Mechanisms of the Electrohydrodimerization of Activated Olefins. IV.* The Protonation of Methyl Cinnamate Anion Radical
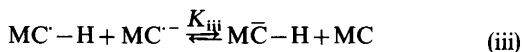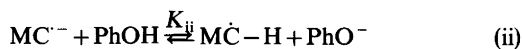
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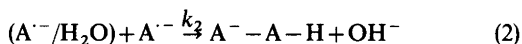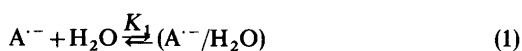
The protonation of methyl cinnamate (MC) anion radical by phenol in DMF was investigated in order to establish whether or not the resulting radicals participate in electrohydrodimerization. The overall reaction was observed to involve 2 e⁻ per molecule of MC consumed, producing the hydrogenated product. Kinetic studies in phenoxide buffers revealed rate law (i), corresponding to mechanism (ii)–(iv). At a constant value (1/1) of the buffer

$$\text{Rate} = k_{obs}[\text{MC}^{·-}]^2([\text{PhOH}]/[\text{PhO}^-])\cdot[\text{PhOH}]/[\text{MC}] \qquad \text{(i)}$$

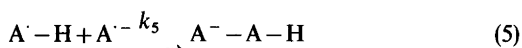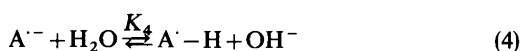$$\text{MC}^{·-} + \text{PhOH} \overset{K_{ii}}{\rightleftharpoons} \text{MĊ-H} + \text{PhO}^- \qquad \text{(ii)}$$

$$\text{MĊ-H} + \text{MC}^{·-} \overset{K_{iii}}{\rightleftharpoons} \text{M\bar{C}-H} + \text{MC} \qquad \text{(iii)}$$

$$\text{M\bar{C}-H} + \text{PhOH} \overset{k_{iv}}{\rightarrow} \text{MCH}_2 + \text{PhO}^- \qquad \text{(iv)}$$

ratio, [PhOH]/[PhO⁻], the rate was directly proportional to [PhOH] up until about 60 mM. The reaction orders in MC·⁻ and MC were deduced from linear sweep voltammetry studies. At high [PhOH], reaction (iv) becomes sufficiently fast that second order kinetics are observed reflecting only forward step (ii). It was concluded that MĊ–H does not undergo coupling reactions and must be excluded as a possible intermediate in electrohydrodimerization.

It has recently been concluded that the mechanism of electrohydrodimerization of activated olefins in water containing solvents involves reactions (1) and (2) and can be described by rate law (3).[1] An essential
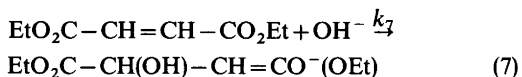
$$\text{A}^{·-} + \text{H}_2\text{O} \overset{K_1}{\rightleftharpoons} (\text{A}^{·-}/\text{H}_2\text{O}) \qquad \text{(1)}$$

$$(\text{A}^{·-}/\text{H}_2\text{O}) + \text{A}^{·-} \overset{k_2}{\rightarrow} \text{A}^- - \text{A} - \text{H} + \text{OH}^- \qquad \text{(2)}$$

$$\text{Rate} = k_2 K_1[\text{A}^{·-}]^2[\text{H}_2\text{O}] \qquad \text{(3)}$$

feature of this mechanism is that the anion radical–water complex formed in step (1) is of such nature that the proton transfer is not complete and hydroxide ion is not released. The reversible protonation of the radical anions (eqn. 4) followed by the coupling reaction (5) was rejected since the rate law (6) predicts inhibition by hydroxide ion which could

$$\text{A}^{·-} + \text{H}_2\text{O} \overset{K_4}{\rightleftharpoons} \text{A}^· - \text{H} + \text{OH}^- \qquad \text{(4)}$$

$$\text{A}^· - \text{H} + \text{A}^{·-} \overset{k_5}{\rightarrow} \text{A}^- - \text{A} - \text{H} \qquad \text{(5)}$$

$$\text{Rate} = k_5 K_4[\text{A}^{·-}]^2[\text{H}_2\text{O}]/[\text{OH}^-] \qquad \text{(6)}$$

