Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. Part V.[1] Kinetics of Thermodynamically Unfavourable Electron Transfer Reactions between Cation Radicals and Aromatic Compounds

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The kinetics of the electron transfer reactions between the cation radicals derived from thianthren, dibenzo-*p*-dioxin, and 9,10-diphenylanthracene with anisole and anthracene in acetonitrile and dichloromethane were investigated. The reactions were found to be complex under the conditions employed being either first or second order in cation radical depending upon the radical ion concentration. The pseudo-second-order reactions were inhibited by the presence of unoxidized substrate. In all cases, the reactions were found to be first order in the compound undergoing oxidation. The disproportionation mechanism was ruled out for the second-order segment of all the reactions, except for that between diphenylanthracene cation radical and anisole, on the grounds that the disproportionation equilibrium constants are much too small to account for the reaction rates observed.

A GREAT deal of interest has been shown in the electron transfer reactions of aromatic ions. Most studies have involved aromatic anion radicals and dianions [2,3] although some have been conducted on aromatic cation radicals.[3,4] The mechanisms of these reactions are generally formulated as simple bimolecular exchange reactions although certain reactions involving dianions and aromatic compounds have been shown to involve initial adduct formation followed by dissociation.[5]

A common feature of the previous work [2-5] is that the reactions studied have been in the direction favoured by equilibrium as in (1) when ΔG° has a negative value. If π_2^+ undergoes an irreversible reaction (2) for which the rate constant (k_2) is known, the overall rate constant can be predicted providing the equilibrium constant for (1) is known. Thus, a system following (1) and (2) can be

$$\pi_1^+ + \pi_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \pi_1 + \pi_2^+ \qquad (1)$$

$$\pi_2^+ + \mathrm{R} \xrightarrow{k_2} \text{products} \qquad (2)$$

studied even though equilibrium (1) is unfavourable.

Here we report a kinetic study of several reactions which involve the oxidation of an aromatic compound to a reactive cation radical by a stable cation radical. These

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[1] (*a*) Part I, U. Svanholm, A. Ronlán, and V. D. Parker, *J. Amer. Chem. Soc.*, 1974, **96**, 5108; (*b*) Part II, U. Svanholm, O. Hammerich, and V. D. Parker, *ibid.*, 1975, **97**, 101; (*c*) Part III, U. Svanholm and V. D. Parker, *ibid.*, 1976, **98**, 997; (*d*) Part IV, *idem.*, *ibid.*, p. 2942.

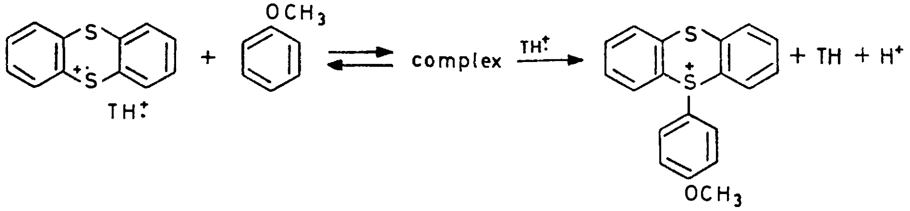
[2] M. Szwarc, *Accounts Chem. Res.*, 1972, **5**, 169.

[3] L. M. Dorfman, *Accounts Chem. Res.*, 1970, **3**, 224.

[4] B. A. Kowert, L. S. Marcoux, and A. J. Bard, *J. Amer. Chem. Soc.*, 1972, **94**, 5538.

[5] J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, 1969, **91**, 7594.

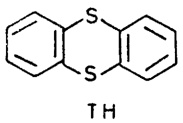
studies revealed that when equilibrium (1) lies far to the left, the simple mechanism (1) and (2) usually does not account for the reactions but instead a more complex mechanism is operative which is characterized by a rate law second order in the stable cation radical. The kinetics closely resemble those observed during the anisylation of the thianthren cation radical [reaction (3)].[1b]



(3)

RESULTS

Two solvents were used in the study of the electron transfer reactions, dichloromethane and acetonitrile. The cation radicals of TH, DBO, or DPA were not stable in either of the solvents which had been purified by standard techniques.* However, the inclusion of trifluoroacetic acid anhydride (TFAn) a very effective nucleophile scavenger, in low concentration (1%) rendered the solvents sufficiently free from nucleophiles so that stable solutions of all three radical ions could be prepared in either of the solvents.[9]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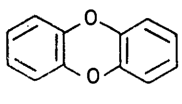
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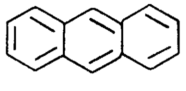
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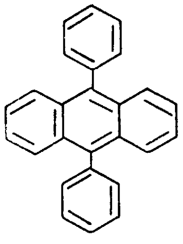
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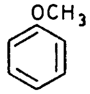
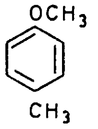


AN



MAN

Thermodynamic Data for the Electron Transfer Reactions.—It has recently been shown that voltammetric data gathered at solid electrodes in aprotic solvents give reliable estimates of $\Delta E°$ values and equilibrium constants for electron transfer reactions between aromatic compounds and aromatic cation radicals.[10] Voltammetric data and the corresponding disproportionation equilibrium constants for the aromatic compounds in both solvents are summarized in Table 1 and equilibrium constants for the electron transfer reactions are gathered in Table 2.

Method for measuring Reaction Rates and the Treatment of Kinetic Data.—The kinetic method used has been described for the pyridination of DPA$^{+\cdot}$.[11] The procedure involved monitoring the decrease in radical ion concentration at the rotating disc electrode (r.d.e.). The stable cation radical was first prepared by anodic oxidation of the aromatic

TABLE 1

Voltammetric data for the oxidation of aromatic compounds

	E_{P_1}		E_{P_2}		K_{disp}	
Compound	*a*	*b*	*a*	*b*	*a*	*b*
DBO	1.45	1.32	2.31	2.02	$10^{-14.6}$	$10^{-11.9}$
			2.45[c]	2.10[d]	10^{-17}	$10^{-13.2}$
TH	1.28	1.16	1.86	1.68	$10^{-9.8}$	$10^{-8.8}$
DPA	1.20	1.14	1.86	1.59	$10^{-11.2}$	$10^{-7.6}$
			1.80[e]		$10^{-10.2}$	
A	1.31	1.17				
	1.31[c]	1.19[d]				
	1.29[e]					
AN	1.80	1.69				
MAN	1.64					

[a] CH_2Cl_2–TFA–TFAn (97 : 2 : 1). Supporting electrolyte $Bu^n{}_4NBF_4$ (0.2M). [b] MeCN–TFAn (99 : 1). Supporting electrolyte $NaClO_4$ (0.1M). [c] CH_2Cl_2–TFA–TFAn (94 : 5 : 1). [d] MeCN–TFA–TFAn (94 : 5 : 1). [e] CH_2Cl_2–TFAn (99 : 1). All potentials are oxidation peak potentials and are given in V *vs.* s.c.e. Voltage sweep rate 100 mV s^{-1}. All measurements were made at 11 °C.

