

References and Notes

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Relative Stabilities of Dications in Strong Acids. Calorimetric Study of Dications Formed from Diesters, Diketones, and Diacid Chlorides¹

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Abstract: The relative heats of protonation of a series of β - and γ -diketones, a series of diesters (RO—C(=O)—(CH₂)_n—C(=O)—OR) with $n = 1-4$, and the relative heats of formation of diacylium ions O=C⁺—(CH₂)_n—C⁺=O ($n = 1-8$) have been measured in 11.5 mol % SbF₅-FSO₃H, neat FSO₃H, or both. A large Baker-Nathan order is observed in substituted diketones. The diprotonated diketones and diesters are of identical stability while the monoprotection of a diketone is more exothermic than diester monoprotection. The heat of protonation of phenyl substituted diketones is less exothermic than alkyl substituted diketones, despite the fact that the absolute stability of the phenyl substituted ions is greater as evidenced by formation of dications under conditions where the alkyl substituted compounds are only monoprotected. In 11.5 mol % SbF₅-FSO₃H, clean formation of diacylium ions is observed at $n \geq 5$, alkyl substituted diketones $n \geq 2$, phenyl substituted diketones $n \geq 1$, and diesters $n \geq 2$. In neat FSO₃H, diprotonated diesters are stable with $n \geq 2$, and diprotonated diketones are stable in 11.5 mol % SbF₅-FSO₃H with $n \geq 2$. These observations are discussed.

With the development of superacid media, a variety of fascinating dications have been characterized.² To date, no thermodynamic stabilities have been measured. The most interesting cases are those in which two positive charges are delocalized in a single π system. However, ions which have two independent single positive charges are simpler to treat and will provide information about charge-charge repulsions which will be necessary for an understanding of the other dications. Accordingly, we have measured calorimetrically the relative stabilities of three series of dications. Our aim was to measure the effect of the charge separation and delocalization on the relative thermodynamic stabilities of the dications.

Results

Diacylium Ions. The ¹H NMR spectra of the species resulting from a series of linear diacid chlorides in superacids together with structural assignments are shown in Table I. The donor-acceptor complex can be distinguished from the cation by the presence of two types of methylene groups in the ¹H NMR spectra. The upfield protons are assigned to the complex. Included are Olah's data from SbF₅-SO₂ solutions.³ Dications in 11.5 mol % SbF₅ in FSO₃H are

formed cleanly at -60° for all diacid chlorides with $n \geq 3$ (n represents the number of methylene groups separating the two carbonyl groups). In the temperature range -20° to +37°, clean conversion of the diacid chloride precursors to diacylium ions only occurs for those compounds in which the two centers of positive charge are separated by five or more methylene groups. In the 11.5 mol % SbF₅ in FSO₃H acid media, succinyl chloride ($n = 2$) forms a monodonor-acceptor, monoacylium ion (2) at temperatures between -60 and +37°. Glutaryl chloride ($n = 3$) forms a dication (1) from -60 to -20° in this acid system. At temperatures above -20°, an equilibrium mixture of the dication (1) and a monodonor-acceptor, monoacylium ion is present. The ¹H

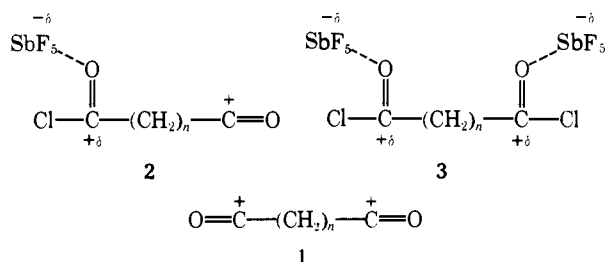


Table I. Proton Chemical Shifts^a of Diacylium Ions

Compd	Solvent	Temp, °C	H _α	H _β	H _γ	Structure
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{O}=\text{C}(\text{CH}_2)_n\text{C}=\text{O} \end{array}$	11.5 mol % SbF ₅ in FSO ₃ H	+20	4.59 (t, J = 7) 3.73 (q, J = 7)			2
	SbF ₅ -SO ₂ ^b	-17	4.60 (t, J = 7) 3.73 (q, J = 7)			2
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{O}=\text{C}(\text{CH}_2)_n\text{C}=\text{O} \end{array}$	11.5 mol % SbF ₅ in FSO ₃ H	-40	4.60	3.38		1
	11.5 mol % SbF ₅ in FSO ₃ H	+30	3.40	2.57		2, 1
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{O}=\text{C}(\text{CH}_2)_n\text{C}=\text{O} \end{array}$	SbF ₅ -SO ₂ ^b	-20, +25	3.08			1
	11.5 mol % SbF ₅ in FSO ₃ H	-20, +25	4.25	2.58		3, 1
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{O}=\text{C}(\text{CH}_2)_n\text{C}=\text{O} \end{array}$	SbF ₅ -SO ₂ ^b	-20	3.18	2.22		1
			1.20	2.52		

^a In parts per million. ^b From ref 3.

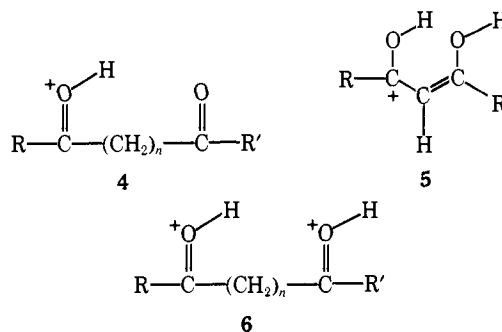
Table II. Relative Stabilities of Some Diacylium Ions and Complexes in 11.5 mol % SbF₅-FSO₃H Formed from

