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Is Resonance Important in Determining the Acidities of Weak Acids or the Homolytic Bond Dissociation Enthalpies (BDEs) of Their Acidic H–A Bonds?

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Abstract: Equilibrium acidities in DMSO for benzoic acid, the enol of 1,3-cyclohexadione, and tropolone have been measured, and the BDEs for their O–H bonds have been estimated by combining the pK_{HA} data with electrochemical data. The acidity data are not in accord with the theory that the polarity of the carbonyl group is the *dominant* factor in making the CO_2H function acidic. Equilibrium acidities in DMSO for the α-C–H bonds in nine nitroalkanes have been measured and the BDEs of their acidic C–H bonds have been estimated in a similar fashion. The radical stabilization energy (RSE) of the $NO_2CH_2^•$ radical is estimated to be 7.6 kcal/mol, relative to the $CH_3^•$ radical, based on the relative BDEs of the $H–CH_2NO_2$ and $H–CH_3$ bonds. The finding of sizable RSEs for radicals of the type $GCH_2^•$, where G is an electron-withdrawing group, such as NO_2, CN, SO_2R, or O═CR, suggests that they behave as π radicals capable of delocalization of the odd electron to heteroatoms, whereas ESR data indicate that they are essentially σ radicals with electron density concentrated primarily on carbon.

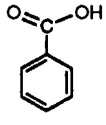
For many years resonance in carboxylate ions, RCO_2^-, was accepted as the prime reason for the greater acidity of carboxylic acids than alcohols. But in 1986 theoretical calculations were presented that suggested that the polarity of the carbonyl group in RCO_2H, rather than resonance in the RCO_2^- anion, was the major factor contributing to the acidity of carboxylic acids.[1,2] Similar theoretical calculations indicated that resonance was also unimportant in carboxamides, and that here too the properties associated with resonance could be explained by electrostatic effects.[3] The supposed unimportance of resonance in carboxylate ions and carboxamides was challenged on several grounds, however. Estimates of energies, based on thermodynamic cycles, indicated that the low energy content for the acetate ion, rather than the high energy content of the undissociated acid, was the *dominant* acidifying factor.[4] Also, calculations indicated that for formic acid vinylogues, $HCO(CH{=}CH)_nOH$, the deprotonation energies decreased as *n* increased, which is opposite to the effect expected if electrostatic effects are the principal acidifying factor controlling carboxylic acid acidities.[5] Finally, Perrin has criticized the calculations[1,2] themselves and has concluded that the atomic charges used were unreliable "especially as evidence against resonance in carboxylate anions and related species,"[6a] but several authors have discounted this criticism.[6b,c] (The most recent calculations indicate that carboxamides are stabilized by about 15 kcal/mol by delocalization effects.[3c])

ESR experiments have for some time discounted the importance of resonance in carbon-centered •C–G-type radicals, where G is CO_2R, CN, or NO_2.[7-9] Theoretical calculations have also failed to show the expected equalization of the C–O bonds in the formyloxyl radical, $HCO_2^•$, which has led to the conclusion that resonance in carboxyl radicals, $RCO_2^•$, is less important than that in the allyl radical.[10]

In this paper we will present data pertinent to (a) the importance of resonance in carboxylate ions and (b) the importance of resonance in carboxyl radicals and in carbon-centered radicals adjacent to electron-withdrawing groups such as C═O, CO_2R, CN, and particularly NO_2.

Results and Discussion

Acidities and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic H–A Bonds in Benzoic Acid, 1,3-Cyclohexadione, and Tropolone. The equilibrium acidities in DMSO of benzoic acid (**1**), 1,3-cyclohexadione (**2**), and tropolone (**3**) shown in Table 1 are nearly identical (pK_{HA} = 11.2 ± 0.2). At first sight this is surprising, but perusal of structural formulas shows that their functional groups are closely related. Thus, 1,3-cyclohexadione has been shown to exist almost entirely in the enol form **2**, and structure **2** can be considered to be a vinylogue[11] of benzoic acid (**1**) in which a CH═CH group has been interspersed between the O═C and OH moieties. Tropolone (**3**) can also be considered to be a vinylogue of **1** in which three CH═CH groups have been interspersed between the O═C and OH moieties. The electrostatic effect of the O═C group on the acidity must be much smaller in **2** than in **1** because of the presence of the two intervening



