Reduction of Dioxygen by an NADH Model Compound and 1,1'-Dimethylferrocene Catalysed by Acids in Homogeneous and Heterogeneous Systems

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An acid-stable NADH model compound, 10-methyl-9,10-dihydroacridine ($AcrH_2$) and 1,1'-dimethylferrocene [$Fe(C_5H_4Me)_2$] are oxidized by dioxygen in the presence of $HClO_4$ in acetonitrile and water. The acid-catalysed two-electron and four-electron reductions of dioxygen by $AcrH_2$ and [$Fe(C_5H_4Me)_2$], respectively, take place more efficiently in the heterogeneous systems using solid acid catalysts [alumina, silica–alumina, HY-type zeolite, and solid superacids (ZrO_2 and Fe_2O_3 treated with H_2SO_4)] activated by calcination at various temperatures. Mechanisms of both the homogeneous and heterogeneous reduction of dioxygen by $AcrH_2$ and [$Fe(C_5H_4Me)_2$] are discussed.

Catalytic reduction of dioxygen has been extensively studied in electrochemical systems.[1,2] However, little is known of the catalytic reduction of dioxygen by mild chemical reductants such as reduced nicotinamide adenine dinucleotide (NADH) which plays a vital role as the electron source in the respiratory chain.[3] In the absence of an appropriate catalyst, triplet dioxygen is unreactive towards NADH or the model compounds because of spin restriction. Thus, in order to achieve the efficient reduction of dioxygen by NADH or the model compounds it is required to remove the spin restriction.

We have previously reported that an acid-stable NADH model compound, 10-methyl-9,10-dihydroacridine ($AcrH_2$), reduces a series of aromatic aldehydes as well as *p*-benzoquinone derivatives in the presence of perchloric acid ($HClO_4$).[4] The reactivity of the acid catalyst may be improved by using appropriate heterogeneous catalysts, since the acid strength, as well as the acidity on the surface of solid acids, can be finely tuned by choosing an appropriate solid acid catalyst and by means of activation, *e.g.*, the calcination temperature.[5–7]

In this study, we report the successful reduction of dioxygen by both a two-electron reductant ($AcrH_2$) and a one-electron reductant [$Fe(C_5H_4Me)_2$] in the homogeneous and heterogeneous systems by using $HClO_4$ and solid acid catalysts, respectively. The acid-catalysed electron transfer pathways of dioxygen, which are spin-allowed processes, in the reduction of dioxygen by $AcrH_2$ as well as by [$Fe(C_5H_4Me)_2$] are discussed based on the Marcus electron-transfer theory.[8]

Experimental

Materials.—Preparation of 10-methyl-9,10-dihydroacridine ($AcrH_2$) and 10-methylacridinium ion ($AcrH^+$) has been described.[9] The dideuteriated analogue of $AcrH_2$, [9,9-$^2H_2$]-10-methyl-9,10-dihydroacridine ($AcrD_2$), was prepared by $LiAlD_4$ reduction of 10-methylacridone.[10,11] 1,1'-Dimethylferrocene was obtained commercially and purified by recrystallization from ethanol. The corresponding ferricenium ion [$Fe(C_5H_4Me)_2$]$^+$ was prepared as described elsewhere.[12] Alumina was obtained from Woelm (No. 02099). The commercial sample of silica–alumina (28% Al_2O_3) was supplied by Shokubai Kasei Kogyo. Na-Y form zeolite, obtained from Gasukuro Kogyo (SK-40), was modified as required by exchange of the sodium ion for ammonium. The maximal level of exchange of ammonium for sodium was achieved by exhaustively exchanging 10 g samples of the Na-Y zeolite with 50 cm^3 aliquots of 0.10 mol dm^{-3} ammonium chloride at 80 °C for 24 h.[13] The solid superacids, ZrO_2 and Fe_2O_3 treated with H_2SO_4 were prepared from $Zr(OH)_2$ (Nakarai Chemicals) and $Fe(NO_3)_3$ (Wako Pure Chemicals), respectively, according to the literature.[14,15] Perchloric acid (70%) was obtained from Wako Pure Chemicals. Reagent grade acetonitrile, dichloromethane, and methanol were purified by the standard methods.[16]

Homogeneous Reduction of Dioxygen.—Typically, $AcrH_2$ (2.5×10^{-5} mol) was added to an n.m.r. tube which contained [$^2H_3$]acetonitrile (CD_3CN) and D_2O (1:1 v/v, 0.50 cm^3). After the reactant solution had been saturated with dioxygen, the reaction was started by the addition of $HClO_4$ (70%, 9.4×10^{-2} cm^3). The oxidized product was identified by comparing the ^1H n.m.r. spectrum with that of the authentic sample $AcrH^+$ [δ 4.62 (s, 3 H, Me)]. The amount of the reduction product, H_2O_2, was determined by the standard method (titration by iodide ion);[17] the aliquots of the product mixture in MeCN was treated with excess NaI and the amount of I_3^- formed was determined by the electronic spectrum (λ_{max} 365 nm, ε_{max} 2.8×10^4 dm^3 mol^{-1} cm^{-1})[18] using a Union SM-401 spectrophotometer.

Rates of formation of $AcrH^+$ and [$Fe(C_5H_4Me)_2$]$^+$ were followed by the rise of the absorption bands due to $AcrH^+$ (λ_{max} 358 nm, ε_{max} 1.80×10^4 dm^3 mol^{-1} cm^{-1}) and [$Fe(C_5H_4Me)_2$]$^+$ (λ_{max} 650 nm, 3.7×10^2 dm^3 mol^{-1} cm^{-1}), respectively.

