

# Kinetics and Mechanism of the Second Order Cyclization of the Cation Radicals Derived from 1,2-Diarylethanes

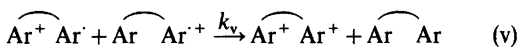
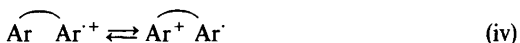
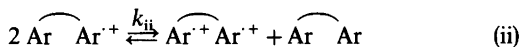
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The cyclization of the cation radical derived from 1,2-bis(3,4-dimethoxyphenyl)ethane in dry acetonitrile or in acetonitrile containing trifluoroacetic acid was observed to follow rate law (i) which is

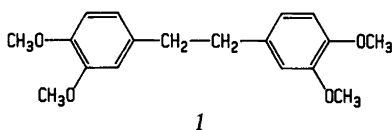
$$\text{Rate} = k_{app} [\text{Ar}-\text{CH}_2\text{CH}_2-\text{Ar}^{\cdot+}]^2 \quad (\text{i})$$

consistent with either disproportionation (ii) followed by cyclization (iii) or cyclization (iv) followed by rate-determining electron transfer (v). A secondary deuterium kinetic isotope effect was de-

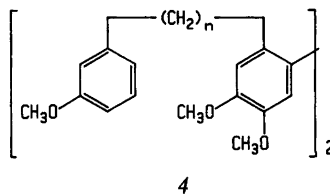
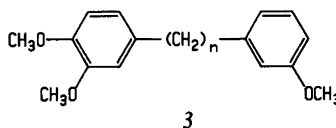
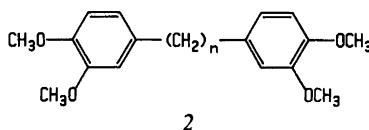


tected when the ring protons were exchanged with deuterium. It was concluded that the most likely mechanism for the cyclization is mechanism (iv)–(v) with rate-determining electron transfer (v).

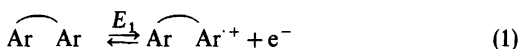
The cyclization of the cation radical (3,4-dimethoxyphenyl)ethane (1) was one of the first examples reported<sup>1</sup> of the general reaction, oxidative intramolecular coupling of alkoxy-substituted biaryl-

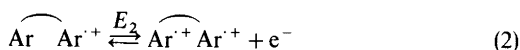


alkanes.<sup>1–30</sup> Most of the mechanistic work has been based upon product studies and cyclic voltammetric evidence. Symmetrically substituted compounds (2) were observed to undergo intramolecular cyclization while unsymmetrical ones (3) gave intermolecular dimers (4).<sup>2</sup> Potential step-sweep



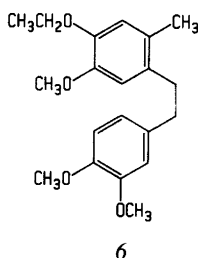
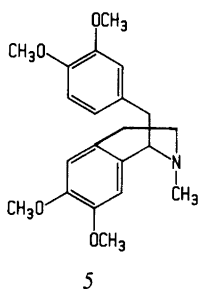
voltammetry experiments, supported by the product studies, indicated that the intramolecular cyclization of 2 involved the dication–diradical as an intermediate. It was suggested that the methylene groups separating the two aryl moieties have an insulating effect so that the potential difference,



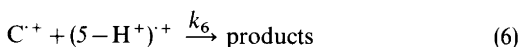
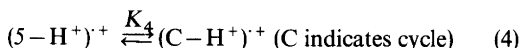
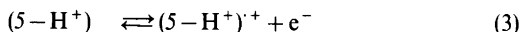


$E_2 - E_1$ , is small for symmetrically substituted compounds (2).<sup>2</sup> In the case of unsymmetrically substituted (3) the aryl moiety with two methoxy groups is oxidized about 0.5 V more easily than the anisyl group. The cation radicals of (3) were observed to undergo intermolecular coupling to give (4).

