5 which had been left for 2 h, nor was any iodine produced when charcoal or boron nitride (0.5 g) was added to the solution (100 cm^3).

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