Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. I. Cyclization of the Tetraphenylethylene Dication

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Abstract: The tetraphenylethylene (TPE) cation radical is long lived in trifluoroacetic acid (TFA) and in dichloromethane–TFA. TPE·+ undergoes a cyclization reaction giving equimolar quantities of 9,10-diphenylphenanthrene (DPP) and TPE. One-electron anodic oxidation of TPE·+ results in the quantitative formation of DPP. The reaction was found to obey the rate law, $v = k_{obsd}[TPE·+]^2/[TPE]$, indicating a disproportionation mechanism. A maximum value of the equilibrium constant for the disproportionation, $2TPE·+ \rightleftarrows TPE^{2+} + TPE$, was estimated to be of the order of 10^{-6} from voltammetric data. The effect of the reaction conditions on the rate indicates that the cyclization step rather than the disproportionation is rate determining. Depending upon the conditions (salt concentration, solvent composition, and temperature), first-order rate constants for the cyclization of the dication (eq 2) were found to be of the order of 50–5000 sec^{-1}. Comparable rate constants for the reaction of the dication were obtained from a rotating disk voltammetric study giving strong support to the suggested mechanism.

I ntramolecular cyclization reactions of anodically generated intermediates have received a great deal of recent attention.[2-6] A potential step voltammetric study[2b] has provided evidence that the mechanism of cyclization of methoxybibenzyls to dihydrophenanthrenes involves the generation of the dication–diradical which cyclizes *via* radical coupling. Several alternative reaction pathways for the anodic cyclization of tetraphenylethylene (TPE) to 9,10-diphenylphenanthrene (DPP) were recently suggested but the existing evidence could not be used to establish a mechanism.[6] The enhanced stability of aromatic cation radicals in media containing trifluoroacetic acid[7,8] suggested the possibility that the lifetime of the TPE cation radical could be extended in order to examine the mechanism of the cyclization reaction. We report the results of a voltammetric and kinetic study of the conversion of TPE·+ to DPP in the TFA–dichloromethane solvent system.

Results

Product Study. The anodic oxidation of TPE at a platinum anode under constant current conditions in TFA–dichloromethane (1:3) resulted in nearly quantitative conversion to DPP. No other products could be detected. DPP was identified by comparison with the authentic compound prepared by the irradiation of TPE in dichloromethane; *i.e.*, voltammetric behavior, mass spectrum, and ultraviolet absorption spectra.[9]

Electrochemical Study. The cyclic voltammogram of TPE in TFA–dichloromethane (1:3) is shown in Figure 1. When the direction of voltage sweep is switched after the first anodic peak (O₁), a corresponding reduction peak (R₁) is observed (Figure 1a). This couple with peak potentials of +1.33 and +1.23 V, respectively, is due to the formation and reduction of the TPE cation radical. When the anodic scan is extended, a second complex oxidation peak (O₂, O₃) appears and a reduction peak (R₃) is observed on the cathodic sweep. Continuous sweeping between +1.0 and +1.7 at a voltage sweep rate of 156 mV/sec resulted after about 10 cycles in the steady-state voltammogram (Figure 1b) which shows a couple (O₃–R₃) as the most prominent feature. The cyclic voltammogram of DPP under identical conditions is shown in Figure 1c. The redox couple, O₃–R₃, matched the steady-state voltammogram of TPE very closely with potentials of +1.58 and +1.48 V for the oxidation and reduction peak, respectively.[10]

The steady-state voltammogram (Figure 1b) was simulated assuming very fast reaction of TPE²⁺ and the measured and simulated voltammograms were almost identical.

Constant current coulometry[11] on solution of TPE (1.0 m*M*) in TFA–dichloromethane (1:3) resulted in the consumption of 1.0 faradays/mol and the formation of TPE·+ [λ_max 486 nm (ε 1.9 × 10⁴ in TFA–dichloromethane (1:3))].[12] The experiments were carried out

(1) (a) University of Copenhagen; (b) Lund Institute of Technology.
(2) (a) A. Ronlán and V. D. Parker, *Chem. Commun.*, 1567 (1970); (b) A. Ronlán, O. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, 95, 7132 (1973).
(3) L. L. Miller, F. R. Stermitz, and J. R. Falck, *J. Amer. Chem. Soc.*, 95, 2651 (1973); 93, 5941 (1971).
(4) M. Sainsbury and R. F. Schniazi, *J. Chem. Soc., Chem. Commun.*, 718 (1972).
(5) J. M. Bobbitt, private communication.
(6) J. D. Stuart and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, 93, 4531 (1971).
(7) O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).
(8) U. Svanholm and V. D. Parker, *Tetrahedron Lett.*, 471 (1972).
(9) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964).

