Kinetics and Mechanisms for Protonation of the Anthracene Anion Radical by β-Dicarbonyl Compounds in Aprotic Solvents

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Three β-dicarbonyl compounds, dimedone, acetylacetone, and ethyl acetoacetate which in solution exist as keto–enol equilibrium mixtures have been used as proton sources in a kinetic and mechanistic study of the protonation of the anthracene anion radical ($A^{-\cdot}$) in dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and acetonitrile (MeCN). It is suggested that the protonation of $A^{-\cdot}$ involves exclusively the enol form of the β-dicarbonyl compound. The interconversion of the keto and enol forms was effectively catalyzed by the enolate ions formed during the reaction and could for that reason be treated as a fast and reversible equilibrium in the kinetic analysis of the experimental data.

The kinetics were studied by derivative cyclic voltammetry and linear sweep voltammetry, and the keto–enol equilibrium constants and approximate rate constants for the enolate-catalyzed keto–enol interconversion were determined by NMR spectroscopy.

For acetylacetone and ethyl acetoacetate the rate constant for protonation of $A^{-\cdot}$ and the equilibrium constant for tautomerization showed only slight dependence on the nature of the solvent. In contrast, both of these constants increased appreciably in the order DMSO < DMF << MeCN for dimedone. The same order was found for the rate constants for protonation of $A^{-\cdot}$ by phenol (PhOH) and benzoic acid (PhCOOH). These results reflect that the enol forms of acetylacetone and ethyl acetoacetate in solution are stabilized by the formation of intramolecularly hydrogen-bonded species the solvation of which is determined mainly by polarity/polarizability effects. In contrast, the solvation of PhOH, PhCOOH and the enol form of dimedone, the structures of which make intramolecular hydrogen-bond stabilization impossible, depends primarily on the hydrogen-bond basicity of the solvent.

The results of the study showed that the attenuating effect of these hydrogen-bond equilibria is a major factor in determining the rate of proton transfer from oxygen acids to, for example, anion radicals of aromatic hydrocarbons under non-aqueous conditions and therefore that great care should be taken when using values of observed rate constants in correlations with other kinetic, thermodynamic or theoretical data.

The mechanism for protonation of anion radicals derived from alternant aromatic hydrocarbons, e.g., anthracene (A), by simple oxygen acids (HB) in apotic, dipolar solvents is now well established.[1-17] The reaction sequence leading to the product, AH_2, includes the four steps, (1)–(4), with (2) being rate determining.

$$A + e^- \rightleftharpoons A^{-\cdot} \quad (1)$$

$$A^{-\cdot} + HB \xrightarrow{k_2} AH^{\cdot} + B^- \quad (2)$$

$$AH^{\cdot} + A^{-\cdot} \xrightarrow{\text{fast}} AH^- + A \quad (3)$$

$$AH^- + HB \xrightarrow{\text{fast}} AH_2 + B^- \quad (4)$$

$$-d[A^{-\cdot}]/dt = 2k_2[HB][A^{-\cdot}] \quad (5)$$

Although the rate law, eqn. (5),[3-16] associated with this scheme appears simple, the detailed interpretation of kinetic data for the reaction is complicated by the participation of HB in parallel hydrogen-bonding equilibria, for example of the types (6) and (7), where HB/B^- is the so-called homoconjugation complex and HB/HB is the dimer of HB.[12-16] (Here and in the following a slash, /, represents a hydrogen-bond).

$$HB + B^- \xrightleftharpoons{K_6} HB/B^- \quad (6)$$

$$HB + HB \xrightleftharpoons{K_7} HB/HB \quad (7)$$

The kinetic contributions from these equilibria are highly dependent on the solvent properties. For example, for the protonation of anthracene anion radical ($A^{-\cdot}$) by phenol

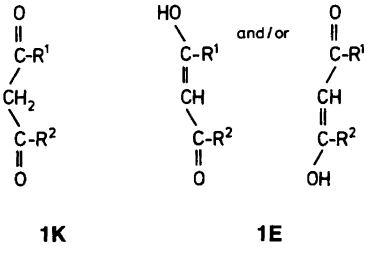
(PhOH) in *N,N*-dimethylformamide (DMF) we have shown that the formation of HB/B^- may be treated kinetically as an essentially irreversible process and a reaction order analysis also indicated the participation of HB/HB in the protonation of $A^{-\bullet}$, eqn. (8).[12,13,17] In contrast, the

$$A^{-\bullet} + HB/HB \xrightarrow{k_8} AH^{\bullet} + HB/B^- \quad (8)$$

analysis of kinetic data for the same reaction carried out in dimethyl sulfoxide (DMSO) showed that reaction (6) in this solvent could be treated kinetically as a fast equilibrium and reaction (7) was found to be displaced to the left so effectively that kinetic contributions from eqn. (8) could not be detected.[16] This difference between reactions carried out in DMF and DMSO was attributed to the stronger hydrogen-bond accepting properties of the latter solvent.

When the proton source is a β-dicarbonyl compound of the type shown in Scheme 1, a more complicated reaction mechanism may be expected, since compounds of this structure generally exist in solution as a mixture of two tautomers of different acidity, the keto form (**1K**) and the enol form (**1E**). Mechanistic complications of this kind were encountered during a study of the protonation of a series of napthalene anion radicals by diethyl malonate in DMF.[18] By application of derivative cyclic voltammetry (DCV)[6] it was found that the rate of interconversion of **1K** and **1E** ($R^1 = R^2 = OEt$) was of the same order of magnitude as the rate of disappearance of the anion radicals and for this reason a detailed analysis of the kinetic data could not be carried out. The study also implied that protonation of anion radicals by β-dicarbonyl compounds may be subject to autocatalysis owing to the increased rate of formation of the kinetically more acidic tautomer caused by base formed during the reaction.

