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EQUILIBRIUM ACIDITIES AND HOMOLYTIC BOND DISSOCIATION ENTHALPIES OF THE ACIDIC C–H BONDS IN DIALKYL MALONATES AND RELATED COMPOUNDS

XIAN-MAN ZHANG AND FREDERICK G. BORDWELL

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

The equilibrium acidities, pK_{HA}, of 18 dialkyl malonates, five alkyl 2-cyanoacetates and nine malononitriles and the oxidation potentials of their conjugate anions, $E_{ox}(A^-)$, were measured in dimethyl sulfoxide solution. The homolytic bond dissociation enthalpies (*BDE*s) of their acidic C–H were estimated by combining their pK_{HA} and $E_{ox}(A^-)$ values. The pK_{HA} values of the dialkyl malonates were found to increase from 15·9 to 16·4 to 18·4 as the dialkyl groups were changed from dimethyl to diethyl to di-*tert*-butyl, but the *BDE*s of the acidic C–H bonds remained constant [95·3 ± 0·3 kcal mol^{-1}) (1 kcal = 4·184 kJ). Introduction of methyl, ethyl, isopropyl and *tert*-butyl groups into the 2-position of diethyl malonate caused the equilibrium acidities to increase by 2·0, 2·4, 3·8 and 8·0 pK_{HA} units, respectively, and the *BDE* values to decrease by 4·4, 3·7, 2·5 and 0·8 kcal mol^{-1}, respectively. Introduction of a phenyl group into the 2-position of diethyl malonate had no effect on the acidity, but weakened the acidic C–H bond by 10 kcal mol^{-1}. The effects on acidity and *BDE* of introducing 3,4,5-$(MeO)_3C_6H_2CO$, CF_3, Me_3N^+, *c*-$C_5H_{10}N$, *p*-MeC_6H_4, *p*-$NO_2C_6H_4$, PhO, F and *c*-$C_5H_5N^+$ groups into the 2-position of diethyl malonate were also examined.

INTRODUCTION

Homolytic bond dissociation enthalpies (*BDE*s) of the H–A bonds in weak organic acids obtained primarily from gas-phase measurements have long been considered to provide the most reliable quantitative information about stabilization energies of the corresponding radicals A· formed by homolytic dissociation:[1]

$$H-A \rightarrow H\cdot + A\cdot \qquad (1)$$

However, direct experimental measurements of the *BDE* values for H–A bonds, especially those in large organic molecules, are often difficult, if not impossible, to carry out owing to the high reactivity of the radicals formed. During the past 6 years we have developed a simple method to estimate *BDE* values for the acidic H–A bonds (O–H, S–H, N–H and C–H) in several hundred weak acids by the combination of equilibrium acidities (pK_{HA}) with the oxidation potentials of the corresponding conjugate anions, $E_{ox}(A^-)$, both measured in dimethyl sulfoxide (DMSO) solution.[2,3] Even though most of the oxidation potentials of the conjugate anions determined by conventional cyclic voltammetry are irreversible, and the constant *C* in the equation

$$BDE = 1{\cdot}37pK_{HA} + 23{\cdot}1E_{ox}(A^-) + C \qquad (2)$$

is empirical, the *BDE* values obtained by equation (2) for a variety of acids have been shown to be in remarkably good agreement [2 kcal mol^{-1} (1 kcal = 4·184 kJ)] with the best available gas-phase values[3] (henceforth, kcal mol^{-1} will be abbreviated as kcal). The empirical constant *C*, which is the sum of the free energy and entropy of the hydrogen atom, is equal to 73·3 kcal when the oxidation potentials of the conjugate anions are referenced to the ferrocenium–ferrocene (Fc^+–Fc) couple.

In this work we extended these studies to obtain acidities and *BDE*s of a number of malononitriles, 2-substituted dialkyl malonates and related compounds.

