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Electron-Transfer Oxidation of 9-Alkylanthracenes and the Decay Kinetics of Radical Cations in Acetonitrile

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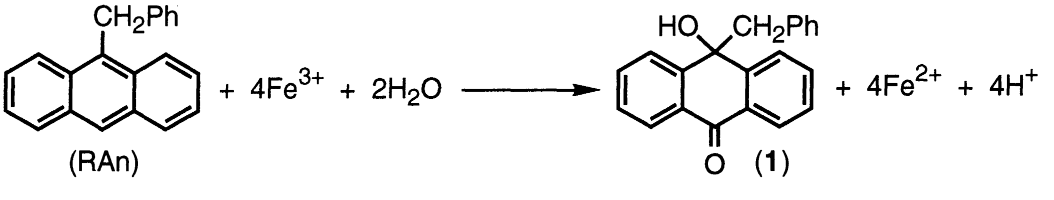
Transient absorption spectra of radical cations of 9-alkylanthracenes ($RAn^{\bullet+}$) formed by the electron-transfer oxidation of 9-alkylanthracenes with $Fe(ClO_4)_3 \cdot 9H_2O$ have been detected by using a stopped flow spectrophotometer. The decay rates of $RAn^{\bullet+}$ obey the second-order kinetics due to the electron-transfer disproportionation reactions, followed by the nucleophilic attack of H_2O on the resulting dications leading to the final ring-oxygenated products.

Electron-transfer oxidation of hydrocarbons has recently attracted considerable interest in view of a drastic change in the reactivity of the radical cations which become much stronger acids, electrophiles, and oxidants than the parent molecules.1-4) For example, the radical cation of toluene has a tremendous acidity ($pKa < -12$)2) and thereby the deprotonation from the alkylbenzene radical cations is the predominant decay process of the radical cations.3) In the case of alkylanthracene radical cations, however, the deprotonation leading to the side chain oxidation has recently been shown to be sluggish relative to nucleophilic attack by nucleophiles leading to the ring oxidation.4) In order to elucidate the reaction mechanism for the ring oxidation it is certainly preferred to analyze the decay kinetics of the radical cations detected directly. To the best of our knowledge, however, there has so far been no report on the direct kinetic analysis of the radical cations, combined with the product analysis.5) This study reports the direct detection of radical cations of 9-alkylanthracenes by $Fe(ClO_4)_3 \cdot 9H_2O$ in acetonitrile (MeCN) and the kinetic analysis of the decay process as well as the characterization of the oxygenated products, providing valuable insight into the mechanistic aspects in radical cation chemistry.

When 9-benzylanthracene (RAn, R = $PhCH_2$) is oxidized by $Fe(ClO_4)_3 \cdot 9H_2O$ in deaerated MeCN, the ring oxidation occurs to yield the four-electron oxidized species, 10-benzyl-10-hydroxy-9(10H)-anthracenone (**1**) as shown in Eq. 1. The product (**1**) was identified by the ^1H NMR spectrum, elemental analysis, and mass spectroscopy.6) The oxidation of other 9-alkylanthracenes (RA; R = Et, Pr^i) by Fe^{3+} also yields the corresponding 10-alkyl-10-hydroxy-9(10H)-anthracenones. Mixing an MeCN solution of $Fe(ClO_4)_3 \cdot 9H_2O$ with RAn (R = Pr^i) in a stopped-flow spectrometer results in an instant appearance of a new absorption band at $\lambda_{max} = 700$ nm due to the radical cation ($RAn^{\bullet+}$)7) as shown in Fig. 1. The decay of the absorbance due to $RAn^{\bullet+}$ (R =



(1)

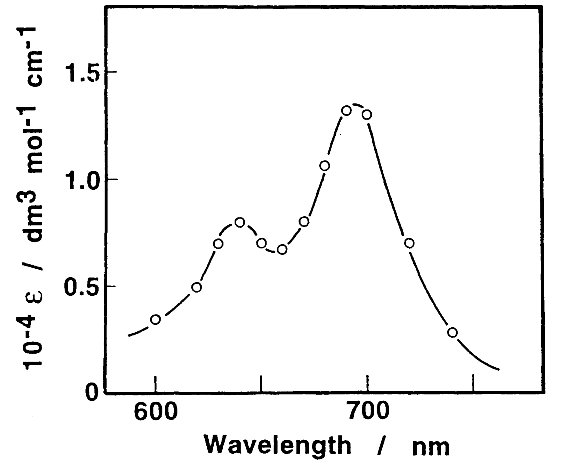


Fig. 1. Transient absorption spectrum of $RAn^{\bullet+}$ (R = Pr^i) formed in the electron-transfer oxidation of RAn by $Fe(ClO_4)_3$ in deaerated MeCN at 298 K.