not be detected.[1] It has since been found that hydroxide ion reacts exceedingly rapidly with esters, such as diethyl fumarate, in N,N-dimethylformamide (DMF) according to eqn. (7).[3] Thus, the activated olefin itself can act as a very effective

$$\text{EtO}_2\text{C} - \text{CH} = \text{CH} - \text{CO}_2\text{Et} + \text{OH}^- \overset{k_7}{\rightarrow}$$
$$\text{EtO}_2\text{C} - \text{CH(OH)} - \text{CH} = \text{CO}^-(\text{OEt}) \qquad \text{(7)}$$

hydroxide ion scavenger and competing reaction (7) could give rise to apparent kinetics that are consistent with rate law (3) even though the mechanism consists of reactions (4) and (5).

The coupling of neutral radicals with anion

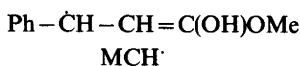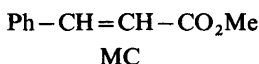* See Refs. 1–3 for other parts in this series.

radicals, as in (5), has been proposed for some other reactions such as the pinacolization of benzaldehyde and benzophenone.[4] Thus, the observation of rate law (3) does not differentiate between the two mechanisms as long as the effect of hydroxide ion is masked by reaction (7). Until recently,[1-3] the mechanism of electrohydrodimerization was considered to be established[5-10] as anion radical dimerization in all cases. This mechanism will not be considered in this paper since the evidence presented already[1-3] overwhelmingly rules it out for the cases that have been tested.

In order to test for the possible participation of neutral radicals in electrohydrodimerization, phenol was chosen as the proton donor. The reason for this was two-fold. In the first place, phenol is a much better proton donor than water and hence is expected to take part in an equilibrium such as (4) much more effectively. Secondly, and perhaps even more important in the present context, phenoxide ion is a much poorer nucleophile (and better leaving group) and is not expected to react readily with the activated olefins. Thus, esters such as diethyl fumarate and methyl cinnamate were expected to be stable in phenol/phenoxide buffers in DMF.

In this paper, the kinetics of the reactions of MC$^{\cdot-}$ in phenol buffers is reported. Reaction orders in anion radical, substrate, phenol and phenoxide ion are established and the reactions of the neutral radical, MC$^{\cdot}$, are described.

RESULTS

In order to clarify symbols used throughout this paper, pertinent structures and identifying symbols are listed below:

$$Ph-CH=CH-CO_2Me$$

MC

$$Ph-\overset{\cdot}{C}H-CH=C(OH)OMe$$

MCH$^{\cdot}$

$$Ph-\overset{-}{C}H-CH=C(OH)OMe \quad PhCH_2CH_2CO_2Me$$

MCH^{-} MCH$_2$

Alternative structures, involving protonation on carbon instead of oxygen, could be written for MCH$^{\cdot}$ and MCH^{-}. There is no evidence for the structures given but they are expected to be more

likely than alternative ones. This point has no effect on the discussion of the mechanism of the reduction of MC, at least in the detail made possible by kinetic measurements.

Kinetic studies in unbuffered DMF. Data obtained by derivative cyclic voltammetry[11-13] kinetic experiments on the reaction between MC$^{\cdot-}$ and phenol in DMF are summarized in Table 1. The kinetic analysis is based on the fact that $v_{\frac{1}{2}}$, the voltage sweep rate at which the ratio of the derivative maxima (R'_I) on the backward and forward scans of a cyclic voltammogram equals 0.500, is proportional to the apparent rate constant of the reaction following charge transfer.[14,15]

The first four rows of data reveal an unusual situation, the rate at constant phenol concentration (25 mM) decreases with increasing substrate concentration indicating an approximate 0.5 reaction order. The next four rows of data show that at constant [MC], the apparent rate constant is directly proportional to [PhOH]. The final five rows indicate the effect of temperature on the apparent rate constant. At a substrate concentration of 2.0 mM and [PhOH] equal to 10 mM, the apparent activation energy was observed to be 9.0 kcal/mol with a linear regression correlation coefficient of 0.999.

