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Aspects of Organomercury Chemistry[1]

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MNDO has been applied with success to two topics of interest in organomercury chemistry, leading to satisfactory interpretations of the structures of sandwich and half-sandwich cyclopentadienylmercury compounds and the addition of mercury cations to olefins. The mechanism of oxymercuration is discussed.

Introduction

Mercury has long been an element of especial interest[2] to both inorganic and organic chemists, partly because of its varied chemistry and partly because its compounds are readily available. Since MNDO has now been parameterized for mercury,[3] we decided to study two topics of interest in the organomercury area, partly in the hope of resolving uncertainties and partly to check the ability of MNDO to deal with an element from the sixth row. The topics studied were (a) sandwich and half-sandwich (cyclopentadienyl)mercury compounds and (b) the addition of mercury cations to olefins (oxymercuration).

Procedure

The calculations were carried out by using the standard MNDO method and parameters,[4] as implemented in the MOPAC[5] package of computer programs. Geometries were optimized by the derivative procedures included in MOPAC with no assumptions other than symmetry in cases where symmetry was deliberately enforced. Transition states were located by the reaction coordinate method[6] or by a new procedure recently developed here[7] and refined by minimizing the scalar gradient of the energy.[6] All stationary points were characterized by calculating force constants.[6] Options for all these procedures are included in MOPAC.

Results and Discussion

A. (η^5-Cyclopentadienyl)mercury Compounds. The bonding in mercury cyclopentadienyl compounds has been shown by experiment to be η^1 and not η^5.[8] Such species also undergo rapid "ring whizzing"[8] by sigmatropic shifts of mercury round the cyclopentadienyl ring. Theoretical considerations, based on a revised set[9] of Woodward–Hoffmann rules,[10] indicate that the migration of mercury takes place by 1,2 shifts rather than by 1,3 shifts. The fluxional nature of these compounds has so far precluded an experimental[8,11,12] distinction between the two possibilities. In the hope of elucidating the structures of these novel compounds and the mechanism of "ring whizzing", we calculated the potential energy (PE) surfaces corresponding to (cyclopentadienyl)mercury cation ($C_5H_5Hg^+$), (Cyclopentadienyl)methylmercury ($C_5H_5HgCH_3$), (cyclopentadienyl)mercury chloride (C_5H_5HgCl), and bis(cyclopentadienyl)mercury ($(C_5H_5)_2Hg$).

While the (η^5-cyclopentadienyl)mercury cation (**1**) was a stationary point on the $C_5H_5Hg^+$ PE surface, this was not a minimum but a hilltop with two negative force constants, corresponding to conversion to **2** or **3**. The (η^1-cyclopentadienyl)mercury cation (**2**) was found to be the global minimum. The heats of formation and geometries calculated for the various stationary points are shown in Figure 1.

The transition state (TS **3**) for the 1,2 shift of mercury in **1** is higher in energy than **1** by only 6 kcal/mol. No TS could be found for an analogous 1,3 shift (**4**). Our results thus strongly support Su's[9] suggestion that "ring whizzing" takes place by 1,2 shifts of mercury round the ring. The low activation energy is also consistent with the fact that the reaction is fast on the NMR time scale under all conditions so far used.

Another possible isomer of **2**, i.e., **5**, was also found to be a minimum on the $C_5H_5Hg^+$ PE surface, higher in energy than **2** by 4.15 kcal/mol. Since our calculations predict a large activation energy (42.78 kcal/mol) for the conversion of **5** to **2**, via the TS **6**, **5** should be a stable species. It should be obtainable from a suitable precursor, e.g., **7**, under stable ion conditions. While no derivatives of **7** seem as yet to have been reported, their synthesis should be feasible.

We found a third minimum (**8**) on the $C_5H_5Hg^+$ PE surface, corresponding to cyclopentadienyl cations with one hydrogen atom replaced by Hg–H and only 11.78 kcal/mol higher in energy than **2**. The calculated barrier to conversion of **2** to **8** by a 1,2 migration of hydrogen from carbon to mercury, via the TS **9**, is very high (65.5 kcal/mol). However, since MNDO is known to overestimate the activation energies for hydrogen migrations,[4] this value is probably too large.

The geometries and the heats of formation calculated for stationary points on the $C_5H_5HgCH_3$ PE surface are shown in Figure 2 and those for C_5H_5HgCl in Figure 3. (η^5-Cyclopentadienyl)methylmercury (**10a**) was found to be a minimum, unlike **1** or the corresponding chloride (**10b**). The barrier separating **10a** from the more stable η^1 isomer (**11a**) was, however, minimal (0.56 kcal/mol). The structure of the corresponding TS (**12a**) seemed at

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(1) Part 78 of the series "Ground States of Molecules". For part 77, see: Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.*, in press.

(2) See, for example: Jensen, F. R.; Rickborn, B. In "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968. Matteson, D. S. In "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974. Negishi, E.-I. In "Organometallics in Organic Synthesis"; Wiley: New York, 1980.

(3) See the first of three papers in this issue.

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(5) QCPE Publication 455, Department of Chem., Indiana University, Bloomington, IN 47405.

