N–H bond dissociation energy, solvation of the lithium cation, and the degree of covalence of the Li–N bond also contribute to the shift of the oxidation potential. In consequence, the choice of the base used for metalations may be a determinant factor when competing reactions can occur by electron transfer. The use of LiHMDS instead of the more generally used lithium dialkylamides may permit such side reactions to be avoided.

Experimental Section

Materials. Diisopropylamine, 1,1,1,3,3,3-hexamethyldisilazane, and 2,2,6,6-tetramethylpiperidine (Aldrich) were distilled over CaH_2 and stored under argon. Tetrahydrofuran (THF) was distilled under Ar over potassium, and hexamethylphosphoramide (HMPA) was heated at 180 °C over CaH_2 for 2 h before distillation under reduced pressure. The lithium amide solutions (0.3 M) were freshly prepared by metalation of the corresponding amine in THF with *n*-butyllithium (Aldrich, 2.5 M in hexane). The solutions were stored at −50 °C under Ar. Solutions of LDA and LiTMP in THF/HMPA were not stable at temperatures higher than −10 °C for more than 5 min. LiHMDS was stable at room temperature, even in the presence of HMPA. Lithium perchlorate (Aldrich, anhydrous) was dried at 200 °C (0.05 mmHg) for 12 h in an electrolyte storage flask. The flask was then flushed with Ar, and THF was transferred from the distillation apparatus via a cannula to give a 0.2 M solution.

Cell and Apparatus. Cyclic voltammetry measurements were performed in a three compartment cell. The working electrode (glassy carbon, V25, Atomergic Chemetals Corp., polished with diamond paste (50000 mesh)) was separated from the counterelectrode (platinum mesh) by a medium porosity fritted glass. A silver wire coated with AgCl, employed as the pseudo-reference electrode, was separated from the working electrode by a fine fritted glass. $LiClO_4$ (0.2 M) was used as the supporting electrolyte. Potentials were measured relative to an internal ferrocene standard ($E_{1/2} = +510$ mV versus SCE). Cyclic voltammograms were recorded with a BAS-100 electrochemical analyzer or with a PAR 173 potentiostat driven by a PAR 175 universal programmer.

NMR Measurements. Solutions of LiTMP (187, 84, and 42 nM) in THF/THF-d_8 were prepared by adding the appropriate amounts of solvent to solid LiTMP (isolated by evaporation of the solvent after metalation as described above). NMR tubes were sealed with rubber stoppers. ^{7}Li NMR spectra were recorded on a General Electric GN-500 (194 MHz) spectrometer. Chemical shifts are reported relative to an external LiCl reference. ^{1}H NMR spectra were recorded on a Nicolet NT-200 (200 MHz), and chemical shifts are reported relative to TMS.

Acknowledgment. We are grateful to the National Science Foundation and to the Robert A. Welch Foundation for support of this work. We thank Dr. Ben Shoulders, J. Wallia, and S. Sorey for assistance with the NMR measurements.

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An Electrochemical Characterization of Dianions: Dilithiated Carboxylic Acids

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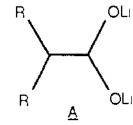
Abstract: The oxidation of dilithiated carboxylic acids has been studied by cyclic voltammetry. The pK_as for the second deprotonation of phenylacetic acid, diphenylacetic acid, and phenylthioacetic acid have been determined by an equilibration method. From the electrochemical results and the pK_a values, the bond dissociation energies were calculated, via a thermodynamic cycle, for the α C–H bonds of the corresponding carboxylate salts. The noncoplanarity of the two phenyl rings for the radical derived from diphenylacetic acid was deduced.

The use of electrochemical methods to obtain physical and chemical information about carbanions has been recently reviewed.[1] For instance, molecular orbital energies, conformation analysis, and the ability to react by electron transfer[2] have been studied. A correlation between the pK_a values of carbon acids and the oxidation potentials of their conjugated bases has been reported by Kern and Federlin.[3] On the basis of gas-phase bond dissociation energies and oxidation potentials of organolithium compounds, Breslow and co-workers have estimated the pK_as of such very weak carbon acids as toluene, propene, and 4,4-dimethyl-2-pentyne.[4] More recently, Bordwell and Bausch have used acidity-oxidation potential values as estimates of relative bond dissociation energies and radical stabilities in DMSO.[5]

Only few studies of dianionic systems, however, have been reported in the literature.[6] Because of their electron-rich character, they represent an interesting target for study by electrochemical methods.

