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(25) As pointed out earlier[1] steady-state kinetics lead to limiting values of k_q^{obsd} given by

$$k_q^{\mathrm{obsd}} = \frac{k_q(k_c + k_d)}{k_{-q} + (k_c + k_d)} \tag{11}$$

$$\text{where } (k_c + k_d) \gg k_{-q} \qquad k_q^{\mathrm{obsd}} = k_q \tag{12}$$

$$\text{where } (k_c + k_d) \ll k_{-q} \qquad k_q^{\mathrm{obsd}} = K_q(k_c + k_d) \tag{13}$$

Since the k_q^{obsd} values are all within an order of magnitude of diffusion controlled and the differing rates of the exciplex appear to little affect the values of k_q^{obsd}, it appears reasonable that eq 12 applies and thus that the quenching is essentially irreversible.

(26) For some of the quenchers, most notably biphenyl, benzonitrile, and acenaphthene (triplet energies, respectively, 69.8, 76.8, and 59.2 kcal/mol[27]), the quencher triplet lies below the excited singlet of **1**. For these exciplexes formation of A^{3*} should be possible; however, in each case rapid energy transfer to generate $\mathbf{1}^{3*}$ (which evidently does not occur) might be expected.

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Gas-Phase Reactivity of Alkenes Toward Methylmercury Cation

Robert D. Bach,* A. Thomas Weibel, Joseph Patane, and Larry Kevan*

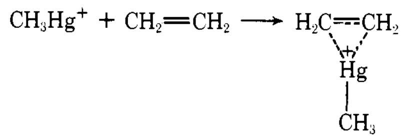
Contribution from the Department of Chemistry, Wayne State University,
Detroit, Michigan 48202. Received January 3, 1975

Abstract: The gas-phase reactivity of the electrophilic methylmercury cation towards a series of alkenes has been determined by ion cyclotron resonance spectroscopy. The rate of mercurinium ion formation was established to increase with increasing methyl substitution on the double bond.

The nature of the intermediates involved in the reaction of alkenes with electrophilic species is of considerable interest to the physical organic chemist. The origin of the differences in the rate of formation and the stability of these complexes with increasing alkyl substitution on the carbon-carbon double bond continues to be a vexing problem. In general, a composite of electronic, steric, and strain effects has been invoked in explanation of the various reactivity trends. On the basis of frontier orbital concepts, an increase in the number of alkyl substituents will increase the energy of the highest occupied molecular orbital (HOMO), thereby increasing the reactivity of the nucleophilic π molecular orbital (MO) toward a specific electron acceptor. An opposing effect resulting from increased alkyl substitution is the increase in steric interactions with the electrophile. The relationship of alkene reactivity to molecular parameters such as ionization potential (energy of HOMO) and steric effects are further complicated by solvation phenomena. Solvation energies are often sufficiently large to render a study of subtle changes in these innate properties untenable. Thus, an unambiguous separation of these rate influencing factors is very difficult and still remains an unsettled question. Recently, gas-phase studies[1] on the acidity of molecules have amply demonstrated the discrepancies between gas-phase and solution behavior.

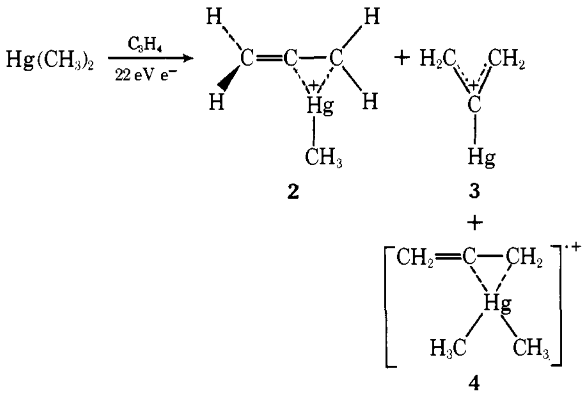
In continuing our mechanistic studies on the oxymercuration reaction, it became clear that data on this electrophilic addition reaction in the gas phase would provide information pertaining to our solution studies[2] and our theoretical investigations[3] of the nature of mercurinium ion intermediates. Although mercurinium ions have been postulated as intermediates in the oxymercuration of alkenes for many years,[4] unequivocal evidence for their existence under actual reaction conditions has not appeared. Olah and Clifford[5] recently reported the first observation of a long-lived mercurinium ion in magic acid solution. They established that these metal-alkene π complexes were stable at temperatures below 243 K.

