Organic and Biological Chemistry

A Molecular Orbital Approach to the Mechanism of Electrophilic Additions to Olefins

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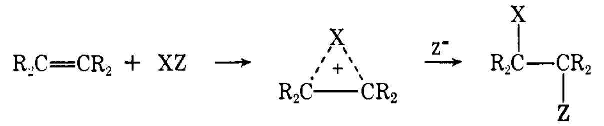
Abstract: The nature of the intermediate formed by the electrophilic addition of H^+, F^+, Cl^+, Br^+, ^+SR, ^+HgX, or Ag^+ to ethylene has been studied by extended Hückel molecular orbital calculations. The trends observed in these calculations are shown to correlate well with experimental data and chemical intuition. Overlap populations, self-consistent charge distributions, and relative energy differences for these ions are given. Total energy differences for two of the charged species are compared by CNDO/2 calculations. The overall mechanism of electrophilic additions to olefins is discussed in light of these calculations. The relative stability of the intermediates involved in these reactions is determined by the extent of perturbation of the olefin by the attacking electrophile. The mode of addition is influenced by the amount of energy required to convert the symmetrical onium ion II to its unsymmetrical form IV.

Despite the extensive research that has been carried out on electrophilic additions to olefins, an all-encompassing mechanism for this class of reactions is still not available. Many of the ambiguities that currently exist are cited in several excellent reviews[2-4] that have been published recently. Much of the discussion of the mechanism of these reactions involves product studies while little effort has been expended on a molecular orbital approach to this problem. In many cases these additions are known to proceed by the formation of olefin-electrophile complexes which subsequently undergo nucleophilic attack to afford the addition product (eq 1). The π-complex intermediates are usually extremely labile and their existence in many cases is questionable and evidence is based on chemical behavior. However, certain metals form isolable π complexes and it is to these species that we owe much of our knowledge in this area. A molecular orbital description of the bonding in these complexes, first used by Dewar,[5] suggests that a σ-type acceptor orbital on the metal is involved in addition to dπ–pπ backbonding from filled metal d orbitals into antibonding orbitals of the olefin. Extended Hückel calculations[6] on potassium trichloro(ethylene)platinate(II), Zeiss' salt, suggested that the 5d (52%), 6s (31%), and 6p (17%) orbitals all play a significant role in the metal–olefin bond based on overlap populations. The dπ–π* interaction accounts for some 31% of the total metal–olefin overlap population in this case. This result is, therefore, in excellent agreement with chemical evidence,[7] supports the suggestion by Dewar[5] that a π-type double bonding has validity, and provides evidence for the reliability of the present method of calculation to analyze this type of bonding. However, it must be emphasized that the extent of this type of bonding is a function of the relative energies of the orbitals involved and is not necessarily general.[6] For example, in these same calculations, the 5s orbital of the silver ion and the 6s orbital of the divalent mercury II cation account for 90 and 98% of the total bonding to the olefin with virtually no involvement of the metal p orbitals. Hence in these cases the dπ–pπ bonds to C_2H_4 accounted for 10% or less of the metal–olefin bond. In this paper, we wish to discuss the relevance of the mode of bonding in metal–olefin complexes, halonium ions, and sulfonium ions to the observed chemical behavior of these intermediates.



$$R_2C{=}CR_2 + XZ \longrightarrow \overset{\displaystyle X}{\overset{+}{R_2C{-}CR_2}} \xrightarrow{Z^-} \underset{\displaystyle Z}{\overset{\displaystyle X}{R_2C{-}CR_2}} \qquad (1)$$

Experimental Section

Extended Hückel (EH) calculations, as developed by Hoffmann,[8a] were carried out and an abstract of the data is presented in tabular form. The coulomb integrals, H_{ii}, were set equal to valence orbital ionization potentials (VOIP)[8b] for the particular orbital in question. The VOIP's for the silver atom were calculated to be 7.58, 3.84,

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and 10.66 for the 5s, 5p, and 4d orbitals,[9] respectively, by averaging over the spectral states given for that element by Moore.[10] VOIP's for mercury are those reported previously.[11] A comparison of the VOIP's given for copper[8b] with those calculated for silver show them to be quite comparable and they could conceivably be used interchangeably when a lack of sufficient data is encountered. The resonance integrals, H_{ij}, were evaluated using the Wolfsberg–Helmholz expression[12] with $K = 1.75$ for both σ and π interactions. The overlap integrals, S_{ij}, were calculated using atomic self-consistent field wave functions. For the metals these were the analytical representations of Herman–Skillman[8c] functions given for the 1+ metal ions by Basch, *et al.*[8b] For all other atoms the double ζ functions of Clementi[13] were employed. By taking maximum advantage of symmetry in both the molecular coordinate system and the local coordinate system in which the overlaps are calculated, the procedure was programmed as a single core load for a CDC 6600 computer.

Charges were iterated to self-consistency using a charge sensitivity factor [CONCH(I)] of 2.00 eV/electron for all VOIP's and eq 2. The self-consistency criterion for charges was taken as a difference of 0.01 e or less in the initial and final atomic charges of any atom for a given cycle.

$$H_{ii}{}^{k} = H_{ii}{}^{0} - \mathrm{CONCH(I)}q^{k-1}\mathrm{(I)} + \frac{qk\mathrm{(I)} - q^{k-1}\mathrm{(I)}}{2} \qquad (2)$$

where q^k(I) is the charge on atom I at cycle k.

The carbon–silver bond distance for the π complex was taken from X-ray data and the average carbon–carbon double bond distance reported was that for silver complexes, 1.36 Å.[14] Unless otherwise specified all calculations with C_2H_4 utilized a C–C bond length of 1.36 Å. An HCH bond angle of 116° and a C–H bond distance of 1.085 Å were used. The C–Ag bond distance (2.44 Å) in the π complex represents a 12% increase over the bond distance in CH_3Ag. Since this is the only experimental bond distance available, all other bond distances for the π complexes reported herein were estimated by increasing the normal covalent C–X bond distance[15] by 12%. The C_2H_4 was located in the XY plane with the Y axis extending through the length of the C–C bond. The attacking electrophile approached the olefin along the positive Z axis and was located symmetrically between the carbon atoms at a distance in angstroms from the center of the C=C bond of 1.375, 1.772, 1.975, and 1.920 Å for F, Cl, Br, and S, respectively, and a distance of 2.347 Å for Hg and Ag.

Results

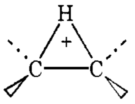
EH calculations concerning the interaction of a positively charged species with an olefin were first reported by Hoffmann,[16] and in more recent calculations he has described the addition of methylene to C_2H_4.[17] Recent calculations on cyclopropyl methyl cation,[18a] bicyclobutonium and related cations,[18b] and on cyclobutyl cation[19] have shown that conformational preferences from the EH method appear to be reasonable. The application of the EH method to charged species has recently been criticized since the success of the EH method with neutral molecules depends upon the approximate cancellation of electron–electron repulsion and nuclear–nuclear interactions. Hence the imbalance created in these terms and parametrization for neutral molecules should afford orbital energies for positively charged species that are too high.[20]

Our conclusions in this work are based principally on a comparison of overlap populations, eigenvectors, and charge distributions. Cases where we have compared total energies involving angle-bending procedures would appear to be reasonable based on a study by Allen[21] who has shown that the EH method reproduces SCF predictions in this area with reasonable success. In no instance have we placed any confidence in the absolute value of the total energy but have instead relied upon relative energies. Despite the theoretical shortcomings of this method, it appears to produce results that conform remarkably well with chemical knowledge of the reactions discussed herein.

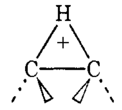
Protonated Ethylene. For the purposes of discussion the interaction of electrophilic reagents with olefins can be divided into two categories. At the extremes of this range are those reagents which only mildly perturb the double bond (true π complexes) and those which perturb the olefinic bond quite strongly.

The ethyleneargentium ion clearly falls into the former category and we shall employ this as a model π complex for a reference point. The simplest bridged cation that falls into the latter category is protonated ethylene, and it is to this complex that we shall first direct our attention.

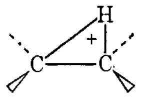
Protonated ethylene was one of the first positively charged species treated by EH calculations.[16] In a recent semiempirical SCF-MO calculation,[20] Ia was found to be only slightly more stable than an ethyl cation. *Ab initio* calculations, however, indicate that the bridged ion Ia is less stable than the nonbridged "classical" cation by 9 kcal/mol.[22]



Ia



Ib



Ic

In agreement with previously reported semiempirical calculations[20] the planar symmetrical protonated ethylene Ia is of lower energy than Ib, where the terminal carbon–hydrogen bonds are bent away from the apical proton in the tetrahedral angle. EH, CNDO/2,[23a] and the Sichel–Whitehead (SW) CNDO/2 parametrization[23b] afforded energy differences between Ia and Ib (1.36 Å) of 3.4, 2.8, and 1.7 eV and 3.6, 2.5, and 1.7 eV at a bond distance of 1.47 Å.[24]

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[9] While an Ag d VOIP of 11.85 eV can be estimated from available data, we chose to use a VOIP of 10.66 eV in order to maximize the possibility for dπ–pπ back bonding. The justification for this choice came from the extremely close parallel between energy level of Cu and Ag. For copper, more data are available and lead unambiguously to the above-mentioned VOIP.