RESULTS AND DISCUSSION

Effects on acidities and *BDE*s of structural changes on malononitrile, acetonitrile, ethyl acetate and ethyl *α*-cyanoacetate

The effects of the structural changes to be considered are summarized in Table 1. The data show that substitution of a phenyl group at the acidic site of malononitrile increases the acidity by 7·1 pK_{HA} units (9·7 kcal), and lowers the *BDE* by about 13 kcal. By comparison, phenyl substitution into acetonitrile increases the acidity by 9·6 pK_{HA} units (13·1 kcal) and also lowers the *BDE*

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Table 1. Equilibrium acidities in DMSO and *BDE*s of malononitriles, acetonitriles and related carboxylic esters

Acid	pK_{HA}[d]	ΔpK_{HA}[e]	$E_{ox}(A^-)$[f]	*BDE*[g]	*ΔBDE*
$CH_2(CN)_2$	11·0	(0·0)	0·063	90	(0·0)
$C_6H_5CH(CN)_2$	4·23	7·1	−0·083	77·1	13
$C_6H_5CH(CN)_2$	4·23	(0·0)	−0·083	77·1	(0·0)
m-$ClC_6H_4CH(CN)_2$	2·66	1·6	−0·086	78·0	−0·9
p-$ClC_6H_4CH(CN)_2$	3·14	1·1	−0·014	77·3	−0·2
p-$MeC_6H_4CH(CN)_2$	4·85	−0·6	−0·154	76·5	0·60
p-$MeOC_6H_4CH(CN)_2$	5·7	−1·5	−0·259	75·1	2·0
CH_3CN[a]	31·3	(0·0)	−0·960	94	(0·0)
$C_6H_5CH_2CN$[a]	21·9	9·6	−0·909	81·1	13
CH_3CO_2Et[b]	~29	(0·0)		~95	(0·0)
$CH_2(CO_2Et)_2$	16·4	12·8	−0·022	95	0
$C_6H_5CH_2CO_2Et$[c]	22·6	6·6	−0·879	84	11
$CNCH_2CO_2Et$	13·1	(0·0)	0·034	92	(0·0)
$CNCH(C_6H_5)CO_2Et$	8·0	5·4	−0·186	80	12

[a] Ref. 4.
[b] Estimated; Ref. 12.
[c] Data of J. A. Harrelson, Jr.
[d] Usually measured against two or more indicators by the overlapping indicator method.[17]
[e] pK_{HA}(parent) − pK_{HA}(derivative), statistically corrected for the number of acidic hydrogen atoms.
[f] Referenced to the Fc–Fc$^+$ couple (0·875 V on our instrument[3]).
[g] In kcal mol^{-1}, estimated by equation (2).

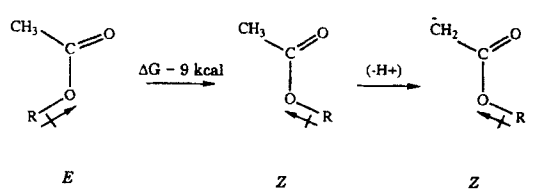
by 13 kcal. Substitution of *m*-Cl and *p*-Cl into the benzene ring of phenylmalononitrile increases the acidity by 1·6 and 1·1 pK_{HA} units, respectively, whereas *p*-Me and *p*-MeO groups decrease the acidity by 0·6 and 1·5 pK_{HA} units, respectively. These effects are similar to those observed for comparable substitutions into the benzene ring of phenylacetonitrile,[4] but only about half as large, owing to the (expected) levelling effect in the stronger acid. The *m*-Cl and *p*-Cl substituents cause small increases in *BDE*s for the malononitriles, and the *p*-Me and *p*-MeO donors cause small *BDE* decreases. Similar effects are observed for these substituents in phenylacetonitriles.[4]