Table 1. The kinetics of the reaction of methyl cinnamate anion radical with phenol in DMF.[a]

[MC]/mM	[PhOH]/mM	T/°C	$v_{\frac{1}{2}}$[b]/V s^{-1}
0.5	25	20	33.5
1.0	25	20	29.0
2.0	25	20	22.7
4.0	25	20	14.7
1.0	10	20	9.5
1.0	20	20	19.0
1.0	40	20	40.3
1.0	80	20	84.0
2.0	10	5.6	5.4
2.0	10	20.7	13.2
2.0	10	30.9	20.0[c]
2.0	10	37.9	30.0[c]
2.0	10	49.6	50.0[c]

[a] Measured by derivative cyclic voltammetry in the presence of Bu$_4$NBF$_4$ (0.1 M) at a mercury electrode. [b] Voltage sweep rate necessary for the ratio of the derivative maxima on the backward and forward scans to equal 0.500. [c] The temperature was adjusted so that $v_{1/2}$ equaled the values shown.

Table 2. Linear sweep voltammetry studies of the kinetics of the protonation of methyl cinnamate anion radical by phenol in un-buffered media.[a]

$v/V s^{-1}$	$-E^P/mV$ [b] at [MC]/mM			
	0.50	1.00	2.00	4.00
0.100	336.8(0.0)	336.6(0.1)	335.3(0.1)	334.2(0.0)
0.200	342.4(0.0)	342.0(0.0)	341.0(0.1)	339.8(0.0)
0.400	350.9(0.1)	349.8(0.0)	348.0(0.0)	342.7(0.1)
1.000	361.2(0.0)	359.1(0.1)	356.0(0.0)	348.6(0.1)

[a] Measurements in DMF at a mercury electrode in the presence of phenol (50 mM) and Bu_4NBF_4 (0.1 M) at 22 °C.
[b] Peak potential measured by derivative linear sweep voltammetry *vs.* a potentiostat bias setting of -1.700 V *vs.* Ag/Ag^+. The numbers in parentheses are the standard deviations in 5 replicate measurements.

The results of a linear sweep voltammetry (LSV) study of the reaction at [PhOH] equal to 50 mM are summarized in Table 2. The voltage sweep rate dependence, $dE^P/d \log v$, was observed to be concentration dependent, ranging from 24.8 mV/decade at [MC] equal to 0.50 mM to 14.0 mV/decade at 4.00 mM.

The results in Tables 1 and 2 indicate a very complex reaction scheme and are highly indicative that a product (or products) of the reaction is exerting an inhibiting effect on the rate. For this reason, no further attempts were made to study the reaction in unbuffered media.

The effect of phenoxide ion on the reaction kinetics. Data obtained for the reaction of MC^{-} with phenol in DMF in the presence of various amounts of PhO^- are summarized in Table 3. The first four rows of data illustrate the inhibiting effect of phenoxide ion and the final entry indicates that the reaction rate is doubled by increasing the phenol concentration by a factor of 2 at $[PhO^-]$ equal to 25 mM.

Kinetics of the reaction in buffered media. The results described in the previous paragraph identify the inhibiting species to be phenoxide ion. A series of experiments were conducted at a buffer ratio, $[PhOH]/[PhO^-]$, equal to 1.0, while the phenol concentration was varied from 10 to 80 mM and the substrate concentration was varied over the range, 0.25 to 4.00 mM. The source of phenoxide ion was from the neutralization of phenol by Bu_4NOH added in methanol solution. In order to hold the concentrations of Bu_4N^+ and methanol constant, the amount of supporting electrolyte (Bu_4NBF_4) in each case was adjusted so that $[Bu_4N^+]$ was 0.10 M and it was necessary to add methanol in some cases so that [MeOH] was 2.34 M. The remainder of the experiments described were conducted in media of the above composition.

