10,10′-Dimethyl-9,9′-biacridine Acting as a Unique Electron Source Compared with the Corresponding Monomer for the Efficient Reduction of Dioxygen, Catalysed by a Cobalt Porphyrin in the Presence of Perchloric Acid

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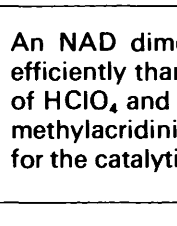
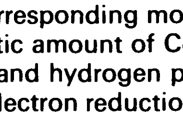
An NAD dimer analogue, 10,10′-dimethyl-9.9′-biacridine [$(AcrH)_2$] reduces dioxygen much more efficiently than the corresponding monomer, 10-methyl-9,10-dihydroacridine ($AcrH_2$) in the presence of $HClO_4$ and a catalytic amount of $CoTPP^+$ (TPP = tetraphenylporphyrin) in acetonitrile to yield 10-methylacridinium ion and hydrogen peroxide. The mechanistic difference between $(AcrH)_2$ and $AcrH_2$ for the catalytic two-electron reduction of dioxygen is revealed based on the detailed kinetic studies.

One-electron reduction of pyridinium and acridinium ions including nicotinamide adenine dinucleotide (NAD^+) results in the formation of the corresponding dimers.[1,2] For example, thermal as well as photoinduced electron transfer from group 14 dimetallic compounds ($Me_3MM'Me_3$; M = M′ = Sn, Ge, Si) to 10-methylacridinium ion ($AcrH^+$) yields 10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] selectively.[3,4] We have recently reported that the dimer [$(AcrH)_2$] acts as a pure two-electron donor in the one-electron reduction of triphenylmethyl cation (Ph_3C^+) compared with the corresponding monomer, 9,10-dihydroacridine ($AcrH_2$), which acts as a normal hydride (two-electron and one-proton) in the two-electron reduction of Ph_3C^+.[5] Such a unique donor property of the dimer may be relevant to the biological significance of the NAD dimer which has hitherto been overlooked, compared with the corresponding monomer (NADH).[6] On the other hand, NADH is known to play a vital role as the electron source in the respiratory chain for the reduction of dioxygen.[7] We have recently reported that a cobalt porphyrin, $CoTPP^+$ (TPP = tetraphenylporphyrin) catalyses the reduction of dioxygen by $AcrH_2$ in the presence of perchloric acid ($HClO_4$) in acetonitrile (MeCN). Here we report that the 10-methylacridine dimer [$(AcrH)_2$] acts as a much more efficient electron donor than the monomer ($AcrH_2$) for the $CoTPP^+$-catalysed reduction of dioxygen in the presence of $HClO_4$ in MeCN. The difference in the mechanisms for the reduction of dioxygen by $(AcrH)_2$ and $AcrH_2$ is clarified based on the detailed kinetic studies.


$(AcrH)_2$


$(AcrH_2)$

Experimental

Materials.—10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] was prepared from 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) by one-electron reduction with hexamethylditin in deaerated MeCN.[3] 10-Methylacridinium iodide was prepared by the reaction of acridine with methyl iodide in acetone, and it was converted into the perchlorate salt ($AcrH^+ClO_4^-$) by the addition of magnesium perchlorate to the iodide salt, and purified by recrystallization from methanol.[8] Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared as described in the literature.[9] The CoTPP was oxidized by dioxygen in the presence of HCl in methanol to obtain tetraphenylporphynatocobalt(III) chloride (CoTPPCl),[10] which was purified by recrystallization from methanol. The perchlorate salt of $CoTPP^+$ was obtained by the metathesis of the chloride salt with $AgClO_4$ and recrystallized from toluene.[11] Perchloric acid (70%) was obtained from Wako Pure Chemicals. Reagent grade acetonitrile was purified by the successive distillation (four times) over P_2O_5 before use.

