JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 104, NUMBER 22 NOVEMBER 3, 1982

Nuclear Magnetic Resonance Examination of Organic Dianions

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Abstract: Dianions have been examined by ^{13}C and ^{17}O nuclear magnetic resonance spectroscopy under long-lived conditions in Me_2SO and THF. Generation of a dianion is accompanied by characteristic changes in the ^{13}C chemical shift, the one-bond ^{13}C–^{1}H coupling constant, and the multiplicity of the ^{13}C resonance. The dianions examined in this way included those of arylacetic acids, thiophenoxyacetic acid, (phenylsulfonyl)acetic acid, 2-indanone, and two β-keto esters. Electron densities at all positions were calculated by comparison of dianion chemical shifts with those of the corresponding neutral species or of suitable neutral models. In the arylacetic acids, a modest amount of negative charge exists on the α-methylene carbon (about −0.25) and in the aryl ring (−0.1 to −0.3, depending on aryl substitution). The sulfur and sulfonyl groups insulate the phenyl ring completely from negative charge, so that the α-carbon bears a higher charge, about −0.4. The α-methylene carbons in 2-indanone and in the β-keto esters possess about −0.2. Charge density is dependent on cation and solvent. A change from K^+ to Na^+ to Li^+ or from Me_2SO to THF decreases the overall charge on carbon, so that oxygen is even more highly charged. Charge densities on oxygen were calculated by difference and were compared with the upfield shifts observed in the ^{17}O spectrum in four of these systems. Extremely large ^{17}O line widths made these measurements relatively inaccurate. The derived shift caused by introduction of a full unit of negative charge was calculated to be about 500 ppm/e$^-$, compared with 160 ppm/e$^-$ for ^{13}C. The ratio of these two factors is close to the expected value from consideration of radial differences between the two atoms.

Carbon-13 nuclear magnetic resonance spectroscopy has proved to be a useful technique in the examination of the structure and charge distribution of carbanions.[2] Spiesecke and Schneider[3] found that the introduction of a full unit of electronic charge causes an upfield shift of about 160 ppm when the structure is otherwise unchanged (constant hybridization). Grutzner[4] has pointed out that this shift is caused by several effects, but its utility in the calculation of charge densities in well-defined cases is not in dispute. Charge distribution has been studied extensively in arylmethyl,[5] aliphatic polyene,[6] cyclopentadienyl,[7] and enolate[8] systems. In the simplest case, the ^{13}C chemical shift of the neutral is subtracted from that of the anion, and the difference is converted to units of negative charge through division by 160 ppm/e$^-$. Corrections for hybridization are required when the carbon in the neutral is not already trigonal. For example, House used shifts in enol acetates as models for the neutrals that correspond to enolate anions.[8] Other problems and exceptions have been discussed by Grutzner.[4] Ion pair structure has been examined by the effects of temperature, solvent, cation, and aryl substitution on ^{13}C chemical shifts.[7,9] For anions of oxygen acids the contact ion pair is favored over the solvent-separated ion pair by higher temperatures, smaller cations (Li^+), and lower solvent polarity and is signified by an upfield shift. Aggregation has been studied through the effects of ^{13}C relaxation times.[7,10] Questions about planarity vs. pyramidality have been probed in the 7-phenylnorborn-7-yl carbanion.[11]

Except for our initial publication,[12] ^{13}C studies of organic dianions have been limited to linear or aromatic systems such as the cyclooctatetraene dianion. In this study we exclude dianions in which both protons are removed from a heteroatom. Dianions in which at least one proton is removed from carbon are important in organic synthesis.[13] Our initial studies[12] were aimed primarily at establishing definitive evidence that dianions exist as such in Me_2SO solution under long-lived conditions. We now report an in-depth study of dianion structure, including examination of

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[1] This research was supported by the National Science Foundation, Grants CHE79-05542 and CHE80-25601.

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[11] Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709–4715.

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charge distribution and ion pair effects. Although magnetic resonance studies of anions heretofore have been limited to ^{1}H and ^{13}C nuclei, we also include an examination of ^{17}O resonances in the present study. In many delocalized anions, such an enolates and nitronates, the preponderance of charge is on oxygen, so that charge density and ion pair effects should be well displayed in the ^{17}O spectrum.

Results

Dianions were prepared directly in NMR tubes by the addition under nitrogen of dimsyl anion to the substrate in Me$_2$SO or of methyllithium to the substrate in tetrahydrofuran (THF). Samples were quenched in D$_2$O and were normally found by ^{1}H NMR spectroscopy to have a single deuterium at exchangeable sites, corresponding in each case to the dianion stage. Only lithium was used as the cation for the THF solutions. For Me$_2$SO, sodium was used for all dianions, and some of the substrates additionally were examined with lithium and potassium. Dianion concentrations were between 0.5 and 1.0 M.

Dianions were successfully observed by ^{13}C NMR spectroscopy for phenylacetic acid (**1**), diphenylacetic acid (**2**), *p*-fluorophenylacetic acid (**3**), *p*-tolylacetic acid (**4**), thiophenoxyacetic acid (**5**), (phenylsulfonyl)acetic acid (**6**), 2-indanone (**7**), diethyl 3-oxo-1,5-pentanedioate (**8**), and ethyl 3-oxo-4-phenylbutanoate (**9**). Under the conditions used, dianions could regularly be observed when the less acidic hydrogen was on a carbon located between two acidifying functionalities (phenyl, carbonyl, sulfonyl, sulfenyl). A single acidifying functionality, as in acetone, was invariably insufficient to produce the dianion.