Heterogeneous Reduction of Dioxygen.—The activation of the solid acid catalyst involved heating it in a quartz tube in air for 5 h at temperatures between 200 and 1 000 °C in an electric muffle furnace (Yamato Kagaku FM-26), then cooling it in a stream of dry oxygen. $AcrH_2$ (1.54×10^{-5} mol) and a magnetic stirring bar were then added to the catalyst and the quartz tube was sealed with a septum. After being stirred for 0.5–18 h at 25 °C, the reaction was quenched by the addition of methanol (2.0 cm^3). The solid acid was then removed by filtration, and the amounts of products were determined in the same manner as described above for the homogeneous system.

The stoicheiometry of the heterogeneous reduction of dioxygen was determined by changing the ratio of the reductant {$AcrH_2$ and [$Fe(C_5H_4Me)_2$]} to dioxygen when the initial amount of dioxygen was maintained constant by filling the reaction tube with an air-saturated CH_2Cl_2 solution (5.0 cm^3) which contained the solid acid catalyst (1.0 g) and various concentrations of $AcrH_2$ or [$Fe(C_5H_4Me)_2$]. The amount of oxygen in the air-saturated CH_2Cl_2 solution was determined

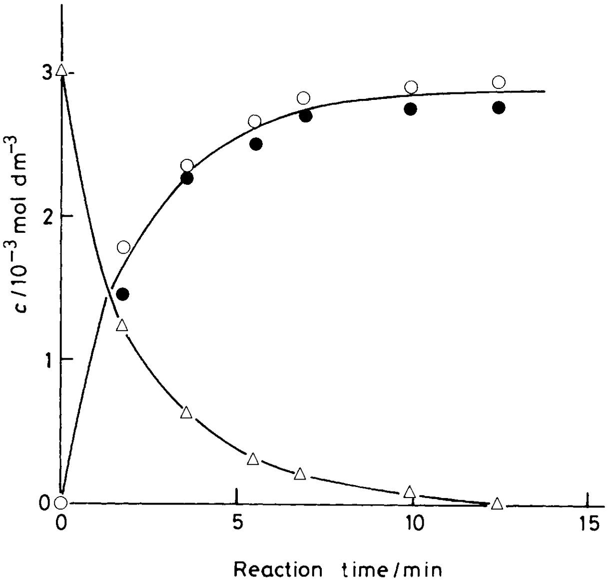


Figure 1. Reduction of dioxygen by $AcrH_2$ in the presence of $HClO_4$ (0.30 mol dm^{-3}) in $MeCN-H_2O$ (1:1 v/v) at 25 °C; $AcrH^+$ (○), H_2O_2 (●), $AcrH_2$(△).

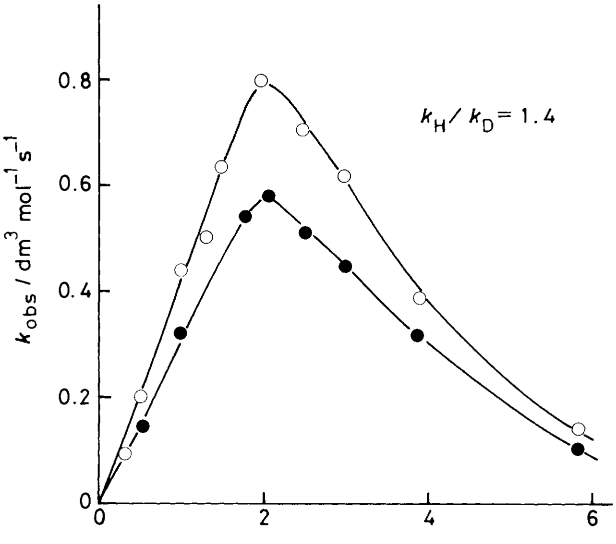


Figure 2. Dependence of the observed second-order rate constant k_{obs} on $[HClO_4]$ for the oxidation of $AcrH_2$ (○) and $AcrD_2$ (●) by dioxygen in the presence of $HClO_4$ in an oxygen saturated aqueous solution at 25 °C.

independently from the photo-oxidation of $AcrH_2$ by excess dioxygen in the presence of excess $HClO_4$ relative to $AcrH_2$, using the same reaction tube as employed for the heterogeneous reduction of dioxygen. It has been confirmed that the photo-oxidation of $AcrH_2$ by dioxygen in the presence of $HClO_4$ yields the same amount of $AcrH^+$ as that of dioxygen contained in the solution.[19]

The surface acidities of alumina, which was activated by calcination at various temperatures, were determined using a Hammett indicator, methyl red {2-[4-(dimethylamino)-phenylazo]benzoic acid, $pK_a = 4.8$}[20] according to the procedure reported in the literature.[21]

An H-shaped Schlenk tube equipped with a Teflon stopcock was used for the heterogeneous reaction of $AcrH_2$ or $[Fe(C_5H_4Me)_2]$ with the activated alumina in the absence of dioxygen. The alumina was introduced into one arm with a Teflon stopcock and it was activated by calcination in air for 5 h at 400 °C in an electric muffle furnace, followed by cooling under vacuum for 0.5 h. A CH_2Cl_2 solution of $AcrH_2$ or $[Fe(C_5H_4Me)_2]$ was added to the other arm and it was thoroughly degassed by successive freeze–pump–thaw cycles and sealed under vacuum. The reaction was started by transferring the reactant solution to the other arm which contained the activated solid catalyst under vacuum. The subsequent procedures were the same as those in the presence of dioxygen described above.