More recently, linear sweep voltammetry (LSV) and convolution potential sweep voltammetry (CPSV) have been applied to the study of the mechanism of the cyclization of two compounds related to (1), (5) and (6).<sup>30</sup> On the basis of the voltammetric results, different mechanisms were



postulated for the oxidative cyclization of (5) and (6). In the acidic media employed (5) is protonated on nitrogen ( $5-H^+$ ). The mechanism in this case was suggested to consist of reactions (3)–(6) which would give rise to rate law (7). Rate law (7) leads



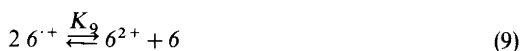
$$\text{Rate} = k_6 K_4 K_5 [(5-H^+)^{\cdot+}]^2 / [H^+] \quad (7)$$

to the prediction that  $dE^p/d \log v = (\ln 10) RT/3F$  and  $dE^p/d \log C_A = 0$  during LSV mechanism analysis. The independence of the peak potential on the substrate concentration can be derived from equation (8) where  $a$ ,  $b$  and  $i$  are the reaction orders in

$$dE^p/d \log C_A = (a + b + i - 1)/(b + 1) (\ln 10) RT/F \quad (8)$$

substrate, cation radical and protons, respectively.<sup>31</sup> An apparent inconsistency in the analysis is that the voltammetric experiments were carried out in strongly acidic media and  $[H^+]$  is expected to be constant under these conditions. This inconsistency was commented on in a footnote and the implication was made that the region near the electrode is not buffered since protons are produced in the reaction. It is, of course, possible that the acidity in the double layer is enhanced but it must be kept in mind that the reaction in question is second order in cation radical and even if  $k_6$  is a diffusion controlled second order rate constant, the reaction layer extends far beyond the immediate vicinity of the electrode. In our opinion, this is adequate reason for rejecting rate law (7) as accounting for the observed LSV results.

A simple disproportionation mechanism (9)–(10) with rate limiting cyclization was postulated to account for the oxidative cyclization of 6. This



mechanism gives rise to rate law (11) and the same

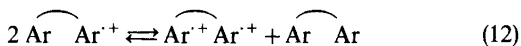
$$\text{Rate} = k_{10} K_9 [\text{6}^{\cdot+}]^2 / [\text{6}] \quad (11)$$

LSV predictions as for (7).

The reason that different mechanisms were postulated for the two reactions, in spite of very similar LSV behaviour, is that the CPSV analyses differed. Two factors should be considered in the evaluation of the latter data. The first is that the systems do not give ideal response and the voltammograms do not have the theoretical shapes necessary for the analysis. This is evident from Fig. 3 of Ref. 30. The second is that the calculations<sup>32,33</sup> upon which the CPSV predictions were made were derived for much simpler systems where the overall wave consists of the transfer of two electrons. During the oxidative cyclization of 5 and 6 and 2 in general, the overall reaction at the LSV wave involves the transfer of four electrons resulting in the dication of the cyclized product.<sup>2,34</sup> This added complication would surely have some effect on the wave shape. Thus, we feel that there is adequate reason to doubt the validity of the conclusions based upon the CPSV analyses in this case.

A further point which should be considered is

that it is not possible to distinguish between cyclization reaction sequences (12)–(13) and (14)–(16) by reaction orders, which is essentially the information



available from the LSV wave,<sup>31</sup> since both give rate law (17).

$$\text{Rate} = k_{\text{app}} [\text{Ar}^{\cdot+} \text{Ar}^{\cdot+}]^2 / [\text{Ar}^{\cdot+} \text{Ar}^{\cdot+}] \quad (17)$$

A possible way to distinguish between the two reaction sequences is to test for a secondary deuterium kinetic isotope effect when the ring protons are replaced by deuterium. Such an effect has recently been demonstrated in a related case, the dimerization of 4-methoxybiphenyl cation radical.<sup>35</sup> The secondary deuterium kinetic isotope effect arises when the carbon atoms attached to the isotopes undergo a change in hybridization,<sup>36</sup>  $sp^2$  to  $sp^3$  in this case. The disproportionation scheme (12)–(13) in the case where electron transfer (12) is rate-determining is not expected to show the kinetic isotope effect while the other mechanism (14)–(16) could when either (14) or (15) are rate-determining.

In this paper we report the results of an LSV kinetic study of the oxidative cyclization of *1*.

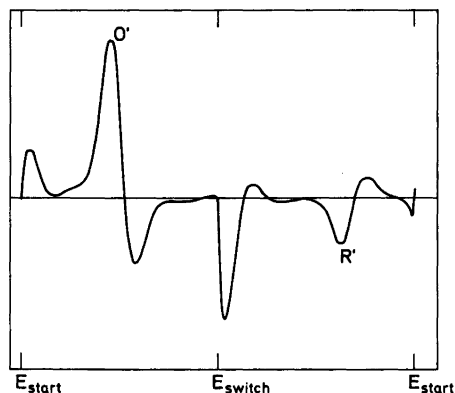


Fig. 1. Derivative cyclic voltammogram for the oxidation of (3,4-dimethoxyphenyl)ethane in acetonitrile–trifluoroacetic acid (19/1) containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) at 243 K and 80 V/s.  $E_{\text{switch}} - E_{\text{start}} = 900$  mV.