Derivative cyclic voltammetry kinetic experiments for the various buffers are summarized in Table 4. The data give evidence for two important

Table 3. The effect of phenoxide ion on the kinetics of the protonation of methyl cinnamate anion radical by phenol.[a]

[MC]/mM	[PhOH]/mM	$[PhO^-]$/mM	$v_{\frac{1}{2}}/V s^{-1}$
0.50	50	0	88
0.50	45	5	75
0.50	40	10	55
0.50	25	25	14
0.50	50	25	29

[a] Measurements in DMF containing Bu_4N^+ (0.1 M) at a mercury electrode at 25 °C.

Table 4. Kinetics of the protonation of methyl cinnamate anion radical in phenol — phenoxide buffers.[a]

[MC]/mM	$v_{\frac{1}{2}}/V s^{-1}$ at $([PhOH]/[PhO^-])/(mM/mM)$				
	10/10	20/20	40/40	60/60	80/80
0.25	—	—	—	49.8	30.0
0.50	6.80	—	—	45.5	29.1
1.00	6.10	12.6	24.0	41.0	26.0
2.00	5.40	12.0	23.2	—	24.0
4.00	—	11.6	23.5	—	—

[a] In DMF containing Bu_4N^+ (0.1 M) and MeOH (2.34 M) at 22 °C. Measurements at a mercury electrode.

Table 5 Voltage sweep rate dependence during the protonation of methyl cinnamate anion radical as a function of the buffer composition.

[MC]/mM	$(dE^p/d \log v)/(mV/decade)$ at $([PhOH]/[PhO^-])/(mM/mM)$				
	10/10	20/20	40/40	60/60	80/80
0.25	19.4	23.0	22.0	25.2	25.0
0.50	21.5	24.9	23.4	23.5	26.7
1.00	19.7	24.0	25.6	25.7	27.8
2.00	20.8	24.6	28.8	28.9	29.3

[a] Each slope given is for four sweep rates, 100, 200, 400 and 1000 mV s^{-1} and 5 replicates were made for each potential measurement as in Table 2. Measurements by derivative LSV at a mercury electrode at 22 °C.

quantities, the reaction orders in MC$^-$/MC and in PhOH. In each of the buffers, the apparent rate constant is very nearly independent of the substrate concentration with a slight decreasing trend in every case. This is indicative of a reaction order in MC$^-$/MC equal to 1.0 and perhaps some inhibiting effect of the phenoxide ion produced during the reaction. The apparent rate constants are found to be very nearly proportional to [PhOH] up to 60 mM and decrease again upon going to a concentration of 80 mM. The phenol concentration dependence indicates a reaction order of 1.0 in phenol in addition to the buffer ratio.

Data from LSV studies of the reaction in the buffers are summarized in Table 5. Each of the values of $dE^p/d \log v$ represent measurements at sweep rates of 100, 200, 400 and 10000 mV s^{-1} with five replicates at each sweep rate. Two trends are apparent in the data. At the lowest concentration of the buffer, $dE^p/d \log v$ appears to be concentration independent and the value 20.4 ± 1.0 is in good agreement with the theoretical value of 19.5

mV/decade predicted for a reaction order (*b*) in anion radical of 2.0 according to eqn. (8).[16] When

$$dE^p/d \log v = (1/(b+1))RT/F \qquad (8)$$

the buffer concentration is increased to 20 mM, the slope is still concentration independent but is higher than predicted for $b=2$. The value observed, 24.1 ± 0.8 mV/decade, indicates a non-integral reaction order in anion radical between 2 and 1. The increasing trend in $dE^p/d \log v$ continues as the buffer concentration is increased and the second trend is observed at buffer concentrations of 40 mM or greater. The value of the slope becomes concentration dependent, increasing with increases in substrate concentration. At a buffer concentration of 80 mM, the slope observed at [MC] equal to 2.00 mM was 29.3 mV/decade which is identical to the value predicted by (8) for $b=1$. In fact, there appears to be a diagonal relationship in going from the lowest buffer and substrate concentration ($b=2$) to the highest concentrations ($b=1$). These

Table 6. Electrode potential dependence on the buffer composition during the protonation of methyl cinnamate anion radical by phenol in DMF.[a]

[MC]/mM	$-E^p/mV$[b] at $([PhOH]/[PhO^-])/(mM/mM)$				
	10/10	20/20	40/40	60/60	80/80
0.25	388.2	383.9	377.6	369.9	376.4
0.50	386.0	381.3	373.9	369.3	374.2
1.00	387.0	382.2	374.2	368.4	373.2
2.00	387.3	384.0	374.7	367.1	372.9
Ave.	387.3(9)	382.9(13)	375.1(17)	368.7(12)	374.2(16)

[a] Measurements at 100 mV s^{-1} from the same data as that used in Table 5.

data indicate competing mechanisms under the conditions of the LSV experiments, one second order in anion radical and the other first order.

