δ 8.4, 19.1, 27.0, 27.3, 27.8, 65.3, 77.7, 93.7, 104.8, 109.9, 120.9, 126.9, 127.7, 128.6, 129.9, 132.3, 131.0, 140.6, and 155.6.

To a solution containing 100 mg (0.7 mmol) of **53** in 35 mL of methylene chloride was added 5 mg of rhodium(II) octanoate. The reaction mixture was stirred at rt for 20 min, and then the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to give 84 mg (90%) of (*Z*)-2-methyl-3-(5-(2-furyl)penten-1-yl)inden-1-one (**54**): IR (neat) 1712, 1600, 1455, and 1310 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.77 (m, 2 H), 2.07 (q, 2 H, *J* = 7.2 Hz), 2.65 (t, 2 H, *J* = 7.2 Hz), 5.89 (d, 1 H, *J* = 1.5 Hz), 5.95 (m, 1 H), 6.12 (m, 1 H), 6.25 (m, 1 H), 6.95 (d, 1 H, *J* = 7.2 Hz), 7.24 (d, 1 H, *J* = 1.5 Hz), 7.14–7.30 (m, 2 H), and 7.38 (d, 1 H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.3, 27.2, 27.3, 33.5, 105.0, 109.9, 119.9, 121.9, 122.6, 127.7, 130.2, 131.7, 132.7, 140.1, 140.8, 144.6, 152.1, 155.4, and 198.8; HRMS calcd for $C_{19}H_{18}O_2$ 278.1308, found 278.1309.

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Registry No. **4**, 142458-55-7; **6**, 142458-56-8; **7**, 124583-37-5; **8a**, 124583-38-6; **8b**, 124583-39-7; **9**, 142458-57-9; **10**, 142458-58-0; **11**, 142458-59-1; **12**, 142458-60-4; (*E*)-**13**, 142458-61-5; (*Z*)-**13**, 142458-62-6; (*E*)-**14**, 142458-63-7; (*Z*)-**14**, 142458-64-8; **15**, 124583-34-2; *cis*-**16**, 142458-65-9; *trans*-**16**, 142458-66-0; **17**, 142458-67-1; **24**, 142458-68-2; **27**, 142458-69-3; **28**, 142458-70-6; **29**, 84-85-5; **30**, 41426-37-3; **31**, 36159-76-9; **32**, 142458-71-7; **35**, 142458-72-8; **36**, 142458-73-9; **44**, 138308-51-7; **45**, 142458-74-0; **46**, 142458-75-1; **51**, 142458-76-2; **52**, 142458-77-3; **53**, 142458-78-4; **54**, 142458-79-5; methyl 2-iodobenzoate, 610-97-9; 3-methyl-1-butyne, 598-23-2; methyl 2-(3-methyl-1-butynyl)benzoate, 142458-80-8; rhodium(II) mandelate, 80911-97-3; methyl 2-bromobenzoate, 610-94-6; 2-methylbutyn-2-ol, 115-19-5; methyl 2-(2-hydroxy-2-methyl-3-butyn-4-yl)benzoate, 33577-96-7; methyl 2-(2-methoxy-2-methyl-3-butyn-4-yl)benzoate, 142458-81-9; 1-ethynylcyclopentanol, 17356-19-3; methyl 2-[2-(1-hydroxycyclopentyl)ethynyl]benzoate, 142458-82-0; rhodium(II) octanoate, 68803-87-2; 1-ethynylcyclohexanol, 78-27-3; methyl 2-[2-(1-hydroxycyclohexyl)ethynyl]benzoate, 142458-83-1; 1-heptyne, 628-71-7; methyl 2-(1-heptynyl)benzoate, 118476-16-7; 4-pentyn-1-ol, 5390-04-5; allyl bromide, 106-95-6; 5-(allyloxy)-1-pentyne, 130018-34-7; methyl *o*-[5-(allyloxy)-1-pentynyl]benzoate, 142458-84-2; methyl 2-ethynylbenzoate, 33577-99-0; 2-bromo-*m*-xylene, 576-22-7; 2-bromoisophthalic acid, 22433-91-6; methyl 2-bromoisophthalate, 39622-80-5; methyl 2-ethynylisophthalate, 142458-85-3; rhodium(II) acetate, 5503-41-3; 1-bromo-3-chloropropane, 109-70-6; 1-chloro-3-furylpropane, 40517-25-7; 5-(2-furyl)-1-pentyne, 142458-86-4; methyl 2-iodophthalate, 610-97-9; methyl *o*-[5-(2-furyl)-1-pentynyl]benzoate, 142458-87-5; 6-(2-furyl)-1-hexyne, 122132-28-9; methyl-*o*-[6-(2-furyl)-1-hexynyl]benzoate, 142458-88-6; furan, 110-00-9.

