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A Theoretical Study on Bromonium Ion and Mercurinium Ion Intermediates[#]

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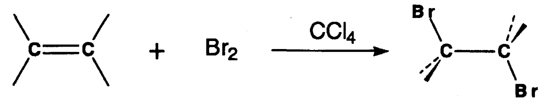
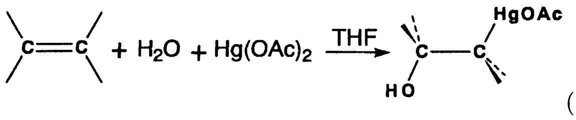
Geometries of two title intermediates brought about by bromination and oxymercuration are studied with PM3 and *ab initio* molecular orbital calculations. For thirteen Br^+ intermediates, the regular Markovnikov type structures are obtained and they depend upon the electronic donating strength. On the other hand, geometries of thirteen $Hg(OCOCH_3)_2$ intermediates are found to be almost the same and of the isosceles-triangle forms. Steric repulsion occurs not between two acetate groups but between one acetate and the substituents attached to olefins.

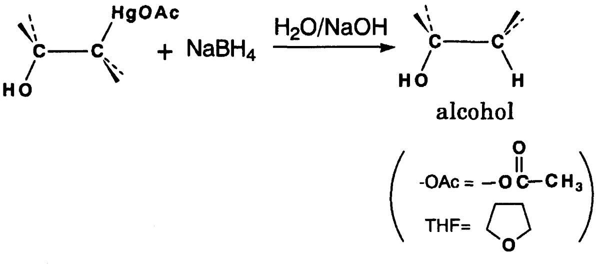
Olefin bromination in Eq. 1 and oxymercuration in Eq. 2 are representative electrophilic additions in organic chemistry.[1)] The stability of bromonium ion and mercurinium ion intermediates (Chart 1) is known to control addition routes. There is a mystery in the reactivity of the oxymercuration. The bromination reactivity follows the regular order. As the alkyl size attached to the olefin double bond increases, the addition rate is enhanced.[2)] However, the oxymercuration rate does not show this expected trend.[3)] The irregularity of the oxymercuration reactivity is ascribed to a "steric effect."



(1)



(2a)



(2b)

Fukuzumi and Kochi showed an elegant spectroscopic meaning of the steric effect.[4)] They proved that the relative rate of the bromination becomes identical with that of the oxymercuration if the steric effect is taken into account in the latter reaction. However, structural and electronic features of this steric effect are still open to question.

bromonium ion intermediate
mercurinium ion intermediate

Chart 1.

This work will deal with geometries of two cyclic-ion intermediates theoretically, and it is attempted to find out what is the steric effect in the mercurinium ion intermediates. Various olefins are adopted to compare systematically structures of intermediates.

Method of Calculations

The bromonium and mercurinium ion intermediates of 13 olefins in Table 1 are calculated using the PM3 method[5)] of version 6 MOPAC.[6)] Olefins are numbered according to the HOMO energies. That is, **1** is the poorest electron donor and **13** is the strongest one. Hereafter, Br^+ and $Hg(OAc)_2$ intermediates of **1**, for instance, are called **1**–Br and **1**–Hg, respectively.

For intermediates of **3** and **4**, *ab initio* calculations are also made to evaluate reliability of PM3 geometries. Valence minimal, double-zeta and effective core potentials of Hay and Wadt (RHF/LANL1MB and RHF/LANL1DZ)[7)] internal in the GAUSSIAN 92[8)] program are used.

All calculations are performed with GAUSSIAN 92 and MOPAC installed both at CONVEX C-220 at the Information Processing Center of Nara University of Education and at CONVEX C-3420 at the Computer Center of Nara University.

Geometries of Bromonium Ion Intermediates

Figure 1 displays optimized geometries of Br^+ intermediates. As expected, unsymmetric alkenes give Markovnikov-type open forms of intermediates. Bridged forms are found only in **3**–Br and **8**–Br. **6**–Br, **7**–Br, and **11**–Br are of the typical open form with tertiary carbonium-ion center. Asymmetric forms of **9**–Br, **10**–Br, and **13**–Br are noteworthy, because the corresponding olefins are of the symmetric form. This feature was reported in our preliminary work of chlorination[9)] as a rapid equilibrium via the symmetric transition state (Chart 2).

