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Gas-Phase Structure of the Bromonium Ion of 2-Methylpropene

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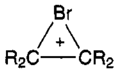
1. Introduction

There has been continued interest, both theoretical[1−6] and experimental,[6−8] in the structure and energetics of three-membered halonium and bromonium ions. Bromine bridging in alkene bromination intermediates is currently believed to be essentially symmetric for ions produced from symmetrically substituted olefins **1** and asymmetric for the ions produced from asymmetrically substituted olefins **2**.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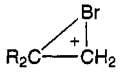
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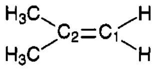
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It is also generally accepted that for alkyl-substituted ethylenes the extent of the asymmetry in **2** depends upon the number and nature of the alkyl group substituents, but even in the most extreme cases where the ion structurally resembles a β-bromocarbocation, there is some weak, but unspecified bridging. In the case of aryl-substituted ethylenes such as styrene or stilbene, the presently available evidence suggests that the cationic intermediates can consist of symmetric, unsymmetric, or completely open β-bromocarbocations.[9] It has been suggested[9a] that bromination of appropriately substituted stilbenes can proceed by two independent pathways leading through closed and open ions. Whether there is an equilibrium between these two ions remains a matter of debate.[9b]

What concerns us here is to what extent the magnitude of asymmetry computed for the bromonium ion of an unsymmetrically alkylated alkene (2-methylpropene, **3**) depends upon the quality of the computational method. The anticipated asymmetry[3] of this species has been alluded to as being tied to the factors that control the Markovnikov mode of addition for the addition of Br^+/X^- to an unsymmetrical olefin, although recent work has demonstrated that other effects such as steric and polarization factors are also important.[10] Herein we present the results of several calculations employing methods of varying sophistication which show that the extent of bridging in the bromonium ion of 2-methylpropene **3** is highly dependent upon the computational method.

2. Calculations and Discussion

Galland and co-workers,[3] using the semiempirical method with the MNDO parametrization, found that the bromonium ion of 2-methylpropene **3** exhibits a C_2-C_1-Br angle of 105° characteristic of an essentially open structure; a similar result was obtained with the AM1 parametrization. Unfortunately, this ion was excluded from Reynolds' studies[4] of the isomers of the bromonium ion of 2-butene in which a flexible basis set was used together with the treatment of electron correlation effects.

In preliminary calculations, using the two best methodologies available to us, we obtained a much smaller C_2-C_1-Br angle of only 75−80° for **3** which, in contrast to the results of Galland *et al.*, is only a few degrees larger than the angle in the bromonium ion of the unsubstituted ethylene.[2,6] Given the striking difference in the calculated C_2-C_1-Br angles, we undertook an investigation of the origin of this difference.

In our previous work on the halonium ion transfer between olefins[6a,b] we used the effective core potential approach (ECP)[11] which is similar to the semiempirical schemes in that only the valence electrons are treated explicitly (while the chemically inert core electrons are represented by a potential). The basis set used were of double ζ valence (DZV) quality to ensure sufficient accuracy; furthermore, they were augmented with polarization functions. The polarization functions, which correspond to atomic orbitals with higher azimuthal quantum numbers than the ones occupied in the ground state of an atom (*e.g.*, d-type functions for a carbon atom), are required for a realistic description of the electron density in molecules. Their absence may lead to large errors in the calculated dipole moments and structural parameters. In the majority of cases, unpolarized basis sets are quite capable of predicting reasonable molecular structures; nevertheless, in many instances the lack of polarization functions leads to qualitatively incorrect structures which may be easily recognized when the experimental ones are known. (For example, H_3O^+ is predicted to be planar, rather than pyramidal, without polarization functions.[12]) However, when the experimental structure is unknown, the only way to make certain that the polarization functions are *not* required is to *include them* in the calculations if only to see their negligible impact. (See recent reviews[13−15] for extensive

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discussion of the importance of polarization functions.) The semiempirical methods use minimal basis sets without polarization functions; the required flexibility is assumed to be included in the empirically adjusted parameters of the method. In recognition of these shortcomings, the methods have been recently reparametrized[16] and the basis sets augmented with d-type polarization functions.[17]