However, the complexity of the kinetic problem is reduced considerably if the interconversion of the tautomers is fast compared with the rate of protonation of $A^{-\bullet}$. If in addition the equilibrium constant for the tautomerization process is known, the scene is set for a detailed discussion of the kinetic data. As a result of an extensive survey we have found three β-dicarbonyl compounds, dimedone, acetylacetone and ethyl acetoacetate, that fulfilled these criteria and in addition gave rise to almost ideal voltammetric behavior when used as proton sources in the protonation of



1K **1E**

R^1 = alkyl, alkoxy; R^2 = alkyl, alkoxy

Scheme 1.

$A^{-\bullet}$. The purpose of the present paper is to show an analysis of the experimental data that in such cases may give access to rate constants associated with well defined proton transfer steps.

Results and discussion

Inclusion of the base-catalyzed interconversion[19–22] of the keto form, BH,* and the enol form, HB,* in the mechanism without making assumptions concerning the relative acidity of the two tautomers, results in the following general reaction sequence (Scheme 2), where B^- is the common conjugate base of BH and HB. The rate law associ-

$$A^{-\bullet} + BH \xrightarrow{k_2^K} AH^{\bullet} + B^- \quad (2K)$$

$$A^{-\bullet} + HB \xrightarrow{k_2^E} AH^{\bullet} + B^- \quad (2E)$$

$$AH^{\bullet} + A^{-\bullet} \xrightarrow{\text{fast}} AH^- + A \quad (3)$$

$$AH^- + BH \xrightarrow{k_4^K} AH_2 + B^- \quad (k_4^K/k_2^K >> 1) \quad (4K)$$

$$AH^- + HB \xrightarrow{k_4^E} AH_2 + B^- \quad (k_4^E/k_2^E >> 1) \quad (4E)$$

$$BH + B^- \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} HB + B^- \quad (K_9 = [HB]/[BH] = k_9/k_{-9}) \quad (9)$$

Scheme 2.

ated with this scheme depends on the relative rates of the proton transfer steps for which the only assumptions made so far, $k_4^K/k_2^K >> 1$ and $k_4^E/k_2^E >> 1$, are based on the fact that AH^- is a considerably stronger base than $A^{-\bullet}$.[23] However, this assumption is not in itself sufficient for the derivation of a feasible rate law and therefore we will now examine the rate and equilibrium properties of reaction (9) for the three β-dicarbonyl compounds included in the study. The paragraphs to follow include discussion of the magnitudes of K_9 and the thermodynamic and kinetic acidities of the keto and enol forms, and before returning to our main subject, the rate of protonation of $A^{-\bullet}$, we will also comment on the choice of measurement techniques and evaluate the possible kinetic contributions from reactions (6)–(8), and we will analyze the kinetic consequences of the base catalysis of the keto–enol interconversion.

Equilibrium constants for the keto–enol interconversion, K_9. The values of K_9 required in the kinetic analysis are not all available in the literature. Thus, in order to have acess to a complete and consistent set of data it was decided to carry out an independent series of measurements of K_9 by NMR spectroscopy (see the Experimental). Preliminary experi-

* Here and in the following the keto form is abbreviated to BH and the enol form to HB.

Table 1. Equilibrium constants, K_9, in three solvents for the interconversion of the keto and enol forms of the β-dicarbonyl compounds employed in this study.[a]

Compound	K_9/M^{-1}		
	DMSO	DMF	MeCN
Dimedone	>100 (94)[b]	>100 (85)[b]	1.9 (2.3)[b]
Acetylacetone	1.4 (1.95)[b] (1.6)[c,d,e]	1.9 (1.9)[e]	1.3 (1.2)[b] (1.6)[c,e]
Ethyl acetoacetate	0.02 (0.023)[c]	0.04	0.04 (0.052)[c]

[a]Measured by NMR spectroscopy at C°_{Acid} = 160 mM and T = 20 °C as described in the Experimental. Data from the literature are given in parentheses. Minimum values are indicated by >. [b]From Ref. 25. [c]From Ref. 26 (T = 33 °C). [d]From Ref. 24. [e]From Ref. 27.

ments showed that the uncatalyzed interconversion of the tautomers is slow on the time scale of this technique and well defined peaks that could be attributed to **1K** and/or **1E** were observed in all cases. The values of K_9 obtained in DMF, DMSO and acetonitrile (MeCN) are summarized in Table 1 and are found to be in accord with available literature values[24-27] (see Table 1).

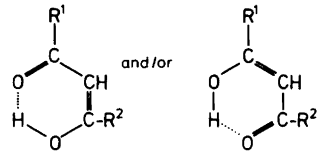
The three β-dicarbonyl compounds cover a wide range of K_9 values from more than 100 for dimedone in DMSO and DMF to 0.02 for ethyl acetoacetate in DMSO. Considering that DMSO, DMF, and MeCN are all aprotic, dipolar solvents, it is noteworthy that the values of K_9 for acetylacetone and ethyl acetoacetate vary only slightly for the three solvents, whereas K_9 for dimedone changes from >100 in DMSO and DMF to 1.9 in MeCN. These results are in keeping with the general observation[25] that K_9 for tautomer pairs of which the enol form is stabilized through intramolecular hydrogen-bonding (Scheme 3), like, in this case, acetylacetone and ethyl acetoacetate,[25-29] is determined mainly by polarity–polarizability effects. These vary only slightly on going through the series DMSO, DMF and MeCN. On the other hand, K_9 for compounds like the cyclic dimedone, the enol form of which cannot gain this extra intramolecular stabilization, is controlled almost completely by the hydrogen-bond basicity of the solvent,[25] which decreases in the order DMSO > DMF >> MeCN.[17,30] (see also the Experimental).

