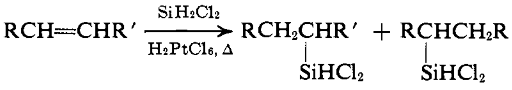
chloroplatinic acid, has proved to be an excellent synthetic route to the formation of a carbon–silicon bond. With internal olefins, however, the terminal adduct is usually the major product[4] in such reactions.

We have discovered that dichlorosilane[5] (H_2SiCl_2) adds directly to internal olefins when catalyzed by chloroplatinic acid to give internally substituted alkyl silanes in excellent yields. Significantly no bond migration[6] occurs with dichlorosilane[7] in contrast to similar reactions with trichlorosilane and chloroplatinic[8] acid.



$$\mathrm{RCH{=}CHR'} \xrightarrow[\mathrm{H_2PtCl_6},\,\Delta]{\mathrm{SiH_2Cl_2}} \underset{\substack{|\\ \mathrm{SiHCl_2}}}{\mathrm{RCH_2CHR'}} + \underset{\substack{|\\ \mathrm{SiHCl_2}}}{\mathrm{RCHCH_2R'}}$$

Table I lists typical results for such dichlorosilane additions.

Table I. Chloroplatinic Acid-Catalyzed Addition of Dichlorosilane to Internal Olefins

Olefin[a]	Temp, °C (time, hr)	Products[b] (% distribution)	Bp, °C (mm)	Yield, %
2-Heptene	150 (8)	2-$C_7H_{15}SiCl_2H$ (64) 3-$C_7H_{15}SiCl_2H$ (36)	55–60 (5)	81
2-Heptene	110 (8)	As above		51
2-Hexene	140 (8)	2-$C_6H_{13}SiCl_2H$ (66) 3-$C_6H_{13}SiCl_2H$ (34)	48–51 (7.5)	89
2-Hexene	72–74 (24)	As above		26
3-Hexene[c]	150 (8)	3-$C_6H_{13}SiCl_2H$[d]	50–55 (12)	56
3-Hexene[c]	150 (24)	3-$C_6H_{13}SiCl_2H$[d]	47–51 (9)	88
2-Pentene	128–130 (8)	2-$C_5H_{11}SiCl_2H$ (69) 3-$C_5H_{11}SiCl_2H$ (31)	131–136 (740)	92

[a] Pure mixtures of cis and trans. [b] All compounds gave acceptable elemental analyses and nmr spectra. [c] Contained 6% 2-hexene as an impurity. [d] Contained 4% 2-$C_6H_{13}SiCl_2H$.

In a typical experiment, 0.10 mol of 2-heptene and 50 μl of chloroplatinic acid in isopropyl alcohol (0.10 g of $H_2PtCl_6 \cdot 6H_2O$ in 2 ml of isopropyl alcohol) were placed in a stainless steel bomb and cooled to −78°. Dichlorosilane (0.20 mol, 14.2 ml) was condensed in a calibrated tube at −78° and then distilled into the bomb under dry nitrogen after which the bomb was heated in an oil bath at 150° for 8 hr. Upon cooling, the excess dichlorosilane was vented and the bomb washed with dry pentane. Solvent removal followed by distillation afforded 16.1 g (81%) (bp 55–60° at 5.0 mm) of a mixture of 2- (64%) and 3- (36%) heptyldichlorosilane: nmr (CCl_4–TMS) δ 0.73–1.87 multiplet and two unresolved singlets (SiH) at δ 5.42 (64%) and 5.48 (36%). *Anal.* Calcd for $C_7H_{16}SiCl_2$: C, 42.20; H, 8.10; Si, 14.10; Cl, 35.60. Found: C, 42.30; H, 8.27; Si, 14.01; Cl, 35.81.

