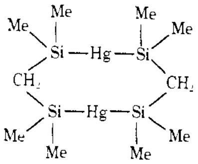
Table I. Proton Magnetic Resonance Parameters for Some Silymercurials

Compound	Solvent[a]	δ (ppm)[b]	$^3J_{Hg-H}$ (Hz)[c]
$Hg(SiMe_3)_2$	CP	1.23	40.8
	CP	1.22	40.0
$Hg(SiMe_2Ph)_2$	CP	1.03	42.5
	THF	1.08	43.5
$Li[Hg(SiMe_2Ph)_3]$	THF	1.08[d]	27.0[d]
$K[Hg(SiMe_2Ph)_3]$	THF	1.08[d]	27.2[d]
$Li_2[Hg(SiMe_2Ph)_4]$	CP	1.07	21.5
	THF	1.35[e]	19.0[e]

[a] Key: CP, cyclopentane; THF, tetrahydrofuran. [b] Methyl resonance reported ppm upfield from internal cyclopentane. [c] Mercury to methyl proton coupling. [d] At −10°C. [e] At −30°C.

observed in other organometallic ion pairs which are usually coordinated with a base. It appears that this entrapment is not restricted to species containing aromatic groups since $Li_2Hg(SiMe_3)_4$ has properties similar to II forming unsolvated, hydrocarbon soluble crystals.

Addition of a coordinating solvent such as THF or DME (1,2-dimethoxyethane) leads to the formation of coordinated derivatives such as $LiHg(SiR_3)_3 \cdot mL$ and $Li_2Hg(SiR_3)_4 \cdot nL$ which give rise to well-defined crystalline materials.[1] In these derivatives it appears that the lithium ions are abstracted from the cage and coordinated by the ether in an effectively irreversible step, since the ether cannot be removed easily from these species and on removal does not give rise to the hydrocarbon-soluble starting material.

Further studies are in progress on these and related species to determine the spectroscopic, chemical, and structural properties.

2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-1,5-mercuracyclooctane was prepared by the method of Bettler and Urry.[5] Greenish yellow single crystals were recrystallized from hot cyclohexane in a sealed tube in the absence of oxygen. The compound crystallizes in the triclinic space group, $P\bar{1}$, with unit cell parameters, a = 6.277 (3) Å, b = 8.408 (3) Å, c = 9.274 (4) Å, α = 92.74 (3)°, β = 94.79 (3)°, γ = 100.14 (2)°, with one molecule of the cyclic $Hg_2Si_4C_{10}H_{28}$ per unit cell. Intensity data were collected with monochromatized Mo Kα radiation by the θ-2θ scan technique on a Syntex $P2_1$ diffractometer. The instability of the crystal required the use of a 4°/min scan rate and the application of a 15% decay factor. Conventional heavy atom techniques followed by full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms resulted in R = 0.062 and R_w = 0.072 for 1809 data for which $I > 3\sigma(I)$.

Lithium tetrakis(dimethylphenylsilyl)mercurate was prepared in a similar manner to previously reported mercurates by the reaction of lithium with bis(dimethylphenylsilyl)-mercury in cyclopentane.[1] The lithium tetrakis(dimethylphenylsilyl)mercurate was isolated through its decreased solubility. Recrystallization from cyclopentane in a sealed tube in the absence of oxygen gave one large single crystal which had to be cut. The crystal was found to be monoclinic, space group $C2/c$, with unit cell dimensions, a = 16.268 (5) Å, b = 10.297 (3) Å, c = 22.389 (6) Å, β = 69.95 (2)°, and with four molecules of $Li_2[Hg(SiMe_2Ph)_4]$ per unit cell. A 4°/min θ-2θ scan gave 1677 data $I > 3\sigma(I)$ consistent with the systematic absences for $C2/c$. The high scan rate was used to reduce decomposition which still required application of a 14% decay factor to account for the loss in intensity due to decomposition. Direct methods were used to solve the structure.[6] Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and constrained isotropic thermal parameters for hydrogen atoms yielded R = 0.029 and R_w = 0.034.