Results

Homogeneous Reduction of Dioxygen by $AcrH_2$ *and* $[Fe(C_5H_4Me)_2]$ *in the Presence of* $HClO_4$.—No oxidation of $AcrH_2$ by dioxygen was observed in MeCN at 25 °C. The addition of $HClO_4$ to an oxygen-saturated MeCN solution of $AcrH_2$ resulted in the slow oxidation of $AcrH_2$ to yield $AcrH^+$, but no significant acceleration of the rate was observed with an increase in the $HClO_4$ concentration ($> 1.0 \times 10^{-3}$ mol dm^{-3}) in MeCN. When a 1:1 (v/v) mixture of MeCN and H_2O was used as a solvent, the oxidation of $AcrH_2$ by dioxygen in the presence of $HClO_4$ took place more efficiently to yield $AcrH^+$, accompanied by the two-electron reduction of dioxygen to H_2O_2, as shown in Figure 1.

The stoicheiometry of the reaction is given by equation (1).

$$AcrH_2 + O_2 + H^+ \xrightarrow{k_{obs}} AcrH^+ + H_2O_2 \quad (1)$$

The rate of formation of $AcrH^+$ obeyed the pseudo-first-order kinetics in the presence of excess O_2 and $HClO_4$, and the pseudo-first-order rate constant was proportional to the concentration of dioxygen, equation (2). The dependence of k_{obs} on

$$d[AcrH^+]/dt = k_{obs}[AcrH_2][O_2] \quad (2)$$

the $HClO_4$ concentration in an aqueous solution is shown in Figure 2. When $AcrH_2$ is replaced by the 9,9′-dideuteriated analogue ($AcrD_2$), the small primary kinetic isotope effect, $k_H/k_D = 1.4 \pm 0.2$ was observed and the k_H/k_D value remains constant with the variation in the $HClO_4$ concentration (Figure 2). The k_{obs} value increases with an increase in the $HClO_4$ concentration but decreases in the high $HClO_4$ concentrations through a maximum at 2.0 mol dm^{-3} (Figure 2). Such a maximal dependence of k_{obs} on $[HClO_4]$ may be attributed to the protonation of $AcrH_2$ in the presence of $HClO_4$, equation (3),[4]

$$AcrH_2 + H^+ \overset{K}{\rightleftharpoons} AcrH_3^+ \quad (3)$$

vide infra. The absorption band due to $AcrH_2$ (λ_{max} 285 nm) disappears due to protonation in the presence of $HClO_4$.[4] In Figure 3, the ratios of unprotonated $AcrH_2$ and $AcrD_2$, determined by the electronic spectra in the presence of $HClO_4$, relative to the initial amount in the absence of $HClO_4$ are plotted against the $HClO_4$ concentration. As seen in Figure 3, essentially no protonation of $AcrH_2$ or $AcrD_2$ occurs in the region $[HClO_4] < 1.0$ mol dm^{-3}, but the fraction of unprotonated $AcrH_2$ or $AcrD_2$ decreases significantly with an increase in the $HClO_4$ concentration > 2.0 mol dm^{-3}. Thus, the decrease in k_{obs} in the high $HClO_4$ concentration range (> 2.0 mol dm^{-3}) may be ascribed to the protonation equilibrium between $AcrH_2$ and $AcrH_3^+$; the latter is inactive for the acid-catalysed reduction of dioxygen. The lower reactivity of $AcrH_2$ in MeCN relative to that in H_2O or $MeCN/H_2O$ (1:1 v/v) may also be ascribed to the much larger protonation equilibrium constant in MeCN ($K = 1.1 \times 10^4$ mol^{-1} dm^3).[4] With such a large protonation equilibrium constant, no

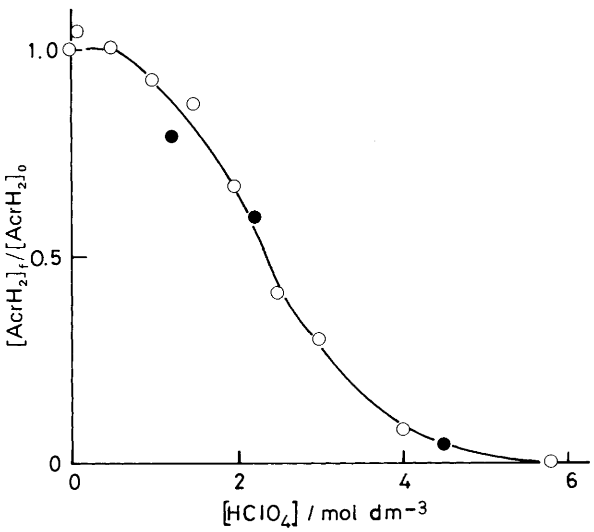


Figure 3. Dependence of the ratio of the concentration of free (unprotonated) $AcrH_2$ (○) or $AcrD_2$ (●) in the presence of $HClO_4$ to the initial concentration in the absence of $HClO_4$, $[AcrH_2$ or $AcrD_2]_f/[AcrH_2$ or $AcrD_2]_0$, on the $HClO_4$ concentration in aqueous solution at 25 °C.