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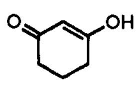

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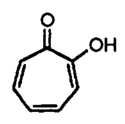

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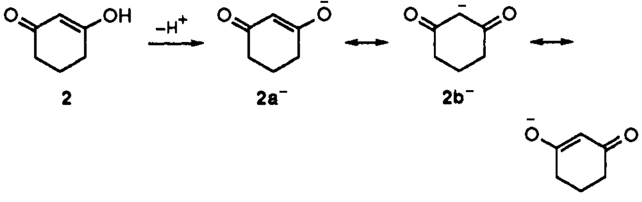
Table 1. Equilibrium Acidities in DMSO and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic HA bonds in Benzoic Acid, 1,3-Cyclohexadione, Tropolone, and Selected Ketones

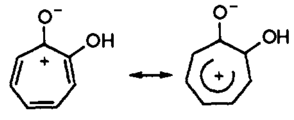
acid	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE (kcal)[c]	ΔBDE (kcal)[g]
benzoic acid	11.2	0.730	105	(0.0)
1,3-cyclohexadione	11.15	0.160	92	13
tropolone	11.37	−0.071	88	17
$MeCOCH_2$–H			93[d]	12
$PhCOCH_2$–H			93[d]	12
$(MeCO)_2CH$–H			92[e]	13
$(PhCO)_2CH$–H			92[e]	13
cyclohexanone			88[f]	17
$Me_2CHCOCHMe_2$			84[f]	21
$PhCOCHMe_2$			86[f]	19

[a] See the Experimental Section. [b] Determined by cyclic voltammetry. [c] Calculated by eq 1. [d] See the text. [e] Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448–4450. [f] Reference 14. [g] ΔBDEs can be considered to provide estimates of radical stabilization energies (RSEs) relative to that of the methyl radical.

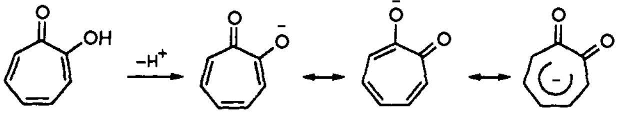
sp^2 carbon atoms, yet the acidities of **1** and **2** are the same. The nearly equal acidities must be a consequence of stabilization of the anions derived from **2** by resonance delocalization of the negative charge, for example, as shown in **2a**⁻ ↔ **2b**⁻ ↔ **2c**⁻. These results support the calculations made by Dewar and Krull on the acidities of vinylogues of formic acid, $HCO(CH{=}CH)_nOH$,[5]



results which are also not in accord with the idea that the electrostatic effect of the carbonyl group is the major factor that makes carboxylic acids more acidic than alcohols. In tropolone (**3**) the plus charge of the C^+–O^- dipole is dispersed over the whole carbon skeleton (**3a** ↔ **3b**) and should exert a much smaller effect on the acidity than it does in **1**, yet here too the acidities in DMSO are the same.



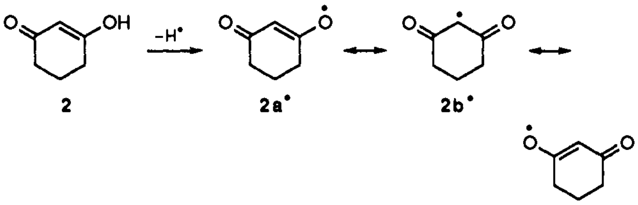
The smaller acidity enhancement by the C^+–O^- dipole in the undissociated acid is evidently offset by a stronger acidifying stabilization of the anion by delocalization of the negative charge (**3a**⁻ ↔ **3c**⁻). This resonance involves the two oxygen atoms, as well as the carbon skeleton. A progressive increase in resonance in the anions along the series **1**, **2**, and **3**



therefore offsets a progressive decrease in the C^+–O^- dipole effect in the undissociated acid.

In view of the high acidity of tropolone in DMSO, relative to that of phenol (pK_{HA} = 18; ΔpK_{HA} = 7), it is apparent that the negative charge in the tropolonide anion is highly delocalized.