The effect of introducing a phenyl group at the acidic site of ethyl acetate is to increase the pK_{HA} by *ca* 6·6 pK_{HA} units (9·0 kcal), an effect smaller by 4·1 kcal than that for $PhCH_2CN$. The difference can be attributed to steric inhibition of solvation in the anion derived from ethyl phenylacetate. The effect of phenyl substitution into ethyl α-cyanoacetate is also smaller ($\Delta pK_{HA} = 5·4$), partly owing to a leveling effect, but steric inhibition of solvation in the anion is also probably a factor. Note also that the effect on the acidity of introducing a second CO_2Et moiety into ethyl acetate is only 12·8 pK_{HA} units compared with 20·5 pK_{HA} units on introducing a second CN group into acetonitrile. On the other hand, in the corresponding radicals solvation is not a factor in determining their stabilities and the effects of introducing a phenyl group are remarkably constant for $CH_2(CN)_2$, CH_3CN, $CNCH_2CO_2Et$ and CH_3CO_2Et, i.e. 12 ± 1 kcal (Table 1).

Conformational effects must also be considered in analyzing the acidities of esters. For the anion derived from methyl acetate theoretical calculations indicate that the *Z* conformer is more stable than the *E* conformer by about 9 kcal[5] (Scheme 1). The *E* conformer, wherein the dipoles complement one another, is less stable but more acidic as a consequence. Conformational effects in dialkyl malonate ions play a key role in deciding the effects of structural changes on their acidities, as will be brought out in the next section.

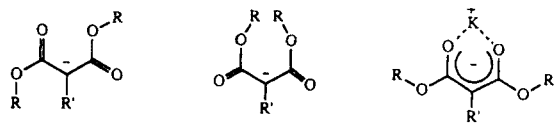
Conformational and alkyl effects on stabilities of dialkyl malonate ions and radicals

The *S*, *W* and *U* conformers of dialkyl malonate anions are shown in Scheme 2. Each of these conformers can exist in *E,Z*, *E,E* or *Z,Z* forms (the *Z* form is that where the R group is on the side of the C=O moiety rather than the CH_3 moiety). When deprotonation of the dialkyl malonate is effected in DMSO solution using the $CH_3S(=O)CH_2^-K^+$ base, the dialkyl malonate ions are usually in the *Z,Z*(*U*) conformation because they are chelated by the K^+ ion, as shown in Scheme 2



E *Z* *Z*

Scheme 1



E,Z(S) *E,E(W)* *Z,Z(U)*

Scheme 2

($\log K_{as} = 2{\cdot}31$[6]). Note that in the *Z,Z(U)* conformation the R–O dipoles are oriented so as to oppose the C=O dipoles, a stabilizing factor. Changing R from Me to Et in the ester functions causes no appreciable change in $\log K_{as}$,[7] but in the present study we have found that a change in R to *t*-Bu eliminates ion pairing, even with Li^+, probably because steric repulsions between the *tert*-butyl groups and the oxygen atoms destabilize the chelate structure. The pK_{HA} values increase progressively as R is changed from Me (15·9) to Et (16·37) to *t*-Bu (18·4) (Table 2), at least partly because of progressive increases in the steric hindrance to solvation of the anion. Chelation is absent in the corresponding radicals, of course,and they, and the parent dialkyl malonates, are free to adopt the most stable conformation available. As a consequence, the *BDE*s remain constant as R is changed from Me to Et to *t*-Bu (95·4 ± 0·2 kcal) (Table 2).

Introducing a methyl group into the 2-position of dimethyl malonate causes a 1·8 pK_{HA} unit (2·5 kcal) decrease in acidity, statistically corrected, and a comparable decrease occurs on introducing a 2-methyl group into diethyl malonate (Table 2). The $\log K_{as}$ values decrease only slightly for these structural changes.[7] These effects, which are similar to the effects of 2-methyl substitutions into $CH_2(CN)_2$ (1·9 kcal) or $CH_2(SO_2Et)_2$ (2·7 kcal), are probably caused by increased steric hindrance to solvation in the corresponding anions. There is a sharp increase in ΔpK_{HA} to 4·2 pK_{HA} units (5·7 kcal) as the 2-alkyl group is changed from *i*-Pr to *t*-Bu (Table 2). This sudden large increase as essentially all access to solvation is cut off is typical of a steric effect.

