

The Association Reactions of Ion Radicals with Neutral Molecules.

III. Equilibrium Constants for Hydrogen Bonding between Water and *p*-Methylbenzylidenemalononitrile Anion Radical in Acetonitrile

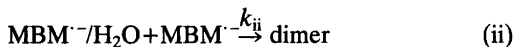
ROBERT ELIASON* and VERNON D. PARKER

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

Recent suggestions that *p*-methylbenzylidenemalononitrile (MBM) anion radical is strongly complexed by water in acetonitrile were shown to be incorrect. The equilibrium constant for reaction (i) was estimated to be equal to $0.31 \pm 0.04 \text{ M}^{-1}$ at



287.2 K by linear sweep voltammetry with $[\text{H}_2\text{O}]$ ranging from 0.28 to 4.11 M. Attempts to determine more precise equilibrium constants by phase selective second harmonic *a.c.* voltammetry failed. The response was deformed and highly irreproducible at all water concentrations and it was not possible to measure reliable potentials. The results of the equilibrium constant determinations indicate that the ratio $[\text{MBM}^{\cdot-}/\text{H}_2\text{O}]/[\text{MBM}^{\cdot-}]$ is of the order of 0.3 at $[\text{H}_2\text{O}]$ equal to 1 M. It had earlier been observed by derivative cyclic voltammetry that water does not accelerate the rate of dimerization at concentrations up to 0.2 M. These results were interpreted to indicate that the rate constant for reaction (ii) is not appreciably greater than that for (iii).



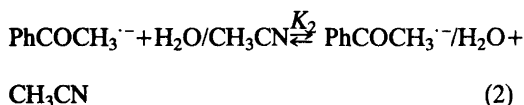
* On sabbatical leave from Southwest State University, Marshall, Minnesota, U.S.A.

The previous papers in this series have established that benzaldehyde and acetophenone anion radicals form 1/1 hydrogen bonded complexes with hydroxylic compounds. Complexes involving more than one molecule of water or alcohols could not be detected by phase selective second harmonic *a.c.* voltammetry (SHAC).^{1,2} Related measurements on the reduction of 9-cyanoanthracene indicated that reaction (1) is so far



displaced to the left that the electrode potential is not affected.³ The contrasting behaviour of the anion radicals of the aromatic carbonyl compounds with that of ANCN^{•-} most likely arises from the fact that charge is localized on the carbonyl groups in the former case which makes hydrogen bonding more favorable while in the case of ANCN^{•-} the dispersed charge renders the energy gain by hydrogen bonding less than that required to break the bond between water and the solvent (solv). On this basis one might predict that complexes between *p*-methylbenzylidenemalononitrile (MBM) anion radical and water would also be unfavorable energetically and would escape detection by electrode potential measurements. In fact, this has been found to be the case for $[\text{H}_2\text{O}]$ up to 0.28 M in *N,N*-dimethylformamide (DMF).⁴

In a recent discussion⁵ it has been claimed that the standard potential for the reduction of acetophenone becomes more positive upon the addition of water by more than 90 mV per log unit of water concentration. This was attributed to the formation of complexes containing more than one water molecule per anion radical. Our results mentioned above using the highly precise SHAC method showed a positive shift of 54.1 mV for a 20 fold increase in [H₂O] in acetonitrile and an excellent fit with theory for reaction (2) with $K_2=21.1\pm 0.6 \text{ M}^{-1}$ at 292.2 K. No evidence for the formation of complexes containing more



than 1 molecule of water per anion radical with [H₂O] up to 0.56 M, the upper limit for which reliable measurements could be made, could be found.

In the same discussion, it was claimed that the standard potential for the reduction of MBM in acetonitrile varies by more than 30 mV per log unit of [H₂O] in acetonitrile between 0.17 and 5.7 M.⁵ This was attributed to a rather strong complexation of the anion radical by water. It is the purpose of this paper to present results which show MBM⁻ does not form a strong complex with water in acetonitrile and that there is

nothing unusual with this substrate as compared to the others that equilibrium measurements have been made on.^{1,2}

RESULTS AND DISCUSSION

The method of choice for the measurement of reversible electrode potentials for the formation of rapidly reacting intermediates is without doubt SHAC. The theoretical relationships for the method⁶ have been realized in a number of different experimental systems.⁷ This method has been employed in the study of association reactions of anion radicals with hydroxylic compounds in the previous two papers in this series.^{1,2} Attempts to use the method in this study were disappointing. Either in the presence or absence of added water in acetonitrile, the SHAC in phase and quadrature components of the *a.c.* current were small and it was not possible to measure meaningful zero current crossing potentials. Such phenomena are characteristic of non-ideal electrode processes where phase shifts accompany adsorption by substrates, products or intermediates.