The BDE data for the acidic H–A bonds of **1**, **2**, **3**, and related compounds shown in Table 1 are relevant to the question of the ability of a carbonyl group to stabilize an odd electron on an adjacent carbon atom. Removal of a hydrogen atom from the O–H group in **2** gives a radical in which the odd electron can be situated on either of two oxygen atoms or on a carbon atom, **2a**• ↔ **2b**• ↔ **2c**•.



Conclusions drawn from ESR studies have discounted the importance of resonance in •C—C=O type radicals,[7–9] the radical derived from **2**,[8] and for the corresponding open-chain $(MeCO)_2CH^\bullet$ radical.[8] For the latter radical, ESR data for the series $CH_3^\bullet$, $MeCOCH_2^\bullet$, $(MeCO)_2CH^\bullet$ have shown that the $\alpha_{CH_3}{}^{H}$ values, which are estimated to be related to empirical spin densities, "decrease only slightly from 23 to 19.3 to 18.6 gauss."[8] This led to the conclusion that delocalization of the odd electron to the oxygen atom of the carbonyl group in the $MeCOCH_2^\bullet$ radical and the oxygen atoms in the $(MeCO)_2CH^\bullet$ radical is unimportant.[8] This conclusion was supported further by the observation that over 75% of the spin density in the tropolonyl radical was on carbon, rather than on the two oxygen atoms.[8] Differences in BDEs relative to that of the CH_3–H bond (105 kcal/mol), or the H–O bond in $PhCO_2H$ (105 kcal/mol) as reference standards, provide another way of estimating relative radical stabilization energies (RSEs).[12] (Henceforth, kcal/mol will be abbreviated as kcal.) It is possible to estimate BDEs for weak acids by combining their pK_{HA} values with the oxidation potentials of their conjugate anions, $E_{ox}(A^-)$, by using eq 1, or the like.[13]

$$\mathrm{BDE}_{HA} = 1.37\mathrm{p}K_{HA} + 23.1E_{ox}(A^-) + 73.3\ \mathrm{kcal} \qquad (1)$$

The BDEs estimated in this way have been found usually to agree with the best literature values[12d] to within ±3 kcal. For benzoic acid (or acetic acid), the BDE estimated by eq 1 is 105 ± 3 kcal, (Table 1), which agrees with the gas-phase BDEs,[12d] and with the gas-phase BDE of 104 ± 2 kcal for the O–H bond in alcohols.[12d] The good agreement between the BDEs for the O–H bonds in carboxylic acids and alcohols is consistent with the conclusion that resonance is unimportant in carboxyl radicals, $RCO_2^\bullet$. The BDE of 92 kcal for the O–H bond in enol **2** is 13 kcal lower than that in benzoic acid (Table 1). This is *not* in agreement with the conclusion that resonance in the radical derived from **2** is unimportant.[7–9] The BDE of 93 kcal estimated for acetone or acetophenone is also not in agreement with the conclusion that resonance in carbon-centered radicals adjacent to carbonyl groups is unimportant (Table 1). (The BDE for the $MeCOCH_2$–H bond of 93 kcal is an average of the BDE of 94 kcal estimated by eq 1[14] and a BDE of 92 kcal determined recently in the gas phase.[15]) These results show that the BDE values for the acidic C–H bonds in $MeCOCH_2$–H and $PhCOCH_2$–H are 12 kcal lower than that for methane, suggesting that the odd