TABLE 2

Apparent equilibrium constants for electron transfer reactions

	K	
Reaction	*a*	*b*
$DBO^+ + AN \rightleftharpoons DBO + AN^+$	$10^{-5.9}$	$10^{-6.3}$
$DPA^+ + AN \rightleftharpoons DPA + AN^+$	$10^{-10.2}$ [c]	$10^{-9.3}$
$DPA^+ + MAN \rightleftharpoons DPA + MAN^+$	$10^{-7.5}$ [c]	
$DPA^+ + A \rightleftharpoons DPA + A^+$	$10^{-1.5}$ [c]	$10^{-2.5}$
$TH^+ + AN \rightleftharpoons TH + AN^+$	$10^{-8.8}$	10^{-9}
$TH^+ + A \rightleftharpoons TH + A^+$		$10^{-0.5}$ [d]

[a] CH_2Cl_2–TFA–TFAn (97 : 2 : 1). Supporting electrolyte $Bu^n{}_4NBF_4$ (0.2M). [b] MeCN–TFAn (99 : 1). Supporting electrolyte $NaClO_4$ (0.1M). [c] CH_2Cl_2–TFAn (99 : 1). [d] MeCN–TFA–TFAn (94 : 5 : 1).

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* Some clarification is necessary regarding the stability of cation radicals in aprotic solvents. A number of papers have appeared describing reversible cyclic voltammetry in aprotic solvents such as acetonitrile,[6] nitrobenzene,[7] and methylene chloride.[8] What is necessary to appreciate are the differences in time scales involved in cyclic voltammetry and kinetic measurements such as those described here. Our experiments required that the ions have half-lives of several minutes and preferably longer while reversible cyclic voltammograms may be obtained from species having half-lives of a second or less.

[6] M. E. Peover and B. S. White, *J. Electroanalyt. Chem.*, 1967, **13**, 93.

[7] L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 5766.

[8] J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, 1967, **89**, 1752.

[9] The stabilizing effect of TFAn has recently been discussed, see O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

[10] (*a*) U. Svanholm and V. D. Parker, *J.C.S. Perkin II*, 1973, 1594; (*b*) U. Svanholm, B. Svensmark Jensen, and V. D. Parker, *ibid.*, 1974, 907.

[11] U. Svanholm and V. D. Parker, *Acta Chem. Scand.*, 1973, **27**, 1454. This technique is readily applied to reactions having a half-life of a few seconds or less. The reactions reported here were all slower having half-lives >1 min.

compound. The concentration of π_1^+ was monitored at a fixed potential *ca.* 200 mV more negative than necessary to reduce the cation radical. In general the reactions were followed for several half-lives.

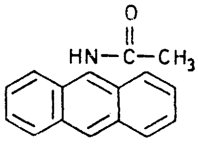
The limitations of the method were evaluated as follows. It was first necessary to determine the response time of the recorder. A Watanabe *X–Y* recorder was used and the response was determined by switching between two different potentials imposed upon the recorder, one corresponding to zero deflection and the other to full scale deflection. In this manner the time required for full scale deflection was determined to be *ca.* 0.4 s. The mixing time for a reactant injected by syringe into the cell was determined by injecting a solution of TH and recording the oxidation current at the r.d.e. which was held at a potential *ca.* 200 mV more positive than necessary to oxidize TH. The mixing times were taken to be the time necessary for the r.d.e. current to reach a constant value after the injection of TH. At small scale deflections an apparent mixing time of *ca.* 0.15 s was observed and this value increased to *ca.* 0.4 s for larger deflections. The latter led to the conclusion that the actual mixing times are <0.2 s and that the response of the recorder makes the apparent mixing time increase at higher scale deflections.

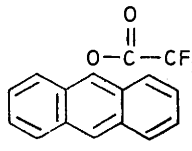
The data, r.d.e. reduction current *vs.* time were first plotted according to a pseudo-first-order reaction, *i.e.* log ($i_{\text{r.d.e.}}$) *vs.* time. In all but special circumstances, substantial curvature was observed indicating that the order in cation radical was greater than unity. R.d.e. reduction currents were then converted to concentrations of cation radical and plotted as pseudo-second-order reactions, *i.e.* $1/[\pi_1^+]$ *vs.* time. The rate plots were usually linear for more than two half-lives. To further insure that the reactions were indeed second order in $[\pi_1^+]$, initial $[\pi_1^+]$ were varied over as wide a range as practical.

The rate constants obtained from plots of $1/[\pi_1^+]$ or log ($i_{\text{r.d.e.}}$) *vs.* time are referred to as k''_{obs} and k'_{obs}, respectively. The value of k''_{obs} generally decreased with increasing $[\pi_1]$ and decreasing $[\pi_2]$ when both π_1 and π_2 were present in sufficient excess so as not to change significantly during reaction. The values of k_{obs} were then converted to k_{app} values independent of $[\pi_1]$ and $[\pi_2]$ by standard procedures. For the pseudo-second-order reactions, plots of $1/k''_{\text{obs}}$ *vs.* $[\pi_1]$ (at constant $[\pi_2]$) gave the dependence on $[\pi_1]$ and log k''_{obs} *vs.* log $[\pi_2]$ (at constant $[\pi_1]$) gave the dependence on $[\pi_2]$. From the observation of pseudo-second-order kinetics, and the $[\pi_1]$ and $[\pi_2]$ dependencies, the form of the rate law was established. The reactions were all observed to be first order in $[\pi_2]$. Thus, the relationship between k''_{obs} and k''_{app} is given by (4) where the constant C was evaluated from the plot of $1/k''_{\text{obs}}$ *vs.* $[\pi_1]$.