(6) (a) McIver, J. W., Jr.; Komornicki, J. *J. Am. Chem. Soc.* **1972**, *94*, 2625. (b) *Chem. Phys. Lett.* **1971**, *10*, 303.

(7) Dewar, M. J. S.; Healy, E.; Stewart, J. J. P. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 227.

(8) (a) Goodfellow, R. J.; Stobart, S. R. *J. Magn. Reson.* **1977**, *27*, 143. (b) Grishin, Yu. K.; Sergeyev, N. M.; Ustynyuk, Yu. A. *Org. Magn. Reson.* **1972**, *4*, 377. See also ref 11 and 12a,b.

(9) Su, C.-C. J. *J. Am. Chem. Soc.* **1971**, *93*, 5653.

(10) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(11) (a) Campbell, A. J.; Cottrell, C. E.; Fyfe, C. A.; Jeffrey, K. R. *Inorg. Chem.* **1976**, *15*, 1326. (b) Campbell, A. J.; Fyfe, C. A.; Goel, R. G.; Maslowsky, E., Jr.; Senoff, C. V. *J. Am. Chem. Soc.* **1972**, *94*, 8387.

(12) (a) West, P.; Woodville, M. C.; Rausch, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 5649. (b) Campbell, C. H.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 3282. (c) Cradcock, S.; Duncan, W. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 194.

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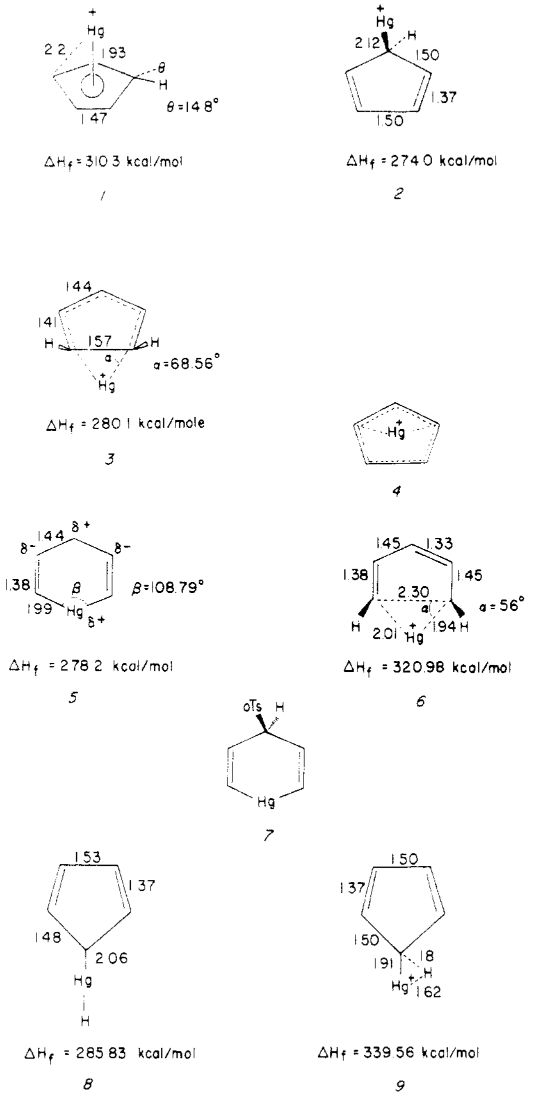

Figure 1. MNDO heats of formations and geometries for **1**–**9**.

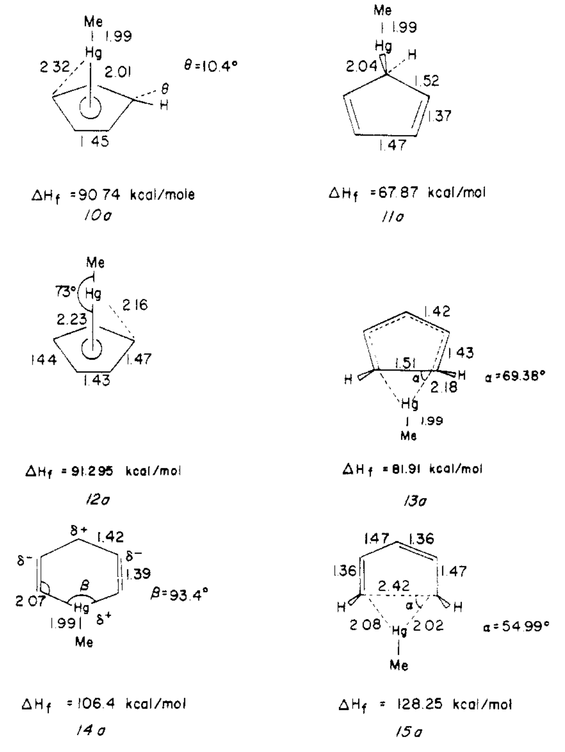

Figure 2. MNDO heats of formations and geometries for **10a**–**15a**.