		$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{ClC}-(\text{CH}_2)_n-\text{CCl} \end{array}$			
n	Temp, °C	ΔH _{s,CCl₄}	ΔH _{s,acid}	ΔH _{Ttrans}	Structure
2	25	2.26 ± 0.05	-32.9 ± 0.5	-35.1 ± 0.5	2
3	+25	1.97 ± 0.05	-33.9 ± 0.5	-35.9 ± 0.5	2, 1
4	0		-34.1 ± 0.5	-36.0 ± 0.5	3, 1
4	+23	1.89 ± 0.05	-35.0 ± 0.5	-36.9 ± 0.5	3, 1
5	25	1.61 ± 0.06	-39.6 ± 0.3	-41.2 ± 0.3	1
6	25	1.81 ± 0.05	-39.4 ± 0.6	-41.2 ± 0.6	1
7	25	1.53 ± 0.10	-39.5 ± 0.4	-41.0 ± 0.4	1
8	25	1.26 ± 0.10	-39.5 ± 0.5	-40.7 ± 0.5	1

NMR of adipyl chloride (*n* = 4) indicates formation of an equilibrium mixture of the dication (1) form and a didonor-acceptor complex (3; at -30°, in this acid medium. For the diacylium ions with *n* ≥ 5, clean formation of diacylium ions (1) was observed, the NMR spectra agreeing with Olah's with allowance for solvent effects.

The relative stabilities of the diacylium ions and some complexes are shown in Table II. As before,⁴ the heats of solution and ionization in the acid, ΔH_{s,acid}, are combined with heats of solution in carbon tetrachloride (ΔH_{s,CCl₄}) to give the relative heats of ion formation from the indicated precursors in the acid (ΔH_{Ttrans}). In agreement with the ¹H NMR data, the relative stabilities of the ions O=C⁺-(CH₂)_n-C⁺=O where *n* ≥ 5 are the same. For the compounds with *n* = 2 and 3, the heat shown is for the formation of a pair of products. Using the relative amounts of the two from the NMR measurements and an additional assumption, a dissection of these into the heats of formation of the diacylium ion and complex could be made. However, the NMR studies and calorimetric studies are done at concentrations so different that we do not feel the equilibrium constant obtained at the ¹H NMR concentrations (ca. 1 M) will be valid at the lower calorimetric concentration (10⁻³ M). It has been established that organic ions present in NMR concentrations have an effect on the acidity of this medium.⁵

Diketones. The ¹H NMR spectra of a series of diketones protonated in various acids are shown in Table III. An examination of the literature^{6,7} reveals that several structures for mono- and diprotonated β-diketones are possible (structures 4-6). Many of the ions in Table III have not appeared in the literature and thus will be analyzed in detail. Spectra were run in the temperature range -60 to +37°. Low temperature spectra were used to verify mono- or diprotonation



on the basis of the hydroxyl proton peak areas. Many of the spectra showed considerable change in the temperature range studied. Using ¹H NMR, Brouwer⁶ has recently observed that, in FSO₃H or H₂SO₄, the ion formed by protonation of β-dicarbonyl compounds has the structure 5 when R is alkyl or aryl and 4 when R and R' are alkoxy. In stronger acid systems (HF-SbF₅, FSO₃H-SbF₅) where diprotonation takes place, the dication has structure 6.^{6,7}

The monocation (5) formed from the protonation of β-diketones can be identified by the presence of only one hydrogen in the central "methylene" group and the downfield shift of the proton resonances relative to a CCl₄ solution of the unprotonated diketone. The existence of dications of structure 6 formed in FSO₃H-SbF₅ mixtures from the diketones is indicated by the chemical shift data, specifically the very low downfield absorption for the methylene group, and the integrated peak areas of both the methylene and the hydroxy groups. For example, the diprotonated form of 2,4-pentadione (R = Me in 6) would have peak areas corresponding to two methylene protons and two hydroxy protons. Using these data, it was obvious that only monoprotection of the alkyl-substituted β-diketones was achieved in either FSO₃H or 11.5 mol % SBF₅ in FSO₃H at -60°. In the latter solvent when R or R' was aryl, diprotonation occurred. At temperatures above 25°, β cleavage of the monoprotectioned species occurred. Subsequent condensation of the methyl ketones then took place. When additional SbF₅ was added, diprotonation of the alkyl diketones was achieved at -60°. As the probe temperature was raised, these spectra changed to a monocation-dication equilibrium mixture and eventually (*T* ≈ 0°) underwent β cleavage to the corresponding acylium ion and protonated methyl ketone. For example, with 3,5-heptanedione, the presence of three ethyl groups, one for the monocation, one for the acylium ion, and one for the protonated methyl ethyl ketone confirms this behavior. Protonated methyl ethyl ketone shows absorptions at δ 3.1 (α-CH₃), 1.4 (β-CH₃), and 3.5 (α-CH₂). The ethyl acylium ion absorbs at δ 4.4 (α-CH₂),

Table III. Proton Chemical Shifts (in ppm) for Diketones in Strong Acid Media^{a,g}