The use of ion cyclotron resonance (ICR) spectroscopy for the study of ion-molecule reactions of heavy metals has not been employed extensively. Foster and Beauchamp[6] have reported gas-phase reactions of $Fe(CO)_5$ and Dunbar and coworkers[7] have described their experimental results on lead, nickel, and chromium derivatives. In a preliminary account we reported[8a] the first observation of the stable mercurinium ion **1** in the gas phase derived from the ion-molecule reaction of methylmercury cation with ethylene (eq 1). We have also reported a similar observation of a mercurinium ion derived from the reaction of CH_3Hg^+ with allene[8b] (eq 2). The product



$$\mathrm{CH_3Hg^+ + CH_2{=}CH_2 \longrightarrow \underset{\underset{\displaystyle CH_3}{|}}{\underset{Hg}{\overset{}{H_2C{=}CH_2}}}} \tag{1}$$

1



2 **3** **4** (2)

Table I. Rates of Mercurinium Ion Formation

Alkene	$k_1(R_2C{=}CR_2HgCH_3^+)^a$ **5**	$k_1(R_2C{=}CR_2Hg^+)$ **6**	$k_1(C_3H_5Hg^+)$ **7**
Isobutylene	1.37 ± 0.34	1.42 ± 0.77	1.46 ± 0.53
1-Butene	1.55 ± 0.17	1.90 ± 0.46	
trans-2-Butene	1.19 ± 0.21	2.22 ± 0.69	1.17 ± 0.43
cis-2-Butene	1.96 ± 0.08	2.70 ± 0.54	3.27 ± 1.0
2-Methyl-2-butene	1.60 ± 0.32	2.54 ± 0.86	2.15 ± 0.08
1,3-Butadiene	1.37 ± 0.27	1.58 ± 0.41	

[a] Rate constants ($\times 10^{10}$ cm^3 mol^{-1} s^{-1}) were calculated from the rate expression: $\log (I_0/(I_0 - X)) = [\text{alkene}]k\tau/2.3$.

ions **2**, **3**, and **4** were formed in the ratio 97:3:(<1), respectively. We have extended our studies to include a kinetic investigation of a series of alkenes in the gas phase. We now report that the reactivity of CH_3Hg^+ toward alkenes *increases* with increasing methyl substitution on the double bond.

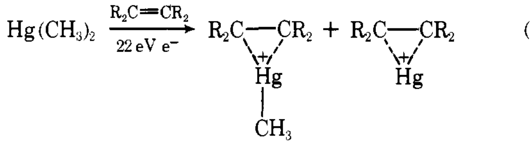
Experimental Section

A modified V-5900 ICR mass spectrometer with a flat cell (drift plates separated by 1.1 cm) was used for these experiments. Instrumental modification and our operating techniques have been described previously.[9] Pressure is measured with a Barocell ionization gauge, which is connected directly to the center of the ICR cell through a ¾ in. tube. These two gauges are calibrated against each other for fast, accurate pressure measurements. Thus, all pressure measurements are independent of molecular type and measure the ICR cell absolute pressures. In addition, the Barocell was independently calibrated against a trapped McLeod gauge system and found to be accurate to ±1.5%.

The method of extended Hückel molecular orbital calculation and the input parameters used have been described elsewhere.[8b] Alkenes were obtained from Matheson Co. and dimethylmercury was purchased from Alpha Inorganic Chemicals, Beverly, Mass. All gases were degassed by freeze-pump-thaw techniques at 77 K before use.