(10) The peak potential separation (100 mV) for both O₁–R₁ and O₃–R₃ was greater than the theoretical value (57 mV) for a reversible one-electron transfer. The charge transfers are in fact reversible and the increased peak separation is due to uncompensated resistance in the solution. The latter was shown by further experiments at lower sweep rate (31 mV/sec) using a smaller electrode and higher supporting electrolyte concentration (0.4 *M*). Under the latter conditions, peak separations for both couples were about 65 mV. All potentials refer to the saturated aqueous calomel electrode.
(11) V. D. Parker, *Acta Chem. Scand.*, 24, 2768 (1970).
(12) The half-life of TPE·+ under these conditions is several hours in the presence of a large excess of TPE. The extinction coefficient was measured by passing the calculated amount of current through a solution containing TPE (10⁻² *M*) to give a solution containing TPE·+ (1.0 × 10⁻³ *M*) and TPE (9.0 × 10⁻³ *M*).
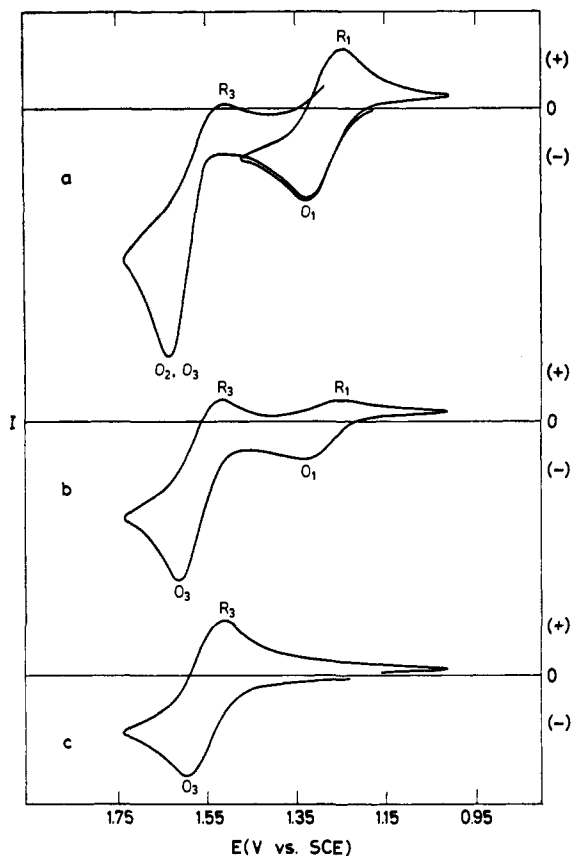
Figure 1. Cyclic voltammograms in TFA–dichloromethane (1:3) containing Bu_4NBF_4 (0.2 M): (a) single sweep voltammogram of TPE (1 mM); (b) steady-state voltammogram of TPE (1 mM); (c) voltammogram of DDP (1 mM).

on 50 ml of solution at 50 mA for a duration of about 3.2 min, conditions under which very little further reaction occurred.

Results of a rotating disk electrode (rde) study are included with the kinetic results.

Kinetic Study. Solutions of $TPE \cdot^+$ in TFA–dichloromethane (1:3) in the presence of excess of TPE were found to decompose at rates second order in $TPE \cdot^+$ (Table I, Figure 2) and inversely proportional to the concentration of unoxidized TPE (Table I) which

Table I. Dependence of the Rate of Cyclization on the Concentration of TPE

$(TPE)_0 \times 10^4$	k_{obsd}, M^{-1} sec^{-1} a,b	k_p, sec^{-1}
2.1	0.37	78
3.1	0.33	103
5.5	0.23	125
9.7	0.09	99
		100 ± 25

a Temperature, 12.5°; solvent composition, TFA–dichloromethane (1:3); (n-Bu_4NBF_4) = 0.2 M. b k_{obsd} is the apparent second-order rate constant for disappearance of $TPE \cdot^+$.

suggested a disproportionation mechanism (eq 1). The stoichiometry followed eq 1 and 2 very closely as

$$2TPE \cdot^+ \rightleftharpoons TPE^{2+} + TPE \quad (1)$$

$$TPE^{2+} \xrightarrow{k_p} DPP + 2H^+ \quad (2)$$
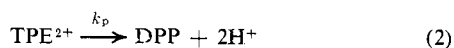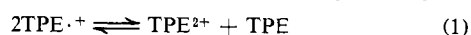
was demonstrated by comparison of the voltammetry