In each case, ^{13}C spectra were recorded for the neutral in Me$_2$SO and THF, if possible for the monoanion in Me$_2$SO, and for the dianion in THF and Me$_2$SO. The monoanions frequently were less stable with respect to condensation and were less soluble than the dianions. The chemical shifts and coupling constants are listed in Table I. Charge densities were calculated for all dianion systems by the method of Spiesecke and Schneider.[3] The difference between dianion chemical shifts and those of the neutral were divided by 160 ppm/e$^-$ to provide the fraction of negative charge introduced at each position. No hybridization correction was necessary for the aromatic carbons or for methyl and methylene carbons that retain all the attached protons. For those carbons that undergo rehybridization, the chemical shift of the neutral species is not relevant. Following the lead of House in his study of electron density in enolate anions,[8] we used enol acetates (typical chemical shift, δ 110) as the model for anions generated next to a carbonyl group. The value is probably a minimum, so that calculated charges may be smaller than actual charges. The calculated charges on carbon are shown in Scheme I.

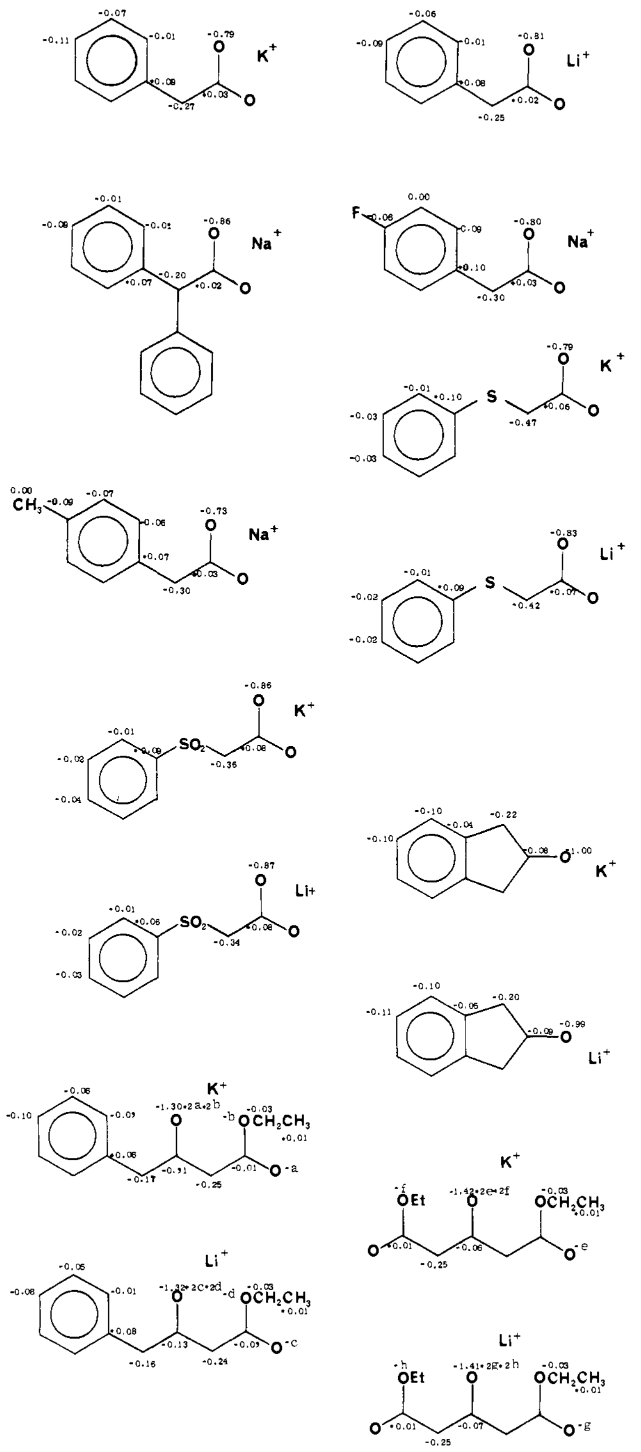
Table II gives the ^{17}O shifts for the neutral species, the monoanion when possible, and the dianion for four of the systems. Isotopic enrichment in ^{17}O (5%) was necessary. Resonances for the charged species are extremely broad, so that very short delay times were used.

Discussion

Production of a dianion is signified by three spectroscopic changes.

(1) The multiplicity of the ^{13}C resonance of the carbon losing the proton is lowered by one component (C2 and C10 in Table I). Thus the α-methylene triplets in **1** and **3**–**9** become doublets, and the doublet in **2** becomes a singlet. In the monoanions, the original multiplicity is retained in all the carboxylic acids. For ethyl 3-oxo-4-phenylbutanoate (**9**), the monoanion has a doublet for C2 and a triplet for C4 (C10 in the table), the dianion has a doublet for both, and the neutral has a triplet for both. The monoanion of the diester **8** was not stable. 2-Indanone (**7**) gave a monoanion with nonequivalent 2-positions, a triplet and a doublet, so exchange is slow on the NMR time scale.

