

Kinetics and Mechanism of the Anodic Dimerization of *trans*-Anethole Studied by Cyclic Voltammetry and Scanning Electrochemical Microscopy

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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The mechanistic study of *trans*-anethole oxidation at platinum electrodes by cyclic voltammetry in acetonitrile shows that reaction occurs by a rapid radical dimerization of the *trans*-anethole radical cation. The use of the scanning electrochemical microscope (SECM) for studying homogeneous kinetics allowed the determination of the very large rate constant for the coupling between two *trans*-anethole radical cations: $\log(k/M^{-1} s^{-1}) = 8.6 \pm 0.4$. Combining this result with the cyclic voltammetric data allowed us to estimate the standard potential of the *trans*-anethole radical cation as $E^\circ = 1.40(4)$ V vs. SCE.

Radical cations of aromatic molecules are widely studied intermediates in organic chemistry and electrochemistry.¹ They are produced by monoelectronic oxidation of electron-rich conjugated molecules at an electrode,¹ or by oxidants such as inorganic ions (Fe^{3+} , Ce^{4+} or Cu^{2+}) or organic ions (such as triarylammonium ions).² It has been long known that the highly reactive radical cations thus formed can react with the parent compound to give, after a second electron exchange, the cycloaddition product.² The peculiarity of these cycloaddition reactions is that the final cyclodimer is uncharged ('a zero electron product') therefore implying that the intermediate dimer is reduced by some reacting partner to yield the final product. Among the possible candidates for the reductant that provides this second electron is the parent compound itself, the cyclodimerization reaction then being a (zero electron) chain reaction.^{2,3}



where (2)+(3) yields



and A is *trans*-anethole and D is the cyclodimer.

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This implies that the intermediate, $D^{\cdot+}$, is more oxidizing than the parent compound, $A^{\cdot+}$, which is quite unusual. Another candidate for the reducing agent is the reduced form of the oxidizing agent initially introduced in solution that would thus be regenerated, the net result being a zero electron catalytic reaction.⁴

Bauld *et al.* have reported very efficient cycloadditions promoted by *tris*(*p*-bromophenyl)ammonium hexachloroantimonate ions.^{3,5-7} In most cases, the oxidizing ammonium ion is introduced in solution together with the starting compound (usually an olefin) or with a mixture of substituted olefins and dienes. In the former case, the cyclodimer is formed, whereas in the latter case Diels-Alder products resulting from the cycloaddition of the olefin and the diene are obtained. The kinetics and mechanism of these ammonium salt-initiated radical cation catalyzed cycloadditions have been studied by spectroscopic techniques.⁸

The attractive possibility of triggering such reactions by generating the radical cation via direct oxidation of the starting material at an anode has also received some attention.⁹⁻¹³ The occurrence of anodically promoted cycloadditions was initially reported by Ebersson *et al.*⁹ who observed the cyclodimerization of some indene derivatives upon their direct oxidation at electrodes, but only under very specific conditions; a very high indene concentration (in the molar range) with a comparatively very low current density ($1-2$ mA cm⁻²) were used.

The possibility of using an anode to induce radical cation catalyzed cycloadditions or Diels–Alder reactions has also been studied.^{10,11} Typically, in these studies a dienophile (an olefin) and a diene (or a similar four π -electron compound) are both present at about the same concentration in solution. Upon anodic oxidation, Diels–Alder products form. The potentials for oxidation of the starting compounds point to an initial oxidation of the diene rather than of the dienophile compound.¹¹ However, in these cases the product analysis and the faradaic yield of the electrolysis in some cases point to the occurrence of a zero electron radical cation catalyzed cycloaddition^{10,11} but in other cases to a fundamentally different reaction involving the successive transfer of two electrons and two protons.¹²

Bauld *et al.* also reported radical cation cycloadditions¹³ or cyclodimerizations¹⁴ triggered by an anode, whether via the direct oxidation of an olefin or via the *in situ* generation of the oxidizing agent (aminium salt ion) that then initializes the cycloaddition reactions.¹⁴ In the latter reference and in most of the other work dealing with the direct oxidation of olefins for preparative purposes,¹¹ the problem of an inhibiting film forming at the anode surface is widely encountered. This problem is generally solved by the use of very low oxidizing electrolysis potentials, sometimes very negative of the peak potential observed for the oxidation of the starting compounds by voltammetry.