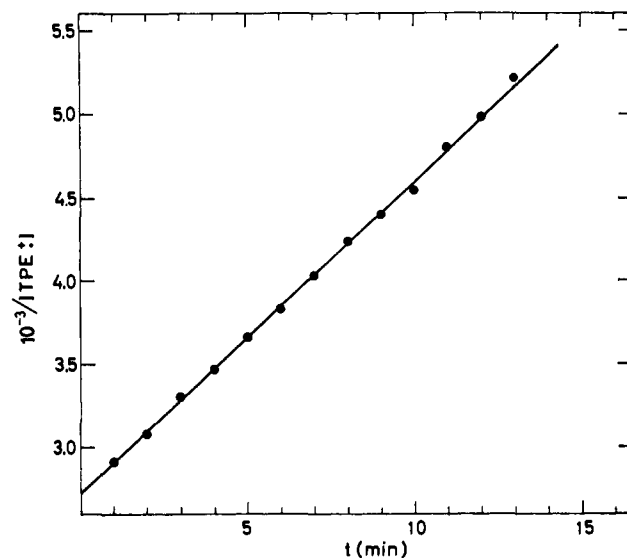Figure 2. Plot of $1/[TPE \cdot^+]$ $vs.$ time for the reaction of $TPE \cdot^+$ in TFA–dichloromethane (1:9) containing Bu_4NBF_4 (0.1 M).

of solutions in which known concentrations of the cation radical had been allowed to react to completion with standard solutions containing TPE and DPP. Thus, the half-regeneration disproportionation mechanism (eq 1 and 2) was selected as a working hypothesis. This mechanism is expected to follow the rate law

$$v = k_p K_{disp}[TPE \cdot^+]^2/[TPE] \quad (3)$$

where k_p is the first-order rate constant for the reaction of TPE^{2+} (eq 2) and K_{disp} is the equilibrium constant for the disproportionation (eq 1). The value of K_{disp} can be estimated from the potential difference ($E_2 - E_1$) for the two charge transfers (eq 4) using an appropri-

$$TPE \underset{+e}{\overset{-e}{\rightleftharpoons}} TPE \cdot^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} TPE^{2+} \quad (4)$$
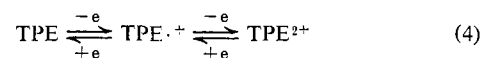
ate form of the Nernst equation, a procedure which has recently been verified to give reliable results.[13,14] The value of $E_2 - E_1$ can be estimated from Figure 1a to be of the order of 360 mV which results in an estimate of K_{disp} of 10^{-6}, a value which must be considered to be a maximum since the rapid reaction of the dication causes the value of E_2 to appear at a less than real potential.[15] The feasibility of the disproportionation mechanism may be ascertained by assuming that k_b (eq 1) is a diffusion controlled second-order rate constant with a value of the order of 10^{10} M^{-1} sec^{-1}, a reasonable assumption since the rate of reaction of aromatic cation radicals with aromatic compounds approach diffusion control.[16] Thus, the maximum possible value of a second-order rate constant for the cyclization of $TPE \cdot^+$, according to the disproportionation mechanism (eq 1 and 2), is given by

$$K_{disp} = k_f/k_b$$

$$k_f = k_b K_{disp} \quad (5)$$

$$(k_f)_{max} = (10^{10} \ M^{-1} \ sec^{-1})K_{disp}$$

(13) U. Svanholm and V. D. Parker, J. Chem. Soc., Perkin Trans. 2, 1594 (1973).
(14) U. Svanholm, B. Svensmark Jensen, and V. D. Parker, J. Chem. Soc., Perkin Trans. 2, in press.
(15) R. S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).
(16) B. A. Kowert, L. S. Marcoux, and A. J. Bard, J. Amer. Chem. Soc., 94, 5538 (1972).

and using a value of 10^{-6} for K_{disp}, a reasonable value of 10^4 M^{-1} sec^{-1} is arrived at for the maximum feasible value of a second-order rate constant. Such considerations have recently been employed to cast doubt on other proposed disproportionation mechanisms.[17]

The effect of unoxidized TPE on the rate of the cyclization is shown by the data in Table I. A plot of 1/(TPE$\cdot^+$) vs. time for a typical run is illustrated in Figure 2. The slope of the rate curve was found to be equal to 22.2 M^{-1} min^{-1} (0.37 M^{-1} sec^{-1}) and is the pseudo-second-order rate constant at (TPE)$_0$ = 2.1 × 10^{-4} M. The data clearly indicate both the inverse dependence upon (TPE) and the second-order relationship in (TPE$\cdot^+$). The third column in Table I gives the rate constant for the reaction of the dication according to the disproportionation mechanism which was obtained by multiplying k_{obsd} by (TPE)$_0$/K_{disp}. In cases where a large excess of TPE was present the second-order rate plots were linear for more than 2 half-lives. In other cases significant changes in (TPE) occurred during the runs and deviation from linearity in the rate plots was observed at lower conversions. In the latter case, the initial linear portion of the data was used (in no case was the plot nonlinear during the first 25% of the reaction) to calculate the rate constants.