Errors in computed (so-called theoretical) structural parameters may result not only from the use of insufficiently flexible basis sets, but also from neglect of electron correlation. In the Hartree–Fock self consistent field (HF SCF) approximation, which is used in both the ECP and semiempirical approaches, the molecular wavefunction is expressed as a single determinant of one-electron molecular orbital functions. This approximation, although very appealing to the practicing chemist, does not properly account for electron correlation effects in the Coulombic repulsion between electrons because each electron is viewed as moving in the average Coulomb field of the other electrons. To go beyond the Hartree–Fock approximation, one must abandon the single determinant form and use of configuration interaction molecular wavefunction which can be expressed as a linear combination of determinants including the Hartree–Fock determinant and determinants derived from it by single and double excitations of electrons to higher orbitals (CISD). The CISD method brings the computed energy differences and molecular structures closer to the experimental values. Since CISD calculations are very costly, it is common to use the second-order Møller–Plesset (MP2) perturbation calculations as a cheaper substitute. In the MP2 method, the perturbation is taken to be the difference between the instantaneous electron repulsion and the averaged one used in the Hartree–Fock method. The post-SCF methods, by exciting electrons from the occupied to empty orbitals, allow for redistribution of electron density so that it more closely resembles that in the observed molecules. The electron correlation corrections are usually small, and their typical effect is the lengthening of bonds; however, as found earlier for the ethylenebromonium ion,[2] if the electron correlation contribution to the bonding is significant, the bond lengths may be shortened.

Sometimes, the single reference MP2 or CISD approach may be inadequate due to the multireference character of the wavefunction. This often happens for molecular geometries far removed from the equilibrium structures. In such cases good results may often be obtained with the density functional theory (DFT).[18,19] Solving the DFT equations gives the electron density of the molecule directly, together with the corresponding total energy.

In the semiempirical methods, the effects of electron correlation are expected to be implicitly included in the empirically adjusted parameters.

As the results depend strongly on the composition of the basis set, we present below a detailed description of the basis sets used in the present work. The smallest, completely unpolarized, basis set (denoted POL0) contained 64 functions and consisted of the DZV contraction of the (4s) basis set of Huzinaga[20] for hydrogen, the DZV contraction of the ECP basis set for all carbon atoms,[11] and the [4s4p] contraction of the ECP basis set for bromine.[11] This basis set was augmented by the addition of d-type polarization functions on the carbon atoms of the ethylene fragment ($\zeta_{d(C)} = 0.80$) and on the bromine atom ($\zeta_{d(Br)} = 0.389$) giving the basis set denoted POL1 with 82 basis functions. The largest basis set, POL2 (with 100 basis functions), was obtained by adding polarization functions on all carbon atoms and on the hydrogen atoms attached to the ethylene fragment ($\zeta_{p(H)} = 1.10$). (All six components of Cartesian d-type Gaussian functions were kept.)

Table 1. Geometry of the Central Fragment[a]

	SCF level				post-SCF level		
basis	C_2–C_1	C_1–Br	C_2–C_1–Br	method	C_2–C_1	C_1–Br	C_2–C_1–Br
AM1	1.46	1.93	108				
MNDO	1.45	1.88	105				
PM3	1.45	1.97	101				
POL0	1.49	2.01	98	MP2	1.48	2.09	80
				CISD	1.50	2.05	90
				DFT-1	1.51	2.09	89
				DFT-2	1.51	2.06	86
POL1	1.48	1.97	92	MP2	1.48	2.01	75
				CISD	1.47	1.99	80
				DFT-1	1.49	2.03	85
				DFT-2	1.49	2.00	82
POL2	1.48	1.97	91	MP2	1.48	2.01	75
				DFT-1	1.49	2.03	85
				DFT-2	1.49	2.01	82
POL1X	1.47	1.97	92	MP2	1.47	2.01	77

[a] Distances in Å, angles in deg. For abbreviations, see text.