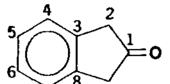
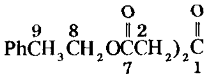
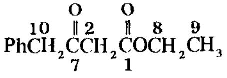
Scheme I



(2) Conversion to the dianion is normally accompanied by a downfield shift of the dianion carbon resonance (C2 and C10 in the table). Introduction of a negative charge by itself would cause an upfield shift. These carbons, however, also are being rehybridized, and conversion to trigonal hybridization brings about a large downfield shift. The net result of these two factors is a downfield shift within the surprisingly narrow range of 26–39 ppm for all the nonsulfur systems (**1**–**4**, **7**–**9**), from the range in the neutrals of δ 40–49 (56 for the diphenyl case **2**) to the range in the dianions of δ 69–88. The changes in the chemical shifts of these carbons in the monoanions of the carboxylic acids are quite small, as they possess little negative charge density on carbon. The dianions of the two sulfur systems (**5** and **6**) exhibit a very small downfield shift. In these cases, the hybridization effect is further offset by a large negative charge density.

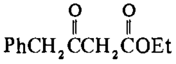
(3) The change in hybridization is accompanied in every case by an increase in the one bond ^{13}C–^{1}H coupling constant of between 10 and 28 Hz. Again, the normal increase in this coupling constant, expected for the approximate change from sp^3 to sp^2