Spectral Measurements.—Electronic absorption spectra were recorded with a Union SM-401 spectrophotometer with a quartz cell (1 mm or 1 cm i.d.), which was placed in a thermostated compartment at 298 K. The stoichiometry of the catalytic reduction of dioxygen by $(AcrH)_2$ in the presence of $CoTPP^+$ and $HClO_4$ in MeCN was determined by measuring the absorbances due to $AcrH^+$ with various initial concentrations of $(AcrH)_2$ and a fixed concentration of dioxygen. The amount of H_2O_2 formed in the two-electron reduction of dioxygen by $(AcrH)_2$ in the presence of $HClO_4$ was determined by the standard method (titration by iodide ion) according to the procedure reported previously.[12]

The concentration of dioxygen in air-saturated MeCN containing the same concentration of $HClO_4$ as employed in determining the stoichiometry of the catalytic two-electron reduction of dioxygen was determined to be 2.6×10^{-3} mol dm^{-3} from the photooxidation of 10-methyl-9,10-dihydroacridine ($AcrH_2$) by dioxygen in the presence of $HClO_4$ (0.80 mol dm^{-3}) in MeCN, as described elsewhere.[7b,13] The dioxygen concentration in air-saturated MeCN determined in this manner was in good agreement with those in aprotic solvents such as alkanes, acetone, alcohol and carbon tetrachloride.[14]

Kinetic Measurements.—Acetonitrile solutions containing various concentrations of dioxygen were prepared by saturating the MeCN solution with a stream of mixture gas (dioxygen and nitrogen) at various partial pressures of dioxygen. The various partial pressures of dioxygen were attained by controlling the flow rates of dioxygen and nitrogen with gas regulators. The concentrations of dioxygen were assumed to be proportional to the partial pressure of dioxygen. Rates of the oxidation of $(AcrH)_2$ were monitored by the rise of the absorption band due to $AcrH^+$ (λ_{max} = 358 nm, $\varepsilon_{max} = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}) in MeCN at 298 K. Rates of the reduction of $CoTPP^+$ by $(AcrH)_2$ were monitored by the rise and decay of the absorption bands at 412 and 434 nm due to CoTPP and $CoTPP^+$,[7b]

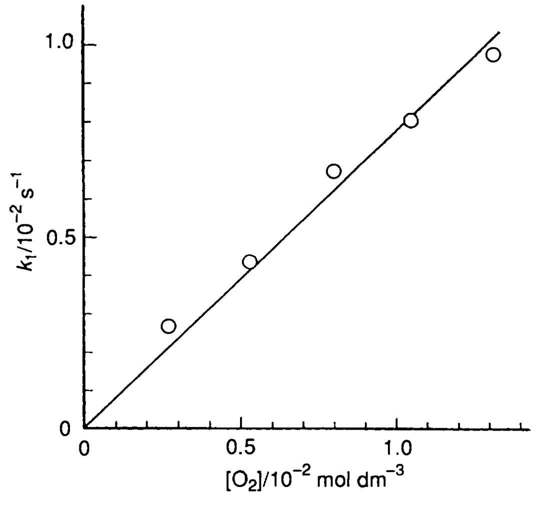


Fig. 1 Plots of k_{obs} *versus* $[O_2]_0$ for the reduction of O_2 by $(AcrH)_2$ (1.0×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (0.80 mol dm^{-3}) in MeCN at 298 K

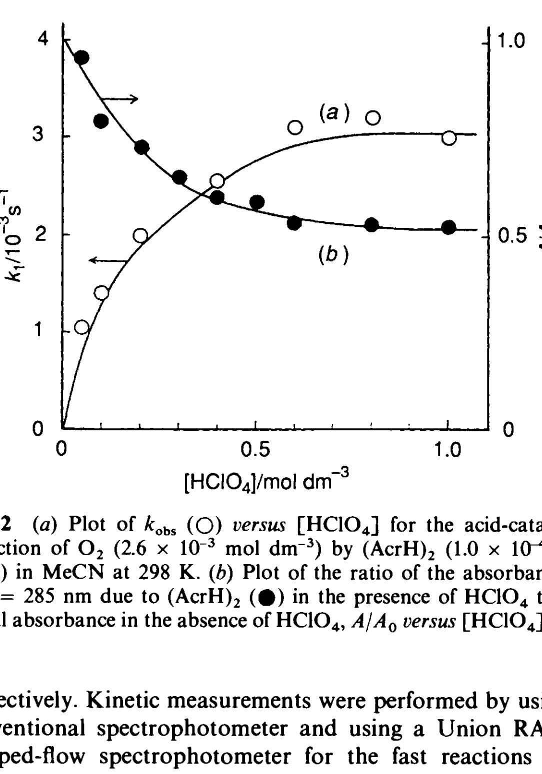


Fig. 2 (*a*) Plot of k_{obs} (○) *versus* $[HClO_4]$ for the acid-catalysed reduction of O_2 (2.6×10^{-3} mol dm^{-3}) by $(AcrH)_2$ (1.0×10^{-4} mol dm^{-3}) in MeCN at 298 K. (*b*) Plot of the ratio of the absorbance at λ_{max} = 285 nm due to $(AcrH)_2$ (●) in the presence of $HClO_4$ to the initial absorbance in the absence of $HClO_4$, A/A_0 *versus* $[HClO_4]$.