The aim of the present work was a mechanistic investigation of the reactions that a radical cation, reported to undergo radical cation catalyzed cyclodimerization when produced by aminium salt oxidation, undergoes if produced at an electrode surface by direct oxidation of the parent compound. For this purpose, we chose the oxida-

tion of *trans*-anethole because its oxidation is considered to result in a model radical cation-catalyzed cyclodimerization reaction that produces the corresponding *trans*-anethole cyclobutane dimer.^{5,8} The direct oxidation of *trans*-anethole (TA) was studied by cyclic voltammetry and scanning electrochemical microscopy (SECM).

Results and discussion

Cyclic voltammetry study. A typical cyclic voltammogram for the oxidation of *trans*-anethole (TA) recorded at a mm-size platinum electrode in acetonitrile is presented in Fig. 1. Although only the two first peaks are shown in Fig. 1, the complete voltammogram shows three successive irreversible peaks. The first one, corresponding to the oxidation of TA, occurs at about 1.35 V vs. SCE. The second and third one occur, respectively, at about 1.7 V and 2.1 V vs. SCE; in this study we focused on the first oxidation peak. If we assume that the direct oxidation of TA at the electrode proceeds via a mechanism equivalent to the one observed in the case of the aminium salt-initiated radical-catalyzed cycloaddition of TA,⁸ then the expected reactions occurring at the electrode can be written as:

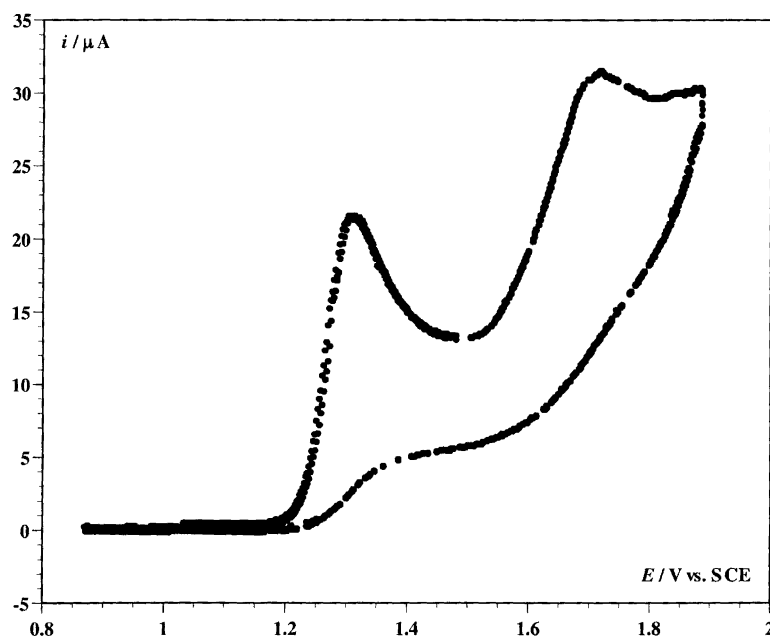
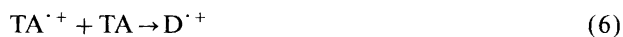
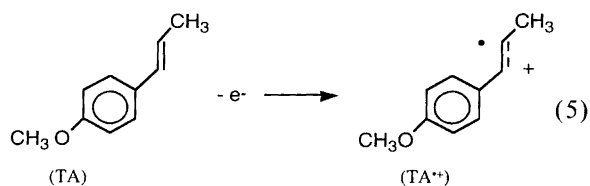
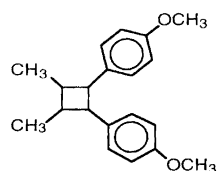


Fig. 1. Cyclic voltammogram of TA 1.5 mM in acetonitrile, TBABF₄ 0.1 M as supporting electrolyte, obtained at a platinum electrode, $d=1$ mm. Scan rate $\nu=0.2$ V s⁻¹.

with the second electron transfer taking place with the parent compound and at the electrode



where D is the final cyclobutane dimer.