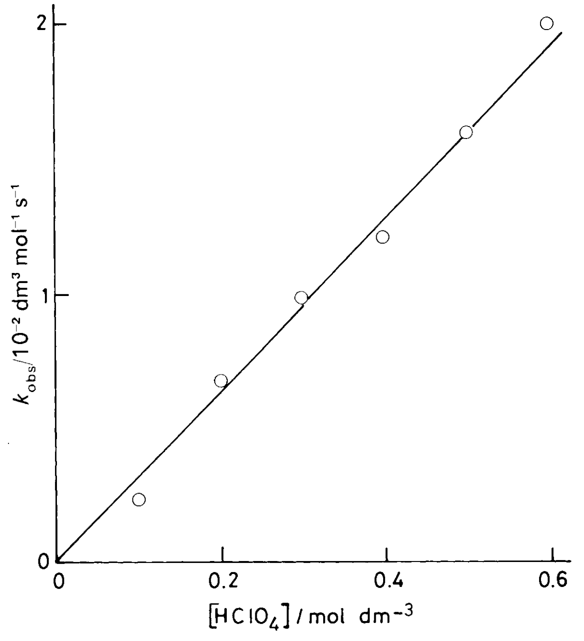


Figure 4. Dependence of the observed second-order rate constant k_{obs} on $[HClO_4]$ for the oxidation of $[Fe(C_5H_4Me)_2]$ by dioxygen in the presence of $HClO_4$ in MeCN at 25 °C.

acceleration of the rate may occur with increased $HClO_4$ concentration ($> 1.0 \times 10^{-3}$ mol dm^{-3}), as described above.

The acid-catalysed reduction of dioxygen is also effected by a mild one-electron reductant, $[Fe(C_5H_4Me)_2]$, in the presence of $HClO_4$ in MeCN to yield $[Fe(C_5H_4Me)_2]^+$, equation (4). In

$$2[Fe(C_5H_4Me)_2] + O_2 + 2H^+ \longrightarrow 2[Fe(C_5H_4Me)_2]^+ + H_2O_2 \quad (4)$$

the presence of excess $[Fe(C_5H_4Me)_2]$ relative to dioxygen, the H_2O_2 formed is further reduced by $[Fe(C_5H_4Me)_2]$ as described later. In contrast with the case of $AcrH_2$, the observed second-order rate constant k_{obs} increases linearly with increased $HClO_4$ concentration in MeCN as shown in Figure 4, since no protonation of $[Fe(C_5H_4Me)_2]$ has been observed in the presence of $HClO_4$ in MeCN.

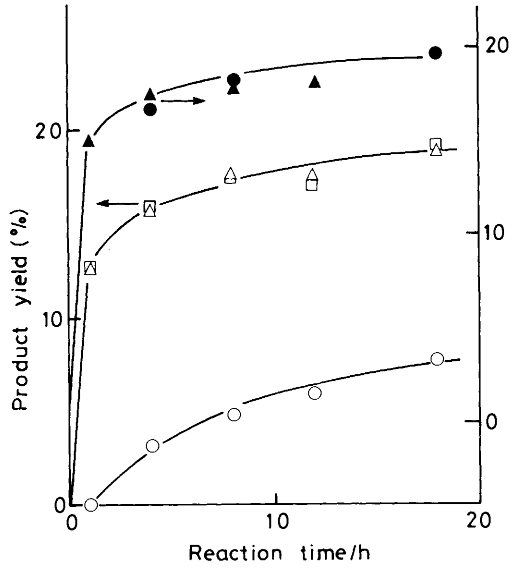


Figure 5. Heterogeneous reduction of dioxygen by $AcrH_2$ in the presence of alumina, activated by calcination at 440 °C for 5 h, in CH_2Cl_2 at 25 °C; the conversion of $AcrH_2$ (●) and the yield of $AcrH^+$ (○) before the addition of MeOH to alumina; the conversion of $AcrH_2$ (▲), the yield of $AcrH^+$ (△) and H_2O_2 (□) after the addition of MeOH to alumina, which results in the desorption of the adsorbed $AcrH^+$ into the homogeneous phase.

Heterogeneous Reduction of Dioxygen by $AcrH_2$ *and* $[Fe(C_5H_4Me)_2]$ *in the Presence of Solid Acids.*—When a CH_2Cl_2 solution of $AcrH_2$ (7.7×10^{-3} mol dm^{-3}, 2.0 cm^3) was introduced onto alumina (0.10 g), activated by calcination at 400 °C for 5 h, the alumina surface turned yellow immediately, indicating the formation of $AcrH^+$ adsorbed on the surface. With prolonged reaction time, the formation of desorbed $AcrH^+$ is observed in the homogeneous phase, and the $AcrH^+$ concentration increases gradually with the reaction time as shown in Figure 5. When MeOH (2.0 cm^3) was added to the reactant solution containing the coloured alumina, at different reaction times, the colour on the surface disappeared and essentially all the $AcrH^+$ and H_2O_2 formed were desorbed into the homogeneous phase (Figure 5). Similarly, the formation of $[Fe(C_5H_4Me)_2]^+$ was observed when $AcrH_2$ was replaced by $[Fe(C_5H_4Me)_2]$. The stoicheiometries of the reduction of dioxygen by $AcrH_2$ and $[Fe(C_5H_4Me)_2]$ were examined using a larger amount of alumina (1.0 g) with which the reactions were brought to completion. The concentrations of $AcrH^+$ and $[Fe(C_5H_4Me)_2]^+$ formed are plotted against the ratios of the concentrations of $AcrH_2$ and $[Fe(C_5H_4Me)_2]$ relative to dioxygen as shown in Figure 6 [(*a*) and (*b*), respectively], which demonstrates that the two-electron and four-electron reductions of dioxygen by $AcrH_2$ and $[Fe(C_5H_4Me)_2]$ proceed in the presence of activated alumina as given by equations (5) and (6),

$$AcrH_2 + O_2 + H^+ \xrightarrow{Al_2O_3} AcrH^+ + H_2O_2 \quad (5)$$

$$4[Fe(C_5H_4Me)_2] + O_2 + 4H^+ \xrightarrow{Al_2O_3} 4[Fe(C_5H_4Me)_2] + 2H_2O \quad (6)$$

respectively. It was confirmed that, essentially, no oxidation of $AcrH_2$ or $[Fe(C_5H_4Me)_2]$ occurred in the absence of dioxygen under otherwise identical conditions.