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Received June 7, 1975

Evidence for Carbocation–Arenesulfonate Ion Pairs in Reactions with Hydroxide and Borohydride Ion

Sir:

Ion pairing is important in SN reactions,[1-3] and we present evidence for ion pairing with arenesulfonate ions in carbocation recombinations with OH^- and BH_4^- in water (cf. ref 4-7). Anionic nucleophilic attack upon both the tri-p-anisylmethyl cation, R^+,[6,7] and Malachite Green (bis(p-dimethylaminophenyl)phenylmethyl cation, MG^+) is inhibited by salts having bulky anions; some examples are shown in Figure 1. These salts also increase both $-H_R$[8] and A-1 reaction rates in water suggesting a role for solvent structure induced ion pairing.[9]

We find difference spectra for mixtures of MG^+ or R^+ and arenesulfonate ions in water with good isosbestic points, showing that there is an interionic interaction. Some examples are shown in Figure 2. Most of these data were obtained with a Cary 118 spectrometer, but the few obtained with a Cary 15 spectrometer agreed with the others. On the assumptions that a 1:1 complex is formed, and that Beer's law is obeyed, we estimate dissociation constants, K_S (Tables I and II), from the difference spectra using eq 1a,b shown for MG^+:

$$\frac{1}{[S^-]} = \frac{(1 - \epsilon_{MG^+S^-}/\epsilon_{MG^+})A_0}{K_s\Delta} - \frac{1}{K_s} \qquad (1a)$$

Where Δ is the difference absorbance, A_0 is the absorbance in the absence of S^-, and K_S is computed using a least-squares fit. Each set of difference spectra was obtained using five–seven different concentrations of the aromatic solute. There was reasonable agreement between independent experiments.

Similar values of K_s (in parentheses) were obtained using the rearranged eq 1b.

$$-\Delta/A_0[S^-] = \epsilon_{MG^+S^-}/\epsilon_{MG^+}K_s - (A_0 - \Delta)/K_sA_0 \qquad (1b)$$

The values of K_s were calculated using a least-squares plot with 95% confidence limits.

Added 2 M sodium perchlorate decreases absorbance of MG^+ by 25%, but only slightly changes λ_{max}. In all experiments MG^+ was present wholly as the monocation, and the difference spectra are identical in pH 4 and 4.5. The difference spectra of R^+ were obtained in 3 M HCl where the

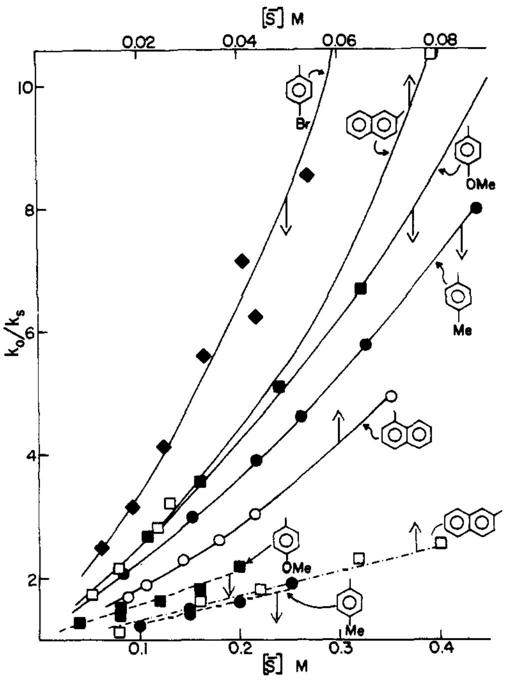


Figure 1. Negative kinetic salt effects at 25.0°: (—) MG^+ with 0.01 *M* NaOH: (· · · · ·) R^+ with 2.5×10^{-4} *M* BH_4^-; (- -) R^+ with 2.5×10^{-4} *M* BH_4^-.