Authentic samples of 1-, 2-, and 3-heptyldichlorosilane were prepared for comparison purposes by treating the appropriate Grignard reagent derived from the isomerically pure 1-, 2-, and 3-bromoheptanes with excess trichlorosilane. The nmr spectrum of 1-heptyldichlorosilane thus prepared showed a triplet for SiH at δ 5.5, while the authentic 2- and 3-heptyl isomers showed unresolved singlets for SiH at δ 5.42 and 5.48, respectively. These differences in chemical shift for the silanic protons proved a valuable diagnostic in analyzing the isomeric mixtures depicted in Table I. Based on the results in Table I the silicon atom of dichlorosilane attached itself preferentially to the less hindered carbon atom, thus favoring formation of the 2 over the 3 isomer by a ratio of about 2:1. Further substantiation for the assignments of the chemical shifts of the silanic protons was forthcoming from the reaction between 3-hexene and dichlorosilane where only the 3 isomer can result (Table I). The nmr spectrum of the product again showed an unresolved singlet for Si–H at δ 5.48.

To establish whether impurities, surreptitiously introduced from the metal of the stainless steel bomb, were responsible for the failure to obtain terminal adducts with dichlorosilane, 2-heptene was treated with trichlorosilane in the same bomb and under identical reaction conditions (chloroplatinic acid, 110°, 8 hr). *n*-Heptyltrichlorosilane was obtained in this case in 83% yield. Clearly the mechanism[9] suggested for trichlorosilane additions requires some modification in the case of similar dichlorosilane additions.

A new area of organosilicon chemistry is now open since, for the first time, internally substituted alkyl silanes can be prepared in convenient quantities by a direct and economical route. Studies are continuing in our laboratory on the stereochemistry of dichlorosilane additions as well as its addition to dienes. Preliminary studies indicate that monoadducts derived from diene substrates can be made to undergo intramolecular cyclizations. Details of these experiments will be published shortly.

Acknowledgment. We wish to thank the National Science Foundation for its financial support of this work.

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[4] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

[5] Obtained from Union Carbide Corp., Sistersville, W. Va.

[6] With 2-butene some terminal adduct could be obtained if the reaction were carried out at lower temperatures. The results in Table I would indicate that the rate of internal addition is increased by higher reaction temperatures.

[7] We have obtained some preliminary evidence that monochlorosilane also can be made to add to internal olefins without rearrangements.

[8] While chloroplatinic acid was initially introduced into the bomb, one is not justified in assuming that it *must* be the active catalyst in these reactions. Decomposition to other active platinum species may well have occurred under the reaction conditions employed. Blank runs made in the absence of initially added chloroplatinic acid gave little or no product, clearly indicating the catalytic effect of some form of platinum.

[9] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

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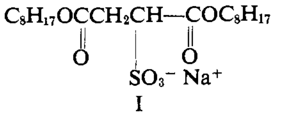
Received July 20, 1972

Catalysis in Water Pools

Sir:

Octane solutions of di-2-ethylhexyl sodium sulfosuccinate (I) dissolve remarkable amounts of water (50 mol/mol of solute).[1] Thus, a 0.1 *M* solution of the sulfosuccinate in octane can incorporate nearly 10% water. This solubilized water is confined in spherical



$$\mathrm{C_8H_{17}O\underset{\substack{\|\\ O}}{C}CH_2\underset{\substack{|\\ SO_3^-\ Na^+}}{CH}{-}\underset{\substack{\|\\ O}}{C}OC_8H_{17}}$$

I

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[1] W. I. Higuchi and J. Misra, *J. Pharm. Sci.*, **51**, 455 (1962).

pools encased by surfactant molecules which have only their ionic heads immersed in the aqueous phase.[2] We report here the first mechanistic study of an imidazole-catalyzed ester hydrolysis occurring within such micellar water.[3] Our objective was to compare the properties of organic molecules in water pools of different sizes with the corresponding properties in bulk water. In this manner we hoped to probe the structure of the inverted micelles.

Before initiating the kinetic investigation we characterized important physical properties of the octane–I–water systems. Light scattering data[4] revealed that the micelles have molecular weights of 8.2×10^3, 2.8×10^4, and 1.9×10^5 at $[H_2O]/[I]$ ratios of 2.2, 8.9, and 36, respectively. This corresponds to 37, 410, and 6400 water molecules per aggregate. The molecular weights were calculated assuming that the micelles are monodisperse and that their structure is independent of [I] at any given $[H_2O]/[I]$ ratio. Kinetic data presented below support these assumptions.