The most interesting feature of this postulated mechanism is its 'zero electron' nature; the electrode can therefore be considered as a catalyst that only initiates the dimerization. Such 'zero electron mechanisms' can conveniently be characterized by cyclic voltammetry.¹⁵ They result in an easily detectable *decrease* of the peak current with decreasing scan rates, faster than the one simply due to diffusion, owing to the fact that at slow scan rate more time is given for reaction (7) to take place. Therefore, the variation of the TA oxidation peak current, i_p , with the scan rate, ν , was studied. The occurrence of the expected 'zero' electron cyclodimerization should have resulted in a decrease of the ratio $i_p/\nu^{1/2}$ with decreasing scan rate, as observed in the case of known 'zero' or electrocatalytic reactions.¹⁵ However, as can be seen in Fig. 2, the ratio remained roughly constant. The slight decrease with increasing scan rate is compatible

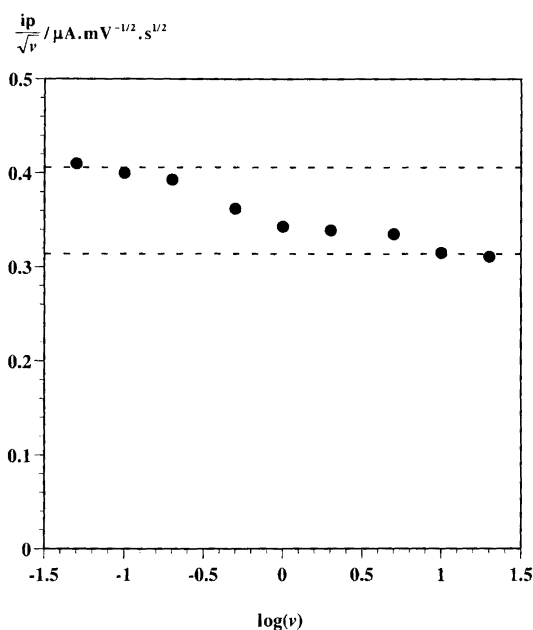


Fig. 2. Cyclic voltammetry of TA at a 1 mm platinum electrode: variation of the ratio of the oxidation peak current (in μA) over the square root of the scan rate (in mV s^{-1}) versus the log of the scan rate ν (in V s^{-1}). TA concentration: 0.35 mM. Acetonitrile, TBABF₄ 0.1 M supporting electrolyte.

with the heterogeneous electron transfer rate starting to interfere in the overall rate of the oxidation process.¹⁶

The fact that the ratio $i_p/\nu^{1/2}$ does not follow the expected trend rules out the possibility of a 'zero electron' cycloaddition being triggered by the direct oxidation of TA at the electrode, under cyclic voltammetry conditions. Further investigations were therefore required to determine the nature of the reaction following the direct oxidation of TA at the electrode.

To determine the number of electrons transferred at the potential of the first peak, steady state cyclic voltammetry at a platinum ultramicroelectrode (UME) was used. The plateau current of the sigmoidal-shaped voltammogram recorded using this technique is much less mechanism-dependent than the height of the transient voltammetric peak recorded at a mm-size electrode.¹⁷ Therefore, the height of the plateau current obtained at the UME is essentially the same as that obtained for the reduction of tetracyanoquinodimethane (TCNQ) or of anthracene at the same concentration. In both cases, the apparent number of electrons transferred was close to one.