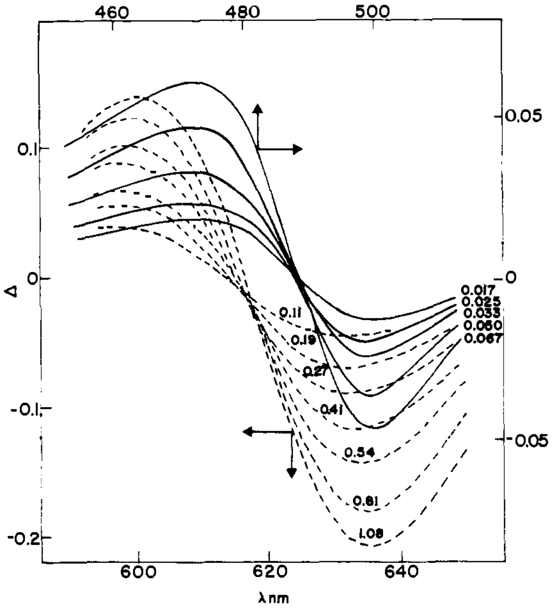


Figure 2. Difference spectra at 25.5° of R^+ with sodium 1-naphthanesulfonate (solid line) and MG^+ with sodium 4-methoxybenzene sulfonate (broken line). The molarities of the arenesulfonates are shown along side each curve.

equilibrium between R^+ and ROH is wholly in favor of the former.

The values of K_S suggest that hydrophobicity and dispersive interactions between MG^+ or R^+ and the aromatic π-system are important (cf. ref 10-12) and *m*-dihydroxybenzene gives similar difference spectra (Tables I and II). The difference spectra of MG^+ with 2-naphthalenesulfonate ion or *m*-dihydroxybenzene are considerably reduced by 3.7 *M* urea and almost disappear in $MeCN{:}H_2O$ 50:50 v/v, suggesting a role for water structure.

The kinetic salt effects in water approximately fit eq 2:

$$k_0/k_s = 1 + [S^-]/K_{kin} \qquad (2)$$

Table I. Dissociative Equilibrium Constants for Complexes of MG^+

Solute	λ (nm)[a]	K_s[b]	$K_{kin}^{OH^-}$[c]	$K_{kin}^{BH_4^-}$[c]
p-$BrC_6H_4SO_3Na$	596	0.43 (0.36) 0.49 (0.54)	0.04	0.05
p-$MeOC_6H_4SO_3Na$	600	0.43 (0.52)	0.06	0.05
p-$MeC_6H_4SO_3Na$	600	0.76 (0.63) 0.62 (0.64)[d]	0.07	0.08
p-$HOC_6H_4SO_3Na$	599	0.19 (0.19)		
1,3-$C_6H_4(OH)_2$	600	0.28 (0.29)		
1-$C_{10}H_7SO_3Na$	601	0.066 (0.061)	0.02	0.02
2-$C_{10}H_7SO_3Na$	605	0.022 (0.022) 0.017 (0.017) 0.023 (0.023)	0.01	0.01

[a] Wavelength used for calculation. [b] At 25.5° and pH 4. [c] At 25.0°. [d] At pH 4.5.

Table II. Dissociative Equilibrium Constants for Complexes of R^+

Solute	λ (nm)[a]	K_s[b]	$K_{kin}^{OH^-}$[c]	$K_{kin}^{BH^-}$[c]
p-$BrC_6H_4SO_3Na$	470	0.33 (0.50)	0.17	0.11 (0.12)
p-$MeOC_6H_4SO_3Na$	470	0.48 (0.51)	0.22	0.18 (0.20)
p-$MeC_6H_4SO_3Na$	470	0.78 (0.64)	0.18	0.31 (0.40)
p-$HOC_6H_4SO_3Na$	470	0.36 (0.30)		
1,3-$C_6H_4(OH)_2$	475	0.43 (0.45)		
1-$C_{10}H_7SO_3Na$	473	0.17 (0.19) 0.13 (0.14)	0.07	0.11
2-$C_{10}H_7SO_3Na$	473	0.06 (0.09) 0.09 (0.11)	0.03	0.05

[a] Wavelength used for calculation. [b] At 25.5° in 3 *M* HCl. [c] At 25.0°; the values in parentheses are in 3 *M* NaCl.