The rate of decomposition of TPE$\cdot^+$ solutions was greatly dependent on the concentration of the salt, tetra-n-butylammonium tetrafluoroborate. Data for runs at four different salt concentrations are tabulated in Table II.

Table II. Dependence of the Rate of Cyclization on the Salt Concentration

(n-Bu$_4$NBF$_4$)	(TPE)$_0$ × 10^4	(TPE$\cdot^+$)$_0$ × 10^4	k_p, sec^{-1} ^{a}
0.089	3.76	4.52	556
0.172	3.77	4.67	854
0.252	3.29	4.16	1.620
0.328	2.91	4.06	2.090

^{a} Temperature, 12.0°; solvent composition, TFA–dichloromethane (1:9).

The reactivity of TPE$\cdot^+$ in solutions made up of the mixed solvent TFA–dichloromethane increased markedly with decreasing fraction of TFA present. In TFA alone, TPE$\cdot^+$ is long lived. The effect of the fraction of TFA present in the mixed solvent upon the rate of the cyclization reaction is demonstrated by the data in Table III.

Table III. Effect of the Solvent Composition upon the Rate of Cyclization

% TFA^{a,b}	(TPE)$_0$ × 10^4, M	(TPE$\cdot^+$)$_0$ × 10^4, M	k_p, sec^{-1}
25	2.54	6.36	50
10	4.2	4.9	280
5	5.7	3.7	860
2	6.6	2.2	5100

^{a} Volume % of TFA in the mixed solvent, cosolvent dichloromethane. ^{b} Temperature, 10.5°; (n-Bu$_4$NBF$_4$), 0.1 M.

The rate of reaction of TPE$\cdot^+$ in the mixed solvent system was greatly affected by the temperature. Two

(17) V. D. Parker, *J. Electroanal. Chem.*, **36**, App. 11 (1972).

series of runs were conducted at different solvent composition over a range of temperatures. The data are summarized in Tables IV (TFA = 25%) and V (TFA =

Table IV. Effect of Temperature on the Rate of Cyclization in TFA (25%)–CH$_2$Cl$_2$^{a}

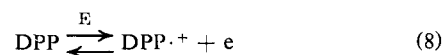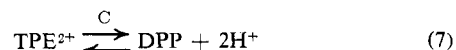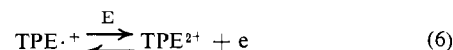| Temp, °C	(TPE)$_0$ × 10^4, M	(TPE$\cdot^+$)$_0$ × 10^4, M	k_p, sec^{-1}
3	2.22	7.59	35
10.5	2.1	7.9	99
13	2.22	7.58	126
15	4.56	4.56	113
22	3.2	5.9	230
27	4.79	4.86	374

^{a} (n-Bu$_4$NBF$_4$) = 0.2 M.

Table V. Effect of Temperature on the Rate of Cyclization in TFA (8.9%)–CH$_2$Cl$_2$^{a}

Temp, °C	(TPE)$_0$ × 10^4, M	(TPE$\cdot^+$)$_0$ × 10^4, M	k_p, sec^{-1}
−2	4.51	3.67	123
9.5	3.51	5.55	237
13	4.59	3.85	622
16.5	3.0	5.85	675
20	4.43	3.62	772
26	5.16	3.83	1520

^{a} (n-Bu$_4$NBF$_4$) = 0.089 M.

8.85%). Plots of log k vs. $1/T$ were linear and gave activation parameters of: E_a = 14.5 kcal/mol and $\Delta S^{\ddagger}$ = 0.5 eu.

The rate of cyclization of the dication was also determined directly by rotating disk electrode (rde) voltammetry at the second wave during oxidation of TPE. The reaction was treated as an ECE reaction (eq 6–8) of the cation radical, TPE$\cdot^+$. The DPP$\cdot^+$ is

$$\text{TPE}\cdot^+ \underset{\longleftarrow}{\overset{E}{\rightleftarrows}} \text{TPE}^{2+} + e \tag{6}$$

$$\text{TPE}^{2+} \underset{\longleftarrow}{\overset{C}{\rightleftarrows}} \text{DPP} + 2\text{H}^+ \tag{7}$$

$$\text{DPP} \underset{\longleftarrow}{\overset{E}{\rightleftarrows}} \text{DPP}\cdot^+ + e \tag{8}$$