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[24] (a) An absolute energy minimization procedure for C_2H_4 predicts a C–C bond length of 1.47 Å.[8a] With our parameters, C_2H_4 is 0.25 kcal/mol more stable at this bond distance than at 1.36 A. Since 1.47 Å[24b] and 1.44 Å[24c] are the observed C–C bond distances in ethylene

Table I. Symmetrically Protonated Ethylene

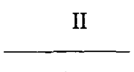
	Q_c	Q_H	Q_{H^+}	ρ_{cc}	ρ_π	π bond order	E_{lumo}	E_{homo}
				1.36 Å				
EH	0.298	0.046	0.218	1.013	0.266		7.05	14.10
CNDO/2	0.107	0.126	0.284			0.703	4.81	25.20
SW CNDO/2	0.133	0.146	0.150			0.622	9.74	19.15
				1.47 Å				
EH	0.297	0.052	0.200	0.936	0.240		7.83	14.14
CNDO/2	0.116	0.131	0.245			0.687	5.46	25.88
SW CNDO/2	0.135	0.155	0.109			0.602	9.76	19.36

In contrast to the CNDO/2 methods, EH calculations suggest that Ia would be more stable at 1.47 than at 1.36 Å by 6.8 kcal/mol. In support of this prediction the overlap population, ρ_{cc}, is reduced on protonation by approximately 24% at either bond length. More significant, however, is the marked reduction in the π-overlap population which is 0.503 and 0.453 (1.47 Å) in C_2H_4. Similarly, the π bond order calculated by CNDO/2 is reduced markedly from 1.00 observed with C_2H_4 (Table I). It seems reasonable that a reduction in double bond character should be accompanied by bond elongation.

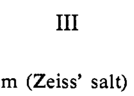
The energy required to move the proton 0.68 Å (held fixed at 1.2 Å above the planar ethylene) from its symmetrical position to a point directly over the carbon atom (Ic) has a direct bearing on the polar addition of hydrogen halides to olefins, particularly where *cis* additions have been observed.[5]

The energy increase on conversion of Ia to Ic was calculated to be 0.62, 1.54, and 0.58 eV's as determined by EH, CNDO/2, and (SW) CNDO/2. The EH overlap population, ρ_{cc}, was reduced to 1.050 from its value in ethylene while the CNDO/2 π bond orders were 0.657 and 0.559 by Pople–Segal and Sichel–Whitehead methods, respectively. It may be concluded that EH calculations on Ia–Ic are in qualitative agreement with CNDO/2 calculations on charge distribution, bond order, and molecular geometry.

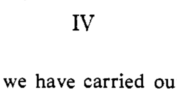
Halonium Ions. The reaction of halogen with olefins has long been recognized as an electrophilic addition. In many cases, the reaction stereospecifically affords a vicinal dihalide by *trans* addition. This observation led Roberts and Kimball[25] to postulate a three-membered ring halonium ion intermediate (II). Subsequently, Dewar[5] suggested that this intermediate could also be described as a π complex (III) in which the π orbital of the olefin forms a dative bond by interaction with the empty valence orbital of the acceptor X^+. One of the salient features of this hypothesis is the possibility for a reverse dative bond to the olefin by unshared p or d electrons on the X^+ interacting with the π^* orbital of the olefin.



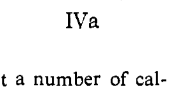
II



III



IV



IVa

Extended Hückel calculations on a symmetrical planar chloronium ion of ethylene indicates a strong interaction between the olefin and Cl^+. In fact, the total overlap population of 0.369 between chlorine and each carbon atom approaches that of the covalent C–Cl bond in methyl chloride for which ρ_{CCl} is 0.580. Estimates of bond strength based on overlap energies give basically the same results.

The charge is well distributed over the molecule with 0.817 electron being transferred from C_2H_4 to the electrophilic Cl^+ (Table II). The chlorine atom utilizes mostly its 3p orbitals with the 3s orbital accounting for only 16.5% of the total overlap population to carbon. The extent of participation of the empty 3d orbitals on chlorine was determined in a separate EH calculation. In this case, the overlap integrals, S_{ij}, were calculated by adjusting the Slater exponents to give an approximate match to calculated SCF overlap integrals. The method of calculation and the input parameters have been described previously.[11] The overall bonding picture in this calculation closely resembled the data described above. All of the contributions from the 3d orbitals on chlorine were antibonding with a ρ of -0.127 and the net ρ_{CCl} was 0.269. In the remaining calculations, the d orbitals on halogen were neglected.

The bonding picture presented above is consistent with a very tightly bound cyclic onium ion intermediate II. In contrast to the nature of the bonding exhibited by the silver π complex with C_2H_4, *vide infra*, the olefin has been strongly perturbed, the contribution of the p_z orbitals to the double bond has been significantly reduced, and a substantial positive charge has accumulated on carbon. This is in accord with a highly reactive intermediate that should be susceptible to nucleophilic attack as is observed experimentally.

In view of the magnitude of the bond order between Cl^+ and C_2H_4 it is not surprising that an energy minimum exists for the symmetrical chloronium ion where some rehybridization at carbon has resulted and the hydrogens are bent away from the chlorine at an angle of approximately 25°. This nonplanar form is calculated to be 21 kcal/mol more stable than a planar C_2H_4 fragment bound to Cl^+. This stabilization is accompanied by an increase in overlap population and the combined ρ_{CCl} to both carbons is 0.804. Of the several molecules selected for this type of calculation, the chloronium ion would appear to have realized the greatest deviation from planarity. In Table II, we have tabulated the energy required to bend the hydrogens down at an angle of 10° for these molecules. The trend that develops as you proceed down the table and as the olefin experiences less perturbation is that the complex remains more nearly

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bonded to platinum (Zeiss' salt) we have carried out a number of calculations with a bond distance of 1.47 Å as a reference point; (b) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, 13, 149 (1960); (c) M. Black, R. H. B. Mais, and P. G. Owston, *ibid.*, 25, 1753 (1969).

(25) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, 59, 947 (1937).

Table II. EH Calculations on Onium Ion Intermediates. Addition of XY^+ to C_2H_4[a]

X–Y	Q_c[b]	QH	Q_X[c]	ρ_{cc}	ρ_π	ρ_{C-X}[d]	ρ_{C-H}[e]	ρ_{X-Y}	E_{lumo}	E_{homo}	ΔE, kcal/mol offset 0.68 Å[f]	ΔE, kcal/mol 10° bend[g]
F	0.578	0.063	−0.410	0.766	0.102	0.477	0.832		4.83	14.46	44.6	
Cl	0.323	0.042	0.183	0.854	0.118	0.738	0.835		4.48	13.09	35.1	−14.8
Br	0.265	0.040	0.309	0.907	0.135	0.680	0.835		4.99	12.31	23.2	
SCH_3	0.181	0.032	0.407 0.105	0.899	0.127	0.769	0.835	0.660	4.56	11.79	23.7	
SCF_3	0.205	0.034	0.471 −0.020	0.905	0.134	0.760	0.835	0.793	4.72	12.20	23.6	
SCl	0.190	0.034	0.565 −0.080	0.881	0.113	0.771	0.835	0.494	4.51	11.38	19.9	
SCN	0.249	0.040	0.612 −0.268	0.916	0.143	0.722	0.834	0.976	6.34	12.00	22.5	
S[h]	0.050	−0.001	−0.094	0.674		1.110	0.841		2.23	10.45		
Hg(II)	0.288	0.047	1.236	1.083	0.251	0.434	0.827		10.45	8.55	7.1	0.2
HgOH	0.171	0.034	1.075 −0.552	1.151	0.323	0.429	0.829	0.401	8.15	13.67		
HgOCHO	0.173	0.034	1.102 −0.586	1.150	0.321	0.433	0.829	0.382	8.15	13.00		
HgF	0.203	0.038	1.210 −0.768	1.127	0.300	0.463	0.828	0.228	8.35	13.96		
$HgCH_3$	0.114	0.027	0.863 −0.201	1.199	0.368	0.337	0.830	0.620	7.91	12.40	1.9	
HgCl	0.143	0.031	0.957 −0.366	1.173	0.325	0.390	0.829	0.563	7.95	12.91	1.3	1.0
HgBr	0.127	0.029	0.877 −0.247	1.185	0.354	0.360	0.830	0.617	7.86	11.85		
Ag	0.058	0.020	0.803	1.233	0.390	0.241	0.832		7.84	12.04	1.6	3.4
AgOH	0.037	0.018	0.701 −0.846	1.247	0.404	0.217	0.833	0.167	7.26	11.76		2.07
	−0.031	0.016		1.329[i]	0.503		0.826		6.64	12.73		

[a] All C–C bond lengths 1.36 Å. [b] All charges are positive unless otherwise indicated. [c] Where X^+ involves more than one atom, the net charge on the remaining atoms is listed below the charge on X. [d] Includes sum of overlap population to both carbon atoms. [e] Where hydrogens are nonequivalent an average ρ is reported. [f] Energy required to offset X^+ by 0.68 Å affording IV. [g] Energy required to bend the hydrogens down along the z axis while keeping the C–H bond length at 1.085 Å. [h] Neutral ethylene sulfide. [i] Total C–C overlap population for C_2H_4.

planar and hence is more nearly a π complex in nature with the s orbital on the electrophile making a larger contribution to the bonding.

The symmetrical planar bromonium ion II has its positive charge more evenly distributed over the three-membered ring as would be expected on the basis of the relative electronegativity of Br^+ which has perturbed the olefin to a lesser extent than Cl^+. The carbon–bromine overlap population was 0.34 as compared to the overlap in methyl bromide where ρ_{CBr} is 0.570. The bonding to ethylene utilized the valence p orbitals on bromine to an even greater extent than was observed for chlorine.

Since fluorine has never been reported to be effective in neighboring group participation, any form of complex including fluorine should be symmetrical, II. Due to the extremely high electronegativity of F^+, C_2H_4 has transferred 1.41 electrons to fluorine. The high positive charge that has therefore accumulated on carbon suggests that this should be an extremely reactive intermediate if it is capable of existing at all.

