

Rate Constants and Activation Parameters for the Cyclization of the Tetraphenylethylene Dication in Acidic Dichloromethane

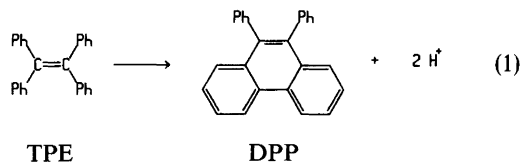
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The kinetics and activation parameters for the cyclization of the tetraphenylethylene dication in dichloromethane–trifluoroacetic acid–trifluoroacetic acid anhydride (8.5/1.0/0.5) containing Bu_4NBF_4 (0.1 M) were determined by derivative linear sweep voltammetry. The rate constant at 298 K was found to be equal to $3.2 \times 10^3 \text{ s}^{-1}$, E_a was observed to be 11.4 kcal/mol and the entropy of activation at 298 K was -6 cal/K mol . The relatively large activation energy is believed to arise from charge–charge repulsion in the transition state. The negative entropy of activation arises because of solvent reorganization around the more localized charges in the transition state.

Cyclization reactions are frequently encountered during the oxidation and reduction of difunctional organic molecules. The intramolecular cyclization of 1,2-diarylethanes during oxidation has been studied in detail.^{1–10} These systems are of special interest due to their relationship to naturally occurring alkaloids.

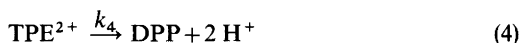
A related cyclization, that of tetraphenylethylene (TPE) to 9,10-diphenylphenanthrene (DPP) during anodic oxidation in acetonitrile (eqn. 1) was reported some years ago.¹¹ The cation radical ($\text{TPE}^{\cdot+}$) was



found to be sufficiently stable so that solution could be prepared and the kinetics of the reaction were

studied.¹² The reaction was observed to follow rate law (2) and a disproportionation mechanism, eqns. (3)–(4), was proposed to account for the data.

$$\text{Rate} = k_{\text{obs}} |\text{TPE}^{\cdot+}|^2 / |\text{TPE}| \quad (2)$$



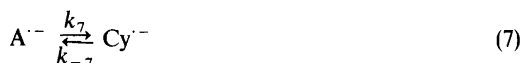
A rotating disk electrode study of the oxidation of the cation radical to the dication supported the mechanism assignment.

Disproportionation mechanisms have been proposed for two related cyclization reactions, those involving 1,2-diarylethane cation radicals⁹ and 1,3-dibenzoylpropane anion radicals.^{13,14} More recently, it has been suggested that the observation of rate laws of the type represented by (2) is not unambiguous evidence for the disproportionation mechanism.¹⁵ The reaction investigated was the cyclization of 1,3-dibenzoyl-1,3-diphenylpropane anion radicals. Under some conditions the reaction was observed to follow simple second order kinetics (5) which could indicate the disproportionation

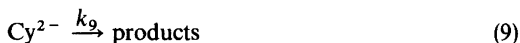
$$\text{Rate} = k_{\text{app}} |\text{A}^{\cdot-}|^2 \quad (5)$$

mechanism with rate-determining electron transfer analogous to (3). However, the apparent activation energy was observed to be only 2.7 kcal/mol which rules out a simple bimolecular reaction. Under linear sweep voltammetry (LSV) conditions, the rate law (6) was more complex and suggested mechanism (7)–(8). In this mechanism, $\text{Cy}^{\cdot-}$ is the

$$\text{Rate} = k_7 k_8 [A^{\cdot-}]^2 / (k_{-7} + k_8 [A^{\cdot-}]) \quad (6)$$



product of cyclization bridging the two carbonyl carbons. The pertinent point is that the apparent rate laws for the disproportionation mechanism (3)–(4) and ion radical cyclization (7)–(8) are not sufficient evidence to establish the mechanism. For example if (8) is considered reversible and is followed by irreversible (9), the anion radical cyclization mechanism gives a rate law identical in form to (2).



There are two other types of evidence which can be used to distinguish between the two mechanisms. The first is the apparent activation energy. In the case cited above, under purely second order conditions the apparent activation energy was too low to be due to rate determining electron transfer. Thus, the magnitude of the apparent activation energy can serve as a guide in the analysis of the mechanism. The second arises from the deuterium kinetic isotope effect when the carbons at the sites of ring closure are substituted with deuterium as illustrated in (10). Values of k_H/k_D in the range 0.7–0.9 have been observed during the dimerization of



arene cation radicals.¹⁶ The secondary deuterium kinetic isotope effect arises when the substituted carbons undergo a change in hybridization,¹⁷ in this case from sp^2 to sp^3 . Under purely second order conditions, the disproportionation mechanism involves rate-determining electron transfer which should not be dependent upon the isotopic substitution. On the other hand, two carbons change hybridization in the ion radical cyclization mechanism and appropriate deuterium substitution would be expected to be accompanied by a deuterium kinetic isotope effect of the usual magnitude.