stable on the time scale of the experiment (Figure 1c) which allows the reaction to be treated as a simple ECE mechanism. Limiting current data were analyzed with working curves used previously for the ECE mechanism for the anodic pyridination of 9,10-diphenylanthracene[18] and were derived using digital simulation techniques[19] as previously discussed for the ECE mechanism.[20] The value of the limiting current at the first wave, that for formation of TPE$\cdot^+$, was used as the value of n_{app} = 1.0 for the second wave. Data for runs at two different supporting electrolyte concentrations are illustrated in Figure 3. The first-order rate constant (k_p) was estimated to be about 100 sec^{-1} (n-Bu$_4$NBF$_4$ = 0.2 M) and 30 sec^{-1} (n-Bu$_4$NBF$_4$ = 0.1 M), respectively.

Discussion

The poorly defined voltammetry observed for the

(18) G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, **91**, 4584 (1969).
(19) S. W. Feldberg, *Electroanal. Chem.*, **3**, 199 (1969).
(20) L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *J. Phys. Chem.*, **73**, 2611 (1969).

oxidation of TPE in acetonitrile[6] made firm mechanistic conclusions for the mode of cyclization to DPP impossible. This is a common problem associated with the study of chemical reactions coupled with electron transfer. A pertinent example of a reaction in which conventional electroanalytical techniques have failed to definitively define the mechanism is the anodic pyridination of 9,10-diphenylanthracene. The original rde study[18] definitely established that the initial electrode reaction was the transfer of a single electron to give the cation radical, and on this basis a concerted two-electron transfer was ruled out and the ECE mechanism was assigned. However, the question was reopened by Marcoux[21] who proposed that although the theoretical working curves for the ECE and disproportionation mechanisms for chronoamperometry were very similar, experimental data more closely fit the disproportionation mechanism and thus the latter mechanism was the most likely. Thus, in order to firmly establish the mechanism it was necessary to obtain kinetic data for the homogeneous chemical reaction of the diphenylanthracene cation radical with pyridine which showed that the reaction was first order in both the cation radical and pyridine[22] and confirmed the original proposal of the ECE mechanism.

The previous study[6] established that DPP is the product of the anodic oxidation of TPE in acetonitrile. The first stage of this study was to verify that DPP is also formed in the TFA–dichloromethane solvent system. The only product that could be detected upon anodic oxidation of TPE in the latter solvent system was DPP. Anodic oxidation of TPE is an excellent means of preparing DPP since the former is oxidized about 500 mV more readily than the latter and thus nearly quantitative conversions can be achieved.

The voltammetric study provided immediate evidence of the stability of TPE·+ in the dichloromethane–TFA solvent system. The cyclic voltammogram of TPE showed a perfectly reversible couple for the oxidation and reduction of TPE–TPE·+ (Figure 1a). The steady-state voltammogram (Figure 1b) in which the voltage sweep was extended to the second stage, i.e., oxidation of TPE·+ to TPE²⁺, revealed that the dication undergoes rapid reaction and the diffusion layer rapidly becomes depleted of substrate leaving the product, DPP. That the immediate product is indeed DPP was verified by the close similarity of the voltammogram of authentic DPP (Figure 1c) with the steady-state voltammogram for TPE (Figure 1b).

When solutions of TPE·+, prepared by partial oxidation of TPE in TFA–dichloromethane, were allowed to decompose, voltammetric analyses of the resulting solutions indicated that within experimental error, 1.0 mol of DPP and 1.0 mol of TPE were formed for every 2.0 mol of TPE·+ which reacted. Thus, the stoichiometry of the reaction is that expected for the disproportionation mechanism (eq 1 and 2) as has been observed for reactions of the thianthrene[23] and perylene[24] cation radicals. Although the latter stoichiometry has been taken as evidence for the disproportionation mecha-
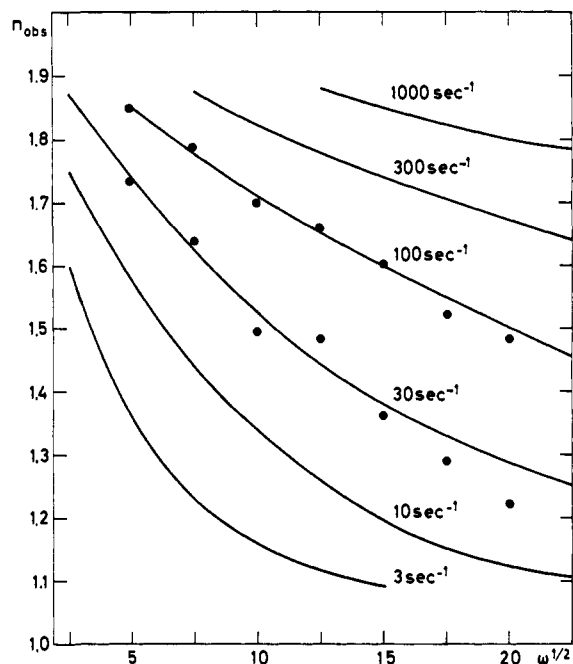
(21) L. S. Marcoux, *J. Amer. Chem. Soc.*, **93**, 537 (1971).
(22) U. Svanholm and V. D. Parker, *Acta Chem. Scand.*, **27**, 1454 (1973).
(23) (a) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 1872 (1969); (b) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969); (c) J. J. Silber and H. J. Shine, *ibid.*, **36**, 2923 (1971).
(24) C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, **36**, 4050 (1971).