Dianions have been shown to react in many cases by electron transfer. For example, attempts to methylate the dipotassium salt of *p*-xylene with an excess of methyl iodide produced exclusively a dibenzyl derivative, presumably via one electron oxidation and dimerization of the generated radical anion.[7] The dianion derived from diisopropylbenzene was shown to dimerize spontaneously.[8] Oxidative coupling of dicarbanions is also described in the literature.[9]

We have chosen to examine in this work dilithiated carboxylic acids (A). They are known for their high stability, ease of preparation, and great utility from a synthetic point of view.[10]



A

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Table I. Oxidation Peak Potentials E_p and Peak Widths ($E_p - E_{p/2}$) for Some Dilithiated Carboxylic Acids in THF/HMPA Mixtures Containing $LiClO_4$ (0.2 M)[b]

compd[a]	T [°C]	% vol HMPA in THF	E_p [V] vs SCE	$E_p - E_{p/2}$ [V]
1	rt	0	−0.29	0.19
	rt	10	−0.53	0.15
	rt	20	−0.55	0.17
	rt	30	−0.62	0.15
2	rt	0	−0.54	0.12
	rt	10	−0.58	0.10
	rt	30	−0.67	0.12
3	rt	30	−0.68	0.13
4	rt	10	−0.65	0.10
5	rt	30	−0.55	0.22
6	rt	0	+0.10	0.10
	−33	0	+0.28	0.14
	rt	10	two peaks	
	rt	30	−0.34	0.13
9	rt	30	−0.40	0.08
10	rt	30	+0.41	0.17
15	−40	10	+0.29	0.34

[a] All dianions were prepared amine-free, either by deprotonation with butyllithium (when possible) or by evaporation of the amine formed from LDA. [b] Scan rate: 100 mV/s.

They are very nucleophilic reagents, reacting, for instance, with alkyl halides, epoxides, aldehydes, ketones, and esters: A good knowledge of their electrochemical properties is highly desirable. For example, they react with α,β-unsaturated esters to produce exclusively 1,4-addition product, a single electron transfer mechanism having been suggested.[11] The synthetic utility of oxidative coupling of dianions has been exploited by Belletire and co-workers[12-14] and by Bergman and Pelcman.[15] These studies suggested a possible electron-transfer mechanism and indeed have also shown that radical anions are formed during the coupling reaction of carboxylic acid dianions with iodine.[16]

Results and Discussion

Choice of Solvent for Cyclic Voltammetry. Because of the high degree of aggregation of dilithiated acids, we first examined their electrooxidizability in DMSO, a strongly solvating medium in which the salts might reasonably be expected to be monomeric.

When any of several dilithiated alkanoic acids were studied in DMSO, an oxidation peak corresponding to monolithiated DMSO was observed, identical with that seen when sodium hydride was added directly to an electrochemical cell containing only DMSO and the supporting electrolyte ($LiClO_4$). Since proton exchange between the dianion and DMSO occurs readily, making DMSO too acidic for our study, we turned to the solvent mixture THF/HMPA with $LiClO_4$ as supporting electrolyte.[17] Oxidation peak potentials (E_p) and the width of the waves ($E_p - E_{p/2}$) are reported in Table I. In order to prevent deformation of the peak shape due to electrode fouling (observed with most of the dianions), the glassy carbon electrode was polished between each measurement. Since no further shifts in peak potentials or peak separation could be observed with larger fractions of HMPA, we assume that solvent mixtures containing 30% HMPA gave monomeric dianions of arylacetic acids and phenylthioacetic acids.

Dilithiated Phenylacetic Acid Derivatives. The cyclic voltammogram of dilithiated phenylacetic acid (**1**) at room temperature in THF is essentially identical with that observed in DMSO: irreversible (even at high scan rate of 5 V/s) but slightly broader ($E_p - E_{p/2}$ = 0.19 V). By addition of HMPA, a cathodic shift was observed which leveled after addition of 25% vol HMPA. An anodic shift of 2.8 mV/K was noticed on lowering the temperature.