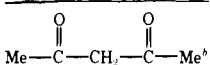
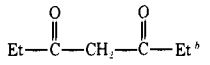
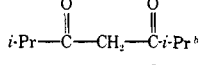
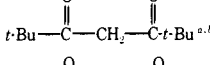
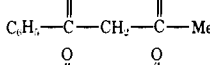
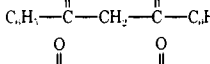
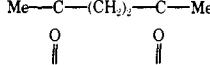
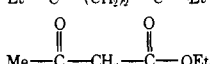
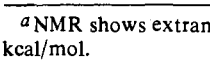
Compd	Temp, °C	OH	R			CH ₂ (CH)	Other groups	Solvent	Structure	
			CH	CH ₂	CH ₃					
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Me}$	37				2.45 (s,7)	6.00 (s, 1)		H ₂ SO ₄ , FSO ₃ H	5	
	-60 → 10	12.0 (s, 1)			2.65 (s, 7)	6.30 (s, 1)		11.5 mol % SbF ₅ in FSO ₃ H	5	
	-60				3.45 (s, 7)	5.50 (s, 2)		1:1 SbF ₅ -FSO ₃ H-SO ₂	6	
$\text{Et}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Et}$	37			2.9 (q, 4, J = 7)	1.42 (t, 5, J = 7)	6.30 (s, 1)		H ₂ SO ₄ , FSO ₃ H	5	
	-60 → 10		12.2 (s, 1)	3.0 (q, 4)	1.50 (t, 7)	6.40 (s, 1)		11.5 mol % SbF ₅ in FSO ₃ H	5	
	-60			3.8 (q)	1.65 (t)	5.40 (s)		Increased concn SbF ₅ in FSO ₃ H	6	
	0 → 25			2.9 (q)	1.40 (t)	6.25 (s)		Increased concn SbF ₅ in FSO ₃ H	5	
					3.8 (q)	1.40 (t)	5.40 (s)			
					4.2 ^b (q)	2.0 (t)		3.1 ^c (s)		
$i\text{-Pr}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-i\text{-Pr}$	37		3.00 (m)		1.42 (d)	6.31 (s, 1)		H ₂ SO ₄ , FSO ₃ H	5	
	-60 → 10	12.3 (s, 1)	3.10 (m, 3)		1.50 (d, 15)	6.3 (s, 1)		11.5 mol % SbF ₅ in FSO ₃ H	5	
	-60		3.80 (br, 2)		1.74 (d, 17)	5.45 (s, 2)		Increased concn SbF ₅ in FSO ₃ H	6	
	0 → 25		<i>d</i>		1.50 (d, 19)	6.35 (s, 1)		Increased concn SbF ₅ in FSO ₃ H	5	
				3.80 (br, 2) <i>d</i>		1.75 (d, 14)	5.40 (s, 2)			
					2.05 (d) ^f		3.1 ^{d,f} (s)			
$t\text{-Bu}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-t\text{-Bu}$	37				1.45 (s, 18)	6.45 (s, 1)		H ₂ SO ₄ , FSO ₃ H	5	
	-60, 0	12.4 (br)			1.45 (s, 18)	6.45 (s, 17)		11.5 mol % SbF ₅ in FSO ₃ H	5	
	-60	14.8 (br)			1.80 (s)	5.50 (s, 2)		1:1 SbF ₅ -FSO ₃ H-SO ₂	6	
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$	37				2.70 (s, 3)	6.83 (s, 1)	7.85 8.57 (m,6)	H ₂ SO ₄ , FSO ₃ H	5	
	-60, 0				3.50 (s)	6.00 (s)	-8.05 -8.60 (m)	11.5 mol % SbF ₅ in FSO ₃ H	6	
$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$	37					7.11 (s, 1)	7.74 8.12 (m, 11)	H ₂ SO ₄ , FSO ₃ H	5	
	-60, 0	-14.2 (s)				6.05 (s)	-8.05 -8.60 (m)	11.5 mol % SbF ₅ in FSO ₃ H	6	
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Me}$	37				-2.75 (s, 7)	-3.45 (s, 4)		H ₂ SO ₄ , FSO ₃ H	4	
	37				-3.05 (s, 7)	-3.80 (s, 4)		11.5 mol % SbF ₅ in FSO ₃ H	6	
	-60, 0				-3.30 (s, 7)	-4.20 (s, 4)				
$\text{Et}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Et}$	37			-3.10 (q, 4)	-1.36 (t, 6)	-3.40 (s, 4)		H ₂ SO ₄ , FSO ₃ H	4	
	-60, 0	-14.8 (s)		-3.55 (q, 4)	-1.65 (t, 6)	-4.10 (s, 4)	3.9 ^e	11.5 mol % SbF ₅ in FSO ₃ H	6	

^aJ = 7 wherever coupling is reported. ^bPeaks for ethyl acylium ion. ^cMethyl peak of methyl ethyl ketone, CH₃ (1.45) CH₂ (3.70). ^dPosition of the septets not locatable. ^ePeak for isopropyl acylium ion. ^fIf no peak is reported, it was not possible to measure accurately. ^gIntegrated peak area rounded off to nearest whole number.

2.0 (β-CH₃). These values are very close to those reported in Table III for 3,5-heptandione in 11.5 mol % SbF₅ in FSO₃H at 25°. In the case of diketones in which the car-

bonyl groups were separated by two methylene groups, the dication was formed in 11.5 mol % SbF₅-FSO₃H, as shown by the chemical shift data and the integrated peak areas. In

Table IV. Relative Heats of Protonation of Some Diketones in FSO₃H and in 11.5 mol % SbF₅-FSO₃H (MA) from Both Ketone and Enol Standard States

Compd	$\Delta\bar{H}_{s,CCl_4}$	$\Delta H_{s,FSO_3H}$	$\Delta H_{T,E}$	ΔH_{TK}	Structure	$\Delta\bar{H}_{s,MA}$	ΔH_{TE}	ΔH_{TK}	Structure
	0.80 ± 0.05	-21.4 ± 0.4	-21.9	-24.0	5	-25.3 ± 0.7	-25.8	-27.9	5
	0.51 ± 0.09	-21.2 ± 0.2	-21.4	-23.5	5	-25.9 ± 1.0	-26.1	-28.2	5
	0.38 ± 0.08	-20.7 ± 0.4	-21.0	-23.8	5	-24.6 ± 0.5	-24.9	-27.7	5
	0.17 ± 0.03	-18.5 ± 0.4	-18.6	-21.9	5	-22.3 ± 0.6	-22.4	-25.7	5
	+6.35 ± 0.14	-15.9 ± 0.2	-22.2 ± 0.2		5	-29.1 ± 1.0	-36.4 ± 1.0		6
	+5.95 ± 0.30	-12.7 ± 0.4	-18.6 ± 0.4		5	-28.8 ± 1.0	-34.7 ± 1.0		6
	+0.88 ± 0.09	-32.8 ± 0.2		-33.7 ± 0.2	6	-38.3 ± 0.5		-39.2 ± 0.5	6
	-0.72 ± 0.10	-29.9 ± 0.7		-30.6 ± 0.7	6	-36.2 ± 0.7		-36.9 ± 0.7	6
	+1.32 ± 0.05					-36.8 ± 0.6		-40.1 ± 0.6	6

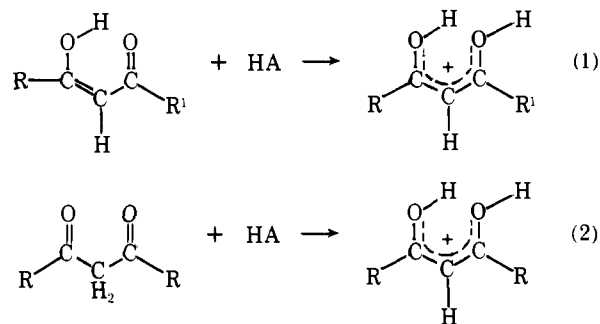
^a NMR shows extraneous peak at ca. 3.98. ^b The values for $\Delta H_{T,E}$ for these compounds in Table I, ref 8, are too exothermic by 0.6 kcal/mol.