respectively. Kinetic measurements were performed by using a conventional spectrophotometer and using a Union RA-103 stopped-flow spectrophotometer for the fast reactions with half-lives < 10 s. All the kinetic measurements were carried out under pseudo first order conditions where the concentrations of dioxygen and $HClO_4$ were maintained at greater than tenfold excess of the concentration of reactant, which is also maintained at greater than tenfold excess of the catalyst concentration whenever possible. Pseudo-first-order rate constants k_1 were determined by a least-squares curve fit by use of a Union System 77 microcomputer. The pseudo-first-order plots were linear for three or more half-lives with the correlation coefficient $\rho > 0.999$.

Results

Two-electron Reduction of Dioxygen with $(AcrH)_2$ *in the presence of* $HClO_4$.—In contrast with the 10-methylacridine monomer ($AcrH_2$) which is only sluggishly oxidized by dioxygen in the presence of $HClO_4$ in MeCN, the corresponding dimer $(AcrH)_2$ is readily oxidized by dioxygen under the same conditions. The stoichiometry of the oxidation of $(AcrH)_2$ with dioxygen in the presence of $HClO_4$ is given by eqn. (1). The two-electron reduction of dioxygen by $(AcrH)_2$

$$(AcrH)_2 + O_2 + 2H^+ \longrightarrow 2AcrH^+ + H_2O_2 \quad (1)$$

was confirmed by the detection of $AcrH^+$ and H_2O_2 formed in the reaction (see the Experimental section).

Rates of oxidation of $(AcrH)_2$ with a large excess of dioxygen and $HClO_4$ obeyed pseudo-first-order kinetics. The pseudo-first-order rate constant (k_1/s^{-1}) increases linearly with an increase in the dioxygen concentration at a fixed concentration of $HClO_4$ (Fig. 1). The dependence of k_1 on the $HClO_4$ concentration at a fixed concentration of dioxygen is shown in Fig. 2(*a*), where the k_1 value increases with an increase in the $HClO_4$ concentration to reach a constant value. Such a saturation in the rate constant is accompanied by a decrease in the absorbance at λ_{max} (285 nm) due to $(AcrH)_2$, which reaches a constant value which is one-half of the original value with an increase in $[HClO_4]$, as shown in Fig. 2(*b*). In the case of $AcrH_2$ the absorbance at λ_{max} = 285 nm due to $AcrH_2$ is known to decrease to zero with an increase in $[HClO_4]$ due to the protonation of $AcrH_2$ [eqn. (2)].[15] Thus, the half-decrease in the absorbance due to

$$AcrH_2 + H^+ \rightleftharpoons (AcrH_2)H^+ \quad (2)$$

$(AcrH)_2$ in Fig. 2(*b*) may be ascribed to the protonation of one acridine moiety of $(AcrH)_2$ [eqn. (3)]. In the case of $AcrH_2$ the

$$(AcryH)_2 + H^+ \rightleftharpoons (AcrH)_2H^+ \quad (3)$$

reducing power is known to be decreased significantly by the protonation,[15] and thereby only the free $AcrH_2$ is active for the reduction of dioxygen.[7] If only the free (unprotonated) dimer $(AcrH)_2$ is also active for the reduction of dioxygen, the dependence of k_1 on $[HClO_4]$ may be given by eqn. (4), where k

$$k_1 = k[HClO_4][O_2]/(1 + K[HClO_4]) \quad (4)$$

and K are the rate constant for the acid-catalysed reduction of dioxygen by free $(AcrH)_2$ and the equilibrium constant for the protonation of $(AcrH)_2$ [eqn. (3)], respectively. According to eqn. (4), k_1 increases with an increase in $[HClO_4]$ to reach a constant value, in agreement with the observation in Fig. 2(*a*). In fact, the K value (6.0 dm^3 mol^{-1}) obtained from the linear plot of k_1^{-1} *versus* $[HClO_4]^{-1}$ agrees well with that (5.6 dm^3 mol^{-1}) obtained independently from the linear plot of $A_0/(A_0 - A)$ *versus* $[HClO_4]^{-1}$ ($[HClO_4]$ = 0.1–1.0 mol dm^{-3}).