The effects of changing the 2-alkyl group in $RCH(CO_2Et)_2$ on ΔBDEs differs from that on anions, as expected, since the corresponding radicals are not chelated. Methyl substitution decreases the *BDE* by about 4·5 kcal for $MeCH(CO_2Et)_2$ vs $CH_2(CO_2Et)_2$ or $MeCH(CO_2Me)_2$ vs $CH_2(CO_2Me)_2$. α-Methyl substitution on carbon-centered radicals derived from hydrocarbons,[1d] ketones[8] or nitroalkanes[9] have similar effects, and the *BDE* of $MeCH(CN)CO_2$-*t*-Bu is 5·2 kcal lower than that of $CH_2(CN)CO_2$-*t*-Bu (Table 2). In the series $RCH(CO_2Et)_2$ the ΔBDEs decrease progressively in the order R = Me (4·4) > Et (3·7) > *i*-Pr (2·7) > *t*-Bu (0·8) kcal, which is consistent with a progressive decrease in $H{-}CR_2\dot{C}(CO_2Et)_2 \leftrightarrow H{\cdot}CR_2{=}C(CO_2Et)_2$ type hyperconjugation.

Conformational and 2-substituent effects on acidities and *BDE*s of $GCH(CO_2Et)_2$ malonates

The acidities and *BDE*s for a variety of 2-substituted diethyl malonates are compared with the acidity of $CH_2(CO_2Et)_2$ and the *BDE* of its acidic C–H bond in Table 3.

Since the structural changes from CH_3CN to $CH_2(CN)_2$, CH_3CN to $CH_2(CN)CO_2Et$ and CH_3CO_2Et to $CH_2(CO_2Et)_2$ lead to large decreases in pK_{HA}, but small increases or decreases in *BDE*s, we would expect

Table 2. Conformational and alkyl effects on the acidities and *BDE*s of dialkyl malonates and alkyl cyanoacetates

No.	Acid.	pK_a[a]	ΔpK_{HA}[d]	$E_{ox}(A^-)$[e]	*BDE*[h]	ΔBDE
1	$CH_2(CO_2Me)_2$	15·9[b]	(0·0)	0·010[f]	95·3	(0·0)
2	$CH_2(CO_2Et)_2$	16·37[c]	(0·0)	−0·022[g]	95·2	(0·0)
3	$CH_2(CO_2$-*t*-$Bu)_2$	18·4[c]	2·0	−0·124[f]	95·6	−0·4
4	$MeCH(CO_2Me)_2$	18·04[b]	1·8	−0·324[f]	90·5	4·8
5	$MeCH(CO_2Et)_2$	18·7[c]	2·0	−0·352[f]	90·8	4·4
6	$EtCH(CO_2Et)_2$	19·1[c]	2·4	−0·346[f]	91·5	3·7
7	*i*-$PrCH(CO_2Et)_2$	20·52[c]	3·8	−0·387[f]	92·5	2·5
8	*t*-$BuCH(CO_2Et)_2$	24·66[c]	8·0	−0·550[f]	94·4	0·8
9	$CNCH_2CO_2$-*t*-Bu	14·1	(0·0)	−0·024	92·1	(0·0)
10	$CNCH(Me)CO_2$-*t*-Bu	14·5	0·1	−0·273	86·9	5·2

[a] Measured in DMSO solution by the overlapping indicator method as described previously,[17] unless indicated otherwise.
[b] Ref. 7.
[c] Ref. 17.
[d] pK_{HA}(derivative) − pK_{HA}(parent), statistically corrected for the number of acidic hydrogen atoms.
[e] Measured in DMSO solution by conventional cyclic voltammetry as described previously,[3] unless indicated otherwise.
[f] Measured by J. A. Harrelson, Jr.
[g] Ref. 12.
[h] In kcal mol^{-1}, estimated using equation (2) with $C = 73{\cdot}3$ kcal mol^{-1}.