Due to the failure to obtain reliable SHAC data for the reduction of MBM in acetonitrile we were forced to rely on linear sweep voltammetry (LSV) data at low sweep rates. The results of measurements of the peak (E^p) and half-peak ($E^{p/2}$) potential at various water concentrations

Table 1. Equilibrium constants for the association of MBM⁻ with water calculated from LSV data.^a

[H ₂ O]/M	ΔE^p ^b /mV	K/M^{-1}	$\Delta E^{p/2}$ ^b /mV	K/M^{-1}
$\nu=0.100 \text{ Vs}^{-1}$				
0.14	0.40	0.12	0.4	0.12
0.28	2.0	0.30	2.0	0.30
0.55	4.7	0.37	4.5	0.35
1.09	8.9	0.38	8.7	0.37
2.13	11.8	0.28	12.1	0.28
4.11	20.5	0.30	19.8	0.28
$\nu=1.00 \text{ Vs}^{-1}$				
0.14	0.6	0.17	0.5	0.13
0.28	2.2	0.32	1.8	0.26
0.55	4.7	0.37	4.1	0.32
1.09	8.2	0.35	7.9	0.33
2.13	10.9	0.25	12.1	0.28
4.11	19.9	0.29	20.4	0.29

^a Measurements on the reduction of MBM (0.5 mM) in acetonitrile containing Bu₄NBF₄ (0.1 M) at 298.2 K.

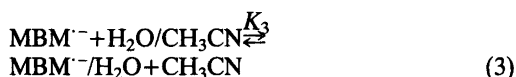
^b The value obtained from the optimization procedure described in the text.

Table 2. Equilibrium constants for the association of $\text{MBM}^{\cdot-}$ with water based on literature data.^a

% H ₂ O	[H ₂ O]/M	log[H ₂ O]	-E ^p (180 V/s) ^b	K ^c /M ⁻¹
0.3	0.17	-0.77	1539.9	—
2.3	1.28	0.11	1526.7	0.39
5.3	2.94	0.47	1516.9	0.41
10.3	5.72	0.76	1506.5	0.405

^a Data taken from Ref. 5. The peak potentials are for the reduction of MBM in acetonitrile containing Et₄NClO₄ (0.1 M) at 295 K. ^b Expressed in mV, no indication was given of the precision of the measurements. ^c Calculated using eqn. (4) as described in the text.

are summarized in Table 1. The measurements were made using the procedure recently described⁸ which employs a second order linear regression analysis in the region of the current maximum to find E^p. Two voltage sweep rates were used, 100 and 1,000 mV/s, which are expected to be well within the purely kinetic region since previous work⁹ has indicated that this is the case even at sweep rates as high as 1.8 V/s. The data resulted in two measures of the equilibrium constant (K₃) for reaction (3) at each [H₂O] and each sweep rate,



i.e. one each resulting from E^p and E^{p/2}. The values of K₃ were obtained using eqn. (4). Since

$$K_3 = (\exp(\Delta E / (RT/F)) - 1) [\text{H}_2\text{O}]^{-1} \quad (4)$$

the reversible potential could not be determined it was necessary to assume that changes in E^p and E^{p/2} on changes in [H₂O] reflect ΔE^{rev} which is the proper quantity to use in eqn. (4). The latter is indeed legitimate providing the process is of the purely kinetic type. Also, because the reversible potential could not be determined, it was necessary to follow an optimization procedure, starting with a guess of E^{rev} and then making appropriate changes to obtain the set of most consistent K₃ values from eqn. (4). For water concentrations ranging from 0.28 to 4.11 M, a good fit to eqn. (4) was found in all 4 cases when the potentials measured at [H₂O] equal to 0.069 M were taken to be the reversible values. This resulted in very much lower K₃ at [H₂O] equal to 0.138 M but minimized any trends in values at all other water concentrations. Thus, this procedure

resulted in K₃ = 0.31 ± 0.04 M⁻¹.