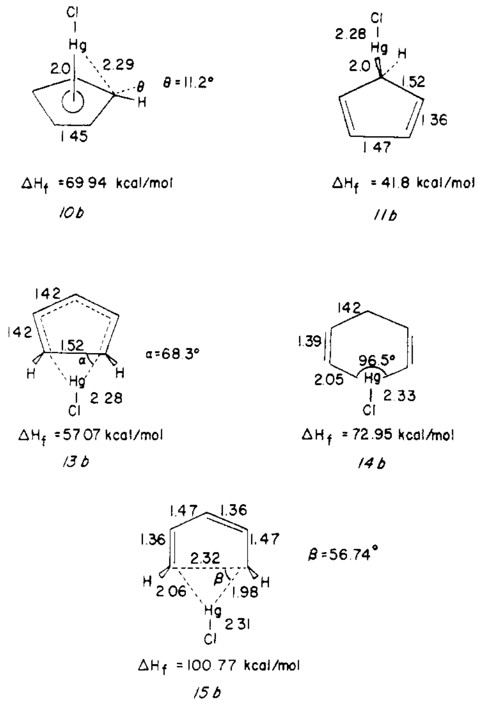

Figure 3. MNDO heats of formations and geometries for **10b**–**15b**.

first sight to imply that it was the TS for a 1,3 sigmatropic shift of hydrogen in **11a**. However, examination of the eigenvector of the force constant (Hessian) matrix corresponding to the imaginary vibration showed that it is in fact the TS for interconversion of **10a** and **11a**. The stability of these η^5 mercury compounds seems to depend on the net charge on the mercury atom, being greater, the less positive it is. As one would expect in view of the electron-donating properties of methyl, the positive charge on mercury is less in **10a** (0.45) than in **10b** (0.62) or **1** (0.80).

The MOs of these compounds present interesting features. Figure 4 shows a partial listing for **1**, **10a**, and **10b**. The occupied bonding MOs in **1** and **10a** are derived from a sp_z hybrid AO and the p_x and p_y AOs of mercury, interacting with the MOs of the cyclopentadienyl moiety. In the case of **10b**, however, the s and p_z AOs of mercury do not mix significantly, presumably because interaction with the electronegative chlorine increases the separation between them.

The activation energy calculated for "ring whizzing" (from TS **13a**) in **11a** is 14.0 kcal/mol. While no experimental value is available for comparison, the rearrangement is still fast on the NMR time scale at 150 K.[8a] This suggests that our calculated value may be somewhat too large. As in the case of **2**, all attempts to locate a TS for a 1,3 shift failed.

We were also able to locate a minimum (**14a**) on the C_6H_8Hg PE surface, related to **5** and involving a trigonal mercury atom. Here, however, the difference (38.5 kcal/mol) in energy between it and the global minimum **11a** was much greater than that (4.1 kcal/mol) between **5** and **2**. The activation energy for conversion of **14a** to **11a**, via the TS **15a**, is predicted to be 21.8 kcal/mol, implying that **14a** will be stable only at low temperatures.

(η^5-Cyclopentadienyl)mercury chloride (**10b**) is a hilltop on the C_5H_5HgCl PE surface, its force constant matrix having two negative eigenvalues, like that of **1**. The rest of the surface is similar to that for $C_5H_5Hg^+$ and need not therefore be discussed in detail. As noted above, Figure 3 shows the heats of formation and geometries calculated for the various stationary points. Here an experimental