Table 3. Acidities and *BDE*s of $GCH(CO_2Et)_2$ malonates and $GCH(CN)_2$

G	pK_{HA}[d]	ΔpK_{HA}[e]	$E_{ox}(A^-)$[f]	*BDE*[g]	*ΔBDE*
$HCH(CO_2Et)_2$	16·37	(0·0)	−0·022	95·2	(0·0)
ArCO[a]	10·7	6·0	−0·249	93·7	1·5
CF_3	10·8	5·1	0·449	98·5	−3·3
$Me_3N^+NO_3^-$[b]	11·8	4·9	0·401	98·7	−3·5
t-Bu	24·7	−8·0	−0·550	94·4	0·8
$C_5H_{10}N$	19·37	−2·7	−0·793	81·5	14
Me	18·7	−2·0	−0·352	90·8	4·4
p-MeC_6H_4	16·5	0·7	−0·471	85·0	10
C_6H_5	16·3	0·37	−0·444	85·4	9·8
PhO	15·1	1·6	−0·245	88·3	6·9
F	14·5	2·2	0·648	90·7	4·5
p-$NO_2C_6H_4$	11·7	5·0	−0·134	86·2	5·0
c-$C_5H_5N^+ClO_4^-$	5·6	11	0·638	95·6	−0·40
$H_2C(CN)_2$	11·0	(0·0)	0·063	89·8	(0·0)
t-$BuCH(CN)_2$	13·2	−2·5	−0·199	86·8	3·0
$H_2NCH(CN)_2$[c]	13·7	−2·4	−0·787	73·9	16
$Me_2NCH(CN)_2$[c]	12·2	−1·2	−0·695	74·0	16

[a] 3,4,5-$(MeO)_3C_6H_2CO$.
[b] $[2\text{-}Me_3NCH(CO_2Et)_2]^+ NO_3^-$.
[c] Ref. 18.
[d] Usually measured against two indicators by the overlapping indicator titration.[17]
[e] pK_{HA}(parent) − pK_{HA}(derivative), statistically corrected for the number of acidic hydrogen atoms.
[f] Referenced to the Fc–Fc^+ couple (0·875 V on our instrument).
[g] In kcal mol^{-1}, estimated by equation (2)

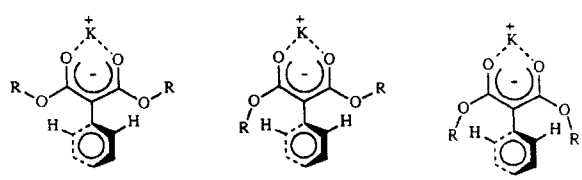
similar, but smaller (because of leveling) effects on introducing an electron-withdrawing group into the 2-position of diethyl malonates. This expectation was realized for 2-(3,4,5-$(MeO)_3C_6H_2$)CO, 2-CF_3 and 2-Me_3N^+ acceptor groups, for which the ΔpK_{HA} values, relative to $CH_2(CO_2Et)_2$, are 6·0, 5·9 and 4·9 pK_{HA} units (statistically corrected), respectively, and the *ΔBDE* values are 1·5, −3·2 and −3·5 kcal, respectively (Table 3).