Supplementary Material Available: ^1H-NMR and ^{13}C-NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Comparison of the Mechanisms of the Bromination and Oxymercuration Reactions of Alkenes

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An NMR method is used to measure the formation constants for complexation of mercuric chloride and silver triflate with a series of alkenes. The trends for mercury complexation parallel the argentation constants. These data are used in a discussion of the mechanism of both the bromination and oxymercuration of alkenes. Arguments are presented that the two electrophilic addition reactions have different rate-limiting steps. In the bromination reaction the rate-determining step is the formation of a bromonium ion intermediate while oxymercuration proceeds by rate-limiting attack by solvent on a mercuronium ion intermediate in agreement with the accepted mechanism.

Introduction

The mechanistic studies to date on the mechanism of electrophilic addition to alkenes,[1] such as the bromination[2] and oxymercuration reactions,[3] have provided considerable data concerning the reactive intermediates involved, the nature of the transition state, and the stereochemistry of the addition step. The rate of bromination is strongly accelerated by alkyl substituents and retarded by electron-withdrawing substituents. Reaction with bromine normally proceeds by an antarafacial addition to nonconjugated alkenes. These observations can be satisfactorily explained on the basis of the formation of a "bromonium ion" as first postulated by Roberts and Kimball.[4a] Olah and Hockswender[4b] proposed that in a nonpolar medium a molecular complex forms which then collapses to the cyclic bromonium ion with loss of Br^-. The bromonium ion was observed[5a] by NMR spectroscopy at low temper-

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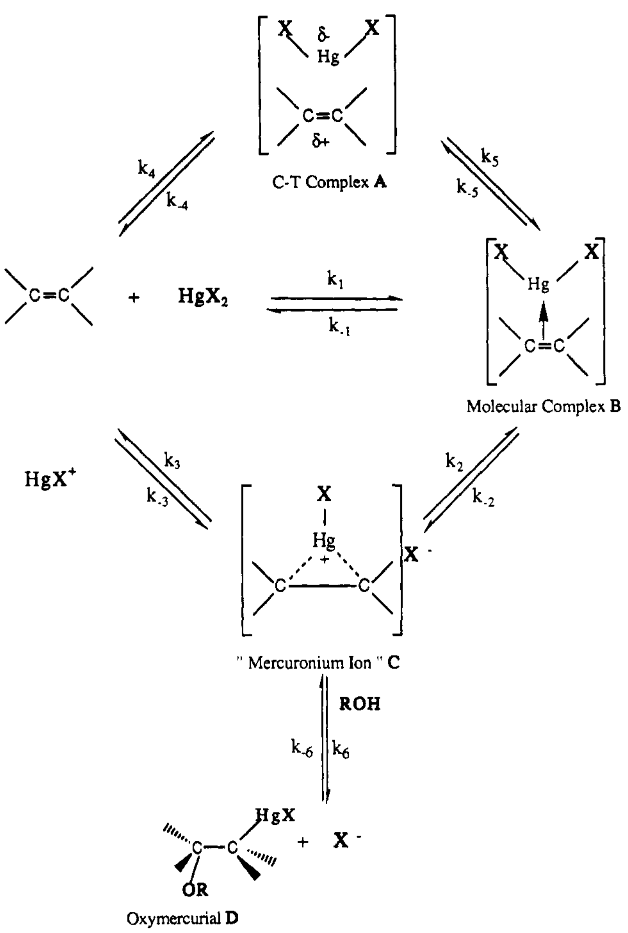
atures in a medium of low nucleophilicity (SbF_6–SO_2). Wynberg and co-workers[5b] have isolated the bromonium ion as the tribromide salt. X-ray crystallographic studies have recently supported the existence of such cyclic bromonium ions.[5c]

The oxymercuration reaction[3b] is thought to involve electrophilic addition of a mercuric salt to an alkene in a fast reversible step leading to a mercuronium ion, which in a rate-determining step is attacked by a nucleophile (solvent) leading to the product called the oxymercurial. The addition product has been shown to have Markovnikov regiochemistry and be predominantly of anti stereochemistry.[3c] Winstein originally proposed that the reaction proceeded through the intermediacy of a "mercurinium ion".[6] This mechanism has been supported by a number of kinetic studies, which have provided evidence consistent with the intermediacy of a positively charged onium ion species.[7] Stable mercuronium ions have been observed in a medium of high acidity by ^1H, ^{13}C, and ^{199}Hg NMR.[8a–c] Mercuronium ions have also been detected in the gas phase.[8d] The fact that the mercuronium ion is very labile is one reason for its elusive nature. Its observation by NMR was possible only by using high concentrations of acid whereby an observable amount of the mercuronium ion accumulated. To date there is no unequivocal evidence that this postulated intermediate exists under the actual oxymercuration reaction conditions.