The thermodynamic and kinetic acidities of the tautomers. From eqn. (9) and the definitions of the *thermodynamic* acidities of BH and HB, eqns. (10K) and (10E), a simple relation for the relative acidity of the two tautomers is easily obtained, eqn. (11). It is seen from eqn. (11) that

$$K^{K}_{10} = [H^+][B^-]/[BH] \quad (10K)$$

$$K^{E}_{10} = [H^+][B^-]/[HB] \quad (10E)$$

$$K^{K}_{10}/K^{E}_{10} = K_9 \quad (11)$$



Scheme 3.

the tautomer present in solution in the lower concentration is the stronger acid. In our case this implies that the keto form of dimedone in DMSO and DMF is a stronger acid than the enol form (K_9 >> 1), whereas the tautomers are of similar acidity for dimedone in MeCN and for acetylacetone in any of the three solvents (K_9 = 1–2). Finally, the enol form is the stronger acid for ethyl acetoacetate in all three solvents (K_9 << 1).

Another useful relation is that between the acidity constant for a particular tautomer, K^{K}_{10} or K^{E}_{10}, and the apparent acidity constant, K_{12}, referring to the keto–enol equilibrium mixture and defined by eqn. (12). Substitution of [BH] and

$$K_{12} = [H^+][B^-]/([BH] + [HB]) \quad (12)$$

[BH] in eqn. (12) by expressions obtained from eqns. (10K) and (10E) results in eqns. (13) and (14), which show that K^{K}_{10} and K^{E}_{10} may conveniently be estimated from the directly accessible equilibrium constants, K_9 and K_{12}.

$$K^{K}_{10} = K_{12}(1 + K_9) \quad (13)$$

$$K^{E}_{10} = K_{12}(1 + K_9)/K_9 \quad (14)$$

Values of pK_{12} for the three β-dicarbonyl compounds used in this study have been reported for DMSO,[24,31,32] and these, together with the data for K_9 (Table 1), resulted in the values of K^{K}_{10} and K^{E}_{10} summarized in Table 2. For comparison this table also contains the acidity constants, pK_A, for two oxygen acids, PhOH and benzoic acid (PhCOOH), used in our earlier studies of protonation of $A^{-\bullet}$.[12-16]

Table 2. Thermodynamic acidities in dimethyl sulfoxide of the β-dicarbonyl compounds and the oxygen acids employed in this study.

Compound	pK^{a}	pK^{K}_{10}[b]	pK^{E}_{10}[c]
Dimedone	11.2[d]	<9.2	11.2
Acetylacetone	13.3[d]	12.9	13.1
Ethyl acetoacetate	14.2[e]	14.2	12.5
Phenol	18.0[f]		
Benzoic acid	11.0[g]		

[a]The acidity constants, K, equal K_{12} for the β-dicarbonyl compounds and K_A for PhOH and PhCOOH; T = 25 °C. [b]Thermodynamic acidity of the keto form calculated from eqn. (13). [c]Thermodynamic acidity of the enol form calculated from eqn. (14). [d]From Refs. 24 and 31. [e]From Ref. 32. [f]From Ref. 33. [g]From Ref. 34.

The data in Table 2 show that the keto form of dimedone is approximately two orders of magnitude more acidic than PhCOOH in DMSO, whereas the acidity of the enol form is similar to that of PhCOOH. The acidities of the keto and enol forms of acetylacetone and ethyl acetoacetate are all intermediate between those of PhOH and PhCOOH. Complete sets of pK_{12} values for the five acids in DMF and MeCN have not been reported, but the published data[33–37] indicate that the values of pK_{12} in DMF are similar to those in DMSO, whereas the pK_{12} values in MeCN are 8–10 units higher than those given in Table 2.

The relative *kinetic* acidity of carbon acids and oxygen acids has been the subject of intensive research.[21,38–44] The general observation is that the intrinsic rate constant, referring to a driving force equal to zero, is several orders of magnitude smaller for carbon acids than for oxygen acids. The fact that the enol form of ethyl acetoacetate is thermodynamically a much stronger acid than the corresponding keto form in all three solvents leaves little doubt that this tautomer is also kinetically the stronger acid. This means that contributions from eqns. (2K) and (4K) may be neglected for this proton source provided that the enol form can be supplied by forward reaction (9) at a sufficient rate. The same conclusion is arrived at for acetylacetone in all three solvents and for dimedone in MeCN; in all these cases the tautomers have similar thermodynamic acidities with values of K_9 only slightly larger than one, ranging from 1.3 to 1.9. Predictions concerning the relative kinetic acidity of the tautomers of dimedone in DMSO and DMF are more difficult to make considering that the pK_{10}^{K} values in these two solvents are at least two units lower than pK_{10}^{E} (Table 2). However, as will become evident later, it is most likely that protonation of $A^{-\bullet}$ by dimedone also takes place via the enol form in these two solvents.

The measurement techniques and the significance of reactions (6)–(8). Before continuing the discussion it is necessary to specify the stoichiometric acid concentrations, which depend on the experimental technique.

The kinetics of the protonation of $A^{-\bullet}$ in the presence of acetylacetone or ethyl acetoacetate were investigated by DCV through measurements of $v_{1/2}$ as earlier described,[6,13,14,16] where $v_{1/2}$ is the voltage sweep rate at which the derivative peak current ratio equals 0.5. The stoichiometric concentration of the acid, C°_{Acid}, was in most cases between 10 and 160 mM at C°_{A} = 1 mM. Preliminary experiments showed that the reaction between $A^{-\bullet}$ and dimedone was too fast to be studied this way, and instead a newly developed linear sweep voltammetry (LSV) procdure[15] involving measurements of $E_{p/4}-E_p$ as a function of v under second-order conditions was applied. Here, E_p is the peak potential and $E_{p/4}$ is the potential at which the current, i, equals $i/4$. The stoichiometric concentrations of A and dimedone in this case were 1.0 mM and 0.5 mM, respectively.