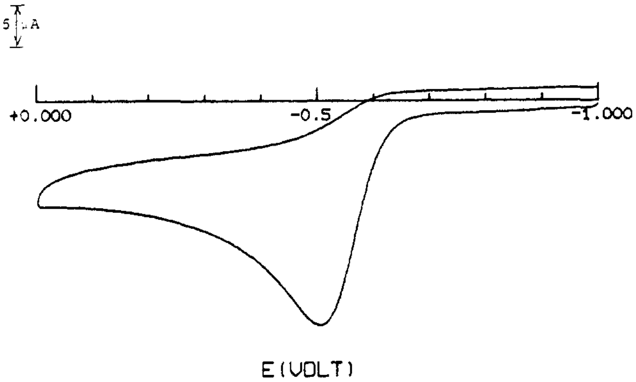

Figure 1. Cyclic voltammetric oxidation of **9**; 0.01 M **9** in 10 vol % HMPA in THF containing 0.2 M $LiClO_4$; 100 mV/s.

The cyclic voltammogram of dilithiated diphenylacetic acid (**2**) in THF containing differing amounts of HMPA consisted also of one relatively narrow irreversible wave ($E_p - E_{p/2}$ = 0.10 V). No reversibility was observed even at −78 °C and high scan rate. A small cathodic shift of 0.12 V was observed on going from pure THF to 30% vol HMPA in THF. Lowering the temperature induced an anodic shift of less than 0.7 mV/deg. Other dilithiated substituted phenylacetic acids (**3**, **4**, and **5**) gave similar cyclic voltammetric behavior.

Dilithiated Phenylthioacetic Acid Derivatives. The cyclic voltammogram of dilithiated phenylthioacetic acid (**6**) in THF at room temperature displayed a single narrow ($E_p - E_{p/2}$ = 0.10 V) irreversible oxidation peak. Lowering the temperature to −33 °C led to an anodic shift of 0.18 V. Upon addition of 10% HMPA, a shoulder appeared in the peak which disappears at temperature below −20 °C. At higher HMPA concentrations, the shoulder became the only observable peak. In 30% vol HMPA, a total cathodic shift of 0.44 V relative to the peak in pure THF was measured. This behavior was attributed to a change of the aggregation degree of the dianion, the most cathodic peak representing the less aggregated species.[18] The electrochemical behavior of dilithiated cyclopropylphenylthioacetic acid (**7**) and 2-phenylthio-6-heptenoic acid (**8**) were similar to **6**; however, the more cathodic peak was always relatively broad, indicating that a kinetic barrier to heterogeneous charge transfer was encountered.

The cyclic voltammogram of *tert*-butylphenylthioacetic acid (**9**) showed also two peaks in 10% vol HMPA in THF at −58 °C. At higher temperatures and HMPA contents, only one single irreversible narrow peak ($E_p - E_{p/2}$ = 0.08 V) was observed (Figure 1). Dilithiated phenoxyacetic acid (**10**) was also examined by cyclic voltammetry. A relatively broad irreversible oxidation wave was observed at a very anodic potential.

Dilithiated Alkanoic Acids. No oxidative peaks could be observed by cyclic voltammetry for any of the dilithiated alkanoic acids we have examined (acetic acid **11**, hexanoic acid **12**, 6-heptenoic acid **13**, cyclobutanecarboxylic acid **14**, and cyclopropylacetic acid **15**, for instance) under any solvent or temperature conditions. Some oxidative current of very low intensity was observed at potentials higher than +0.4 V versus SCE. We believe that this poor electrochemical behavior is caused by strong aggregation of the dianions. The milky viscous appearance of the dianion THF solution (sometimes even when HMPA is present in the medium) reflected the great extent of this aggregation. It has been reported, for instance, that the alkylation of straight chain aliphatic acids gives unsatisfactory yield in THF[19] and that the use of HMPA as cosolvent would permit this problem to be overcome.