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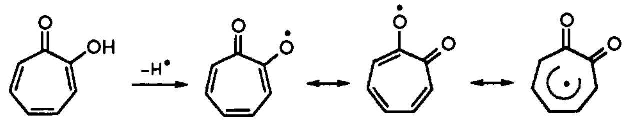
electrons in the corresponding radicals are strongly delocalized to the carbonyl group (RSE = 12 kcal). The data obtained for numerous α-substituted acetones and acetophenones supports this conclusion.[14] On the other hand, the presence of a second MeCO or PhCO group, as in $(MeCO)_2CH_2$ or $(PhCO)_2CH_2$, provides little or no *additional* stabilization of the radical (Table 1). The BDE data, therefore, indicate that the RSEs of the radicals in the $CH_3^\bullet$, $MeCOCH_2^\bullet$, and $(MeCO)_2CH^\bullet$ series are (0.0), 12, and 13 kcal, respectively. The ESR $a_{CH_3}{}^{H}$ values appear to be consistent with this order since the difference between the $CH_3^\bullet$ and $MeCOCH_2^\bullet$ radicals is 3.7 G, whereas that between the $MeCOCH_2^\bullet$ and $(MeCO)_2CH^\bullet$ radicals is only 0.7 G.[8] We note in this respect that the ΔBDE of 13 kcal between the $CH_3^\bullet$ and $(MeCO)_2CH^\bullet$ radicals is comparable to the ΔBDE between the $PhCO_2^\bullet$ radical and the 1,3-cyclohexadionyl radical (Table 1).

An ESR analysis of the tropolonyl radical shows that over 75% of the spin density is located on the carbon skeleton, indicating that delocalization of the odd electron between the two equivalent oxygen atoms $\mathbf{3a}^\bullet \leftrightarrow \mathbf{3b}^\bullet$ is unimportant. This is consistent with the ESR and BDE data for the radicals derived from **2**. On the other hand, the ΔBDE of 17 kcal for the O–H bond in tropolone relative to that in benzoic acid indicates that delocalization of the odd electron to the carbon skeleton, as depicted by $\mathbf{3c}^\bullet$, provides strong resonance stabilization.



3 $\mathbf{3a}^\bullet$ $\mathbf{3b}^\bullet$ $\mathbf{3c}^\bullet$

A detailed study of the ^{13}C and ^{17}O hyperfine splitting constants of the 2-cyclohexanonyl radical by ESR spectroscopy led to the conclusion that this radical is approximately 30% allylic with a small (15%) spin density on oxygen.[9a] A similar ESR study of the $EtCOCH_2^\bullet$ radical estimated that 84% of the spin density was on carbon.[9b] It was concluded that delocalization of this magnitude with the unusually high barriers to rotation around the C-1–C-2 bond in the acetonyl and 1,1-dimethylacetonyl radicals (9.4 and >10 kcal, respectively) was reasonable.[9a] Our estimates using eq 1 place the BDE of the acidic C–H bond for cyclohexanone at 88 kcal, that for $PhCOCHMe_2$ at 86 kcal, and that for $Me_2CHCOCHMe_2$ at 84 kcal. (The latter two are models for $Me_2CHCOCH_3$.) The corresponding RSEs are 17, 19, and 21 kcal, respectively, indicating extensive delocalization of the odd electron.