Figure 3. Rde rate constants for the cyclization of TPE²⁺ in TFA–dichloromethane (1:3): (a) (Bu₄NBF₄) = 0.2 M; (b) (Bu₄NBF₄) = 0.1 M. The solid lines are the working curves.

nism,[23,24] it should be pointed out that any other mechanism going to a two-electron oxidation product would also exhibit the same stoichiometry, for example, the direct cyclization of TPE·+ (eq 9 and 10). Therefore,
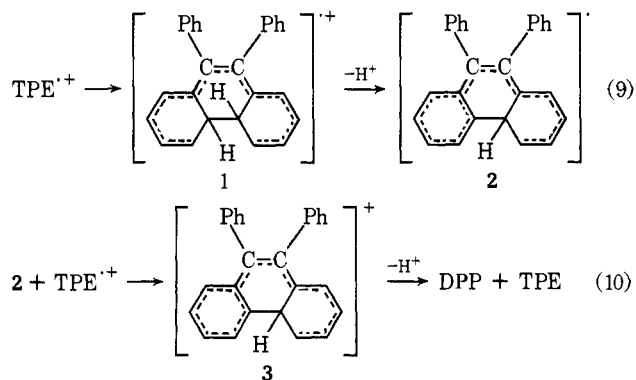
the observed stoichiometry, i.e., half-regeneration, is a necessary condition for the disproportionation mechanism but cannot be considered as evidence for the latter.

The kinetic data fit the disproportionation rate law (eq 3) lending strong support for that mechanism (eq 1 and 2). Still the question remains as to which step is rate determining. The approach used to shed light upon this question was to vary the reaction conditions and to compare the results observed with those expected for the two possibilities, i.e., disproportionation (eq 1) or cyclization of the dication (eq 2) being rate determining. The equilibrium constant, K_{disp} (eq 1), estimated from voltammetry was found to be independent or very nearly independent of the temperature, the supporting electrolyte concentration, and the solvent composition over the range investigated. Thus, if the back reaction, that of TPE²⁺ with TPE, is diffusion controlled or nearly so as is reasonable to expect from previous work,[16] the rate of the forward reaction, disproportionation, would be independent of the conditions. The fact that a linear

Figure 4. The dependence of the reaction of TPE·+ on the concentration of Bu₄NBF₄.
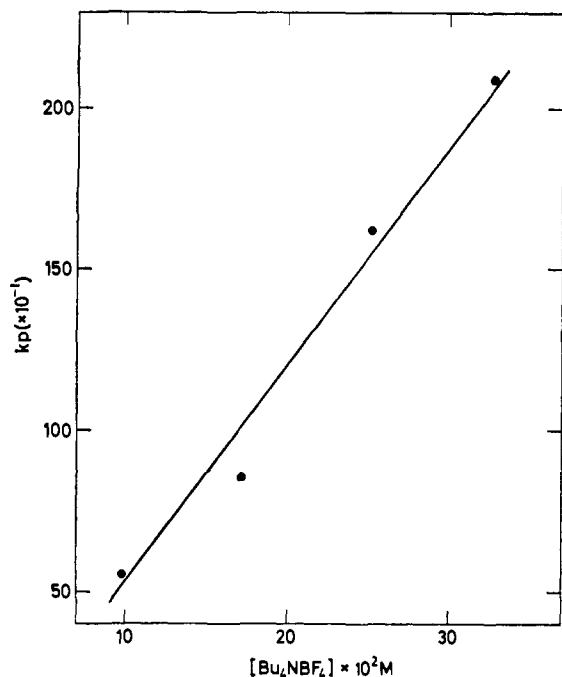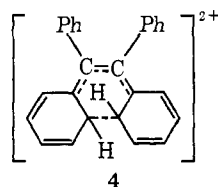

