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10,10'-Dimethyl-9,9'-biacridine Acting as a Novel Organic Outer-Sphere Electron-Transfer Reagent

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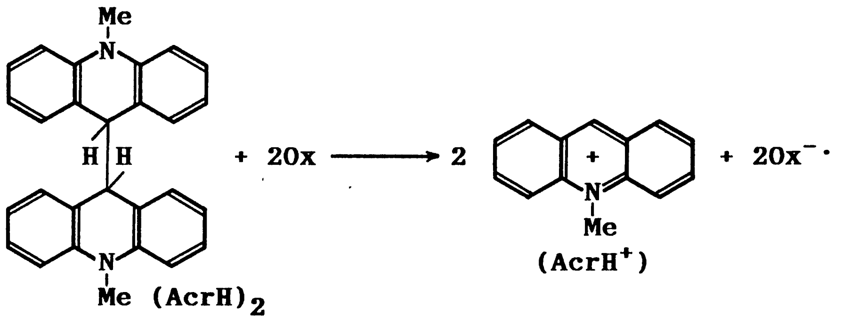
Rates of Electron-transfer (ET) reactions from 10,10'-dimethyl-9,9'-biacridine [$(AcrH)_2$] to various inorganic and organic one-electron oxidants depend solely on the one-electron reduction potentials of the oxidants irrespective of the size of the oxidants, indicating that $(AcrH)_2$ acts as a novel outer-sphere organic ET reagent.

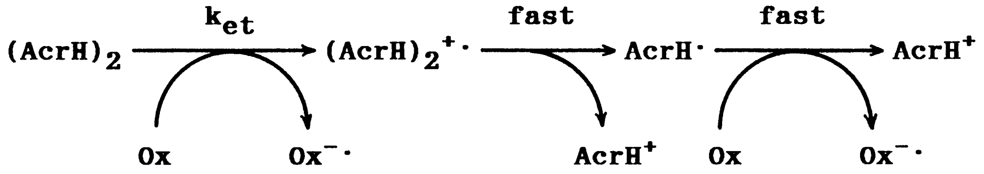
The outer-sphere mechanism for electron-transfer (ET) reactions has been extremely useful and successful in predicting the ET rates of a number of inorganic redox reagents in terms of the Marcus simple and classical theory.$^{1)}$ This concept requires no specific knowledge of the transition-state structure, since rates of the outer-sphere ET reactions having nonbonded transition states can be described only in terms of the thermodynamic parameters of each independent reductant and oxidant. In contrast, transition-state structures play important roles in mechanistic thinking in organic redox chemistry, since bonding is so important in transition states of organic redox reactions. Thus, well documented cases of outer-sphere ET reactions involving organic redox reagents are rare as Eberson and Shaik have recently pointed out.$^{2,3)}$ We report herein that there is an exception for such generalization and that 10,10'-dimethyl-9,9'-biacridine [$(AcrH)_2$] acts as a novel organic outer-sphere ET reagent.

Upon mixing of $(AcrH)_2$$^{4)}$ with a neutral organic oxidant (Ox) such as 7,7,8,8-tetracyano-p-quinodimethane (TCNQ), tetracyanoethylene (TCNE), or p-benzoquinone derivatives in deaerated MeCN at 298 K, Ox is readily reduced to the corresponding radical anion ($Ox^{-\cdot}$), accompanied by the formation of 10-methylacridinium ion ($AcrH^+$).$^{5-7)}$ The stoichiometry is given by Eq. 1,$^{5,7)}$ where $(AcrH)_2$ acts as a two-electron donor in the one-electron-reduction of Ox. The rates of formation of $Ox^{-\cdot}$ obey second-order kinetics, showing the first-order dependence on each reactant concentra-



(1)

tion,8) indicating that the initial electron transfer from $(AcrH)_2$ to Ox is the rate-determining step, followed by facile cleavage of the C-C bond of $(AcrH)_2^{+\cdot}$ to yield $AcrH^+$ and AcrH· (Scheme 1).9) The second electron transfer from AcrH· to Ox (Scheme 1) may be much faster than the initial



Scheme 1.

electron transfer, since the one-electron oxidation potential of AcrH· is largely negative (E^0_{ox} = -0.43 V vs. SCE).6) In such a case the observed second-order rate constant (k_{obs}) corresponds to $2k_{et}$. Such electron transfer also takes place in the case of inorganic one-electron oxidants; $CoTPP^+$ (TPP = tetraphenylporphyrin) and ferrocenium ions.