The previous examples with substituted phenylthioacetic acids **6**–**9** have shown that a strong anodic shift was observed with increase in aggregation degree. The same effect may be expected

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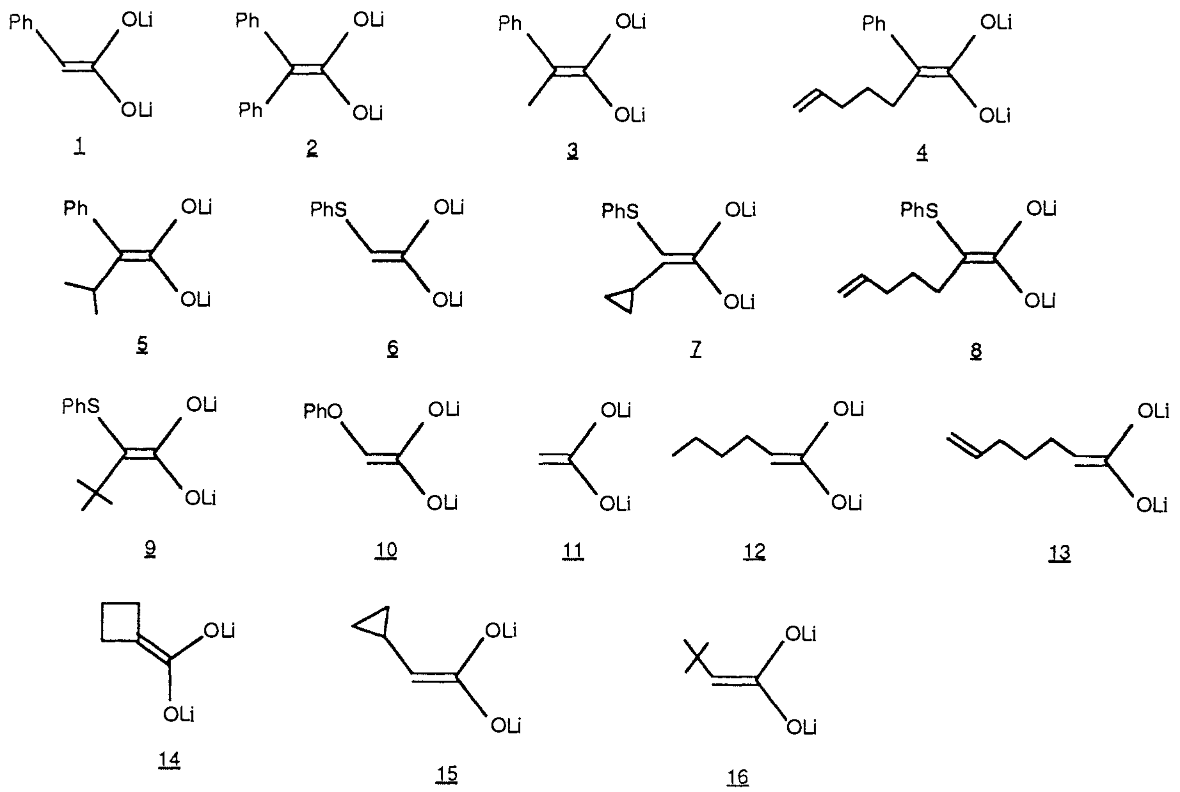
Chart I



for alkanoic acid dianions, with their very high association degree (polymers) explaining the almost complete disappearance of oxidation peaks. A similar phenomenon was also observed by House, who reported the absence of oxidation peaks in the cyclic voltammogram of the aggregated organocuprate $Me_4Cu_2Li_2$.[2]

Yellow octahedral crystals of the dianion of diphenylacetic acid were obtained from THF solutions. ^1H NMR of these crystals, quenched in CD_3COOD, showed that they were constituted as a 1:1 complex with THF. They were unfortunately not suitable for X-ray structural analysis (polycrystalline form).

Dilithiated *tert*-butylacetic acid (**16**) formed a clear solution in THF, and a broad oxidation peak was observed in the cyclic voltammogram at a relatively anodic potential.