$$k''_{\text{obs}} = k''_{\text{app}}\,[\pi_2]/(\mathrm{C} + [\pi_1]) \qquad (4)$$

Products from Oxidation of Aromatic Compounds.—Two substrates were chosen which give reactive cation radicals. Anthracene (A) gives a cation radical which reacts with the solvent to give AAA when generated in MeCN–TFA [12] and TA when generated in CH_2Cl_2–TFA.[13] The pseudo-first-order rate constant for the reaction of A^+ with MeCN has been determined as 125 s^{-1} at 11 °C.[12] TA did not survive the work-up procedure and 9-anthrone was the isolated product. This was readily shown by matching cyclic voltammograms of TA prepared by oxidation of A in the presence of sodium trifluoroacetate [13] with those obtained after oxidation of A with the stable cation radicals. The isolated product, 9-anthrone, is not electroactive in the potential range accessible in these solvents.


AAA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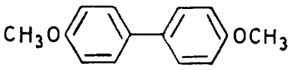
DMB

The cation radical of AN is far more reactive than that of A. In CH_2Cl_2–TFA, it rapidly dimerizes to 4,4′-dimethoxybiphenyl (DMB), which undergoes further electron transfer to the stable cation radical.[14] DMB^+ is readily identified by cyclic voltammetry and its visible absorption spectrum. In acetonitrile, AN^+ does not form the dimer. The products are unknown but most likely result from reactions of AN^+ with solvent. Pseudo-first-order rate constants for the reactions of AN^+ in MeCN are apparently $>10^3$ s^{-1}, out of the range accessible to study by r.d.e. voltammetry.

Reactions of DBO^+ with AN.—The reactions of DBO^+ with AN in both MeCN and CH_2Cl_2 were accompanied by the quantitative regeneration of DBO as shown by the magnitude of the limiting current for oxidation of DBO at the rotating disc electrode after the reaction. The reaction of DBO^+ with AN in CH_2Cl_2 resulted in the formation of DMB according to the expected stoicheiometry ($3\,DBO^+ + 2\,AN \longrightarrow 3\,DBO + DMB^+ + 2\,H^+$). The latter was shown by comparing cyclic voltammograms of solutions after reaction with those from mixtures of authentic DMB and DBO. The products from the reaction of DBO^+ with AN in MeCN were not identified; AN^+ apparently undergoes several competing reactions in that solvent.

Kinetic data for the reaction between DBO^+ and AN in both solvents are summarized in Table 3 (second order in DBO^+, $[DBO^+]$ *ca.* 5×10^{-4}M) and Table 4 (first order in DBO^+, $[DBO^+]$ *ca.* 10^{-5}M). Both first- and second-order data are illustrated by the rate plots in Figure 1.

A plot of log k''_{obs} (in CH_2Cl_2) *vs.* log [AN] was linear with unit slope showing that the reaction is first order in [AN] (Figure 2). A plot of $1/k''_{\text{obs}}$ (Table 3) *vs.* $[DBO]_0$ at a constant anisole concentration resulted in equation (5) for the second-order rate constant, k''_{app}, in CH_2Cl_2. The dependence of $1/k''_{\text{obs}}$ on $[DBO]_0$ was obtained at two different [AN] values, 1.84×10^{-2}M (runs 1—7) and 18.4×10^{-2}M (runs 14—20). The data are plotted in Figure 3 for both sets of experiments.

$$k''_{\text{app}} = k''_{\text{obs}}\,[\mathrm{DBO}/[\mathrm{AN}] \qquad (5)$$

Sufficient data were not gathered in MeCN to establish

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[12] O. Hammerich and V. D. Parker, *J.C.S. Chem. Comm.*, 1974, 245.

[13] U. Svanholm and V. D. Parker, unpublished work. Details of trifluoroacetoxylation reactions of aromatic compounds will appear later.

[14] A. Ronlán, K. Bechgaard, and V. D. Parker, *Acta Chem. Scand.*, 1973, **27**, 2375.

definitely the order in [AN] and [DBO] but reasonably constant values of k''_{app} (Table 3) were observed by assuming first order in [AN] and inverse order in [DBO].

TABLE 3

Pseudo-second-order electron transfer reaction between DBO^+ and AN

Run no.	10^4[DBO]/ M	$10^4[DBO^+]$/ M	10^3[AN]/ M	k_{obs}/ l mol^{-1} s^{-1}	k_{app}/ l mol^{-1} s^{-1} [a]
1	5.0	4.57	1.84	6.44	0.175
2	7.0	2.22	1.84	4.37	0.166
3	17.4	2.61	1.84	1.88	0.178
4	12.2	2.74	1.84	2.55	0.169
5	27.1	2.87	1.84	1.24	0.183
6	26.8	3.13	1.84	1.16	0.169
7	22.0	3.0	1.84	1.56	0.187
8	21.8	3.13	3.68	3.41	0.202
9	22.0	3.0	5.52	4.96	0.198
10	18.6	6.37	5.52	5.06	0.171
11	23.6	1.34	5.52	4.47	0.191
12	24.3	6.52	5.52	4.88	0.215
13	21.7	3.26	9.20	9.19	0.217
14	19.3	4.11	18.4	20.2	0.212
15	4.67	4.55	18.4	75.1	0.191
16	9.11	4.96	18.4	38.7	0.191
17	14.0	4.96	18.4	24.8	0.189
18	20.0	4.68	18.4	17.3	0.189
19	24.6	4.68	18.4	15.1	0.202
20	24.8	4.82	18.4	13.7	0.185
21	20.0	3.66	46.0	46.3	0.202
22 [b]	4.25	5.75	18.4	1.08	2.5×10^{-3}
23 [c]	4.92	5.08	27.6	0.244	4.4×10^{-4}
24	7.02	2.02	1.84	29.3	1.88
25	8.53	1.05	1.84	48.8	2.26
26	17.7	2.32	1.84	23.6	2.27
27	7.16	2.11	0.92	24.2	1.89

Runs 1—23: CH_2Cl_2–TFA–TFAn (97 : 2 : 1), supporting electrolyte $Bu^n_4NBF_4$ (0.1M). Runs 24—27: MeCN–TFAn (99 : 1), supporting electrolyte $NaClO_4$ (0.1M). Temperature: 11 °C.