Table I. Carbon-13 Chemical Shifts^{a} and One-Bond Coupling Constants^{b}

system	charge	solvent	cation	C1	C2	$\mathrm{C3}^{c}$	$\mathrm{C4}^{d}$	$\mathrm{C5}^{e}$	$\mathrm{C6}^{f}$	$\mathrm{C7}^{g}$	$\mathrm{C8}^{h}$	$\mathrm{C9}^{i}$	$\mathrm{C10}^{j}$
$\mathrm{Ph\overset{2}{C}H_2\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		172.6 s	40.7 t (128)	135.0 s	128.6 d (165)	129.3 d (155)	126.5 d (160)				
	0	THF		172.6 s	41.4 t (128)	136.1 s	128.8 d (160)	130.0 d (161)	127.2 d (162)				
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	175.9 s	45.9 t (126)	139.7 s	127.6 d (157)	129.4 d (158)	125.1 d (152)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{K^+}$	177.5 s	71.4 d (140)	149.4 s	127.5 d (152)	117.4 d (153)	108.2 d (167)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	177.7 s	71.4 d (145)	149.4 s	127.6 d (149)	118.5 d (158)	109.1 d (160)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	175.4 s	74.4 d (146)	148.3 s	127.0 d (152)	120.4 d (156)	111.5 d (159)				
	−2	THF	$\mathrm{Li^+}$	172.6 s	76.5 d (140)	150.3 s	130.5 d (154)	125.5 d (157)	118.6 d (158)				
$\mathrm{Ph_2\overset{2}{C}H\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		173.2 s	56.2 d (129)	139.4 s	128.4 d (161)	128.3 d (161)	126.8 d (160)				
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	175.4 s	61.6 d (127)	143.7 s	127.3 d (156)	128.6 d (165)	125.0 d (160)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	175.8 s	84.7 s	150.2 s	126.6 d (159)	126.5 d (158)	113.9 d (158)				
p-$\mathrm{FPh\overset{2}{C}H_2\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		172.5 s	39.7 t (129)	131.2 s	131.2 d (161)	114.9 d (164)	161.2 s				
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	174.8 s	44.7 t (129)	136.3 s	130.9 d (159)	114.1 d (163)	160.3 s				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	177.2 s	69.1 d (140)	146.6 s	117.1 d (160)	114.2 d (164)	151.3 s				
p-$\mathrm{\overset{7}{C}H_3Ph\overset{2}{C}H_2\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		172.6 s	40.3 t (130)	135.5 s	128.7 d (157)	129.1 d (157)	131.8 s	20.5 q (127)			
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	176.1 s	45.3 t (125)	136.5 s	128.2 d (149)	129.2 d (158)	133.6 s	20.7 q (126)			
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	177.1 s	70.1 d (142)	146.8 s	118.6 d (150)	118.3 d (150)	116.8 s	20.7 q (126)			
$\mathrm{PhS\overset{2}{C}H_2\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		170.8 s	35.3 t (141)	136.6 s	128.2 d (160)	128.1 d (163)	126.2 d (162)				
	0	THF		170.8 s	36.3 t (141)	137.4 s	129.5 d (161)	129.6 d (161)	126.8 d (161)				
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	170.7 s	35.9 t (139)	136.6 s	129.0 d (163)	127.5 d (160)	125.7 d (160)				
	−2	$\mathrm{Me_2SO}^{k}$	$\mathrm{K^+}$	180.7	34.8	151.4	127.9	123.0	121.8				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	182.3 s	36.6 d (164)	150.9 s	127.7 d (157)	123.9 d (159)	121.7 d (162)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	180.1 s	*l*	150.1 s	127.5 d (163)	124.4 d (159)	122.0 d (163)				
	−2	THF	$\mathrm{Li^+}$	180.4 s	45.7 d (165)	148.0 s	128.1 d (158)	125.6 d (160)	123.1 d (159)				
$\mathrm{PhSO_2\overset{2}{C}H_2\overset{1}{C}O_2H}$	0	$\mathrm{Me_2SO}$		163.9 s	60.1 d (140)	139.1 s	129.1 d (167)	127.9 d (168)	133.9 d (163)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{K^+}$	176.1 s	62.2 d (153)	152.1 s	127.9 d (158)	125.1 d (166)	127.5 d (160)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	177.0 s	64.2 d (168)	152.2 s	127.8 d (159)	125.0 d (164)	128.9 d (162)				
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	176.3 s	64.9 d (166)	151.9 s	127.9 d (163)	124.8 d (165)	128.5 d (161)				
	0	$\mathrm{Me_2SO}$		214.3 s	43.6 t (138)	138.1 s	126.9 d (160)	124.8 d (160)					
	0	THF		212.9 s	44.2 t (132)	139.3 s	127.7 d (165)	125.5 d (155)					
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	183.4 s	91.6 d (151)	153.7 s	125.9 d (148)	114.8 d (164)	121.7 d (158)	112.2 d (161)	134.7 s	42.0 t (120)	
	−2	$\mathrm{Me_2SO}$	$\mathrm{K^+}$	169.7 s	79.1 d (147)	131.2 s	110.9 d (147)	108.4 d (151)					
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	169.9 s	80.0 d (148)	131.0 s	111.3 d (148)	108.1 d (149)					
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	167.0 s	82.8 d (157)	129.9 s	111.3 d (147)	107.2 d (150)					
	−2	THF	$\mathrm{Li^+}$	163.1 s	79.1 d (179)	127.2 s	114.7 d (149)	111.1 d (155)					
 $\mathrm{Ph\overset{9}{C}H_3\overset{8}{C}H_2O\underset{7}{\overset{\overset{O}{\|}}{C}}\overset{2}{C}H_2)_2\underset{1}{\overset{\overset{O}{\|}}{C}}}$	0	$\mathrm{Me_2SO}$		197.1 s	48.9 t (131)					166.8 s	60.7 t (148)	13.9 q (127)	
	0	THF		195.8 s	49.2 t (131)					167.3 s	61.4 t (142)	14.3 q (127)	
	−2	$\mathrm{Me_2SO}$	$\mathrm{K^+}$	187.3 s	75.4 d (151)					167.6 s	55.2 t (146)	15.5 q (125)	
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	187.9 s	75.8 d (149)					168.1 s	55.6 t (144)	15.6 q (125)	
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	186.3 s	75.7 d (151)					168.6 s	55.5 t (144)	15.6 q (125)	
	−2	THF	$\mathrm{Li^+}$	187.9 s	77.7 d (153)					171.0 s	58.6 t (143)	15.5 q (125)	
 $\mathrm{Ph\overset{10}{C}H_2\underset{7}{\overset{\overset{O}{\|}}{C}}\overset{2}{C}H_2\underset{1}{\overset{\overset{O}{\|}}{C}}O\overset{8}{C}H_2\overset{9}{C}H_3}$	0	$\mathrm{Me_2SO}$		167.0 s	48.4 t (131)	134.0 s	128.3 d (160)	129.7 d (159)	126.7 d (162)	200.9 s	60.5 t (144)	14.0 q (127)	48.8 t (128)
	0	THF		167.6 s	48.7 t (130)	135.1 s	129.1 d (159)	130.4 d (160)	127.7 d (159)	200.0 s	61.3 t (147)	14.4 q (127)	49.9 t (128)
	−1	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	169.3 s	80.6 d (155)	140.3 s	127.8 d (157)	129.3 d (155)	125.3 d (159)	186.6 s	56.0 t (148)	15.1 q (126)	49.4 t (136)
	−2	$\mathrm{Me_2SO}$	$\mathrm{K^+}$	165.1 s	74.4 d (147)	147.4 s	127.4 d (151)	119.8 d (153)	111.2 d (166)	178.4 s	55.9 t (140)	15.9 q (134)	87.3 d (142)
	−2	$\mathrm{Me_2SO}$	$\mathrm{Na^+}$	165.7 s	74.8 d (150)	147.0 s	127.2 d (154)	120.7 d (158)	112.4 d (163)	177.4 s	56.8 t (146)	15.7 q (126)	88.1 d (145)
	−2	$\mathrm{Me_2SO}$	$\mathrm{Li^+}$	165.6 s	76.2 d (149)	146.5 s	127.3 d (152)	121.6 d (162)	113.4 d (169)	175.3 s	56.2 t (140)	16.0 q (126)	88.8 d (149)
	−2	THF	$\mathrm{Li^+}$	163.5 s	76.7 d (150)	144.8 s	127.8 d (155)	124.3 d (158)	118.2 d (154)	168.4 s	58.8 t (133)	15.6 q (127)	94.2 d (148)

[a] In ppm from $\mathrm{Me_4Si}$. [b] In Hz; the multiplicity precedes the coupling constant. [c] Aromatic ipso carbon; for 2-indanone see structure. [d] Aromatic ortho carbon; for 2-indanone see structure. [e] Aromatic meta carbon; for 2-indanone see structure. [f] Aromatic para carbon; for 2-indanone see structure. [g] Tolyl methyl carbon in 4 or carbonyl β to phenyl in ethyl 3-oxo-4-phenylbutanoate (9); for 2-indanone see structure. [h] Methylene carbon in ethyl groups; for 2-indanone see structure. [i] Methyl carbon in ethyl groups; for 2-indanone see structure. [j] Benzylic carbon in ethyl 3-oxo-4-phenylbutanoate (9). [k] Low solubility prevented obtaining the coupled spectrum. [l] Solvent overlap.