Determination of the pK_a. In order to correlate the measured oxidation peak potential of dilithiated carboxylic acids with the stabilization energy of the radical anion, it was necessary to determine the pK_a for the second deprotonation of the carboxylic acid.[20] Recently, an intense interest for acidity measurements in THF solution has grown. UV–vis spectroscopy[21] and ^{13}C NMR[22] have been used to monitor these equilibria. None of these methods was appropriate for our study since the dianions generated with LDA were slightly colored by impurities, and the ^{13}C NMR spectra were complicated by aggregation.

We have been able to follow the transmetalation equilibria between two carboxylic acids by quenching an equilibrated solution with deuteriated acetic acid (Figure 2). About 12 h stirring at room temperature were needed to reach equilibrium prior to quenching. Similar results were obtained when approaching the equilibrium from the left or right side as written. In order to show that the deuteriation was much faster than the equilibration reaction (k_{d1} and $k_{d2} \gg k_1$ and k_2) we have conducted the following control experiment: a solution in THF/HMPA (5:1) of the carboxylate salt was mixed with the dianion at room temperature. The mixture was then cooled to −78 °C and stirred for 3 min before quenching. No more than 5% of deuterium was incorporated in the monoanionic species, whereas the dianion was quantitatively deuteriated.

This control has been done for each couple we have studied, in both directions. The relative pK_as measured by this method are reported in Table II. The results are very interpretable within an experimental error of ±0.2 pK_a unit: pK_a (phenylthioacetate) < pK_a (phenylacetate) < pK_a (diphenylacetate).

Table II. pK_a Differences Measured by Equilibration in HMPA, 20% in THF ($A^{2-} + B^- \rightleftharpoons A^- + B^{2-}$)

A^{2-}	B^-	pK_a(A) − pK_a(B)[a] ±0.2 pK units
$C_6H_5C(Li)H_2COOLi$	$C_6H_5SCH_2COOLi$	+0.4
$C_6H_5C(Li)HCOOLi$	$(C_6H_5)_2CHCOOLi$	−0.4 (−0.1)
$(C_6H_5)_2C(Li)COOLi$	$C_6H_5SCH_2COOLi$	+0.8 (+0.5)
$(CH_3)_3CC(Li)HCOOLi$	$C_6H_5SCH_2COOLi$	>2
$Ph_2C(Li)COOLi$	Ph_3CLi	+0.3
$PhSC(Li)HCOOLi$	Ph_3CLi	+0.4 (+0.1)
$PhCHCOOLi$	Ph_3CLi	+0.8 (+0.5)

[a] Values in parentheses are statistically corrected for the number of acidic protons.

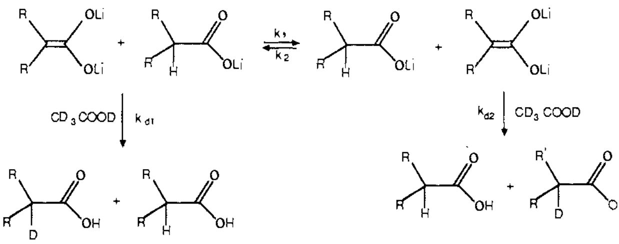


Figure 2. Determination of the transmetalation equilibrium constant between mono- and dilithiated carboxylic acids by deuteriation with CD_3CO_2H, k_{d1} and $k_{d2} \gg k_1$ and k_2.

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(20) Only pK_as in water measured by bromination rates are reported for the second deprotonation of carboxylic acids: pK_a (CH_3COOH) = 24.0, a value very similar was found for the deprotonation of esters: pK_a ($CH_3COOC_2H_5$) = 24.5; Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439. See also the following (which appeared while this article was in press): Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1988**, *110*, 4418.