Of particular significance to the mechanism of the opening of a cyclic halonium ion intermediate is the potential energy surface described by moving the X^+ along the C–C bond axis. For this motion, the Z coordinate of X^+ was held constant. *cis* opening of the three-membered ring halonium ion from the front side would most likely require more extensive carbon–halogen bond breaking in the transition state prior to the formation of a carbon nucleophile bond than *trans* addition. The trend seen developing in Table II is that electrophiles which are tightly bound to the olefin, principally by more directed sp hybrid orbitals, require considerably more energy to form an unsymmetrical ion IV than those metal–olefin complexes where s orbtials are principally involved in the bonding (Table III).

A comparison of the energies required to convert symmetrical halonium ions, II, to their unsymmetrical form IV suggests that bromine is a better bridging atom than chlorine and that an unsymmetrical fluoronium ion would be extremely unstable in good accord with experimental behavior. This is supported by the charge distribution and overlap populations (Table IV) for the unsymmetrical ions where ρ_{CX} is 0.214, 0.208, and 0.056 for Br, Cl, and F as the neighboring groups. The stabilization of the adjacent carbonium ion is due to a lone pair of p electrons on halogen since the halogen s orbitals are antibonding to the distant carbon in all three cases. This is in excellent agreement with the qualitative picture usually envisioned of a lone pair being involved in neighboring group participation.

In the unsymmetrical halonium ions the extent of halogen s character involved in the carbon–halogen bond is 21.5, 35.3, and 56.2% for Br, Cl, and F. It is difficult to explain why the fluorine s orbital with a VOIP of −40.12 eV would mix with a p orbital at −18.65 eV to this extent, and why the amount of

Table III. Bonding Mode of Ligands XY^+ to C_2H_4[a]

X–Y[b]	Bonding of X to C_2H_4, %; ρ_{C-X}[c] s	p	d	Bonding of Y to X, %; ρ_{X-Y} s	p	d
F	25.1 (0.0600)	74.9 (0.1790)				
Cl	16.5 (0.0609)	83.5 (0.3082)				
Br	7.1 (0.0241)	92.9 (0.3159)				
SCH_3	17.4 (0.0668)	82.6 (0.3180)		35.3 (0.2331)	64.7 (0.4269)	
SCF_3	19.2 (0.0729)	80.8 (0.3068)		31.9 (0.2533)	68.1 (0.5400)	
SCl	16.8 (0.0648)	83.2 (0.3207)		24.9 (0.1227)	75.1 (0.3711)	
SCN	22.9 (0.0827)	77.1 (0.2784)		26.7 (0.2609)	73.3 (0.7147)	
Hg(II)	97.8 (0.2123)	0.00	2.2 (0.0048)			
HgOH	68.0 (0.1461)	28.4 (0.0610)	3.6 (0.0077)	52.0 (0.2164)	48.0 (0.2000)	(−0.0156)
HgOCHO	67.8 (0.1468)	28.6 (0.0619)	3.6 (0.0078)	52.9 (0.2101)	47.1 (0.1873)	(−0.0150)
HgF	73.3 (0.1699)	23.2 (0.0539)	3.4 (0.008)	47.6 (0.1196)	52.4 (0.1316)	(−0.0236)
$HgCH_3$	52.4 (0.0883)	44.6 (0.0752)	3.0 (0.0051)	67.3 (0.4171)	30.1 (0.1864)	2.60 (0.0161)
HgCl	63.5 (0.1236)	33.4 (0.0651)	3.1 (0.0060)	53.2 (0.3050)	46.8 (0.2678)	(−0.0096)
HgBr	60.6 (0.1089)	36.6 (0.0658)	2.8 (0.0050)	54.9 (0.3415)	45.1 (0.2811)	(−0.0053)
Ag	93.8 (0.1253)	(−0.0134)	6.2 (0.0083)			
Ag[d]	84.8 (0.1192)	9.0 (0.0127)	6.2 (0.0087)			
AgOH	90.6 (0.1021)	(−0.0041)	9.4 (0.0106)	57.2 (0.1001)	42.8 (0.075)	(−0.0079)

[a] All C–C bond lengths 1.36 Å with the ligand symmetrically disposed. [b] X is defined as the attacking electrophile and Y may be any substituent attached to X. [c] The total overlap population may be found in Table II. [d] VOIP of the 5p orbital on silver = −4.77 eV.

Table IV. Unsymmetrical Onium Ion Intermediates. X^+ Offset 0.68 Å

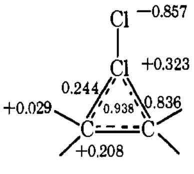
X–Y	Q_{C_1}	Q_{C_2}	ρ_{CC}	ρ_π	ρ_{C_1-X}	ρ_{C_2-X}
F	0.634	0.560	0.827	0.0632	0.056	0.297
Cl	0.371	0.287	0.905	0.126	0.208	0.377
Br	0.299	0.236	0.957	0.156	0.214	0.335
SCH_3	0.198	0.164	0.945	0.148	0.243	0.389
SCF_3	0.236	0.181	0.951	0.153	0.238	0.386
SCl	0.187	0.180	0.930	0.136	0.233	0.403
SCN	0.286	0.219	0.963	0.162	0.213	0.382
Hg	0.332	0.235	1.093	0.256	0.134	0.270
$HgCH_3$	0.123	0.074	1.216	0.381	0.092	0.200
HgCl	0.166	0.095	1.190	0.356	0.114	0.232
Ag	0.069	0.034	1.245	0.403	0.079	0.127

sp mixing decreases as the valence s and p orbitals approach one another in energy. EH calculations on methyl fluoride, using Cusachs' formula[26] for treating off-diagonal elements, would appear to agree since it gives a ρ_{CF} of 0.435 with a slight antibonding contribution from the fluorine 2s orbital. By comparison, the Wolfberg–Helmholz[12] treatment predicts greater than 50% s orbital involvement. However, calculations on the fluoronium ions II and IV, according to Cusachs' formula,[26] showed 46.5 and 32.8% fluorine 2s contribution to the C–F bond with an energy difference between the two isomeric ions of 56.5 kcal/mol. Obviously this point needs further clarification.

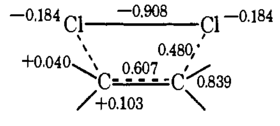
Calculations on an unsymmetrical ion, IVa, where the carbon bonded to halogen has tetrahedral geometry, and a normal covalent carbon–halogen bond distance, result in a substantial increase in energy. The sp^2–sp^3 chloronium ion and bromonium ion are less stable than IV by 29.4 and 26.5 kcal/mol and the overlap population between halogen and the adjacent planar carbonium ion is only 0.039 and 0.068, respectively. These data strongly suggest that a classical carbonium ion is likely to result only in cases where stabilization is possible through other groups attached directly to the positively charged carbon.

Since in the above discussion we have placed emphasis on the total energy difference between ions of varying geometry, we felt compelled to examine the energy difference between II and IV by the CNDO/2 method[23b] where electron–electron and nuclear–nuclear interactions are considered. We hope to establish by these comparisons that our conclusions based on EH calculations are meaningful. The acidity of Cl^+ in the symmetrical ion II was in excellent agreement with the EH method with 0.811 electron being transferred from C_2H_4. The π bond order was reduced from 1.00 in C_2H_4 to 0.474. The total energy difference between II and IV was calculated to be 18.5 kcal/mol by CNDO/2 and 35.1 kcal/mol by the EH method. Although the absolute values of these energy differences are not in good agreement, both methods of calculation suggest that a substantial energy barrier to isomerization exists.

Addition of Molecular Chlorine. Kinetic evidence suggests that chlorination of olefins involves addition of molecular chlorine to the olefin[2,3] which subsequently forms a chloronium ion II when simple olefins are involved. The most logical precursor to II is depicted in V where the Cl–Cl bond is polarized and the developing positive charge can be evenly distributed over the ethylene molecule in the transition state prior to expulsion of chloride ion and formation of II. To examine this mechanism by EH calculations we placed a



V



VI

Cl_2 molecule (Cl–Cl distance = 1.988 Å) normal to the plane of the ethylene and above the C–C bond midpoint. The distance between the near chlorine atom and the bond midpoint was varied from 2.57 to 1.77 Å, *i.e.*, from nearly van der Waals distance to nearly a normal C–Cl covalent distance. In each case, the net interaction between the ethylene and Cl_2 was antibonding with a maximum in ρ_{CCl} of −0.188 near 2.17 Å. However, with the nearest chlorine at 1.772 Å and the Cl–Cl bond length elongated by 10%, an appreciable interaction resulted. The C_2H_4 π-bond

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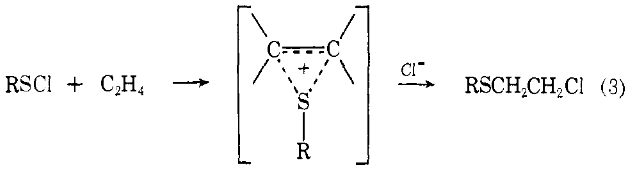
(26) L. C. Cusachs, *J. Chem. Phys.*, 43, S157 (1965).

overlap population was reduced to 0.195; a carbon–chlorine bond developed and a strong antibonding interaction between the chlorine atoms that had a ρ_{ClCl} of -0.545 resulted. The charge distribution and overlap population are those given in V. When the Cl–Cl bond distance was elongated 20%, ρ_{CCl} increased to 0.319 and almost a full negative charge had developed on the departing chloride ion. Bond elongation (100%) afforded results virtually indistinguishable from those reported for II (Table II) with the more distant chlorine atom being essentially a nonbonded ion. Increasing the Cl–Cl bond distance in V by 10, 20, and 100% resulted in a net stabilization, after a correction for the energy decrease associated with elongating the bond length in Cl_2, of 26, 122, and 267 kcal/mol, respectively. These values are obviously exaggerated but the trend is in the right direction and suggests that the olefin can compete favorably with chloride ion for the acidic Cl^+.