Results and Discussion

In a typical experiment dimethylmercury was introduced into the ion cyclotron resonance spectrometer at $1.1\text{-}2.0 \times 10^{-4}$ Pa ($0.80\text{-}1.5 \times 10^{-6}$ Torr), and with 3.5×10^{18} J (22 eV) ionizing electrons $Hg(CH_3)_2^+$ (25-30%), CH_3Hg^+ (40-42%), and Hg^+(30-34%) were observed at room temperature. Pulsed electron beam modulation in the ICR cell gave absorption type signals. When $0.53\text{-}3.9 \times 10^{-3}$ Pa of alkene was introduced through a second inlet, two prominent new peaks having masses corresponding to $R_2C{=}CR_2HgCH_3^+$ and $R_2C{=}CR_2Hg^+$ were observed (eq 3). The formation of **6** was a very minor product with ethylene and allene. However, with an increase in alkyl substitution and the polarizability of the molecule, its intensity is markedly increased and with substituted alkenes it is the major product of the reaction (see rate constants in Table I, which are proportional to the ion intensity). An additional product, $C_3H_5Hg^+$ (**7**), was also observed with the isomeric butenes and will be discussed below.



$$Hg(CH_3)_2 \xrightarrow[22\text{ eV } e^-]{R_2C{=}CR_2} R_2C\text{—}CR_2(\overset{+}{Hg}CH_3) + R_2C\text{—}CR_2(\overset{+}{Hg}) \quad (3)$$

5 **6**

At the expense of some sensitivity the mercury isotopes (198-204 amu) were resolvable at high resolution. Ion ejection experiments were used to determine the manner of ion formation. In all cases the product ions **5** and **6** were formed by the reaction of CH_3Hg^+ and Hg^+ with the neutral alkene. Double resonance experiments in which $C_2H_4^+$ was irradiated showed no effect on **1**; this also indicates that formation of **1** does not occur by collision of $C_2H_4^+$ with dimethylmercury. Similar observations have been reported for the reaction of CH_3Hg^+ with allene.[8b]

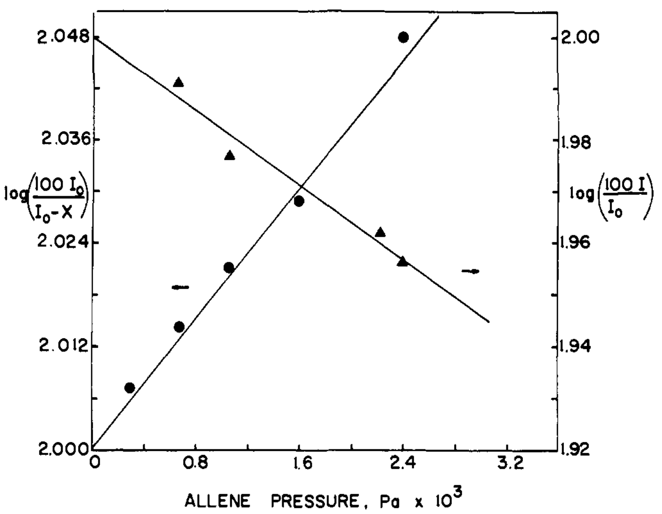


Figure 1. Kinetic plots of the appearance of $CH_3HgX^+(X = R_2C{=}CR_2)$ vs. the alkene pressure in dimethylmercury-alkene mixtures. I_0 is the CH_3Hg^+ intensity at zero alkene pressure.

Under experimental conditions pertaining to the ICR experiments, the ion residence time is about 3×10^{-3} s. Thus, the product ions **5** and **6** are clearly stable for this period of time at room temperature. This is so much longer than typical metastable ion lifetimes ($\sim 10^{-5}$ s) that we regard these alkene π complexes as truly stable gas-phase species.