The accepted rate expression for oxymercuration includes the equilibrium constant for the formation of the positively charged mercuronium ion as outlined in Scheme I; rate = $K_3k_6[HgX_2][\text{alkene}]$. The earliest attempt to measure K_3 was in 1939 when the complexation of $Hg(NO_3)_2$ with cyclohexene was measured in water by a distribution method.[6] Conductivity measurements were used to study the complexation of $HgCl_2$ in aqueous acid,[9] and a gas chromatographic method was utilized to measure the complexation of $Hg(OCOCF_3)_2$ with cyclohexene.[10] However, it is quite possible that these efforts actually measured the formation of covalent adducts as well as π-complexes. Various Hammett–Taft types of analyses of the rates of oxymercuration have been attempted to gain an understanding of the influence of the substituents upon the nature of the transition state.[7,11] Based on these studies, Halpern and Tinker[7c] and others have postulated either symmetric[7c] or unsymmetric[7d,e] bridged onium ions as intermediates. A study of the structural effects of the alkene on the oxymercuration reaction leads to the conclusion that the intermediate formed may be either an open or a bridged ion depending upon the nature of the substituent.[11b] Strongly electron-donating substituents favor open ions, and bridged intermediates are formed in the absence of electronic factors that can stabilize β-metallo carbenium ions.[11b] Tidwell has concurred with Olah's view[12] that oxymercuration involves a continuum of ions.

Scheme I. Mechanism of Oxymercuration



Fukuzumi and Kochi, in a recent effort to unify the mechanism for bromination and oxymercuration, detected charge-transfer bands for the complexation of alkenes with bromine and mercuric salts.[13] They measured the differences in the charge-transfer spectral energies of a series of alkyl-substituted alkenes with reference to a common alkene and defined a "steric term" ε as

$$\epsilon = \Delta E/2.3RT$$

where $\Delta E = E - E_0 = \Delta\omega = \Delta h\nu_{ct} - \Delta I$; ΔI is the difference in the ionization potential of the alkene and the reference alkene (1-pentene), $\Delta h\nu_{ct}$ is the difference in the charge-transfer spectral energies of the two alkenes, and ω is the interaction energy term. The term ε approximates a correction factor which reflects the difference between the calculated and measured charge-transfer energy and is dependent upon the steric factors involved in the complex formation. The ε term was utilized to interrelate the bromination and oxymercuration reactions and the following relationship was derived:

$$\log\,[k/k_0]_{Br_2} + \epsilon_{Br_2} = \log\,[k/k_0]_{HgX_2} + \epsilon_{HgX_2}$$

Despite the fact that the reactivity patterns of the alkenes are quite different (Figure 1) and the two addition reactions generally follow opposite trends, when the steric interaction term was evaluated independently as ε and included in the relative reactivity a nearly linear correlation between these two processes was observed. It was con-

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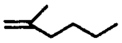
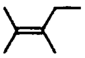
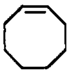
Table I. Formation Constants for the Complexation of Alkenes with $HgCl_2$ and Ag^+

alkenes	rel rate oxymercuration[a]	K_{eq}, $HgCl_2$		K_{eq}, Ag^+			IP,[d] eV	strain[e] energy, kcal/mol
		K_{obs}[b]	K_{rel}	K_{obs}[b]	K_{rel}	K_{rel}[c]		
	1.0	2.02	1.0	17.8	1.0	1.0	9.48	0.07
	0.035	0.40	0.198	3.07	0.172	0.07	9.09	0.05
	10.0	1.3	0.64			0.488	9.12	
	0.26	0.81	0.40	3.27	0.184	0.054	8.68	1.60
	0.012	0.09	0.045	*f*		0.0067	8.27	4.60
	0.21	0.335	0.166	15.31	0.86	0.242	8.95	2.61
	0.00042	0.10	0.050			0.966	8.97	8.81
	0.77	*g*		430[h]	24.2	14.42	8.95	23.62
	2.1[i]	*g*		900[h]	50.6	250	8.91	17.85

[a] Hg(OAc) in THF/H_2O from ref 5a. [b] NMR measurements were taken in methanol. [c] Argentation constants measured by gas chromatographic techniques, ref 14. [d] Ionization potentials from ref 27. [e] Alkene strain energies from ref 24. [f] *K* is too small to measure. [g] *K* is too large to measure accurately and adducts are formed. [h] Values have a large standard deviation. [i] Relative rate from ref 25.

cluded that "when the steric terms for the olefin–bromine and olefin–mercury(II) interactions are included, the relative reactivities of various olefins to electrophilic bromination and mercuration are identical".[13] This highly interesting, unprecedented relationship was interpreted to signify that related transition states are actually involved in these apparently dissimilar processes and that the relative reactivities in bromination and oxymercuration are expected to be the same in the absence of steric differences among olefins.

These observations imply that the transition states and hence the rate-determining steps for both bromination and oxymercuration must be related. These conclusions stand in contrast to the previously accepted idea that the rate-determining step in bromination is the formation of the intermediate and that for oxymercuration it is the attack of the nucleophile on an intermediate, and that these differences in the mechanisms are manifested in the different rate trends for the two reactions. Any overall mechanism that encompasses both reactions must account for the fact that the rate of bromation increases nearly linearly over 6 powers of 10 with increased alkyl substitution while oxymercuration rates are barely measurable for tetrasubstituted alkenes (Table I).