Table II. Oxygen-17 Chemical Shifts[a]

system	charge	chemical shift,[b] ppm	line width,[c] Hz
$PhCH_2CO_2H$	0	260	350
	−1[d]	270	450
	−2	−100	6000
 $PhCH_2\overset{\overset{2}{O}}{\overset{\|}{C}}CH_2\overset{\overset{1}{O}}{\overset{\|}{C}}OEt$	0 (O-1)	570	350
	0 (O-2)	120	200
	−1 (O-1)	50	5000
	−1 (O-2)	50	5000
	−2 (O-1)	100	7000
	−2 (O-2)	−100	7000
 $(EtO\overset{\overset{2}{O}}{\overset{\|}{C}}CH_2)_2\overset{\overset{1}{O}}{\overset{\|}{C}}$	0 (O-1)	580	200
	0 (O-2)	350	160
	−2 (O-1)	100	5500
	−2 (O-2)	100	5500
2-indanone	0	560	200
	−1	60	300
	−2	60	5000

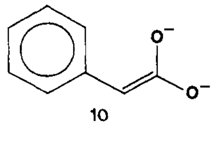
[a] Solutions in THF with Li^+ as cation, unless otherwise specified. [b] From H_2O. [c] Width at half-height. [d] In H_2O.

hybridization, is partially offset by the effect of the negative charge.

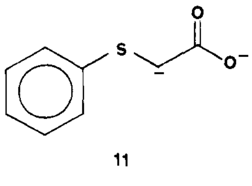
Other carbons also are affected by the introduction of the second negative charge. The carboxyl carbons (C1 in Table I) undergo a downfield shift, the aromatic ipso carbons (C3) a downfield shift, and the aromatic para carbons (C_6) an upfield shift. All these changes may be explained in terms of shielding effects of the negative charge.

The Spiesecke–Schneider method provided the charge densities that have been displayed in Scheme I for the dianions. In the arylacetic acids, the α-carbon develops about −0.25 of a charge, and about −0.10 or more is delocalized into the aromatic ring. The largest aryl delocalization is found in the tolyl system, in which the methyl group appears to stabilize adjacent charge through polarization. The sulfenyl and sulfonyl groups in **5** and **6** effectively insulate the phenyl groups from the charge, since charge accumulation in the rings is negligible. As a result, the charge on the dianion carbon increases to between −0.34 and −0.47. 2-Indanone has quite a large amount of charge that is delocalized into the aromatic ring (close to −0.50), but the usual amount of charge (−0.22) is at each of the α-carbons. Possibly ring fusion in this system permits better orbital overlap than in the freely rotating aryl systems. In addition, negative charge is being supplied to the aryl ring from two sites. The keto esters have the usual charge on the α-carbons (−0.13 to −0.25) and in the aromatic ring (−0.10 to −0.14). Some charge alternation is seen in these systems. Thus the aromatic ipso carbon is almost always positive in the dianion, compared with the same carbon in the neutral. The larger negative charge density on the dianion carbon appears to polarize the adjacent carbons positive.

The values in Scheme I indicate that the most important resonance structure for the arylacetic acids is **10**, which shows negative charge at the points of highest density. The higher charge density at the α-carbon in the sulfenyl and sulfonyl compounds does not reduce the amount of charge on the two oxygens, because of the absence of aryl delocalization. Structure **11** (and the corresponding structure with charge on the other oxygen) therefore represents one important aspect of charge delocalization for these two molecules. The keto esters **8** and **9** are very extensively delocalized, so that there is no single good representation of these dianions.



10



11

Charge delocalization is also influenced by the identity of the cation and by the solvent. The overall effect of the change from K^+ to Na^+ to Li^+ invariably is polarization of charge from carbon to oxygen, and a solvent change from Me_2SO to THF further enhances this charge polarization. The changes from K^+ to Na^+ usually are small, so that in these cases the cation may be somewhat removed from the dianion, as in the solvent-separated structure. Thus in phenylacetic acid, the dianion carbon C2 is at δ 71.4 for both K^+ and Na^+ in Me_2SO, but shifts to 74.4 for Li^+ in the same solvent and then to 76.5 for Li^+ in THF. These downfield shifts result from a loss of electron density from C2 to oxygen. Large changes in chemical shifts and hence in charge densities are also seen for the para and meta carbons in phenylacetic acid. Apparently there is some reorganization of the cation or of solvent with respect to the aromatic ring, but details are not clear. In contrast, these same aromatic carbons in the sulfenyl and sulfonyl systems (**5** and **6**) exhibit little dependence on cation identity. The small negative charge density in the aromatic ring and the lack of a cation effect suggest little phenyl–cation interaction for **5** and **6**. In agreement with phenylacetic acid, the dianion carbon (C2) of the sulfur systems shows the same sharp downfield shifts and hence lower negative charge density with Li^+ and with THF (34.8 for K^+, 36.6 for Na^+, 42.5 for Li^+ in Me_2SO, and 45.7 for Li^+ in THF for thiophenoxyacetic acid), so that this carbon appears to be close to the lithium cation. Alternatively, the Li^+ effects could be the result of different degrees of solvation rather than the location of the cation.