[a] $k''_{app} = k''_{obs}[DBO]_0/[AN]$. [b] Temperature −30 °C. [c] Temperature −55 °C.

TABLE 4

Pseudo-first-order electron transfer reaction between DBO^+ and AN

Run no.	10^4[DBO]/ M	$10^5[DBO^+]$/ M	10^2[AN]/ M	$10^3k'_{obs}$/ s^{-1}	$10^2k'_{app}$/ s^{-1} [a]
28	10	1.88	9.2	1.09	1.18
29	10	0.81	9.2	1.09	1.18
30	10	0.64	9.2	1.05	1.14
31	10	0.49	9.2	1.28	1.39
32	10	0.54	18.4	2.57	1.40
33	10	0.68	4.6	0.68	1.48
34	20	0.58	9.2	1.05	1.14
35	5	0.70	9.2	1.48	1.61
36	100	0.75	9.2	1.60	1.74
37	10	0.82	9.2	1.25	1.36

Solvent: CH_2Cl_2–TFA–TFAn (97 : 2 : 1). Supporting electrolyte $Bu^n_4NBF_4$ (0.1M). Temperature 11 °C.

[a] $k'_{app} = k'_{obs}/[AN]$.

The effect of temperature on the rate of the reaction between DBO^+ and AN in CH_2Cl_2 was examined briefly (runs 1—22 and 33). The slope of a plot of log k_{app} *vs.* $1/T$ was found to be equal to -2.58×10^{-3} which corresponds to $\Delta H^\ddagger$ 11.2 kcal mol^{-1}.

The reaction of DBO^+ with AN in CH_2Cl_2 at radical ion concentrations < *ca.* 10^{-5}M gave good pseudo-first-order rate plots (Figure 1b). The rate was found to be indepen-

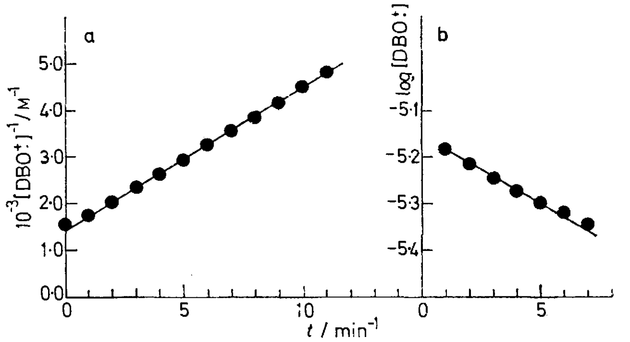

FIGURE 1 a, Rate plot for the pseudo-second-order electron transfer reaction between DBO^+ and AN ($[DBO^+]_0 = 6.4 \times 10^{-4}$M, $[DBO]_0 = 1.9 \times 10^{-3}$M, $[AN]_0 = 5.5 \times 10^{-2}$M); b, rate plot for the pseudo-first-order electron transfer reaction between DBO^+ and AN [$(DBO^+]_0 = 8.2 \times 10^{-6}$M, $[AN]_0 = 9.2 \times 10^{-2}$M). CH_2Cl_2–TFA–TFAn (97 : 2 : 1), $Bu^n_4NBF_4$ = 0.1M, Temperature 11 °C

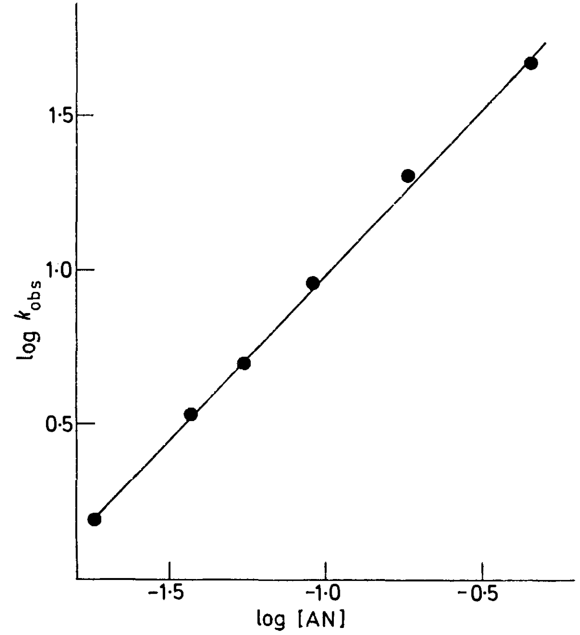

FIGURE 2 Dependence of k''_{obs} on $[AN]_0$ for the pseudo-second-order electron transfer reaction between DBO^+ and AN in CH_2Cl_2–TFA–TFAn (97 : 2 : 1) at 11 °C. $[DBO]_0$ = 2.0—2.2 × 10^{-3}M (runs 7—9, 13, 18, 21)

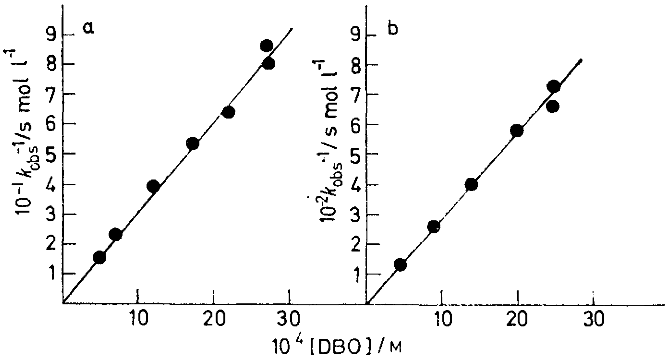

FIGURE 3 Plots of $1/k''_{obs}$ *vs.* $[DBO]_0$ for the pseudo-second-order electron transfer reaction of DBO^+ with AN: a, $[AN]_0 = 1.84 \times 10^{-2}$M; b, [AN] = 18.4×10^{-2}M

dent of [DBO] (runs 28—36) and directly proportional to [AN] (runs 28—37). The data are summarized in Table 4.