We chose to take an alternative approach to this problem by measuring the formation constants for the complexation of alkenes with Hg(II) in order to understand the effect of steric interactions on the magnitude of the formation constants for these weakly bound π-type complexes. These equilibria have not been measured by conventional methods. Since comparable alkene–Ag^+ complexes have been well characterized by gas chromatographic techniques,[14] we have also examined these by NMR to provide a comparison between the steric interactions involved in these metal–alkene complexes. The similarity of the bonding mode of Ag^+ and HgX^+ with a double bond suggests that silver ion should serve as a suitable model cation to examine structural reactivity relationships of π-complexes.[15]

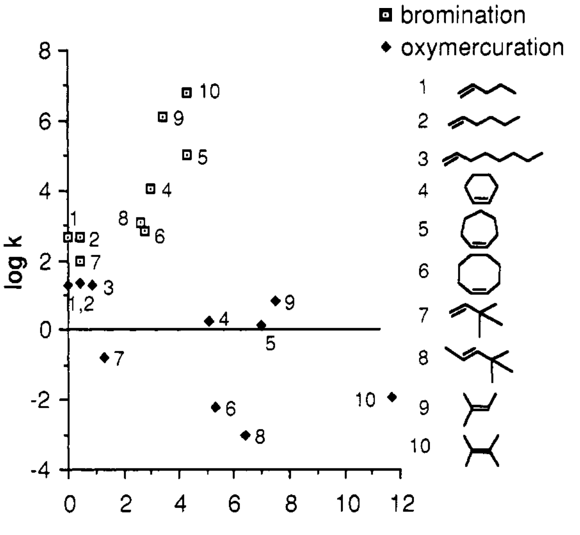


Figure 1. Relationship between the reactivity of a series of alkenes in the bromination and oxymercuration reactions in methanol and the steric factor ϵ relative to 1-pentene (data from ref 13).

Measurement of Equilibrium Constants

In previous reports[16] we have described a very sensitive NMR probe that measured the equilibrium constants for the interaction of MeHg(II) with a variety of cyclic and acyclic ligands. The ^{199}Hg nucleus is very sensitive to both the primary ligands and the immediate solvation shell surrounding the metal, and this is reflected in the large

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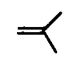
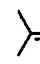
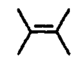
Table II. Relative K_{eq} and HOMO Energy Levels for Neutral Alkenes and Their Radical Cations

alkene	E_{HOMO}, eV[a] neutral alkene	E_{HOMO}, eV[a] radical cation	stabilization energy, kcal/mol, rad. cation[a]	rel K_{eq}[b] Ag^+	rel. K_{eq}[b] $HgCl_2$
	-9.1	-19.6		6.19[c]	
	-8.6	-18.1	14.0 (14.8)	1.16	6.03[d]
	-8.2	-17.4	25.2 (27.3)	3.0[c]	3.88
	-8.1	-16.7	25.7 (26.7)	0.20[e]	
	-7.8	-16.0	35.0 (37.0)	0.21	2.42
	-7.5	-15.3	(45.6)	*f*	0.27

[a] Reference 26 (HF/4-31G//STO-3G, the values in parentheses are STO-3G). [b] Relative to cyclohexene. [c] Reference 14. [d] 1-Hexene. [e] *trans*-2-Octene. [f] Too small to measure.

range of chemical shifts extending over 4000 ppm.[17] Since the equilibrium involving the metal and the ligand is rapid on the NMR time scale, only one resonance, which is the weighted average of the signals of the uncomplexed and the complexed metal species, is observed.

For the equilibrium involving the interaction of a mercuric salt with added alkene ligand L, it follows that

$$\underset{(a-x)}{R_2C{=}CR_2} + \underset{(b-x)}{HgX_2} \overset{K_f}{\rightleftharpoons} \underset{(x)}{[\text{complex}]}$$

if one assumes no prior dissociation or association of the reactants. In these experiments the initial concentration of alkene (a) remains constant while the concentration of the ligand (b) is varied. The equilibrium constant may then be expressed in terms of the reciprocal of the observed change in chemical shift as follows:[16]

$$\Delta\delta^{-1} = K_f^{-1}(\delta_x - \delta_0)^{-1}b^{-1} + (\delta_x - \delta_0)^{-1} \qquad (1)$$

The procedure employed in the evaluation of K_f is to substitute the experimental parameters $\Delta\delta$, δ_0 (the initial chemical shift of a), and vary the two adjustable parameters K_f and δ_x (the chemical shift of fully complexed a) until the calculated chemical shifts correspond to the experimental $\Delta\delta$ values within given error limits.[16,18] The general nonlinear curve-fitting program KINFIT-4[19] was used with the appropriate equations given here (eq 1) and elsewhere.[16] This general method for measuring formation constants has been amply demonstrated by several groups.[20]

The argentation constants for the alkenes were determined by an analogous method in which the ^{13}C chemical shift changes of the sp^2 carbon of the alkene upon complexation with the Ag^+ species were measured. For the unsymmetrical alkenes, the K_f were calculated by utilizing the ^{13}C shift change of both alkene carbons. The two values were in good agreement with one another, within experimental error limits. The formation constants for the complexation of the series of substituted acyclic and cyclic alkenes with silver trifluoromethanesulfonate (AgOTf) and $HgCl_2$ were measured in methanol, which has been the solvent of choice for many of the kinetic studies. AgOTf was chosen because of its high solubility and because it is capable of complexing strongly with alkenes.[21] Mercuric chloride was used as the Hg(II) electrophile since it does not add to normal unstrained alkenes and only reacts very slowly with strained alkenes.