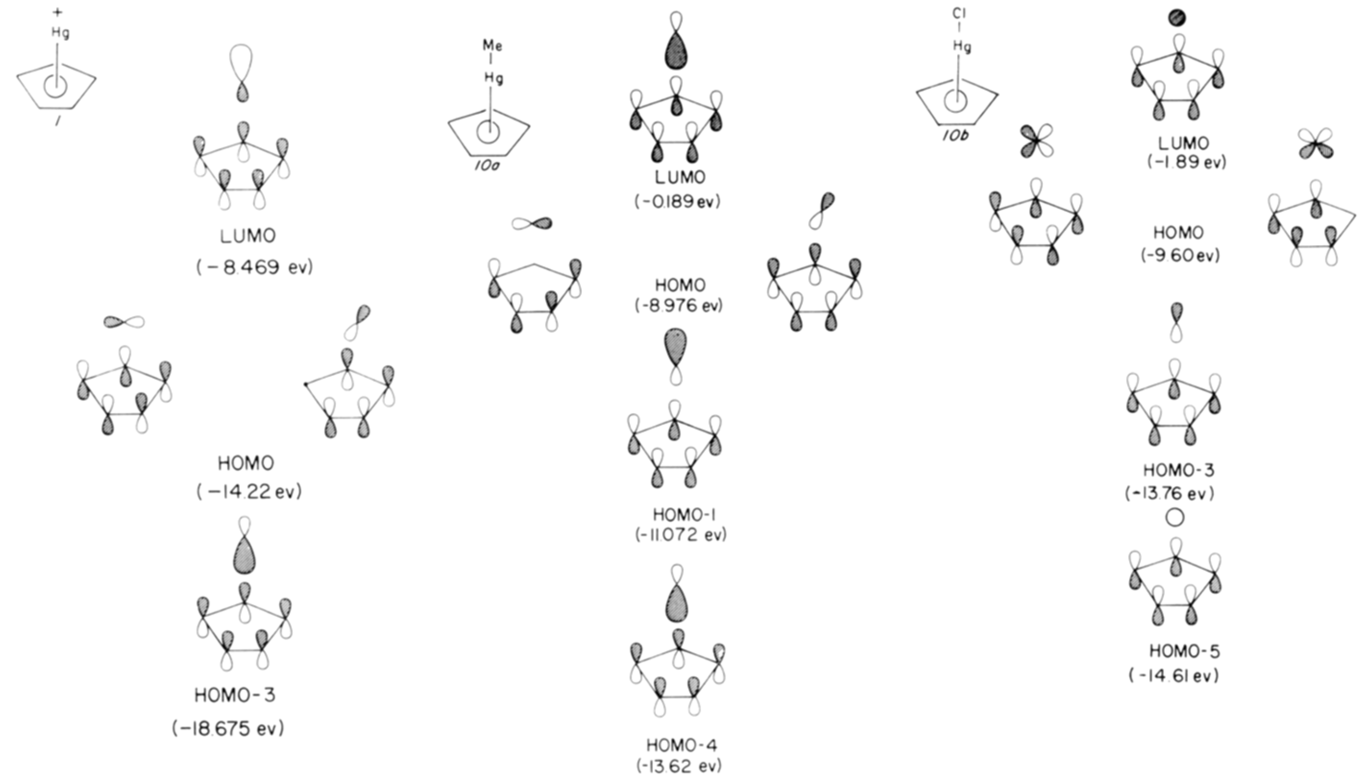

Figure 4. MNDO MO diagrams for **1**, **10a**, and **10b**.

activation energy (10 kcal/mol) has been reported[11] for the "ring whizzing" reaction, in reasonable agreement with our calculated value (15.3 kcal/mol). The former referred, however, to the solid state where crystal packing forces might be expected to increase the activation energy for any molecular rearrangement. Our calculated value seems in any case to be again somewhat too large.

Figure 5 shows the heats of formation and geometries calculated for stationary points on the bis(cyclopentadienyl)mercury PE surface. Since this is entirely analogous to that for (cyclopentadienyl)methylmercury and since the relative energies of the various species are also similar, there is no need for any independent discussion. The only point of interest is the possible existence of the sandwich species mercurocene (**16**), which was calculated by imposing D_{5d} symmetry. While necessarily a stationary point, this was not a minimum on the PE surface. Indeed, its force constant matrix had *four* negative eigenvalues, corresponding to four independent modes of rearrangement to bis η^1 isomers. This result agrees with the available experimental evidence,[12] which shows that bis(cyclopentadienyl)mercury exists only as the bis η^1 isomer. From our previous experiences with MNDO,[13] we have observed that MNDO underestimates the stability of bis(η^5-cyclopentadienyl) compounds. Even with the consideration of this point the importance of **16** on this PE surface is probably minimal.

An experimental activation energy (6.15 kcal/mol) has been reported[11] for "ring whizzing" in **11c**. This again is less than our calculated value (14.2 kcal/mol) for the 1,2 shift, and here again no TS could be found for rearrangement by 1,3 migration of mercury.

Table I. Heats of Formation (H_f; kcal/mol at 25 °C) for the Species Involved in the Reactions Studied Here

	H_f	
compd	calcd	obsd
Hg^{2+}	679.29	690.84[a]
Hg^+	222.46	256.83[a]
$HgCH_3^+$	218.85	222.11[a]
C_2H_4	15.3	12.5[b]
$CH_3CH:CH_2$	4.9	4.9[b]
NH_3	−6.3	−11.0[b]

[a] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Richard, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982** *11*, 150. [b] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

B. Addition of Mercury Cations to Olefins. While the addition of mercury cations to olefins has been studied experimentally both in the gas phase[14] and in solution,[15] the only theoretical calculations so far reported[16] were based on the EH method and are therefore of dubious significance.[17] Here we describe a detailed MNDO study of the additions of mercuric ion (Hg^{2+}), mercurous ion (Hg^+), and methylmercury cation (CH_3Hg^+) to various olefins. Table I shows the heats of formation calculated for the reactants, together with experimental values for comparison. The agreement is acceptable.

The addition of Hg^{2+} to ethylene is predicted by MNDO to be extremely exothermic ($\Delta H = -140$ kcal/mol), leading to an unsymmetrically bridged ion (**17**). The symmetrically bridged ion **18** is predicted to be less stable than **17** by 14.7 kcal/mol, being indeed the TS for the interconversion of two mirror-image unsymmetrically bridged ions. The