## RESULTS AND DISCUSSION

*Cyclic voltammetric oxidation of 1.* The derivative cyclic voltammogram observed during the oxidation of *1* in acetonitrile–trifluoroacetic acid (AN/TFA, 19/1) containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) at a voltage sweep rate ( $v$ ) of 80 V/s at a platinum electrode is illustrated in Fig. 1. Similar voltammetric behaviour was observed when the solvent was AN. The potential difference between  $O'$  and  $R'$  was observed to be 265 mV at  $-30^\circ\text{C}$ . Normalized potential sweep voltammetry (NPSV),<sup>37</sup> which gives a direct comparison of the experimental LSV wave with theoretical data, gave a slope of  $1.009 \pm 0.004$  when experimental data measured under the conditions given above were

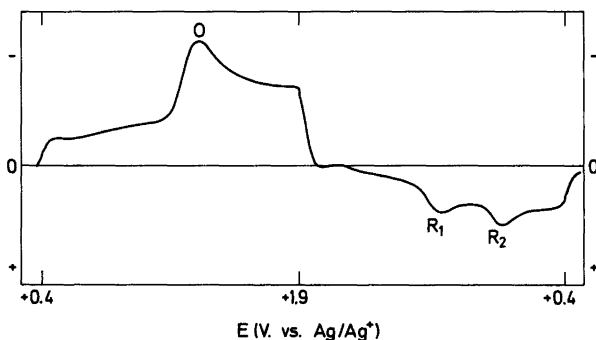
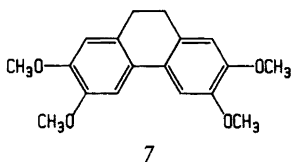


Fig. 2. Cyclic voltammogram for the oxidation of *1* in AN/TFA (19/1) containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) at 100 V/s and  $-30^\circ\text{C}$  at a platinum electrode.

correlated as the Y axis *vs.* theoretical data for Nernstian charge transfer as the X axis. This analysis rules out the possibility that  $O' - R'$  is due to a quasi-reversible oxidation of *1*. The NPSV slope for a quasi-reversible process with a cyclic voltammetric peak separation of 275 mV is much greater than unity.<sup>38</sup> An indication of the nature of the process giving rise to  $R'$  can be obtained from the cyclic voltammogram measured at 100 V/s over an extended potential range illustrated in Fig. 2. On the reverse scan two reduction peaks,  $R_1$  and  $R_2$ , are evident. The first,  $R_1$ , corresponds to  $R'$  in Fig. 1. A comparison with voltammograms already published<sup>2,34</sup> showed that  $R_1$  and  $R_2$  are due to the reduction of the dication and cation radical, respectively, of the cyclized product (7).



**LSV kinetic study.** Preliminary experiments carried out in AN which had been passed through neutral alumina indicated that  $dE^p/d \log v$  was of the order of 30 mV/decade. Under similar conditions it has been found that the yield of cyclized products is low.<sup>30</sup> When the water concentration is kept to a very low level by carrying out the voltammetry experiments in AN in the presence of alumina<sup>39</sup> the reaction appears to approach second order kinetics in cation radical. Data measured under these conditions are summarized in Table 1. Each peak

potential listed is the mean of five measurements and the numbers in parentheses are the standard deviations. The precision, even at the exceedingly low concentrations (0.05 mM), is noteworthy. The last column gives  $dE^p/d \log v$  obtained by linear regression analysis of the peak potential data. The last row of data gives the corresponding values of  $dE^p/d \log C_A$ . The data can be analyzed using the LSV equations (8) and (18). For a reaction second order in  $I^{+\cdot}$ , application of (18)<sup>31</sup> results in

$$dE^p/d \log v = 1/(b+1)(\ln 10)RT/F \quad (18)$$

$dE^p/d \log v$  equal to 19.3 mV/decade and assuming that  $a$  and  $i$  are 0, eqn. (8) predicts  $dE^p/d \log C_A$  to be -19.3 mV/decade. Solving (8) and (18) simultaneously for  $b$  then results in a value of 1.65. This result, along with the fact that the reaction tends to first order in  $I^{+\cdot}$  when water is less rigorously excluded, suggests that the kinetics correspond to competing reaction mechanisms, the major one (~83%) being second order and the minor component (~17%) first order in  $I^{+\cdot}$ .