Results and Discussion

The mechanism of the oxymercuration reaction can be described as a continuum of equilibria, which may be depicted as in Scheme I. The "C-T complex", A, is a transient charge-transfer complex as observed utilizing UV spectroscopy.[13] The molecular complex, B, is a thermodynamically stable, outersphere molecular complex,[22] whose formation constant ($K_1 = k_1/k_{-1}$) we have been able to measure. The formation constants for the charge-transfer complexes are usually measured utilizing the Benesi–Hildebrand[23] procedure. The formation constants for the alkene–HgX_2 C-T complexes are difficult to measure accurately by this method. However, estimated values of 0.8 ± 0.1 for cyclohexene, 0.4 ± 0.1 for *cis*-cyclooctene with $HgCl_2$ in methanol are of the same order of magnitude as our measured formation constants (see Table I) for the equilibria represented by K_1. The charge-transfer complex involves an electron transfer from an occupied molecular orbital on the alkene to a higher lying virtual orbital on the acceptor.

An examination of the data presented in the Table I reveals that the trends in the formation constants for the complexation of the alkenes roughly parallel one another for both Ag^+ and Hg(II). However, the increase in complexation is not linear with increasing strain energies,[24] although highly strained alkenes such as norbornene and *trans*-cyclooctene do complex strongly with silver ion.[25] In contrast, 1-octene exhibits a rate of oxymercuration comparable to that of *trans*-cyclooctene and greater than that

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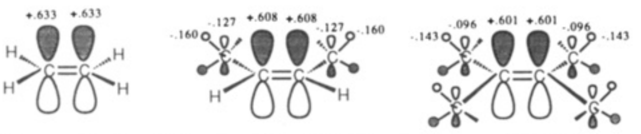

Figure 2. Coefficients of the HOMO of ethylene, (*Z*)-2-butene, and tetramethylethylene showing the interaction of the π-bond with the filled π_{CH_2} orbitals on the methyl groups.

of norbornene, suggesting that there is minimal relief of strain in the transition state. Normally, alkyl substitution on the alkenes is expected to increase the reactivities (by raising the HOMO) of the alkenes toward electrophiles. However, the formation constant data presented in Table I are contrary to such an expectation.

The ionization potential of an alkene constitutes an important component of the activation process for an electrophilic addition. In the absence of steric or solvent considerations, a very simple perturbation of an alkene is to remove one of its π-electrons. We have used ab initio calculations to determine the total energies for a series of alkenes and their corresponding radical cations.[26] The results in Table II clearly indicate that a methyl group imparts a stability to the HOMO of both the alkene and its radical cation, but the magnitude of this electronic effect is larger for the radical cation than for the neutral alkene. The stabilization energies for the isodesmic reaction $R_1R_2C{=}CR_3R_4^+ + CH_2{=}CH_2 \rightarrow R_1R_2C{=}CH_2 \rightarrow R_1R_2C{=}CR_3R_4 + CH_2{=}CH_2^+$ are summarized in Table II. This stabilizing effect of 10–15 kcal/mol for each additional methyl group is reflected in the relatively low ionization potential (E_{HOMO}) of the more highly substituted alkenes and is primarily due to the strong hyperconjugative stabilization of the radical cation relative to the neutral alkene.[27] The formation of a molecular complex involves the transfer of π-electron density into a suitable empty orbital on the electrophile without significant rehybridization at the carbon atoms. Thus, the corresponding radical cation should serve as a suitable model to assess the effects of an alkyl substituent on the stability of an alkene that has been extensively perturbed by an attacking electrophile.

The enhanced nucleophilicity of alkyl-substituted alkenes has been attributed to a raising of the energy of the HOMO of the alkene and an attendant lowering of the ionization potential. The more highly substituted alkenes have traditionally been referred to as having "electron-rich" double bonds. Ironically, the π-bond contribution to the HOMO of alkenes actually *decreases* with increasing alkyl substitution. Since the filled orbitals of the alkyl groups with π-symmetry mix in an antibonding manner into the higher lying alkene π-bond, the π-contribution to the HOMO of an alkene in a normalized wave function is diminished as a consequence of the out-of-phase contribution of the filled π_{CH_2} orbitals of the methyl (alkyl) groups (Figure 2). A lower lying bonding interaction of these orbitals is largely responsible for the increased thermodynamic stability of more highly substituted alkenes.[26] The origin of the increased reactivity of more highly substituted double bonds toward electrophiles should be attributed to the *increased energy* of the frontier π-MO which makes it a better "electron donor" and not to its electron "richness".