$CoTPP^+$*-catalysed Two-electron Reduction of Dioxygen with* $(AcrH)_2$ *in the Presence of* $HClO_4$.—The rates of oxidation of $(AcrH)_2$ by dioxygen in the presence of $HClO_4$ were enhanced significantly by the addition of a catalytic amount of $CoTPP^+$ or CoTPP. The stoichiometry of the $CoTPP^+$-catalysed reduction of dioxygen by $(AcrH)_2$ is determined from the spectral titration. As shown in Fig. 3, one $(AcrH)_2$ molecule reduces one dioxygen molecule to yield two $AcrH^+$ molecules. Thus, the two-electron reduction of dioxygen by $(AcrH)_2$ [eqn. (1)] is catalysed by $CoTPP^+$. Rates of the catalytic oxidation of $(AcrH)_2$ with excess amounts of dioxygen and $HClO_4$ in the presence of a catalytic amount of $CoTPP^+$ obeyed pseudo-first-order kinetics. The pseudo-first-order rate constant (k_1/s^{-1}) increases linearly with an increase in the $CoTPP^+$ concentration, as shown in Fig. 4(*a*), which confirms that $CoTPP^+$ acts as an efficient catalyst in the oxidation of $(AcrH)_2$ by dioxygen (2.6×10^{-3} mol dm^{-3}) in the presence of $HClO_4$ (1.0×10^{-3} mol dm^{-3}) in MeCN. Under the same conditions the k_1 value in the absence of $CoTPP^+$ is 1.0×10^{-4} s^{-1}, which is 10^5 times smaller than the k^1 value in the presence

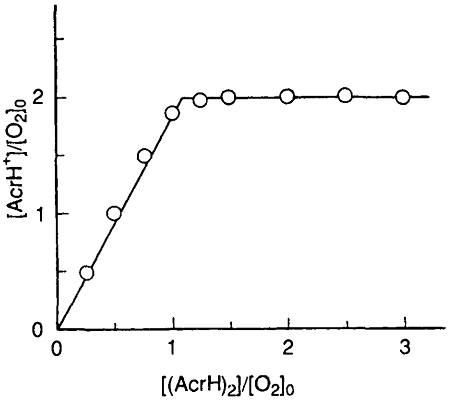


Fig. 3 Plot of the ratio of the $AcrH^+$ concentration formed in the oxidation of $(AcrH)_2$ by dioxygen in the presence of $CoTPP^+$ (1.0×10^{-4} mol dm^{-3}) and $HClO_4$ (0.10 mol dm^{-3}) to the initial concentration of dioxygen (2.6×10^{-3} mol dm^{-3}), $[AcrH^+]/[O_2]_0$ *versus* $[(AcrH)_2]/[O_2]_0$

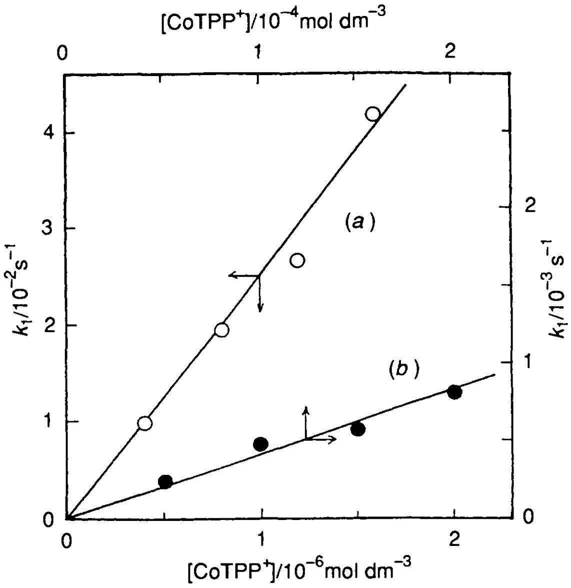


Fig. 4 (*a*) Plot of k_{obs} *versus* $[CoTPP^+]$ for the $CoTPP^+$-catalysed reduction of dioxygen (2.6×10^{-3} mol dm^{-3}) by $(AcrH)_2$ (1.0×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (1.0×10^{-3} mol dm^{-3}) in MeCN at 298 K. (*b*) Plot of k_{obs} *versus* $[CoTPP^+]$ for the $CoTPP^+$-catalysed reduction of dioxygen (2.6×10^{-3} mol dm^{-3}) by $AcrH_2$ (1.0×10^{-3} mol dm^{-3}) in the presence of $HClO_4$ (2.0×10^{-3} mol dm^{-3}) in MeCN at 298 K.[7b]