Effects of CN, CO_2Et, and Related Functions on RSEs of Carbon-Centered Radicals. ESR data for radicals of the type $^\bullet C{-}C{=}O$, $^\bullet C{-}CN$, or $^\bullet C{-}CO_2R$ have been shown to have spin densities almost completely on the α-carbon atom,[7–9] which has been interpreted to mean that delocalization of the odd electron to the carbonyl, cyano, nitro, or ester function is unimportant.[8] On the other hand, the BDE of $H{-}CH_2CN$ is reported in the McMillen–Golden 1982 review to be 93 kcal.[12d] More recent measurements give a value of 95.5 kcal in the gas phase and 94.5 in aqueous solution.[16] These data indicate a ΔBDE (or RSE) of about 11 kcal for the CN group, relative to 105 kcal for $H{-}CH_3$. Less information is available for the BDE of the α-H–C bond in esters. A BDE of 98.8 ± 3.7 kcal has been estimated from a gas-phase thermodynamic cycle.[17] The acidities of CH_3CO_2R esters and the stabilities of the corresponding conjugate anions are too low to make an estimate using eq 1. An extrapolation of the BDE for the acidic C–H bond in CH_3CO_2Et can be made from the BDE of 84 kcal for the acidic C–H bond in $PhCH_2CO_2Et$, however, if we assume that the Ph effect on the BDE of the acidic C–H bond in CH_3CO_2Et will be the same as the Ph effect on the BDE of the C–H bond in CH_3CN (94–82 = 12 kcal). This extrapolation gives a BDE of 96 kcal for the acidic C–H bond in CH_3CO_2Et. Ph_3P substitution for an acidic hydrogen atom in CH_3CN gives a cation, $Ph_3P^+CH_2CN$, where the BDE of the acidic C–H bond is 94.5 kcal, i.e., essentially the same as that for CH_3CN. This is true also for the BDE of the acidic C–H bond in $Ph_3P^+CH_2Ph$ (BDE estimated, 87.5 kcal versus 88 kcal for $H{-}CH_2Ph$). For $Ph_3P^+CH_2CO_2Et$ the BDE of the acidic C–H bond is estimated to be 97.7 kcal.[18] The average of these three estimates is BDE = 97.5 kcal for the acidic C–H bond in CH_3CO_2Et, but this seems to be on the high side. If this value is accepted, this places the $H{-}CH_2CO_2Et$ BDE about 7.5 kcal below the BDE of the C–H bond in methane. The ΔBDEs, for $H{-}C{-}C{=}O$, $H{-}C{-}C{\equiv}N$, and $HC{-}CO_2Et$, are then 12, 11, and 7.5 kcal, respectively, indicating that there is sizable delocalization of the odd electrons in the corresponding radicals, $^\bullet C{-}C{=}O$, $^\bullet C{-}C{\equiv}N$, and $^\bullet C{-}CO_2Et$, to these electron-withdrawing functions. The ΔBDE for $PhSO_2CH_2{-}H$ is estimated to be 6 kcal relative to $CH_3{-}H$.[19] For the related radical, $EtSO_2CH_2^\bullet$, the ESR data indicate that the spin density on carbon is 100%.[9b] From these results we see the ΔBDE data consistently indicate much greater delocalization from carbon in carbon-centered radicals to electron-drawing groups than is indicated by ESR spin densities. This appears to be true for donor groups as well. For example, ΔBDEs vs $CH_3{-}H$ in $GCH_2{-}H$ methanes where G is Me, MeO, RS, and PhS indicate RSEs of 7, 12, 12, and 12 kcal, respectively,[19] whereas ESR data indicate that the percent of spin density on carbon in $MeCH_2^\bullet$, $EtOCH_2^\bullet$, $EtSCH_2^\bullet$, and $PhSCH_2^\bullet$ radicals is 93, 81, 74, and 77%, respectively.[9b] Note also that a plethora of ΔBDE data show that R_2N is a far better donor than RO,[19] whereas ESR data suggest that a $MeO{-}C^\bullet{-}CO_2Me$ ("captodative") radical is more stable than a corresponding $H_2N{-}C^\bullet{-}CO_2Me$ radical.[20] It should be noted in this regard that Rüchardt and co-workers have pointed out that no clear relationship between spin delocalization, as detected by ESR, and thermochemical stabilization energies has been formulated.[21] Substitution of a second electron-withdrawing group of the same kind at the acidic site increases the ΔBDE by only 1, 4, and 2.5 kcal for C=O, CN, and CO_2Et functions, respectively.[22] The smaller ΔBDE effects for a second electron-withdrawing function, despite the extended conjugation provided thereby, may be a consequence of destabilizing the corresponding radical by electron withdrawal.[23]

Acidities and BDEs of Nitroalkanes. The pK_{HA} and BDE values for nitromethane and a number of its derivatives are shown in Table 2. Examination of Table 2 shows that nitromethane has a pK_{HA} of 17.2 in DMSO solution. Its acidity is estimated to be about 39 pK_{HA} units (53 kcal) greater than that of methane in DMSO. In the gas phase nitromethane is about 59 kcal more acidic than methane.[17] Nitromethane therefore has a high intrinsic acidity that is not greatly enhanced by solvation in DMSO. As a consequence its acidity is not altered much by changes in the carbon skeletons of its simple alkyl derivatives. The average pK_{HA} for the first six entries in Table 2, CH_3NO_2, $MeCH_2NO_2$, Me_2CHNO_2, $c\text{-}C_3H_5CH_2NO_2$, $c\text{-}C_5H_9NO_2$, and $c\text{-}C_6H_{11}NO_2$, is 16.7 ± 1.2 pK_{HA} units. On the other hand, the pK_{HA} values in 50% MeOH–H_2O for CH_3NO_2, $MeCH_2NO_2$,