It will be recalled that it was claimed⁵ that the standard potential for the reduction of MBM is shifted in a positive direction 30 mV per log unit of [H₂O]. Since our LSV data contradict this statement we examined the original data upon which this statement is based. The data are reproduced in Table 2 and the % water reported⁹ is converted to a concentration scale. It is immediately obvious that an arithmetic error has been made.⁵ The log[H₂O] actually encompasses 1.53 units and the peak potential was observed to shift by 33.4 mV. Furthermore, as would be expected from eqn. (4) E^p is not linear with log[H₂O]. The same optimization procedure as used with our data resulted in the most consistent set of K₃ when the reversible peak potential was taken at that measured at [H₂O] equal to 0.17 M. This resulted in K₃ = 0.4 at 295 K, a value slightly larger than we estimate from our own data.

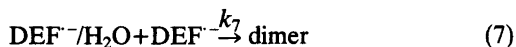
In addition to the arithmetic error,⁵ the conclusions of the original study⁹ have been misquoted. The conclusions of that study were, in fact, that the rate of the reaction with the rate determining step written as (5) is practically insensitive to the water concentration. This was then contrasted



with previous results for the dimerization of acetophenone by the following statement which is a direct quotation. "This may be interpreted as due to the difference in bulkiness of the atom groups where the negative charge of the anion radical is mostly located; (C(CN)₂ here and O in the other case), which results in a smaller solvation and a smaller influence of solvation on the coupling rate". It is obvious that the reader in the year 1975 would have had to interpret this discussion to mean that MBM^{·-} is so weakly

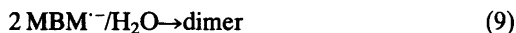
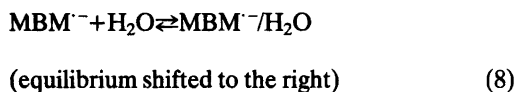
associated with water that the rate of reaction is unaffected and the mechanism is described by the coupling of two uncomplexed anion radicals as put forth in eqn. (5).

But, a number of new findings have been published in this field since 1975. The most pertinent one to this discussion is that it has been demonstrated that the dimerization of diethyl fumarate (DEF) anion radical takes place by mechanism (6)+(7).¹⁰ This mechanism has re-



cently been thoroughly investigated and both K_6 and k_7 were evaluated along with ΔH_6° and ΔH_7^\ddagger .¹¹ Equilibrium (6) was not formulated to include the solvent in the original papers but this must be taken into account in view of the recent discussions.^{1,2} In fact, the main objective of the new discussion⁵ of the role of water in the dimerization of anion radicals was to show that this is not a general mechanism.

The reader of the 1983 discussion⁵ of the results on the effect of water on the dimerization of $\text{MBM}^{\cdot-}$ ⁹ is led to believe that the data indicate and were interpreted as evidence for mechanism (8)+(9). *This is very far from the truth.* In the



first place the original data as well as our own indicate that equilibrium (1) lies to the left in most circumstances. Even when $[\text{H}_2\text{O}]$ is as high as 1 M, the ratio $[\text{A}^{\cdot-}/\text{H}_2\text{O}]/[\text{A}^{\cdot-}]$ is equal to about 0.3. Thus, the predominant species present at this and lower water concentrations is the uncomplexed anion radical. Secondly, the original conclusion⁹ is precisely the opposite to what is being claimed now.⁵

The question may arise as to how reliable the estimates of K_3 from the LSV data are. First of all, the process is obviously not ideal as is clearly indicated by the failure to obtain normal SHAC response. Also, eqn. (4) is not consistent with the

data for the lowest water concentrations in either our work or from the previous study.⁹ Thus, we emphasize that eqn. (4) *approximately* holds for the reduction of MBM in acetonitrile containing water at concentrations of 0.28 M and greater. We suspect that the reason for the non-ideality of the electrode process which becomes more severe in dry solvent may be connected with the fact that two equivalents of strong base, *i.e.* the dimer dianion or hydroxide ion, are produced for each product forming reaction and that the base influences the overall process. This problem should become less severe as the water concentration is increased since the activity of the base would diminish.

Measurements of the peak potential for the reduction of MBM in *N,N*-dimethylformamide (DMF) at 100 V/s failed to reveal a positive shift of E^p with $[\text{H}_2\text{O}]$ up to 0.28 M.⁴ The peak potential was constant to ± 2 mV. However, the equilibrium constant for the association of acetophenone anion radical with water was observed to be about 3 times as great in acetonitrile as in DMF.² If the same ratio of equilibrium constants for the two solvents hold for $\text{MBM}^{\cdot-}$ and water we would predict a value of about 0.1 in DMF. The previous LSV data⁴ do not rule out the association of $\text{MBM}^{\cdot-}$ with water in DMF with an equilibrium constant of that magnitude. However, it could not be much greater and still be consistent. In any event, the DMF work supports our view that K_3 is no greater than about 0.3 M^{-1} .