H₂SO₄, only monoprotonation was achieved while, in FSO₃H, these molecules eventually underwent cleavage similar to the β diketones.

Heats of protonation of a series of dicarbonyl compounds were measured using the basic calorimetric procedures described for the acylium ions. The heats of solution (ΔH_s) were measured at 25° for the diketones in neat FSO₃H and at 10° in 11.5 mol % SbF₅ in FSO₃H. ΔH_s for the diesters was measured at 25° in neat FSO₃H while, in 11.5 mol % SbF₅ in FSO₃H, the calorimeter temperature was 10°. All $\Delta\bar{H}_{s,CCl_4}$ were measured at 25°. The data for some of the diketones were taken from the literature.⁸

The relative heats of protonation of the diketones in FSO₃H and in 11.5 mol % SbF₅-FSO₃H are shown in Table IV. There are some difficulties with the standard state for the β -diketones. Several of them exist as the enol, and not enough data are available to correct this to the ketone standard state. The data in Table IV have been corrected to the enol or ketone standard state using the enthalpy cycle previously employed.⁸ This was done in order to have data directly comparable to those for the diesters. In correcting the data, the heat of keto-enol tautomerism and the equilibrium constants in carbon tetrachloride are necessary. These are not available so the equilibrium constants for the neat diketones were used.⁹ The enthalpies were estimated by assuming that the entropy of isomerization was the same for these β -diketones as for 2,4-pentanedione (3.4 eu). While these corrections introduce some uncertainty, particularly for protonation of the compounds as diketones rather than as enols, the substituent effects are much larger than any possible error in the correction. Heats of transfer of the β -diketones reported in Table IV and referring to the enol as standard state are for the reaction shown in eq 1, and those referring to the ketone form as standard state are for the reaction shown in eq 2.

Diesters. Determination of the structures of the cations formed when a series of diesters was protonated in various strong acid solvents was accomplished using chemical shift data and the integrated peak area of the OH group. The



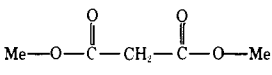
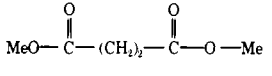
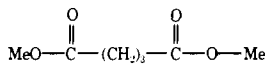
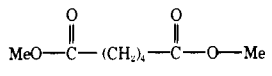
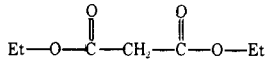
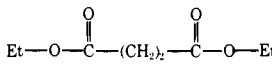
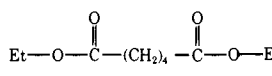
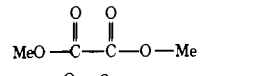
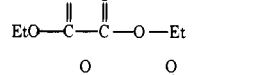
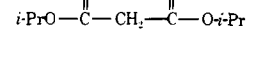
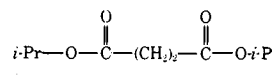
data are shown in Tables V and VI. The monocations formed in these cases exist in two forms which rapidly equilibrate and exchange protons with the acid solvent. This prevents the observation of the OH signal so the structural assignment has to be based on comparison of the methylene absorption with reported literature values.^{6,7,10}

At temperatures below 0°, the β -diesters formed dications in 11.5 mol % SbF₅ in FSO₃H as indicated by the downfield shift of the proton absorptions relative to the unprotonated forms. Furthermore at -60°, the OH signal was observable and integration of the peak area showed two protons present. As in the case of the diketones, separation of the carbonyl groups by two or more methylene groups resulted in diprotonation of the diesters. Unlike the diketones, clean diprotonation was observed in both FSO₃H and 11.5 mol % SbF₅ in FSO₃H. In all cases this was shown by the chemical shift values and the integrated peak areas of the OH group. Clean spectra of monoprotonated diisopropyl malonate were not obtained. Even at -60° the spectrum showed large peaks corresponding to protonated isopropyl alcohol. Diisopropyl succinate was clearly monoprotonated at -60°, but warming to -30° produced protonated isopropyl alcohol. Both the malonate and the succinate decomposed to unidentifiable products when warmed to 0°.

Several β -diesters with substituents on the methylene group between the two carbonyls were investigated (Table V). Using the same procedures as those for the simple diest-

Table V. Proton Chemical Shifts (in ppm) for Diesters in Strong Acid Media^a

$$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\alpha}{\text{CH}_2}-\overset{\beta}{(\text{CH}_2)_{n-2}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}$$