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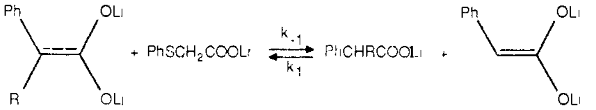
Table III. Absolute pK_a Values in 20% vol HMPA in THF

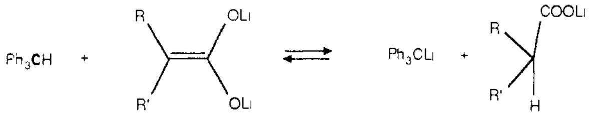
compd	pK_a ± 0.2 pK units
$(C_6H_5)_2CHCOOLi$	30.7
$C_6H_5SCH_2COOLi$	30.6
$C_6H_5CH_2COOLi$	30.2
$(CH_3)_3CCH_2COOLi$	>33

In order to convert our relative pK_a scale to an absolute one, we have looked at equilibration with an indicator of suitable pK_a. Fluorene (pK_a = 22.4 in THF[21b]) was completely deprotonated in a few minutes by dilithiated diphenylacetic acid. When triphenylmethane (pK_a = 31.0[21b]) was used, the characteristic deep red color of triphenylmethyllithium appeared very slowly. As the deprotonation reaction was very slow, we were able to use the same technique as before (D^+-quenching) to monitor the equilibrium. (The same type of control experiments described above were also done for this system.)

The resulting pK_a values are also shown in Table II. Lithium phenylacetate was found again to be more acidic than lithium diphenylacetate. The acidity of lithium phenylthioacetate had dramatically decreased and became very similar to that of diphenylacetate. We have used this last value for the absolute pK_a determination of phenylthioacetate (Table III), the relative value obtained by the transmetalation equilibration having been assumed to be distorted by electronic repulsion, eq 1. The coulombic repulsion between dilithiated phenylthioacetic acid and phenylacetate is much greater than the electronic repulsion of dilithiated phenylacetic acid (delocalized dianion) and phenylthioacetate. As a result, the decrease of the k_{-1} attributable to electron repulsion is more important than the decrease of k_1. Such problems do not occur in a transmetalation equilibrium with triphenylmethane, eq 2. Since coulombic repulsion appears only between the carboxylate and triphenylmethyllithium, this factor is almost independent of the nature of R and R′. Nevertheless, this repulsion is partially responsible for the low acidity of carboxylates relative to esters[24] in THF. The decreased acidity of phenylacetate compared to diphenylacetate appears at first surprising. However, the same effect was observed for phenylacetophenone (pK_a = 17.9) and diphenylacetophenone (pK_a = 18.7).[23] This was attributed to steric inhibition of resonance. The same argument may be proposed in our case since the OLi group can be considered to be very bulky because of solvation and aggregation.



(1)



(2)

Relative Radical Anion Stabilization Energies. From the measured oxidation peak potentials and pK_a measurements, it is possible to determine the heat of reaction for the isodesmic process depicted in eq 3. The choice of triphenylmethane as standard was dictated by the fact that the bond dissociation energy, the pK_a, and the oxidation potential of the lithiated derivative are all well known. The free energy for this reaction is given by the difference of bond dissociation energies (BDE), eq 4. For a given compound R–H, the BDE may be expressed as a function of the acidity of RH [pK_a(R–H)] and the oxidation potential of R^-, eq 5. The relation (eq 6) for $\Delta G°$ is obtained by introducing the expression for the BDEs (eq 5) into eq 4.

$$\underset{\substack{|\\ H}}{RR'CCOOLi} + (C_6H_5)_3C\cdot \longrightarrow RR'C\dot{C}OOLi + (C_6H_5)_3CH \quad (3)$$

$$\Delta G° = BDE(C{-}H)_{Ph_3CH} - BDE(C{-}H)_{RR'CHCOOLi} \quad (4)$$

$$BDE = pK_a + E_{ox} + \text{constant} \quad (5)$$

$$\Delta G° = pK_a + E_{ox}\ (\text{kcal/mol}) \quad (6)$$

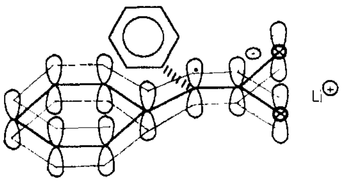
Table IV. Free Energies for the Isodesmic Process (eq 3) and Estimated Bond Dissociation Energies for the α-CH Bond of RR′CHCOOLi

R	R′	pK_a[a]	E_{ox}[b] [V]	$\Delta G°$ [kcal/mol]	BDE[c] [kcal/mol]
Ph	H	0.5	0.53	11.5	86
Ph	Ph	0.3	0.51	11.3	86
PhS	H	0.1	0.81	18.5	93