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Table 2. Acidities and BDEs of the C–H Bonds in Nitroalkanes in DMSO

nitroalkane	pK_{HA}[a]	$E_{OX}(A^-)$[b]	BDE (kcal)[c]
CH_3NO_2	17.2	0.024	97.4
$MeCH_2NO_2$	16.7	–0.207	91.4
Me_2CHNO_2	16.8	–0.413	86.8
$c\text{-}C_3H_5CH_2NO_2$	16.5	–0.327	88.4
$c\text{-}C_5H_9NO_2$	16.0	–0.364	86.8
$c\text{-}C_6H_{11}NO_2$	17.90	–0.399	88.6
$PhCH_2NO_2$	12.2	–0.289	83.4
$PhSCH_2NO_2$	12.0	–0.165	86.0
$PhCH_2OCH_2NO_2$	17.1	–0.448	86.1

[a] Standard deviations were all ±0.05, or less. The indicators used were the following: ISFH (9-isopropylthiofluorene; pK_{InH} = 16.9) and PFH (9-phenylfluorene; pK_{InH} = 17.9) for CH_3NO_2. PSFH (9-phenylthiofluorene; pK_{InH} = 15.4) for $CH_3CH_2NO_2$. PFH and PSFH for Me_2CHNO_2. PSFH for $c\text{-}C_3H_5CH_2NO_2$ and $c\text{-}C_5H_9NO_2$. PFH for $c\text{-}C_6H_{11}NO_2$. HZFO2P (9-fluorenone 2,4-dichlorophenylhydrazone; pK_{In} = 11.98) for $PhSCH_2NO_2$. $PhSO_2FH$ (9-phenylsulfonylfluorene; pK_{InH} = 11.55) for $PhCH_2NO_2$. PFH for $PhCH_2OCH_2NO_2$. [b] Determined by cyclic voltammetry. [c] Calculated by eq 1.

Table 3. Comparison of Structural Changes on the Homolytic Bond Dissociation Enthalpies for Substituted Nitroalkanes and Acetophenones

acid[a]	BDE (kcal)[b]	ΔBDE (kcal)	acid[c]	BDE (kcal)[d]	ΔBDE (kcal)[e]
CH_3–H	105		CH_3–H	105	
CH_3NO_2	97.4	(0.0)	CH_3COPh	93	(0.0)
$MeCH_2NO_2$	91.4	6.0	$MeCH_2COPh$	88	5.0
Me_2CHNO_2	86.8	10.6	$Me_2CHCOPh$	86	7.0
$c\text{-}C_3H_5NO_2$	88.4	9.0	$c\text{-}C_3H_5COPh$		
$c\text{-}C_5H_9NO_2$	86.8	10.6	$c\text{-}C_5H_9COPh$		
$c\text{-}C_6H_{11}NO_2$	88.6	8.8	$c\text{-}C_6H_{11}COPh$	88	5.0
$PhCH_2NO_2$	83.4	14.0	$PhCH_2COPh$	82.5	10.5
$PhSCH_2NO_2$	86.0	11.4	$PhSCH_2COPh$	81.5	11.5
$BzOCH_2NO_2$	86.1	11.3	$MeOCH_2COPh$	80.5	12.5
			Me_2NCH_2COPh	72	21

[a] See Table 2 for the pK_{HA} values. [b] Taken from Table 2. [c] Data taken from ref 14. [d] Calculated using eq 1. [e] ΔBDEs can be considered to provide estimates of radical stabilization energies (RSEs) relative to that of the methyl radical[12] (see, however, ref 27).

$MeCH_2NO_2$, and Me_2CHNO_2 decrease progressively from 11.11 to 9.63 to 8.85,[24] the greater sensitivity to structural change being due to strong hydrogen bonding of water to the negatively charged oxygen atoms in the nitronate ions, $H_2C{=}NO_2^-$, $MeCH{=}NO_2^-$, and $Me_2C{=}NO_2^-$. In DMSO, solvation occurs through the positive charge on the sulfur atom in $Me_2S^+{-}O^-$, and solvation is weaker and less specific, leading to an average 6.8 pK_{HA} increase in pK_{HA}, relative to that in aqueous methanol.