The situation is quite different for 2-indanone, in which Li^+ has a larger effect on the aryl carbons than on the dianion carbons. These results may be related to the physical movement of the cation from over the aryl ring (K^+) toward oxygen (Li^+). 2-Indanone is unique in this series of compounds in having only a single oxygen atom. In contrast to the acetic acids and the keto esters, in which both cations could conceivably be complexed with separate oxygens, 2-indanone may require the location of one cation closer to the negative charge on carbon. Change of the cation from K^+ to Li^+ then could exhibit larger effects on the aryl chemical shifts.

The two keto esters have several possible stable conformations from rotation about partial double bonds, in contrast to the previous examples. Our spectra show only a single set of resonances, so that either only one form is present or multiple forms are interconverting rapidly on the NMR time scale. For the diester **8**, chemical shift changes between K^+ and Na^+ are insignificant, but small changes with Li^+ may indicate alterations either in the ion pair structure or in the conformer populations. There is no clear evidence for chelation. The monoester **9** is somewhat more sensitive to cation identity. In particular, the dianion carbon labeled C10 in Table I (benzylic) and the meta and para aromatic carbons lose substantial negative charge with Li and THF. Much of this displaced charge moves to the keto carbon (C7 in Table I).

The negative charge on oxygen may be calculated from the carbon charge densities by difference. These numbers are given in Scheme I for all nine systems. When charge exists on nonequivalent oxygens, some charges are represented by letters. The carboxylic acid oxygen all bear a negative charge of −0.7 to −0.9. The single oxygen in 2-indanone carries a charge of about −1.0. The charge in the keto esters cannot be allotted specifically to the distinct carbonyl oxygens, but the sum of the charge can be calculated by difference.

We can use the calculated negative charges and the observed ^{17}O shifts to calculate the Spiesecke–Schneider factor for oxygen, corresponding to 160 ppm/e^- for carbon. Lippmaa and co-workers examined the change in the ^{17}O resonance on ionization of nitropyrroles and estimated that the upfield shift caused by a full negative charge would be 350–400 ppm.[14] Because of rapid relaxation through the quadrupolar interaction (spin = $^5/_2$), ^{17}O has extremely large line widths, sometimes on the order of several thousand hertz. A very short pulse delay must be used in order to avoid losing the signal entirely.

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We failed to observe any ^{17}O resonances of the charged species at natural abundance (0.037%), so we enriched four of the substrates to 5% ^{17}O. At this level of labeling, we found relatively sharp resonances for all four neutrals (half-height of 150–350 Hz) and extremely broad resonances for most charged species (300–7000 Hz). With peaks this wide, errors in position measurement are large. In every case, we examined as a control an identical sample with ^{17}O at natural abundance. These controls provided an assurrance that our unpleasingly broad peaks were real. Nonetheless, the possibility of error is large. Concentrations again were 0.5–1.0 M. For the monoanions, solubility frequently was quite limited in the solvent (THF). The monoanion data in Table II are lacking in some cases, were measured in water in others (and hence are not directly comparable), and are less reliable in all. Fortunately, the dianion resonances were better defined.

Upfield shifts occur from the neutral to the dianion oxygen in all cases. Division of the 360-ppm change for phenylacetic acid by the calculated charge of −0.81 on each oxygen gives a shift for a unit negative charge of 440 ppm. Division of 510 ppm for 2-indanone by −0.99 gives an analogous value of 510 ppm. For the keto esters, the calculation must take into consideration the combined charges. Thus for ethyl 3-oxo-4-phenylbutanoate, the sum of the upfield shifts is 690 ppm, and the sum of the charges is calculated to be −1.32, so that the unit charge shift is 520 ppm. In diethyl 3-oxo-1,5-pentanedioate, the calculation is less clear, because only one very broad peak was observed for the dianion. It may be that the expected two peaks are superimposed or that a second broad peak was not detected. If the data are taken as displayed in Table II (a superposition is assumed), the sum of the shifts is 980 ppm (the shift for O-2 must be doubled for statistical reasons), and the calculated charge is −1.53, for a unit shift of 640 ppm. Clearly, this figure is the least reliable of the group. The average of the first three figures is 490; with the fourth figure included the average is 530. The results compare well to Lippmaa's value.[14] Because the carbon negative charges are minimum values, the calculated oxygen charges are maximum values, and these calculated unit shifts are minimum values. Kintzinger and co-workers[15] found that the slope for the plot of ^{17}O shifts of aliphatic ethers (ROR′) vs. ^{13}C shifts for analogous methylene groups (RCH_2R') is 2.96, and the slope of the plot of 7-oxanorbornanes vs. C7 of norbornanes is 2.84. This factor of about three was related to the orbital expansion term $\langle r^{-3}\rangle$ in the expression for the paramagnetic shift. Thus oxygen is more electronegative than carbon, holds its electrons more closely, and has a larger paramagnetic effect. The Spiesecke–Schneider factor of 160 for ^{13}C, multiplied by 3, is 480, or very close to the average value that we have observed of about 500.

The extreme broadness of ^{17}O signals, coupled with its low natural abundance, may prevent ^{17}O NMR spectroscopy from becoming a practical method for measuring charge density on oxygen. The breadth of the signals is partially offset by the large shifts that accompany the introduction of negative charge. The consistency of the results reported herein suggests that improvement of experimental or instrumental factors may provide better results. Our measurements were made on an iron core magnet at 90 MHz. Clearly, some improvement in the experiment could be obtained by the use of superconducting field.