All top views demonstrate that Br stays along the

[#]This paper is dedicated to the late Professor Hiroshi Kato.

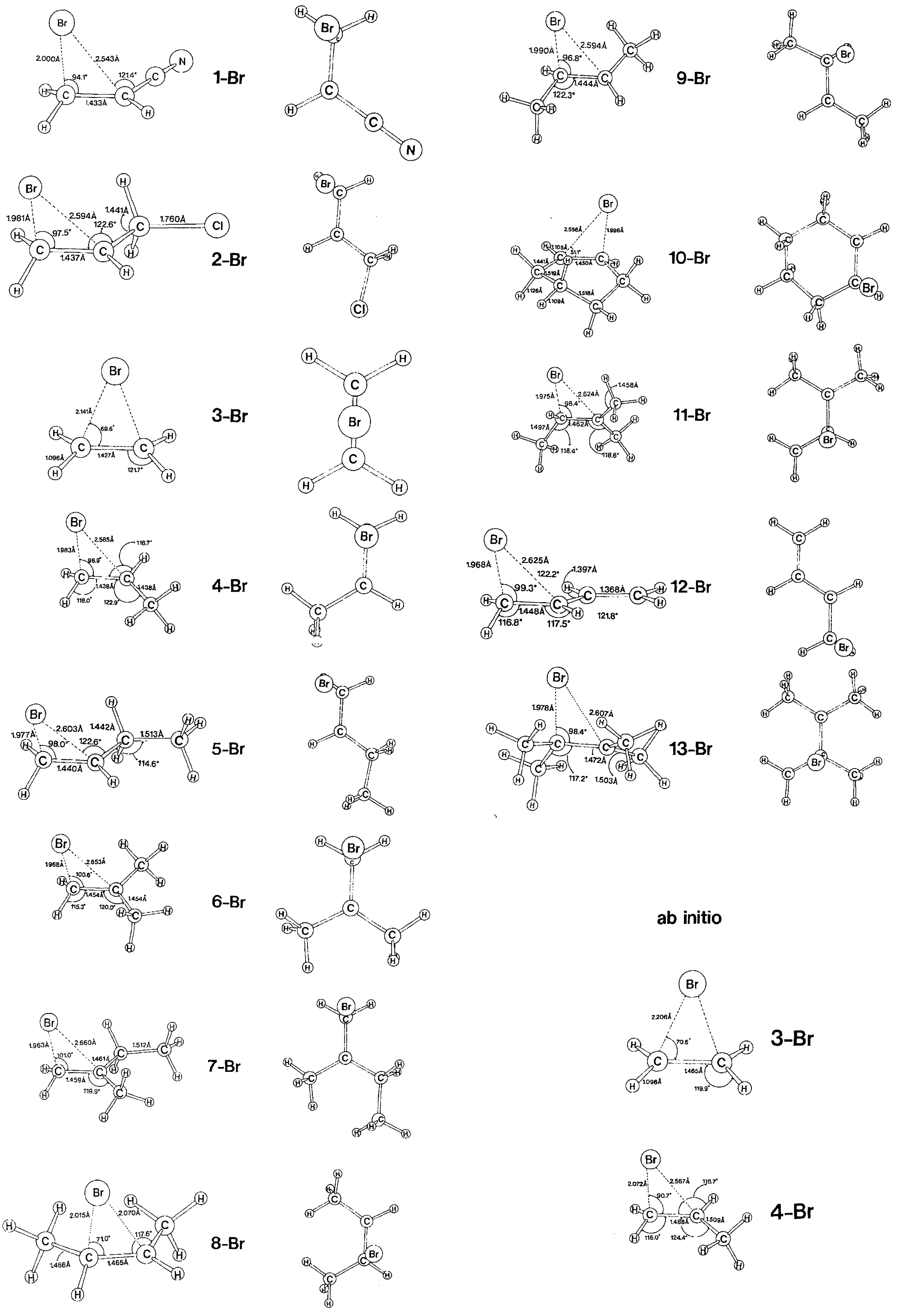
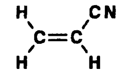
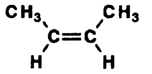
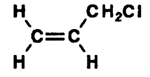
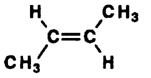
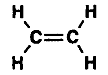
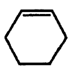
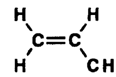
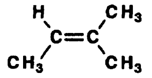
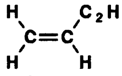
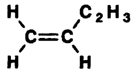
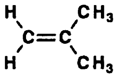
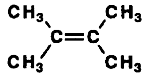
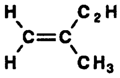


Fig. 1. Thirteen PM3- and two *ab initio* optimized geometries of bromonium ion intermediates. For PM3 geometries, side and top views are shown.