Going back to cyclic voltammetry at mm-size electrodes (i.e. in the linear diffusion regime), the variation of the peak potential with the scan rate allows the easy determination of the order of the reaction following the oxidation.¹⁸ For the oxidation of TA at platinum electrodes, plots of the peak potential, E_p , versus $\log \nu$, such as the one presented in Fig. 3, were obtained. Provided that the scan rate was kept below a few tens of V s^{-1} , the peak potential varied linearly by 20(3) mV per log unit scan rate. At higher scan rates, the slope of the peak variation increased to reach values as high as 60 mV

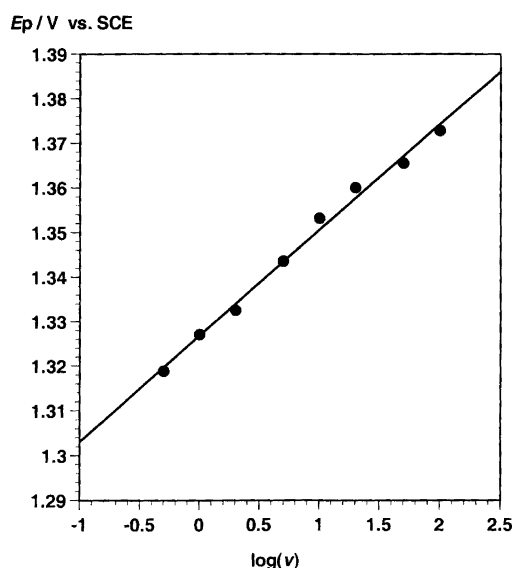


Fig. 3. Cyclic voltammetry of TA at a 1 mm platinum electrode: variation of the peak potential of the TA oxidation wave (E_p in V vs. SCE). Slope: 23 mV/decade ν . TA concentration: 1.5 mM. Acetonitrile, TBABF₄ 0.1 M supporting electrolyte.

(data not shown). This confirms that, at fast scan rates, the kinetic control changes from the chemical reaction to the heterogeneous electron transfer reaction,¹⁶ and makes the determination of the standard potential of the TA radical cation formed at the electrode and of its dimerization rate constant much more difficult. The problem was even worse when carbon was used as the electrode material, because the effect of the slow heterogeneous electron transfer was observed at much lower scan rates, indicating a slower heterogeneous electron transfer rate between carbon and TA than between platinum and TA.

At either Pt or C, no peak was observed on the reverse scan of the voltammogram for the highest scan rates used (up to a few hundred V s^{-1}). This precluded any estimation of the standard potential of the TA radical cation from the cyclic voltammetry data alone.

Nevertheless, the peak potential variation of 20 mV per log unit scan rate observed on platinum at the slowest scan rates (from 200 mV s^{-1} up to a few tens V s^{-1}) is sufficient to point to a dimerization reaction.¹⁸ This was confirmed by studying the variation of the peak potential, at a given scan rate, with the log of the TA concentration. As can be seen in Fig. 4, a 20 mV decrease of the peak potential per log unit of the TA concentration is observed.

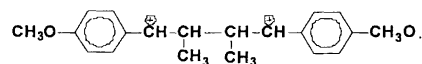
The observed variations of the peak potential of +20 mV per log unit of the scan rate and of -20 mV per log unit of the TA concentration are characteristic of a simple radical-radical dimerization mechanism,¹⁹ for which the theoretical slope values are +19.7 mV and -19.7 mV, respectively. We obtained similar results with dichloromethane as solvent.

Therefore the reaction observed to occur at the elec-

trode under our experimental conditions was



TA_2^{2+} is the initially formed dication:²⁰



The observed linear dependence of the peak potential versus $\log v$ is theoretically related to both the dimerization rate constant and the standard potential of the radical cation of TA by eqn. (11),¹⁸

$$E_p = E^\circ + 26.7 - 19.7 \log[RTkC/(Fv)] \quad (\text{at } 25^\circ\text{C}) \quad (11)$$

where E° and E_p , expressed in millivolts, are respectively the standard potential of the TA radical cation and the peak potential, k is the rate constant for dimerization, C , the TA concentration, v , the scan rate and F , the Faraday constant. Therefore the experimental E_p vs. $\log(v)$ graph can give access to E° or k provided one of them is known, i.e., can be determined independently.