The results in the previous paragraph suggested that acetonitrile containing TFA to reduce the water activity<sup>40</sup> would be a more suitable medium to study the cyclization kinetics in. Results of measurements in AN/TFA(19/1) are summarized in Tables 2 and 3 carried out at 18 and 0°C, respectively. Some drift in the reference electrode was observed in this solvent system. The most convenient method to determine the LSV slopes under these conditions was found to be to switch back and forth between sweep rates of 100 and 1000 mV/s. The sequence of measurement used was  $v$

Table 1. Derivative linear sweep voltammetry analysis of the kinetics of the cyclization of  $I^{+\cdot}$  in acetonitrile.<sup>a</sup>

$C_A/\text{mM}^b$	$E^p$ at $v/\text{mV s}^{-1}$				$dE^p/d \log v^c$
	100	200	400	1000	
0.05	227.9(0.3)	234.3(0.4)	241.0(0.5)	250.3(0.5)	22.4
0.10	224.4(0.1)	231.5(0.2)	238.4(0.3)	249.0(0.3)	24.5
0.20	221.5(0.1)	227.0(0.1)	233.8(0.1)	244.0(0.3)	22.6
0.40	216.6(0.0)	221.5(0.1)	228.2(0.2)	237.7(0.2)	21.3
0.80	—	215.7(0.1)	222.4(0.3)	231.9(0.2)	23.2
$dE^p/d \log C_A^c$	-12.2	-15.7	-15.7	-16.0	

<sup>a</sup> Measurements at 18°C at a platinum electrode in solvent containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) in the presence of neutral alumina. The peak potentials are expressed in mV *vs.* a potentiostat bias setting of +1.000 V relative to an  $\text{Ag}/\text{Ag}^+$  reference electrode. <sup>b</sup> Substrate concentration. <sup>c</sup> Expressed in mV/decade.

Table 2. Derivative linear sweep voltammetry analysis of the kinetics of the cyclization of  $I^{\cdot+}$  in AN/TFA at 18 °C.<sup>a</sup>

$C_A/\text{mM}$	$dE^p/d \log v^b$				Ave.
	1	2	3	4	
0.05	20.2	22.0	20.7	18.9	20.5(1.3)
0.10	22.9	20.2	20.9	23.6	21.9(1.6)
0.20	20.8	22.3	21.0	19.5	20.9(1.1)
0.40	21.8	19.6	20.6	22.8	21.2(1.4)
0.80	18.1	19.1	17.6	16.6	17.9(1.0)
$dE^p/d \log C_A^c$	-21.6	-23.6	-20.9	-23.6	-22.4(1.4)

<sup>a</sup> Solvent ratio (19/1) containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M). Measurements at a platinum electrode. <sup>b</sup> The difference in potentials measured at 100 and 1000  $\text{mV s}^{-1}$  expressed in mV/decade. <sup>c</sup> Expressed in mV/decade.

Table 3. Derivative linear sweep voltammetry analysis of the kinetics of the cyclization of  $I^{\cdot+}$  in AN/TFA at 0 °C.<sup>a</sup>

$C_A/\text{mM}$	$dE^p/d \log v^b$				Ave.
	1	2	3	4	
0.05	18.5	16.6	17.8	19.7	18.2(1.3)
0.10	16.2	16.6	17.2	16.8	16.7(0.4)
0.20	16.2	18.9	14.9	17.6	16.9(1.7)
0.40	14.3	15.2	15.1	14.2	14.7(0.5)
$dE^p/d \log C_A^c$	-18.1	-17.8	-19.8	-17.2	-18.2(1.1)

<sup>a</sup> Solvent ratio (19/1) containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M). Measurements at a platinum electrode. <sup>b</sup> The difference in potentials measured at 100 and 1000  $\text{mV s}^{-1}$  expressed in mV/decade. <sup>c</sup> Expressed in mV/decade.