The electrode peak potentials measured at 100 mV s^{-1} in each of the sets of experiments used to obtain the slopes in Table 5 are listed in Table 6. These data show that the peak potentials at 100 mV s^{-1} are very nearly concentration independent. Correlation of the average values for buffer concentrations ranging from 10 to 60 mM results in dE^p/d log[PhOH] of 23.4 mV/decade. The theoretical value is given by eqn. (9) where X refers to phenol.[16] This indicates that the reaction order in

$$dE^p/d \log C_X = (x/(b+1))RT/F \qquad (9)$$

phenol (x) is equal to 1.0 in this buffer range providing the value of b is such that dE^p/d log v is equal to 23.4 mV/decade. In view of the data in Table 5, this is very nearly the case. Thus, the LSV data support that obtained from derivative cyclic voltammetry (Table 4) and indicate that the reaction is first order in buffer and phenol up to a concentration of 60 mM.

The value of temperature studies in electrode mechanism analysis has recently been emphasized.[17] In order to attempt to detect a change in mechanism with changes in buffer concentration, apparent activation energies were determined by making measurements in the temperature range, +20 to −16 °C, in each of the buffers with a substrate concentration equal to 1.00 mM. The method used was that described recently which does not require the evaluation of rate constants.[14] At each temperature v was adjusted so that R_1^i was equal to 0.500 and the activation energy could then be calculated from equation (10).[14] The data are summarized in Table 7. There does not appear to be a trend in the

$$d \ln v_{\frac{1}{2}}/d(1/T) = -E_a/R \qquad (10)$$

data and the average value is 9.3±0.6 kcal/mol. Thus, any change in mechanism that may take place with change in buffer concentration is not reflected in the apparent activation energy.

The coulometric n *value for the protonation of the* MC$^{\cdot-}$. The coulometric n value, the number of electrons per molecule of substrate consumed, is a very important quantity in determining whether or not any coupling reactions of MC$^{\cdot}$ are taking place. LSV peak currents for purely kinetic waves can be used to determine n but this is normally

Table 7. Apparent activation energies for the protonation of methyl cinnamate anion radical in phenol − phenoxide buffers.[a]

Buffer[b]	E_a/kcal mol^{-1}	r[c]
10/10	9.5	0.994
20/20	9.7	0.998
40/40	8.3	0.999
60/60	9.8	1.000
80/80	9.2	0.999
Ave.	9.3(6)	

[a] Measurements by derivative cyclic voltammetry as in Ref. 14. Measurements in DMF containing MC (1.00 mM), Bu$_4$N$^+$ (0.1 M), methanol (2.34 M) at a mercury electrode. [b] [PhOH]/[PhO$^-$] in mM/mM. [c] Correlation coefficients for linear regression analysis at five temperatures ranging from about +20 to −16 °C.

somewhat approximate since the peak current is dependent upon, among other quantities, the diffusion coefficient of the substrate. This is usually not known and model substances must be used which are expected to have similar diffusion coefficients. However, in the present case the latter approximation is not necessary since the peak current for the reduction of MC under conditions where only one electron is transferred, i.e. hydrodimerization in DMF containing low concentrations of water, can be used as the standard reaction. The peak currents for 1.00 mM solutions of MC

Table 8. Coulometric n values for the protonation of methyl cinnamate anion radical by phenol in DMF.[a]

[PhOH]/mM	[PhO$^-$]/mM	I^p/μA	n_{app}[b]
0	0	0.992(0.006)	1.00
10	10	1.986(0.026)	2.00
20	20	1.939(0.026)	1.96
40	40	1.889(0.006)	1.90
60	60	1.984(0.044)	2.00
80	80	1.988(0.012)	2.00
Ave.			1.97(4)