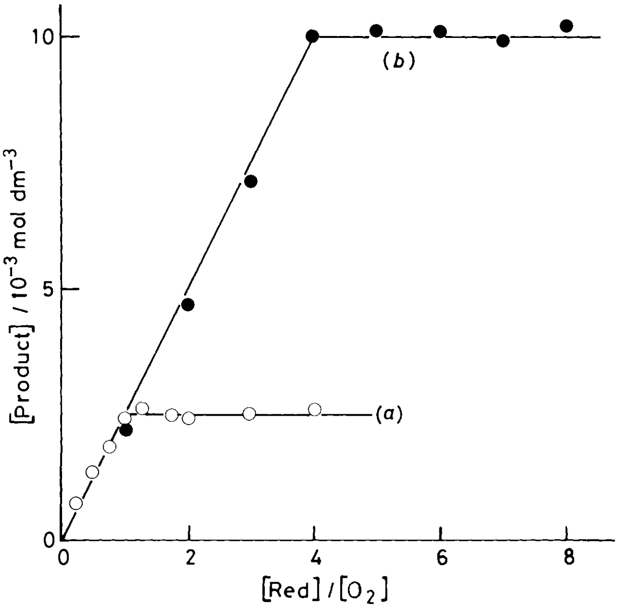


Figure 6. Plots of the concentrations of the products [$AcrH^+$ (○) and [$Fe(C_5H_4Me)_2]^+$ (●)] formed in the heterogeneous reduction of dioxygen by (*a*) $AcrH_2$ and (*b*) [$Fe(C_5H_4Me)_2$], respectively, in the presence of alumina, activated by calcination at 400 °C for 5 h, in CH_2Cl_2, *vs.* the ratio of the concentrations of the reductants (Red: $AcrH_2$ and [$Fe(C_5H_4Me)_2$]) to the initial concentration of dioxygen, [Red]/[O_2].

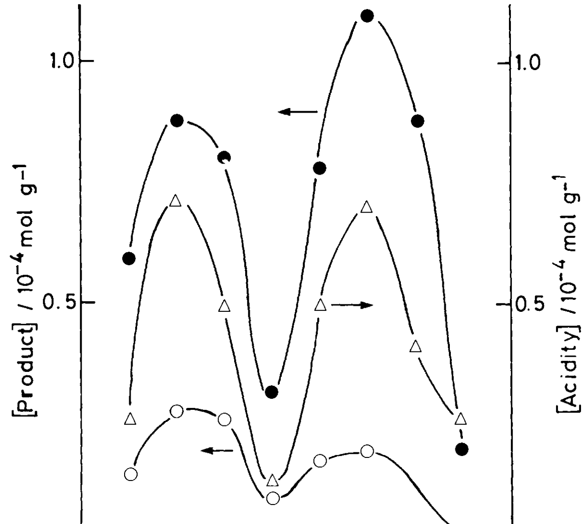


Figure 7. Plots of the amounts of products [$AcrH^+$ (○) and [$Fe(C_5H_4Me)_2]^+$ (●)] formed in the heterogeneous oxidation of $AcrH_2$ and [$Fe(C_5H_4Me)_2$], respectively, by dioxygen in the presence of alumina in CH_2Cl_2 [mol g^{-1} (Al_2O_3)], and the acidity ($H_0 < 4.8$) of alumina (△) *vs.* the calcination temperature of alumina (5 h in air).

The ratio of product yields to alumina (mol g^{-1}), as well as the acidity of the activated alumina (mol g^{-1}) titrated by a Hammett indicator methyl red ($pK_a = 4.8$), one dependent upon the calcination temperature of alumina are shown in Figure 7, where the product yields and the acidity exhibit the same maxima at 400 and 800 °C. A similar dependence of the acidity of alumina on the calcination temperature has been reported previously.[22]

Table. Heterogeneous oxidation of $AcrH_2$ (1.54×10^{-5} mol) by dioxygen in the presence of various solid acids (0.10 g, activated by calcination at 400 °C for 5 h) in CH_2Cl_2 (2.0 cm^3) for 8 h at 25 °C.