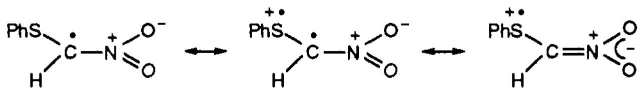
Substitution of a phenyl group for one of the hydrogen atoms of nitromethane increases the acidity by 5.2 pK_{HA} units (7.1 kcal), and a like substitution of a PhS group increases the acidity by 5.4 pK_{HA} units (7.4 kcal). These effects are similar to, but smaller than, the effects estimated for Ph and PhS substitution for an acidic hydrogen atom of CH_3CO_2Et (7.5 and 8.5 pK_{HA} units, respectively). The effect of phenyl on the acidity is much larger than that of a benzyloxy group, however, which is negligible (Table 2).

Examination of Table 2 shows that the BDE of nitromethane is 97.4 kcal, 7.6 kcal below that of methane. This ΔBDE suggests that the NO_2 group resembles the $PhSO_2$ or CO_2Et group (ΔBDEs of 6 and 7.5 kcal, respectively) in its ability to delocalize an odd electron, and that its delocalizing ability is considerably below that of MeC=O, PhC=O, and CN groups (12, 12, and 11 kcal, respectively). It seems likely that the powerful field/inductive effects of NO_2, $PhSO_2$, and CO_2Et groups may destabilize $^\bullet CH_2NO_2$ and like radicals.[23]

Effects of Structural Changes on BDEs of Nitroalkanes and Acetophenones. A comparison of structural changes on BDEs of nitroalkanes and acetophenones brings out a number of similarities.

In earlier studies, the PhC=O group has been shown to act as a strong electron acceptor when attached to a carbon-centered radical bearing donor groups. For example, the ΔBDEs for the combined donor–acceptor effects for α-substituted acetophenones bearing Ph, PhS, MeO, and Me_2N donor groups are 22.5, 23.5, 24.5, and 33 kcal, respectively, relative to CH_3–H (105 kcal) (Table 3). These effects can be used as estimates of radical stabilization energies (RSEs), i.e., donor–acceptor ("captodative") effects.[25] The donor–acceptor combined effects are nearly as large for α-Ph, α-PhS, and α-BzO nitromethanes as for the corresponding acetophenones, i.e., 21, 19, and 19 kcal, respectively. Here too they can be considered to be a consequence of extended conjugation, e.g. 4a–4c.

The effects of α-methyl substitution on the BDEs of nitromethane and acetophenone are similar to those on methane. The methyl group in $MeCH_2$–H lowers the BDE of methane by 6.9 kcal, and the two methyl groups in Me_2CH–H lower the BDE by 10 kcal.[12d] These effects are to be compared with the effects of 6 and 10.6 kcal for the substitution of one and two α-Me groups into nitromethane and 5 and 7 kcal for substitution of one and two α-Me groups into acetophenone. (More recent data for the BDEs of $MeCH_2$–H and Me_2CH–H bonds suggest smaller effects, 4.6 and 5.8 kcal, respectively.[26])