In this paper we address the first mechanism criterion, that of the activation energy. The pre-

dominant contribution to the activation energy for the disproportionation mechanism of ion radical cyclization is expected to come from the cyclization of the doubly charged ion as in (4) for an example. Prior to this study, activation parameters were not available for any model systems undergoing the cyclization reaction. The purpose of the work presented here was to establish the activation parameters for reaction (4) to make the data available for comparison with other systems of unknown mechanism.

RESULTS AND DISCUSSION

The kinetic method. All kinetic measurements were carried out in dichloromethane–trifluoroacetic acid–trifluoroacetic acid anhydride (8.5:1.0:0.5). The first derivative of the linear sweep voltammogram for the oxidation of TPE at -33°C is illustrated in the figure. The first peak (p_1) is due to the oxidation to $\text{TPE}^{\cdot+}$ which is stable under the reaction conditions. The second peak (p_2) is the one describing the chemistry of interest and consists of the oxidation to TPE^{2+} which reacts to form DPP which is oxidized to $\text{DPP}^{\cdot+}$. The voltammetry for these two redox systems have been reported earlier.¹² The exact nature of the process occurring at p_3 is unknown but it corresponds to an overall two electron oxidation. At low sweep rates, the relative

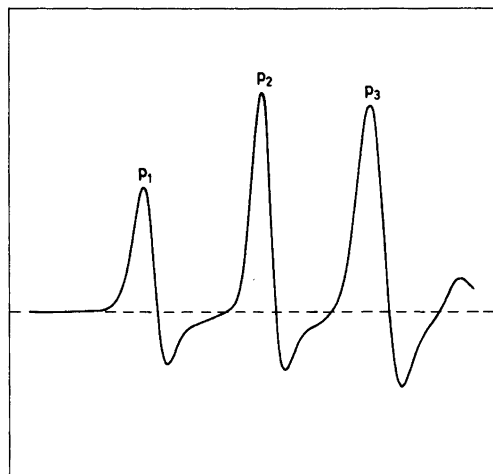


Fig. 1. Derivative linear sweep voltammogram for the oxidation of tetraphenylethylene in dichloromethane–trifluoroacetic acid–trifluoroacetic acid anhydride (8.5:1.0:0.5) containing Bu_4NBF_4 (0.1 M) at -33°C . Voltage sweep rate = 10 V s^{-1} .

peak heights are 1:2:2 for $p_1:p_2:p_3$. Because p_2 involves both TPE^+ and DPP , this peak and the reduction counterpart cannot be used for derivative cyclic voltammetry kinetics. However, p_1 involves only the substrate TPE and p_3 only the product DPP^+ and the ratio $p_3:p_1$ or $p_3:p_2$, can be used to determine the rate constant for the cyclization of TPE^{2+} .

Theoretical data were obtained by digital simulation¹⁸ using the measured potentials for the processes occurring at p_1 , p_2 and p_3 . The calculations assumed, based on experimental observations, that the process occurring at p_3 give a purely kinetic wave. This is necessary in the analysis so that the peak height is a measure of the amount of TPE^{2+} consumed at p_2 . Calculations were carried out over a range of rate constants, normalized for changes in sweep rate. Since these calculations are specific to this system, they will not be reported here. Any other system with different electrode potentials for the three waves would require a complete set of calculations for a kinetic analysis.

Since TPE^+ is stable under the reaction conditions, a convenient method of analysis was observed to be a potential program consisting of a step to a value mid-way between p_1 and p_2 and then a potential sweep encompassing p_2 and p_3 after a hold time long enough for TPE to be depleted in the reaction layer. Carrying out experiments in this manner made the contribution from back reaction (3) negligible. The ratio (p_3/p_2) obtained experimentally could then be used in conjunction with theoretical data to obtain k_4 .

Kinetics of the cyclization of TPE^{2+} . Kinetic experiments were carried out at -31.1°C with the substrate concentration varied from 0.50 to 2.00 mM. At each substrate concentration, $p_3:p_2$ was held at either 0.500 or 0.700 by making appropriate adjustments in the voltage sweep rate. Any change taking place in the apparent rate constant would then be reflected in changes in the sweep rate.¹⁹ The correspondence of the two rate constants derived at each concentration is a good indication of the fit of the experimental data to the theoretical model. The very close correspondence in all three pairs indicate an excellent fit. Although the rate constants measured at $|\text{TPE}|$ equal 0.50 mM are little higher than at the other two concentrations, the standard deviation in the rate constants was observed to be less than $\pm 10\%$. The latter indicates that the kinetics are first order and describe the cyclization of the dication. This is the principal

advantage of using the potential step to deplete the reaction layer of TPE . If this were not done the kinetic scheme would be more complicated because of the necessity to contend with reverse reaction (3).