Reactions of TH^+ with Aromatic Compounds.—The reaction of TH^+ with anisole to produce a sulphonium salt [equation (1)] was first described by Silber and Shine[15] and studied in detail in our laboratory.[1b]

The product of the reaction of TH^+ with A in MeCN–TFA (95 : 5) was identified by comparison of the cyclic voltammograms of solutions after reaction with solutions of AAA.

The yield of the amide was estimated to be nearly quantitative based on the expected stoicheiometry; $2TH^+ + A + H_2O \longrightarrow 2TH + AAA + 2H^+$ Kinetic data for the reaction in the same solvent are presented in Table 5.

TABLE 5

Pseudo-first-order electron transfer reaction between DPA^+ and AN

Run no.	10^3[TH]/ M	$10^6[TH^+]$/ M	10^5[A]/ M	$10^{-4}k''_{obs}$/ l mol^{-1} s^{-1}	$10^{-6}k''_{app}$/ l mol^{-1} s^{-1}
44	5	7.33	5	3.9	3.9
45	10	9.07	5	1.5	3.0
46	2.5	8.0	5	7.0	3.5
47	10	16.9	5	1.2	2.4
48	10	14.7	5	1.5	3.0
49	10	7.69	10	3.1	3.1

Temperature 11 °C. MeCN–TFA (95 : 5), supporting electrolyte $NaClO_4$ (0.1M).

[a] $k''_{app} = k''_{obs}[TH]_0/[A]$.

Although $[TH]_0$ was varied over only a small range, the plot of $1/k_{obs}$ *vs.* $[TH]_0$ is significant. An intercept (runs 44—48) $< 10^{-5}$ was observed. Since $[TH]_0$ was varied from 2.5 to 10×10^{-3}M, the reaction rate was observed to be inversely proportional to that concentration.

Reactions between DPA^+ and Aromatic Compounds.—Products of the reactions of AN^+ in CH_2Cl_2 and A^+ in both CH_2Cl_2 and MeCN produced by electron transfer to DPA^+ were shown to be DMB, TA, and AAA by a combination of cyclic voltammetric and visible spectral measurements on the solutions after reaction. Exact yields were not determined but estimated yields were in all cases >75%.

Kinetic results showed that the reaction between DPA^+ and AN follow both a first- and a second-order rate law, the importance of which can be adjusted by varying the concentration of DPA^+.* Data in both solvent systems are summarized in Tables 6 (pseudo-second-order runs) and 7 (pseudo-first-order runs). The data are limited (Table 6) for the intercept analysis, but a plot of $1/k''_{obs}$ *vs.* $[DPA]_0$ passes very near the origin. However, $[DPA]_0$ was necessarily small in order to give a reasonably fast reaction rate and thus the apparent intercept of zero cannot be taken to be significant. The k''_{app} values were calculated assuming first order in [AN] and inverse order in [DPA]. The reaction first order in $[DPA^+]$ was found to be independent of $[DPA]_0$ and first order in [AN]. Pseudo-first-order rate constants for the reaction in MeCN were of the order of 10^2 greater than the corresponding values in CH_2Cl_2.

Conditions were not found for the reaction between DPA^+ and A which produced data solely due to either the first- or the second-order reaction pathway and the data gathered are not tabulated. However, in CH_2Cl_2–TFAn (99 : 1) second-order conditions were approached at $[DPA^+]_0$ equal to 5.0×10^{-5}M (k''_{app} 1.5×10^4 l mol^{-1} s^{-1} at 11 °C). At higher cation radical concentrations the reaction was too fast to follow by the technique used.

TABLE 6

Pseudo-second-order electron transfer reaction between DPA^+ and AN

Run no.	10^4[DPA]/ M	$10^4[DPA^+]$/ M	[AN]/ M	k''_{obs}/ l mol^{-1} s^{-1}	$10^4k''_{app}$/ l mol^{-1} s^{-1} [a]
50	4.96	7.63	0.46	0.311	3.35
51	2.46	3.02	0.46	0.685	3.87
52	10.2	7.18	0.46	0.158	3.50

CH_2Cl_2–TFAn (99 : 1), supporting electrolyte $Bu^n_4NBF_4$ (0.1M). Temperature 11 °C.

[a] $k''_{app} = k''_{obs}[DPA]_0/[AN]$.

TABLE 7

Pseudo-second-order electron transfer reaction between TH^+ and A

Run no.	10^4[DPA]/ M	$10^4[DPA^+]$/ M	[AN]/ M	$10^5k'_{obs}$/ s^{-1}	$10^4k'_{app}$/ s^{-1} [a]
53	5.04	0.65	0.46	7.79	1.69
54	4.89	0.88	0.46	6.67	1.45
55	4.20	0.34	0.46	6.19	1.35
56	4.96	0.76	0.92	14.3	1.55
57	9.85	0.92	0.92	12.4	1.35
58	2.52	0.84	0.46	7.00	1.52
50	5.11	0.84	0.46	7.00	1.52
60	2.52	0.76	0.46	7.14	1.55
61	2.31	2.19	0.092	132	143
62	2.44	1.09	0.092	109	118
63	1.98	0.58	0.092	125	136

Temperature 11 °C. Runs 53—60: CH_2Cl_2–TFAn (99 : 1), supporting electrolyte: $Bu^n_4NBF_4$ (0.1M). Runs 61—63: MeCN–TFAn (99 : 1), supporting electrolyte $NaClO_4$ (0.1M).

[a] $k'_{app} = k'_{obs}/[AN]$.

DISCUSSION

The reversible electron transfer reaction (1) of the stable cation radical π_1^+ with an aromatic compound (π_2) to give the reactive cation radical (π_2^+) follows rate law (6) which was derived by applying a combination of equilibrium and steady state approximations[17] assuming that the net rate of change of (π_2^+) is zero. If k_2[R] is small compared to $k_{-1}[\pi_1]$, (6) reduces to (7). In any

$$-d[\pi_1^+]/dt = k_1k_2[\pi_1^+][\pi_2][R]/(k_{-1}[\pi_1] + k_2[R]) \quad (6)$$

$$-d[\pi_1^+]/dt = k_2K_1[\pi_1^+][\pi_2][R]/[\pi_1] \quad (7)$$

case, the rate of the reaction is expected to be directly proportional to $[\pi_1^+]$ as long as $[\pi_2]$, $[\pi_1]$, and [R] do not

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* These data demonstrate the advantage of using the r.d.e. for following the kinetics of radical ion reactions.[11] While it is possible to analyse complex data from simultaneous first- and second-order reactions,[16] a much more satisfactory procedure is to separate the two reaction pathways by adjustment of the radical ion concentration. Using the r.d.e., the concentration range of radical ion can be adjusted by a factor of the order of 10^4. Concentration ranges greater than a factor of *ca.* 10 are usually the practical limit for following reactions by absorption spectroscopy.