[a] Measurements at 100 mV s^{-1} in DMF containing Bu$_4$N$^+$ (0.1 M) and MC (1.00 mM). All solutions other than that for the first entry also contained methanol (2.34 M). Measurements at a mercury electrode at 22 °C. [b] Calculated by dividing the peak current by that obtained in the absence of the buffer.

in DMF and DMF containing the buffers are listed in Table 8. The numbers in parenthesis are the standard deviations in 10 replicate measurements. The values at the two extremes of the buffer concentration were observed to be equal to 2.00 and the average value to 1.97 ± 0.04. Thus, there can be little doubt that $2 \, e^-$ per molecule of MC reduced are involved under all conditions where phenol is present.
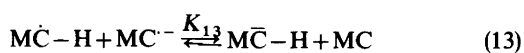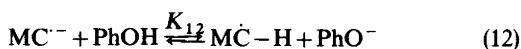
DISCUSSION

The following facts are clear from the data presented in the preceeding sections. (i) The reaction is very complex in unbuffered media due to the inhibition by phenoxide ion. The latter is complicated by the fact that two PhO^- are produced for each MC consumed. (ii) At low buffer concentration, the reaction order in $MC^{\cdot-}$ is 2 and approaches 1 at high buffer and substrate concentrations. (iii) The reaction order in phenol appears to be 1 in either buffered or unbuffered DMF. (iv) The reaction order in $MC^{\cdot-}/MC$, obtained from the derivative cyclic voltammetry experiments is 1. The latter taken with the LSV results at low buffer concentrations indicates a -1 order in MC under those conditions. This result can also be implied from the LSV data alone and the latter also indicates that a competing reaction in which the reaction order in MC is 0 is taking place at the higher buffer concentrations. (v) The apparent activation energy is independent of the buffer concentration and must therefore be essentially the same for both of the competing mechanisms. (vi) The reaction involves the transfer of two electrons per molecule of MC under all conditions studied in the presence of phenol.

The data at the lowest buffer concentration (10 mM) appears to be the simplest situation encountered in that the reaction order is 2.0 in $MC^{\cdot-}$ and -1.0 in MC. Under these conditions, the kinetics of the reaction can be described by rate law (11). A mechanism which appears to be completely consistent with the data under these conditions consists of equilibria (12) and (13) followed by protonation (14). The apparent rate constant, k_{obs}, is then

$$\text{Rate} = k_{obs}[MC^{\cdot-}]^2([PhOH]/[PhO^-]) \cdot [PhOH]/[MC] \qquad (11)$$

$$MC^{\cdot-} + PhOH \overset{K_{12}}{\rightleftharpoons} M\dot{C} - H + PhO^- \qquad (12)$$

$$M\dot{C} - H + MC^{\cdot-} \overset{K_{13}}{\rightleftharpoons} M\bar{C} - H + MC \qquad (13)$$

$$M\bar{C} - H + PhOH \overset{k_{14}}{\rightarrow} MCH_2 + PhO^- \qquad (14)$$

described by (15).

$$k_{obs} = k_{14} K_{12} K_{13} \qquad (15)$$

This mechanism can also account for the appearance of a competing mechanism at higher substrate and phenol concentrations. Since the buffer ratio was held constant at 1.0, the product of $[MC^{\cdot-}]$ and $[PhOH]$ must remain constant as long as reaction (12) is at equilibrium. On the other hand, assuming that equilibrium (13) is fast under all conditions which appears to be justifiable, the steady state concentration of $M\bar{C} - H$ increases directly with increases either in the phenol or the substrate concentrations. Thus, the rate of reaction (14) is enhanced to the second power of the increase in $[PhOH]$ and to the first power of the increase in substrate concentration. When the rate of (14) is sufficiently enhanced, it will no longer determine the rate and the kinetics will only reflect the rate of the forward step (12). If this is correct the rate law for the apparent competing reaction is (16). It is therefore likely that there is no competing reaction

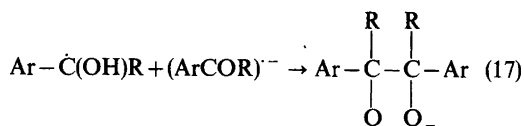$$\text{Rate} = k_1[MC^{\cdot-}][PhOH] \qquad (16)$$

at all but that the rates of reactions (12) to (14) are in rather delicate balance and small changes in the concentrations of the intermediates can cause the overall rate of the reaction to be determined by different steps.