In an effort to gain a more fundamental understanding of the effects of solvent on alkene-metal complex formation, we have also measured the rates of mercurinium ion formation in the gas phase. The kinetic measurements for bimolecular formation of **5** and **6** were simplified by employing pseudo-first-order conditions with an excess of alkene; $d(\mathbf{5})/dt = k'[CH_3Hg^+]$, where $k' = k_{\text{expt}}[\text{alkene}]$. Thus, rate constants for formation of **5** were measured by plotting $\log (I - X)$ vs. the pressure of alkene, where I = intensity of CH_3Hg^+ and X = intensity of **5**, as measured from the observed intensities corrected by their respective masses, and the slope = $k\tau/2.303$, where τ is the measured reaction or residence time[9] in the ICR cell.[10]

The data given in Figure 1 show that the reaction exhibits pseudo-first-order kinetic behavior over the pressure range studied. The intensity of **5** is linearly proportional to the alkene pressure in all cases, which is consistent with the proposed mechanism. If a substantial portion of the reverse reaction occurs, then the kinetic equations are changed and linearity with alkene pressure is not expected. It is also immediately apparent from the data summarized in Table II that the rate of π-complex formation *increases* with increasing methyl substitution. This observation in itself is significant because it is generally assumed that exothermic reactions forming a single product of the type A + B → C are not efficient because the thermally excited product ion C must dispose of its excess energy or else revert back to reactants. Other examples of an ion association reaction involving lead[7a] and iron-65 containing species have been reported. Thus, heavy metals seem to assist in stabilizing association products. We have recently pointed out that the mercurinium ion derived from allene is formed with about 20% efficiency.[8b] Our overall data suggest that mercurinium ion formation from alkene and CH_3Hg^+ is a major pathway.

Table II. Comparison of Mercuration Rate Constants and Argentation Equilibrium Constants

Alkene	k_1 ($\times 10^{-10}$ cm^3 mol^{-1} s^{-1})[a] formation of **1**	k_1 ($\times 10^{10}$ mol^{-1} s^{-1})[b] loss of CH_3Hg^+	Hydroxy mercuration relative rate[c]	Relative argentation equilibrium constant[d]
Ethylene	0.38 ± 0.05 (1.0)[e]	2.7 ± 0.4	1.00	1.00
Propylene	0.83 ± 0.13 (2.2)	2.9 ± 0.3	19.6	0.41
1-Butene	1.6 ± 0.2 (4.2)	1.6 ± 0.1	15.6	0.35
Isobutylene	1.4 ± 0.3 (3.7)	3.7 ± 0.9	>200	0.17
trans-2-Butene	1.2 ± 0.2 (3.2)	5.2	0.33	0.06
cis-2-Butene	2.0 ± 0.1 (5.3)		1.1	0.24
2-Methyl-2-butene	1.6 ± 0.3 (4.2)	5.2	1.24[f]	0.04
2,3-Dimethyl-2-butene			0.61[g]	0.004
Allene	1.4 ± 0.5 (3.7)	1.5 ± 0.5		0.04
1,3-Butadiene	1.4 ± 0.3 (3.7)	3.9 ± 1.3		0.19

[a] Rate constants were calculated from the rate expression: log $(I_0/(I_0 - X)) = [\text{alkene}]k\tau/2.3$. [b] Rate constants were calculated from the rate expression: log $(I/I_0) = [\text{alkene}]k\tau/2.3$. [c] Values taken from ref 15, where $k = 5.1 \times 10^3$ M^{-1} s^{-1} for ethylene at 298 K using $Hg(ClO_4)_2$ in H_2O. [d] Argentation constants were taken from ref 20, where the equilibrium constant $K_1 = 22.3$ for ethylene at 314 K. [e] Relative rate of formation of **1**. [f] Estimated from the rate of 2-methyl-2-pentene, which is 1.24 times greater than cyclohexene.[15] Cyclohexene has essentially the same rate constant as ethylene ((5 ± 1) × 10^3 M^{-1} s^{-1}).[16] [g] Estimated by comparison to cyclohexene (see footnote *f* above).