[15] J. J. Silber and H. J. Shine, *J. Org. Chem.*, 1971, **36**, 2923.

[16] A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, 1973, **95**, 659.

[17] (*a*) A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, 2nd edn., p. 195; (*b*) H. S. Johnston, 'Gas Phase Reaction Rate Theory,' Ronald Press, New York, 1966, pp. 298 and 332; (*c*) C. W. Pyun, *J. Chem. Educ.*, 1971, **48**, 195.

change significantly during the reaction, *i.e.* pseudo-first-order conditions. Thus, the observation of pseudo-second-order kinetics for the reactions studied here immediately indicates that equations (1) and (2) do not account for the major reaction taking place under the conditions employed. The fact that pseudo-first-order kinetics could be observed by going to very low cation radical concentrations indicates that (1) and (2) may be operative under those conditions. What is apparent from this study is that the thermodynamically unfavourable equilibria (1) allow for another electron transfer mechanism to take place, *i.e.* one which is second order in cation radical.

The reaction studied most extensively was that of DBO$^+$ and AN. At [DBO$^+$] $>10^{-4}$M (Table 3), the reaction was found to be second order in cation radical but became first order at concentrations *ca.* 10^{-5}M (Table 4). Under pseudo-second-order conditions, the reaction was observed to be first order in [AN] and inverse first order in [DBO], *i.e.* log plots of k_{obs} *vs.* [AN] had unit slope and plots of $1/k_{\text{obs}}$ *vs.* [DBO] gave intercepts equal to zero. Thus, the rate law can be written as (8).

$$-\mathrm{d}[\mathrm{DBO}^+]/\mathrm{d}t = k''_{\text{obs}}[\mathrm{DBO}^+]^2[\mathrm{AN}]/[\mathrm{DBO}] \quad (8)$$

The products of the reaction were established to be DBO and DMB$^+$, the latter arising from the dimerization of AN$^+$. The observation of the anisole cation radical dimer as the product of the reaction following electron transfer allows us to make a conclusion important in arriving at the overall mechanism of the reaction. If the dimerization of AN$^+$ was the rate-determining step, the reaction would be second order in AN. The fact that the reaction is clearly first order in [AN] conclusively shows that the dimerization is preceded by a slower rate-determining step.

Two mechanisms can be written which follow rate law (8). The disproportionation mechanism (9) and (10) is consistent with (8) as long as (9) is a fast equilibrium and if (10) lies very far to the right, *i.e.* is essentially irreversible.

$$2\ (\pi_1{}^+) \rightleftharpoons \pi_1{}^{2+} + \pi_1 \quad (9)$$

$$\pi_1{}^{2+} + \pi_2 \rightleftharpoons \pi_1{}^+ + \pi_2{}^+ \quad (10)$$

The other mechanism that fits the rate law is similar to the mechanism recently proposed for the anisylation of TH$^+$ (3). Two rapid equilibria (11) and (12) involving complexation of the aromatic ion and aromatic compound,[18] followed by electron transfer to a second aromatic ion to give the dication complex which dissociates to two aromatic ions [reaction (13)] precede the product-forming reactions (14) of $\pi_2{}^+$. The equilibrium and steady state approximations [17] assuming the net rate of change of [$\pi_2{}^+$] is zero leads to the rate equation (15). The rate law can be reduced to (16) by assuming the term $k_{-13}[\pi_1{}^+]$ is negligible compared with k_{14}. This seems to be a reasonable assumption since (13) would be expected to lie far to the right and [$\pi_1{}^+$] in this work was generally *ca.* 10^{-4}M.

$$\pi_1{}^+ + \pi_2 \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} (\pi_1/\pi_2)^+ \quad (11)$$

$$(\pi_1/\pi_2)^+ + \pi_1{}^+ \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} (\pi_1/\pi_2)^{2+} + \pi_1 \quad (12)$$

$$(\pi_1/\pi_2)^{2+} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} \pi_1{}^+ + \pi_2{}^+ \quad (13)$$

$$\pi_2{}^+ \xrightarrow{k_{14}} \text{Products} \quad (14)$$

$$-\mathrm{d}[\pi_1{}^+]/\mathrm{d}t = \frac{2\ k_{14}k_{13}K_{11}K_{12}[\pi_1{}^+]^2[\pi_2]}{[\pi_1](k_{14} + k^{-}{}_{13}[\pi_1{}^+])} \quad (15)$$

$$-\mathrm{d}[\pi_1{}^+]/\mathrm{d}t = 2\ k_{13}K_{11}K_{12}[\pi_1{}^+]^2[\pi_2]/[\pi_1] \quad (16)$$

A comparison of the observed pseudo-second-order rate constant for the reaction of DBO$^+$ with AN with the maximum possible value, assuming a diffusion controlled reaction of DBO^{2+}, according to the disproportionation mechanism [19] (Table 1) allows us to eliminate that mechanism. The disproportionation mechanism (9) + (10) assuming fast equilibrium (9) leads to rate law (17).[20,21] The rate constant (k_{10}) can be related to k''_{app} by (18).

$$-\mathrm{d}[\pi_1{}^+]/\mathrm{d}t = 2\ k_{10}K_{\text{disp}}[\pi_1{}^+]^2[\pi_2]/[\pi_1] \quad (17)$$

$$k_{10} = k_{\text{obs}}[\pi_1 1/2\ K_{\text{disp}}[\pi_2] = k_{\text{app}}/2\ K_{\text{disp}} \quad (18)$$

The value of K_{disp} in CH_2Cl_2–TFA–TFAn (97 : 2 : 1) is *ca.* 10^{-15} (Table 1) while k''_{app} under the same conditions is equal to 0.2 l mol^{-1} s^{-1}. Using these values in (18) leads to a value of 10^{14} for k_{10}, a factor of *ca.* 10^4 greater than a diffusion controlled second-order rate constant.