Since Cl_2 adds *cis* to olefins in some instances we briefly examined the horizontal interaction of Cl_2 with C_2H_4 affording structure VI. The chlorine molecule, at a normal Cl–Cl bond length, was symmetrically placed 1.772 Å above the plane of the double bond. The charge distribution and overlap populations are those given in VI. The carbon–carbon bond order was reduced considerably due to an antibonding π contribution where ρ was -0.234. A strong antibonding interaction between the chlorines and between each chlorine and its adjacent (β) carbon atom ($\rho = -0.345$) would suggest that the transition state for a four-centered *cis*-molecular addition to ethylene would be unfavorable.[27] The total energy of VI is considerably higher than those calculated for V at various stages of bond elongation of Cl_2. Perhaps a more realistic model for this transition state would be to elongate the Cl–Cl bond to reduce internuclear repulsions with concomitant rehybridization at carbon. The number of degrees of freedom involved in this calculation discouraged us from doing it. When the above calculation was repeated on VI with Cl–Cl, 2.171 Å above the plane of the double bond, an antibonding situation between chlorine and carbon resulted with little perturbation of the double bond; $\rho_{cc} = 1.318$.

Sulfonium Ions. As a reference point for charge distribution and overlap population in sulfonium ion intermediates, we carried out an EH calculation on ethylene sulfide (Table II). Coordinates for the three-membered ring were calculated from the experimental geometry of ethylene sulfide[28a] and the bond angles for the hydrogens were assumed to be the same on those reported for cyclopropanone.[28b] With these parameters, we calculate a covalent carbon–sulfur single bond to have an overlap population of 0.555 with a relatively small buildup of charge at any atom of the molecule (Table II). The orbitals on sulfur involved in the bonding to carbon consisted largely of 3p orbitals with a contribution of 19.5% from the 3s orbital on sulfur. The d orbitals were not included in these calculations.

Much of our knowledge of sulfonium ions comes from studies on the addition of sulfenyl halides to olefins (eq 3). Although under certain conditions free-radical addition can occur, we will restrict our discussion to the ionic mechanism. The ionic additions exhibit a high degree of *trans* stereospecificity, which by analogy to halonium ion intermediates has led to the suggestion that a bridged ion VII is involved here also. The orientation of addition is now thought to be largely anti-Markovnikov.[29] Most commonly used as substituents on sulfur in mechanistic studies of this reaction are methane-, benzene-, and 2,4-dinitrobenzenesulfonyl chloride. Our choice of R for these calculations is obviously limited by size and complexity. Therefore, in addition to CH_3– we have used –Cl and $-CF_3$ as electron-withdrawing substituents and –CN as a π-type acceptor. The results are summarized in Tables II and III.



VII

EH calculations on the simulated addition of CH_3S^+ to C_2H_4 suggested a slightly greater interaction than that observed with Cl^+ with a ρ_{cs} of 0.385. However, the π system of C_2H_4 is not as severely disrupted and a smaller positive charge on carbon has developed suggesting this complex to be less reactive than a chloronium ion. The orbitals involved in the bonding are quite similar to those utilized in ethylene sulfide. The 3p orbitals on sulfur accounted for the major portion of the bonding supporting the contention, based on extent of perturbation of the olefin and the relatively large ρ_{cs}, that VII more closely resembles a three-membered ring than a π complex. Calculations with the CH_3 group in the *YZ* plane approximating an sp^2-hybridized sulfur were found to be 23 kcal/mol less stable than for the complex where the sulfur assumed a nonplanar approximately sp^3 geometry and the CH_3 group was symmetrically placed between the two carbons and protruded into the *YZ* plane at a 54° angle. All calculations reported are with this geometry.

On comparison of the four sulfonium ions, we find the acidity of RS^+ toward C_2H_4 to be arranged in the order $SCN^+ > SCF_3^+ > SCl^+ > SCH_3^+$ with 0.656, 0.549, 0.515, and 0.488 electrons being transferred from the C_2H_4, respectively. In agreement with this order is the positive charge on carbon and the carbon–carbon overlap population (Table II). In all four examples, the π-overlap populations, ρ_{cs}, appear to be rather insensitive to the substituent Y on sulfur; however, the trends are in general agreement with chemical behavior. The π acceptor being the most acidic electrophile induced the greatest positive charge on sulfur, thereby most readily effecting *trans* addition by nucleophilic attack on the bridged intermediate VII.

Mercury(II) Cation. The reaction of Hg^{2+} with olefins in an aqueous media affords an adduct which is often referred to as an oxymercurial. The Hg^{2+} is

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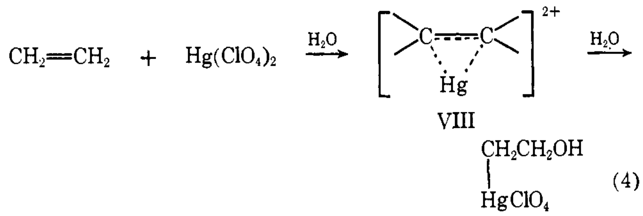
[27] We are grateful to the referee for pointing out that this four-center addition is a forbidden reaction in the Woodward–Hoffmann sense.

[28] (a) R. L. Shoemaker and W. H. Flygare, *J. Amer. Chem. Soc.*, 90, 6263 (1968); (b) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, 91, 1896 (1969).

[29] W. H. Mueller and P. E. Butler, *ibid.*, 90, 2075 (1968), and references cited therein.

generated from $Hg(ClO_4)_2$ which is completely dissociated in H_2O and the reaction is generally thought to proceed *via* a mercurinium ion intermediate (eq 4).


VIII

(4)

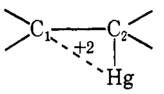
In a recent study on the hydroxymercuration of olefins, Halpern[30] suggested that a transition state was involved that had a considerable amount of carbonium ion character but found no kinetic evidence for a Hg^{2+}–olefin π-complex intermediate.

Our calculations show the bonding strength between C_2H_4 and mercury(II) cation to be intermediate between the chloronium ion II and a silver π complex. The C_2H_4 transferred 0.764 electron to mercury developing a sufficient positive charge on carbon to induce nucleophilic attack by solvent. These facts are in good agreement with Halpern's observation on the hydroxymercuration of substituted olefins where an excellent correlation between log k and Taft's σ^* ($\rho^* = -3.3$) was observed, suggesting that considerable positive charge had developed on carbon in the transition state. By comparison with the overlap observed with the silver complexes, which are isolable, it would appear that π complexes, of Hg^{2+}, should be quite capable of forming. However, VIII is an extremely reactive species and it is, therefore, not surprising that it has escaped detection to date, even by nmr techniques, since a detectable concentration of the π complex is never allowed to accumulate. Thus a very fine line between a reaction intermediate and a transition state exists in this case since a rapid preequilibrium between olefin and Hg^{2+} was observed.[30] An upper limit for the equilibrium constant for formation of VIII has been estimated[30] to be $\sim 10^2$ which is comparable to the measured equilibrium constant for the known silver π-complex formation with C_2H_4.

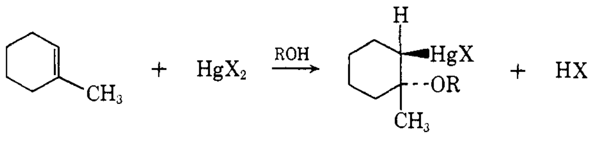
The olefin–mercury bonds consist almost entirely of the 6s orbital on mercury interacting with the π orbital of ethylene. In the mercurinium ion (VIII) the 5d orbitals of Hg(II) are essentially nonbonding so that the interaction between metal ion and olefin does not involve a synergistic back donation of metal d electron density as was found for Zeiss' salt.[6] This is certainly not surprising since for the Hg the separation of 5d and 6s orbitals is 5.2 eV while for Pt the separation is only 0.8 eV, from their respective VOIP's. The withdrawal of the 5d electrons from the valence shell into the core for Hg with the concomitant loss of $d\pi$–π^* bonding results in a much larger net transfer of electron density from ethylene than in the Pt case. This is in good agreement with the relative reactivity of their π complexes. In this respect, Ag^+ might be expected to be intermediate but in fact the reactivity of Ag^+–olefin complexes is very low, resembling Pt, while our calculations show that the mode of bonding more closely resembles Hg(II) rather than the Pt(II) case. There are probably several factors involved in this. With its lower charge Ag(I) would be expected to be less acidic than either Pt(II) or Hg(II).

The Ag 6s VOIP is very low at 7.58 eV and since the silver ion can be thought of as formally forming only one rather weak bond to the olefin π cloud, it is not too surprising that the 5s orbital is employed without any hybridization with $4d_{z^2}$ which would involve promotion. Thus, even though we find little $d\pi$–π^* back donation in this case, the calculations do mirror the low reactivity of Ag^+–olefin complexes and show that in contrast to the Pt(II) case the small positive charge buildup in this case is due to the weak σ acceptor properties of the silver 5s orbital.

The calculated total energy of VIII with a C–C bond length of 1.36 Å was 0.6 kcal more stable than the mercury complex with a C–C bond length of 1.47 Å. By analogy to the bond length observed for the silver complex, the C–C bond length in VIII should be approximately 1.36 Å. At that distance an energy minimum existed for the symmetrical complex with the hydrogens bent down along the Z axis at an angle of $\sim 7°$. The potential energy surface for shifting the Hg^{2+} along the C–C axis was considerably more shallow than that observed for the halonium ion. Thus, the mercury can be readily displaced forming an unsymmetrical ion IX in the direction that affords the most stable carbonium ion yielding exclusive Markovnikov addition and affording a transition state with positive character[30] that can be stabilized by the neighboring group mercury (Table IV). The overlap population between mercury and the adjacent carbon atom (C_2) was due entirely to the relatively diffuse 6s orbital on mercury. This configuration was more stable than the aforementioned sp^2–sp^3 unsymmetrical form by 29 kcal/mol with the Hg–C_1 overlap population in that configuration being reduced to 0.030 and a substantial positive charge, +0.427, existed on the carbonium ion. Hence the formation of a classical carbonium ion is seriously impeded in this complex also. These facts suggest that VIII more closely resembles a π complex than a three-membered ring structure.