When an alkene interacts with a neutral mercuric salt, the molecular complex B initially formed can dissociate to a mercuronium ion C (Scheme I) by the loss of X^-. An ionic salt such as $Hg(NO_3)_2$, which is highly ionized in a polar solvent ($\log K_f = 0.83$)[28] such as water or methanol, can lead directly to the mercuronium ion as depicted by the equilibrium $K_3 = k_3/k_{-3}$. This π-complex clearly has a sufficient amount of charge delocalization that a nucleophilic solvent could attack it in a rate-limiting step leading to the formation of an oxymercurial D. This picture is consistent with the currently accepted mechanism for oxymercuration,[3b,25] which proposes a rapid preequilibrium formation of the mercuronium ion and a rate-limiting attack by the nucleophile on this species. When the mercuric salt used is not highly dissociated, for example $HgCl_2$ ($K_{diss} = 1.23 \times 10^{-7}$),[28] then $K_1 = k_1/k_{-1}$ and the corresponding ionization to the mercuronium ion $K_2 = k_2/k_{-2}$ would be expected to be small and dissociation to the mercuronium ion could become rate limiting. Since $HgCl_2$ is only slightly dissociated in polar solvents (<1% in water), it is unreactive toward most typical alkenes, and one would only expect to see a slow rate of oxymercuration. For such a covalent mercuric salt the rate-limiting step may indeed be k_2, the formation of the mercuronium ion. The lack of reactivity of $HgCl_2$ with normal alkenes could be attributed to a lack of dissociation of the molecular complex to the mercuronium ion. If the rate-limiting step were to be a loss of a Cl^-, then one might anticipate that tetramethylethylene should exhibit a faster rate than ethylene since the tetrasubstituted alkene can stabilize the positive charge more effectively (see Table II). However, the silver complex of tetramethylethylene does not form strongly, indicating that either steric interactions or solvation effects due to the hydrophobic nature of the four alkyl groups must dominate. The same is very likely true for the mercuronium ion. Further, such data clearly preclude a classical open carbenium ion[5d,e] as being involved in the rate-limiting step since the more highly substituted alkene would exhibit a faster rate of addition. The lack of molecular rearrangement in the oxymercuration of substituted norbornenes and *cis*-di-*tert*-butylethylene[25] also argues against an intermediate with a high degree of positive charge at carbon.

If one assumes a steady-state concentration of mercuronium ions to be present under typical oxymercuration conditions, then the overall rate constant should be: $k_{obs} = k_6K_3$ where K_3 is the formation constant for the mercuronium ion. Since the mercuronium ion and the silver–alkene π-complex have similar bonding characteristics, the formation constants for these species should be similar. For a mercuric salt such as $Hg(NO_3)_2$, which is highly dissociated, the formation of the mercuronium ion would be rapid and reversible, and it is reasonable to expect this highly electrophilic metal cation to form such a π-complex with little or no activation barrier. Equilibrium is rapidly established during measurement of the comparable argentation constants. An increase in the electrophilicity of the mercuric salt does result in an increased rate of oxymercuration.[13] However, this could also be a consequence of an increase in k_3. If we examine the rate data and formation constant data summarized in Table I, it is clear that although the trends in the formation constants parallel the trends in the rate constants, the magnitude of the differences in the rates is significantly greater. For example, while the K_{eq} for $HgCl_2$ decreases by a factor of 5.1 on going from 1-hexene to 2-octene, the corresponding rate decreases by a factor of 28.6. The increase in K_{eq} from *trans*-2-octene to 2-methyl-1-hexene is about 3-fold while the rate changes by a factor of almost 300. Along similar

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lines, the rate falls off by a factor of 22 on going from tri- to tetrasubstituted alkenes, while the related formation constant decreases by a factor of 9. These trends are indicative of a large steric requirement in either the formation of the mercuronium ion k_3 or the attack of the nucleophile on the mercuronium ion k_6, or both. Since the magnitude of the absolute values of the formation constants is small (Table I), the rate trends observed are consistent with the suggestion that the rate decreases are due to a steric inhibition to the attack of the solvent on the reactive intermediate, i.e. k_6.

In the absence of steric inhibition, one would anticipate that an electrophilic addition to a highly substituted alkene that involves an electron-transfer component should exhibit an enhanced rate. However, the measured formation constants presented (Table I) clearly decrease with increased alkyl substitution. The different extent to which alkyl groups impart stability to an adjacent electron-deficient carbon in these two electrophilic processes points to yet another major distinction between them. The increased demand for hyperconjugative stabilization in the transition state for bromination is reflected in the rate trends noted and is consistent with the failure to observe reversible bromonium ion formation from the dibromide product under typical bromination conditions. Reversible formation of both mercuronium ion C (k_{-3}) and oxymercurial D (k_{-6}) are known to take place with ionic mercuric salts.[9,10] If mercuronium ion formation was in fact rate-limiting, a comparable stabilizing influence would be anticipated.

