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The Mechanisms of the Dimerization of Benzaldehyde Anion Radical in Ethanol and Aqueous Ethanol Buffers

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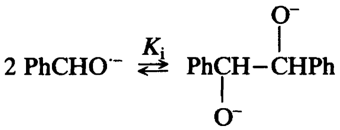
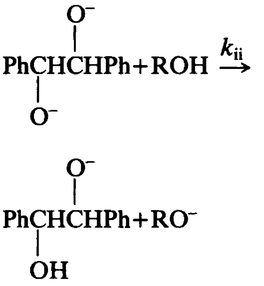
Benzaldehyde anion radical undergoes dimerization in ethanol and aqueous ethanol containing Bu_4NOH (>10 mM) by a mechanism consisting of the reversible dimerization (i) followed by protonation reaction (ii). This mechanism was demonstrated by showing the applicability of rate law (iii) to the data.



$$2\,\mathrm{PhCHO}^{\cdot -} \overset{K_i}{\rightleftarrows} \mathrm{Ph}\underset{\mathrm{O}^-}{\underset{|}{\mathrm{C}}}\mathrm{H}-\overset{\mathrm{O}^-}{\overset{|}{\mathrm{C}}}\mathrm{HPh} \qquad \text{(i)}$$

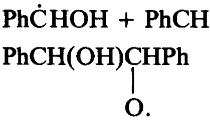


$$\mathrm{Ph}\overset{\overset{\mathrm{O}^-}{|}}{\underset{\underset{\mathrm{O}^-}{|}}{\mathrm{C}}}\mathrm{HCHPh}+\mathrm{ROH} \xrightarrow{k_{ii}} \mathrm{Ph}\overset{\overset{\mathrm{O}^-}{|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{HCHPh}+\mathrm{RO}^- \qquad \text{(ii)}$$

$$\text{Rate} = k_{ii}K_i[\mathrm{PhCHO}^{\cdot -}]^2[\mathrm{ROH}] \qquad \text{(iii)}$$

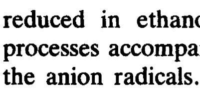
A primary deuterium kinetic isotope effect was observed and the rate of the reaction was observed to be independent of $[Bu_4NOH]$ as long as the latter was greater than about 20 mM. At lower $[Bu_4NOH]$ or in the presence of HOAc another mechanism competes which is first order in benzaldehyde anion radical. The latter was demonstrated by derivative cyclic voltammetry reaction orders approaching 1 and by linear sweep voltammetry in the presence of HOAc. The coulometric n value was observed to be 1 regardless of the conditions indicating that dimerization takes place under all conditions studied. The most likely first order reaction mechanism was suggested to be protonation (iv) followed by attack on the substrate (v) and further reduction.

$$\mathrm{PhCHO}^{\cdot -}+\mathrm{ROH} \xrightarrow{k_{iv}} \mathrm{Ph\dot{C}HOH} + \mathrm{RO}^- \text{ (rate determining)} \qquad \text{(iv)}$$



$$\mathrm{Ph\dot{C}HOH} + \mathrm{PhCHO} \rightarrow \mathrm{PhCH(OH)}\underset{\mathrm{O.}}{\underset{|}{\mathrm{C}}}\mathrm{HPh} \qquad \text{(v)}$$

An alternative mechanism involving reaction (vi) instead of (v) was deemed less likely since the rate of (vii) is expected to be near the diffusion controlled limit and this would at least compete with (vi) and result in n values greater than unity.



$$\mathrm{Ph\dot{C}HOH} + \mathrm{PhCHO}^{\cdot -} \rightarrow \mathrm{PhCH(OH)}\underset{\mathrm{O}^-}{\underset{|}{\mathrm{C}}}\mathrm{HPh} \qquad \text{(vi)}$$

$$\mathrm{Ph\dot{C}HOH} + \mathrm{PhCHO}^{\cdot -} \rightarrow \mathrm{Ph\bar{C}HOH} + \mathrm{PhCHO} \qquad \text{(vii)}$$

A number of aromatic carbonyl compounds are reduced in ethanolic buffers in one electron processes accompanied by rapid dimerization of the anion radicals.[1,2] On the basis of extensive linear sweep voltammetry (LSV) studies, Nadjo and Savéant [3] concluded that the dimerization mechanism consists of reactions (1)–(3), which may be described by rate law (4) where the apparent rate constant (k_{app}) is equal to k_2K_1.