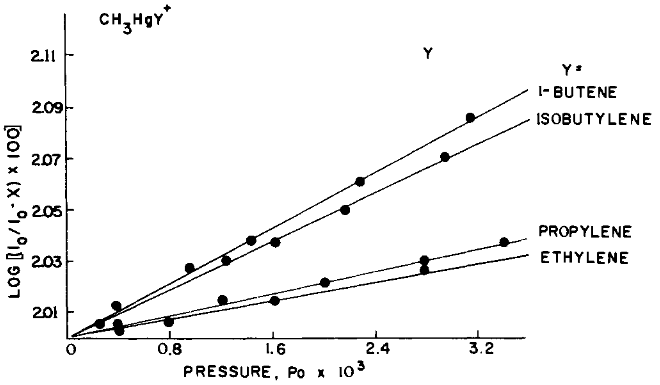


Figure 2. Kinetic plots of the disappearance of $HgCH_3^+$ (▲) and the appearance of $C_3H_4HgCH_3^+$ (●) vs. allene pressure in dimethylmercury-allene mixtures. The dimethylmercury pressure is 2.6×10^{-4} Pa (2.0×10^{-6} Torr), I_0 is the $HgCH_3^+$ intensity at zero allene pressure, I is the $HgCH_3^+$ intensity, and X is the $C_3H_4HgCH_3^+$ intensity.

Ion fragmentation does occur, as evidenced by the relatively large amounts of **7** observed (Table I). This ion most likely arises by homolytic carbon-carbon bond cleavage resulting in loss of a methyl radical from **6**. Ion ejection experiments, where a second rf pulse irradiated Hg^+, established that the major pathway for formation of **6** was a reaction of C_4H_8 with Hg^+. However, one cannot exclude the possibility that **6** derives in part from loss of $CH_3\cdot$ from the thermally excited mercurinium ion **5**.

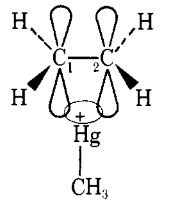
Pseudo-first-order rate constants for the loss of CH_3Hg^+ were also measured by plotting log I/I_0 vs. the pressure of alkene, where I = intensity of CH_3Hg^+ at time t and I_0 = intensity of CH_3Hg^+ at zero alkene pressure. As noted previously,[8b] there is not a 1:1 correspondence between loss of CH_3Hg^+ and appearance of **5** with the possible exceptions of 1-butene and allene[8b] (Figure 2). Two additional reactions of CH_3Hg^+ were observed that could account for this fact.

$$CH_3Hg^+ + CR_2{=}CR_2 \longrightarrow CH_3Hg + CR_2{=}CR_2^+ \quad (4)$$

$$(CH_3)_2Hg + CR_2CR_2^+ \longrightarrow CH_3Hg^+ + CR_2{=}CR_2 + CH_3 \quad (5)$$

When ethylene was introduced into the ICR cell, the intensity of CH_3Hg^+ increased. In other experiments, as the alkene pressure increased, the intensity of the CH_3Hg^+ peak increased and then decreased. Thus, the observed rate constant for loss of CH_3Hg^+ is the net result of the ion-molecule reactions described by eq 3-5.

We also wish to suggest the most probable structure for the product ions observed, based upon extended Hückel molecular orbital calculations. One of the difficulties inherent in postulating the existence of intermediate ions on the basis of MO calculations is that the role of solvent in stabilizing charged species is difficult to ascertain. Our ICR experiments clearly indicate that mercury-alkene π complexes are capable of existence in the gas phase in the absence of solvent molecules. The ions derived from the interaction of CH_3Hg^+ and an alkene may exist either as a symmetrically bridged π complex such as **8** or as the classical ion **9** with sp^2 hybridization at C_1 and sp^3 hybridization at C_2. Our calculations suggest that **8** is 171 kJ/mol (40.9 kcal/mol) more stable than the nondelocalized ion **9**. Proton transfer with rearrangement to the ethyl cation, $CH_3C^+HHgCH_3$, is calculated to be endothermic by ~670 kJ/mol. These data are in good agreement with experimental NMR evidence,[5] where the importance of bridging in mercurinium ions in solution has been firmly established. A symmetrically bonded π complex such as **8** may be construed as an internally solvated carbocation, where a majority of the positive charge is localized on the metal. This is especially true with mercurinium ions, since the polarizable carbon-mercury σ bond is very efficient at stabilizing an adjacent empty π orbital on carbon by σ-π hyperconjugation. Recent experimental[11] and theoretical[3] evidence have provided ample evidence for the significance of this mode of stabilization of adjacent cationic centers. Stabilization by σ-π hyperconjugation is particularly effective in the unsymmetrical mercurinium ion **10**, where the C-Hg σ bond and the π orbital are coplanar. Indeed, the energy difference between **9** and **10** is small in marked contrast to an onium ion, where the neighboring group