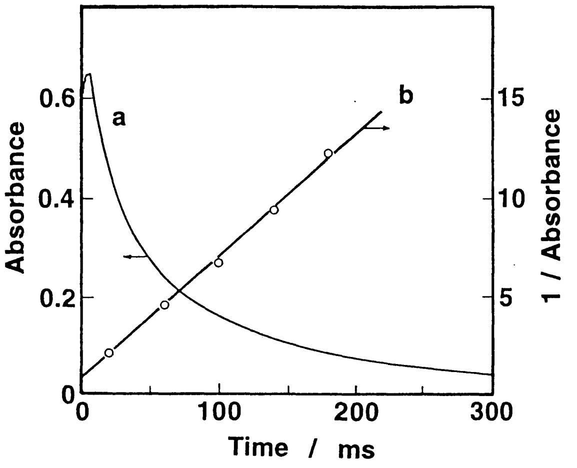


Fig. 2. (a) Decay of the absorbance due to $RAn^{\bullet+}$ (R = $PhCH_2$) formed in the electron-transfer oxidation of RAn (6.25×10^{-4} mol dm^{-3}) by $Fe(ClO_4)_3$ (3.04×10^{-2} mol dm^{-3}) in deaerated MeCN at 298 K, and (b) the second-order decay plot of 1/absorbance vs. time.

$PhCH_2$) at λ_{max} = 720 nm shown in Fig. 2a obeys the second-order kinetics (Eq. 2) as demonstrated by

$$-d[RAn^{\bullet+}]/dt = k_{obsd}[RAn^{\bullet+}]^2 \qquad (2)$$

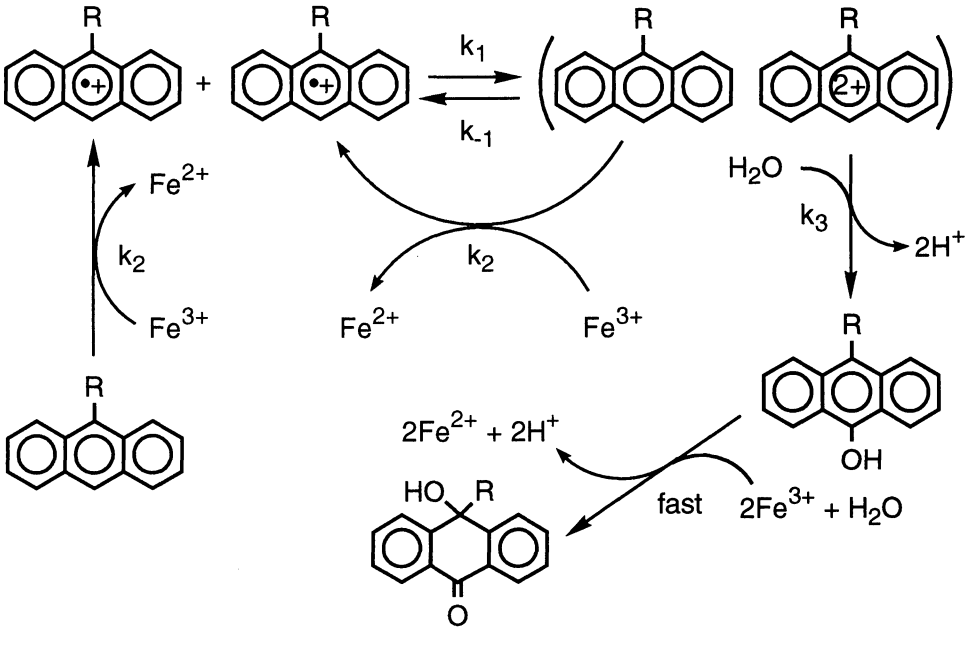
the linear plot of 1/absorbance *vs.* time in Fig. 2b. From the intercept at time = 0 of the linear plot of 1/absorbance *vs.* time is obtained the initial absorbance at 720 nm, which is proportional to the initial concentration of RAn. Thus, the extinction coefficient (ε_{max}) is obtained from the initial absorbance, the initial concentration of RAn, and the optical path length (2 mm). The radical cations of other alkylanthracenes ($RAn^{\bullet+}$; R = Me, Et, $PhCH_2$) are also detected in the reactions of RAn with Fe^{3+}. The absorption maxima (λ_{max}) and the extinction coefficients (ε_{max}) of $RAn^{\bullet+}$ are listed in Table 1, together with the one-electron oxidation potentials (E^0_{ox}) of RAn, which were determined by the fast cyclic voltammetry measurements.[8]