Solid acid	Yield of $AcrH^+$ (%)	Conversion of $AcrH_2$ (%)
Al_2O_3	18	18
SiO_2–Al_2O_3[a]	28	72
HY-type zeolite	1.3	59
H_2SO_4–Fe_2O_3[b]	13	22
H_2SO_4–ZrO_2[b]	9.1	15

[a] 28% Al_2O_3. [b] Treated with H_2SO_4.[14,15]

The reactivities of other solid acids, silica–alumina (28% Al_2O_3), HY-type zeolite, and the solid superacids (ZrO_2 and Fe_2O_3, treated with H_2SO_4),[14,15] were also examined for the oxidation of $AcrH_2$ by dioxygen in CH_2Cl_2. The yields of $AcrH^+$ as well as the conversion of $AcrH_2$ are listed in the Table, where identical experimental conditions were maintained for all the solid acids (0.10 g), which were activated by calcination in air for 5 h, the reaction time being 8 h at 25 °C. The conversion of $AcrH_2$ increases with increased acid strength of the catalyst[5–7] in the order $Al_2O_3 < SiO_2$–$Al_2O_3 \simeq$ HY-type zeolite which was converted from NH_4Y-type by calcination (Table). However, the strongest solid superacid so far reported,[14] *i.e.*, ZrO_2 treated with H_2SO_4, showed the least reactivity. The yield of $AcrH^+$ was always smaller than the conversion of $AcrH_2$, except for the case of alumina (Table). In such a case, only a part of the $AcrH^+$ was desorbed into the homogeneous phase, and the colour of the catalyst surface due to the adsorbed $AcrH^+$ did not disappear completely on addition of MeOH. In particular, most $AcrH^+$ molecules formed remained inside the core of HY-type zeolite (Table).

Discussion

Outer-sphere Pathway in the Acid-catalysed Homogeneous Reduction of Dioxygen by [$Fe(C_5H_4Me)_2$].—The electron transfer from [$Fe(C_5H_4Me)_2$] to dioxygen in MeCN is highly endothermic based on the one-electron oxidation potential of [$Fe(C_5H_4Me)_2$] (E°_{ox} *vs.* SCE 0.26 V)[12] and the one-electron reduction potential of O_2 (E°_{red} *vs.* SCE −0.86 V)[23] in MeCN. In fact, no oxidation of [$Fe(C_5H_4Me)_2$] by dioxygen occurred in MeCN. In the presence of $HClO_4$, however, the one-electron reduction potential of O_2 is known to be shifted in the positive direction, caused by the protonation of the one-electron reduction product, *i.e.*, $O_2^{-\bullet}$ [equation (7)], according to equation (8) where F is the Faraday constant, and $2.3RT/F$

$$HO_2\bullet \overset{K_1}{\rightleftharpoons} O_2^{-\bullet} + H^+ \qquad (7)$$

$$E_{red} = E^\circ(O_2/O_2^{-\bullet}) + (2.3RT/F)(\log[H^+] - \log K_1) \qquad (8)$$

corresponds to 59 mV at 25 °C. From the reported values of $E^\circ(O_2/O_2^{-\bullet})$,[23] pK_1 (=12) in an aprotic solvent,[25] the one-electron reduction potential of O_2 in the presence of 0.10 mol dm^{-3} $HClO_4$ in MeCN can be estimated as −0.21 V using equation (8).

The rate constant k_{12} of outer-sphere electron transfer can be estimated by the Marcus relation, equation (9),[8] where k_{11} and

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad (9)$$

k_{22} are the rate constants of the self-exchange of the reductant (1) and of the oxidant (2), respectively and K_{12} is the equilibrium constant of the electron transfer, which is obtained from the one-electron oxidation potential of the reductant (E°_{ox}) and the one-electron reduction potential of the oxidant (E°_{red}) using equation (10). The parameter f in equation (9) is given by

$$\log K_{12} = (-2.3RT/F)^{-1}(E^\circ_{ox} - E^\circ_{red}) \qquad (10)$$

equation 11),[8] where Z, the frequency factor, is taken as

$$\log f = (\log K_{12})^2/[4 \log(k_{11}k_{22}/Z^2)] \qquad (11)$$

1×10^{11} dm^3 mol^{-1} s^{-1}. The k_{11} value of $[Fe(C_5H_4Me)_2]^+/[Fe(C_5H_4Me)_2]$ has been reported as 8.3×10^6 dm^3 mol^{-1} s^{-1},[26] however, the k_{22} value of $O_2/O_2^{-\bullet}$ is known to vary depending on the system.[27] The most appropriate k_{22} value may be taken as 6.9×10^{-5} mol^{-1} dm^3 s^{-1},[27] which was obtained by applying the Marcus theory to the electron transfer from $O_2^{-\bullet}$ to ferricenium cation, the reverse reaction of the present case. Thus, from the reported values of k_{11} and k_{22} together with the one-electron redox potentials of $[Fe(C_5H_4Me)_2]$ and O_2, described above, the k_{12} value of the electron transfer from $[Fe(C_5H_4Me)_2]$ to O_2 in the presence of 0.10 mol dm^{-3} $HClO_4$ in MeCN at 25 °C, can be evaluated at 1.0×10^{-3} dm^3 mol^{-1} s^{-1} using equations (9)–(11).

The observed rate constant k_{obs} of the oxidation of $[Fe(C_5H_4Me)_2]$ by O_2 in the presence of $HClO_4$ corresponds to twice the rate constant of the electron transfer from $[Fe(C_5H_4Me)_2]$ to O_2 [equation (12)], since the initial electron transfer, which is rate-determining, may be followed by the facile second electron-transfer from $[Fe(C_5H_4Me)_2]$ to $HO_2^\bullet$ in the presence of $HClO_4$ in MeCN [equation (13)]. The second electron transfer is highly exothermic since the reduction potential of $HO_2^\bullet$ in the presence of $HClO_4$ is by 1.3 V more positive than that of O_2.[25] Thus, the experimental rate constant k_{et} of the electron transfer [equation (12)] in the presence of 0.10 mol dm^{-3} $HClO_4$ in MeCN is obtained as 1.2×10^{-3} dm^3 mol^{-1} s^{-1} ($= k_{obs}/2$ in Figure 4), which agrees well with the calculated k_{12} values (1.0×10^{-3} dm^3 mol^{-1} s^{-1}, *vide supra*). Such an agreement indicates that the oxidation of $[Fe(C_5H_4Me)_2]$ by dioxygen in the presence of $HClO_4$ proceeds *via* an outer-sphere electron transfer from $[Fe(C_5H_4Me)_2]$ to dioxygen [equation (12)].