Since hydrogen-bonding effects are only of minor importance for strongly conjugated carbon acids[45] the discussion of the effects of eqns. (6) and (7) may be limited to the enol form, HB, and the corresponding base, B^-. A common characteristic of the β-dicarbonyl compounds is that the negative charge in B^- is delocalized by resonance over a structural segment encompassing two equivalent or nearly equivalent oxygen atoms. Thus, the negative charge density at oxygen is low in these anions and accordingly their ability to act as hydrogen-bond acceptors is smaller than that for anions with only one oxygen atom, for example PhO^-. As an illustration of this, the value of K_6 for dimedone in DMSO, 1.6×10^2 M^{-1}, is approximately one order of magnitude smaller than that for PhOH, 2.3×10^3 M^{-1}, in the same solvent.[31,33] This moderate value of K_6 for dimedone in DMSO causes $[HB/B^-]$ in the reaction layer to be negligibly small at C°_{Acid} = 0.5 mM. The values of K_6 for dimedone in DMF and MeCN are not known, but are supposedly larger than that in DMSO. However, as shown later, the protonation of $A^{-\bullet}$ by dimedone is a very fast process and for this reason the interference from eqn. (6) is expected to be negligible as found in a similar LSV study of the protonation of aromatic hydrocarbon anion radicals by different oxygen acids.[15] The values of K_6 for acetylacetone and ethyl acetoacetate in all three solvents are expected to be even smaller than those for dimedone owing to the intramolecular hydrogen-bond stabilization of the enol form of these two acids (Scheme 3) and accordingly the effect of eqn. (6) is expected to be negligible for these two compounds as well.

The formation of the intramolecularly hydrogen-bonded species also competes effectively with the formation of intermolecularly hydrogen-bonded dimers. Thus, for acetylacetone and ethyl acetoacetate the kinetic effects of eqn. (7), and consequently of eqn. (8), were deemed insignificant. For dimedone the values of K_9 in DMSO and DMF strongly favor the enol form, which, due to its cyclic carbon skeleton, cannot form an intramolecularly hydrogen-bonded structure. However, for reasons given above the measurements involving this acid had to be carried out at very low concentrations, C°_{Acid} = 0.5 mM, which favor the left-hand side of eqn. (7). This, together with the expressed hydrogen-bond basicity of DMF and DMSO, which further diminishes the amount of dimer,[16] led to the conclusion that contributions from eqns. (7) and (8) for dimedone in DMF and DMSO are negligible. The amount of dimedone dimer in MeCN is not easy to predict, but the experimental results (see later) demonstrated that contributions from eqns. (7) and (8) are also apparently insignificant in this case.

Thus, the general conclusion is that the kinetic contributions from eqns. (6)–(8) are small for all three β-dicarbonyl compounds in all three solvents and may be neglected in the kinetic analysis of the experimental data without appreciable loss of accuracy of the resulting rate constants.

The rate and the kinetic consequences of the base-catalyzed keto–enol interconversion. The uncatalyzed equilibration of a keto–enol mixture is usually a slow process,[27,28] and the NMR measurements that gave rise to the values of K_9 given in Table 1 showed that dimedone, acetylacetone and ethyl acetoacetate are not exceptional in this respect. However, the important point in the present context is the rate of formation of HB in the presence of the enolate ion, B^-, which is inevitably produced during the proton transfer steps, (2E) and (4E).

Rough estimates of the rate constants, k_9, were obtained by NMR spectroscopy for acetylacetone and ethyl acetoacetate in DMSO and MeCN for solutions containing known amounts of B^- (see the Experimental). The values of k_9 for acetylacetone and ethyl acetoacetate in DMSO were both in the range $(2–4)\times10^4$ M^{-1} s^{-1}, while the values for MeCN were approximately one order of magnitude smaller. Measurements could not be carried out in DMF owing to hydrolysis of the solvent during the prolonged exposure to base necessary in this type of work. The question now is whether these values of k_9 are sufficiently large to ensure that reaction (9) may be treated as a fast equilibrium process.

The kinetic consequences of the magnitude of k_9 are dependent on the values of K_9 and the ratio, k_9/k_2^E. The smaller the value of K_9, the larger is the value of k_9/k_2^E necessary to maintain equilibrium conditions. The limits of k_9/k_2^E corresponding to a maximum error of 10 % in k_2^E were calculated by digital simulation (see the Experimental) for proton sources with K_9 values in the range 0.02–2.0. The results of these calculations at $C^\circ_{Acid}/C^\circ_A \geq 10$ and $K_9 = 0.02$ (ethyl acetoacetate) showed that equilibrium conditions prevail as long as $k_9/k_2^E > 1$. This limit decreases with increasing K_9 and when $K_9 \approx 1.5$ or larger (acetylacetone and dimedone) the situation is reached in which the deviations from equilibrium conditions are insignificant even at $k_9/k_2^E = 0$. In other words, a gradual change is observed from low values of K_9, where a certain minimum value of k_9/k_2^E is required in order for the amount of B^- formed during reactions (2E) and (4E) to be sufficient to maintain reaction (9) at equilibrium, to larger values of K_9 where equilibrium (9) is displaced to the right so effectively that deviations from equilibrium behavior are insignificant.

An important and experimentally verifiable consequence of this is that the value of the observed rate constant, k_{obs}, is predicted to be *invariant* to addition of B^- to the solution in the cases where the amount of B^- formed during reactions (2E) and (4E) is sufficient to govern the equilibrium conditions. On the other hand, in the kinetic region where the ratio k_9/k_2^E is too small to maintain reaction (9) at equilibrium, the value of k_{obs} will be observed to increase upon addition of B^-. The results from digital simulation showed that addition of B^- is in fact an extremely sensitive method of testing for deviations from equilibrium behavior of reaction (9). For example, addition of an amount of B^- corresponding to $C^\circ_{B^-}/C^\circ_A = 2$ may result in an increase in k_{obs} of 30–100 % depending upon the actual values of C°_{Acid}/C°_A and k_9/k_2^E.

Another indication of non-equilibrium conditions is the observation of apparent reaction orders,[13] $d\log v_{1/2}/d\log C^\circ_{Acid}$, larger than unity. This is caused by the fact that the deviations from equilibrium behavior of reaction (9) will increase with decreasing values of C°_{Acid}/C°_A, and accordingly the values of k_{obs} become smaller and smaller relative to that for the equilibrium situation.