SECM study of the oxidation of TA in acetonitrile. The use of SECM as a tool for the study of homogeneous kinetics has been described for several mechanisms,²¹ including dimerization.²² The experiment is carried out by approaching an ultramicroelectrode (tip) at which the chemical reaction of interest is electrochemically triggered towards a larger planar electrode (substrate) which collects the intermediate species formed at the tip. As the tip-substrate distance is made smaller, i.e., the electrode-substrate diffusional transit time is made small enough to be in the range of the intermediate species lifetime, a collection current starts to flow in the substrate. By plotting the ratio of this substrate (collector) current, I_s , over the tip (generator) current, I_t , as a function of the tip-substrate distance, d , the rate constant of the chemical reaction following the electron transfer at the electrode can be determined.

The main advantage of the technique is that it is a stationary steady-state technique, i.e., it does not require fast measurements of transient currents. The other advantage is that the tip is biased at a sufficiently positive potential so that the electron transfer at the electrode is fast enough not to interfere with the dimerization rate measurement. This characteristic is of interest in our case where we have seen that the heterogeneous electron transfer between the platinum electrode and TA hampered the measurement of the dimerization reaction by cyclic voltammetry.

For our study of the oxidative dimerization of TA, the reactions taking place in the tip/substrate domain are sketched in Fig. 5. The substrate potential is set at a value corresponding to the foot of the wave of the oxidation of TA, i.e., at a potential at which the radical

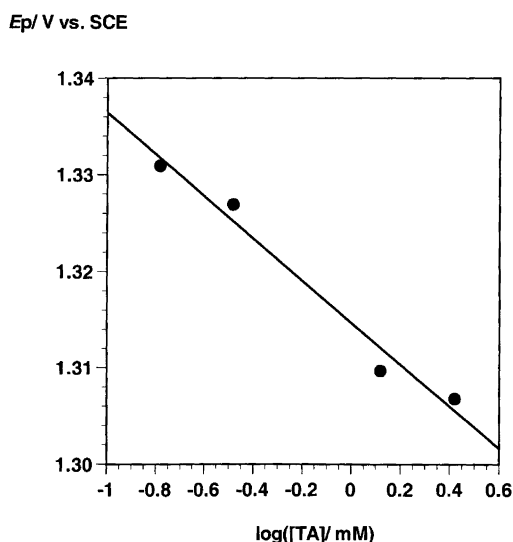


Fig. 4. Cyclic voltammetry of TA at a 1 mm platinum electrode: variation of the peak potential of the TA oxidation wave (E_p in V vs. SCE) versus the log of the TA concentration ([TA] in mM). Slope: 21.7 mV/decade [TA]. Scan rate $v = 0.2 \text{ V s}^{-1}$. Acetonitrile, TBABF₄ 0.1 M supporting electrolyte.

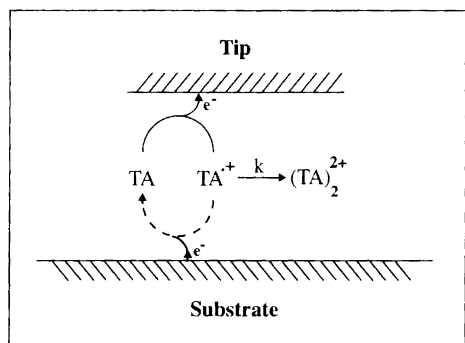


Fig. 5. Schematic of SECM measurements: diffusional and chemical processes occurring within the tip-substrate domain during the TA oxidation.

cation, TA^+ , can be collected and reduced back to TA, which is fed back to the tip. Acetonitrile was preferred over dichloromethane as the solvent because of its lower volatility.