$$[Fe(C_5H_4Me)_2] + O_2 + H^+ \xrightarrow{k_{et}} [Fe(C_5H_4Me)_2]^+ + HO_2^\bullet \qquad (12)$$

$$[Fe(C_5H_4Me)_2] + HO_2^\bullet + H^+ \xrightarrow{\text{fast}} [Fe(C_5H_4Me)_2]^+ + H_2O_2 \qquad (13)$$

Inner-sphere Pathway in the Acid-catalysed Homogeneous Reduction of Dioxygen by $AcrH_2$.—The Gibbs energy change of the hydride transfer from $AcrH_2$ to O_2 at pH = 7 (ΔG_h) is obtained as -83 kJ mol^{-1} from the two-electron oxidation potential of $AcrH_2$ [$E(AcrH_2/AcrH^+)$ *vs.* NHE -0.078 V][28] and the two-electron reduction potential of O_2 [$E(H_2O_2/O_2)$ *vs.* NHE 0.355 V)[24] in neutral aqueous solution. Thus, the hydride transfer from $AcrH_2$ to O_2 is highly exothermic even in a neutral aqueous solution. However, essentially no reaction occurred in neutral aqueous solution. Such unreactivity of dioxygen towards $AcrH_2$ despite the favourable energetics may be ascribed to the triplet ground state of dioxygen, since hydride transfer from the singlet $AcrH_2$ to the triplet O_2 is spin-forbidden. In order to make dioxygen reactive, the spin restriction needs to be removed. In general, there are four reaction pathways that remove the spin restriction of dioxygen, namely those *via* (*a*) free radicals, (*b*) singlet oxygen, (*c*) interaction with transition-metal complexes, and (*d*) electron transfer.[27] In the present case, the last one, *i.e.*, electron transfer from $AcrH_2$ to O_2, may be the most probable pathway, since no free radicals, singlet oxygen, or transition-metal complexes are involved in this system which consists of only $AcrH_2$, O_2, and $HClO_4$, although the one-electron reduction of dioxygen is usually energetically unfavourable because of the low reduction potential.[23–25] In the presence of $HClO_4$, however, the one-electron reduction becomes energetically more favourable compared with that in the absence of an acid, according to equation (8). In fact, the electron transfer from a mild one-electron reductant $[Fe(C_5H_4Me)_2]$ to O_2 was made possible in the presence of $HClO_4$ in MeCN, *vide supra*.

Based on the above discussion, the reaction scheme for the reduction of dioxygen by $AcrH_2$ in the presence of $HClO_4$ may be given by equation (14), where the acid-catalysed electron transfer from $AcrH_2$ to O_2 is followed by the hydrogen transfer from $AcrH_2^{+\bullet}$ to $HO_2^\bullet$ to yield $AcrH^+$ and H_2O_2. According to equation (14), the observed second-order rate constant is given by equation (15), under the conditions for which the protonation of $AcrH_2$ [equation (3)] is negligible (*e.g.*, $[HClO_4] \ll 2.0$ mol dm^{-3} in Figure 3). The small primary kinetic isotope effect ($k_H/k_D = 1.4 \pm 0.2$, Figure 2) is ascribed to the competition between the hydrogen transfer (k_H) and the back electron transfer (k_b) in equation (15). In an extreme case, $k_H \gg k_b$, k_{obs} becomes equal to k_{et} and thereby there should be no kinetic isotope effect. Under the experimental conditions employed in this study, no free radicals may escape from the cage in equation (14), since the deviation from simple second-order kinetics [equation (2)] would occur if some radical chain reactions (*e.g.*, autoxidation) were involved.[19]

$$AcrH_2 + O_2 + H^+ \underset{k_b}{\overset{k_{et}}{\rightleftharpoons}} (AcrH_2^{+\bullet}HO_2^\bullet) \xrightarrow{k_H} AcrH^+ + H_2O_2 \qquad (14)$$

$$k_{obs} = k_{et}k_H/(k_b + k_H) \qquad (15)$$

The Marcus relation can be applied also for the estimation of the rate constant of outer-sphere electron transfer from $AcrH_2$ to O_2 in the presence of $HClO_4$ in an aqueous solution. The k_{12} value is calculated as 7.7×10^{-8} dm^3 mol^{-1} s^{-1} from the reported values of k_{11} (1×10^9 dm^3 mol^{-1} s^{-1}),[9] k_{22} (6.9×10^{-5} dm^3 mol^{-1} s^{-1}),[27] E°_{ox} (0.80 V *vs.* SCE),[9] and E_{red} at pH = 0 (-0.12 V *vs.* SCE),[24,25] using equations (9)–(11). Thus, the calculated value is 5.6×10^6 times smaller than the observed rate constant (0.43 dm^3 mol^{-1} s^{-1} at pH = 0 in Figure 2). Although the k_{22} value of $O_2/O_2^{-\bullet}$ is known to vary depending on the system,[27] the maximum k_{12} value of the outer-sphere electron transfer, obtained by the relation $k_{12} = Z\exp[-F(E^\circ_{ox} - E_{red})/RT]$, is 2.8×10^{-5} dm^3 mol^{-1} s^{-1}, which is still 10^4 times smaller than the observed value. Thus, the electron transfer from $AcrH_2$ to O_2 in the presence of $HClO_4$ [equation (14)] may proceed *via* an inner-sphere pathway. Such a 10^4 to 10^6 rate advantage of an inner-sphere pathway relative to the corresponding outer-sphere pathway has well been established in various electron-transfer reactions.[9,29,30]