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$$-\dot{C}-O^- + H^+ \overset{K_1}{\rightleftharpoons} -\dot{C}-OH \quad \text{(at equilibrium)} \qquad (1)$$

$$-\dot{C}-OH + -\dot{C}-O^- \xrightarrow{k_2} -C(OH)-C-O^- \quad \text{(rate determining)} \qquad (2)$$

$$-C(OH)-C-O^- + H^+ \rightleftharpoons -C(OH)-C-OH \qquad (3)$$

$$\text{Rate} = k_{\text{app}}(-\dot{C}-O^-)^2\,[H^+] \qquad (4)$$

The reaction was also studied by *a.c.* polarography and the data were found to be consistent with the second order dimerization but no attempt was made to verify the proton donor term in rate law (4).[4] Nadjo and Savéant's justification for assuming the reaction to be first order in proton donor was based on the observation that the apparent rate of dimerization was dependent upon the pH of the buffer used decreasing in the order, veratrol (pH ~13.6), phenol (pH ~15.7) and Bu_4NOH.

The most significant aspect of this mechanism is that reaction (2) must take place with the exclusion of the thermodynamically favourable electron transfer reaction (5).

$$-\dot{C}-OH + -\dot{C}-O^- \xrightarrow{k_5} -\bar{C}-OH + -C=O \qquad (5)$$

We find this possibility unlikely * since (5) may be predicted to take place at very near the diffusion controlled limit. This implies that the maximum possible value of k_2 is very close to that of k_5 and it is more likely that it is considerably smaller. Furthermore, in a related system the protonation of methyl cinnamate in phenolic buffers, where the first step is reaction (1), only reaction (5) follows and results in an overall 2e reduction.[5]

The question which should be answered before accepting Nadjo and Savéant's mechanism is as follows. Is the dimer-forming reaction preceded by protonation equilibrium (1)? To answer this question one should consider the complete equation which takes into account the conjugate base of the proton donor (6).

$$-\dot{C}-O^- + HA \overset{K_6}{\rightleftharpoons} -\dot{C}-OH + A^- \qquad (6)$$

$$\text{Rate} = k_2K_6[-\dot{C}-O^-]^2[HA]/[A^-] \qquad (7)$$

Neither of the previous kinetic studies [3,4] resulted in data pertaining to the reaction order in A^-. Thus, the mechanism of the dimerization of anion radicals of carbonyl compounds in ethanolic buffers was not known at the outset of this study.

In this paper we report the results of kinetic studies of the dimerization of benzaldehyde anion radical in ethanolic and aqueous ethanolic buffers. Our data were found to be incompatible with the Nadjo-Savéant mechanism and we conclude that proton transfer does not take place before the formation of the dimer dianion.

RESULTS

The reaction of benzaldehyde anion radical in basic ethanol. The Nadjo-Savéant [3] mechanism (1)–(3) requires, according to rate law (7), that the rate of the reaction be inversely proportional to the concentration of the conjugate base of the strongest acid in the medium. In ethanol containing small amounts of water the latter is hydroxide ion. The data in Table 1 show that at $[OH^-]$ up to about 12 mM the apparent rate constant, proportional to $v_{0.4}$, depends upon the base concentration. The quantity, $v_{0.4}$, is the voltage sweep rate necessary for the ratio of the derivative of the peak currents during derivative cyclic voltam-

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* It is possible that reaction (5) is slow but in general this second step of the ECE_h mechanism takes place preferentially over other possible reactions of the neutral radical.