In order to determine the tip-substrate distance, a stable redox species (i.e., one not undergoing any reaction after having been reduced or oxidized and not interfering with the studied TA oxidation), was added to the solution. In our case, TCNQ was used for this purpose. The tip was initially biased at a potential corresponding to the diffusion controlled reduction of TCNQ and lowered toward the substrate. As the tip-substrate distance is made smaller, part of the stable anion radical $TCNQ^{\cdot-}$ flux produced at the electrode reaches the substrate, is oxidized back to TCNQ and fed back to the tip thus increasing the tip current. At any distance, the ratio of the tip current, I_t , over the tip current at large tip-substrate separation, $I_{t,\infty}$, can be calculated and the tip-substrate distance, d , determined using previously published working curves.²³

Once the tip was brought to the desired distance from the substrate, the tip potential was scanned anodically toward potential regions at which the oxidation of TA occurred and the tip and substrate currents were measured. At a sufficiently close tip-substrate separation a collection current is found at the substrate (see Fig. 6). The ratio, I_s/I_t , was plotted as a function of the log of the dimensionless parameter $K = Ckd^3/(aD)$ [k = the dimerization rate constant; d , the measured tip substrate distance; C , the TA concentration; a , the electrode radius, and D , the TA diffusion coefficient $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$]²⁴ and fitted to the theoretical working curve corresponding to a dimerization²⁵ by adjusting the value of the dimerization rate constant k (see Fig. 7). As can be seen, the experiment was repeated for several TA concentrations, and for tip sizes of 5 and 1 μm diameter. In every case, a good fit was obtained between the experimental data and the working curve confirming the occurrence of a dimerization mechanism and allowing the determination of the dimerization rate constant of the TA^+ reaction: $\log(k/\text{M}^{-1} \text{ s}^{-1}) = 8.6 \pm 0.4$. To the best of our knowledge, this value corresponds to the fastest dimerization rate

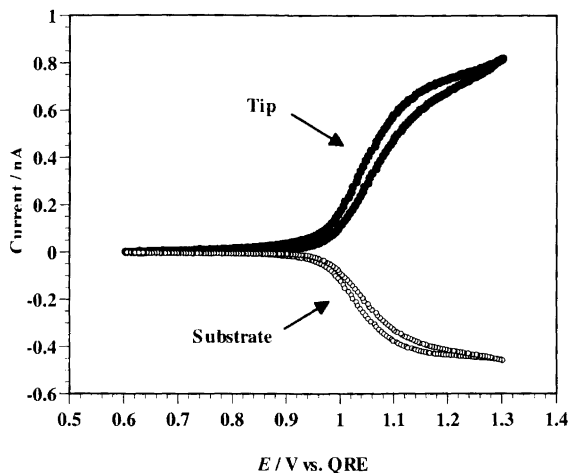


Fig. 6. SECM voltammogram of TA (1.5 mM) recorded at a tip-substrate separation of about 1 μm . The tip was scanned at 100 mV s^{-1} . The x-axis represents the tip potential expressed versus a quasireference electrode (QRE). The tip was a 5 μm diameter platinum electrode and the substrate a 60 μm diameter gold disk held at a potential of 0.6 V vs. QRE. Acetonitrile, TBABF₄ 0.1 M supporting electrolyte.

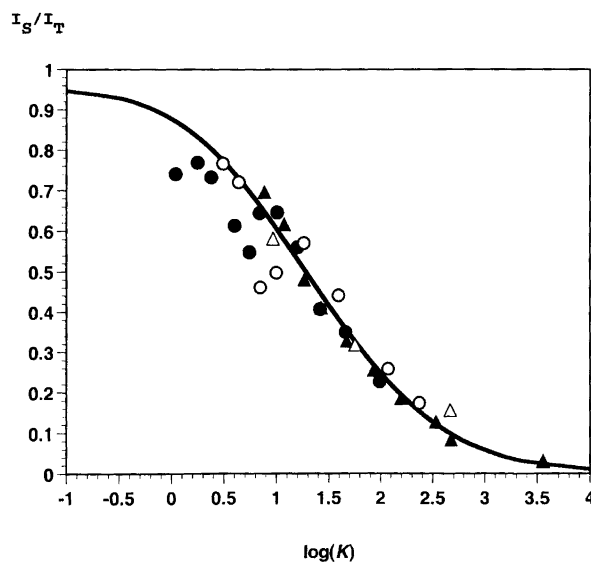


Fig. 7. SECM measurements: variation of the collection efficiency, defined as I_s (substrate current)/ I_t (tip current) as a function of the log of the dimensionless kinetic parameter $K = Ckd^3/(aD)$ (see the text). The experimental data (dots) are fit to the theoretical curve for the following conditions:

Symbol	$2*a/\mu\text{m}$	[TA]/mM	$\log(k)$
●	5	0.19	9
○	5	0.37	8.3
▲	5	0.77	8.7
△	1	0.77	8.3

[Average $\log(k/\text{M}^{-1} \text{ s}^{-1}) = 8.6 \pm 0.4$].

constant measured by SECM. The determination of such a high rate constant by cyclic voltammetry would have required scan rates as high as several thousand V s^{-1} , far above the limit at which the heterogeneous electron transfer rate was observed to interfere with the measurement.

Determination of the standard potential of the radical cation $\text{TA}^{\cdot+}$. From the variation of the peak potential with scan rate measured by cyclic voltammetry, the independent knowledge of the dimerization rate constant allows one to estimate, by using eqn. (11) together with the data of Fig. 3, the value of the standard potential for the half-reaction $\text{TA}^{\cdot+} + e = \text{TA}$ as $E^\circ = 1.40 \pm 0.04 \text{ V}$ vs. SCE.

Discussion

The study of the direct oxidation of *trans*-anethole in acetonitrile by cyclic voltammetry allowed us to rule out, under the conditions of the study, the occurrence of a 'zero' electron cycloaddition that would have taken place through a radical–substrate coupling mechanism. Although the reaction following the TA oxidation was too fast to be studied by cyclic voltammetry, this technique demonstrates a simple one electron radical cation–radical cation dimerization mechanism. Similar conclusions were drawn from cyclic voltammetry measurements in dichloromethane. The study of TA oxidation by SECM in acetonitrile confirmed the occurrence of a one electron dimerization and allowed the measurement of the coupling rate constant between two $\text{TA}^{\cdot+}$ radical cations, k , as $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

One electron per molecule radical cation–radical cation dimerization mechanisms are also reported in the literature for the coupling of radical cations of compounds similar to TA, such as the 3,4-dimethoxypropenylbenzene²⁶ or the 4,4'-dimethoxystilbene.²⁷ However, for this latter compound it is also reported that a one electron radical cation–substrate coupling mechanism is a minor²⁷ or even the major²⁸ dimerization path. The rate constant we report here for the radical–radical coupling of TA, the highest measured so far by SECM, is four orders of magnitude greater than that corresponding to the dimerization of the 4,4'-dimethoxystilbene cation radical (probably for steric reasons).

Our study indicates that under our experimental conditions, no coupling occurs between the electrogenerated radical cation and the parent *trans*-anethole. Although such a radical–substrate mechanism cannot be excluded as a minor process, its observation under our conditions is unlikely, because cyclic voltammetry measurements involve a high concentration of the radical cation in the immediate vicinity of the electrode, making a radical–radical reaction the most favorable process. In other words, a radical–substrate attack could only be detectable if its rate $k_{\text{rsc}} [\text{TA}^{\cdot+}][\text{TA}]$ was of the same order of magnitude as the rate of the radical–radical process

$k[\text{TA}^{\cdot+}]^2$. This would require that the ratio $(k_{\text{rsc}}[\text{TA}]/k[\text{TA}^{\cdot+}])$ become significant, which does not occur in the radical cation rich, parent *trans*-anethole poor, reaction layer at the electrode surface, especially with the high radical–radical bimolecular rate constant measured.²⁹