On the other hand, we would expect the introduction of donor groups into the 2-position of $CH_2(CO_2Et)_2$ to lead to relatively small increases or decreases in pK_{HA} values, but (usually) decreases in *BDE*s that will vary from small to large, depending on the nature of donor and its ability to achieve effective overlap with the orbital at C-2 bearing the odd electron. The acidifying effects (ΔpK_{HA} values) were found to be *c*-$C_5H_{10}N$ (−2·7) < *p*-MeC_6H_4 (0·2) < C_6H_5 (0·4) < PhO (1·6) < F (2·2) < *p*-$NO_2C_6H_4$ (4·4) < *c*-$C_5H_5N^+$ (11) in pK_{HA} units (Table 3). The decrease in acidity caused by the piperidino group, *c*-$C_5H_{10}N$, is not surprising since four-electron repulsions exist between the carbanion site and the lone pair on nitrogen in the anion and the steric inhibition of solvation by the piperidino group may also be a factor. The failure of the 2-C_6H_5 or 2-*p*-MeC_6H_4 groups to increase the acidity is at first sight surprising, however, particularly in view of the 6·6 pK_{HA} unit (9 kcal) increase in acidity caused by the substitution of a phenyl group at the acidic site of ethyl acetate (Table 1). Clearly the *Z,Z(U)* confirmation of the $^-C(CO_2Et)_2$ moiety in the diethyl phenylmalonate anion must restrict the orientation of the phenyl group to a position orthogonal to the carbanion p-orbital (Scheme 3). This must be true also for the diethyl *p*-methylphenylmalonate anion, where the ΔpK_{HA} is also near zero, and for the diethyl *p*-nitrophenylmalonate ion, where ΔpK_{HA} is 5·0. In the latter the field/inductive effect of the *p*-nitro group is responsible for the increase in acidity. (The acidifying effect in *p*-nitrophenylacetonitrile, where the resonance effect of the *p*-nitro group and also the field/inductive effect are operative, is $\Delta pK_{HA} = 9{\cdot}6\ pK_{HA}$ units.[4])

An examination of scalar molecular models of diethyl phenylmalonate anions shows that there is steric repulsion between the *ortho*-hydrogen atoms of the benzene ring and the oxygen atoms of the alkoxyl groups in the *Z,Z(U)* conformer, and that the repulsive steric interactions become progressively worse in the *E,Z(U)* and *E,E(U)* conformations.

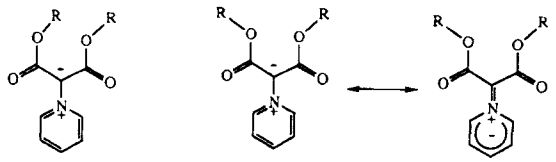
The rationalization of the failure of α-phenyl or α-*p*-methylphenyl groups to increase the acidity of diethyl malonate just given requires that the corresponding malonate anions be chelated by K^+ ion. The effect of ion pairing with potassium ion was therefore checked in pK_{HA} measurements using 9-phenylthiofluorene as the indicator. For diethyl 2-phenylmalonate the pK_{HA} uncorrected for ion pairing was found to be 16·42 and the pK_{HA} corrected for ion pairing was found to be 16·64. The calculated $K_{as} = 6{\cdot}07 \pm 1{\cdot}2 \times 10^2$ or $\log K_{as} = 2{\cdot}78$ compared with $\log K_{as} = 2{\cdot}31$ reported for the diethyl malonate ion.[6] For diethyl 2-*p*-methylphenylmalonate ion, $\log K_{as}$ with K^+ ion was found by a similar experiment to be 2·42.

The 11 ΔpK_{HA} unit increase in acidity caused by the 2-pyridinium group contrasts sharply with the negligible acidifying effect of the 2-phenyl group. The positive charge on the pyridinium group on nitrogen counteracts the adjacent negative charge in the anion, and apparently negates chelation. The ylide is therefore free to adopt a conformation where overlap is feasible, such as the *E,Z(W)* or the *Z,Z(W)* conformation (Scheme 4). The 11 pK_{HA} unit (15 kcal) increase in acidity is 3 pK_{HA}



Z,Z(U) *E,Z(U)* *E,E(U)*

Scheme 3



E,Z(W) *Z,Z(W)*

Scheme 4

units less than observed for $PhCOCH_2^+NC_5H_5Br^-$,[10] and 5 pK_{HA} units greater than that for the Me_3N^+ group in $[Me_3NCH(CO_2Et)_2]^+NO_3^-$ (Table 3). The greater acidifying effect of the pyridinium group than the Me_3N^+ group is due to the delocalizing effect of the aromatic ring[10] (Scheme 4).