Activation parameters of the cyclization of TPE^{2+} . The same procedure for measuring the rate constants for the cyclization of the dication was used for experiments carried out over a 32 K temperature range. Once again the rate constants derived from the two different $p_3:p_2$ ratios were in excellent agreement. Arrhenius correlation of the two data sets resulted in activation energies of 11.6 and 11.2 kcal/mol with corresponding activation entropies of -5.4 and -7.0 cal/K mol. In both cases the correlation coefficient was -0.998 . The probable error in E_a was estimated by taking the errors in $v_{0.5}$ into account for data at the two extreme temperatures. This resulted in values of 11.4 and 12.2 kcal/mol and the conclusion that the error in E_a is of the order of ± 0.5 kcal/mol. This is consistent with the fact that the value estimated from $v_{0.7}$ data differed from that using $v_{0.5}$ by 0.4 kcal/mol. An error of 0.5 kcal/mol in E_a corresponds to an error of ± 1.8 cal/K mol in ΔS^\ddagger . This again is reflected in the two values given in Table 2.

Conclusions. The activation energy for the cyclization of the tetraphenylethylene dication is of the same order of magnitude as was observed previously for the dimerization of 4-methoxybiphenyl cation radicals.¹⁶ This is most likely due to loss of conjugation and to the localizing of the positive charge. The negative activation entropy could arise from the restriction of rotations in the transition state during

Table 1. Rate constants for the cyclization of tetraphenylethylene dication in acidic dichloromethane.^a

C_A/mM^b	$p_3:p_2^c$	$v/V \text{ s}^{-1}$	k/s^{-1}
0.50	0.500	19.3(1.9)	40.5
0.50	0.700	11.1(0.7)	39.8
1.00	0.500	16.2(1.0)	34.0
1.00	0.700	9.9(0.7)	35.5
2.00	0.500	16.2(1.6)	34.0
2.00	0.700	9.7(0.9)	34.8
			36.4(2.9)

^a Measurements in dichloromethane-trifluoroacetic acid-trifluoroacetic acid anhydride (8.5:1.0:0.5) at -32.1°C . ^b Tetraphenylethylene concentration. ^c The ratio of derivative peak 3 to peak 2 heights during linear sweep voltammetry as described in the text.

Table 2. The effect of temperature on the rate of cyclization of tetraphenylethylene dication.^a

T/K	$v_{0.5}/V\ s^{-1\ b}$	k/s^{-1}	$v_{0.7}/V\ s^{-1\ b}$	k/s^{-1}
273.2	326(6)	604	178.2(2.5)	563
263.1	117.5(7.0)	226	65.6(2.5)	215
251.6	45.1(4.7)	90.8	27.5(2.4)	94.8
241.2	16.1(1.5)	33.8	9.6(1.0)	34.4
E_a (kcal/mol)	11.6		11.2	
k_{298} (s^{-1})	3.4×10^3		3.0×10^3	
ΔS_{298}^\ddagger (cal/K mol)	-5.4		-7.0	
r^c	-0.998		-0.998	

^a Conditions as in Table 1. ^b The voltage sweep rates necessary for $p_3:p_2$ to equal 0.500 and 0.700. ^c Correlation coefficient from the Arrhenius correlation.

cyclization or to increased ordering of the solvent. In any case ΔS_{298} was not observed to be very large, only -6 cal/K mol as compared to -30 cal/K mol in the related cyclization of the anion radical of 1,3-dibenzoyl-1,3-diphenylpropane.¹⁵ This comparison suggests that the restriction of rotations in the transition state in the latter reaction is much more severe. This is not unexpected since the carbonyl groups of the anion radical are separated by three methylenes and rotations are relatively free until bond formation begins.

The data reported here, along with that from other recent studies^{15,16} provide a basis for the analysis of the mechanism of dimerization and cyclization reactions utilizing activation parameters. Mechanism assignments which include such studies as well as the determination of reaction orders are on much safer grounds than those based on experimental rate laws alone.

EXPERIMENTAL

The instrumentation and data retrieval system was the same as used in other recent publications.^{15,16,20} TFA was reagent grade and used without further purification. Reagent grade dichloromethane containing the supporting electrolyte (Bu_4NBF_4) was passed through a column of neutral alumina before use.

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