Kinetic measurements. After this preparatory discussion we will now analyze the rate law resulting from Scheme 2. In addition to the assumptions already made for the magnitudes of k_4^K/k_2^K and k_4^E/k_2^E, it seems indisputable that the steady-state approximation applies for $AH^\bullet$ and AH^-, which was also assumed in the derivation of rate law (5).[3–16] All together this leads to rate law (15). Now, if only the enol form of the β-dicarbonyl compound participates in the protonation of $A^{-\bullet}$ as suggested above, rate law (15) reduces to (16). Finally, if the equilibrium condition is ful-

Table 3. Values of the rate constants, k_{obs} and k_2^E, for the protonation of the anthracene anion radical by β-dicarbonyl compounds.[a]

Compound	Solvent					
	DMSO		DMF		MeCN	
	k_{obs}	k_2^E	k_{obs}	k_2^E	k_{obs}	k_2^E
Dimedone[b]	1.8×10^{6c}	1.8×10^{6c}	3.6×10^{6c}	3.6×10^{6c}	1.6×10^8	2×10^8
Acetylacetone[d]	2.1×10^4	4×10^4	3.8×10^4	6×10^4	2.1×10^4	4×10^4
Ethyl acetoacetate[e]	3.8×10^3	2×10^5	9.8×10^3	3×10^5	4.0×10^{3f}	1×10^5
PhOH[e]	2.6×10^{3g}		5.4×10^{3h}		3.0×10^5	
PhCOOH[b]	8.4×10^5		3.0×10^{6i}		1.6×10^8	

[a]Measured in solvent containing Bu_4NBF_4 (0.1 M) at $T = 20$ °C and $C^\circ_A = 1$ mM and given in units of M^{-1} s^{-1}. The values of k_2^E are calculated from eqn. (17) and rounded off to one digit as for reasons discussed in the text, they are less accurate than the directly measured values of k_{obs}. For PhOH and PhCOOH the values of k_{obs} are equal to k_2. [b]From $E_{p/4}-E_p$ measurements as described in Ref. 15; $C^\circ_{Acid}/C^\circ_A = 0.5$. [c]The values of k_{obs} for dimedone in DMSO and DMF are equal to k_2^E (see the text). [d]From DCV measurements at C°_{Acid} in the range 10–40 mM (DMSO) or 2.5–20 mM (DMF and MeCN). [e]From DCV measurements at C°_{Acid} in the range 10–160 mM. [f]Value obtained at $C^\circ_{Bu_4NOH} = 4$ mM. [g]From Ref. 16. [h]From Ref. 12. [i]From Ref. 15.

filled for reaction (9), we arrive at rate law (17), where [Acid] = [BH] + [HB]. This rate law will be the basis for our discussion of the experimental results.

$$-d[A^{-\bullet}]/dt = 2(k_2^K[BH] + k_2^E[HB])[A^{-\bullet}] \quad (15)$$

$$-d[A^{-\bullet}]/dt = 2k_2^E[HB][A^{-\bullet}] \quad (16)$$

$$-d[A^{-\bullet}]/dt = \frac{2k_2^E K_9}{1+K_9}[Acid][A^{-\bullet}] = 2k_{obs}[Acid][A^{-\bullet}] \quad (17)$$

The values of k_{obs} for protonation of $A^{-\bullet}$ obtained as described above are summarized in Table 3, which also contains values of k_2^E (see below).

Dimedone. The values of K_9 for dimedone in DMSO and DMF are both larger than 100 and therefore too large for conclusions to be drawn concerning the magnitude of k_9 and k_{-9}. At the same time $K_9 > 100$ implies that [Acid] ≈ [HB] and therefore rate law (17) degenerates to (16), which is equivalent to rate law (5) with $k_2 = k_{obs} = k_2^E$. The fit of the experimental values of $E_{p/4}-E_p$ obtained at different voltage sweep rates to the working curve, $E_{p/4}-E_p$ versus $\log [k_2 C_A^\circ RT/(\nu nF)]$, was, in general, very good and comparable to that for data obtained earlier by the same technique for the protonation of $A^{-\bullet}$ by PhCOOH.[15] The values of k_2^E obtained in this way were 1.8×10^6 M^{-1} s^{-1} (DMSO) and 3.6×10^6 M^{-1} s^{-1} (DMF). Now, *if* the thermodynamically more acidic keto form had been the proton donor and we still assume reaction (9) to be fast and reversible, it follows from eqns. (11) and (17) that $k_2^K = k_{obs}(1 + K_9) > 10^8$ M^{-1} s^{-1}, which approaches the value for a diffusion controlled process in these two solvents.[46] We find this an improbably large value for proton transfer between two carbon centers, and our conclusion is, as also indicated above, that $k_{obs} = k_2^E$ for dimedone in DMSO and DMF.

In MeCN with $K_9 = 1.9$ the equilibrium concentration of the enol form, [HB], is considerably smaller than [Acid]. Also in this case, the fit of the experimental data to the working curve was good as shown in Fig. 1. However, owing to the considerable computer time involved, theoretical data at $\log [k_2 C_A^\circ RT/(\nu nF)] > 3.3$ were not available, but it is noteworthy that an almost perfect match is observed in the entire kinetic region between the data for dimedone and the data for protonation of $A^{-\bullet}$ by PhCOOH, which follows mechanism (1)–(4),[15] including the part corresponding to $\log [k_2 C_A^\circ RT/(\nu nF)] > 3.3$ (Fig. 1).

The LSV technique used in this case is based on the depletion of the proton donor in the reaction layer and experience has shown that even minor deviation from the mechanism on which the working curve is based show up very clearly as a mismatch of the theoretical and the experimental data. The fact that an almost perfect match of the data for dimedone and PhCOOH is observed strongly indicates that reaction (9) for dimedone in MeCN under the influence of the B^- generated during reactions (2E) and (4E) responds as a fast equilibrium and that participation of the dimer of dimedone in the proton transfer reaction, eqn. (8), is insignificant. Accordingly, k_2^E may be estimated from eqn. (17) resulting in the value 2×10^8 M^{-1} s^{-1}.