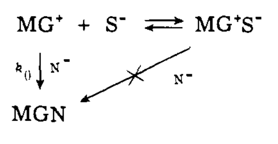
Table III. Second-Order Rate Constants for Reactions of MG^+ and R^+[a]

Carbocation	OH^-	BH_4^-
MG^+	1.59	33.8
R^+	6.7×10^3	1.3×10^6

[a] Second-order rate constants l. mol^{-1} sec^{-1} at 25.0° for reaction in the absence of added salt.

where k_s and k_0 are the second-order rate constants in the presence and absence of added salts. The values of K_{kin} are estimated from the initial slopes of plots of k_0/k_s vs. salt concentration (Figure 1). The kinetic salt effects are similar for reactions of OH^- and BH_4^-, but they are larger for MG^+ than for R^+ (Tables I and II). The reactions with R^+ were followed using a stopped flow spectrophotometer, with 5×10^{-2} OH^- or 2.5×10^{-4} *M* BH_4^-. Reactions with MG^+ were followed conventionally using 10^{-2} *M* OH^- or 2×10^{-3} *M* BH_4^-. The reactions with BH_4^- were in weakly alkaline solution ($1\text{-}2.5 \times 10^{-3}$ *M* OH^-), and the observed rate constants were corrected for the contributions of reactions with H_2O, and where necessary OH^-. The second-order rate constants for reaction of OH^- and BH_4^- with MG^+ and R^+ in the absence of added salts (Table III) were observed using up to 5×10^{-2} OH^- and 3×10^{-4} and 3×10^{-3} *M* BH_4^- for R^+ and MG^+, respectively. They are in reasonable agreement with earlier results.[4,7] As expected BH_4^- is a much better nucleophile than OH^- and similar to azide ion in its nucleophilicity toward carbocations. Although eq 2 fits the reaction scheme shown for MG^+ (Scheme I), the values of K_s, determined spectrally, are

Scheme I



(N^- = OH^-, BH_4^-)

consistently larger than those of K_{kin} (Tables I and II). For reactions of R^+ this difference could be due to the spectral measurements being made in highly acidic solutions, whereas the rate measurements are made in dilute alkali, but this explanation seems improbable because the kinetic salt effects due to the arenesulfonates are little affected by added 3 M NaCl, and differences between K_s and K_{kin} are less for R^+ than for MG^+ (Tables I and II).

There are several explanations for the different values of K_s and K_{kin}. (i) Our estimation of K_s depends on the assumption that free carbocations are in equilibrium with one species of ion pairs, but there may be a family of ion pairs and the difference spectra may detect only those in which the ions are closely associated. (ii) In addition to the formation of relatively unreactive ion pairs there should be an unfavorable primary kinetic salt effect upon the reactions of oppositely charged ions, although the relatively small effects of salts having small anions, e.g., Cl^-, suggests that these primary effects are not large.[6,7] (iii) The special positive salt effect upon SNI reactions in nonpolar solvents is explained in terms of an increased rate of dissociation of a solvent separated ion pair,[1] and if ionic recombination in water involves prior formation of an ion pair, e.g., MG^+N^- (cf. ref 4), such a pair could be split unproductively by an arene sulfonate ion, e.g., Scheme II, and this splitting should be more important in reactions of the less reactive MG^+.