Conclusions

We have found that ^{13}C NMR spectroscopy provides a practical method for demonstrating the existence of dianions in solution and for measuring charge densities in these delocalized systems. In arylacetic acids, about a quarter of a negative charge is located on the benzylic carbon, and −0.1 to −0.28 in the aromatic ring, depending on aryl substitution. Placement of a S or SO_2 between the aryl group and the carbon α to carboxyl fully insulates the aryl ring from the charge. The charge density on the α-carbon increases to −0.3 to −0.5. In 2-indanone, each α-carbon bears a charge of about −0.2, and the aryl ring contains nearly −0.5. The increased delocalization of charge into the aryl ring results from the near planarity of the system, the absence of phenyl rotation, and the presence of only one oxygen atom. The keto esters ethyl 3-oxo-4-phenylbutanoate (**9**) and diethyl 3-oxo-1,5-pentanedioate (**8**) have about −0.2 on the α-methylene carbons, and in the case of **8** the phenyl ring bears only −0.1. These charge densities are strongly dependent on the identity of the cation and the solvent. The trend from K^+ to Na^+ to Li^+ in Me_2SO and to Li^+ in THF generally shows a loss of charge on carbon and a gain on oxygen, as the cation becomes more closely bonded to oxygen.

The charge densities on carbon were calculated from the chemical shift differences between the neutral and the dianions, divided by the Spiesecke–Schneider factor of 160 ppm/e^-. The charge densities on oxygen were calculated by difference from those on carbon. Comparison of these calculated values with the observed shifts in the ^{17}O spectra of four enriched dianions defines an analogous factor of about 500 ppm/e^- for oxygen. Because of extremely large line widths, this value still has a large variance.

Experimental Part

NMR spectra were obtained on a Varian CFT-20 (^{13}C), a JEOL FX-90Q (^{17}O), a Perkin-Elmer R20B (^1H), and a Varian T60 (^1H). IR spectra were recorded on a Perkin-Elmer 283. Melting points are uncorrected. In Me_2SO solution, the solvent was taken as the ^{13}C reference (40.5 ppm downfield from Me_4Si). In THF solution, Me_4Si was the ^{13}C reference. The ^{17}O reference in both solutions was external D_2O, and the values were corrected to ppm H_2O by subtraction of 3 ppm.

Preparation of Dianions in Me_2SO. Into a clean, dry NMR tube (either 8 or 10 mm) was placed a 4-mm sealed NMR tube containing D_2O for lock. This insert was placed in the center of the larger tube with a Teflon spacer constructed to allow free passage of solution. The substrate was then weighed into the NMR tube, which was capped with a rubber septum and sealed with Parafilm. The system was then alternately evacuated and filled with prepurified N_2 by means of a needle inserted through the septum. This cycle was repeated until all air had been replaced by N_2. The system, under N_2, was cooled in an ice bath, and a solution of $CH_3SOCH_2^-$ with either Li^+, Na^+, or K^+ in Me_2SO or of MeLi in THF was added slowly via syringe. This solution was then allowed to react slowly, with cooling when necessary. The NMR tube was shaken to mix the solution thoroughly. The spacer/insert assisted the mixing. The system was allowed to stand for about 30 min. The N_2 supply was then removed by pulling the needle out, and the spectra were then recorded. The dianions were prepared as 0.5–1.0 M solutions in 1–2 mL of solvent.

Recovery and Deuteration of the Starting Materials. To the dianion solution in the NMR tube, under N_2, was added 1.0 mL of D_2O with cooling. The mixture was then placed in a separatory funnel. The aqueous layer was made barely acidic with 1.0 M HCl and then was extracted with diethyl ether. The ether layer was washed several times with dilute HCl, dried, and concentrated under reduced pressure. The recovered starting material was then weighed and the deuteration assessed by ^1H NMR spectroscopy. Hydroxyl deuterium was exchanged under these conditions, and deuterium on carbon was found to be reduced during workup for several samples. Yields and extent of deuteration were as follows: phenylacetic acid (90% yield, 68% monodeuteration on CH_2), thiophenoxyacetic acid (66% yield, 95% monodeuteration on CH_2), (phenylsulfonyl)acetic acid (50% yield, 95% monodeuteration on CH_2), 2-indanone (89% yield, 95% monodeuteration on each CH_2), diethyl 3-oxo-1,5-pentanedioate (89% yield, no estimate of deuteration because of back exchange), and ethyl 3-oxo-4-phenylbutanoate (95% yield, 95% deuteration at the benzylic CH_2, 60% deuteration at CH_2 between the two carbonyls).

Purification of Me_2SO. In a 100-mL, round-bottomed flask was placed 50 mL of Me_2SO and 2.5 g of CaH_2. This solution was heated at 70 °C under N_2 for 2 h, and the Me_2SO was then distilled at 60 °C (0.5 mm). This dry Me_2SO was syringed into a 100-mL, round-bottomed flask containing 1.0 g of $NaNH_2$ and redistilled at 60 °C (0.5 mm).

Preparation of Solutions of LiH in Me_2SO. In a clean, dry, 50 mL, round-bottomed flask was placed 398 mg (50 mmol) of LiH. The flask was then sealed with a rubber septum and placed under N_2 by means of a needle. Purified Me_2SO (25 mL) was added slowly by syringe with cooling. The reaction solution was then allowed to come to room temperature.

Reaction of $NaNH_2$, NaH, or KH in Me_2SO. This procedure followed that used in preparing solutions of LiH in Me_2SO, with the exception of the base used. Particular care must be taken with KH, which is very

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reactive and evolves gas rapidly upon reaction.