All calculations were done using the compact effective potentials of Stevens *et al.*[11] using GAMESS[21] and Gaussian92[22] programs. The calculations were done without imposing any restrictions on the symmetry on the ion, using three semiempirical parametrizations (AM1, MNDO, and PM3) and three *ab initio* methods (ECP SCF, ECP MP2, and ECP CISD). For all methods except CISD, we ascertained that a genuine local minimum, rather than a transition state, was located. (To this end, we evaluated the energy Hessian and performed the harmonic vibrational analysis followed by tracing the intrinsic reaction coordinate path for the cases when one negative eigenvalue of the Hessian (for MNDO and AM1) indicated that a transition state (corresponding to the rotation of one methyl group) was initially located.)

The optimized structural parameters are given in Table 1. The largest values of the CCBr bond angle were obtained with the AM1 and MNDO methods. The PM3 value, 101°, is closest to the angle of 98° obtained with a completely unpolarized basis set in SCF calculations. This is close to the value of 96° obtained for the chlorine analogue by Yamabe *et al.*[1] who used an unpolarized 3-21G basis. Addition of a single set of polarization functions on the CCBr fragment (POL1) reduces the angle to 92°; further extension of the polarization space

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Table 2. SCF Atomic Charges at Optimized Geometries[a]

	basis POL0			basis POL1			basis POL2		
method	Br	C_1	C_2	Br	C_1	C_2	Br	C_1	C_2
MPA	0.17	−0.32	−0.11	−0.02	−0.01	−0.25	−0.03	0.13	−0.26
NPA	0.13	−0.44	0.55	0.15	−0.38	0.53	0.16	−0.38	0.50
MKA	0.07	−0.39	0.67	0.11	−0.26	0.57	0.11	−0.26	0.54

[a] Key: MPA, Mulliken population analysis; NPA, natural population analysis; MKA, Merz−Singh−Kollman scheme of fitting charges to electrostatic potential.

Table 3. Atomic Charges at Optimized Geometries[a]

	basis POL0			basis POL1		
method	Br	C_1	C_2	Br	C_1	C_2
SCF	0.17	−0.32	−0.11	−0.02	−0.01	−0.25
MP2	0.29	−0.22	−0.29	0.11	0.04	−0.27
CISD	0.21	−0.26	−0.18	0.05	−0.06	−0.27

[a] Mulliken population analysis.

by adding functions on all carbons and the ethylene hydrogens (POL2) results in a modest reduction of the angle to about 91°. Using a double set of polarization functions[23] on the atoms of the CCBr fragment (this basis is denoted as POL1X in Table 1) gives an SCF geometry close to that obtained with POL1.

The electron correlation effects at the MP2 level lead to a dramatic reduction of the CCBr bond angle by about 18°, while at the CISD level the reduction is about 8−11°, depending on the basis set. At the CISD level, the angle is only about 10° larger than the CISD value obtained by Hamilton and Schaefer[2] in all-electron calculations on the bromonium ion of ethylene with a comparable basis set.

Two types of functionals were used in the DFT calculations: DFT-1 and DFT-2. In the former, the Becke exchange functional with gradient correction[24] was used together with the gradient-corrected correlation functional of Lee, Yang, and Parr.[25] In the DFT-2 functional, the gradient-corrected exchange functional of Perdew was employed.[26] Results in Table 1 show that the two DFT methods predict very similar structures of the bromonium ion. The DFT C_2-C_1-Br angle is larger than the MP2 values and is close to the CISD values, regardless of the basis set.

Results of the harmonic vibrational analysis show that the ion is very flexible: the computed harmonic vibrational frequency for the motion corresponding to the C_2-C_1-Br bending mode (which may be viewed as the C_2-Br bond stretch) is only 206 cm^{-1} in the MP2 approach, 132 and 146 cm^{-1} in DFT-1 and DFT-2 calculations, respectively. To investigate this bending motion in more detail, we performed complete optimization of all structural parameters except for the angle $\phi = \angle C_2-C_1-Br$. The values of the angle ϕ were selected in the range 60−140°. Expecting that the wavefunction may have multiconfigurational character, we used only the DFT methods in addition to the SCF methodology. We used only the largest basis set, POL2, in these calculations.