The rate law derived for the complexation mechanism reduces to the observed rate law (8) by substituting (19) in (16).

$$k''_{\text{app}} = 2\ k_{13}K_{11}K_{12} \quad (19)$$

Although similar to the rate law observed during the anisylation of TH$^+$, which was assigned the complexation mechanism,[1b] an important difference exists between (16) and (20).

$$-\mathrm{d}[\mathrm{TH}^+]/\mathrm{d}t = k''_{\text{app}}[\mathrm{TH}^+]^2[\mathrm{AN}]/(\text{constant} + [\mathrm{TH}]) \quad (20)$$

The constant in the denominator of (20), which was evaluated by the intercept on the $1/k''_{\text{obs}}$ *vs.* [TH] plot, brings about a considerable deviation from inverse first order in [TH]. In the case of the pseudo-second-order reaction between DBO$^+$ and AN, the intercept on the plot of $1/k''_{\text{obs}}$ *vs.* [DBO] was found to be zero within the limits of experimental error. Since the absence of an intercept has very strong bearing upon the acceptability of the complexation mechanism (11)—(14), the effect of [DBO] on k''_{obs} for the reaction of DBO$^+$ with AN was investigated particularly carefully.

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[18] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43**, 2712.

[19] V. D. Parker, *J. Electroanalyt. Chem.*, 1972, **36**, App. 8.

[20] L. S. Marcoux, *J. Amer. Chem. Soc.*, 1971, **93**, 471.

[21] (*a*) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, 1969, **91**, 1872; (*b*) Y. Murata and H. J. Shine, *J. Org. Chem.*, 1969, **34**, 3368.

Two sets of experiments were conducted at different [AN]. In both cases the intercept was exceedingly small, equal to zero within experimental error. The fact that the complexation mechanism gives two different rate laws for the two reactions, TH^+ with AN and DBO^+ with AN, and that these rate laws (16) and (20) are consistent with those observed, gives strong support to those mechanisms. The essential difference between the complexation and disproportionation mechanisms is that in the latter there is not time for π_1^{2+} to find π_2 after it is formed, *i.e.* π_2 must be associated with nascent π_1^{2+}.

Pseudo-first-order kinetics were also observed for reactions of DBO^+ and DPA^+ with AN. Since the product forming reaction of AN^+ is dimerization, the steady state approximation, applied to the simple electron transfer mechanism for the specific case DNO^+ + AN [equations (21) and (22)], leads to (23) or rate law (24), second order in $[DBO^+]$. In addition to being first order in $[DBO^+]$, the reaction rate was observed to be

$$2\,DBO^+ + 2\,AN \underset{k_{-21}}{\overset{k_{21}}{\rightleftharpoons}} 2\,DBO + 2\,AN^+ \qquad (21)$$

$$2\,AN^+ \xrightarrow{k_{22}} DMB + 2\,H^+ \qquad (22)$$

$$k_{21}[DBO^+]^2[AN]^2 = k_{22}[AN^+]^2 + k_{-21}[DBO]^2[AN^+]^2 \qquad (23)$$

$$-d[DBO^+]/dt = k_{22}\frac{k_{21}[DBO^+]^2[AN]^2}{k_{22} + k_{-21}[DBO]^2} \qquad (24)$$

independent of [DBO] and first order in [AN], therefore mechanism (21) + (22) can only be valid if the rate of (22) is large compared with that of (21) in both directions thus giving the observed rate law (25) (Table 4). Thus, the simple electron transfer mechanism probably occurs

$$-d[DBO^+]/dt = k_{21}[DBO^+][AN] \qquad (25)$$

but is only observed when the complex mechanism is slowed down by working at low $[DBO^+]$.

The Marcus theory [22] for electron transfer rates for equilibria such as (1) has been subjected to experimental test for reactions of both cation radicals and anion radicals with aromatic compounds.[3] As predicted by theory [22] the reactions were found to proceed at rates near the diffusion controlled limit for reactions with negative values of $\Delta G°$.[3] Since all the reactions studied here have positive $\Delta G°$ values in the forward direction, the reverse reactions being thermodynamically favourable would be expected to proceed at rates approaching the diffusion-controlled limit. For the reactions which were found to obey pseudo-first-order kinetics at low radical ion concentrations the observed second-order rate constants are gathered in Table 8. A pseudo-first-order reaction was not observed for the reaction of TH^+ with A; however a maximum value of k_1 was estimated from the half-life of TH^+ in run 49. The equilibrium constants for reaction (1), K_1, calculated from voltammetric data (Table 2) are given in column 2. Second-order rate constants calculated for the reverse reactions (1) using the relationship, $k_{-1} = k_1K_1$, are listed in the third column. The values of k_{-1} are all considerably lower than the diffusion controlled limit which would appear to be inconsistent with the Marcus theory.

TABLE 8

Calculated second-order rate constants for the reactions of aromatic cation radicals with aromatic compounds

Reaction [a]	k_1/ l mol^{-1} s^{-1}	K_1	k_{-1}/ l mol^{-1} s^{-1}	(k_{-1})/ l mol^{-1} s^{-1} corrected
DBO^+ + AN	1.4×10^{-2}	1.3×10^{-6}	1.1×10^4	10^7
TH^+ + AN [b]	1.5×10^{-3}	1.6×10^{-9}	9.4×10^5	10^9
TH^+ + A [c]	$<1.7 \times 10^{-1}$	3.2×10^{-1}	$<5.3 \times 10^3$	
DPA^+ + AN	1.5×10^{-4}	1.6×10^{-11}	9.4×10^6	10^{10}

[a] All reactions in CH_2Cl_2–TFA–TFAn (97 : 2 : 1) except TH^+ + A, at 11 °C in the presence of $Bu^n_4NBF_4$ (0.2M). [b] From ref. 1*b*. [c] Solvent was MeCN–TFA (95 : 5) in the presence of $NaClO_4$ (0.1M).