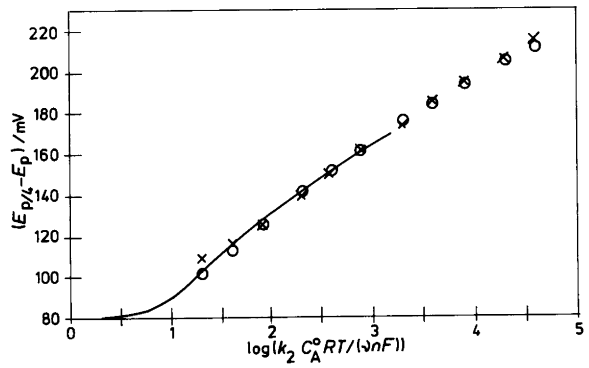


Fig. 1. Theoretical data (full line) for $E_{p/4}-E_p$ at t = 25 °C for rate law (5) at C_{Acid}°/C_A° = 0.5. The experimental points are for protonation of $A^{-\bullet}$ by dimedone (C_{Acid}° = 0.5 mM) (×) and PhCOOH (C_{PhCOOH}° = 0.5 mM) (○) in MeCN (0.1 M Bu_4NBF_4).

Acetylacetone. Acetylacetone in itself is easily reduced and in order to avoid interference from unwanted electrode processes the DCV measurements in the presence of this proton source had to be carried out at $C_{Acid}^\circ < 40$ mM. Measurements in DMSO in the concentration range 10–40 mM resulted in $k_{obs} = 2.1\times10^4$ M^{-1} s^{-1}, and addition of Bu_4NOH was found to leave k_{obs} unchanged. This leaves little doubt that reaction (9) fulfills the equilibrium criterion and the value of k_2^E calculated from eqn. (17) is 4×10^4 M^{-1} s^{-1}. Together with the value of k_9 for acetylacetone in DMSO, taken as 3×10^4 M^{-1} s^{-1}, this gives a k_9/k_2^E ratio close to unity, which compared with the limits given above supports the assumption that the forward reaction (9) in this case is sufficiently fast for the keto–enol interconversion to be treated as a fast equilibrium.

For DMF and MeCN apparently contradictory results were obtained. It was found that k_{obs} calculated from rate law (17) increased with increasing values of C_{Acid}° in the range 2,5–20 mM indicating that the forward reaction (9) participated in determining the overall rate, but at the same time k_{obs} was insensitive to addition of Bu_4NOH indicating that reaction (9) fulfilled the equilibrium criterion. We are most inclined to rely on the latter observation, since the data obtained at the higher values of C_{Acid}° might have been particularly affected by background problems. Rate law (17) thus results in the values 6×10^4 M^{-1} s^{-1} for DMF and 4×10^4 M^{-1} s^{-1} for MeCN. Taking 3×10^3 M^{-1} s^{-1} as the value of k_9 for acetylacetone in MeCN we obtain $k_9/k_2^E \approx 0.1$, which, again, supports the suggestion that reaction (9) may be treated as a fast equilibrium process.

Ethyl acetoacetate. Ethyl acetoacetate is the acid most likely to exhibit non-equilibrium behavior owing to the low value of K_9 and therefore, the protonation of $A^{-\bullet}$ was more thoroughly investigated in this case.

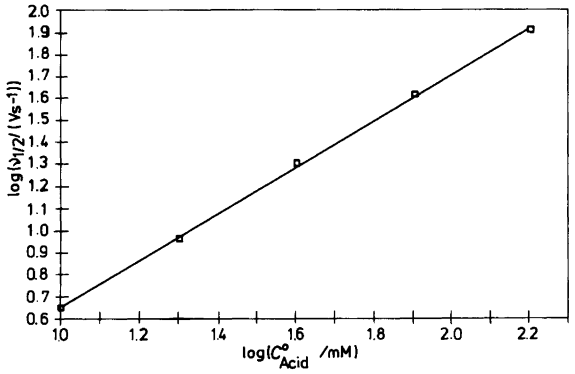


Fig. 2. Reaction order analysis of DCV data for the protonation of $A^{-\bullet}$ by ethyl acetoacetate in DMSO (0.1 M Bu_4NBF_4); C°_A = 1 mM and C°_{Acid} = 10–160 mM.

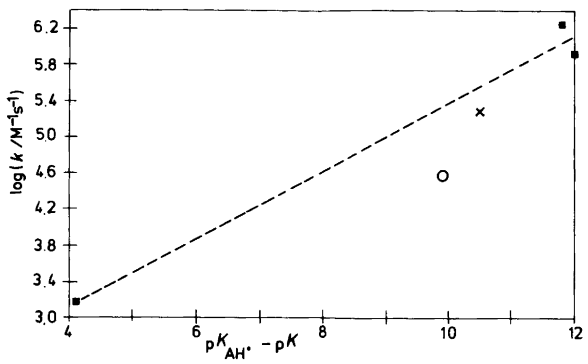


Fig. 3. Brønsted-type plot of log k (k_2 or k_2^E from Table 3) versus pK ($K = K_A$ or K_2^E from Table 2). The regression line (-----) is defined by the data for PhOH, PhCOOH and the enol form of dimedone (see the text). The data point (○) is for acetylacetone and (×) is for ethyl acetoacetate. A value of 23 was used for the pK_A of $AH^{\bullet}$.[23]

In DMSO the apparent reaction order, d log $v_{1/2}$/d log C°_{Acid}, obtained in the range C°_{Acid} = 10–160 mM (Fig. 2), was 1.06 and trends in the data were not observed. Moreover, experiments involving addition of Bu_4NOH at C°_{Acid} = 160 mM had no effect on k_{obs}.