IX

Substituted Mercury Derivatives. The reaction of an ionic mercuric salt with an olefin in an alcoholic solvent is usually referred to as an oxymercuration reaction. The mercuric salt, HgX_2, dissociates and the electrophile ^+HgX forms a π complex, X, with the olefin that is solvated by the alcohol solvent yielding an alkoxymercurial (eq 5). In alcohol solvent the substituent X on the electrophile is either bonded to the mercury or exists as an intimate ion pair in the transition state of the reaction.[11] With simple unstrained olefins, *trans* addition to the mercurinium ion X is observed with the oxy group becoming attached to


(5)

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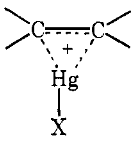
(30) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

the more electropositive carbon, *i.e.*, a Markovnikov addition. Mercuric salts typically used in this reaction are $Hg(ClO_4)_2$, $Hg(NO_3)_2$, and $Hg(OAc)_2$. In the absence of hydroxylic solvents these salts readily add to olefins to yield 1:1 adducts by essentially the same mechanism. The more covalent $HgCl_2$ reacts slowly with more reactive olefins while $HgBr_2$ is essentially unreactive. Alkly- and arylmercuric acetate have only been observed to react with allenes.[11] The more covalent salts are linear and probably use well-developed sp hybrids in their bonding.



X

Our calculations suggest that the mercurinium ion which most closely resembles the Hg^{2+}–olefin complex is that derived from ^+HgF. This correlates well with experimental data since mercuric fluoride is almost completely ionic and a high positive charge on mercury would be anticipated. At an estimated Hg–F bond distance of 2.03 Å, fluorine is weakly bonded to mercury as evidenced by the low ρ_{Hg-F} resulting in a change in the bonding mode to C_2H_4 with some p character developing.

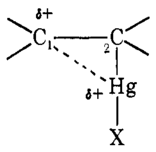
The mercurinium ions formed with ^+HgOH and ^+HgOCHO are comparable in the extent to which they have perturbed the C_2H_4 and in the nature of the bonding to ethylene. The reduced positive charge on carbon, relative to the complex with Hg^{2+}, correctly predicts that $Hg(OAc)_2$ reacts more slowly with olefins than Hg^{2+} [derived from $Hg(ClO_4)_2$].

Mercuric bromide, which is unreactive toward ethylene, exhibited only a weak interaction with considerable p character being involved in the bonding to ethylene. As would be anticipated for a highly covalent Hg–Br bond, the mercury utilizes its 6s and 6p orbitals to nearly an equal extent in its bonding to bromine. In fact, the data in Table III suggest that the Hg–Y bond is largely sp in nature for all the examples studied. The d orbitals on mercury all exhibit an antibonding interaction with Y, except in the case of the methyl group which does not have an unshared pair of electrons.

The methylmercury cation, $^+HgCH_3$, appears to be the least electrophilic cation in this series. The methyl substituent is the least electronegative and enjoys the highest overlap population to mercury of the compounds studied. The trend within the mercury group is that an increase in the covalency of the Hg–X bond as suggested by ρ_{X-Y} results in a reduction of the acidity of the electrophile, ^+HgX. In fact, the low overlap population with the olefin which bears relatively little positive charge at carbon and the high ρ_{CC} correctly suggests that $^+HgCH_3$ should exhibit a low reactivity toward unsaturated centers.

The reactivity of ^+HgCl toward C_2H_4 is slightly greater than that observed for ^+HgBr as expected on the basis of their relative reactivity toward olefins. The mercurinium ion appears to be closer to the silver complex in properties than the three-membered ring chloronium and sulfonium ion intermediates. Appreciable double bond character remains in the olefin and total energy arguments suggest that this complex should be planar. It is of interest to note the low energy requirement for moving the ^+HgCl, as well as $^+HgCH_3$, along the C–C bond axis. One plausible explanation for this is the additional p character involved in the bonding which allows a lower energy, more directed, covalent bond to C_2 in XI to form. The sp^2–sp^3 form of the chloromercurinium ion (IVa) is 39 kcal/mol less stable than III, strongly suggesting that addition should occur by nucleophilic attack on either III or IV with *trans* stereospecificity.

Also evident in this study is the observed increase in reactivity of the mercuric salt toward olefins as the extent of mercury 6s character involved in the π complex increases. It is conceivable that a more directed sp hybrid on the covalent mercury cation is less efficient in forming a three-centered bond with the two carbon atoms of the olefin than a more diffuse 6s orbital. This is also consistent with the neighboring group trend, ρ_{C_1X}, where Hg^{2+} is more efficient in stabilizing the positive charge on C_1 than the more directed π-bonding complexes formed with ^+HgCl and $^+HgCH_3$ in the unsymmetrical complex XI (Table IV).



XI

Silver Complex. The planar symmetrical silver π-complex III represents an energy minimum and is more stable than the unsymmetrical form IV by 1.6 kcal/mol. Rehybridization of one of the carbon atoms affording an sp^2 carbonium ion adjacent to an sp^3 carbon atom bonded to silver (C–Ag = 2.06 Å) was destabilized by 32 kcal/mol relative to III. However, since no allowance was made for C–C bond elongation, in this case or in any of the aforementioned sp^2–sp^3 complexes, only the relative change in energy should be considered. The silver–carbonium ion overlap population in IVa was reduced to 0.023 and ρ_{C-C} to 1.167. This represents an appreciable destabilization since the ρ_{C-C} in ethylene (1.36 Å) is 1.329.

Effecting a slight rehybridization at carbon by bending the hydrogens down along the *Z* axis by 5, 10, and 20° results in a total energy increase of 1.8, 3.4, and 6.0 kcal/mol, while a similar distortion of ethylene resulted in a destabilization of 0.3, 2.1, and 5.1 kcal/mol, respectively. This is in direct contrast to the calculated results[6] with the platinum–ethylene π complex, Zeiss' salt, where an energy minimum was observed where the hydrogens were bent out of plane and away from the platinum by 20–25°. This, however, is not surprising since the metal–olefin interaction in the latter case was stronger with a ρ_{C-Pt} of 0.192, and with substantial $d\pi$–π^* bonding.[6] The extent of d-orbital participation in the silver complex is considerably smaller than in the complex with platinum which has a d^8 configuration and thus an empty d orbital. The charge distribution on these distorted complexes was not significantly changed from III and the overlap population increased slightly with a ρ_{C-Ag} of 0.127. By contrast, we calculated a ρ_{C-Ag} for methyl-silver of 0.461 emphasizing the weakness of the silver–olefin bond. As expected, destabilizing the π system by an out-of-plane deformation resulted in a slight increase in the $d\pi-\pi^*$ contribution to about 8% of the total bonding. The relatively small $d\pi-\pi^*$ back-bonding observed with silver is consistent with a small C–C bond elongation (~0.03 Å) in this complex. A large contribution of this sort should destabilize the π system and result in bond lengthening. This is observed with Zeiss' salt where the carbon–carbon bond distance is ~1.44 Å and where we have attributed a substantial portion of the bonding to be of the $d\pi-\pi^*$ type.[6]

cis-Olefins complex with silver ion more strongly than their corresponding *trans* isomers. It has been suggested[31] that destabilization of the π system, by twisting adjacent p orbitals on carbon, to relieve steric interactions characteristic of *cis*-planar disubstituted olefins, occurs to a degree that is compensated for by a reduction in nonbonded interactions. It may also be inferred from Gardner's[31] data that the ΔG° for isomerization of the 2-butenes on formation of their silver complexes is reduced to nearly zero while the $\Delta G_{25}{}^\circ$ of isomerization of *cis*-2-butene to *trans*-2-butene is 0.7 kcal/mol.[32] EH calculations on the symmetrical silver complex III where the planar CH_2 groups of the ethylene molecule have been rotated in opposite directions by an angle θ equal to 5, 10, 20, and 30° of twist about the double bond resulted in a total energy increase of 3.0, 8.0, 24.1, and 50.3 kcal/mol, respectively (Figure 1). A corresponding destabilization for C_2H_4 was 1.5, 5.8, 23.2, and 51.8 kcal/mol, respectively.[33] Although the energy required to twist III is greater than that of C_2H_4, we have not included a substituted olefin in our calculations. In support of a twisted π complex, when θ equals 10° ρ_{C-C} and ρ_{C-Ag} are 98.8 and 99.3% of their original value in III. Additional experimental evidence for this concept comes from kinetic studies by Kreevoy.[34] Deoxymercuration of the hydroxymercurial derived from the isomeric 2-butenes gave a value of only +0.05 kcal/mol for the $\Delta G_{25}{}^\circ$ of isomerization of *erythro*-3-chloromercuri-2-butyl alcohol to the *threo* isomer. These reactions, involving chloromercurinium ion intermediates, suggest that the *cis* methyl–methyl repulsions must be reduced to nearly zero in the transition state. Our calculations are consistent with these data since we observed energy increases of 1.0, 5.8, 24.6, and 55.5 kcal/mol for the twisted symmetrical mercurinium III (X = $^+$HgCl) where θ equals 5, 10, 20, and 30°. In addition, ρ_{C-Hg} with θ equal to 20° was 98% of its value in planar III. It should also be pointed out that the variation in total energy with twist could be affected adversely by the charge iteration procedure since there are ten essentially nonbonding electrons on the metal. The total energy change reflects changes in the energy of bonding electrons and the nonbonding electrons are destabilized slightly as electrons flow from ethylene to the metal upon twisting the double bond. It is difficult to determine precisely the value of the charge iteration factor for these heavy metals, or for any atom for that matter, but we feel the value of 2.0 eV/electron to be approximately correct.[35]

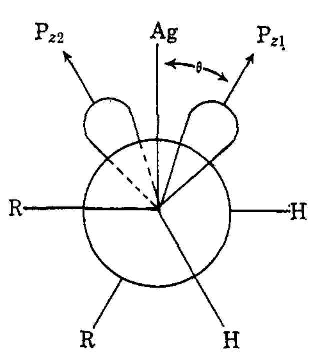


Figure 1.