On the other hand, $(AcrH)_2$ can quench the fluorescence of 9,10-dicyanoanthracene and pyrene as well as the emission of $[Ru(bpy)_3]^{2+*}$ (* denotes the excited state) by electron transfer (Eq. 2 in the case of

$$(AcrH)_2 + [Ru(bpy)_3]^{2+*} \xrightarrow{k_{et}} (AcrH)_2^{+\cdot} + [Ru(bpy)_3]^{+} \qquad (2)$$

$[Ru(bpy)_3]^{2+*}$). The rate constants (k_{et}) for the photoinduced ET reactions of $(AcrH)_2$ were determined by quenching experiments of the fluorescence of the aromatic compounds and luminescence of $[Ru(bpy)_3]^{2+*}$ by $(AcrH)_2$ in MeCN at 298 K as described previously.6,10) The k_{et} values for both thermal and photoinduced ET reactions are listed in Table 1, together with the one-electron reduction potentials (E^0_{red}) of the oxidants.11)

The plot of log k_{et} vs. E^0_{red} in Fig. 1 demonstrates a typical dependence of the rate constant on E^0_{red} for outer-sphere ET reactions; the log k_{et} value increases linearly with an increase in the E^0_{red} value with a slope of 1/(2.3RT) (= 16.9 at 298 K) to reach a diffusion limited value

Table 1. Rate Constants (k_{et}) for Electron Transfer from $(AcrH)_2$ to Various Organic and Inorganic Oxidants in MeCN at 298 K

No.	Oxidant	E^0_{red} *vs.* SCE / V[a)]	k_{et} / $dm^3\ mol^{-1}\ s^{-1}$
1	*p*-bromanil	0.00	2.3
2	*p*-chloranil	0.01	2.4
3	Ph_3C^+	0.21	1.8×10^3
4	TCNQ	0.19	3.8×10^3
5	TCNE	0.22	3.8×10^3
6	2,3-dicyano-*p*-benzoquinone	0.28	1.1×10^4
7	$[Fe(n\text{-}BuC_5H_4)_2]^+$	0.25	2.0×10^4
8	$[Fe(MeC_5H_4)_2]^+$	0.26	2.1×10^4
9	$[Fe(C_5H_5)(n\text{-}BuC_5H_4)]^+$	0.31	8.1×10^4
10	$[Fe(C_5H_5)(t\text{-}AmylC_5H_4)]^+$	0.32	1.1×10^5
11	$CoTPP^+$	0.35	1.8×10^5
12	$[Fe(C_5H_5)_2]^+$	0.37	2.3×10^5
13	$[Fe(C_5H_5)(HgClC_5H_4)]^+$	0.36	2.8×10^5
14	$[Ru(bpy)_3]^{2+}$	0.78	5.3×10^9
15	pyrene	1.23	1.6×10^{10}
16	9,10-Dicyanoanthracene	1.91	2.0×10^{10}

a) Ref. 11.

(k_{et} = 2.0×10^{10} $dm^3\ mol^{-1}\ s^{-1}$). The E^0_{red} value at the intersection of the two broken lines in Fig. 1 corresponds approximately to the one-electron oxidation potential of $(AcrH)_2$ (E^0_{ox} = 0.59 V), which is smaller than that of the corresponding monomer; 10-methyl-9,10-dihydroacridine ($AcrH_2$: E^0_{ox} = 0.80 V).[6)] The k_{et} values for both photoinduced and thermal ET reactions of $(AcrH)_2$ depend solely on the E^0_{red} values, irrespective of the very different size (bulkiness) or type of oxidants including organic and inorganic compounds (Table 1). Thus, the dimer $[(AcrH)_2]$ acts as not only a unique two-electron donor without release of a proton (Eq. 1) but also

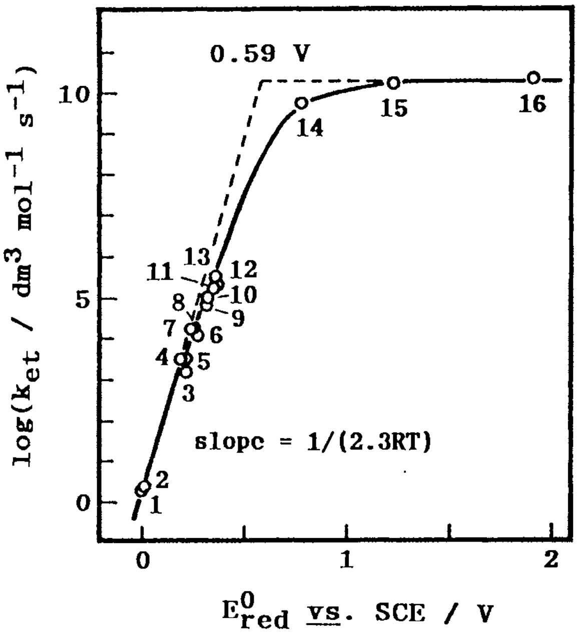


Fig. 1. Plot of log k_{et} *vs.* E^0_{red} for the ET reactions of $(AcrH)_2$ in MeCN at 298 K. The numbers refer to oxidants in Table 1.

a novel outer-sphere ET organic reagent. The outer-sphere mechanism may be only the choice left for the ET reactions of $(AcrH)_2$, since the steric hindrance of the dimer, together with the facile cleavage of the C-C bond upon the one-electron oxidation (Scheme 1) may prevent any specific orbital interaction with oxidants. In contrast, it has well been established that the corresponding monomer ($AcrH_2$) acts as a donor of hydride ion (two electrons and a proton) instead of two electrons.[6,7]

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