Compd	Temp, °C	OH	R		α -	β -	Solvent	Structure
			CH ₂	CH ₃	CH ₂	CH ₂		
	37			4.35 (s, 6)	4.10 (s, 2)		FSO ₃ H	Monoprotonated
	24			4.40 (s, 6)	4.25 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Monoprotonated
	0			4.85 (s, 6)	4.92 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	-60	13.9 (s, 6)		4.85 (s, 6)	4.95 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	37			4.71 (s, 6)	3.73 (s, 4)		FSO ₃ H	Diprotonated
	-60	13.4 (s, 2)		4.70 (s, 7)	3.70 (s, 4)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	37			4.70 (s, 6)	3.3 (t, 2)	2.2 (m, 4)	FSO ₃ H	Diprotonated
	-60, 0	12.9 (s, 2)		4.65 (s, 6)	3.25 (t, 2)	2.45 (m, 4)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	37			4.68 (s, 6)	2.80 (m, 4)	1.95 (m, 4)	FSO ₃ H	Diprotonated
	-60, 0			4.70 (s, 6)	2.81 (m, 4)	1.95 (m, 4)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	-60, +37		4.89 (q, 4, J = 7)	1.62 (t, 6, J = 7)	4.05 (s, 2)		FSO ₃ H	Monoprotonated
	+24		4.95 (q, 4)	1.65 (t, 6)	4.28 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Mixture (mono- and diprotonated)
	0		5.01 (q, 4)	1.68 (t, 6)	4.58 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Mixture (mono- and diprotonated)
	-60		5.10 (q, 4)	1.73 (t, 6)	4.60 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	37		5.12 (q, 4)	1.68 (t, 7)	3.65 (s, 2)		FSO ₃ H	Diprotonated
	0		5.12 (q, 4)	1.72 (t, 6)	3.16 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	-60	13.0 (s, 2)	5.14 (q, 4)	1.73 (t, 6)	3.65 (s, 2)		11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	37		5.08 (q, 4)	1.68 (t, 6)	3.12 (m, 4)	2.00 (m, 4)	FSO ₃ H	Diprotonated
	-60, 0	12.3 (s, 2)	5.11 (q, 4)	1.72 (t, 6)	3.15 (m, 4)	2.02 (m, 4)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
	-60			4.60 (q, 4)			11.5 mol % SbF ₅ in FSO ₃ H	Monoprotonated
	-60		5.10 (q, 4)	1.70 (t, 6)			11.5 mol % SbF ₅ in FSO ₃ H	Monoprotonated
	-60, 0		5.6 (h)	1.65 (d)			FSO ₃ H	Diprotonated
	-60, -30		6.4 (h)	1.75 (d)		4.30 (s, 2)	FSO ₃ H	Monoprotonated
			5.6	1.65		4.30	11.5 mol % SbF ₅ in FSO ₃ H	Monoprotonated
		6.4	1.75		4.30	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated	
	-30		6.00 (m)	1.73 (d)		3.60 (s, 2)	FSO ₃ H	Monoprotonated
	0		6.00 (m)	1.73 (d)		3.60 (s, 2)	FSO ₃ H	Monoprotonated
	-60	12.7	5.40 (m)	1.65 (d)		3.40 (s, 2)	FSO ₃ H	Diprotonated
			6.00	1.75		3.60	11.5 mol % SbF ₅ in FSO ₃ H	Monoprotonated

^aJ = 7 wherever coupling is indicated by splitting of the absorption signal; integrated peak area is rounded off to the nearest whole number; if no peak is reported, it was not possible to measure accurately; d = doublet; q = quartet; h = heptet; s = singlet; t = triplet; m = multiplet.

ers, it was determined that these compounds were diprotonated in 11.5 mol % SbF₅ in FSO₃H, while only monoprotection occurred in neat FSO₃H.

Ethyl acetoacetate and acetyl acetate were diprotonat-

ed in 11.5 mol % SbF₅ in FSO₃H and monoprotection in neat FSO₃H.

The diethyl esters of fumaric and maleic acid have been investigated in various strong acid media and showed mark-

Table VI. Proton Chemical Shifts (in ppm) for Miscellaneous Compounds in Strong Acid Media^a

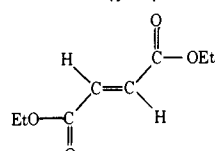
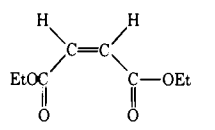
$$1. \text{CH}_3\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}_1}{\underset{\text{R}_2}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$$

Compd	Temp, °C	CH ₂	CH ₃	R ₁	R ₂	Solvent	Structure
R ₂ = H; R ₁ = Me	-40, 0	4.75 (q, 4)	1.60 (t, 6)	4.05 (q, 1)	1.80 (s, 3)	FSO ₃ H	Monoprotonated
	-40, 0	5.00 (q, 4)	1.70 (t, 6)	4.20 (q, 1)	2.00 (d, 4)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
R ₁ = Me; R ₂ = Me	-40, 0	4.85 (q, 4)	1.60 (t, 6)	1.85 (s, 3)	1.85 (s, 3)	FSO ₃ H	Monoprotonated
	-60, 0	5.00 (q, 4)	1.70 (t, 7)	1.90 (s, 3)	1.90 (s, 3)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
R ₁ = H; R ₂ = Ph	-60, 0	5.40 (q, 4)	1.80 (t, 6)	5.90 (s, 1)	7.80 (m, 7)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated

$$2. \text{R}_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}_2$$

Compd	Temp, °C	OH	R ₁	R ₂		Solvent	Structure	
				CH ₂	CH ₃			
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Et}$	+37		2.80 (s, 3)	4.40 (s, 2)	4.83 (q, 2)	1.62 (t, 3)	FSO ₃ H	Monoprotonated
	-60, 0	13.9	3.40 (s, 3)	5.30 (s, 2)	5.50 (q, 2)	1.85 (t, 3)	11.5 mol % SbF ₅ in FSO ₃ H	Diprotonated
$\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Me}$	+37		2.80 (s, 2)	5.40 (s, 3)		2.80 (s, 3)	FSO ₃ H	Monoprotonated
	-60, 0	14.3	2.90 (s, 2)	6.10 (s, 3)		3.20 (s, 3)	11.5 mol % SbF ₅ in FSO ₃ H	Mixture (mono- and diprotonated)