In conclusion we point out that there is an apparent trend in values of equilibrium constants for the association of anion radicals with water and structure. The large planar aromatic systems such as the aromatic hydrocarbons and their derivatives such as 9-cyanoanthracene form anion radicals with highly dispersed charge. These do not associate with water to an extent that the equilibria affect the reversible electrode potentials. At the other extreme smaller molecules such as benzaldehyde, acetophenone, and diethylfumarate form anion radicals which have more localized centers of charge and thus form relatively strong hydrogen bonds with proton donors. The charge in these cases is most likely localized to some extent on oxygen. The reversible potentials for the reduction of these substances are shifted in the positive direction by increasing water concentration. Finally, MBM is an intermediate case. The charge is somewhat

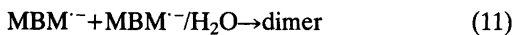
dispersed but is more concentrated on the $-\text{C}(\text{CN})_2$ moiety. This gives rise to anion radicals which do form hydrogen bonds with water in aprotic solvents and the association can be detected by reversible potential measurements.

We believe that all anion radicals form hydrogen bonds with water. What makes the equilibria less favorable is that water associates quite strongly with all of the polar aprotic solvents to form 1/1 hydrogen bonded complexes according to (10).



The thermodynamic properties of these equilibria have been summarized in the previous paper in this series.² This aspect of the role of water has been completely neglected in the most recent⁵ as well as in the earlier^{9,12} discussions. In fact in earlier discussions solvation is described in terms of the collection of a shell of water molecules around the anion radical. In our opinion none of the proposals⁵ regarding the role of water have any validity in view of the total neglect of the all-important equilibria (10).

As far as the mechanism of the dimerization of MBM^- in acetonitrile containing water is concerned we are forced to the conclusion that at low water concentration reaction (5) is the best description since the uncomplexed anion radical predominates and the rate is independent of $[\text{H}_2\text{O}]$. At water concentrations of the order of 1 M there is a significant fraction of $\text{MBM}^-/\text{H}_2\text{O}$ but the rate of the reaction does not notably change. This can only indicate that the rate of reaction (11) does not differ appreciably from that of (5). Obviously, at very high $[\text{H}_2\text{O}]$ the



complexed anion radical will become the predominant species. Under these conditions it is clear that reaction (9) will become important. However, even at $[\text{H}_2\text{O}]$ equal to 10 M, $[\text{MBM}^-/\text{H}_2\text{O}]/[\text{MBM}^-]$ is still only 3 and under these conditions all three of the reactions 5, 11 and 9, would be expected to take place. Whether reactions 5, 11 and 9 are simple or two step mechanisms is another point which need not be discussed here.

Experimental. The cells, electrodes, instruments and data handling procedures were the same as has previously been described.¹³ The peak and half-peak measurements were carried out as before.⁸ The MBM had been prepared for a previous study.⁴

Acknowledgement. This investigation was supported by a grant from the Norwegian Council for Science and the Humanities. We gratefully acknowledge this support.

REFERENCES

1. Parker, V. D. *Acta Chem. Scand. B* 38 (1984) 125.
2. Parker, V. D. *Acta Chem. Scand. B* 38 (1984) 243.
3. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B* 37 (1983) 379.
4. Lerflaten, O. and Parker, V. D. *Acta Chem. Scand. B* 36 (1982) 225.
5. Savéant, J. M. *Acta Chem. Scand. B* 37 (1983) 365.
6. McCord, T. G. and Smith, D. E. *Anal. Chem.* 41 (1969) 1423.
7. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 91.
8. Eliason, R. and Parker, V. D. *J. Electroanal. Chem.* 170 (1984) 347.
9. Nadjo, L., Savéant, J. M. and Tessier, D. J. *Electroanal. Chem.* 64 (1975) 143.
10. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 147.
11. Parker, V. D. *Acta Chem. Scand. B* 37 (1983) 393.
12. Lamy, E., Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 50 (1974) 141.
13. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 97.

Received January 4, 1984.