[a] Values are corrected for statistical factors. [b] E_p (triphenylmethyllithium) = −1.15 V SCE at room temperature in 30% vol HMPA in THF (ref 4: E_p = −1.18 V SCE at room temperature in 10% vol HMPA in THF). [c] On the basis of a value of 75 kcal/mol for triphenylmethane.[22]

The use of E_{ox} obtained from irreversible oxidation peak potentials may cause some problems. However, if the irreversibility of the peak is caused by a rapid dimerization of the radicals formed[25] and not by irreversible charge transfer (normally characterized by broad peaks), it has been shown that the half-wave oxidation potentials may be deduced with reasonable accuracy from the oxidation peak potentials by applying a small correction factor.[4] As this correction factor is not highly dependent of the substrate, its relative contribution will cancel, making it possible to use the oxidation peak potentials for the estimation of ΔE_{ox}.

$\Delta G°$ values and estimated BDEs for the α-CH bonds of the lithium carboxylates are reported in Table IV. For compounds of similar structure, differences in BDEs are a good approximation for the relative stabilities of the radicals. The BDE values obtained for lithium diphenylacetate and phenylacetate (86 kcal/mol) are about the same as that for toluene (88 kcal/mol) in the gas phase.[26] This result is probably caused by steric restriction of the radical delocalization onto one phenyl ring, the other phenyl ring being orthogonal to the planar radical center (structure B). The high BDE value measured for phenylthioacetate (93 kcal/mol) shows that the stabilization of the radical C by capto-dative effects is rather small.



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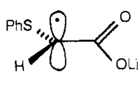

C

Experimental Section

Materials. Commercially available phenylacetic acid, diphenylacetic acid, 2-phenylpropanoic acid, phenylthioacetic acid, phenoxyacetic acid, hexanoic acid, 6-heptenoic acid, cyclobutane carboxylic acid, and *tert*-butylacetic acid were purified by recrystallization or distillation before use. The other acids were prepared by alkylation of phenylacetic acid (**4** and **5**), heptenoic aid (**8**), *tert*-butylacetic acid (**9**), and cyclopropylacetic acid[16] (**7**), according to the procedure of Petragnani.[10] Tetrahydrofuran (THF) was distilled under argon over potassium; hexamethyl phosphoramide (HMPA) was distilled over CaH_2. $LiClO_4$ (Aldrich, anhydrous) was dried for 12 h at 200 °C (0.01 mmHg) in an electrolyte storage flask. The flask was then flushed with Ar, and THF was transferred from the distillation apparatus via cannula to give a 0.2 M solution.

Cell and Apparatus. Cyclic voltammetry measurements were performed in a three compartment cell. The working electrode (glassy carbon V 25, Atomergic Chemetals Corp., polished with diamond paste 50 000 mesh) was separated from the counterelectrode (platinum mesh)

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(24) pK_a (*tert*-butyl phenylacetate) = 19.6 in THF: Kaufman, M. J.; Gronert, S.; Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 602.

(25) Preparative electrolysis of dilithiated carboxylic acids is known to produce dimeric product.[16]

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by medium porosity fritted glass. A silver wire coated with AgCl, employed as the pseudo-reference electrode, was separated from the working electrode by a fine fritted glass. $LiClO_4$ (0.2 M) was used as supporting electrolyte. Potentials were measured relative to an internal ferrocene ($E_{1/2}$ = 510 mV versus SCE) or anthracene ($E_{1/2}$ = −1.94 V versus SCE) standard. Cyclic voltammograms were recorded with a BAS-100 or a PAR 173 potentiostat driven by a PAR 175 Universal programmer.

Preparation of the Dianion Solutions. The acid (10 mmol), dissolved in THF, was slowly added to a 1 M LDA solution (20 mL) diluted with 12 mL of THF. The reaction mixture was stirred at room temperature for 3 to 5 h, and the solvent was evaporated under vacuum, yielding the solid dianion as a powder. A stock solution (0.3 M) was prepared by dissolution of the dianion in THF.