Scheme II

$$\begin{tikzcd}
MG^+ \arrow[r, shift left, "N^-"] & MG^+N^- \arrow[l, shift left] \arrow[r] \arrow[d, shift left, "N^-"] & MGN \\
& MG^+ArSO_3^- \arrow[u, shift left, "ArSO_3^-"] &
\end{tikzcd}$$

The carbocations, R^+ and MG^+, have delocalized charge, and they should be polarizable and relatively hydrophobic, and it is these properties which apparently dictate interactions with the aromatic solutes, irrespective of charge (Tables I and II). For a given salt K_s and K_{kin} come closer in magnitude as the binding with the carbocations increases.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

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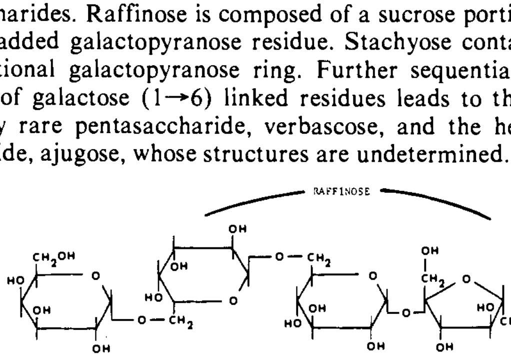
Received February 24, 1975

Conformation of the Tetrasaccharide Stachyose

Sir:

Stachyose ($C_{24}H_{42}O_{21}\cdot xH_2O$), *O*-α-D-galactopyranosyl-(1→6)-*O*-α-galactopyranosyl-(1→6)-*O*-α-D-glucopyranosyl (1→2)-α-D-fructofuranoside, is a tetrasaccharide which is widely distributed in the botanical world. It is usually concentrated in plant storage organs (roots, seeds, tubers, etc.), and is often found associated with sucrose and raffinose. These three sugars are the most common plant oligosaccharides. Raffinose is composed of a sucrose portion and one added galactopyranose residue. Stachyose contains an additional galactopyranose ring. Further sequential addition of galactose (1→6) linked residues leads to the relatively rare pentasaccharide, verbascose, and the hexasaccharide, ajugose, whose structures are undetermined.



Stachyose, which crystallizes as a hydrate, represents the first tetrasaccharide structure to be fully characterized by X-ray single-crystal analysis. It crystallizes in the orthorhombic space group $P2_12_12$ with a = 12.801 (6) Å, b = 24.026 (5) Å, and c = 10.856 (6) Å. Crystalline stachyose probably varies in its hydration. Assuming four molecules of stachyose per unit cell, and four water molecules per stachyose molecule, the calculated crystal density is 1.469 g cm^{-3}. With five molecules of water per stachyose molecule, it is 1.505 g cm^{-3}. French et al.[1] reported an experimental crystal density of 1.485 g cm^{-3}, which would correspond to approximately 4.4 water molecules per stachyose molecule. (The commercial sample was labeled as a pentahydrate which might lose water in storage.)

Cu Kα radiation (λ 1.54178) was used to collect 3120 independent reflections with a maximum 2θ of 127.3°. At a later date, 2312 additional independent reflections were collected from the same crystal using Mo Kα radiation (λ 0.71069). The final data set included the full diffracting sphere for Cu radiation and also some reflections available only to Mo radiation. The molybdenum data were put on the same scale as the copper data and used to get normalized structure factor magnitudes $|E|$ which were then used to solve the structure by direct methods. A partial structure was obtained by application of the symbolic addition procedure for noncentrosymmetric crystals.[2] This fragment was then developed into the full structure by the tangent formula refinement and expansion.[3] Full-matrix three-dimensional least-squares refinement[4] (using only the 3120 Cu reflections) is being carried out and difference maps have been calculated to locate the H_2O molecules. The crystallographic R factor, with isotropic thermal factors for all atoms and four water molecules included, is now 0.155. Further difference maps seem to indicate alternative positions for H_2O molecules. There may be a disorder involving two distinct networks of H_2O molecules. The H_2O molecules will certainly play a significant role in packing of the molecules in the crystal. The packing will be described after refinement has been completed.

Figure 1 illustrates the results of the X-ray analysis on stachyose as well as the results of structure studies on sucrose[5] and raffinose.[6] The carbon atoms of the first galactose residue are conventionally numbered, while the numbers on the second galactose, the glucose, and the fructose