Table 1. Alkenes for the Present Bromonium and Mercurinium Ion Intermediates in the Order of HOMO Levels Calculated by RHF/STO-3G Method

1	 acrylonitrile	8	 *cis*-2-butene
2	 allyl-chloride	9	 *trans*-2-butene
3	 ethylene	10	 cyclohexene
4	 propene	11	 2-methyl-2-butene
5	 1-butene	12	 1,3-butadiene
6	 2-methyl-propene	13	 2,3-dimethyl-2-butene
7	 2-methyl-1-butene		

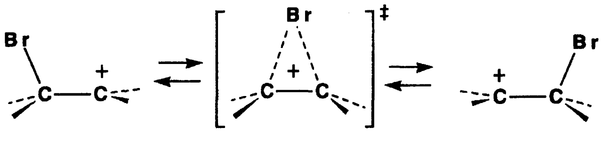


Chart 2.

olefin C–C axis to accept the π electronic charge. That is, intermediate geometries reflect the electron-donating strength of olefins.

For **3**–Br and **4**–Br, PM3 geometries are compared with *ab initio* ones. Significant differences are not found between them.

Geometries of Mercurinium Ion Intermediates

Figure 2 shows geometries of the Hg electrophile and its anion radical. $Hg(OAc)_2$ is found to be of D_{2d}-type symmetry. When an electron is added to $Hg(OAc)_2$, a bent form is generated. However, two acetate ions are still distant with each other, suggesting that the steric crowd inside the electrophile is negligible at the $Hg(OAc)_2$ attack to olefins.

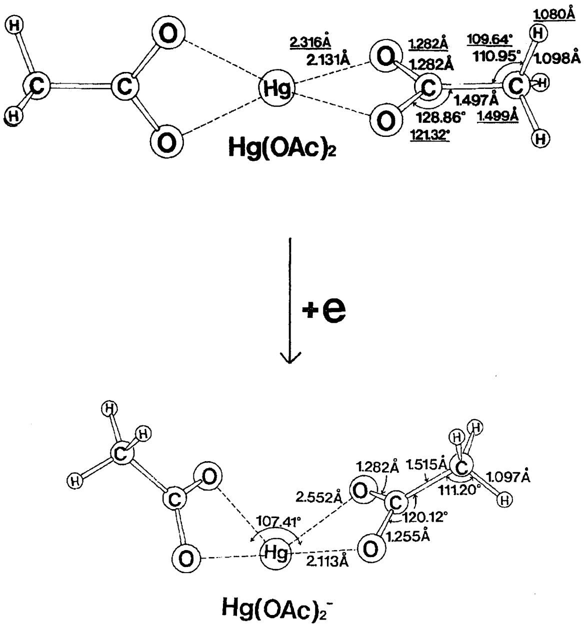


Fig. 2. PM3 geometries of mercury (II) diacetate and its anion radical. Underlined numbers denote *ab intio* (RHF/LANL1DZ) geometric data.

Figure 3 shows Hg-intermediate geometries. Surprisingly, all the intermediates have almost the same bridge form regardless of substituents to olefin (Chart 3)! That is, the Markovnikov rule is not applicable to the mercurinium ion intermediate. Also, the extent of the AcO–Hg–OAc bending in the $Hg(OAc)_2$ electrophile is not so different, 120—140°. It is understandable that the electron-donating strength of olefins cannot be concerned with the oxymercuration reactivity.

Top views exhibit that the Hg atom is deviated from the olefin C–C axis except in **3**–Hg and **8**–Hg. This deviation arises from the steric repulsion between the alkyl substituents in the olefin and one –OAc group in the electrophile. To prove this, two olefin–Hg^{2+} complexes (**4**–Hg^{2+} and **13**–Hg^{2+}) are calculated and are shown in Fig. 4. In both complexes, Hg^{2+} is found to be just on the olefin C–C axis, whereas in **4**–Hg and **13**–Hg of Fig. 3 the Hg atom is not on the C–C axis. With maintenance of the isosceles triangle, the involvement of the steric repulsion will lead to unstable mercurinium intermediates.