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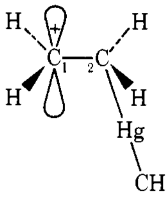

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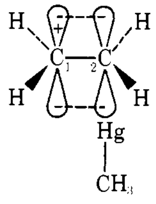

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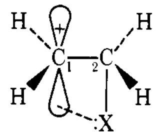


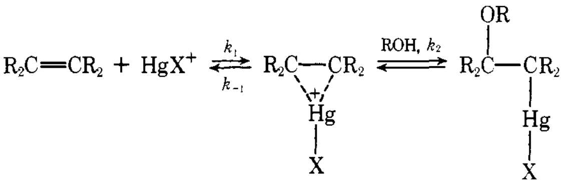
11

is halogen **11** (X = Cl, Br, I). Intuitively, the internally stabilized bridged intermediate should be even more important in the gas phase than in solution, where the carbonium ion center in **9** may be stabilized by solvent interaction.

One measure of the strength of the metal-alkene bond (i.e., the extent of perturbation of the π MO) is to compare the Mulliken overlap population[12] ρ (ρ may be taken as an estimate of the relative bond order between two atoms) of an alkene π MO to that in its complexed state. For example, extended Hückel (EH) calculations show that for ethylene, $\rho_\pi = 0.53$, while the C_1–C_2 π-bond overlap in the π-complex **8** has been reduced to 0.368. The positive charge on C_1 in **10** is stabilized principally by σ–π hyperconjugation. In contrast, both EH and CNDO/2 calculations suggest that with a chloronium or bromonium ion the charge on C_1 is mainly stabilized by electron density on halogen (i.e., neighboring-group participation), as depicted in **11**.[3a]

MO calculations indicate that the bonding in silver[13,3a] and mercury[3a] π complexes is due largely to overlap of the filled π orbital of the alkene with the vacant s orbital of the metal. The amount of dπ–pπ back-bonding of metal electron density with the antibonding π-orbital of the alkene is minimal. The extent of back-bonding, however, will be influenced by the effect of alkyl substituents on the energy of the lowest unoccupied molecular orbital (LUMO), which is the π^* orbital of the alkene. In order to determine the trend in orbital energies anticipated with substituted alkenes, we have carried out ab initio molecular orbital calculations[14] on ethylene, propylene, and *trans*-2-butene. Using a STO-3G basis set we found the energy of the HOMO to be −9.12, −8.59, and −8.10 eV and the energy of the LUMO to be 8.93, 9.03, and 9.10 eV, respectively. Thus, alkyl substitutions cause both HOMO and LUMO to increase in energy. This should favor the σ-type bond to the metal, but should destabilize dπ–pπ back-bonding of d electrons on the metal with the π^* orbital of the alkene. Unfortunately, the relative importance of these two types of bonding cannot yet be reliably studied by theoretical means.