The above calculations with Ag^+ exhibited an antibonding contribution of the 5p orbital on silver. In an effort to examine the effect of the VOIP chosen for the silver p orbital on the bonding, calculations were carried out with a VOIP for the p orbital of −4.77 eV.[9] With this change the 5p orbital was bonding to C_2H_4 to the extent of 9% with the s and d contributions being 85 and 6%. In view of the uncertainty of the p VOIP the best estimate at this time is that the p orbitals on silver are not significantly involved in the bonding to ethylene. This situation is not appreciably altered when a hydroxyl group is placed 2.38 Å, the silver–oxygen ionic bond distance,[14] from the silver ion in III. Solvation of the silver complex III by water or the silver gegenion should tend to reduce the acidity of the silver ion. Thus, the silver hydroxide–C_2H_4 complex is more weakly bound than the Ag–C_2H_4 complex. However, the orbitals involved in the bonding to C_2H_4 have not changed to the extent noted with $^+$HgOH; the p orbital on silver is still slightly antibonding.

The overlap population of Ag^+ with C_2H_4 of 0.241 is of sufficient magnitude to suggest an interaction leading to a π-complex formation. The lack of perturbation of C_2H_4, with the π-bond order of the olefinic double bond still large, the overlap population being reduced only 7%, and the low positive charge on carbon comprise a poor site for nucleophilic attack at carbon. These factors, in addition to the unfavorable formation of a carbon–silver bond, correctly suggest that silver ion should *not* catalyze additions to olefins as do the corresponding complexes with mercury cations.

Discussion

The approximations inherent in the EH method have been discussed by Blyholder and Coulson.[36] They have concluded that the method in general, while not appropriate for high accuracy, can provide satisfactory qualitative results on molecules that cannot at the present time be conveniently handled by full molecular Hartree–Fock methods. The results of the calculations

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(31) P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind.* (*London*), 1363 (1958).

(32) Rossini, *et al.*, "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p 737.

(33) These values are high since 0.2, 0.8, and 1.8 kcal/mol have been reported as the required energy to twist ethene 5, 10, and 15°, respectively, about the double bond: F. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 183.

(34) M. M. Kreevoy, L. L. Schaleger, and J. C. Wave, *Trans. Faraday Soc.*, **58**, 2433 (1962).

(35) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967); S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6669 (1968).

(36) G. Blyholder and C. A. Coulson, *Theoret. Chim. Acta*, **10**, 361 (1968).

in the present paper have provided considerable insight into the nature of the intermediates resulting from electrophilic attack on ethylene.

The most conspicuous aspect of these calculations is the correlation between the extent of perturbation of the olefinic double bond and the known reactivity of the electrophile itself. Also of particular relevance to the nature of the transition state formed was the potential energy surface described by moving X^+ along the C–C bond axis forming an unsymmetrical onium ion. In this section, we will discuss the mechanism of electrophilic addition to olefins not only as a consequence of the above calculations but also in consideration of the abundance of experimental data available on this subject.[2,3] This is especially pertinent since the calculations cannot take solvent and temperature effects into consideration, and since we have not included substitued olefins in the present study.

The weakest interaction noted above was that between silver ion and ethylene. This complexation was first treated quantitatively by Winstein and Lucas[37] with simple olefins while Andrews and Keefer[38] have studied aromatic and Traynham[39] acyclic olefin complexes. Silver complexes are generally quite unstable but a number of them have been isolated and X-ray measurements made.[14] A recent and extensive study on the equilibrium constants of formation of olefin–silver complexes utilizing gas chromatographic techniques has been reported by Muhs and Weiss.[40] Of particular relevance to this paper, since the coordination chemistry of silver(I) is closely paralleled by copper(I), is a study on the complex formation constants of olefins and copper(I) based on the coulometric generation of Cu(I).[41] In contrast to the excellent correlation between the equilibrium constants reported by Muhs and Weiss and the formation constants of the corresponding Cu(I) complexes, the argentation constants reported by Traynham[39] deviated widely with no apparent pattern. The lack of correlation observed by Traynham is most likely attributable to the experimental method which involved transfer of the olefin from carbon tetrachloride to water as well as silver complex formation.[42] The conclusion based on these equilibria constants, that the extent of complex formation with aqueous silver ion parallels the relative ring strain in the olefins, is subject to further consideration.

The three most important factors that influence the stability of an olefin–silver complex appear to be steric, strain, and electronic effects. The olefin is bonded to the silver almost exclusively by its π electrons with little or no σ bonding being involved. The silver atom utilizes principally its relatively diffuse 5s orbital with an estimated maximum[9] of 6% of the bonding being of the $d\pi-\pi$ double bond type suggested by Dewar.[5] Our calculations further indicate that this π complex should be relatively planar with a low potential energy surface for moving the silver atom along the carbon–carbon bond axis. Alkyl substitution on the double bond should, therefore, increase the basicity of the olefin by inductive effects while electron-withdrawing substituents or out-of-plane deformations of the double bond should destabilize the π system and enhance back donation into the antibonding orbitals on the double bond. Steric effects obviously outweigh any inductive effects due to alkyl substitution since increasing the number of substituents about the double bond of alkenes, dienes, and cyclic olefins causes a reduction in the equilibrium constant for compounds within that class.[40] This may be considered to be a reflection of the low positive charge on carbon with the silver complex, where stabilization of a carbonium ion by alkyl substitution is unimportant, since "π-complex" intermediates that are involved in addition reactions (*e.g.*, chlorination) that develop a high positive charge on carbon in the transition state may be stabilized by hyperconjugation and a rate enhancement is observed with increasing substitution on the double bond.[23] Moreover, aryl or vinyl substituents can stabilize an incipient carbonium ion during addition to the double bond, but these substituents, in addition to an adverse steric effect, serve to deactivate the double bond toward silver π-complex formation.

In general, the higher the energy content of an olefin the more readily it will form a silver complex. As noted above, *cis*-acyclic olefins complex more strongly than their *trans* isomers. To a first approximation, the best compromise between destabilization due to twisting about the double bond and the relief of nonbonded interactions will be attained. The principles involved here are similar to those used to explain differences in heats of hydrogenation.[43] There is not necessarily a correlation between argentation equilibrium constants and heats of hydrogenation as noted by Gardner,[31] since it should be emphasized that the rate of formation of the silver complex and the position of equilibrium are more dependent on the *relief* of strain on going to complex than on the extent of strain inherent in the olefin. This point is amply demonstrated by Muhs and Weiss[40] where they estimate an equilibrium constant for complexation of *trans*-cyclooctene to be >1000. In this case, the highly strained olefin[44] is twisted in the ground state and further twisting and relief of strain is obviously accommodated by the spherical 5s orbital on silver in the complex.

Experimentally, the relative stereospecificity of the alkoxymercuration of optically active 1,2-cyclononadiene was shown by Bach[11] to be directly related to the nature of the mercuric salt utilized in the reaction. Our calculations also suggest that there are marked differences in the nature of the bonding of ^+HgX to C_2H_4 as X is varied. The extent of bonding of ^+HgX to the olefin is seen to parallel the reactivity of the mercuric salt. We envision this reaction to proceed by formation of a π complex that can readily polarize to the unsymmetrical form IV with the developing positive charge on the adjacent carbon atom

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(37) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **60**, 836 (1938).

(38) N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **78**, 2210 (1956), and references cited therein.

(39) J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956); J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(40) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

(41) J. M. Harvilchuck, D. A. Aikens, and R. C. Murray, Jr., *Inorg. Chem.*, **8**, 539 (1969).

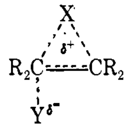
(42) Contrasting results between silver ion complexation in solution and by vpc have also been observed by B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

(43) R. B. Turner, D. E. Nettleton, and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958).