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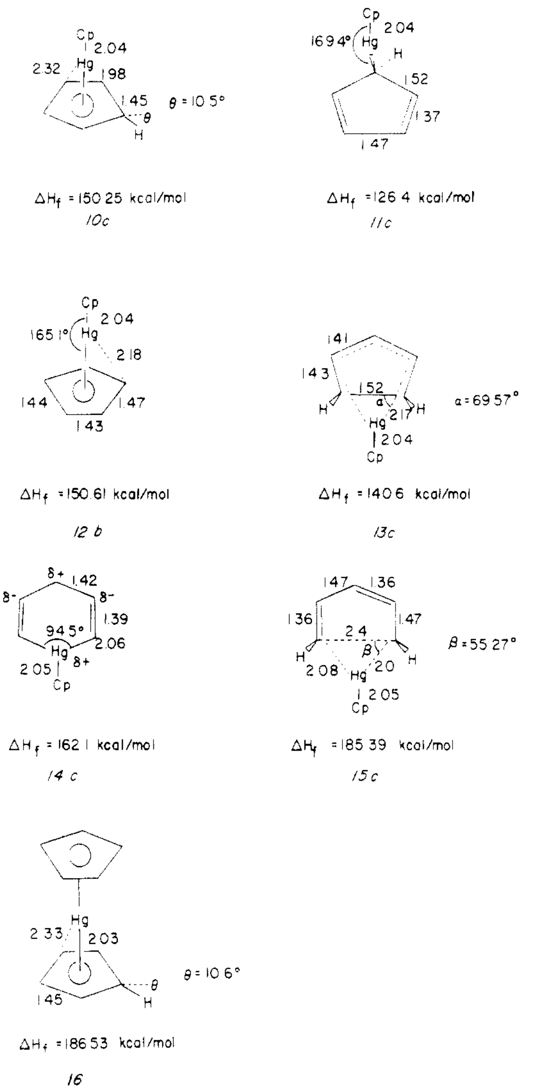
(13) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, Jr., K. M. *J. Am. Chem. Soc.* **1984**, *106*, 6773. Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 777.

(14) (a) Bach, R. D.; Weibel, A. T.; Patane, J.; Kevan, L. *J. Am. Chem. Soc.* **1976**, *98*, 6237. (b) Bach, R. D.; Patane, J.; Kevan, L. *J. Org. Chem.* **1975**, *40*, 257. (c) Bach, R. D.; Gaughofer, J.; Kevan, L. *J. Am. Chem. Soc.* **1972**, *94*, 6860.

(15) (a) Bach, R. D.; Richter, R. F. *J. Org. Chem.* **1973**, *38*, 3442. (b) Bach, R. D.; Richter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 4747. (c) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1971**, *93*, 1261, 2830.

(16) (a) Scherr, P. A.; Glick, M. D.; Siefert, J. H.; Bach, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 1782. (b) Bach, R. D.; Scherr, P. A. *J. Am. Chem. Soc.* **1972**, *94*, 220. (c) Bach, R. D.; Henneike, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 5589. See also ref 13.

(17) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558.



ΔH_f = 150.25 kcal/mol *10c*

ΔH_f = 126.4 kcal/mol *11c*

ΔH_f = 150.61 kcal/mol *12b*

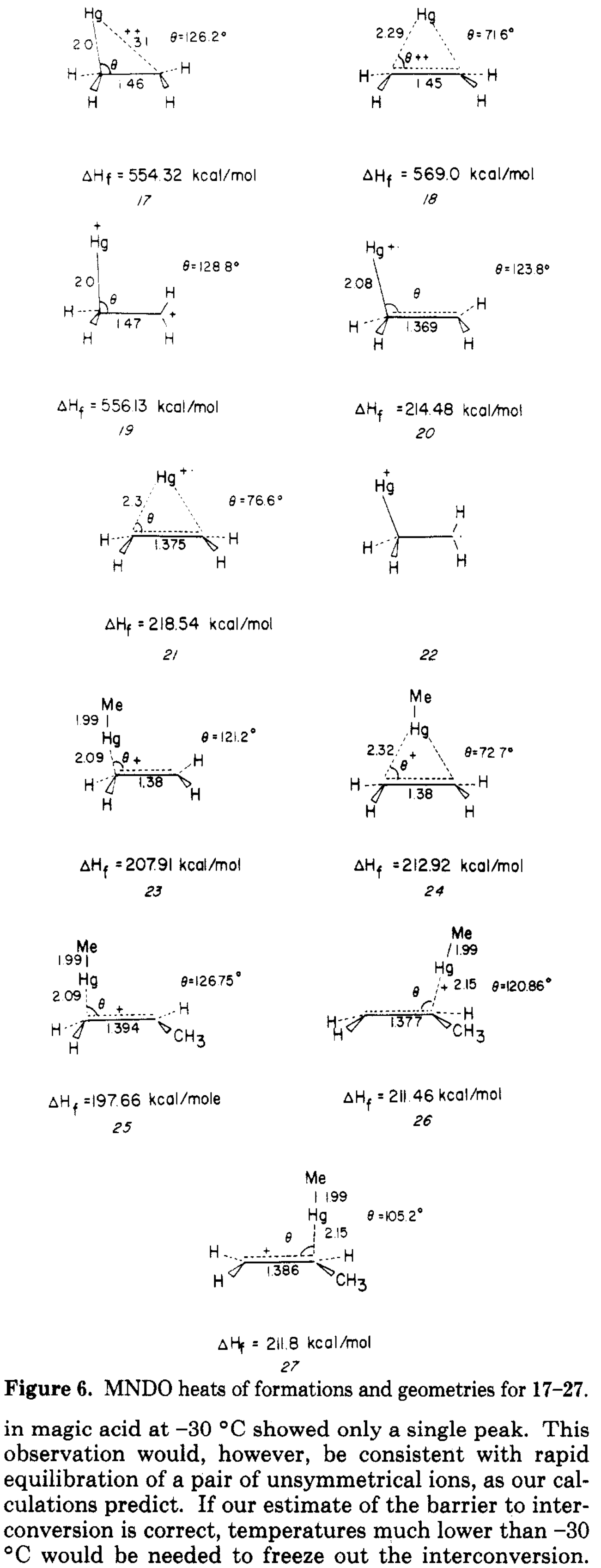
ΔH_f = 140.6 kcal/mol *13c*

ΔH_f = 162.1 kcal/mol *14c*

ΔH_f = 185.39 kcal/mol *15c*

ΔH_f = 186.53 kcal/mol *16*

Figure 5. MNDO heats of formations and geometries for **10c–15c** and **16**.