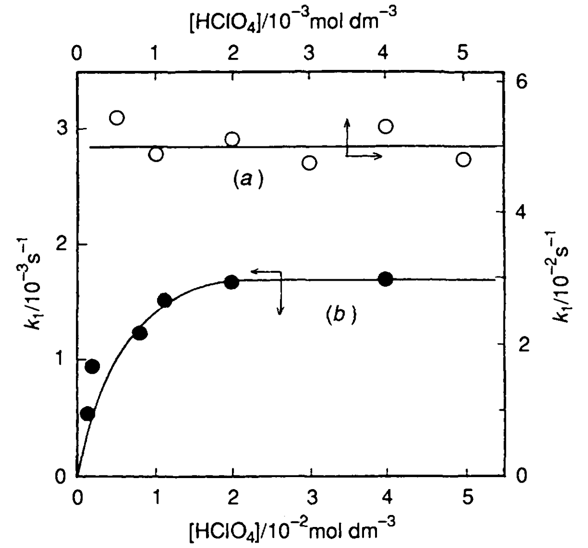


Fig. 5 (*a*) Plot of k_{obs} *versus* $[HClO_4]$ for the $CoTPP^+$-catalysed reduction of dioxygen (2.6×10^{-3} mol dm^{-3}) by $(AcrH)_2$ (1.0×10^{-4} mol dm^{-3}) in the presence of $CoTPP^+$ (2.0×10^{-6} mol dm^{-3}) and $HClO_4$ in MeCN at 298 K. (*b*) Plot of k_{obs} *versus* $[HClO_4]$ for the $CoTPP^+$-catalysed reduction of dioxygen (2.6×10^{-3} mol dm^{-3}) by $AcrH_2$ (2.0×10^{-3} mol dm^{-3}) in the presence of $CoTPP^+$ (2.0×10^{-4} mol dm^{-3}) and $HClO_4$ in MeCN at 298 K.[7b]

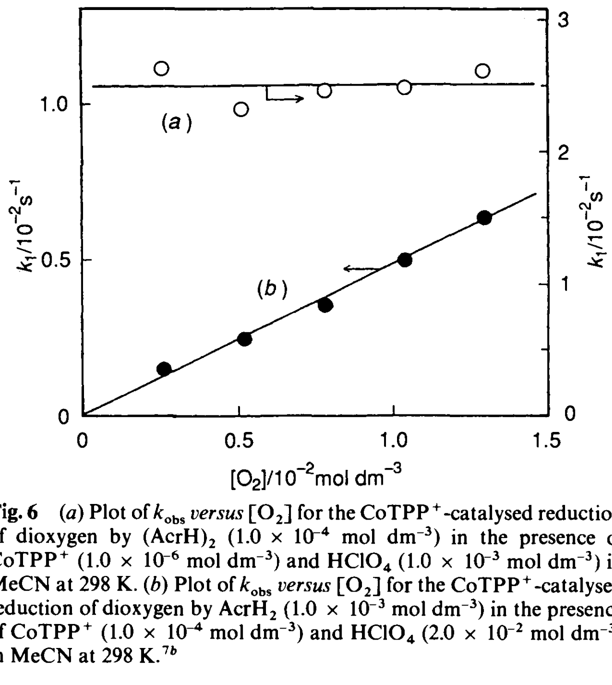


Fig. 6 (*a*) Plot of k_{obs} *versus* $[O_2]$ for the $CoTPP^+$-catalysed reduction of dioxygen by $(AcrH)_2$ (1.0×10^{-4} mol dm^{-3}) in the presence of $CoTPP^+$ (1.0×10^{-6} mol dm^{-3}) and $HClO_4$ (1.0×10^{-3} mol dm^{-3}) in MeCN at 298 K. (*b*) Plot of k_{obs} *versus* $[O_2]$ for the $CoTPP^+$-catalysed reduction of dioxygen by $AcrH_2$ (1.0×10^{-3} mol dm^{-3}) in the presence of $CoTPP^+$ (1.0×10^{-4} mol dm^{-3}) and $HClO_4$ (2.0×10^{-2} mol dm^{-3}) in MeCN at 298 K.[7b]