Table VII. Relative Heats of Protonation for Diesters in FSO₃H

Compd	Temp, °C	ΔH _T	ΔH _P	ΔH _{s,CCl₄}	Protonation	
$\text{MeO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_n-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Me}$	n = 1	25	-21.3 ± 0.1	-19.6 ± 0.1	+1.65 ± 0.05	Mono
	n = 2	25	-30.2 ± 0.4	-29.0 ± 0.4	+1.22 ± 0.07	Di
	n = 3	25	-33.3 ± 0.2	-32.6 ± 0.2	+0.74 ± 0.04	Di
$\text{EtO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_n-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Et}$	n = 1	25	-19.4 ± 0.3	-18.6 ± 0.3	+0.82 ± 0.00	Mono
	n = 2	25	-30.8 ± 0.3	-30.2 ± 0.3	+0.54 ± 0.01	Di
	n = 3	25	-33.7 ± 0.4	-33.7 ± 0.4	+0.00 ± 0.00	Di
	n = 4	25	-33.6 ± 0.6	-33.6 ± 0.6	+0.00 ± 0.00	Di
	25	-23.2 ± 0.5	-22.8 ± 0.5	+0.38 ± 0.03	Mono	
	25	-20.7 ± 0.7	-19.7 ± 0.7	+1.02 ± 0.05	Mono	
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Et}$	25	-17.0 ± 0.2	-17.0 ± 0.2	+0.00 ± 0.00	Mono	

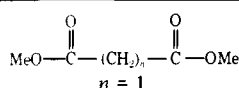
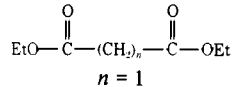
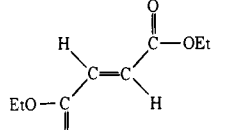
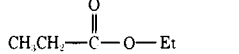
edly different behavior.¹¹ The chemical shift data indicated that, at -80° in FSO₃H, diethyl maleate is monoprotonated while the fumarate is diprotonated. At 0°, however, both species are only monoprotonated. In 11.5 mol % SbF₅ in FSO₃H, both are diprotonated.

Relative heats of protonation of the diesters in neat FSO₃H and in 11.5 mol % SbF₅-FSO₃H are shown in tables VII and VIII.

Discussion

The effect of charge-charge repulsion is well known in organic chemistry. Extensive study of the ionization of dicarboxylic acids has shown that this effect falls off with increasing distance between the centers of charge and remains essentially constant once a minimum distance is achieved.^{12,13} Few studies of the effect of charge-charge re-

Table VIII. Relative Heats of Protonation for Diesters in 11.5 mol % SbF₅ in FSO₃H

Compd	Temp, °C	ΔH_T	ΔH_P	$\Delta H_{S,CCl_4}^a$	Protonation	
 $n = 1$	5	-31.7 ± 0.6	-30.0 ± 0.6	$+1.65 \pm 0.05$	Mono-di	
	-60	-35.4 ± 1.8	-33.7 ± 1.8		Di	
	$n = 2$	8 ^b	-42.2 ± 2.1	-41.0 ± 2.1	$+1.22 \pm 0.03$	Di
		20	-45.3 ± 0.9	-44.0 ± 0.9	$+1.22 \pm 0.03$	
	$n = 3$	7	-47.8 ± 0.3	-47.1 ± 0.3	$+0.74 \pm 0.04$	Di
 $n = 1$	3	-32.2 ± 1.0	-31.2 ± 1.0	$+0.82 \pm 0.0$	Mono-di	
	-60	-36.4 ± 1.8	-35.7 ± 1.9		Di	
	$n = 2$	4	-35.8 ± 1.0	-35.2 ± 1.0	$+0.57 \pm 0.01$	
	$n = 3$	8	-47.6 ± 0.8	-47.6 ± 0.8	$+0.00 \pm 0.00$	Di
	$n = 4$	24	-48.6 ± 1.2	-48.7 ± 1.2	$+0.00 \pm 0.00$	Di
	0	-33.7 ± 0.9	-33.4 ± 0.9	-0.38 ± 0.03	Di	
	0	-32.9 ± 0.6	-31.9 ± 0.6	$+1.02 \pm 0.05$	Di	
	7	-21.5 ± 1.7	-21.5 ± 1.7	$+0.00 \pm 0.00$	Mono	

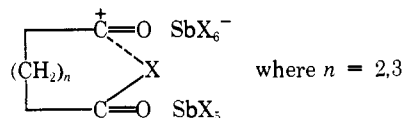
^a Measured at 25°C. ^b Introduced as a supercooled liquid.

pulsion in carbon dications have been reported. Thus, the purpose of this study was to investigate the effect of the following factors on charge-charge repulsion: 1. distance between the charged centers; 2. dispersion of charge at the cationic centers by alkyl, aryl, and alkoxy groups.

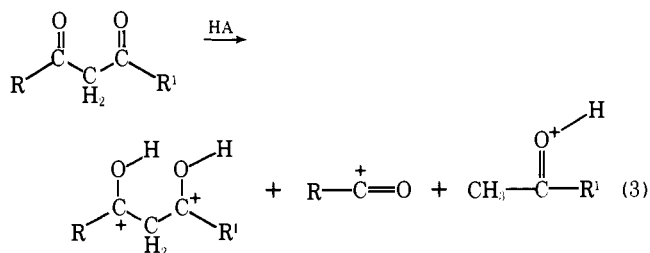
The observation by Olah³ that diacylium ions were formed starting with glutaryl fluoride in SbF₅-SO₂ solutions made the series of dicarboxylic acid halides ideal for studying the energies involved in charge-charge repulsions. However, it became readily apparent that, in 11.5 mol % SbF₅ in FSO₃H, the dications were only stable at very low temperatures (-30 to -60°). Thus, at the temperature used for calorimetric analysis (0 and 25°), a dichotomy of behavior was observed for the diacid chlorides in 11.5 mol % SbF₅ in FSO₃H. The ¹H NMR data (Table I) showed that the dications were only formed when the two centers of positive charge were separated by five or more methylene groups. The calorimetric data (Table II) reflect this trend in that the adipoyl compound ($n = 4$) is ca. 4 kcal/mol less stable than the pimiloyl compound ($n = 5$), and the same heat is observed for all compounds with $n \geq 5$. The similarity in the heats of formation of the diacylium ions and the mono-donor-acceptor complex indicates that the enthalpies for the two processes are similar. Also, the relative heats of formation of the diacylium ions with $n \geq 5$ might be expected to be twice that of Et-C⁺=O ($\Delta H_{R^+} = -19.4 \pm 0.3$).¹⁴ Actually, they are slightly more exothermic than that, yet less exothermic than twice the value for the acetyl cation (-21.2 ± 0.2).¹⁴ It is apparent that the two charges are quite independent.