4a **4b** **4c**

Summary and Conclusions. The observation that the equilibrium acidities in DMSO solution for benzoic acid (**1**), the enol of 1,3-cyclohexadione (**2**), and tropolone (**3**) are nearly identical (pK_{HA} = 11.2 ± 0.2) shows that resonance in the carboxylate ion, and the related ions, is the *major* factor making carboxylic acids more acidic than alcohols, rather than the polar effect of the carbonyl group. The BDEs of the O–H bonds in **2** and **3** are estimated to be 13 and 17 kcal weaker, respectively, than the BDE of the O–H bond in benzoic acid (**1**), showing that there is strong delocalization of the odd electron in the corresponding radicals to carbon. The estimate that the BDE for the acidic C–H bond in acetone is weaker by 12 kcal than the C–H bond in methane (i.e., ΔBDE = 12 kcal) contradicts the conclusion from ESR data that resonance in the $MeCOCH_2^\bullet$ radical, or related ketonic radicals, is unimportant, but the estimate that ΔBDE for the C–H bond in $(MeCO)_2CH$–H is 13 kcal is in agreement with the conclusion drawn from ESR data that resonance involving the *two* oxygen atoms in the $(MeCO)_2CH^\bullet$ radical is unimportant. The ΔBDEs for GCH_2–H bonds [kcal in parentheses for the acceptors MeCO (12), PhCO (12), CN (11), CO_2Et (7.5), $PhSO_2$ (6), and NO_2 (7.6) and for the donors Me (7), EtO (12), EtS (12), and PhS (12)] contradict the conclusion drawn from ESR data that resonance in the corresponding $GCH_2^\bullet$ radicals is unimportant, if we equate these ΔBDEs with radical stabilization energies (RSEs). The RSEs for the carbon-centered radicals formed by combining the PhS and BzO donors with the NO_2 acceptor in eq 1 are almost as large as the RSEs for combining PhS and MeO donors with the PhC=O acceptor, e.g., 19 kcal for the $PhS{-}C^\bullet{-}NO_2$ radical.[27]

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Experimental Section

Materials. All compounds were checked for purity by ^{1}H NMR and melting point for solids. 1,3-Cyclohexadione, tropolone, nitromethane, nitroethane, 2-nitropropane, nitrocyclopentane, and nitrocyclohexane were commercial samples (Aldrich). Cyclopropylnitromethane was prepared by Judith A. Hautala.[28] Phenylnitromethane was a gift from James R. Keeffe. Phenylthionitromethane and benzoxynitromethane were gifts from A. G. M. Barrett.[29]

Cyclic Voltammetry. Oxidation potentials of the conjugate anions were measured in DMSO using a three-electrode system consisting of a platinum disc working electrode, a platinum wire auxiliary electrode, and a Ag/AgI in DMSO reference electrode. Tetraethylammonium tetrafluoroborate (0.1 M) was used as the electrolyte. Two drops of a 150–200 mmol solution of CH_3SOCH_2K in DMSO were added to a 5–10 mmol solution of the weak acid in DMSO and a cyclic voltammogram was recorded at a scan rate of 100 mV/s. This procedure was repeated at least twice to make sure that there was a significant increase in the anodic peak current as the anion concentration increased. The oxidation potentials were reported with reference to the Fc/Fc^+ couple measured under similar conditions.

The cyclic voltammograms of the anions derived from the nitroalkanes have wave widths in the normal region of 50–70 mV. A second strong oxidation peak of unknown origin is usually also observed. In acetonitrile the potentials of the first peaks are about 20 mV less positive and the second oxidation peak is much weaker.

Equilibrium acidities were measured in DMSO by the overlapping indicator method.[30] The pK_{HA} value for benzoic acid (11.02) has been reported earlier.[31] The pK_{HA} values for 1,3-cyclohexanedione (enol) and tropolone, both measured against 9-fluorenone 2,4-dichlorophenylhydrazone, were found to be 11.15 ± 0.01 (identical to that of 4,4-dimethyl-1,3-cyclohexanedione[31]) and 11.37, respectively. The NMR for 1,3-cyclohexanedione (**2**) in DMSO fails to show the presence of a methylene group. Arnett and Harrelson have shown that 5,5-dimethyl-1,3-cyclohexanedione also exists completely in the enol form.[32] The pK_{HA} of tropolone has been corrected for homohydrogen bonding; $\log K_{hb} = 2.1$. For phenol $\log K_{hb} = 3.4$.[33]

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(27) The assumption that ΔBDEs can be equated to RSEs has often been criticized because changes in ground (or initial) state energies have not been considered. It is conceivable, for example, that part of the 7.6 kcal/mol lower BDE for the H–C bond in $H–CH_2NO_2$ than for that in $H–CH_3$ could be caused by weakening of the H–C bond in $H–CH_2NO_2$ by an increase in the ground state energy of CH_3NO_2, relative to that of CH_4. A referee has criticized our interpretations of radical stabilizations solely in terms of allylic-type resonance and has suggested that $^{\bullet}CH_2–C^+–O^- \leftrightarrow {}^+CH_2–C^{\bullet}–O^-$ type resonance may be important. (See also ref 10b.)

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