Where possible, the dianions were also prepared amine-free by deprotonation with butyllithium. Since identical results were attained with and without amine bases, we infer that the procedure for evaporative removal of diethylamine effectively produced free lithium salts uncomplicated by amine complexation effects described previously.[27,28]

Diphenylacetic acid was directly deprotonated with 2 equiv of *n*-butyllithium at 0 °C in THF. Phenylacetic acid was also directly metalated with *n*-butyllithium at −78 °C (slow addition); the reaction mixture was then allowed to warm to room temperature.

All the dianion solutions were very stable at room temperature in the presence of HMPA. Yellow octahedral crystals of dilithiated diphenylacetic acid were obtained after deprotonation of 2 mmol acid in 6 mL of THF with 4 mmol *n*-butyllithium (2.5 M) by maintaining the solution at −20 °C for 2 days.

In all cases, chemical trapping and characterization of alkylated products (isolated in ≥90% yield) derived from the dianions verified that the dianions indeed were formed under these conditions, as has been previously reported by others.[19,29] Although the dianions attack THF at elevated temperatures, no decomposition (as adjudged by yield of alkylation product) occurred at temperatures below 40 °C within the several hours necessary for these experiments.

The pale yellow color observed in these experiments is routinely observed when LDA is used as a base.[10] It is caused by the reaction of LDA with THF since no substrate decomposition product is observed after quenching the dianion solution. The colored product has no influence on the dianion cyclic voltammetry since scans of dianions prepared from LDA or from BuLi were identical. For example, the same electrochemical behavior was observed for the dianion of phenylthioacetic acid prepared in situ by this method and that purified by recrystallization of the dilithium salt.

The milky viscous appearance of the dilithiated alkanoic acids is attributed to strong aggregation rather than to formation of LiOH.[10] Aggregation proved to be a complication for obtaining ^{13}C NMR spectra because of the high substrate concentrations involved in those experiments, whereas cyclic voltammograms were obtained at much lower concentrations where aggregation was not significant.

pK_a Determination. (1) Equilibrium measurements: 1 mmol of the dilithiated acid (I) in 5 mL of THF/HMPA (4:1) was added to 1 mmol of the lithium carboxylate (II). The solution was stirred at room temperature. After 1 h, a homogeneous solution was generally formed, and the solution was stirred for 20 more h. The solution was then quickly cooled to −78 °C, and CD_3COOD (1 mL) was added to the reaction mixture. The usual workup gave the partially deuteriated acid. The deuterium content for each compound was determined by proton NMR, ^{13}C NMR, and mass spectroscopy. The equilibrium constant was always determined by approaching the equilibrium from both sides.

(2) Control experiments: The lithium carboxylate was dissolved in 5 mL of THF/HMPA (4:1) before addition of the dianion. The resulting solution was stirred for 3 min at room temperature before quenching as previously described at −78 °C.

Equilibration with triphenylmethane as indicator was accomplished in similar fashion, with triphenylmethane replacing the carboxylate salt II.

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Laser-Induced Fluorescence, Far-Infrared Spectroscopy, and Luminescence Quenching of Europium Zeolite Y: Site-Selective Probes of Extraframework Cations

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Abstract: In this paper, the far-infrared and laser-induced fluorescence spectra of ion-exchanged, dehydrated europium zeolite Y are reported. Both techniques indicate that europium ions locate in three major sites. The appearance of bands due to parity-forbidden transitions in the fluorescence spectra indicates that the local symmetry of these sites is either C_s, C_n, or C_{nv}. The migration of europium ions between these sites was observed following oxidation of the zeolite at 400 °C. The luminescence intensity was quenched by oxygen, obeying Stern–Volmer kinetics. The spectra recorded in the presence of oxygen indicate that the quenching is site selective. The recognition of molecules entering the pore system of the zeolite by an optical response is one of the goals of this study.

1. Introduction

Zeolite molecular sieves currently play an indispensable role in many technologically and economically important applications. Of primary importance are their uses as acidic cracking catalysts,[1] builders in detergents,[2] and fillers in the paper industry.[3] In the past 5–10 years, the characterization of these materials has become increasingly crucial to their future development in many new

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