In Fig. 3, two *ab initio* geometries, **3**–Hg and **4**–Hg, are compared with PM3 ones. The *ab initio* Hg···C distance, ca. 3.1 Å, is larger than that, ca. 2.5 Å, of PM3.

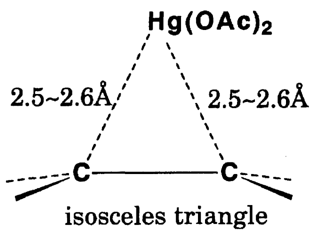


Chart 3.

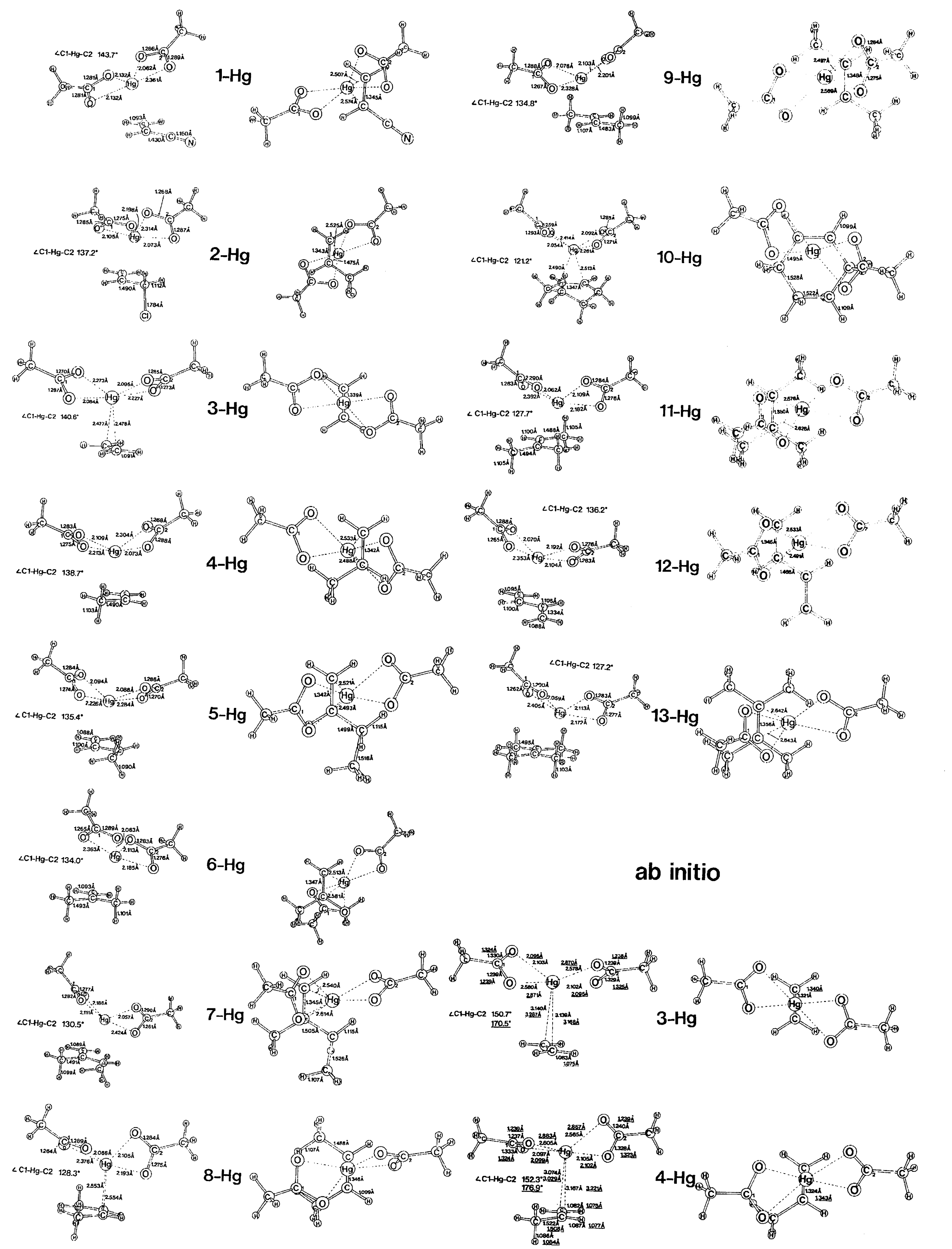


Fig. 3. Thirteen PM3- and two *ab initio* (RHF/LANL1MB and RHF/LANL1DZ) optimized geometries of mercurinium ion intermediates.