Table 1. The effect of base on the rate of reaction of benzaldehyde anion radical in ethanol.[a]

$[OH^-]$/mM [b]	$v_{0.4}$/V s^{-1} [c]	$v_{0.4}[OH^-]$/V mM s^{-1}
1.0	125.9	125.9
2.0	90.9	182
4.0	57.9	232
8.0	45.1	361
12.0	37.7	452
16.0	34.6	554
20.0	34.1	682

[a] In solvent containing Bu_4NBF_4 (0.1 M). Measurements by DCV at a mercury electrode at 18.7 °C. [b] Added as a 25 % solution of Bu_4NOH in methanol. [c] The voltage sweep rate necessary for the derivative current ratio to equal 0.400.

metry (DCV) to equal 0.400.[6] However, the product $v_{0.4}[OH^-]$ is not constant as rate law (7) requires. At $[OH^-]$ greater than 12 mM, $v_{0.4}$ appears to be independent of the base concentration.

A further requirement of rate law (7) is that the reaction be second order in $PhCHO^{\cdot-}$. In terms of DCV reaction orders,[6] this requirement calls for the ratio $v_{1/2}$/[PhCHO] to be constant at a given buffer concentration. The substrate concentration was varied in five different buffers. The results are shown in Table 2. Only in the most concentrated buffer (20 mM) is a reasonably good fit to second order kinetics observed. The data indicate that the reaction order in $PhCHO^{\cdot-}$ is greater than 1 but less than 2 in the other buffers. For example, in the 4 mM buffer a 10-fold increase in substrate concentration resulted in only a 4-fold increase in $v_{1/2}$.

Since the data for the 20 mM buffer approximates that expected for a second order dimerization, a temperature study was carried out on the rate of reaction of benzaldehyde anion radical in this medium. The kinetics were studied by double potential step chronoamperometry (DPSC) and $\tau_{1/2}$ is the pulse width at which the ratio of the normalized current $(=i_b/i_f(1-2^{-1/2})$ is equal to 0.500. The observed apparent second order rate constants were evaluated using eqn. (8).[7]

$$k_{app} = 0.830([PhCHO]\tau_{1/2})^{-1} \qquad (8)$$

Table 2. Effect of substrate concentration on the rate of reaction of benzaldehyde anion radical in ethanol containing base.[a]

$[OH^-]$/mM	[PhCHO]/mM	$v_{1/2}$/V s^{-1}	$v_{1/2}$/[PhCHO]
2.0	0.10	62.2	622
2.0	0.20	72.0	360
2.0	0.40	104.1	260
4.0	0.10	31.3	313
4.0	0.20	47.8	239
4.0	0.40	73.9	185
4.0	1.00	123.3	123
8.0	0.10	17.6	176
8.0	0.20	29.2	146
8.0	0.40	48.3	121
8.0	1.00	86.1	86
12.0	0.10	14.6	146
12.0	0.20	20.7	103.5
12.0	0.40	39.1	97.8
12.0	1.00	73.3	73.3
20.0	0.10	8.65	86.5
20.0	0.20	21.3	106.5
20.0	0.40	36.9	92.3
20.0	1.00	67.2	67.2

[a] Measurements by DCV at a mercury electrode at 18.7 °C in solvent containing Bu_4NBF_4 (0.1 M).

Table 3. The effect of temperature on the rate of dimerization of benzaldehyde anion radical in basic ethanol.[a]

T/K	$\tau_{1/2}$/ms [b]	$k_{app}{}^{c}$/M^{-1}s^{-1}
272.3	3.14	2.64×10^5
291.3	2.37	3.50×10^5
303.6	2.02	4.11×10^5
311.8	1.75	4.74×10^5

[a] Measurements by DPSC on a solution containing benzaldehyde (1.0 mM), Bu_4NOH (20 mM) and Bu_4NBF_4 (0.1 M). [b] The pulse width necessary for the normalized current ratio to equal 0.500. [c] Calculated from theoretical data for the simple dimerization mechanism, $k=0.830/C_{PhCHO}\tau_{1/2}$. The Arrhenius activation energy was equal to 2.5 kcal/mol with a correlation coefficient of 0.998.