The fact that the observed activation energy, 9.3 ± 0.6 kcal mol^{-1}, is independent of the buffer concentration strongly suggests that it is a reflection of only forward reaction (12). This conclusion is strongly supported by related work. The activation energy for the protonation of anthracene anion radical in DMF has been observed to be equal to 8.8 ± 0.5 kcal mol^{-1}, which is within experimental error of that for $MC^{\cdot-}$.[18]

The question regarding the possible intermediacy of neutral radicals in hydrodimerization of activated olefins appears to be answered. There is no evidence in this work that the neutral radical undergoes coupling reactions, either with substrate, an anion radical, or self dimerization. This has only been demonstrated when MC is the substrate but it
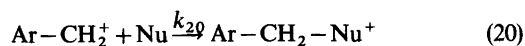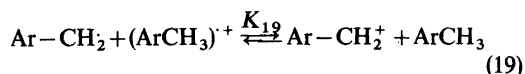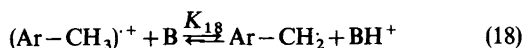
would appear to be very unlikely that the small structural changes involved in going to the other activated olefins would completely change this situation. On this basis, it appears safe to conclude that the anion radical — water complex mechanism is the most likely mechanism of electrohydrodimerization under the usual conditions, i.e. in aprotic solvents in the presence of low concentrations of weak proton donors.[1] Once the neutral radical is formed by the complete transfer of the proton from the donor, the favored reaction than becomes electron transfer to give the carbanion which is rapidly protonated.

The results reported here cast very serious doubt on the conclusion of Nadjo and Savéant regarding the mechanism of pinacol formation during the reduction of aromatic carbonyl compounds.[4] They propose that the primary step in the reaction is the coupling between the neutral radical and the anion radical as in (17). It is difficult to understand why

$$Ar-\dot{C}(OH)R+(ArCOR)^{\cdot -} \rightarrow Ar-\underset{\underset{O}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{O_-}{|}}{\overset{\overset{R}{|}}{C}}-Ar \quad (17)$$

this step becomes favorable relative to electron transfer in this case. There surely is enough doubt to warrant a reinvestigation of these systems under carefully controlled conditions.

In conclusion, attention can be drawn to a completely analogous system involving cation radicals. The reaction of hexamethylbenzene $(Ar-CH_3)$ cation radical in acetonitrile with very low water concentration involves a mechanism consisting of two equilibria (18) and (19) followed by the reaction of the benzylic cation (20). The rate law proposed when water is effectively removed was (21), exactly analogous to (11).[19]

$$(Ar-CH_3)^{\cdot +} + B \overset{K_{18}}{\rightleftharpoons} Ar-\dot{C}H_2 + BH^+ \quad (18)$$

$$Ar-\dot{C}H_2 + (ArCH_3)^{\cdot +} \overset{K_{19}}{\rightleftharpoons} Ar-CH_2^+ + ArCH_3 \quad (19)$$

$$Ar-CH_2^+ + Nu \overset{k_{20}}{\longrightarrow} Ar-CH_2-Nu^+ \quad (20)$$

$$Rate = k_{20}K_{18}K_{19}[Ar-CH_3^{\cdot +}]^2 \times$$
$$([B]/[BH^+])[Nu]/[Ar-CH_3] \quad (21)$$

It is surely becoming increasingly evident that the reactions of ion radicals in general, anions and cations, are far more complex than was believed a few years ago.

EXPERIMENTAL

The chemicals used, methyl cinnamate, phenol and tetrabutylammonium hydroxide, were reagent grade and used without further purification. Procedures for the purification of solvent and electrolyte were those reported in recent work from this laboratory.[13] The instrumentation and data handling procedures were the same as reported earlier.[13]

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