Dielectric constants of the octane–I–water system were found to resemble that of octane ($\epsilon = 1.95$) much more than that of water ($\epsilon = 78.5$) even at high water concentrations. Thus, $\epsilon = 2.33$, 2.47, 2.70, and 4.9 for solutions containing 1.0, 2.9, 5.8, and 16.7% water, respectively.[5] Since the dielectric constant is only a macroscopic parameter, we secured a more intrinsic measure of solvent polarity with the aid of Phenol Blue and pyridine 1-oxide. Phenol Blue has an absorbance maximum which is sensitive to solvent (λ_{max} 552 nm in cyclohexane, λ_{max} 668 nm in water).[6] When Phenol Blue was dissolved in an octane–I solution containing 1% water, the dye displayed λ_{max} 550 nm. We conclude that the Phenol Blue does not partition into the aqueous phase and that the intermicellar liquid is pure hydrocarbon. Similarly, we obtained spectra of pyridine 1-oxide, a water-soluble compound whose absorbance maximum in several solvents has been correlated with Z values.[7] The Z value for micellar water was found to equal that of bulk water at a $[H_2O]/[I]$ ratio of 32. At a ratio of 3.1, where solubilized water is no doubt largely bound by the ionic portion of I, the polarity lies midway between that of bulk water and methanol according to this particular spectroscopic criterion.

We also investigated the water pools using 2-toluidinylnaphthalene-6-sulfonate (TNS), a fluorescent probe. A fluorescent probe is a compound whose fluorescent properties change according to the local environment. For example, the quantum yields of TNS fluorescence in water, methanol, and 1-butanol are 0.0008, 0.34, and 0.57, respectively.[8] The quantum yields of TNS in several octane–I–water solutions are listed in Table I.[9] Since TNS will not dissolve in octane solutions of I when no water is present, the probe molecules must reside within the water pools. We surmise from the low quantum yields of TNS at the high water concentrations that the water structure is rather normal. Icelike water would have led to much higher values.[10] If the efficiency of TNS fluorescence reflects mainly solvent polarity,[8] then the quantum yields of 0.33 and 0.32 in Table I indicate that the micellar polarity at low $[H_2O]/[I]$ ratios resembles that of methanol. Alternatively, the water molecules bound to the surfactant ions in the small pools may have difficulty reorienting their dipoles during the excited-state lifetime; this solvent constraint would enhance the fluorescent emission.[11,12]

Table I. Quantum Yields of TNS Fluorescence in Octane Solutions of Di-2-ethylhexyl Sodium Sulfosuccinate (I) and Water at 25.0°

$[H_2O]/[I]^a$	Quantum yield	$[H_2O]/[I]^a$	Quantum yield
0.9	0.33	9.3	0.061
1.9	0.32	16.0	0.045
3.1	0.21	20.0	0.044
3.7	0.17	39.0	0.026
5.6	0.10		

^{a} $[I] = 5.95 \times 10^{-2}$ *M* or 9.94×10^{-2} *M*.

Solutions of I in octane are capable of solubilizing water containing large amounts of imidazole. This imidazole exists exclusively in the water pools because the amine is insoluble in dry octane solutions of I. When *p*-nitrophenyl acetate in a water-insoluble organic solvent is added to the octane–I–water–imidazole system, the ester undergoes a catalyzed hydrolysis whose rate constants at 25.0° are presented in Table II. A summary of our conclusions based on these data follows.

The observed rate constant is proportional to the imidazole concentration within the water pools at constant $[H_2O]$ and [I]. Consequently, transfer of ester from the organic phase to the aqueous phase is not rate limiting. However, partitioning of the substrate into the pools is certainly an important preequilibrium process. This is proven by the relative hydrolytic rates of *p*-nitrophenyl acetate, propionate, caproate, and laurate (56:16:1.7:1.0). The rate ratio of acetate to propionate (3.5) approximates the relative partition coefficient of the two esters in octane–water (4.6). When the imidazole concentration in the water is constant, the rate of *p*-nitrophenyl acetate hydrolysis is a linear function of the $[H_2O]/[I]$ ratio. The larger the pool size, the faster the reaction. Again, this is understandable in terms of transfer of the substrate from octane to water across the surfactant boundary. We also performed a series of runs using solutions in which the concentrations of I and water were lowered simul-

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(2) M. B. Mathews and E. Hirschhorn, *J. Colloid Sci.*, **8**, 86 (1953).