When the geometry optimization is performed without any symmetry constraints (i.e., C_1 point group), the methylene group rotates around the C_2-Br axis is about $\phi = 120°$ which leads to the planar conformation of the β-bromo carbocation, with all heavy atoms in one plane. (The motion of the methylene groups may be alternatively viewed as the rotation of the methyl groups along the C_1-C_2 bond.) Because the phenomenon occurred at relatively low energy (about 6−8 kcal/mol), we calculated the structure and the cut through the potential energy hypersurface along the ϕ angle for the rotated species. To study each of the two surfaces separately, we restricted the point symmetry to C_s, which prevented the rotation of the methylene group. The relative energies of the two species, calculated with respect to the minimal total energy of the normal structure as calculated with each method, are shown on Figure 2.

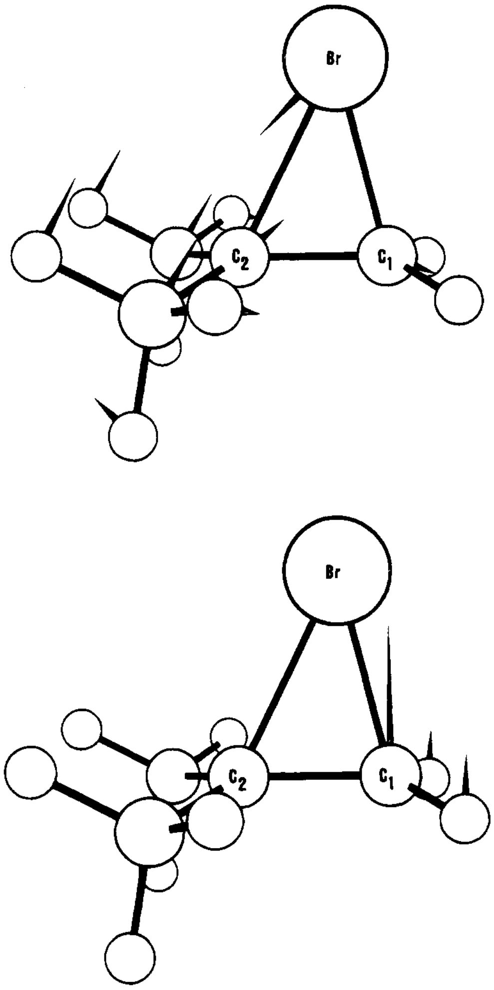

Figure 1. Atomic displacements in the MP2-calculated bends C_2-C_1-Br (top) and C_1-C_2-Br (bottom).

The results show that the potential energy surface is very flat along the bending mode C_2-C_1-Br: large-amplitude bending results in only moderate change in the potential energy. For example, variation of ϕ by ±10−15° leads to energy increase of only 2 kcal/mol. What is more interesting, however, is that the angle may

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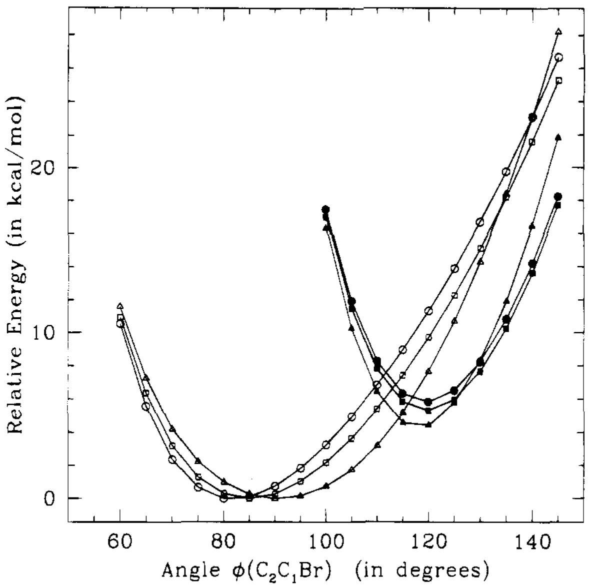

Figure 2. Energy changes during the opening of the CCBr angle: Δ = RHF, □ = DFT-1, ○ = DFT-2; open symbols refer to the normal conformation of **2**, solid symbols to the planar conformation of β-bromocarbocation.