Table 1. The Absorption Maxima (λ_{max}) and Extinction Coefficients (ε_{max}) of 9-Alkylanthracene Radical Cations ($RAn^{\bullet+}$), the One-Electron Oxidation Potentials (E^0_{ox}) of RAn, and the Observed Second-Order Rate Constants (k_{obsd}) for the Decay of $RAn^{\bullet+}$ Generated by Electron-Transfer Oxidation of RAn with $Fe(ClO_4)_3 \cdot 9H_2O$ (3.22×10^{-2} mol dm^{-3}) in Deaerated MeCN at 298 K

RAn	λ_{max}[a] / nm	ε_{max}[b] / dm^3 mol^{-1} cm^{-1}	E^0_{ox} *vs.* SCE / V	k_{obsd}[b] / dm^3 mol^{-1} s^{-1}
R = CH_2Ph	720	1.2×10^5	1.20	1.3×10^5
Pr^i	700	1.3×10^5	1.14	5.2×10^5
Et	700	1.3×10^5	1.14	9.5×10^5
Me	680	1.3×10^5	1.14	3.0×10^6

a) The experimental error is ±10 nm. b) The experimental error is ±10%.

The second-order decay may be ascribed to the disproportionation of two $RAn^{\bullet+}$ molecules to give the corresponding dication (RAn^{2+}) and RAn as shown in Scheme 1. Although the electron transfer between the radical cations may be endergonic,9) the subsequent facile electron transfer from RAn to Fe^{3+} as well as addition of H_2O to RAn^{2+} results in the overall four electron oxidation of RAn to yield 10-alkyl-10-hydroxy-9(10H)-anthracenone (Scheme 1).10) By applying the steady state approximation to the RAn^{2+}-RAn pair in Scheme 1, the observed second-order decay rate constant k_{obsd} is given by Eq. 3. Judging from the initial fast electron transfer from RAn to Fe^{3+}, it is well assumed that $k_2[Fe^{3+}] >> k_3[H_2O]$. In such a case Eq. 3 is rewritten by Eq. 4, which predicts a linear correlation between k_{obsd}^{-1} and $[Fe^{3+}]^{-1}$. In fact, the plot of k_{obsd}^{-1} *vs.* $[Fe^{3+}]$ gives a straight line being in agreement with Eq. 4, as shown in Fig. 3. The deprotonation of $RAn^{\bullet+}$ may be negligible under the present experimental conditions, since no side-oxidation takes place and there is no appreciable contribution of the first-order decay of $RAn^{\bullet+}$. Moreover, the addition of $HClO_4$ (3.9×10^{-2} mol dm^{-3}) to the RAn-Fe^{3+} system resulted in little



Scheme 1.