However, recall that, because of electrode fouling problems, preparative scale electrolysis of olefins reported to have resulted in the formation of zero electron products (cyclodimers or Diels–Alder adducts) are typically carried out at potentials very negative of the oxidation peak of the parent compound.^{11,13} This means that they take place at very low current densities. Radical cation concentration at the electrode surface is directly proportional to the current density, i , since $i = FD[\text{radical cation}]/\delta$, δ being the thickness of the diffusion layer. This implies that electrolysis takes place under conditions of very low radical cation concentration at the electrode surface. For example, in the first report of an anodically promoted cycloaddition by Ebersson,⁹ the working current density of 1–2 mA would correspond to a radical concentration at the electrode of about 1 mM for a parent compound concentration of the order of one molar [assuming typical values for the diffusion coefficient ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and for the thickness of the diffusion layer ($\approx 10 \mu\text{m}$)]. Clearly, these preparative scale electrolysis conditions favor radical cation–parent compound additions over radical cation–radical cation dimerizations.

In the case of aminium ion triggered cyclodimerizations of *trans*-anethole,^{5,8,14} we determined from the value of the standard potential of the *trans*-anethole radical cation that it is possible to obtain a definitive value for the driving force of the *trans*-anethole oxidation by the tris(4-bromophenyl)aminium ion ($E^\circ = 1.09 \text{ V}$ vs. SCE in acetonitrile as measured by us) as 0.31 V ($+7 \text{ kcal mol}^{-1}$). The oxidation of *trans*-anethole by the aminium salt is therefore quite endergonic and only takes place because it is followed by a subsequent reaction of the radical cation. The radical cation can thus be considered as a transient species whose concentration is always negligibly small in solution making any radical cation–radical cation dimerization very unlikely.

Experimental

The supporting electrolyte, tetra-*n*-butylammonium tetrafluoroborate (TBABF₄, Fluka, Buchs, Switzerland) was used as received. All other chemicals, except *trans*-anethole, were of the purest available grade and were from Aldrich (Milwaukee, WI). *trans*-Anethole was a generous gift from T. Aplin and N. L. Bauld. Acetonitrile was stored over molecular sieves. The reference electrode used for the cyclic voltammetry measurements consisted of a silver wire immersed in a silver perchlorate solution separated from the working solution by fritted glass. This electrode was calibrated against the ferrocene/ferrocinium couple taking a standard potential for this couple as $E_{\text{Fc}/\text{Fc}^+}^\circ = 0.405 \text{ V}$ vs. SCE. The SECM cell and

electrode preparation were as reported earlier^{21b} except for the quasireference electrode that was a platinum wire instead of a silver wire. Fouling of the electrode during the cyclic voltammetry measurements was not observed, provided that the scan rate was kept above 0.2 V s^{-1} and the electrode was not biased at potentials more than a few hundred millivolts positive to the first wave of the *trans*-anethole oxidation. The SECM instrument was described previously.³⁰ All the kinetic experiments were conducted at 25°C .

Conclusion

A mechanistic study of *trans*-anethole oxidation at platinum electrodes in acetonitrile points to a rapid dimerization of the *trans*-anethole radical cation ($k = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). No evidence of a zero electron radical cation catalyzed cyclodimerization of *trans*-anethole was observed. The occurrence of such a catalytic mechanism previously reported during the aminium salt initiated oxidation of *trans*-anethole^{5,8} is probably due in this case to the endergonic nature of the oxidation of *trans*-anethole by the aminium salt that results in a very small concentration of the *trans*-anethole radical cation, thus favoring the radical cation–parent *trans*-anethole reaction at the expense of the radical cation–radical cation dimerization reaction. The occurrence of the catalytic cycloaddition or cyclodimerization of compounds similar to *trans*-anethole, reported to take place during oxidative preparative scale electrolysis,^{11,13} probably results from the fact that they are conducted under conditions of very small current densities which implies very small concentrations of the radical cation at the electrode with respect to the parent compound. Combining SECM and cyclic voltammetry measurements allowed the estimation of the standard potential of the *trans*-anethole radical cation: $E^\circ = 1.40 \pm 0.04 \text{ V vs. SCE}$.

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