An alternative mechanism may involve the formation of the hydroperoxonium ion, HO_2^+, formally protonated dioxygen [equation (16)], which accepts a hydride ion from $AcrH_2$ [equation (17)]. However, HO_2^+ has only been recognized in

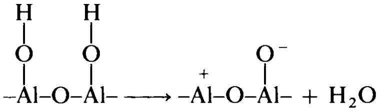
$$H^+ + O_2 \rightleftharpoons HO_2^+ \qquad (16)$$

$$AcrH_2 + HO_2^+ \longrightarrow AcrH^+ + H_2O_2 \qquad (17)$$

the mass spectrum in the fragmentation of H_2O_2 after electron impact,[31] and is unlikely to exist in H_2O. The spin state of HO_2^+ is not known, either. Moreover, if one-step hydride transfer from $AcrH_2$ to HO_2^+ is operative, it would be difficult to account for the small kinetic isotope effect ($k_H/k_D = 1.4 \pm 0.2$, Figure 2), since the reported k_H/k_D values for hydride-transfer reactions of NADH model compounds are in the range 4.4—6.0.[10,32]

Mechanisms of Heterogeneous Reduction of Dioxygen in the Presence of Solid Acid Catalysts.—As discussed above, dioxygen can be activated by the presence of acid which enhances the oxidizing ability of dioxygen towards $AcrH_2$ as well as $[Fe(C_5H_4Me)_2]$. Compared with such a homogeneous system, a heterogeneous system has the advantage of being able to control the acid strength as well as the acidity, since many solid acids including solid superacids are known, and the surface acid strength and acidity can be finely tuned by various means of activation.[5–7] In fact, the acidity of alumina ($H_0 < 4.8$) varies depending on the calcination temperature (Figure 7). The reactivity of dioxygen towards $AcrH_2$ as well as $[Fe(C_5H_4Me)_2]$ also varies in parallel with the variation of the acidity (Figure 7).

Alumina surfaces after removal of adsorbed H_2O are known to have a layer of hydroxy groups.[5–7] The removal of two neighbouring hydroxy groups from the surface by calcination may be accompanied by the formation and desorption of H_2O to leave an oxide ion in the outermost surface layer and an exposed, incompletely co-ordinated aluminium ion in the next lower layer, as shown by equation (18).[6] The oxide ion defect



$$-\overset{\substack{\text{H}\\|\\\text{O}\\|}}{\text{Al}}-\text{O}-\overset{\substack{\text{H}\\|\\\text{O}\\|}}{\text{Al}}- \longrightarrow -\overset{+}{\text{Al}}-\text{O}-\overset{\substack{\text{O}^-\\|}}{\text{Al}}- + \text{H}_2\text{O}$$

(18)

described by Peri[33] is known to act as an electron donor site to give the radical anions upon the adsorption of various electron donors.[34–36] On the other hand, the exposed aluminium ion has been reported to be responsible for the formation of the perylene radical cation upon the absorption of perylene in the presence of dioxygen.[37] However, there has been controversy concerning the formation of the radical cation,[37–39] since it is difficult to distinguish between the perylene radical cation and anion by e.s.r. and electronic spectroscopy, and the presence of electron-donor sites on the activated alumina surface has been well established.[34–36] In the present case, however, there is no question about the formation of $[Fe(C_5H_4Me)_2]^+$ and $AcrH^+$. There has also been controversy concerning the effects of dioxygen: whether oxygen serves as an electron acceptor[37,40] or as a catalyst to increase the oxidizing power of the exposed aluminium ions due to the inductive effect of adsorbed dioxygen.[41] In the present case, there is no question about the stoicheiometric two-electron and four-electron reduction of dioxygen by $AcrH_2$ and $[Fe(C_5H_4Me)_2]$, respectively, as shown in Figure 6.

Thus, the exposed aluminium ion, acting as a Lewis acid site,[5–7] can activate dioxygen such that it can accept an electron from $AcrH_2$ and $[Fe(C_5H_4Me)_2]$. The decrease in the acidity as well as in the product yields as the calcination temperature is raised from 500 to 600 °C (Figure 7) may be caused by surface sintering effects since migration of oxide and aluminium ions may occur at this temperature.[6] The migration of protons may also occur above 600 °C to result in further dehydroxylation, creating more defects, and thereby the acidity, as well as the product yields, increase again from 600 to 800 °C (Figure 7). The considerable decrease in the acidity as well as the product yields above 800 °C (Figure 7) may be due mainly to the decrease in the surface area, caused by the irreversible change of the alumina phase from γ-Al_2O_3 to α-Al_2O_3.[34]

The increase in the conversion of $AcrH_2$ with increased Brønsted acid strength (Table),[5–7] except for the solid superacids (ZrO_2 and Fe_2O_3 treated with H_2SO_4), suggests that the Brønsted acid site may also serve as an active site for the activation of dioxygen for the reduction. The decrease in the conversion of $AcrH_2$ in the case of the solid superacids (Table) indicates the importance of an appropriate acid strength to achieve the efficient acid-catalysed reduction of dioxygen by $AcrH_2$ as observed also in the homogeneous system (Figure 2).

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