Further examination of Kochi's data[13] reveals a number of interesting consequences due to structural changes in the alkene. It is very instructive to plot the steric parameter ϵ versus the log of the relative rates of bromination and oxymercuration (Figure 1). This dramatically demonstrates that the relative rates versus the steric parameter ϵ show distinctively opposing trends as stressed previously.[13] While the relative rates increase with increasing ϵ for the bromination of acyclic alkenes, the relative rates of oxymercuration correspondingly decrease but in a random manner. Also of interest is the fact that the changes in ϵ ($\Delta\epsilon$) for $Hg(OAc)_2$ are larger than the corresponding $\Delta\epsilon$ for Br_2 addition to the same set of alkenes. Thus, these data demonstrate that with increasing alkyl substitution (increasing ϵ_{Br_2}), the rates of bromination increase, while the corresponding increase in the steric parameter for oxymercuration ($^{\epsilon}Hg(OAc)_2$) is attended by a decrease in the rate.

Among the mechanistic discrepancies that must be reconciled is the origin of differences in the steric factor ϵ. A series of equilibria comparable to that shown for oxymercuration (Scheme I) may be envisaged for the bromination reaction. Steric effects clearly manifest themselves in the equilibrium constant for formation of B (K_1) and C-T complex formation A (K_4) with $HgCl_2$. Parallel behavior was noted with AgOTf complexation (i.e. K_3). In each case increasing alkyl substitution should make the reverse reaction (k_{-1}, k_{-3}, k_{-4}) faster due to steric repulsion and increased demand for solvation. Both reactions exhibit faster rates in more polar solvents which could be either a consequence of rate-limiting bromonium ion formation or an increase in K_3 for mercurinium ion formation which will be reflected in the observed rate constant for overall addition. Indeed, the increase in the steric factor ϵ noted with increased substitution is accompanied by a decrease in charge-transfer complexation, but a dramatic, nearly linear increase (correlation coefficient = 0.81) in the rate of bromination (Figure 1). These facts are all consistent with rate-limiting bromonium ion formation.[13]

The mechanistic picture for oxymercuration is far more complex. A change in the ionic nature of the mercuric salt or in the solvent can effect rate changes in the oxymercuration of isobutylene of 10^6. Trimethylethylene and 1-hexene have similar rates of oxymercuration, but ϵ differs by a factor of nearly 19 (Figure 1).[13] The dramatic decrease in oxymercuration rate on going from a tri- to a tetrasubstituted double bond is quite consistent with a decrease in k_3 and in k_6 due to steric inhibition of nucleophilic attack on the mercuronium ion. In our opinion, these data are consistent with a difference in the mechanism of these reactions and therefore *different rate-limiting steps* for the two electrophilic additions.

In conclusion, the evidence in support of the formation of the bromonium ion in the rate determining step is fairly conclusive.[2] We feel that our results tend to support the accepted mechanism for oxymercuration, viz. a rapid preequilibrium leading to the formation of a cyclic mercuronium ion which in a subsequent rate-limiting step is attacked by the nucleophile.[3] At the minimum our data suggest that a second step following alkene π-complexation is involved in the oxymercuration reaction. It is reasonable to assume that this rate-limiting step involves attack by solvent on the mercuronium ion. Unfortunately, this mechanistic question remains unresolved since an explicit partition of the two requisite rate constants k_3 and k_6 is not yet feasible.

Experimental Section

Materials. Mercuric chloride was recrystallized from methanol. Methanol used for spectral measurements was distilled from magnesium activated with iodine and stored under argon. All other solvents were of spectroscopic grade. All the alkenes were commercially available and were used as received (>98% by GC), except cyclohexene and *cis*-cyclooctene which were distilled and norbornene which was sublimed (40 °C) prior to use. *trans*-Cyclooctene was prepared according to a literature procedure[29] and collected by gas chromatography on a 6-ft 25% NMPN (3-nitro-3-methylpimelonitrile) on Chromosorb P-NAW (60–80-mesh) column at 70 °C, or a 20-ft 10% SE-30 on Chromosorb P column at 90 °C.

Measurement of ^{199}Hg Spectra. All the ^{199}Hg spectra[17] were measured using a Nicolet NT-300 spectrometer as described previously[16] at a frequency of 53.670 20 MHz. The spectra represent 4096 scans measured in 10-mm sample tubes utilizing a solution of 1.0 M $HgCl_2$ in CH_3OD as the external lock and reference. No proton decoupling was used. No bulk susceptibility corrections were made.

Fresh stock solutions of $HgCl_2$ were prepared before each set of experiments. Calculated amounts of the ligands were carefully measured (using 10–100-μL syringes) into a 2-mL volumetric flask containing a solution of $HgCl_2$, mixed well, and then transferred to the NMR tube using a Pasteur pipette.

Measurement of ^{13}C Spectra. The ^{13}C spectra for the argentation constant determinations were measured on the JEOL JNM-FX60 spectrometer at 15.03 MHz. The spectra were measured in CH_3OD–CH_3OH (3:2) solvent using tetramethylsilane as the internal standard. Calculated amounts of silver triflate were added to freshly prepared 0.1 M samples of the alkene. Appropriate amounts of a solution of sodium triflate were added to keep the ionic strength constant at 0.5 M.