Measurements at 4 temperatures ranging from 273.2 to 311.8 K, resulted in an Arrhenius activation energy of 2.5 kcal/mol with a correlation coefficient of 0.998 (Table 3).

The reaction of benzaldehyde anion radical in aqueous ethanolic buffers. Since previous studies [1–4] were carried out in ethanol containing appreciable quantities of water, the effect of $[H_2O]$ on the apparent second order rate constants was determined. The data in Table 4 show the effect of water added to solutions 20 mM in Bu_4NOH on the apparent rate constants. In the two independent sets of experiments, approximately 50 % increases in k_{app} were observed in going from added water of 0 to 1.12 M. The reaction order in water was determined from eqn. (9)

$$k_{app} = k_0 + k_w[H_2O] \tag{9}$$

where k_0 is the apparent rate constant in the absence of *added* water. If eqn. (9) is an adequate description of k_{app}, dividing the $k_w[H_2O]$ term by the concentration of added water should result in a constant which is the third order rate constant for the reaction second order in $PhCHO^{\cdot-}$ and first order in water. The last column in Table 4 shows that the data fit eqn. (9) remarkably well and that k_w is equal to $1.18(\pm0.13)\times10^5$ M^{-2}s^{-1}.

The effect of $[Bu_4NOH]$ at 3 different water concentrations was determined. The data in Table 5 show that $v_{1/2}$ measured at buffer concentrations of 50, 25 and 10 mM are essentially independent of $[Bu_4NOH]$. Once again, the apparent second order rate constants increased with increasing water concentration.

Another feature of the Nadjo-Savéant mechanism [3] is that it predicts a small deuterium *equilibrium* isotope effect when the proton donor in reaction (6) is labelled with deuterium. In general, the values of K_H/K_D are normally close to unity while primary deuterium kinetic isotope effects k_H/k_D are generally >2.[8] In order to test for an equilibrium or a kinetic isotope effect, the kinetics were studied in solutions where either H_2O or D_2O were added. Since the Bu_4NOH was available as a 25 % solution in methanol, it was not possible to have solvent in which all hydroxylic groups contained D. The data in Table 6 show the effect of increasing the proportion of deuter-

Table 4. The effect of water concentration on the rate of dimerization of benzaldehyde anion radical in basic ethanol.[a]

$[H_2O]$	$v_{1/2}$/V s^{-1}	$10^{-5}k_{app}$/M^{-1}s^{-1}	10^{-5} k_W/M^{-2}s^{-1} [b]
0	37.2	3.50	0
0.28	40.8	3.84	1.21
0.56	43.2	4.07	1.02
1.12	51.8	4.88	1.23
0	33.0	3.10	0
0.28	35.9	3.38	1.00
0.56	41.0	3.85	1.34
0.84	43.3	4.07	1.15
1.12	48.2	4.53	1.28
k_W/M^{-2}s^{-1}			1.18×10^5

[a] At 18.7 °C in solutions containing benzaldehyde (0.5 mM), Bu_4NOH (20 mM) and Bu_4NBF_4 (0.1 M) at a mercury electrode. [b] Apparent third order rate constant due to the water added to the system.

Table 5. The effect of water and base on the rate of dimerization of benzaldehyde anion radical in aqueous ethanol.[a]

$[Bu_4NOH]$/mM	$[H_2O]$/M	$v_{1/2}$/V s^{-1}	
50	0.56	48.9	50.1±1.9 ($k_{app}=2.35\times10^5$ M^{-1} s^{-1})
25	0.56	49.2	
10	0.56	52.3	
50	1.39	64.8	64.9±3.7 ($k_{app}=3.05\times10^5$ M^{-1} s^{-1})
25	1.39	61.2	
10	1.39	68.6	
50	2.78	98.5	92.3±4.7 ($k_{app}=4.39\times10^5$ M^{-1} s^{-1})
25	2.78	89.3	
10	2.78	92.0	

[a] Measurements by DCV in solvent containing benzaldehyde (1.0 mM) and Bu_4N^+ (0.1 M) at 18.2 °C at a mercury electrode.