of 1.0×10^{-5} mol dm^{-3} $CoTPP^+$. The k_1 values for the $CoTPP^+$-catalysed two-electron reduction of dioxygen by the monomer ($AcrH_2$) are also plotted as a function of $[CoTPP^+]$ for comparison in Fig. 4(*b*), demonstrating that $(AcrH)_2$ is a much more efficient electron donor than $AcrH_2$.

The dependence of k_1 for $(AcrH)_2$ on $[HClO_4]$ at fixed concentrations of $CoTPP^+$ and O_2 is also compared with that of $AcrH_2$ as shown in Fig. 5 Although the k_1 value for $(AcrH)_2$ is constant with change in $[HClO_4]$, the k_1 value for $AcrH_2$ increases with an increase in $[HClO_4]$ to reach a plateau value.[7] The dependence of k_1 on $[O_2]$ at fixed concentrations of $HClO_4$ and $CoTPP^+$ also exhibits a marked contrast between $(AcrH)_2$ and $AcrH_2$ as shown in Fig. 6, where the k_2 value for $(AcrH)_2$ is independent of $[O_2]$ [part (*a*)], but that of $AcrH_2$ is proportional to $[O_2]$ [part (*b*)].[7] According to the results in Figs. 4–6 the rate of formation of $AcrH^+$ for the $CoTPP^+$-catalysed reduction of O_2 by $(AcrH)_2$ is given by eqn. (5), where

$$d[AcrH^+]/dt = k_{obs}[(AcrH)_2][CoTPP^+] \qquad (5)$$

k_{obs} is the observed rate constant, which is independent of $[HClO_4]$ and $[O_2]$ under the present experiment conditions. On the other hand, the corresponding second-order rate constant (k_{obs}) of the monomer ($AcrH_2$) is dependent on $[HClO_4]$ and $[O_2]$, as given by eqn. (6), where k'_{obs} and K' are

$$k_{obs} = k'_{obs}[HClO_4][AcrH_2][O_2]/(1 + K'[HClO_4]) \qquad (6)$$

the observed third-order rate constant and the equilibrium constant of the protonation of $AcrH_2$ [eqn. (2)], respectively. The k_{obs} values of $(AcrH)_2$ and $AcrH_2$ thus obtained are listed in Table 1.

Oxidation of $(AcrH)_2$ *by* $CoTPP^+$ *in the Absence of Dioxygen.*—In the absence of dioxygen, $AcrH_2$ is oxidized by $CoTPP^+$ to yield $AcrH^+$ and CoTPP [eqn. (7)].[7b] The $(AcrH)_2$ is

Table 1 Rate constants for the reduction of dioxygen by $(AcrH)_2$ in the presence of $HClO_4$ in MeCN; the $CoTPP^+$-catalysed reduction of dioxygen by $(AcrH)_2$ and $AcrH_2$ in the presence of $HClO_4$ in MeCN; and the reduction of $CoTPP^+$ by $(AcrH)_2$ and $AcrH_2$ in deaerated MeCN at 298 K

Oxidant	k_{obs} for $(AcrH)_2$/dm^3 mol^{-1} s^{-1}	k'_{obs} for $AcrH_2$[a]/dm^3 mol^{-1} s^{-1}
O_2[b]	1.2	[c]
$CoTPP^+$[d]	1.0×10^5	5.7
$CoTPP^+$[e]	2.3×10^4	8.5[f]

[a] Ref. 7(*b*). [b] $[HClO_4] = 0.80$ mol dm^{-3}. [c] Too small to be determined accurately. [d] In the absence of dioxygen. [e] In the presence of dioxygen. [f] $[HClO_4] = 4.0 \times 10^{-4}$ mol dm^{-3}, $[O_2] = 2.6 \times 10^{-3}$ mol dm^{-3}.