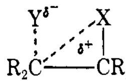
(44) The *trans* isomer is destabilized by 9.2 kcal/mol relative to its *cis* isomer: C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Elmsford, N. Y., 1962, p 38.

being stabilized by the mercury in addition to any stabilization of the incipient carbonium ion to be derived from substituents on the olefin.[45] This is consistent with the observed Markovnikov addition and the *trans* stereospecificity observed for this reaction. The mercurinium ion intermediates appear to be either planar or slightly out of plane depending upon the extent of bonding of the mercuric salt to the olefin. Experimental results with allenes indicate that some rehybridization at carbon has occurred and that the mercurinium ions with these 1,2-dienes are not linear.[46] In support of this suggestion an X-ray study of a rhodium–allene π complex has recently shown the allene moiety to be bent at an angle of 158°.[47]

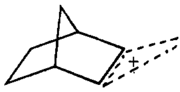
In a kinetic study of the hydroxymercuration reaction, Halpern[30] suggested that the rate-limiting step was a bimolecular reaction between Hg^{2+} and the olefin with no evidence for a mercurinium ion being observed. It seems reasonable that the relative differences in K_{eq} for argentation and that for forming a mercurinium ion, with a given pair of olefins, should be approximately comparable if both are π complexes. The argentation K_{eq} for *trans*-cyclooctene and 2-norbornene cited above differ markedly. However, the relative rates of methoxymercuration of these two olefins with mercuric acetate are not significantly different.[48] This observation is consistent with a transition state involving the solvation of an initially formed mercurinium ion intermediate by methanol as the rate-determining step. Although the preequilibrium[30] with $^{+}HgOAc$ is probably more rapidly established with *trans*-cyclooctene, *cis* addition to these olefins requires a higher energy transition state than *trans* addition (*vide infra*). Either the intermediate formed with an olefin and Hg^{2+}, which is extremely reactive, represents an especially low energy well on the reaction coordinate, or it is virtually nonexistent and resembles the transition state. This, however, does not preclude the possibility of longer lived mercurinium ions existing with less reactive substituted mercury cations such as $^{+}HgOAc$ and $^{+}HgCl$.[45] Our chemical intuition and the data presented here suggest that a mercurinium ion, although more reactive than a silver complex, should be of lower energy than a halonium ion. The fact that mercurinium ions have escaped detection while direct evidence for bromonium, chloronium, and iodonium ions has been obtained from nmr studies[49] could well be attributable to the mechanisms involved. The halonium ion is most likely formed by electrophilic attack on the olefin by a polarizable halogen molecule, X_2. Reversibility of this process would require a nucleophilic displacement of olefin by X^-. EH calculations and the mechanistic implications of halogen addition suggest that C_2H_4 competes favorably with Cl^- for the acid Cl^+. By contrast, the formation of a mercurinium ion is readily reversible,[30,50] dissociating into the olefin and the relatively stable ^{+}HgX. Moreover, halonium ions were observed at low temperature and in the absence of a nucleophilic solvent, while attempts to date to observe the mercurinium ion by nmr have been in hydroxylic solvents where a detectable concentration is obviously not allowed to accumulate.[51] To date, only circumstantial evidence for the intermediacy of mercury π complexes exists. However, recent work with optically active allenes[11,46] and optically active *trans*-cyclooctene[48,52] provides additional support for their existence.



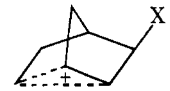
XII



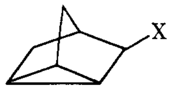
XIII



XIV



XV



XVI

a, X = HgX
b, X = SR
c, X = Br
d, X = Cl

Although the controversy about the involvement of π complexes in the rate-limiting step of electrophilic addition to olefins still exists, there is general agreement that the *trans* stereospecificity in these reactions involves a transition state like XII which is energetically favored[53] over the *cis*-transition state XIII. Front-side displacement not only involves serious interactions of the attacking nucleophile with X, but also with the bonding electrons that comprise the C–X bond. The latter problem should be more prevalent with the tightly bound halonium and sulfonium ions where p orbitals are largely involved in the bonding. The circumstances surrounding *cis*-electrophilic additions to olefins are not yet completely understood, but an excellent discussion of the available data for *cis* addition to strained olefins has been reported by Traylor.[4] For example, oxymercuration of 2-norbornene involves electrophilic attack on the double bond from the *exo* direction, XIVa, with *cis* addition. However, addition of RSCl and Br_2 proceeds by *exo*-electrophilic attack with *endo* attack of the nucleophile to open the three-membered ring affording *trans* adduct. An explanation for this behavior is not obvious and this is one of the ambiguities that prompted the present study. The orientation of addition to norbornenes has been attributed to steric, torsional,[54] twist-strain,[55] and electronic effects. Our calculations suggest that the mer-

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(45) This is in excellent accord with the properties of a mercurinium ion reported in an extensive study on acid-catalyzed deoxymercuration by M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and previous papers.

(46) R. D. Bach, *Tetrahedron Lett.*, 5841 (1968); W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968); W. L. Waters and E. F. Kiefer, *ibid.*, **89**, 6261 (1967).

(47) T. Kashiwagi, N. Yasuoki, N. Kasai, and N. Kukudo, *Chem. Commun.*, 317 (1969).

(48) R. D. Bach, unpublished results.

(49) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947 (1968); G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).

(50) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(51) W. Kitching, A. J. Smith, and P. R. Wells, *Chem. Commun.*, 370 (1968).

(52) V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organometal. Chem.*, **17**, 323 (1969).

(53) A value of $\sim$5 kcal/mol for the $\Delta H°$ of the isomerization of the *trans*- to the *cis*-transition state for deoxymercuration, involving a mercurinium ion intermediate, can be inferred from data given by M. M. Kreevoy, J. W. Gilje, L. T. Ditsch, W. Batorewicz, and M. A. Turner, *J. Org. Chem.*, **27**, 726 (1962).

(54) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

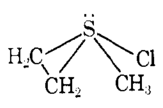
(55) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).

curinium ion, XIVa, can readily form an unsymmetrical ion IV which can greatly reduce bond oppositions in the transition state for *cis* addition, XIII. This is particularly true in view of the relatively long carbon–mercury bond distance in the π complex of ~2.3 Å. This process requires less energy[56a] than that required for inversion of configuration at carbon effecting a *trans* addition by *endo* attack of the nucleophile on XIVa. On the other hand, *trans* addition would be predicted with XIVb and XIVc, if the energy required to form an unsymmetrical three-membered ring is greater than the combined energies required to deform the bicyclic system. In these examples, if carbon–nucleophile bond formation develops concomitantly with C–X bond breaking, a lowering of the transition state energy should result. This process is favored by a *trans* attack. There is a good correlation between the calculated perturbation of the olefin and the positive charge on carbon in the ethylene complexes and the observed extent of rearrangement in XIVa–d. No rearrangements are observed on formation of mercury π complexes. The cyclic sulfonium ion intermediate XIVb does not afford any detectable products derived from the nonclassical ion XVb but gives up to 13% of XVI when the more electrophilic sulfenyl halides are used. On bromination and chlorination of 2-norbornene, the minor product is the *trans*-dihalide with the major products being XVIc and XVId and products derived from XVIc and XVId.[2–4] The bromine and chlorine bridging is in competition with participation by the C_1–C_6 bond (and in the latter case quite favorably) affording extensive strain-induced rearrangement. The trend noted here is in good agreement with what would be anticipated on the basis of neighboring group participation[56b] by X and hence the energy required to form an unsymmetrical ion.

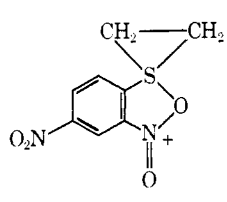
Although 2-norbornene is a strained olefin, it apparently has some flexibility as demonstrated by its greater K_{eq} for argentation (62) than that observed for 2,5-norbornadiene (33.7).[40] One possible consequence of this geometric flexibility is the same orientation of ^+HgX and RS^+ to 7,7-dimethylnorbornene as was observed with 2-norbornene which is considerably less hindered to *exo* attack.[3,4] Epoxidation, involving a simple 1,2-*cis* addition that exhibits the same general trends observed for chlorination, bromination, hydroboration, and other additions to this olefin, gives principally *endo* addition with 7,7-dimethylnorbornene.[3,4] It should be noted that the "exceptions" to the anticipated results based on steric considerations involve addition *via* a positively charged three-membered ring intermediate with subsequent ring opening by *exo-* or *endo*-nucleophilic attack. This attack should be greatly facilitated by formation of the unsymmetrical ion IV relieving methyl group nucleophile interactions in the transition state. Geometric and electronic effects are clearly more important than the steric effects with these intermediates[4] especially in view of the observed *endo* attack of ^+HgX to 7-hydroxymethyl-2-norbornene affording the *trans* adduct[55] by intramolecular attack on the *endo*-mercurium ion.

The addition of PhSCl and CH_3SCl to alkyl-substituted olefins, principally in the anti-Markovnikov sense,[29] is in agreement with a relatively stable cyclic sulfonium ion intermediate. The highly symmetrically episulfonium ion II is apparently bound tightly enough to the olefin to resemble a σ-bonded three-membered ring which undergoes nucleophilic attack at the least-hindered carbon atom as is observed with epoxides. Phenyl substitution on the olefin can stabilize an unsymmetrical episulfonium ion by resonance, and Markovnikov addition occurs. With highly electronegative substituents on sulfur, the episulfonium ion is destabilized, the positive charge at carbon increases, and Markovnikov addition also results since inductive effects become important. This suggestion is supported by kinetic studies where considerably more positive charge develops on sulfur and at carbon in the transition state than was present in the ground state[57] with the rate of reaction being much faster in polar than in nonpolar solvents. In the case of symmetrical alkenes, *trans* addition is well established[58] while *trans* addition to *cis*- and *trans*-2-phenyl-2-butene[59] and acenaphthylene[29] suggest that sulfenyl halides also add *trans* with aryl-substituted olefins. The fact that *cis* additions are not observed with these reactions could be a combination of the stability of the cyclic sulfonium ion and steric hindrance due to the substituent on the sulfur atom. These results suggest that unsymmetrical episulfonium ions are sufficiently stabilized by sulfur to prevent their forming open classical carbonium ions, thereby affording *trans* addition to olefins *via* transition-state XII where bond formation in the product-forming step is of considerable importance.