Finally, we wish to comment upon the relevance of our gas-phase studies to the comparable reactions in solution. The generally accepted[2,4] mechanism for the oxymercuration of alkenes in protic solvents involves a rapid preequilibrium of alkene with the mercurinium ion **12** with a subsequent rate-limiting attack by solvent on this intermediate π complex (eq 6). The overall reaction rate is decreased with increasing alkyl substitution with 1,1-disubstituted alkenes exhibiting the fastest rate and tetramethylethylene reacting ~16 times slower than ethylene[15] (see Table II). There is still controversy about the involvement of mercurinium ions as discrete intermediates in the oxymercuration reaction. Kinetic evidence to support their intermediacy has not been observed.[16] However, if these π complexes are not involved, then one must invoke a termolecular AdE3 mechanism.[17] We emphasize that these ions have been observed by NMR techniques,[5] by a potentiometric study[18] of ethylene in aqueous mercuric perchlorate at very high acid concentrations, and in the gas phase.[8] If one assumes that a steady-state concentration of mercurinium ion is present under typical oxymercuration conditions, then one should observe a rate constant $k' = k_2K_{eq}$, where K_{eq} is that for mercurinium ion formation (eq 6). Since there is no data available concerning the magnitude of this equilibrium constant, we suggest that the trends noted for silver ion complexation with alkenes should parallel those for mercury. MO calculations[3a] suggest that the bonding characteristics and the positive charge at carbon for π complexes of ethylene with CH_3Hg^+ and Ag^+ are quite similar.



$$R_2C{=}CR_2 + HgX^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{\diagdown + \diagup\\ Hg\\ |\\ X}}{R_2C{-}CR_2} \overset{ROH,\ k_2}{\rightleftharpoons} \underset{\substack{|\\ Hg\\ |\\ X}}{\overset{\substack{OR\\ |}}{R_2C{-}CR_2}} \qquad (6)$$

12

Infrared studies[19] of a series of alkenes with solid silver tetrafluoroborate showed that the strength of the silver-alkene bond is primarily dependent upon the basicity of the π-MO. An increase in perturbation of the double bond stretching frequency was noted with increasing alkyl substitution. A linear correlation of this stretching frequency with the alkene ionization potential was observed. Consistent with these data is a theoretical study[13b] which suggests that the calculated enthalpy of complex formation of Ag^+ with alkenes increases with increasing methyl substitution on the double bond. Interestingly, the most stable silver complexes in crystalline form and chloroform solution had two alkenes bonded to each silver ion. Thus, the theoretical calculations[13b] (gas phase) and the thermodynamic data for Ag^+ complexation in the absence of solvent are parallel to our kinetic studies of gas-phase reactions of CH_3Hg^+ with alkenes.

The complex strength (argentation constant) of alkenes with Ag^+ (Table II) in solution markedly *decreases* with an increase in methyl substitution.[20] It has also been noted that the heat of dissociation of solid $AgNO_3{\cdot}C_2H_4$ of 44.3 kJ/mol (10.6 kcal/mol) is about twice as large as the value (24 kJ/mol) for this complex in an aqueous solution.[21a] The structural features that are mainly responsible for determining the stability of these complexes are also closely related to those that determine the stability of complexes of solid iodine, where similar trends are observed.[21b] However, tetramethylethylene undergoes bromination in solution at a rate of 3.2×10^3 faster than ethylene.[22] This has been attributed to the inductive electron release of the methyl groups, which increases the energy of the HOMO and also stabilizes the positive charge at carbon as the cyclic bromonium ion develops. The relative rate differences for bromination are much greater in CH_3OH than in the less polar solvent $CF_2ClCFCl_2$.[23]

The apparent differences between metal complex stability and rates of bromination cannot be attributed to solvent effects alone. A combination of gas-phase[24] and solution[25] data have established the relative stability of cyclic bromonium ions to be the *same in the gas phase and in solution.* It was also shown that the bromonium ions were considerably more stable in the gas phase than in solution.[24]

In conclusion, our rate studies on gas-phase mercurinium ion formation parallel the trend noted for argentation constants in the absence of solvent and exhibit a trend opposite to metal π complexes[20] in solution, where the effect of the alkyl groups is greatly attenuated by solvent interaction. Obviously, the mode of stabilization of these alkene-electrophile complexes also plays a major part in determining their relative stabilities.