(3) Hydroxide ion catalyzed ester hydrolyses in aqueous liquid-crystalline systems have already been described: K. S. Murthy and E. G. Rippie, *J. Pharm. Sci.*, **59**, 459 (1970); S. I. Ahmad and S. Friberg, *J. Amer. Chem. Soc.*, **94**, 5196 (1972); S. Friberg and S. I. Ahmad, *J. Phys. Chem.*, **75**, 2001 (1971).

(4) Measurements were made at 30.0° with a Brice-Phoenix Series 2000 light scattering photometer and a Brice-Phoenix Model BP-2000-V differential refractometer.

(5) Dielectric constants were determined at 25.0° by the heterodyne-beat method using frequencies of 5000 and 54,000 Hz.

(6) L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, 63, 3214 (1941).

(7) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(8) G. M. Edelman and W. O. McClure, *Accounts Chem. Res.*, **1**, 65 (1968).

(9) Quantum yields were determined with a Farrand spectrofluorometer at 25.0° using quinine sulfate in 0.1 *N* H_2SO_4 ($\phi = 0.55$) as a standard.

(10) W. O. McClure and G. M. Edelman, *Biochemistry*, **5**, 1908 (1966).

(11) B. Chance, C. Lee, and J. K. Blasie, Ed., "Probes of Structure and Function of Macromolecules and Membranes," Academic Press, New York, N. Y., 1971, p 13.

(12) When a probe bound to a protein fluoresces with a large quantum yield, it is usually assumed that the probe is situated in a hydrophobic pocket.[6] Since we obtained large quantum yields with the small pools, and since these pools can hardly be regarded as nonpolar, we question the relationship between fluorescent emission and hydrophobicity.

Table II. Observed Rate Constants for the Imidazole-Catalyzed Hydrolysis of *p*-Nitrophenyl Acetate in Water Pools Dissolved in Octane at 25.0°

[Imidazole][a]	[I][b]	$[H_2O]$[c]	R[d]	10^3k_{obsd}, sec^{-1}
0.805	0.105	2.76	26	6.68[e]
0.805	0.105	2.76	26	6.70
0.805	0.104	2.76	26	6.82
0.805	0.0523	1.38	26	3.76
0.805	0.0262	0.689	26	2.08
0.805	0.0131	0.344	26	1.15
0.805	0.105	1.10	10	2.34
0.402	0.099	3.86	39	4.50
0.402	0.105	2.76	26	3.20
0.402	0.0523	1.38	26	1.79
0.402	0.105	1.10	10	1.13
0.201	0.099	3.86	39	2.22
0.200	0.105	2.76	26	1.66
0.200	0.104	2.73	26	1.72
0.200	0.0523	1.38	26	0.950
0.100	0.105	2.76	26	0.783
0.100	0.0523	1.38	26	0.489

[a] Total concentration of imidazole in the water pools. [b] Concentration of di-2-ethylhexyl sodium sulfosuccinate in the octane–water solution. [c] pH 8.00. [d] $R = [H_2O]/[I]$. [e] The corresponding bimolecular rate constant ($9.1 \times 10^{-3}\ M^{-1}\ sec^{-1}$) is approximately 53 times slower than that for the same reaction in bulk water.

taneously by dilution with pure octane. The rate constants were found to decrease proportionally with the dilution factor. The simplest explanation is that the concentration of the micelles—but not their size—decreases with decreasing [I] as long as a constant $[H_2O]/[I]$ ratio is maintained. Such behavior was assumed in calculating molecular weights from light scattering data.

Only a small solvent isotope effect was observed when deuterium oxide was substituted for water ($k_{H_2O}/k_{D_2O} = 1.10$). We infer that imidazole within the micelles, as in bulk water,[13] performs as a nucleophile rather than as a general base toward *p*-nitrophenyl acetate.