However, one other fact must be taken into consideration. The oxidation potentials of AN in both solvent systems and that for A in acetonitrile were measured under conditions where AN^+ and A^+ were undergoing rapid reactions following electron transfer. Thus, the apparent oxidation potentials are less positive than the true values. If we estimate the kinetic shift of the measured potential from the reversible value for the oxidation of AN to be of the order of 180 mV, we arrive at the conclusion that the true values of K_1 for reactions of AN are smaller than those given in Table 2 by a factor of *ca.* 10^3. Values of k_{-1} calculated using corrected values of K_1 are listed in the last column of Table 8. The latter treatment gives a value of *ca.* 10^{10} l mol^{-1} s^{-1} for the reaction of DPA with AN^+. In fact all k_{-1} values calculated in this manner are $>10^7$ l mol^{-1} s^{-1} as predicted by the Marcus theory. Since the rate of dimerization of AN^+ is unknown an exact correction of K_1 cannot be made the $k\text{so}^{-}_{1}$ values given in Table 8 are approximate. The estimate of a 180 mV kinetic shift of the oxidation peak for AN seems reasonable since the reactions which follow are too rapid to study at the rotating disc electrode. On the other hand, the rate constant for the reaction of A^+ with acetonitrile is known [12] and this gives an estimate of *ca.* 50 mV for the kinetic shift. Therefore, corrections of K_1 for A are much smaller.

Pseudo-second-order in cation radical rate laws were also observed for the reactions of TH^+ with A (Table 5) and DPA^+ with AN (Table 6). Neither of these reactions were investigated as thoroughly as the DBO^+ + AN reaction; however the data indicate that the same rate law applies for these reactions as well.

The only reaction for which the disproportionation mechanism is feasible is that between DPA^+ and AN. Disproportionation seems unlikely (but not ruled out) for the latter reaction in view of the following. Another related reaction, DPA^+ + MAN, occurs at nearly the same rate as when π_2 is AN. The electron transfer

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[22] R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; 1957, **26**, 867, 862; 1965, **43**, 679, 2654, 3477; *Discuss. Faraday Soc.*, 1960, **29**, 21; *J. Phys. Chem.*, 1963, **67**, 853.

equilibrium (26), according to voltammetric data (Table 1), lies 10^3 times further to the right than the corresponding equilibrium involving AN. Thus, the disproportionation mechanism predicts that DPA^+ should react much faster with MAN than with AN.

$$DPA^{2+} + MAN \rightleftharpoons DPA^+ + MAN^+ \qquad (26)$$

The order of reactivity observed for $\pi_1{}^+$ was DPA^+ (1), TH^+ (10), and DBO^+ (10^3). This is the approximate order of the oxidizing power of the radical ions and in terms of mechanism [(11)—(14)] must be a reflection of the relative values of K_{12}. However, it must be kept in mind that K_{11} is also dependent on the identity of $\pi_1{}^+$. We would expect K_{11} in the case of TH^+ to be greater than that for the other radical ions since TH^+ has been shown to undergo self association [16,23] while equilibrium (27) cannot be detected for the other two cations.

$$2\,\pi_1{}^+ \rightleftharpoons (\pi_1\text{-}\pi_1)^{2+} \qquad (27)$$

The expected temperature effect according to mechanism [(11)—(14)] is very difficult to assess. Both K_{11} and K_{13} would be expected to be temperature dependent but in opposite ways. The electron transfer equilibrium (K_{12}) should not be greatly affected by temperature. The observed activation parameters show that the overall effect of lowering the temperature is to decrease substantially the rate of reaction. Since no concrete conclusions can be drawn from the temperature effect, it was not examined more carefully.

This study has shown that when a simple electron transfer mechanism between cation radicals and aromatic compounds is energetically unfavourable another mechanism second order in cation radical can operate. The overall result is the same, the aromatic compound is oxidized and the cation radical is reduced. We have also observed pseudo-second-order kinetics for the reaction of DBO^+ and A even though this reaction is energetically favourable, ΔG° —0.2 eV. The latter reaction is being investigated more carefully and will be described later.

EXPERIMENTAL

Acetonitrile and dichloromethane were reagent grade and passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid and trifluoroacetic acid anhydride were Fluka (purum grade) and used as obtained.

The apparatus used for voltammetric measurements has been described.[24] The cell used both for the kinetic study and for the preparation of the cation radical solutions was a cylindrical, round bottom, jacketted container with openings for the auxiliary electrode compartment, reference electrode, inert gas supply, thermometer, and a Beckman rotating disc electrode. The temperature was controlled either with tap water or with a cryostat. The cation radical solutions were prepared by partial oxidation of solutions of the compounds in the solvent systems. Oxidations were carried out at constant current at a large area platinum gauze electrode. Current was passed for a time calculated to give the desired concentration of cation radical. The concentration of cation radical was determined exactly after oxidation by the magnitude of the limiting reduction current at the r.d.e. The limiting current was followed as a function of time for several minutes and little or no decrease in cation radical concentration was observed before adding the aromatic compound (π_2). The procedure used for carrying out the kinetic runs was that previously described.[11] The method is illustrated for the most rapid reaction studied, TH^+ with A, by Figure 4. The line ab recorded at the end of the reaction shows the decay in current over 18 s.

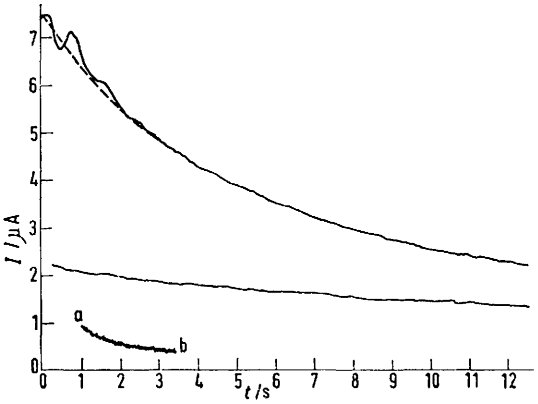

FIGURE 4 The decrease in cation radical reduction current during the reaction of TH^+ with A (run 47). Potential of the rotating disc electrode = +1.0 V *vs.* s.c.e. Rotation rate = 50 r.p.s. Line ab was recorded on a time scale of 20 s cm^{-1} and residual current after complete reaction was <0.25 µA

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[24] O. Hammerich and V. D. Parker, *J.C.S. Perkin I*, 1972, 1718.