It should be noted that a small discrepancy between the ¹H NMR data reported here and that of Olah and Comisarow³ exists. That is, the ¹H NMR spectra of adipoyl chloride is essentially identical in both acid media. However, both spectra contain a distorted triplet at about δ 3.2 which Olah and Comisarow do not report in their ¹H NMR data. It is believed that this peak along with the partially hidden multiplet at ca. 2.2 represents a dicomplex. The ¹H NMR

data in Table I show that, although glutaryl ($n = 3$) chloride forms a dication at low temperature in both acid media, upon warming this becomes a monodonor-acceptor monoacylium ion in 11.5 mol % SbF₅ in FSO₃H. The glutaryl ($n = 3$), like the succinyl ($n = 2$) compound, tends to form a monodonor-acceptor complex monoacylium ion, presumably due to the fact that stabilization through a cyclic species is possible.³



Monoprotonated diketones are, in general, very stable species, undergoing no significant changes in the temperature range -60 to +25°. At temperatures above this, cleavage occurs followed by condensation of the simple ketone formed in the cleavage. Diprotonated diketones are considerably less stable in the temperature range -60 to +25°. The diketones tended to form equilibrium mixtures of the mono- and diprotonated forms when the temperature was raised above -20°. Subsequent warming of a diprotonated diketone above 0° resulted in cleavage to an acylium ion and protonated methyl ketone as shown in eq 3.

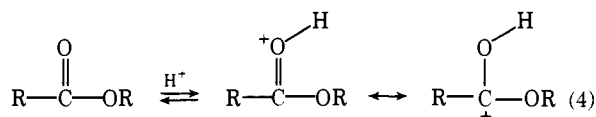


The γ -diesters showed a pattern of behavior similar to the diketones, although the acid strength necessary to achieve diprotonation was less than for the β -diketones. The

calorimetric data (Table IV) show a larger Baker-Nathan effect in neat FSO₃H and in 11.5 mol % SbF₅ in FSO₃H for the β-diketones. This has been discussed previously.⁸ Although it was not possible to examine the diisopropyl or di-*tert*-butyl γ-diketones due to difficulties in synthesizing these compounds, it appears from the dimethyl and diethyl cases that a Baker-Nathan effect is present in the diprotonated γ-diketones.

The ¹H NMR data in Table III show that diprotonation for the mono- or diphenyl substituted β-diketones is achieved under conditions where the dialkyl substituted diketones are only monoprotated. This indicates that, as expected, phenyl groups are more efficient in dispersing charge in these ions than an alkyl group. In direct contrast, a comparison (Table IV) of the heats of transfer of methyl vs. phenyl substituted diketones reveals a marked destabilization when methyl is replaced by phenyl. This is true both in the monoprotated and the diprotonated form. These contrasting facts further support the notion that the less exothermic heats of transfer (when methyl is replaced by phenyl) encountered here and in other systems^{8,15,16} are due largely to ground state interaction in the phenyl substituted compounds. An argument based on steric hinderance to solvation¹⁷ or ion size⁸ will also rationalize these data. Comparison of the heats of diprotonation of the γ-diketones in FSO₃H with those for acetone (−19.1 ± 0.1)¹⁸ and 2-pentanone (−18.8 ± 0.2)¹⁸ reveals that significant repulsive interactions reduce the stability of the diions by ca. 5.5 kcal/mol. The monoprotation of the diketones is significantly more exothermic than that of a monoketone. It seems likely that this is due to hydrogen bonding to the unprotonated oxygen atom.

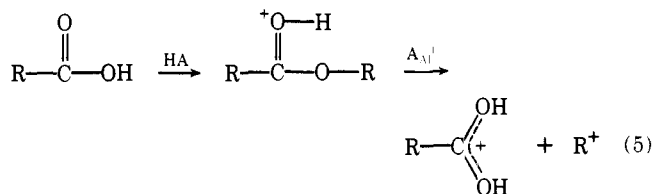
In protonated diesters, the positive charge can be delocalized onto the alkoxy groups and the effects of charge-charge repulsion should be less than in the diketones. It has been shown that protonation of diesters in strong acid media occurs on the acyl oxygen atom.¹⁰ In the acid systems employed here, the equilibrium between the ester and its protonated form shown in eq 4 lies far to the right. Olah



and Westerman¹⁹ have pointed out that the chemical shifts (preferably ¹³C, but also ¹H) should represent the weighted average of the cationic species and the ester form with which it is in equilibrium. Furthermore, these authors have argued that, in acid systems containing less than an equimolar amount of SbF₅ in FSO₃H (such as the 11.5 mol % acid used in this study), for some esters the equilibrium does not lie as far to the right. A comparison of our ¹H NMR chemical shifts with the values of Olah and Westerman indicates that, in diethyl malonate (where charge-charge repulsions are expected to be significant), the equilibrium between the mono- and diprotonated forms does shift toward the monoprotated ester as the acid strength is decreased. It should not be overlooked that at −60° (see Table V) dimethyl and diethyl malonate were diprotonated in both 11.5 mol % SbF₅ in FSO₃H and the equimolar acid employed by Olah and Westerman. With diesters having *n* = 2, the difference in chemical shifts between the protonated and neutral precursor indicates that the equilibrium point, insofar as it can be measured by ¹H NMR, is the same for the FSO₃H and its mixtures with SbF₅ and the esters are diprotonated. It has been observed previously by Gillespie^{20,21} that the acidity of 10 mol % SbF₅ in FSO₃H is essentially the same as a 1:1 equimolar mixture of SbF₅ in FSO₃H. For all cases in which a comparison is possible, the

proton chemical shifts reported by Olah in SbF₅-FSO₃H-SO₂ are ~0.5 ppm further downfield than those we observe. The reason for this large solvent effect is not clear.