$$AcrH_2 + 2CoTPP^+ \longrightarrow AcrH^+ + 2CoTPP + H^+ \quad (7)$$

oxidized much more efficiently by $CoTPP^+$ than $AcrH_2$, also yielding $AcrH^+$ and CoTPP [eqn. (8)]. The rate of formation of

$$(AcrH)_2 + 2CoTPP^+ \longrightarrow 2AcrH^+ + 2CoTPP \quad (8)$$

of CoTPP obeyed pseudo-first-order kinetics under conditions such that the concentrations of $(AcrH)_2$ were maintained at greater than tenfold excess over that of $CoTPP^+$. The pseudo-first-order rate constant (k_1/s^{-1}) was proportional to the $(AcrH)_2$ concentration. Then, the observed second-order rate constant is obtained as 1.0×10^5 dm^3 mol^{-1} s^{-1} as listed in Table 1, where the much smaller k_{obs} value of $AcrH_2$ [7b] is also given for comparison.

Discussion

Mechanism of the Two-electron Reduction of Dioxygen by $(AcrH)_2$ *in the Presence of* $HClO_4$.—The 10-methylacridine dimer $(AcrH)_2$ has been reported to act as a stronger one-electron reductant than the corresponding monomer $(AcrH_2)$.[5] On the other hand, dioxygen is a much stronger one-electron oxidant in the presence of $HClO_4$ in MeCN, since the one-electron reduction potential of O_2 in the presence of $HClO_4$ is shifted significantly in the positive direction.[16–18] Thus, the oxidation of $(AcrH)_2$ by dioxygen in the presence of $HClO_4$ [eqn. (1)] may be initiated by the acid-catalysed electron transfer from $(AcrH)_2$ to dioxygen [eqn. (9)]. The facile cleavage

$$(AcrH)_2 + O_2 + H^+ \longrightarrow (AcrH)_2^{\cdot +} + HO_2^{\cdot} \quad (9)$$

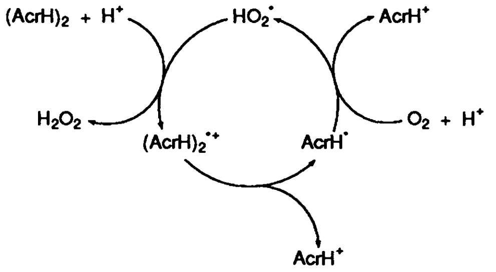
of the C–C bond of the resulting radical cation $(AcrH)_2^{\cdot +}$ to give $AcrH^+$ and $AcrH^{\cdot}$ [eqn. (10)][5] may follow the electron

$$(AcrH)_2^{\cdot +} \longrightarrow AcrH^+ + AcrH^{\cdot} \quad (10)$$

transfer, resulting in the two-electron reduction of dioxygen, since the subsequent electron transfer from $AcrH^{\cdot}$ ($E^0_{ox} = -0.43$ V)[8] to $HO_2^{\cdot}$ in the presence of $HClO_4$ may be highly exergonic,[18] yielding $AcrH^+$ and H_2O_2 [eqn. (11)]. The $HO_2^{\cdot}$

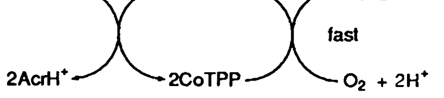
$$AcrH^{\cdot} + HO_2^{\cdot} + H^+ \longrightarrow AcrH^+ + H_2O_2 \quad (11)$$

radicals formed by the acid-catalysed electron transfer from $(AcrH)_2$ to O_2 [eqn. (9)] might initiate the radical chain reactions as shown in Scheme 1, where the acid-catalysed electron transfer from $(AcrH)_2$ to $HO_2^{\cdot}$ to yield $(AcrH)_2^{\cdot +}$ and H_2O_2, followed by the facile cleavage of the C–C bond of $(AcrH)_2^{\cdot +}$ [eqn. (10)], and the acid-catalysed electron transfer from the resulting $AcrH^{\cdot}$ radical to dioxygen to regenerate $HO_2^{\cdot}$. In such a case, however, the kinetic formulation would be clearly different from the simple second-order kinetics observed in Fig. 1, as is demonstrated in similar radical chain reactions for the acid-catalysed photooxidation of $AcrH_2$ by dioxygen.[13]

