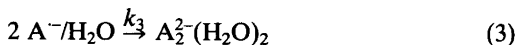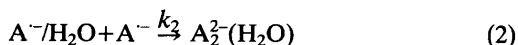# The Mechanism of the Dimerization of Acetophenone Anion Radical in Acetonitrile. The Formation and the Dimerization of the Anion Radical – Water Complex

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Anion radicals form 1:1 complexes with water which in some cases enhance the rate of dimerization. So far, the only dimerization mechanism of this type that has been demonstrated involves equilibrium (1) followed by dimer forming reaction (2).[1-3] The corresponding dimerization of the complex (3) has been claimed to be important in the dimerization of 9-cyanoanthracene anion radical[4] but this has been shown to be erroneous.[5]

$$A^{-} + H_2O \overset{K_1}{\rightleftharpoons} A^{-}/H_2O \qquad (1)$$

$$A^{-}/H_2O + A^{-} \overset{k_2}{\to} A_2^{2-}(H_2O) \qquad (2)$$

$$2\ A^{-}/H_2O \overset{k_3}{\to} A_2^{2-}(H_2O)_2 \qquad (3)$$

The rate constant for reaction (2) has been estimated to be of the order of 10^6 times as great as that for the dimerization of uncomplexed diethyl fumarate anion radical.[2] This large rate difference is most likely due to less charge repulsion in the transition state for reaction (2) as compared to the dimerization of the uncomplexed anion radical. One might expect that the same factor could cause k_3 to be much larger than k_2.

The reason that reaction (3) has not been observed is that K_1 is in most cases so small that it cannot be measured. A large peak potential shift has been reported during voltammetry studies of the reduction of acetophenone in acetonitrile upon the addition of water.[6] This implies that K_1 may be large in this case. High substrate concentrations were employed in the voltammetric study[6] and since the anion radical undergoes a rapid second order reaction the potentials are not very reliable. The purpose of this work was to determine K_1 (A^{-}=acetophenone anion radical) and to study the kinetics of the reactions of the complex.

Reversible electrode potentials were determined for the reduction of acetophenone in acetonitrile containing water. Second harmonic A.C. voltammetry was used for the measurements at a substrate concentration of 0.1 mM. The data are gathered in Table 1. It was not possible to go to higher water concentrations because of a phase shift in the A.C. response most likely due to adsorption phenomena. The value of K_1 at 292.2 K was observed to be 16.6 M^{-1}.

Table 2. The influence of base and substrate concentration on the rate of dimerization of acetophenone anion radical in acetonitrile.[a]

C_A[b]/mM	[Bu$_4$NOH]/mM	$\tau_{0.4}$/ms	$(\tau_{0.4}C_A)^{-1}$
0.50	0	3.80	–
0.50	2.0	4.75	–
0.50	4.0	5.11	0.391
1.00	4.0	2.90	0.345
1.50	4.0	1.88	0.355
2.00	4.0	1.42	0.352

[a] In solvent containing Et$_4$NBF$_4$ (0.1 M) and H$_2$O (0.55 M) at 18.7 °C. [b] Substrate concentration.

Table 1. Determination of the equilibrium constant for the association of acetophenone anion radical with water in acetonitrile.[a]

[H$_2$O]/mM	$-E_{zc}$(300 Hz)[b]/mV	ΔE_{rev}/mV	(K_1/M^{-1})[c]
0	342.8(0.1)	–	–
27.8	333.2(0.2)	9.6	16.7
55.6	326.5(0.2)	16.3	16.4

[a] In solvent containing Et$_4$NBF$_4$ (0.1 M) and acetophenone (0.1 mM) at 292.2 K. [b] The quadrature component zero current crossing potential of the second harmonic A.C. signal referred to a bias potential of -1.400 V. vs. Ag/Ag^{+} in acetonitrile. The numbers in parentheses are the standard deviations in 5 replicate measurements. [c] Calculated from the expression, $K_1 = (\exp(\Delta E_{rev}/(RT/F)) - 1)/[\text{H}_2\text{O}]$.

Table 3. The reaction order in water during the dimerization of acetophenone anion radical in acetonitrile.[a]

$[H_2O]/M$	$[A^{\cdot-}/H_2O]/[A^{\cdot-}]$	$\tau_{0.4}/ms$	$(\tau_{0.4}[H_2O])^{-1}$
0.0556	0.923	52.2	0.345
0.111	1.85	21.9	0.411
0.166	2.76	10.5	0.574
0.221	3.67	6.46	0.700
0.276	4.58	4.39	0.825
0.331	5.49	3.55	0.851
0.386	6.41	2.62	0.989
0.441	7.32	2.06	1.10
0.498	8.27	1.72	1.17
0.550	9.13	1.48	1.23

[a] In solvent containing Et_4NBF_4 (0.1 M) and acetophenone (1.0 mM) at 19.1 °C.

The kinetics of the reactions of acetophenone anion radical in the same media were studied by double potential step chronoamperometry. Some deviation of the kinetics from second order were observed with the apparent rate constants decreasing with increasing substrate concentrations. This is indicative of the generation of an inhibiting species during reaction. The data in Table 2 show both the inhibition by hydroxide ion and a reasonably good fit to second order kinetics in a buffered solution. The quantity measured was $\tau_{0.4}$ which is the pulse width necessary to maintain the current ratio at a constant value equal to 0.400.[7]

The data in Table 3 show the effect of water on the rate of the dimerization. The second column gives the ratio, $[A^{\cdot-}/H_2O]/[A^{\cdot-}]$, calculated from the equilibrium expression. The column headed $(\tau_{0.4}[H_2O])^{-1}$ is the reaction order approach criterion for a reaction first order in water.[7] The data indicate that as $[A^{\cdot-}/H_2O]/[A^{\cdot-}]$ becomes larger the reaction order in water approaches 1. The apparent reaction order which can be derived from the data in the last column has to be corrected for the increase in the ratio of complexed to uncomplexed anion radical shown in the second column of Table 3. Thus, under conditions where equilibrium (1) is shifted to the right the reaction is still accelerated by water and appears to be first order in water.

Under conditions where (1) is far enough to the right that reaction (2) is insignificant, the kinetics are consistent with reversible reaction (3) followed by protonation reaction (4). The inhibition could be due to some reversibility of (4).

$$A_2^{2-}(H_2O)_x + H_2O \xrightarrow{k_4} HA_2^-(H_2O)_x + OH^- \qquad (4)$$

Since nothing is known about the association of the dianion with water the number of H_2O is designated as x.

This work shows that when K_1 is large as it is when A is acetophenone that the species undergoing dimerization is the anion radical–water complex. There is no evidence for the association of the anion radicals with more than one molecule of water.

1. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 149.
2. Parker, V. D. *Acta Chem. Scand. B 37* (1983). *In press.*
3. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B 37* (1983). *In press.*
4. Amatore, C., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem. 139* (1982) 193.
5. Parker, V. D. *Acta Chem. Scand. B 37* (1983) 163.
6. Savéant, J. M. and Tessier, D. *J. Electroanal. Chem. 61* (1975) 251.
7. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 233.