One final experiment deserves mention. Two octane–I–water solutions were prepared, one containing imidazole and the other containing an ionic substrate, *p*-nitrophenyl *p'*-guanidinobenzoate hydrochloride (*p*-NPGB), in the water pools. These solutions were equilibrated at 25.0°, mixed, and observed spectrophotometrically at 400 nm. The *p*-NPGB was found to hydrolyze at a significant rate, although 57 times slower than *p*-nitrophenyl acetate at equal concentrations of imidazole, water, and I.[14] Clearly, imidazole in one set of micelles is able to "communicate" with *p*-NPGB in the second set. Either the water pools merge and separate rapidly (despite their surfactant shells), or else the reactants travel among the micelles with surprising ease.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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[13] T. C. Bruice and S. J. Benkovic, *J. Amer. Chem. Soc.*, **86**, 418 (1964).

[14] *p*-NPGB reacts 12 times slower with imidazole in bulk water than does *p*-nitrophenyl acetate.

[15] Recipient of a Camille and Henry Dreyfus Foundation Teacher–Scholar Grant and an NIH Career Development Award.

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Received May 31, 1972

Electron Spin Resonance Studies of Ion Pairs in Solutions of Cation Radicals

Sir:

The technique of electron spin resonance (esr) spectroscopy has had great success in recent years in providing detailed information on the ion pairs existing in solutions of anion radicals in various solvents and with several different counterions.[1,2] The effects observed include hyperfine splittings from the counterion, *g* shifts from the free ion value, perturbation of proton hyperfine splittings, and the study of several types of equilibria. Somewhat surprisingly, no observations of ion-pair effects in solutions of cation radicals have been reported and it is the purpose of this communication to present esr evidence for the existence of ion pairs in these solutions.

The usual methods of preparation of cation radicals include oxidation by compounds such as H_2SO_4, $AlCl_3$, $SbCl_5$, BF_3, etc., in solvent of high dielectric constant. Certainly these conditions are not favorable for the observation of effects due to the formation of ion pairs. The counterions in these systems are not simple species, and the solvents have high solvating powers thus preventing close approach of the ion pairs. Oxidation with bromine or iodine is sometimes successful with easily oxidized compounds and under these conditions one might expect the counteranion to be simply Br^- or I^-. Combining these oxidants with solvents of lower dielectric constant would seem most likely to produce effects due to ion-pair formation.

In view of the above considerations, the 1,2,4,5-tetramethoxybenzene (TMB) cation radical was selected as a model system in which to search for the effects of ion pairing. $TMB\cdot^+$ has previously been generated by electrochemical oxidation[3] and by chemical oxidation in H_2SO_4 and $AlCl_3$–CH_3NO_2,[4] and its esr spectrum is characteristically simple ($a^H_{OCH_3} = 2.20$ G, $a^H_{CH} = 0.85$ G) consisting of groups of 1:2:1 triplets. The oxidation potential of TMB is 0.82 V[3] which indicates that oxidation by bromine should also be successful. This proved to be the case and allowed us to investigate $TMB\cdot^+$ in a variety of solvents. In each case the radical was produced by reaction in an evacuated system using dried and degassed solvents. For bromine oxidations care was taken to use the minimum amount of bromine required to produce an esr signal.[5] The radical was identified in each solvent by its proton splittings which remained essentially constant in all solvents. The most interesting results were those of the *g* factors which are shown in Table I. The large positive *g* shifts observed for the bromine–chloroform and bromine–methylene chloride systems are attributed to the formation of ion pairs in these solvents. Solvent effects alone have much less effect on the *g* value as seen from the results using aluminum chloride as the oxidizing agent (see Table I).

Assuming that ion pairs are formed in $CHCl_3$ and CH_2Cl_2, one might ask why hyperfine splittings from the

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[1] M. C. R. Symons, *J. Phys. Chem.*, 71, 139 (1967).

[2] T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6421 (1971), and references cited therein.

[3] A. Zweig, W. G. Hodgson, and W. H. Jura, *ibid.*, 86, 4124 (1964).

[4] W. F. Forbes and P. D. Sullivan, *J. Chem. Phys.*, **48**, 1411 (1968).

[5] In this way effects due to the presence of molecular bromine are thought to be minimal.