Table 6. Deuterium kinetic isotope effect studies on the dimerization of benzaldehyde anion radical in aqueous ethanol.[a]

[PhCHO]/mM	$[H_2O]$/M	$10^{-6}k_{app}$/$M^{-1}s^{-1}$	$(k_H/k_D)_{app}$	Active[b] H/D
0.50	5.56 (H_2O)	1.62	1.03	1.38
0.50	5.56 (D_2O)	1.57		
0.25	11.2 (H_2O)	2.23	1.57	0.61
0.25	11.2 (D_2O)	1.42		
0.20	13.9 (H_2O)	2.85	3.50	0.47
0.20	13.9 (D_2O)	0.813		

[a] In solvent containing Bu_4OH (0.04 M), methanol (0.9 M) and Bu_4NBF_4. [b] The ratio of hydroxylic H to hydroxylic D in the solvent to which D_2O was added.

ated hydroxylic groups in the solvent. The last column gives the ratio of hydroxylic H to hydroxylic D in the solvent after D_2O was added. The most interesting feature of the data is that at high active H/D ratio (1.38) a low value of the apparent kinetic isotope effect was observed but when D became more abundant. $(k_H/k_D)_{app}$ increased significantly to 1.57 when the H/D ratio was 0.61 and finally to 3.50 at H/D equal to 0.47. These data lead to two conclusions; (i) the D is mostly present as CH_3OD and CH_3CH_2OD in the solvent with excess hydroxylic H and (ii) a relatively large primary deuterium kinetic isotope effect is evident as the amount of hydroxylic D is increased. No attempt was made to calculate the intrinsic k_H/k_D since the exact distribution of D in the hydroxylic groups of solvent containing ethanol, methanol and water is not known.

The reaction order in $PhCHO^{\cdot-}$ was determined in solvent containing water (2.78 M) and Bu_4NOH (40 mM). The data in Table 7 show the fit to second order kinetics over a 10-fold

Table 7. The effect of substrate concentration on the apparent rate constants for the dimerization of benzaldehyde in aqueous ethanol.[a]

[PhCHO]/mM	$v_{1/2}$/V s^{-1}	$10^{-5}k_{app}$/$M^{-1}s^{-1}$
0.10	13.3	10.7
0.20	21.1	8.58
0.40	41.4	8.42
0.60	60.7	8.23
1.00	86.6	7.04

[a] In solvent containing water (2.78 M), Bu_4NOH (0.04 M) and Bu_4NBF_4 (0.09 M).

concentration range. The data fit is relatively good with k_{app} equal to $8.60(\pm1.32)\times10^5$ $M^{-1}s^{-1}$. The value measured at the lowest substrate concentration is responsible for much of the deviation.

The data in Table 8 were obtained to determine the effect of temperature on the apparent rate constants for the dimerization of $PhCHO^{\cdot-}$ in aqueous ethanol. At a very high water concentration (16.7 M) the Arrhenius plot was not linear and the apparent activation energy was close to 0. However, if the data measured at 282.5 K are omitted the linearity is reasonably good and E_a is about 1.9 kcal/mol. At $[H_2O]$ of 5.56 M the linearity was better with E_a about 3.9 kcal/mol.