Silver Trifluoromethanesulfonate. Silver oxide was prepared using an adaptation of the procedure by Whitesides[30] by slow addition of a solution of $AgNO_3$ (17.0 g, 0.1 mol) in water (50 mL) to a well-stirred solution of 1.0 M NaOH (150 mL, 0.15 mol). The dark brown solid was washed well with water (5 × 50 mL) followed by ether (3 × 25 mL) and resuspended in water (100

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mL). The well-stirred slurry was cooled to 0 °C, and trifluoromethanesulfonic acid (9.0 mL, 0.102 mol) was slowly added over a period of 1 h. The reaction mixture was brought to room temperature and stirred for an additional 1 h, filtered, and concentrated to dryness to afford 25.3 g (98.5%) of an off-white solid. The solid was recrystallized from warm ether–hexane (1:1) and washed well with ice cold ether–hexane (1:1) until colorless. The white crystalline solid was then dried in vacuo to yield 24.6 g (96%). The solid was stored in a dark desiccator. IR (Nujol): 1630 (s), 1250 (s), 1170 (s), 1020 (s) cm^{-1}.

Sodium Trifluoromethanesulfonate. An adaptation of the procedure of De Levie[31] was used. Na$_2$CO$_3$ (5.3 g, 0.05 mol) was carefully added in several small portions to a well-stirred solution of trifluoromethanesulfonic acid (8.85 mL, 0.1 mol) in acetone–CH$_2$Cl$_2$ (2:1, 120 mL). The red solution was stirred until the evolution of CO$_2$ ceased. The solution was then diluted with CH$_2$Cl$_2$ (100 mL) and cooled to −78 °C. The precipitate formed was filtered and washed with small aliquots of cold CH$_2$Cl$_2$ (to decolorize the solid) and dried to yield 17.0 g (100%) of an off white solid. Recrystallization from acetone–CH$_2$Cl$_2$ followed by washing with cold CH$_2$Cl$_2$ yielded 16.05 g (93%) of a white hygroscopic solid. IR (KBr): 1610 (w), 1385 (w), 1280 (sh), 1260 (s), 1230 (sh), 1195 (sh), 1170 (s), 1040 (s), 635 (s), 515 (w), 420 (m) cm^{-1}.

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Stereochemistry of the Reversible Cyclization of ω-Formylalkyl Radicals

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The reactions of 6-bromo-4-(1′,1′-dimethylethyl)hexanal (4), 5-bromo-3-(1′,1′-dimethylethyl)pentanal (11), and 5-bromo-4-(1′,1′-dimethylethyl)pentanal (17) with tributylstannane have been investigated in detail. The major products are the debrominated aldehydes and cycloalkanols which arise from the cyclization of the intermediate ω-formylalkyl radicals. The stereochemical outcome of the cyclization of these radicals is dependent on the stannane concentration. At high concentrations of stannane the cyclization is essentially irreversible with the cycloalkoxy radicals being trapped before β-scission can occur. Under these conditions the relative amount of cis and trans cycloalkanols formed are equal to the ratio of the rate constants for the two modes of cyclization; both 4 and 17 show a small preference for trans cyclization, but 11 gives equal amounts of the two diastereomers. When the stannane concentration is lowered, the lifetime of the cycloalkoxy radicals increases allowing β-scission to occur. Thus, the cis and trans cycloalkoxy radicals approach a thermodynamic equilibrium which is reflected in the relative yields of the cis and trans cycloalkanols.

The formation of carbon–carbon bonds through intramolecular addition of carbon-centered radicals to alkenes, alkynes, and other unsaturated centers is of considerable mechanistic interest[1] and synthetic utility.[2] Such cyclizations of substituted 5-hexenyl radicals have been studied in detail,[1] and the factors controlling the stereochemical outcome are well understood.

A useful guideline[3] for the ring closure of substituted 5-hexenyl radicals states that 1- or 3-substituted radicals preferentially give cis disubstituted products, while 2- and 4-substituted radicals give mainly trans. The explanation for the behavior of species substituted at C(2), C(3), or C(4) rests on the hypothesis that the transition structure resembles the chair form of cyclohexane, the most favorable conformer of which will contain the substituent in a pseudoequatorial position. A theoretical study,[4] involving an approach based on a combination of molecular orbital and molecular mechanics methods, provided a means for calculating the cis/trans ratio of the cyclization products. Such calculations show very good correlation with experimentally measured data.[4] A later refinement by Spellmeyer and Houk[5] demonstrated that the inclusion into the scheme of a low-energy boatlike transition structure for the formation of the lesser diastereoisomer led to closer correlation between calculated and measured data. This has recently been confirmed by experiment.[5b]

Cyclizations involving intramolecular homolytic addition to the carbonyl group of ketones[6] or aldehydes[7–9] have

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