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Nuclear Magnetic Resonance Studies on Anion-Exchange Reactions of Alkylmercury Mercaptides[1]

Robert D. Bach* and A. Thomas Weibel

Contribution from the Department of Chemistry, Wayne State University
Detroit, Michigan 48202.

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Abstract: NMR experiments aimed toward elucidation of the mechanism of anion exchange of alkyl mercurials is described. Mercaptide anion exchange in RHgSR′/RHgSR″ systems exhibits second-order kinetic behavior. Evidence is presented that anion exchange proceeds through a four-center bridged intermediate with total exclusion of an ionic pathway.

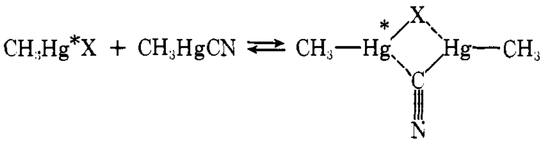
The importance of alkylmercury mercaptides (RHgSR′) as a class of compounds has become increasingly obvious with recent disclosures of widespread mercury contamination in the environment. Methylmercury derivatives[2a] have received particular attention, since these compounds are produced in living systems from a variety of organic and inorganic mercury species. The unusually strong covalent bond between mercury and sulfur has prompted the suggestion[2b] that alkylmercury derivatives are carried through complex biological systems containing the sulfhydryl group (ORG-SH) as mercaptides by the exchange process given in the equation

$$\mathrm{RHgSR' + ORG{-}SH \rightleftharpoons RHgS{-}ORG + R'SH} \qquad (1)$$

Indeed, the generic term mercaptan was coined because of the avidity of thiols for ionic mercury. The biosynthesis of methylmercury has, in fact, been shown to be stimulated in the presence of mercaptans.[3]

Despite the biological significance of sulfur as a ligand, spectral and structural studies on these organomercurials have only recently been carried out. The vibrational spectrum of CH_3HgSCH_3[4] and the infrared and mass spectral properties of C_6H_5HgSCN[5] have been reported. Spectral studies of the complexation of CH_3HgSCN with SCN^- have also been published.[6] Although a number of NMR studies on sulfur-containing mercurials have appeared,[7-13] a systematic NMR investigation of the mechanism of the exchange reaction of a methylmercury mercaptide with a sulfhydryl group has never been reported.

NMR studies have shown that rapid intermolecular-exchange reactions of methylmercury halides and pseudohalides proceed by a second-order pathway. The exchange has been established as proceeding by transfer of the ligand on mercury without carbon-mercury bond rupture.[7,14] A mechanism involving the four-center bridged transition state **1** was invoked for the CH_3HgCN/CH_3HgX exchange process (eq 2).



1

$$\rightleftharpoons \mathrm{CH_3HgX + CH_3Hg^*CN} \qquad (2)$$

However, a pre-exchange equilibrium in which solvent-separated ion pairs were formed could not be excluded.

The controversy concerning an ionic mechanism versus a pathway utilizing covalently bound species forming a bridged transition state in mercury-exchange reactions had its origin in a series of papers by Hughes, Ingold, and co-workers.[15] They stated that one alkyl mercury exchange of RHgX with $^*HgBr_2$ could not be explained on the basis of a "closed" or bridged transition state. More recently, arguments that the proposed alkyl group exchange via an "open transition state" violates the principle of microscopic reversibility have been presented.[16] This criticism, however, has since been challenged.[17] Thus, the mechanism for alkyl and anion exchange in RHgX compounds still remains in question.

In the present study, we report a series of NMR experiments aimed toward elucidation of the mechanism of anion exchange of alkyl mercurials. Our data provide the first unequivocal evidence for anion exchange involving a four-center bridged intermediate in the exchange of an alkyl mercury mercaptide with the total exclusion of an ionic mechanism. We have also developed a model system that has provided fundamental information concerning viable pathways for methylmercury migration in biological systems.