The reaction of benzaldehyde anion radical in ethanol containing acetic acid. The reaction under these conditions was too rapid to study using DCV or DPSC. The results of an LSV study are summarized in Table 9. The reaction orders in $PhCHO^{\cdot-}$ (b), PhCHO (a) and HOAc (x) were calculated from experimental LSV data using eqns. (10), (11) and (12), respectively.[9]

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

$$dE^p/d\log C_A = \ln 10(RT/F)(a+b-1)/(b+1) \qquad (11)$$

$$dE^p/d\log C_X = \ln 10(RT/F)x/(b+1) \qquad (12)$$

Values of $dE^p/d\log v$ were observed to be equal to $29.2(\pm1.1)$ mV/decade over an eightfold range of substrate concentration. The theoretical value for a first order reaction of primary intermediate $PhCHO^{\cdot-}$ at 11 °C is 28.1 mV/decade which is within the limits of error of the experimental value. The reaction orders in PhCHO and HOAc were observed to be 0.2 and 0.8, respectively.

The observation of kinetics first order in $PhCHO^{\cdot-}$ in media containing HOAc suggested that protonation accompanied by further reduction might be taking place under these conditions. In order to test for this possibility the coulometric n value was determined by LSV measurements. For a rapid reaction following charge transfer, the height of the LSV wave at low v is independent of the rate of the reaction and is proportional to the number of electrons per molecule reacting. The data in Table 10 were obtained on solutions of benzaldehyde in ethanol and in ethanol containing either HOAc or

Table 8. The effect of temperature on the rate of dimerization of benzaldehyde anion radical in aqueous ethanol.[a]

T/K	$[H_2O]$/M	$v_{1/2}$/V s^{-1}	$10^{-6}k_{app}$/ $M^{-1}s^{-1}$
300.6	16.7	117.3	4.62
291.2	16.7	95.9	3.90
282.5	16.7	120.4	5.04
272.1	16.7	75.1	3.27
301.7	5.56	50.2	1.97
291.2	5.56	47.1	1.92
283.2	5.56	42.0	1.76
272.6	5.56	23.6	1.03

[a] In solvent containing benzaldehyde (0.20 mM), Bu_4NOH (0.04 M) and Bu_4NBF_4.

Table 9. Linear sweep voltammetry study of the dimerization of benzaldehyde anion radical in ethanol containing acetic acid.

	mV/decade	Reaction order
$dE^p/d\log v$ [a]	29.2±1.1	1.0 in $PhCHO^{\cdot-}$
$dE^p/d\log C_{PhCHO}$ [b]	−5.3±0.4	~0.2 in PhCHO
$dE^p/d\log C_{HOAC}$ [c]	−25.0±0.5	~0.8 in HOAc

[a] Measurements at 0.25, 0.50, 0.75, 1.00 and 2.00 mM in PhCHO in ethanol at [HOAc]=10 mM at 11.1 °C. [b] Measurements at 100, 200, 400 and 1000 mV s^{-1} under the same conditions as *a*. [c] Measurements at [HOAc]=4, 8, 12, 16, 24 and 32 mM at 18.3 °C.

Table 10. Determination of the apparent number of electrons transferred during the reduction of benzaldehyde in ethanol.[a]

Conditions	Relative peak current [b]	n_{app} [c]
EtOH	1.01(±0.0)	1.01
EtOH−HOAc (4 mM)	0.99(±0.2)	0.99
EtOH−Bu_4NOH (20 mM)	1.00(±0.1)	1.00

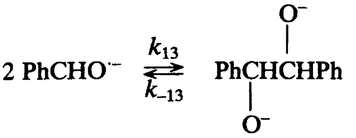
[a] Measurements by LSV in solvent containing PhCHO (0.5 mM) and Bu_4NBF_4 (0.1 M) at 18.3 °C at a mercury electrode. [b] LSV peak current measured at 200 mV s^{-1}. [c] The apparent number of electrons per molecule of PhCHO transferred assuming a value of 1.00 for the reaction in the presence of Bu_4NOH.

Bu_4NOH. Since it is established that the reaction is a dimerization under the latter conditions,[1–4] this can serve as the standard for $n=1.00$. The relative peak currents for all three solutions containing benzaldehyde (0.50 mM) measured at 200 mVs^{-1} were within a ±1 % range. This means that the overall reaction under all conditions involves le reduction and hence dimerization in all three cases.