Figure 5. The dependence of the reaction of TPE·+ on the concentration of TFA.

increase in rate was observed with increasing salt concentration (Table II) strongly suggests that the disproportionation step is not rate determining. The linear dependence is illustrated in Figure 4. The rate of the reaction was more profoundly affected by the solvent composition (Table III). In going from 25 to 2% TFA, the calculated first-order rate constant for cyclization of the dication (k_p) increased by a factor of 10^2. Extrapolation of the data of Figure 5 results in an estimate of a 10^6 rate increase in going from 100 to 0.1% TFA. If the latter were to be attributed to a change in K_{disp}, a change in $E_2 - E_1$ (eq 4) of about 60 mV/decade of rate change would be expected. Yet, the values estimated for E_2 and E_1 were nearly identical at the two solvent compositions. On this basis we can virtually rule out the disproportionation as being rate determining. It is of interest to note that a plot of log k_p vs. log (% TFA) gave a straight line (Figure 5).

The large solvent effect (Table III) suggests that the reactivity of TPE²⁺ is greatly diminished by solvation with TFA. A similar effect has been observed during the hydroxylation of the thianthrene cation radical (Th·⁺). In aprotic solvents, Th·⁺ reacts rapidly with low concentrations of water[23a,b,25] but nearly reversible voltammetry was observed in TFA–H₂O (1 : 1).[6]

If the rate-determining step for the cyclization of TPE·⁺ is eq 2, a transition state such as 4 must be in-

$$\left[\begin{array}{c} Ph \qquad Ph \\ C=C \\ H \\ \\ H \end{array} \right]^{2+}$$

4

volved. In going from TPE²⁺ to 4, the aromaticity of two benzene rings is destroyed, and therefore a localiza-

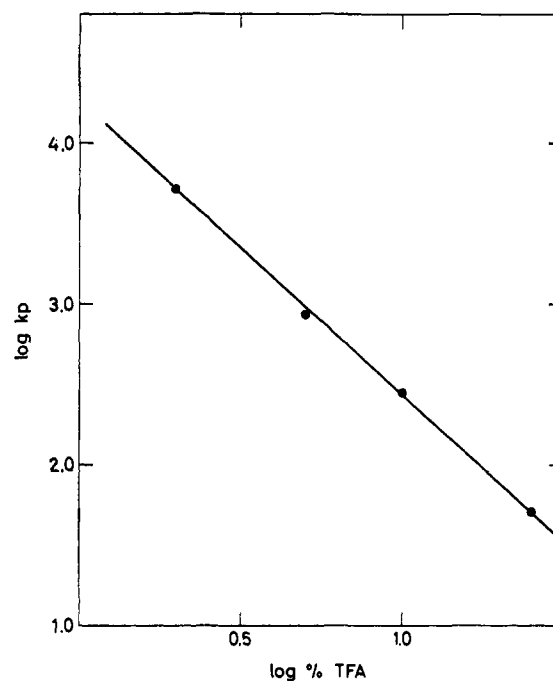(25) V. D. Parker and L. Eberson, *J. Amer. Chem. Soc.*, 92, 2488 (1970).

tion of charge has taken place. Thus the transition state (4) is more polar than TPE²⁺ and a positive salt effect is expected. Indeed, the rate of reaction was observed to be directly dependent on the salt concentration. The activation energy, $E_a = 14.5$ kcal/mol, could also be a reflection of the loss of resonance energy in going from TPE²⁺ to 4. The near zero value of $\Delta S^{\ddagger}$ could be a consequence of the rigid, planar nature of TPE²⁺ with a very small change in geometry required in going to the transition state.[26]

Results from the rde study of the kinetics provided very convincing further support for the disproportionation mechanism. At a solvent composition of TFA–dichloromethane (1:3), temperature of 10.5°, and (Bu₄NBF₄) of 0.1 M, the value of k_p from the rde data was estimated to be of the order of 30 sec⁻¹ while the value from the homogeneous kinetic study was calculated to be equal to 50 sec⁻¹. The effect of doubling (n-Bu₄NBF₄) in the rde work was in the right direction, increasing k_p from 30 to 100 sec⁻¹. Thus, excellent agreement was observed between the rde and homogeneous kinetic results. There seems to be little doubt that the mechanism of the cyclization of TPE·⁺ is the disproportionation pathway (eq 1 and 2) and that the rate-determining step is eq 2.