Thus, at first glance this appears to be an ideal system, and application of rate law (17) gives $k_2^E = 2\times10^5$ M^{-1} s^{-1}. However, this value together with $k_9 \approx 3\times10^4$ M^{-1} s^{-1} results in $k_9/k_2^E \approx 0.15$, which makes the assumption of a fast and reversible reaction (9) questionable. The simulations showed that an increase in k_{obs} up to approximately 20 % would have been expected upon addition of base to the voltammetry solution, but none was observed. We believe that this most likely reflects experimental uncertainty in the value of k_9, which is only a rough estimate, as already mentioned.

In DMF a slight increase in k_{obs} with increasing C°_{Acid} was observed in the range 10–160 mM resulting in d log $v_{1/2}$/d log C°_{Acid} = 1.13. Addition of Bu_4NOH (4 mM) to a solution with C°_{Acid} = 20 mM resulted in an increase of k_{obs} close to 10 %. Thus, this system constitutes a borderline case and the rate constant, 3×10^5 M^{-1} s^{-1}, calculated from eqn. (17) must therefore be regarded as a minimum value.

Addition of Bu_4NOH (4 mM) to the MeCN solution with C°_{Acid} = 20 mM resulted in an increase in k_{obs} of 35 %, clearly indicating that the forward reaction (9) in this case participates in determining the overall rate of the reaction. Addition of more Bu_4NOH did not lead to a further increase in k_{obs}. The value of k_{obs}, 1.0×10^5 M^{-1} s^{-1}, obtained in the presence of 4 mM Bu_4NOH results in $k_9/k_2^E \approx 0.03$ and introduction of this value into the simulation resulted in a predicted increase in k_{obs} of approximately 50 % upon addition of Bu_4NOH (4 mM), which is in fair agreement with the observed value of 35 %. Reaction order measurements in the presence of 4 mM Bu_4NOH resulted in a value of d log $v_{1/2}$/d log C°_{Acid} equal to 1.03, which to within the experimental error, is identical with the theoretical value. The rate constants given in Table 3 for this combination of proton source and solvent were therefore obtained at $C^\circ_{Bu_4NOH}$ = 4 mM.

The dependence of the rate constants on the solvent and the relationship between the kinetic and thermodynamic acidities. Inspection of the data for k_2 and k_2^E in Table 3 shows that the rate constants for protonation of $A^{-\bullet}$ by PhOH, PhCOOH and dimedone increase appreciably in the order DMSO < DMF << MeCN, whereas k_2^E for acetylacetone and ethyl acetoacetate shows only little dependence on the solvent. For the β-dicarbonyl compounds the effect of solvent on k_2^E is similar to that observed for K_9 and most likely reflects the same phenomenon, i.e. that the enol forms of acetylacetone and ethyl acetoacetate in solution exist mainly as the intramolecularly hydrogen-bonded species shown in Scheme 3, whereas PhOH, PhCOOH and the enol form of dimedone, for which this intramolecular stabilization is not possible, interact more strongly with the solvent through hydrogen bonds.[47,48]

This difference in behavior is also illustrated by the Brønsted type plot of the data obtained in DMSO shown in Fig. 3 from which it is seen that the values of log k ($k = k_2$ or k_2^E) and pK ($K = K_A$ or K_{10}^E) are not linearly related as might have been expected. First it is noted that the data point (○) for acetylacetone, one of the two compounds forming an intramolecularly stabilized enol form, is located well below the regression line (------) arbitrarily defined by the data points for the three acids that interact strongly with solvent. The deviation would correspond to an error in k_2^E of a factor of six or an error in pK_{10}^E of approximately two pK units, both of which are much larger than the experimental uncertainty of these data. Also the data point (×) for the other intramolecularly stabilized enol form, that of ethyl acetoacetate, is located below the regression line, but the deviation is smaller for this species. Secondly, it should be noted that within the group of compounds interacting strongly with the solvent we find that k_2^E for dimedone

(1.8×10^6 M^{-1} s^{-1}) is a factor of 2.1 larger than k_2 for PhCOOH (8.4×10^5 M^{-1} s^{-1}) despite the fact that the PhCOOH is the thermodynamically stronger acid by 0.2 pK units. Also, this difference appears to be larger than may be accounted for by experimental uncertainty. Thus, we conclude that the absence of a linear relationship between log k and pK is real and most likely reflects differences in the nature and strength of the hydrogen bonds to be broken in the proton transfer reaction. This suggests that the transition state for proton transfer from any of the five acids to $A^{-\bullet}$ is characterized by considerable weakening or even complete breakage of either an intermolecular hydrogen bond, as for PhOH, PhCOOH and the enol form of dimedone, or an intramolecular hydrogen bond, as for the enol forms of acetylacetone and ethyl acetoacetate. Consequently, it is to be expected that the magnitudes of k_2 and k_2^E for PhOH, PhCOOH and the enol form of dimedone will depend strongly on the hydrogen-bond basicity of the solvent, whereas the protonation of $A^{-\bullet}$ by the enol forms of acetylacetone or ethyl acetoacetate is expected to be much less dependent on the solvent owing to the intramolecular nature of the hydrogen bond to be broken.

The results of this study show that the attenuating effect of the hydrogen-bond equilibria discussed above is a major factor in determining the rate of proton transfer from oxygen acids to, for example, anion radicals of aromatic hydrocarbons under non-aqueous conditions. Thus, the values of the rate constants given in Table 3 are smaller than those that would have been observed in the absence of the hydrogen-bond interactions and therefore, great care should be taken in using values of k_2 and k_2^E, or even worse, values for k_{obs}, in correlations with other kinetic, thermodynamic or theoretical data. Further discussion of these and related problems will be the subject of forthcoming papers from this laboratory.