$$k_{obsd} = \frac{k_1(k_2[Fe^{3+}] + k_3[H_2O])}{k_{-1} + k_2[Fe^{3+}] + k_3[H_2O]} \qquad (3)$$

$$k_{obsd}^{-1} = k_1^{-1}[1 + (k_{-1}k_2[Fe^{3+}])^{-1}] \qquad (4)$$

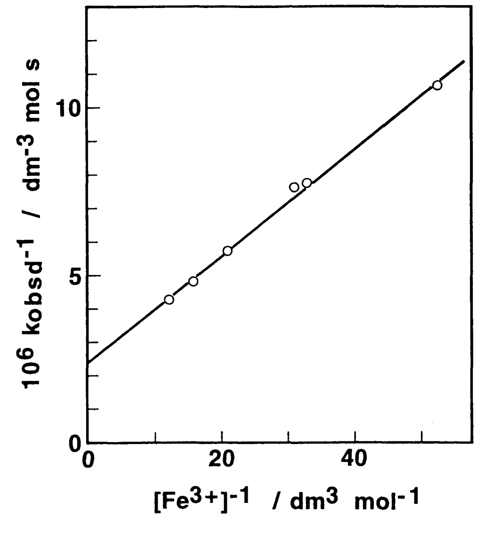


Fig. 3. Plot of k_{obsd}^{-1} *vs.* $[Fe^{3+}]^{-1}$ for the decay of $RAn^{\bullet+}$ (R = $PhCH_2$) formed in the electron-transfer oxidation of RAn (6.25×10^{-4} mol dm^{-3}) by $Fe(ClO_4)_3$ in MeCN at 298 K.

change in the k_{obsd} value. In contrast, the addition of H_2O (0.37 mol dm^{-3}) to the above system resulted in a 35% increase in the k_{obsd} value, being consistent with Eq. 3. Thus, the 9-alkylanthracene radical cation acts as a strong one-electron oxidant, which can accept an electron from the radical cation itself, rather than a strong acid to be deprotonated, in contrast with the case of alkylbenzene radical cation. The electron-transfer disproportionation of $RAn^{\bullet+}$ produces an extremely strong electrophile, *i.e.*, RAn^{2+}, which is subjected to the nucleophilic attack of H_2O, leading to the final ring-oxygenated product (Scheme 1).

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5) The decay kinetics of the arene radical cations has so far been analyzed by indirect electrochemical methods, but the mechanisms remains to be solved; V. D. Parker, *Acta Chem. Scand.*, **B39**, 227 (1985).
6) The isolated yield of **1** was 80%. Found: C, 83.50; H, 5.26%; MS(*m/z*) M^+, 301. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.39%; M, 301. The ^1H NMR measurements were performed using a JNM-GSX-400 NMR spectrometer. **1**: ^1H NMR ($CDCl_3$) δ 2.61 (s, 1H), 3.22 (s, 2H), 6.13 (d, 2H, J = 7.3 Hz), 6.89 (t, 2H, J = 7.5 Hz), 7.04 (t, 1H, J = 7.5 Hz), 7.45 (t, 2H, J = 7.8 Hz), 7.66 (t, 2H, J = 7.8 Hz), 7.90 (d, 2H, J = 7.8 Hz), 8.03 (d, 2H, J = 7.8 Hz).
7) The absorption spectrum of $RAn^{\bullet+}$ in Fig. 1 is essentially the same as that of anthracene radical cation generated by the electrochemical oxidation, photoinduced electron transfer, and γ-irradiation; J. M. Masnovi, J. K. Kochi, E. F. Hilinski, and P. M. Rentzepis, *J. Am. Chem. Soc.*, **108**, 1126 (1986); M. A. Rodgers, *Trans. Faraday Soc.*, **67**, 1029 (1971); T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).
8) The fast cyclic voltammetry measurements were performed on a Fuso Model HECS 972 potentiostat-galvanostat by using the platinum microelectrode (10 μm i.d.) at the sweep rate of 2000 V s^{-1}.
9) The disproportionation equilibrium constant K_1 (= k_1/k_{-1}) of 9,10-diphenylanthracene radical cation has been reported as $10^{-8.1}$ from the difference in the E^0_{ox} values of the anthracene and the radical cation, although the highly irreversible nature of the one-electron oxidation of $RAn^{\bullet+}$ in this study has precluded the determination of the K_1 values; J. O. Howell and R. M. Wightman, *J. Phys. Chem.*, **88**, 3915 (1984).
10) The oxygen in the product may come from crystal water of $Fe(ClO_4)_3 \cdot 9H_2O$, since the reactions were carried out in the absence of oxygen in dehydrated MeCN.

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