ΔH_f = 554.32 kcal/mol *17*

ΔH_f = 569.0 kcal/mol *18*

ΔH_f = 556.13 kcal/mol *19*

ΔH_f = 214.48 kcal/mol *20*

ΔH_f = 218.54 kcal/mol *21*

22

ΔH_f = 207.91 kcal/mol *23*

ΔH_f = 212.92 kcal/mol *24*

ΔH_f = 197.66 kcal/mole *25*

ΔH_f = 211.46 kcal/mol *26*

ΔH_f = 211.8 kcal/mol *27*

Figure 6. MNDO heats of formations and geometries for **17–27**.

structures calculated for **17** and **18** are shown in Figure 6. In the case of carbocations, MNDO is known[4] to favor classical structures over nonclassical (π complex) ones by several kilocalories per mole and a similar tendency has been noted in the case of the boron hydrides.[18] On the other hand, MNDO has predicted bromonium[19] and iodonium[20] ions to be symmetrical and cyclic. In view of the relatively large difference between the heats of formation calculated for **17** and **18**, the prediction that the former is the more stable seems therefore fairly strong.

If the terminal methylene group in **17** is rotated through 90°, **19** is generated. This is the TS for interconversion of the two rotational isomers of **17**. The difference in energy between **17** and **19** is calculated to be only 1.82 kcal/mol, implying that there is little interaction between the mercury atom and the β carbon atom, that the carbon–carbon π bond is completely broken, and that the bond between mercury and the adjacent carbon atom is a normal σ bond. Indeed, the calculated bond orders of these bonds are 1.12 and 0.98, respectively.

The experimental[15] evidence for the addition of mercuric ion to olefins has been interpreted in terms of symmetrical adducts **18**. The NMR spectra[15c] of solutions of such ions in magic acid at −30 °C showed only a single peak. This observation would, however, be consistent with rapid equilibration of a pair of unsymmetrical ions, as our calculations predict. If our estimate of the barrier to interconversion is correct, temperatures much lower than −30 °C would be needed to freeze out the interconversion.

Halpern et al.[21] have shown that the TS involved in attack by a nucleophile on the intermediate adduct has a large amount of carbocationic character. No kinetic evidence was found for the formation of a π complex intermediate. Our conclusions are therefore consistent with the available experimental evidence concerning the mechanisms of these reactions. There is no unequivocal

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[18] Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231. Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569.

[19] Dewar, M. J. S.; Healy, E. *J. Comput. Chem.* **1983**, *4*, 542.

[20] Dewar, M. J. S.; Healy, E., unpublished results.

[21] Halpern, J.; Tinker, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 6427.

evidence that "nonclassical" intermediates are involved.

Addition of mercurous ion (Hg^+) to ethylene is predicted to be exothermic by 23.3 kcal/mol, much less than the value for Hg^{2+}. This of course would be expected. The structures and heats of formation of the various species on the corresponding PE surface are shown in Figure 6. As in the preceding case, the global minimum is again the classical structure **20**, not the nonclassical structure **21**, the latter being higher in energy by 4.1 kcal/mol and corresponding to the TS for interconversion of two classical species **20**. Here the barrier to interconversion is even lower than in the previous case so it should be correspondingly more difficult to freeze out equilibration.

Next we tried to locate the TS **22** for rotation about the CC bond in **20**. To do this, we had to impose symmetry because otherwise dissociation occurred to vinyl cation and CH_3HgH. The barrier to rotation was 25.6 kcal/mol, implying that the carbon–carbon bond in **22** retains its double bond character. The calculated CC bond order is indeed 1.57. Evidently **20** is *not* a normal π complex. It is best regarded as a charge-induced dipole (CID) complex, the mercury ion polarizing the carbon–carbon double bond without completely breaking it. The barrier to rotation about it is less than that (65 kcal/mol) in ethylene primarily because the CH_3Hg group can form a covalent bond to carbon in the biradical-like TS. It is interesting to note that Fukuzumi and Kochi[22] have found evidence for the formation of such intermediates during oxymercuration reactions.

Bach et al.[14a] have observed **20** in an ICR spectrometer. They assumed it to be a π complex (**21**) on the basis of the EH[16c] calculations referenced above.[16] The EH method is, however, unreliable as a guide to molecular structures and/or energies.[17] The experimental results are consistent with the interpretation given here.

The addition of the methylmercury cation to olefins has been studied both in the gas phase[14] and in solution,[15] and EH calculations for it have also been reported.[16] As before, the latter predicts the product from ethylene to be a symmetrical π complex (**24**) whereas our MNDO calculations predict it to be an unsymmetrically bridged species (**23**), lower in energy than **24** by 5 kcal/mol. The calculated (MNDO) geometries of the two ions are shown in Figure 6. As in the case of the Hg^+ adduct, the C=C bond in **24** is still strong, its bond order being the same (1.6) as in **23**. Thus **24**, like **20**, is best formulated as a CID complex.