Standardization of the Me_2SO Solutions. To 5.0 mL of a known amount of 1.0 M HCl was added 1.0 M of the Me_2SO solution with cooling. The resulting aqueous solution was titrated to an end point with 1.5 M NaOH.

Preparation and Standardization of the Solutions of Methyllithium in THF. A two-necked, 100-mL, round-bottomed flask was fitted with a gas inlet adapter, a rubber septum, and a magnetic stirring bar. The gas inlet was attached to either aspirator or N_2. To this system was added 50 mL of CH_3Li in diethyl ether. The ether was then removed under reduced pressure. The system was opened to N_2, and 25 mL of dry THF was added by syringe. The system once again was placed under reduced pressure, and the THF was removed. The system was then again opened, and 25 mL of THF was added by syringe.

Standardization of the Solutions. To 5.0 mL of dry benzene in a two-necked, 100-mL, round-bottomed flask was added a small crystal of 1,10-phenanthroline. One neck of the flask was fitted with a septum, and N_2 was brought in through a needle. In the second neck was placed a septum, through which was placed a buret containing 1.0 mL of *sec*-butyl alcohol in xylene. To the benzene was added 1.0 mL of the MeLi–THF solution. The *sec*-butyl alcohol was then used to titrate the solution to an end point.

(Phenylsulfonyl)acetic acid was prepared by the method of Pasto and co-workers.[16] The resulting solid was recrystallized in hexane: mp 109–111 °C (lit.[16] mp 113–114 °C); yield 40%, IR 1725, 1325, 1245, 1150 cm^{-1}.

Ethyl 3-oxo-4-phenylbutanoate was prepared by the procedure of Kiang et al.[17] The compound was purified with a silica gel column and $CHCl_3$ as the mobile phase: R_f 0.8; yield 27.8 g (47%); NMR ($DCCl_3$) δ 7.24 (s, 5, arom), 4.17 (q, 2, CH_2O), 3.83 (s, 2, $COCH_2CO$), 3.41 (s, 2, $PhCH_2CO$), 1.20 (t, 3, CH_3); IR 2980 (m), 1740 (s), 1715 (s) cm^{-1}.

Registry No. 1, dianion, 67157-48-6; **2**, dianion, 67157-44-2; **3**, dianion, 67157-50-0; **4**, dianion, 67157-49-7; **5**, dianion, 57557-41-2; **6**, dianion, 67157-45-3; **7**, dianion, 67157-47-5; **8**, dianion, 67157-46-4; **9**, dianion, 83026-88-4.

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Polymer Films on Electrodes. 10. Electrochemical Behavior of Solution Species at Nafion–Tetrathiafulvalenium Bromide Polymers

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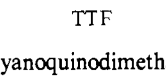
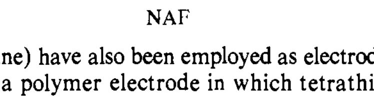
Received February 19, 1982

Abstract: The electrochemical behavior of solution species at electrodes consisting of a conductive polymer layer, produced by incorporation of tetrathiafulvalenium (TTF^+) bromide into the cation-exchange polymer Nafion, on various substrates (Pt, Ta, SnO_2, n-Si) is described. The voltammetric behavior of the solution species $Fe(CN)_6^{3-}$ and FeY^{2-} (where Y^{4-} = ethylenediaminetetraacetate) at the Nafion–TTF^+ electrodes was consistent with models of electrodes partially covered with electronically conductive sites. Microscopic investigation of the electrode showed that the incorporated TTF^+ forms electroactive domains and conductive nonelectroactive crystals from electrochemical cycling. The nonelectroactive crystals have the same stoichiometry as the one-dimensional organic conductor $TTFBr_{0.7}$. In the electrodeposition of copper onto the TTF^+ polymer electrode, most deposited on the $TTFBr_{0.7}$, indicating that they were the major source of electronic conduction within the polymer. When the TTF^+ polymer was applied to the surface of an n-type Si electrode, the lifetime of the semiconductor electrode for the photooxidation of Fe(II) species was improved.

Polymer electrodes consist of thin (~0.1–10 μm) polymer layers on conductive (metal or carbon) substrates.[1-3] These include polymers containing electroactive groups in the polymer backbone and polyelectrolyte layers in which electroactive ions are held by electrostatic binding.[2] In these materials charge is transported by diffusion and migration of the ions as well as by electron hopping between electroactive sites. Electronically conductive polymers[3] and the related one-dimensional organic metals[4] (e.g., TTF–TCNQ, where TTF is tetrathiafulvalene and TCNQ is tetracyanoquinodimethane) have also been employed as electrodes. We recently described a polymer electrode in which tetrathiafulvalenium (TTF^+) was incorporated into a layer of the perfluorinated sulfonate polymer Nafion (NAF) and proposed that charge transfer through this layer occurred by both electronic and ionic conduction (i.e., was a "biconductive" polymer layer).[5] The evidence for this electronic conductivity with incorporated TTF^+ was the significantly higher charge transfer through this layer compared to that of Nafion layers containing other ions, such as $Ru(bpy)_3^{2+}$. In this paper we describe more detailed studies of


TTF


$-(CF_2CF_2)_x(CFCF_2)_y-$ with $O(C_3F_6)OCF_2CF_2SO_3^-Na^+$ on CF

NAF

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