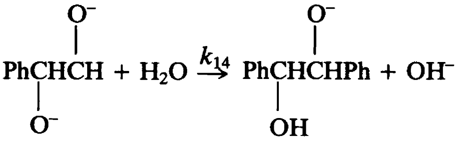
DISCUSSION

The most significant kinetic evidence which requires discarding the Nadjo-Savéant mechanism [3] is the failure to observe inverse first order in hydroxide ion and the observation of a *kinetic* rather than an *equilibrium* deuterium isotope effect in media containing hydroxylic D and H. This demonstrates a general trend. The Nadjo-Savéant paper [3] was published in 1971. At that time most mechanistic papers published in the area of organic electrochemistry were based on measurements by a single technique and usually at a single concentration and a single temperature. Nadjo and Savéant used only linear sweep voltammetry which is an indirect kinetic technique since the response of the primary intermediate is not observed. The latter was in spite of the fact that the rate of the reaction is low enough for the use of direct kinetic techniques such as DPSC and cyclic voltammetry. Nadjo and Savéant used only two substrate concentrations in the study of a second order reaction. Today, this type of mechanistic evidence is not acceptable. The importance of temperature [10] and concentration [6,10] effects in the study of electrode mechanisms has recently been emphasized. In reactions involving proton transfers, deuterium kinetic isotope effects have recently been employed in the study of organic electrode processes.[10–16] The determination of apparent activation energies during the study of electrode processes has become common.[5,6,10,13,14,16–36] In short, acceptable electrode process mechanistic evidence today is comparable to that generally presented in physical organic reaction mechanism studies.[37]

Most of the previous work has been carried out in aqueous ethanol.[1–4] The evidence is strong that in aqueous ethanolic buffers the reaction is a second order dimerization of $PhCHO^{\cdot-}$. Second order behaviour was observed over a tenfold range of substrate concentration (Table 7). In three different hydroxide ion buffers (Table 5) the apparent rate constant was observed to be independent of $[OH^-]$. In these media there is a primary deuterium kinetic isotope effect when hydroxylic H is replaced by hydroxylic D (Table 6). The apparent activation energy is dependent on $[H_2O]$ and was observed to be about 3.9 kcal/mol at $[H_2O]$ equal to 5.6 M and about 1.9 kcal/mol at $[H_2O]$ of 16.7 M (Table 8). A significant portion of the reaction goes through a mechanism that is first order in water (Table 4). When $[H_2O]$ is 1.12 M about 50 % of the reaction goes by that mechanism and at $[H_2O]$ equal 16.7 M greater than 90 % of the rate can be attributed to the mechanism first order in water and second order in $PhCHO^{\cdot-}$. Thus, under the latter conditions the results suggest mechanism (13)+(14) and the corresponding rate law (15).



$$2\,\mathrm{PhCHO}^{\cdot-} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} \mathrm{Ph}\underset{\underset{O^-}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{O^-}{|}}{\mathrm{C}}\mathrm{HPh} \qquad (13)$$



$$\mathrm{Ph}\underset{\underset{O^-}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{O^-}{|}}{\mathrm{C}}\mathrm{H} + H_2O \xrightarrow{k_{14}} \mathrm{Ph}\underset{\underset{OH}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{O^-}{|}}{\mathrm{C}}\mathrm{HPh} + OH^- \qquad (14)$$

$$\text{Rate} = k_{14}K_{15}[\mathrm{PhCHO}^{\cdot-}]^2[H_2O] \qquad (15)$$

It is necessary that proton transfer takes place in an irreversible step to account for the independence on $[OH^-]$ of the observed rate constants as well as the primary k_H/k_D. This mechanism also predicts that the apparent activation energy $(E_a)_{app}$ should depend upon $[H_2O]$ and decrease with increasing water concentration. This is obvious from expression (16)

$$(E_a)_{app} = (\ln A - \ln k_{app})RT \qquad (16)$$

which takes into account that k_{app} is a *pseudo* second order rate constant directly proportional to the water concentration.