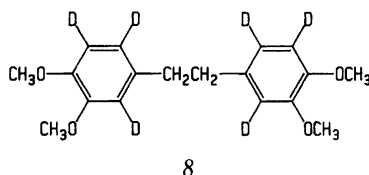
equal to 100 then 1000 then 100 then 1000. The numbers in column 1 of both Table 2 and Table 3 are the differences in  $E^p$  between the first 100 and the first 1000  $\text{mV/s}$  measurement. Column 2 is for the first 1000 and the second 100, column 3 for the second 100 and the second 1000, column 4 is the difference in  $E^p$  for the first 100 and the second 1000  $\text{mV/s}$  measurement. Each  $E^p$  used in the analysis was the mean of 5 measurements. The somewhat larger than usual standard deviations listed in the average column reflects the slow reference potential drift during the measurements. At 0 °C the numerical values of  $dE^p/d \log v$  and  $dE^p/d \log C_A$  are +18.0 and -18.0 mV/decade when  $b$  is 2 and  $a$  and  $i$  are 0 as is evident from eqns. (8) and (18). The observed values were +16.6(1.4) and -18.2(1.1), respectively, both within experimental error of the theoretical values (Table 3). The slopes obtained at 18 °C were +20.5(1.5) and -22.4(1.4) which are slightly greater

than the theoretical values, +19.3 and -19.3, for  $dE^p/d \log v$  and  $dE^p/d \log C_A$ , respectively. The larger deviation in the latter value is probably a consequence of the reference potential drift mentioned earlier.

*Analysis for a possible secondary deuterium kinetic isotope effect.* The LSV kinetic results presented above indicate that in AN/TFA (19/1) the cyclization of  $I^{\cdot+}$  follows rate law (19). This is the situation

$$\text{Rate} = k_{\text{app}}[I^{\cdot+}]^2 \quad (19)$$

where it may be possible to differentiate between cyclization mechanism (12)–(13) and (14)–(16) by the secondary deuterium kinetic isotope effect as was described earlier. For this analysis, compound 8 was prepared by exchanging the ring hydrogens of  $I$  with deuterium in trifluoroacetic acid (d) containing trifluoromethanesulfonic acid.



At any given value of  $v$ , deuterium kinetic isotope effects ( $k_H/k_D$ ) can be calculated from the difference in  $E^p$  observed for the H and D isomers using eqn. (20).<sup>41</sup> Thus, for  $k_H/k_D$  of 0.7 and 0.9, negative shifts

$$\Delta E^p = \log(k_H/k_D) \, dE^p/d \log v \quad (20)$$

in  $E^p$  of 3.1 and 0.9 mV are expected for a reaction order in cation radical of 2 at 298 K.

Ordinarily, the measurements of a 1 mV peak potential difference in two different solutions does not represent any special problem with the precision that we are able to attain.<sup>42</sup> However, the reference potential drift that we observe in the AN/TFA solutions make this type of measurement rather uncertain. In order to attempt to detect the effect, pairs of solutions containing **1** and **8** in concentrations identical within experimental error were made up. The accuracy of the concentrations is important since the peak potentials shift linearly with  $\log C_A$ . After removing the electrodes from one solution and placing them in another, several minutes are usually required for the potential to settle down to a constant value under ordinary conditions. In this particular case, the initial rapid change in potential with time settled down in a few minutes to a slowly drifting value. The procedure used was first to make a set of 15 measurements on a solution of either **1** or **8**, the interval between measurements being constant at about 30 s. After the first 5 measurements, the change in successive values was 0.2 mV or less. After the completion of

the first set of 15 measurements, measurements were begun on the solution of the other form. The alternating measurements were continued until 10 sets had been gathered for each solution. The procedure was carried out on three different pairs of solutions. In all three cases, the oxidation of **1** was observed at a potential positive of the potential for the oxidation of **8**, with peak potential differences ranging from 0.9 to 3.2 mV. In view of the potential drift problem encountered in the measurements in solvent containing TFA, the same procedure was carried out on two pairs of solutions in acetonitrile with neutral alumina in the cell. Once again  $E_H^p - E_D^p$  was positive, 1.0 and 1.1 mV, and this time there was no potential drift problem. The data along with the values of  $k_H/k_D$  calculated using eqn. (20) are summarized in Table 4. Secondary deuterium kinetic isotope effects ranging from 0.69 to 0.90 were obtained.