The ΔBDEs for diethyl 2-substituted malonates were found to be *c*-$C_5H_{10}N$ (14) > *p*-MeC_6H_4 (10) > C_6H_5 (9·8) > *p*-$NO_2C_6H_4$ (9) > PhO (6·9) > F (4·5) > Me (4·4) > 3,4,5-$(MeO)_3C_6H_2CO$ (1·5) > H (0·0) > *c*-$C_5H_5N^+$ (−0·4) > CF_3 (−3·3) > Me_3N^+ (−3·5 kcal). The substantial weakening of the acidic C–H bond by the piperidino group is expected since extensive weakening of acidic C–H bonds by α-amino groups has been observed in other instances. For example, the *BDE* of the acidic C–H bond in $PhCOCH_2NMe_2$ is 21 kcal lower than that in $PhCOCH_3$.[11] The 10 kcal weakening of acidic C–H bonds in 2-C_6H_5- and 2-*p*-$MeC_6H_4CH(CO_2Et)_2$ results because the π-orbitals of the phenyl ring can achieve coplanarity with the p-orbital holding the odd electron in the corresponding radical by using a conformation such as the *Z,Z(W)* conformation shown in Scheme 4. The 6·9 kcal bond-weakening effect of PhO is normal, but the 4·5 kcal bond-weakening effect for a fluorine atom is unexpectedly large compared with 3 kcal for fluorine in $H-CH_2F$.[1d] The presence of an α-CF_3 group generally strengthens acidic C–H bonds,[11] as observed for the 3·3 kcal effect in $CF_3CH(CO_2Et)_2$. The 1·5 kcal stabilizing effect of the 3,4,5-$(MeO)_3C_6H_2CO$ group is consistent with the small effects observed for introducing a second α-carbonyl group adjacent to a O=C–Ċ-type radical.[12] The failure of the $C_5H_5N^+$ group to exert a bond-weakening effect is contrary to its behavior in $PhCOCH_2^+NC_5H_5$, $C_5H_5N^+CH_2CN$ and $C_5H_5N^+CH_2CO_2Et$ substrates, where 5·9, 5·4 and 5·0 kcal bond-weakening effects were observed, respectively.[10] This result suggests that delocalization of the odd electron in the radical cannot be very important, despite the evidence for delocalization of the negative charge in the $C_5H_5N^+{}^-C(CO_2Et)_2$ anion (Scheme 4). This behavior is not unprecedented, however, since there is evidence to indicate that solvation forces on anions can enforce conformational changes in congested systems that will permit stabilization by delocalization, whereas radicals cannot. For example, the *p*-NO_2 group in *p*-$NO_2C_6H_4CHPh_2$ increases the acidity by 19 kcal apparently by stabilizing the corresponding carbanion, but has little or no effect on the *BDE*.[13] Also, the Ph_3P^+ group when present in $Ph_3P^+CH_2CO_2Et$ and similar substrates exerts an enormous acidifying effect (by polarizability) but has little or no effect on the *BDE*.[14] Note that the $C_5H_5N^+$ group does not strengthen the acidic C–H bond in diethyl malonate, as does the Me_3N^+ group (Table 3), which suggests that it does have a small delocalizing effect on the radical.

CONCLUSIONS

The effects on acidities and *BDE*s of the acidic C–H bonds of introducing a variety of groups into the 2-position of diethyl malonate have been examined. The most intriguing results were (a) the 11 kcal acid-weakening effect of the 2-*tert*-butyl group, attributed to steric hindrance to anion solvation, which was accompanied by only a 0·8 kcal homolytic bond-weakening effect, (b) a meager 0·5 kcal acid-strengthening effect of a 2-phenyl group, attributed to a chelating effect of K^+ on the anion, which confines the phenyl group to an orthogonal position relative to the chelate ion plane; this was accompanied by a 9·8 kcal homolytic bond-weakening effect, the unchelated radical being able to adopt a conformation favorable for delocalization of the odd electron, and (c) a 15 kcal acid-strengthening effect of a 2-pyridinium group attributed to negating the chelating effect and enforcing a favorable conformation for overlap in the ylide, accompanied by a homolytic bond-weakening effect only large enough to offset the bond-strengthening effect of the positive charge.