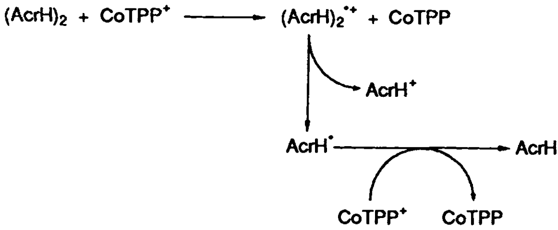


Scheme 1

Comparison of Mechanisms for the $CoTPP^+$*-catalysed Reduction of Dioxygen by* $(AcrH)_2$ *and* $AcrH_2$.—Since the rate of the $CoTPP^+$-catalysed reduction of dioxygen in the presence of $HClO_4$ is independent of $[HClO_4]$ and $[O_2]$ [Figs. 4(*a*) and 5(*a*)], the rate-determining step may be the oxidation of $(AcrH)_2$ by $CoTPP^+$ to yield $AcrH^+$ and CoTPP, the latter being known to be readily oxidized by dioxygen in the presence of $HClO_4$ to regenerate $CoTPP^+$.[19,20] In fact, $(AcrH)_2$ can be oxidized efficiently by $CoTPP^+$ in the absence of dioxygen in MeCN [eqn. (8)]. Thus, the reaction mechanism for the $CoTPP^+$-catalysed reduction of dioxygen may be as shown in Scheme 2. The two-electron oxidation of $(AcrH)_2$ by $CoTPP^+$ may consist of rate determining electron transfer from $(AcrH)_2$ to $CoTPP^+$, followed by facile cleavage of the C–C bond of $(AcrH)_2^{\cdot +}$ [eqn. (10)] and subsequent electron transfer from $AcrH^{\cdot}$ to $CoTPP^+$ as shown in Scheme 3.

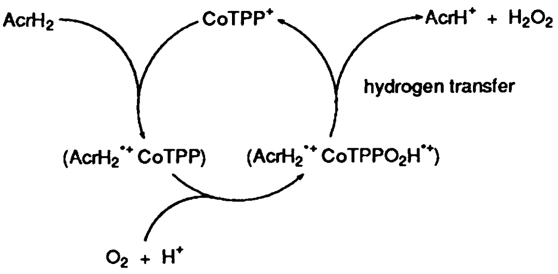


Scheme 2



Scheme 3

In contrast to the case of $(AcrH)_2$, the rate of the $CoTPP^+$-catalysed reduction of dioxygen by $AcrH_2$ is dependent on both $[HClO_4]$ and $[O_2]$ [Figs. 4(*b*) and 5(*b*)]. In this case electron transfer from $AcrH_2$ to $CoTPP^+$ is more endergonic than electron transfer from $(AcrH)_2$, since $(AcrH)_2$ is a stronger one-electron reductant than $AcrH_2$.[5] Moreover, the electron transfer yields $AcrH_2^{\cdot +}$ which is much more stable than the dimer radical cation $[(AcrH)_2^{\cdot +}]$.[5] Thus the only energetically feasible reaction following electron transfer from $AcrH_2$ to $CoTPP^+$ is hydrogen abstraction from $AcrH_2^{\cdot +}$ by $CoTPPO_2H^{\cdot +}$, which is formed as an intermediate for the acid-catalysed oxidation of $CoTPP^+$ by dioxygen, as shown in Scheme 4.[7b] In such a case the reduction of $CoTPP^+$ by $AcrH_2$ and the oxidation of $CoTPP^+$ by dioxygen are no longer independent of each other, since electron transfer from $AcrH_2$ to $CoTPP^+$ coincides with the acid-catalysed oxidation of CoTPP by O_2 and hydrogen transfer from $AcrH_2^{\bullet +}$ to $CoTPPO_2H^{\bullet +}$ (Scheme 4).[7b]



Scheme 4

Although there is no definitive evidence presented for the radical intermediates postulated in Scheme 3, the kinetic formulation for the $CoTPP^+$-catalysed reduction of dioxygen by the dimer $[(AcrH)_2]$ (Scheme 2) is essentially the same as that of the catalytic reduction of dioxygen by ferrocene derivatives, they being inorganic one-electron reductants (the rate is independent of $[HClO_4]$ and $[O_2]$).[19] Thus $(AcrH)_2$, albeit an organic reductant, acts as a unique two-electron donor without loss of hydrogen compared to the corresponding monomer ($AcrH_2$), which acts as a normal hydride donor in the catalytic reduction of dioxygen.

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