*The mechanism of the cyclization reaction.* In either AN with low water content or in AN/TFA, the LSV kinetic studies indicate that the major reaction pathway gives rise to rate law (19). This rate law is equally consistent with disproportionation mechanism (12)–(13) or that involving cyclization of the cation radical (14)–(16). In either case electron transfer, either (12) or (15) must be the slow step. The mechanism must take into account the secondary deuterium kinetic isotope effect observed during the comparison of the reactions of  $1^{\cdot+}$  with those of  $8^{\cdot+}$ . Reaction (12) which involves only the transfer of electrons between cation radicals does not involve any hybridization changes of the carbons which are subsequently bonded in the cyclized product. Thus, the observation of  $k_H/k_D$  ranging from 0.7 to 0.9 makes the disproportionations mechanism highly unlikely. On the other hand, reaction (14) does involve a change in hybridization of the two carbons through which the two rings are joined in the product. The change in hybridization from  $sp^2$  to

Table 4. The secondary deuterium kinetic isotope effect for the cyclization of  $1^{\cdot+}$  and  $8^{\cdot+}$ .

Solution	Solvent	$E_H^p - E_D^p/\text{mV}^a$	$k_H/k_D$
1	AN/TFA	3.2(0.6)	0.64–0.74
2	AN/TFA	1.3(0.9)	0.77–0.95
3	AN/TFA	0.9(1.0)	0.80–1.01
4	AN <sup>b</sup>	1.0(0.5)	0.84–0.94
5	AN <sup>b</sup>	1.1(0.6)	0.82–0.94

<sup>a</sup> The potential difference measured at 100 mV/s in solutions containing either **1** or **8** with a substrate concentration of 0.5 mM. <sup>b</sup> Measurements in the presence of alumina.

$sp^3$  in forward reaction (14) is expected to be accompanied by a kinetic isotope effect in the range observed.<sup>35,36</sup> Thus, the kinetic data suggest that the mechanism of cyclization of  $1^{\cdot+}$  involves initial cyclization of the cation radical (14) followed by electron transfer reaction (15). It must be pointed out that there is a high degree of uncertainty in the value\* of  $k_H/k_D$  due to the difficulties in measurement of the electrode potential difference to a high degree of precision. However, in the numerous experiments on which the data in Table 4 are based, no negative values of  $E_H^p - E_D^p$  were observed, i.e.  $k_H/k_D$  in all cases was found to be less than unity.

The two mechanisms (12)–(13) and (14)–(16) are a special case of the two mechanisms of electrodimmerization, radical ion dimerization or radical ion-substrate coupling that are currently under discussion.<sup>35,43,44</sup> It is perhaps not surprising that mechanism (14)–(16) is a favorable reaction pathway in view of the fact that the charged and uncharged rings are held in close proximity for the intramolecular coupling reaction. In order for the ion radical dimerization analog, dication diradical cyclization in this case, to occur second order electron transfer (12) must first take place. No data are available for the equilibrium constant for reaction (12) but it must surely be less than unity and probably  $10^{-2}$  or smaller. Thus, the radical–substrate analog (14) is more favorable during the cyclization reactions than in the intermolecular reactions. Previous work has shown that the intermolecular radical ion–substrate reaction is a favorable reaction pathway.<sup>35,43,44</sup>

The question arises as to why the cyclization of  $1^{\cdot+}$  follows rate law (19) while that for the related cation radical of 6 is consistent with rate law (17). A significant structural difference between 1 and 6 is that one of the rings in 6 does not have an unsubstituted position *para* to an alkoxy group. This then requires that the intramolecular coupling take place at a substituted ring position. This factor could change the balance between mechanisms (12)–(13) and (14)–(16) in favor of the disproportionation. The same argument can be put forth for the cyclization of  $5^{\cdot+}$ . However, in this case the apparent kinetics are consistent with rate law (19), providing the arguments against rate law (7) are accepted. There are no data available to distinguish

between rate-determining (12) or (15) in this case. The added complication of protonation equilibria of the side-chain nitrogen makes this system very much more complicated.

## EXPERIMENTAL

The practical aspects of making LSV kinetic measurements have been described in detail.<sup>42</sup> The solvent and electrolyte handling procedures were the same as those described in related work.<sup>35,45</sup>

Deuteration of 1 was carried out by dissolving in trifluoroacetic acid (d) containing trifluoromethanesulfonic acid and allowing to stand at room temperature as described in a previous preparation.<sup>35</sup>

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\* The uncertainty is in the magnitude of the effect, not the existence of an isotope effect.

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