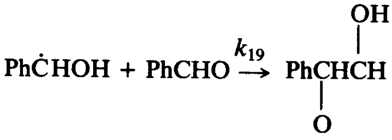
We are forced to be somewhat more speculative for the reaction second order in $PhCHO^{\cdot-}$ at lower $[H_2O]$. When $[OH^-]$ is 20 mM and water is not intentionally added the kinetic data approximately fit rate law (17).

$$\text{Rate} = k_{\text{app}}[\text{PhCHO}^{\cdot-}]^2 \qquad (17)$$

What must be kept in mind is that the solvent is a potential proton donor and that methanol is introduced since the Bu_4NOH was a 25 % solution in that solvent. The [MeOH] in solutions 20 mM in Bu_4NOH was of the order of 0.5 M. Thus, it is likely that the same mechanism is followed under conditions where water is not added with EtOH and MeOH taking the place of water in reaction (14). As in all reactions involving the solvent it is impossible to determine the reaction order in ethanol. The reaction order in methanol was not determined since the uncertainty of the role of ethanol would still be present.

When water was not intentionally added and $[\text{OH}^-]$ was <12 mM, the reaction order in $\text{PhCHO}^{\cdot-}$ was observed to be >1 but <2 (Table 2). Under these conditions the apparent number of electrons transferred was still 1.0 which is indicative of a dimerization mechanism (Table 10). The apparent rate constant under these conditions decreases with increasing $[\text{OH}^-]$ but not in a well-defined manner (Table 2). These results suggest that proton transfer to the anion radical occurs under these conditions and is consistent with either the Nadjo-Savéant mechanism or with (18)+(19) and rate law (20).

$$\text{PhCHO}^{\cdot-} + \text{ROH} \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} \text{Ph}\dot{\text{C}}\text{HOH} + \text{RO}^- \qquad (18)$$



$$\text{Ph}\dot{\text{C}}\text{HOH} + \text{PhCHO} \xrightarrow{k_{19}} \text{PhCH}(\text{OH})\text{CH}(\text{O}) \qquad (19)$$

$$\text{Rate} = k_{18}k_{19}[\text{PhCHO}^{\cdot-}][\text{PhCHO}][\text{ROH}]/(k_{-18}[\text{RO}^-] + k_{19}[\text{PhCHO}]) \qquad (20)$$

The data in Table 2 do not distinguish between these two possibilities. However, as mentioned earlier, the thermodynamically favored electron transfer reaction (5) is expected to be very close to diffusion controlled and should compete effectively with reaction (2). The overall result expected for these competing mechanisms is that a significant fraction of the two electron reduction product would be formed and the observed apparent n values should be greater than 1. This is not observed, either in this study or in previous work.[1-4] On this basis, mechanism (18)+(19) is consistent with the data while the Nadjo-Savéant mechanism is not.

In order to gain a little more insight into the dimerization mechanism when the reaction order in $\text{PhCHO}^{\cdot-}$ is less than 2, studies were carried out in ethanol containing low concentrations of acetic acid (HOAc). The reaction remains a one electron reduction (Table 10) under these conditions. The results of the LSV study were revealing. The reaction order in $\text{PhCHO}^{\cdot-}$ was observed to be 1.0 within experimental error (Table 9) while that in HOAc was 0.8 and in PhCHO was 0.2. These results are once again consistent with mechanism (18)+(19), where ROH is HOAc, being the major reaction pathway.

From the results discussed in the previous paragraphs, it appears safe to conclude that two mechanisms account for the dimerization of benzaldehyde anion radical in ethanol. In the presence of water and hydroxide ion, the predominant mechanism is (13)+(14). In less basic solvent mechanism (18)+(19) becomes important and predominates in acidic solvent.

EXPERIMENTAL

Absolute ethanol was used without further purification. Tetrabutylammonium hydroxide was Fluka (practical) and was available as a 25 % solution in methanol. The instrumentation, electrodes, cells and data handling procedures were those described earlier.[38]

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