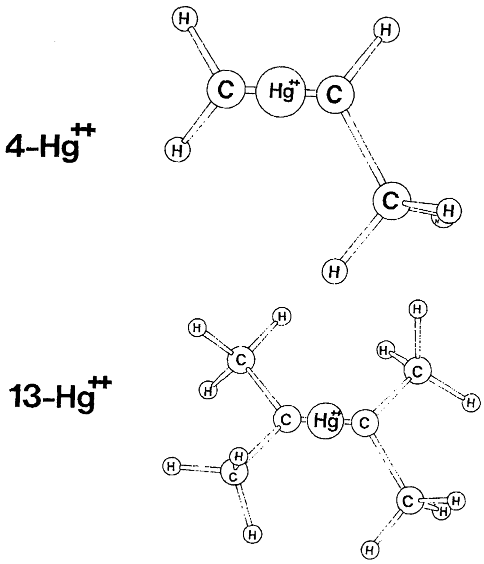


Fig. 4. PM3 optimized geometries of propene–Hg^{2+} and 2,3-dimethyl-2-butene–Hg^{2+} complexes.

Therefore, in *ab initio* **4**–Hg, the deviation of the Hg position in the top view is smaller than that in the PM3 **4**–Hg. Thus, the PM3 method overestimates the steric repulsion to some extent. But, the similar isosceles triangle shape is obtained also in the *ab initio* **4**–Hg. As far as *ab initio* MO results are concerned, LANL1MB (valence-minimal) and LANL1DZ (underlined numbers, valence double-zeta) have given similar geometries. Only the angle, ∠C1–Hg–C2, shows an appreciable difference. The RHF/LANL1DZ method gives a larger angle than the RHF/LANL1MB one. This means that the RHF/LANL1MB and PM3 methods overestimate the interaction between the olefin and Hg, and consequently give a large sp hybridization in Hg. Except the angle, the similarity indicates that computed data are enougth reliable for the mechanistic discussion to be valid.

Comparison of Properties of Two Intermediates

Figure 5 shows complexation energies. Bromonium ion intermediates reflect roughly the electron donating strength of olefins, whereas the stability of mercurinium ion ones is insensitive to the kind of olefins or becomes decreased slightly as the alkyl size increases. The same trend is observed in the electronic charge migrated by the complexation in Fig. 6. The abnormally small quantity of **3**–Br is due to the back charge transfer (CT) in the symmetric (C_{2v}) form (Chart 4). Except **3**–Br, all bromonium ion intermediates are of the asymmetric form leading to the forbiddeness of the back CT and further to the largely migrated charge at Br^+.

The extent of charge-transfer interactions is reflected in the dfference of geometries of Br and Hg intermediates, as the olefinic C–C bond lengths in Figs. 1 and 3 show (ca. 1.43 Å in Br intermediates and ca. 1.34 Å in Hg intermediates). When the olefin π MO interacts with the Br^+ 4p atomic orbital, Br^+ moves toward the right-side carbon to attain the maximum MO overlap. Due to the strong interaction, there is a clear site selectivity (Chart 5). In constrast, the interaction between the olefin π MO and the Hg 6sp hybridized orbital is so weak that the Hg position is almost insensitive to the shape of π MO. For the olefinic π MO, Br^+ is a hard acid and Hg^{2+} is a soft acid. Thus, the latter acid is too soft for the Markovnikov's selectivity to be effective.