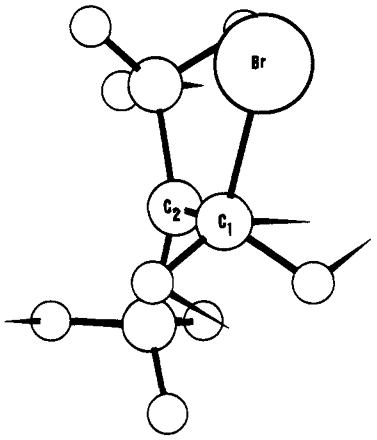

Figure 3. Atomic displacements in the lowest-frequency mode calculated in the DFT-1 method.

increase by 30–40° from its equilibrium value and yet the potential energy increases by only 4–6 kcal/mol. At this point, the cuts of the potential energy surfaces for the two species intersect. As a consequence, the methyl substituents may exhibit rotational motion along the C_2–C_1 bond. Comparison with the energy gap of 22–29 kcal/mol calculated by Hamilton and Schaefer[2] for the ethylenebromonium ion and 2-bromoethyl cation shows that, as expected, the substitution of the α hydrogens by methyl groups significantly increases the stability of the planar β-bromocarbocation relative to the closed bromonium ion.

The harmonic vibrational analysis performed at the fully optimized structure of the planar β-bromo carbocation shows that the ion appears to be a true local minimum on the energy hypersurface. However, the lowest vibrational frequency is very small, only 13, 36, and 45 cm^{-1} in the SCF, DFT-1, and DFT-2 calculations, respectively. The nuclear motion in that mode, shown in Figure 3, will clearly lead back to the normal conformation of **2** via essentially a swinging motion of the methylene group around the C_2–Br bond. It is not unlikely that a change in the computational parameters (basis set, electron correlation scheme, geometry optimization thresholds, etc.) may in fact show that the structure is a transition state in analogy with the finding of Hamilton and Schaefer for 2-bromoethyl cation.[2]

The charge distribution was studied using three different schemes of population analysis: the Mulliken scheme, the natural population analysis (NPA) of Weinhold,[27] and the electrostatic-potential based method of Kollman (MKA).[28] Only the SCF densities, obtained with the various basis sets, were analyzed. The results show the typical strong dependence of the Mulliken population analysis on the basis set. (Somewhat better stability is shown by the charges obtained by adding the hydrogen charges to the heavy atom: in this case, the carbon C_1 carries the charge of 0.13, 0.41, and 0.44 for the basis sets POL0, POL1, and POL2, respectively.) Both NPA and MKA charges are quite stable with change in the basis set and consistent with each other. These two methods assign large positive charge to the carbon C_2, negative charge to the carbon C_1, and predict that the bromine atom is essentially neutral.

3. Conclusions and Observations

The demonstration that the computed geometry of the asymmetric bromonium ion of **3** is markedly dependent upon the method employed, the inclusion of the electron correlation, and of polarization functions, renders suspect all conclusions about geometry and reactivity made on the basis of calculations using semiempirical methods with old parametrization.[3,10] The computed structure of the ion becomes more symmetric (more bridged) as the quality of the computational method improves. Such a structure fits nicely with the observed kinetic substituent effects for bromination of methylated ethylenes which imply a fairly symmetrical charge distribution in the 1,1-disubstituted transition states.[29] The present conclusions concur with the earlier findings of Lischka and Köhler,[31] Zurawski,[30] and Raghavachari *et al.*[32] who recognized the fundamental role played by the electron correlation in determining the relative stability of the classical *vs* nonclassical structures of carbocations.

The computed harmonic vibrational frequency for the motion corresponding to the C_2–C_1–Br bending mode (which may be viewed as the C_2–Br bond stretch) is only 132, 146, and 206 cm^{-1} in the DFT-1, DFT-2, and MP2 calculations, respectively. The corresponding value for the C_1–C_2–Br bend (C_1–Br stretch) is 515, 539, and 539 cm^{-1} in the DFT-1, DFT-2, and MP2 calculations, respectively (Figure 1). These values may have some significance in interpreting the nature of the factors

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responsible for the Markovnikov addition: the potential energy surface along the C_2-C_1-Br mode is very flat and may be easily disturbed by the incoming nucleophile.[33]

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