Experimental Section

DPP from Anodic Oxidation of TPE. TPE (656 mg, 2.0 mmol) in TFA–dichloromethane (1:3, 100 ml) containing n-Bu₄NBF₄ (0.1 M) was subjected to anodic oxidation at a platinum gauze electrode in a two-compartment cell at a constant current of 100 mA. After the consumption of 2.0 faradays/mol, the solvent was removed under vacuum from the anolyte. The residue was dissolved in a minimum amount of dichloromethane and chromatographed on aluminum (Woelm W 200 neutral). After evaporation

(26) As pointed out by referee I, the entropy effect measured over a small temperature range cannot be taken as strong evidence for transition state 4. On the other hand, the value observed is consistent with 4.

of the solvent, the residue was recrystallized from chloroform–ethanol, white needles, mp 239° (lit.[27] 239–240°), 92% after recrystallization. The uv absorption spectrum agreed with that published for DPP.[9]

Techniques and apparatus used for voltammetry and coulometry have previously been described.[11,28] TFA was reagent grade and used without further purification. Reagent grade dichloromethane was passed through a column of neutral aluminum immediately before use. Reagent grade TPE was recrystallized before use.

Kinetics. Solutions of TPE·+ in the solvent system were prepared by partial oxidation at a low constant current (12.5 mA) of solutions of TPE. The concentration of both TPE·+ and TPE were determined by the magnitude of the limiting reduction and oxidation currents, respectively, at the rde. The concentration of TPE·+ was continuously monitored by the value of the limiting current at +0.8 V. The reaction cell was water jacketed and the temperature was controlled either by tap water or by a kyrostat (Ultra DK 80 DW). Second-order rate constants were calculated from plots of 1/[TPE·+] vs. time.

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Complexation Kinetics of Dineopentylmagnesium with *l*-Sparteine

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Abstract: The equilibrium between *l*-sparteine (Sp), dineopentylmagnesium, and the 1:1 complex R₂Mg·Sp in THF–dimethoxymethane has been characterized and the kinetics of ligand magnesium exchange were investigated with the techniques of nmr line-shape analysis. Rates of ligand exchange which turn out to be much slower than for other tertiary amines give rise to rate laws for the forward and reverse reaction whose molecularity is identical with that found on the left and right sides of reaction 1. At 60°, $1/\tau_{R_2Mg} = 32$ (Sp) and $1/\tau_{comp} = 10.4$ sec⁻¹, and the corresponding Eyring activation parameters are $\Delta H^{\pm} = 20$ kcal/mol and $\Delta S^{\pm} = 8.2$ eu. These results on comparison to other work lead to the conclusion that the slow step in the exchange process involves a conformational inversion of sparteine in a monodentate 1:1 complex from cisoid to transoid, thus allowing the approach of ether to magnesium.

Primary organomagnesium compounds in solution at equilibrium undergo fast inversion at carbon bonded to metal,[1,2] carbon–metal bond exchange, and metal base (ether and amine) coordination exchange.[3,4] Ordinarily for primary organomagnesium compounds at −20 to 100° in the presence of ethers and tertiary amines only the inversion process is on the nmr time scale, and its mechanism has been studied with the methods of nmr line-shape analysis.[1,2] In contrast to inversion, both bond and coordination exchange are very much faster, too fast for nmr methods. These processes have so far eluded kinetic study and although various proposals have been made nothing is presently known about their mechanisms.

In this paper we present the first kinetic study of coordination exchange of an organomagnesium compound complexed to a tertiary amine.

For some time it has been apparent that *l*-sparteine[5] (**1**), an optically active, naturally occurring tertiary diamine, is an excellent ligand toward metal ions. For

1
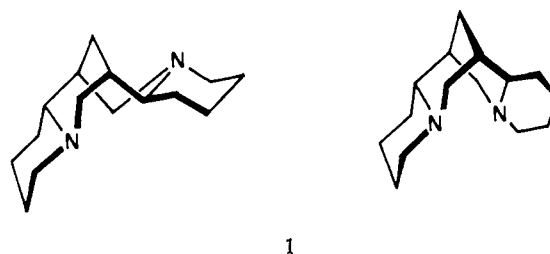
instance, periodically it is rediscovered that addition reactions of certain organometallic compounds carried out in the presence of sparteine result in products with different degrees of optical purity. These reactions include the metalation of isopropylferrocene by butyllithium,[6] the reactions of α-phenethyllithium,[7] butyllithium additions to carbonyl compounds,[7] the formation of allenes from *gem*-dibromocyclopropanes and butyllithium,[7] 1,4-addition reactions of Grignard reagents,[8] and the addition of the Reformatsky reagent to benzaldehyde.[9] The implication of these results is that *l*-sparteine, by complexing with the respective organometallic, imparts a chiral environment about the carbon–metal bond and thus induces asymmetry into the transition states for the different reactions.[5-9]

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