The addition of methylmercury cation to propene **25** was next studied, to assess the course of addition to an unsymmetrical olefin. Only two minima were found on the PE surface, corresponding to the two isomeric CID complexes **25** and **26**. Their calculated heats of formation and geometries are shown in Figure 6. As expected on the basis of the known polarization of the C=C bond in propene **25** is the more stable, by 3.8 kcal/mol. Indeed, the other isomer **26** is marginally stable, the barrier separating it from **26** being only 0.634 kcal/mol (via TS **27**). One can conclude that reactions of methylmercury cation with other unsymmetrical olefins will likewise lead to CID complexes in which mercury is adjacent to the more negative end of the C=C bond.

Mechanism of Oxymercuration

Addition of a mercury compound of the type RHgOX to an olefin is generally believed to involve electrophilic attack by the corresponding mercury ion (RHg^+) on the CC double bond of the olefin. It has been commonly assumed in the past that the result is a π complex (e.g., **24**) which then reacts with the nucleophile trans to the apical group, accounting for the observed stereospecific trans addition. Our calculations, however, seem to imply rather strongly that such adducts are *not* π complexes but CID complexes, with mercury attached unsymmetrically to the C=C bond. While the predicted mode of attachment of mercury to an unsymmetrical olefin corresponds to the observed Markownikov regiospecificity, it is by no means obvious that addition of an anion to such a species should take place preferentially trans to mercury.

To clarify this point, we carried out model calculations for the cis and trans additions of NH_3 to **23**.

The cis adduct **29** was a stationary point on the corresponding PE surface, but not a minimum. It was in fact the TS for rotation about the CD bond. The only minimum we could find was the trans adduct **28**. The calculated difference in energy between **28** and **29**, i.e., the calculated barrier to rotation, was 7.9 kcal/mol.

The TS's for trans (**30**) and cis (**31**) addition were found by studying the reverse reactions, i.e., the dissociations of **28** and **29** to **23** and ammonia. The form of the calculated PE surface is interesting in that the path for cis addition terminates not in a minimum but a TS. Analogous situations have been found in several other cases.[23] The heats of formation and geometries calculated for **28**–**31** are shown in Figure 7. The activation energies for the reverse reactions were 23.6 and 23.5 kcal/mol, respectively. The activation energy for cis addition of ammonia to **23** to form **29** is thus higher by 8.0 kcal/mol than that for trans addition to form **28**, the actual calculated activation energies being 12.0 (via **33**) and 4.0 (via **32**) kcal/mol. Our calculations therefore correctly predict the overall reaction to lead to trans adduct and the calculated difference between the two activation energies would be sufficient to make it essentially stereospecific.

Our calculations admittedly refer to a neutral nucleophile (NH_3) whereas the species involved in oxymercuration is an anion (XO^-). The electrostatic attraction between mercury and the latter would be expected to favor cis addition. Reactions of this kind are, however, carried out in polar solvents where electrostatic interactions between ions are greatly reduced. Indeed, reactions involving the generation of ions from neutral reactants do not normally take place in the gas phase and calculations for them are correspondingly meaningless. This is why we studied the reaction of **23** with ammonia rather than, e.g., acetate ion. However, cis addition should certainly be assisted by a negative charge on the nucleophile and a CID complex should be perfectly capable of adding cis. If our interpretation of the intermediates is correct, one might therefore expect to find special cases where oxymercuration leads to cis adducts, whereas if the intermediates are π complexes, trans addition would be expected in all cases.

While oxymercuration normally takes place by trans addition, as expected on the basis of the π complex mechanism, there are exceptions. Oxymercuration of norbornene, in particular, leads predominantly to cis-exo adduct.[24] This has been commonly attributed to a difference in mechanism, oxymercuration of norbornene being assumed to take place by a concerted (pericyclic) addition without formation of intermediate ions. There is, however, no evidence for this suggestion, and the product formed is inconsistent with it. Analogous reactions that are known

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[22] Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783.

[23] Dewar, M. J. S.; Ford, G. P. *J. Mol. Struct.* **1979**, *51*, 281. Dewar, M. J. S.; Merz, K. M., Jr. *THEOCHEM*, in press. Dewar, M. J. S.; Merz, K. M., Jr., unpublished results.

[24] (a) Traylor T. G. *Acc. Chem. Res.* **1969**, *2*, 152. (b) Reference 15b.