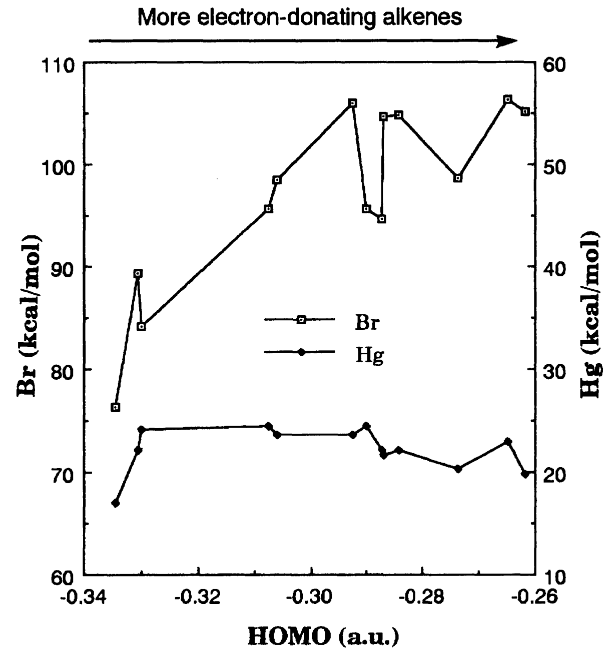


Fig. 5. Binding energies in kcal mol^{-1} between Br^+ or $Hg(OAc)_2$ and alkenes.

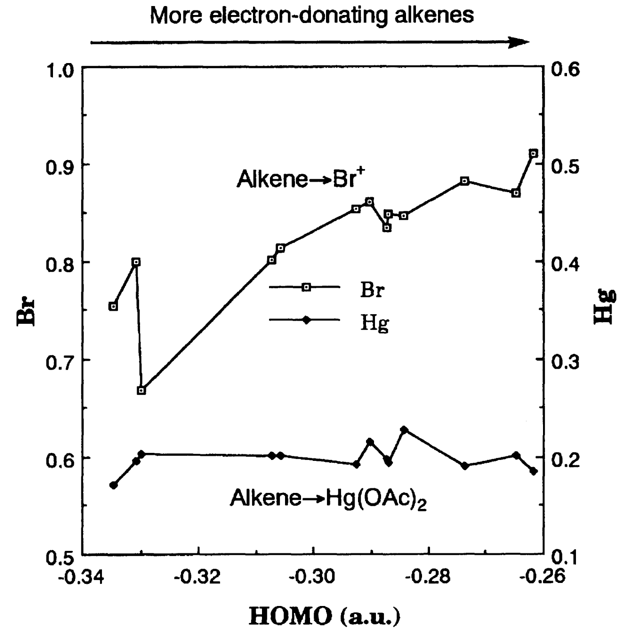
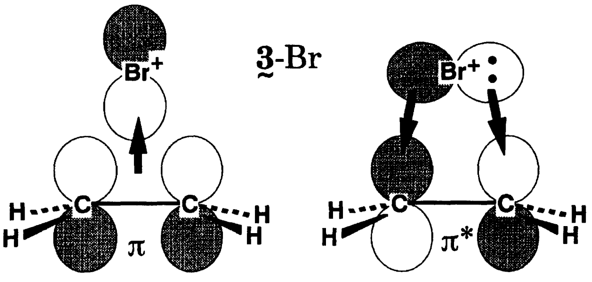
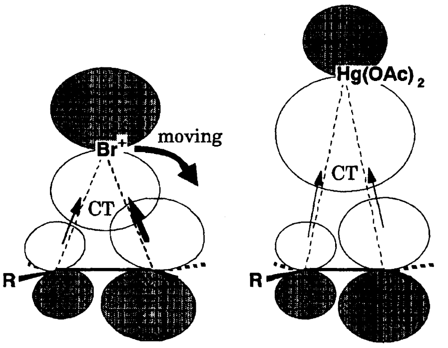


Fig. 6. Electronic charges transferred from alkene to Br^+ or $Hg(OAc)_2$.



CT back CT

Chart 4.



Strong CT Interaction Weak CT Interaction

Chart 5.

Concluding Remarks

This work has dealt with geometric and electronic natures of thirteen bromonium and mercurinium ion intermediates theoretically. While Br intermediates follow the Markovnikov-type donor–acceptor relation, Hg intermediates are insensitive to the relation. All the shapes of the latter intermediates are similar isosceles triangles regardless of alkenes. The steric repulsion between one –OAc and the alkyl substituent of olefins reinforces the deviation of the Hg position, which is the source of the irregularity of the oxymercuration stated in the Introduction.

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