The ¹H NMR data for the diesters in Table V confirm the fact that these compounds are better able to minimize charge-charge repulsions than the diketones. For example, the acid strength required for diprotonation (FSO₃H) of the malonate (*n* = 1) esters is significantly less than for the diketones in which *n* = 1. Furthermore, the malonates were stable in their diprotonated form to a higher temperature than the analogous diketones in every case. Not surprisingly, it was found that, when the temperature was raised above 0°, the diisopropyl esters deteriorated rapidly and irreversibly to give unidentifiable products.²² Esters of secondary or tertiary alcohols are known to cleave by an A_{AL}1 mechanism to give protonated acids and carbonium ions.¹⁷



The calorimetric data for the diesters in both FSO₃H and 11.5 mol % SbF₅ in FSO₃H show some interesting behavior. It has been previously mentioned that dications from the diacid chlorides showed no charge-charge repulsion when the two centers were separated by 5 or more methylene groups. With the diesters, the effect of charge-charge repulsion is negligible once the two centers of positive charge are separated by three or more methylene groups. However, the value is somewhat larger than twice the heat of protonation of ethyl acetate (−17.4 ± 0.1). Ethyl propionate would be a better model compound. This certainly emphasizes the effect that spreading the charge at the individual cationic centers has on charge-charge repulsions. The data on the dimethoxy esters in Tables VII and VIII are particularly relevant to this point, as are the diethoxy compounds.

The lack of substituent effect when ethoxy replaces methoxy in this series of compounds may be significant. However, since the *i*-Pr and *t*-Bu diesters could not be studied calorimetrically, the existence of a normal substituent order (rather than a Baker-Nathan order) for these compounds could not be confirmed.

Diethyl fumarate is apparently more stable than diethyl maleate both in the monoprotated form and the diprotonated forms. Furthermore, a comparison of these compounds with the saturated analog diethyl succinate in FSO₃H shows that the ethylene linkage has a considerable destabilizing effect. This is based on the fact that the ¹H NMR data indicate only monoprotation in the case of the fumarate and maleate, while the succinate is cleanly diprotonated. The calorimetric data also reflect this trend.

A comparison of the heats of protonation for the diketones and diesters is interesting. As previously observed,^{9,18} ester protonation is less exothermic. The greater ease of formation of the diprotonated esters certainly indicates greater absolute stability than found with the protonated ketones. Once again we have a situation in which the heat of protonation to give the most stable ion is least exothermic. The necessary solvent effects can be combined to yield a rationalization and our knowledge of solvent effects in these systems too inadequate to support or refute a solvent based explanation. Alternatively, if replacing an alkyl group by an alkoxy stabilized both ground state and the ion, but stabilized the ground state more, the observed pattern would be produced.

Experimental Section

The calorimeter and its operations have been previously described.^{4,8} Most of the compounds were commercially available. Liquid were dried over molecular sieves (Linde 4A) and distilled. Solids were recrystallized and vacuum dried over P₂O₅. Those acid chlorides not available were prepared from the corresponding acid with SOCl₂. All diketones were commercially available except for 2,6-dimethyl-3,5-heptanedione²³ and 3,6-octanedione²⁴ which were prepared using standard techniques. Those diesters not commercially available were prepared from the corresponding diacid chloride and the appropriate alcohol.

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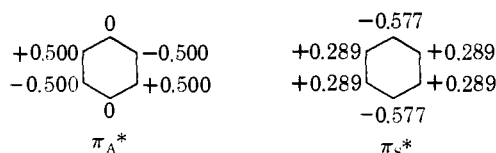
Bonding Studies in Group 4 Substituted Anilines. VI. Assignment of Coupling Constants and CNDO/2 Description of the Radical Anions of *o*-, *m*-, and *p*-Trimethylsilyl-*N,N*-dimethylaniline¹

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Abstract: The radical anions of *o*-, *m*-, and *p*-trimethylsilyl-*N,N*-dimethylaniline, generated by reduction with potassium in mixed ether solvents at low temperatures, have been studied by ESR spectroscopy. By metallation and lithium-halogen exchange reactions, appropriate deuterated and methylated analogs have been prepared, which permit unambiguous experimental assignment of all the hyperfine coupling constants for the radical anions. In every case, the highest spin density is shown to occur at the ring position para to the trimethylsilyl substituent. The coupling constants are consistent with a mixing of the symmetric and antisymmetric π^* orbitals of benzene and are correlated with the π spin densities obtained from CNDO/2 calculations. In spite of the strongly electron-donating dimethylamino group, the trimethylsilyl group is the major influence on the spin distributions in the radical anions. Based on the CNDO/2 results, the effect is apparently due to large interactions of both the silicon p and d orbitals with the aromatic π^* system.

The technique of electron spin resonance (ESR) spectroscopy has been widely applied to the investigation of substituent effects in monosubstituted benzene derivatives² and multiply substituted aromatics.^{3,4} Substitution at the benzene nucleus removes the degeneracy of the lowest lying π^* (e_{2u}) orbitals of benzene giving rise to radical anions of substituted benzenes in which the unpaired electron is found in a predominantly antisymmetric (A) or symmetric (S) state.^{2a} Electron-donating substituents such as alkyl substitu-



ents cause only small perturbations of the benzene π^* orbitals, slightly raising the energy of the S state and giving radical anions whose ESR spectra may be interpreted in terms of interactions between the S and A states.⁵ Electron-withdrawing substituents, on the other hand, stabilize the S state and give radical anions typified by large hyperfine splitting (hfs) for the proton para to the substituent and smaller coupling constants for the ortho and meta protons.³ In a recent study, Sipe and West found that, in the anion radicals of trimethylsilyl- or trimethylgermylalkylbenzenes, the organometal substituent dominates the ordering of the MO energy levels by accepting electron density more effectively than the alkyl substituents release it.⁴ This result is consistent with the small perturbations of the aromatic systems produced by alkyl substituents⁵ and naturally raises the question as to what the dominating influence will be