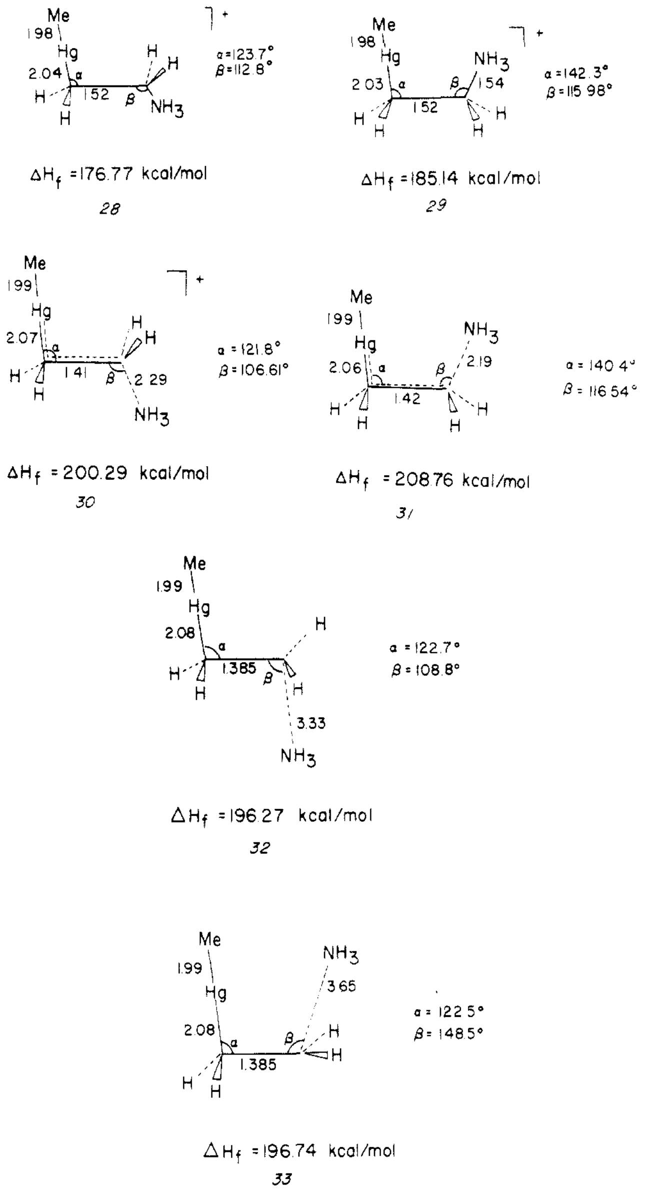


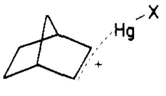
Figure 7. MNDO heats of formations and geometries for **28–33**.

to proceed by concerted addition take place cis-endo, not cis-exo.[25] Nor can the intermediate in the addition be a classical carbenium ion, as Brown[26] has suggested, because such an ion would be expected to undergo Wagner-Meerwein rearrangements, which are not observed.

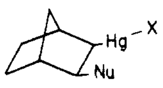
Our proposed mechanism, involving CID complexes as intermediates, accounts for all the available evidence in a unified manner, with no need for ad hoc assumptions.

In mercuration of an olefin, the initial attack by the mercury cation is expected to take place at the more negative end of the olefinic double bond. This accounts immediately for the observed Markownikov-type regioselectivity. Also, for reasons indicated above, the overall addition normally takes place trans.

Consider now addition to norbornene. The corresponding CID complex is expected to have the exo structure **34** because steric effects will favor exo addition, as they do in normal electrophilic additions to norbornene. In such an electrophilic addition, the intermediate ion is either a π complex formed by the 2,3 CC bond as donor or a classical carbenium ion which immediately rearranges to the corresponding (nonclassical but probably unsymmetrical) 2-norbornyl cation. If the former, subsequent reaction with a nucleophile necessarily leads to trans addition. If the latter, the result is a mixture of the products from the nonclassical ion, i.e., the cis adduct and an exo-2-cis-7-disubstituted norbornane.[24] However, in addition of RHg^+ to norbornene, the initial adduct is expected to be a CID complex (**34**) where the CC double bond is still essentially intact. Addition of a nucleophile to the CID complex therefore encounters the same steric effects as the initial addition of RHg^+ to the C=C bond in norbornene because the carbon atoms forming the double bond are still trigonal. Addition therefore tends to take place exo, leading to cis adduct **35**.



34



35

where for example

X = oAc

Nu = ōAc

Note that rapid Wagner–Meerwein rearrangements *have* been observed[15c] in the case of the adduct from norbornene and mercuric ion (Hg^{2+}). This again would be expected on the basis of our calculations because the adduct in this case is predicted to be a classical carbocation, not a CID complex. Subsequent attack by an anion would then be expected to take place trans to mercury.

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Registry No. **1**, 97975-71-8; **2**, 97975-72-9; **5**, 97975-73-0; **7**, 97975-81-0; **8**, 97975-74-1; **10a**, 97975-75-2; **10b**, 12071-53-3; **10c**, 97975-76-3; **11a**, 34310-40-2; **11b**, 1003-26-5; **11c**, 18263-08-6; **14a**, 97975-82-1; **14b**, 97975-83-2; **14c**, 97975-77-4; **16**, 12083-67-9; **18**, 157-14-2; **19**, 97975-78-5; **21**, 97975-79-6; **22**, 97975-80-9; **23**, 97975-84-3; **24**, 38831-99-1; **25**, 97975-85-4; **26**, 97975-86-5; **28**, 97997-01-8; Hg^{2+}, 14302-87-5; Hg^+, 22542-11-6; $HgCH3^+$, 22967-92-6; C2H4, 74-85-1; CH3CH:CH2, 115-07-1; NH3, 7664-41-7; norbornene, 498-66-8.

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