Final remarks concerning the accuracy of the kinetic data. The use of β-dicarbonyl compounds as proton sources during electroanalytical measurements under non-aqueous conditions is attractive since their pK values make them suitable for the protonation of electrogenerated bases as for example anion radicals. However, the kinetic analysis of data for proton transfer reactions that involve tautomeric proton sources will, for obvious reasons, be more complex than the analysis of data for reactions involving proton sources that exist in solution only as one tautomer, and the analysis requires, in addition to the primary kinetic data, the rate and equilibrium data for eaction (9) to be accessible. The degree of precision and accuracy of these additional data will be reflected in the resulting proton transfer rate constants, which for this reason will be less accurate than those obtained in kinetically less complicated cases. An additional experimental problem is that often it is impossible to obtain the necessary parameters, such as K_9, under the same conditions as those employed in a voltammetric study, i.e. in the same concentration range and in the presence of supporting electrolyte, and this may introduce additional uncertainty in the resulting kinetic data. Another problem that may result in a lower level of accuracy in the present case is the assumption that protonation of $A^{-\bullet}$ and AH^- takes place exclusively via the enol forms of the β-dicarbonyl compounds. For the three compounds included in this study, we believe that the assumption is well based, but it is also obvious that it would be practically impossible to detect participation of the keto form in the protonation processes to a degree of 5–10 % of the total reaction. Altogether this implies that the data for k_2^E given in Table 3 are of lower accuracy than for example those we have reported earlier for the protonation of $A^{-\bullet}$ by simple oxygen acids like phenols and benzoic acids. [12–16] However, there appears to be no way to overcome this problem at present.

Experimental

Reagents, electrodes, cells and instrumentation. Anthracene, tetrabutylammonium tetrafluoroborate, dimethyl sulfoxide and *N,N*-dimethylformamide were of the same origin as previously reported.[12,15] Dimedone (Fluka, *puriss.*) and tetrabutylammonium hydroxide (Fluka, *purum*, 40 % in water) were used as received. Acetylacetone (Fluka, *puriss.*) and ethyl acetoacetate (Fluka, *puriss.*) were distilled prior to use. The solutions of tetrabutylammonium tetrafluoroborate (0.1 M) in dimethyl sulfoxide, *N,N*-dimethylformamide or acetonitrile (Merck, spectroscopic grade) were passed through a column filled with neutral alumina (Woelm, W200) immediately before the measurements were made.

The electrodes, cells and electrochemical instrumentation were as previously reported.[12]

NMR measurements. NMR spectra were recorded on a Bruker AM 250 instrument at 5.9 Tesla. Both ^1H and ^{13}C NMR spectra were used in the determination of K_9 except for the ^{13}C NMR spectra obtained in DMF-d_7, which were unsuitable owing to solvent–signal overlap. Nearly identical values of K_9 were found from both types of spectra to within experimental error. The signal-to-noise ratio was generally higher in the ^1H NMR spectra, which for that reason were used exclusively for the determination of the minimum values of K_9 for dimedone in DMSO-d_6 and DMF-d_7. The spectra were recorded with a pulse delay sufficient to ensure complete relaxation between the pulses. The concentration, C°_{Acid}, was 160 mM and a control experiment showed that the value of K_9 for acetylacetone in DMF-d_7 was independent of concentration in the range 60–160 mM, as was also the case when DMSO was the solvent.[24] Another control experiment showed that the temperature dependence of K_9 in DMSO was negligible in the range T = 20–30 °C.

The NMR spectra exhibited separate sharp lines for the two tautomers in the absence of a basic catalyst demonstrating that the keto–enol interconversion is slow under these

conditions. However, addition of base, Bu_4NOH (1.5 mM), resulted in substantial line broadening indicating a much faster conversion rate. From the ^1H NMR spectra the line widths were measured and as the chemical shifts were unchanged this allowed an estimate of the lifetimes, τ, of the tautomers. The results are those given in the text.

Considerable broadening of the ^{13}C NMR signals for the oxygen bearing carbons and the methylene carbons was observed for the enol form of dimedone in DMSO-d_6 in the absence of the basic catalyst. Broadening was also observed for the enol form in MeCN-d_3, but to a degree significantly less than that observed in DMSO-d_6. The effect on the signal for the methylene protons measured from the ^1H NMR spectrum obtained in MeCN-d_3 amounted to less than 1 Hz. These observations are suggested to reflect that hydrogen bonding of the enol form of dimedone to the solvent is much more important in DMSO than in MeCN.

Digital simulations. The theoretical data for the mechanism consisting of the reactions (1), (2E), (3), (4E) and (9), with (9) responding as a fast equilibrium, were obtained by application of an explicit formulation of the diffusion problem followed by evaluation of the homogeneous kinetic terms by help of the integrated rate law as previously described.[12] The value of $E^\circ - E_{sw}$ was 0.2 V, where E_{sw} is the potential at which the voltage sweep is reversed. In the cases where the rate of the keto-to-enol conversion had to be taken into account, the kinetic problem was handled by means of a Runge-Kutta method described in detail elsewhere.[49] The input parameters were K_9, k_9/k_2^E, $k_2^E C_A^\circ RT/(\nu nF)$, C_{Acid}°/C_A°, and $C_{B^-}^\circ/C_A^\circ$. A value of $C_{B^-}^\circ/C_A^\circ$ equal to zero corresponds to the purely autocatalytic case where the amount of B^- in solution is only that formed during reactions (2E) and (4E). The equilibration fo the keto–enol system was assumed to be established at the initiation of the potential sweep. The homogeneous kinetics were described by the five differential eqns. (18)–(22).

$$d[A]/dt = k_2^E[A^{-\bullet}][HB] \quad (18)$$

$$d[A^{-\bullet}]/dt = -2k_2^E[A^{-\bullet}][HB] \quad (19)$$

$$d[BH]/dt = -k_9[BH][B^-] + k_{-9}[HB][B^-] \quad (20)$$

$$d[HB]/dt = -2k_2^E[A^{-\bullet}][HB] + k_9[BH][B^-] - k_{-9}[HB][B^-] \quad (21)$$

$$d[B^-]/dt = 2k_2^E[A^{-\bullet}][HB] \quad (22)$$

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