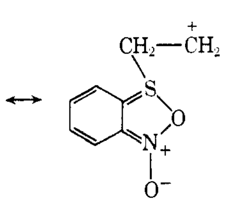
Recent nmr evidence indicates that episulfonium ions have a marked propensity to coordinate with nucleophiles in solution.[60] EH calculations on the coordinated episulfonium ion XVII led these authors to suggest that other episulfonium salts may also be coordinated (XVIII). We wish to point out that the highly electrophilic 2,4-dinitrosulfenyl halide complex



XVII



XVIII



XIX

is intramolecularly coordinated and thus bears a full positive charge that may be stabilized by resonance as depicted in XIX. This possibility does not exist

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(56) (a) The sum of the total steric and torsional effects for 2-norbornene have been estimated to be on the order of 5–8 kcal/mol based on the differences in transition state energies for *cis* and *trans* oxymercuration, and an estimate of the effect of neighboring group participation on the rate and orientation of addition: R. D. Bach, unpublished results. Using a different argument, Traylor[55] has concluded that twist strain raises the transition state for *trans* addition by more than 4 kcal/mol. (b) C. A. Clark and D. L. H. Williams, *J. Chem. Soc. B*, 1126 (1966).

(57) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961); C. Brown and D. R. Hogg, *Chem. Commun.*, 357 (1965).

(58) G. H. Schmid and V. M. Cslzmadia, *Can. J. Chem.*, **44**, 1338 (1966).

(59) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3883 (1949).

(60) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969).

for the neutral species XVII or for the comparably coordinated complex formed with PhSCl. We feel that this provides an attractive explanation for the observed Markovnikov addition of 2,4-dinitrosulfenyl chloride to propene[33] involving a carbonium ion intermediate while PhSCl and CH_3SCl added in the opposite sense by an apparent SN-2-like mechanism, as suggested above.

The addition of Cl_2 and Br_2 to symmetrical olefins occurs with a high degree of *trans* stereospecificity. This would be expected from a highly symmetrical halonium ion where bond making by halide ion in the transition state, XII, is important. The unsymmetrical halonium ion, IV, can result in Markovnikov addition. By analogy, I^+ should form the most stable halonium ion and our calculations are in agreement with the experimental trend of $Br^+ > Cl^+ > F^+$ in this capacity. In support of this suggestion a stabilized bromonium ion has recently been isolated.[61]

In certain cases stabilized carbonium ions can compete favorably with chlorine and bromine[62] bridging resulting in both *cis* and *trans* addition.[3] Nmr evidence[46] indicates β-fluorocarbonium ions have an open classical structure resulting in nonstereospecific addition with the *cis*-difluoride being formed preferentially.[63] By analogy to the behavior of highly reactive mercurinium ions,[30] it is conceivable that fluorine adds to olefins by collapse of a strongly perturbed olefin to product without an intermediate being involved. As anticipated, the propensity toward *cis* addition varies inversely with the stability of the bridged ion. A mechanism consistent with our results is the formation of a molecular complex between the olefin and the halogen molecule which collapses to a halonium ion intermediate. The substituents on the olefin determine whether the halonium ion is symmetrical, II, or unsymmetrical, IV, while the halogen will determine the extent of bridging, which is extremely low in the case of fluorine. *cis* addition may result from collapse of an ion-pair intermediate comprised of the unsymmetrical ion IV and the departing halide ion in which case solvent effects and conformational effects will influence the product distribution.[3] The planarity of the double bond of the halonium ion should also effect the *cis–trans* ratio. Rehybridization at carbon results in a bond-angle compression from 120 to 109° increasing steric interactions between substituents on the double bond. However, it should be possible to relieve these bond oppositions to some extent by twisting the double bond as suggested above for silver and mercury complexes. With a nonplanar symmetrical ion (*e.g.*, chloronium ion) *trans* addition requires inversion at carbon and the torsional strain for this process should be greater than for a *cis* addition or collapse of a planar carbonium ion IVa to product.

The stereospecific *trans* addition of chlorine to *cis*- and *trans*-di-*t*-butylethylene recently prompted Fahey[64] to assign the stabilization of a chloronium ion a value of at least 9.3 kcal/mol. An argument was presented that the steric repulsions between the *t*-butyl groups destabilized the *cis* isomer by 9.3 kcal/mol and that the energy of the bridged chloronium ion must be greater than that of the starting olefin. Thus, the chlorine bridging effectively offset the steric interactions and prevented free rotation, thereby providing a semiquantitative lower limit of the energy of a symmetrical chloronium ion. The above arguments suggest that this stabilization energy should be reduced from 9.3 kcal/mol to compensate for internal relief of strain due to twisting about the double bond. This same argument can be applied to the oxymercuration of *trans*-cyclooctene (which is strained by 9.2 kcal/mol) which also does not proceed *via* a carbonium ion intermediate.[4,48] A lower limit of the stability of a bridged mercurinium ion has been estimated to be comparable to the stabilization energy of an allylic carbonium ion.[11]

The electrophilic addition of hydrogen halides to olefins is probably the most difficult to study and the least well understood of this type of reaction. Dewar and Fahey[5] have concluded on the bases of their studies with acenaphthylene that the addition of DBr is an ionic addition involving classical carbonium ions as intermediates that afford mostly *cis* adducts *via* an undissociated ion pair. The conclusion reached by these workers is that classical carbonium ion structures are more stable than isomeric π complexes with apical protons. However, a more recent study[65] on the addition of DBr to *cis*- and *trans*-2-butene suggested a radical process to be involved that isomerized the olefins at a rate much faster than the rate of ionic addition, thereby affording identical mixtures of 60% *threo*- and 40% *erythro*-3-deuterio-2-bromobutane from either olefin under the "usual" conditions of 1 *M* DBr in acetic acid. A highly stereoselective *trans* addition (85 ± 1%) of DBr to these olefins was noted when a freeze-degassed acetic acid-O-*d* solution was used under helium and in the dark. This observation is consistent with a protonated ethylene intermediate or an AdE3 type transition state. Semiempirical molecular orbital calculations suggest the planar symmetrical form Ia to be more stable than the unsymmetrical form Ic but are of little value in deciding between Ia and a classical ethyl carbonium ion. However, by analogy to the other "onium" ion intermediates, symmetrically protonated ethylene should have a relatively planar double bond since the spherical 1s orbital of the apical proton should not cause extensive rehybridization at carbon. Certainly the perturbation of the olefinic system and the positive charge developed on carbon are conducive to nucleophilic attack on the protonated olefin. With highly substituted or aryl-substituted olefins, where stable carbonium ions may form, a classical carbonium ion mechanism should prevail affording both *cis* and *trans* adducts. Additional careful experimental work is needed to clarify this problem.

In conclusion, we have found extended Hückel molecular orbital calculations to be extremely useful in suggesting many of the mechanistic possibilities described in this study. In the above discussion, we have set forth some guidelines that may influence the

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(61) J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Commun.*, 907 (1969).

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path of electrophilic additions. However, in general this treatment is an oversimplification and it is still impossible at this time to present an overall theory that adequately treats all such electrophilic additions.

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Mechanistic Photochemistry of γ-Hydroxy-γ-phenylbutyrophenone. The Nature of the 1,4-Biradical Intermediate

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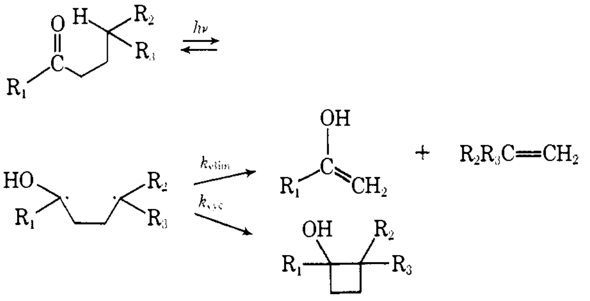
Abstract: The mechanistic photochemistry of γ-hydroxy-γ-phenylbutyrophenone (**1**) and its β,γ-dideuterio derivative (**2**) has been investigated. The presence of a biradical intermediate formed by γ-deuterium abstraction upon photolysis of **2** has been established by the formation of deuterium–hydrogen exchanged ketone **3**. A deuterium isotope effect on the rate constant for γ-hydrogen abstraction of 1.7 is observed. A kinetic analysis shows that bond rotations in the biradical are about five times slower than reabstraction of hydrogen or elimination to give acetophenone.

Reactions postulated to proceed through 1,4-biradical intermediates[1] have attracted considerable attention. Among the better known examples of such reactions are the thermal[2] and photochemical[2b,3] 2 + 2 addition of haloethylenes to dienes, the thermal and photochemical decomposition of cyclic azo compounds,[4] the 2 + 2 photoaddition of ketones[5] and thioketones[6] to olefins, the isomerization of olefins by "energy transfer" from carbonyl excited states,[5c,f,7] and the type II photoelimination and cyclization reactions of carbonyl compounds having a γ-hydrogen.[8–19] Previous investigations have established that the biradical intermediates formed by γ-hydrogen abstraction by the n,π* carbonyl excited state of dialkyl and aryl alkyl ketones give rise to both elimination and cyclization products (eq 1). Early evidence for the biradical intermediate was provided by (1) the



(1)

formation of both a vinylcyclobutanol and a cyclohexenol from 6-hepten-2-one,[8] (2) observation of an inverse deuterium isotope effect on the quantum yield of dialkyl ketone photoelimination,[9,10] and (3) the formation of cyclization and elimination products with identical rate constants for a number of ketones.[10–12] The fact that some carbonyl compounds optically active at the γ-carbon form cyclization or elimination products with some retention of configuration[13,14] has caused speculation that a concerted reaction mechanism might be involved in these reactions. However, small amounts of retention of configuration during cyclization are compatible with the formation of a short-lived biradical for which cyclization occurs faster than bond rotation.[15] The recent study of dialkyl ketone photochemistry by Yang and Elliott[16] has shown that whereas triplet alkanones react with concurrent racemization at the γ-carbon, singlet alkanones do not. Thus, the triplet biradical undergoes

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[1] Unfortunately, the terms biradical and diradical have been used loosely and interchangeably.

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