EXPERIMENTAL

The dialkyl malonates, malononitriles and alkyl cyanoacetates, except for those for which the preparations are described below, were commercial samples or gifts from other laboratories.

Diethyl 2-phenoxymalonate was prepared following a literature method;[15] m.p. 53–54 °C; lit. m.p. 53–54 °C; ^1H NMR ($CDCl_3$), δ 1·21 (t, 6H), 4·18 (q, 4H), 5·05 (s, 1H) and 6·95 (m, 5H).

Diethyl 2-piperidinomalonate was prepared as follows. To 3·41 g (0·04 mol) of piperidine (Aldrich) in 25 ml of dry diethyl ether was added dropwise 4·78 g of diethyl 2-bromomalonate (Aldrich) in 10 ml of dry diethyl ether and the mixture was stirred at room temperature for 24 h. The white precipitate (piperidinium bromide, *ca* 3 g) was removed by filtration. The residual crude product was purified by flash chromatography with a mixture of hexane and ethyl acetate (10 : 1, vv) as eluent. The pure compound was a light-yellow liquid.

^{1}H NMR ($CDCl_3$), δ 1·30 (t, 6H), 1·4–3·0 (m, 10H), 4·0 (s, 1H) and 4·18 (q, 4H). Analysis: calculated for $C_{12}H_{21}NO_4$, C 59·20, H 8·78, N 5·76; found, C 59·41, H 8·77, N 5·53%. MS: m/z 243 ($M^{+\cdot}$, 25%); 170 (100%).

Diethyl 2-(*p*-nitrophenyl)malonate was prepared following the literature method to synthesize ethyl 2-cyano-2-(*p*-nitrophenyl)acetate.[16] To 4·49 g (0·04 mol) of potassium *tert*-butoxide suspended in 100 ml of dry DMSO was added dropwise 6·41 g (0·04 mol) of diethyl malonate (Aldrich) in 15 ml of dry DMSO and the mixture was stirred at room temperature for 10 min. Then 4·04 g (0·02 mol) of *p*-nitrobromobenzene in 15 ml of DMSO was added dropwise to the resulting solution and the mixture was heated in the range 70–80 °C for 4 h. The cooled mixture was diluted with 2 M HCl solution and extracted with diethyl ether. The organic layer was dried with $MgSO_4$ overnight. Removal of the ether and diethyl malonate under reduced pressure gave a solid. Recrystallization from ethanol and hexane gave pure crystals, m.p. 56–57 °C. ^{1}H NMR ($CDCl_3$), δ 1·2–1·4 (m, 6H), 4·15–4·30 (m, 4H), 4·72 (s, 1H),7·62 (d, 2H) and 8·25 (d, 2H).

The equilibrium acidities of the weak acids in DMSO were measured by the overlapping indicator titration method as described previously.[17] The log K_{as} constants for ion pairing with potassium ion were determined as described previously.[6] The oxidation potentials of the conjugate anions were measured by conventional cyclic voltammetry as described previously.[3] The working electrode consisted of a 1·5 mm diameter platinum disc embedded in a cobalt glass seal. It was polished with a 0·05 μm Fisher polishing aluminum or cleaned with an ultrasonic instrument and rinsed with ethanol before each run. The counter electrode was platinum wire (BAS). The reference electrode was Ag/AgI, but the reported oxidation potentials were all referenced to the ferrocenium–ferrocene couple ($E_{1/2}$ = 0·875 V vs the Ag/AgI couple in our instrument[3]).

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