Aspects of Electrophilic Bromination of Alkenes in Solution. Theoretical Calculation of Atomic Charges in Bromonium Ions

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Abstract: The first results of a theoretical study of bromination reactions in solution are presented, with an illustration of the parameters used to describe the solvation effects in the framework of the polarizable continuum model (PCM). The distribution of the positive charge on the atoms of some bromonium ions is calculated, using Bader's procedure on the wave functions obtained in vacuo, in dichloroethane, and in methanol. These results provide new insights about the nature of bromonium ions and the reversibility of their formation reactions.

Introduction

The electrophilic addition of Br_2 to alkenes is certainly one of the best known organic reactions,[1,2] and its mechanism has been extensively studied. The generally accepted reaction scheme consists of several steps.[3]

Despite the great amount of work devoted to this reaction, some aspects have not yet been fully explained: in recent years, the interest of many researchers has concentrated on the first stages of this reaction, leading to the bromine/alkene complex[4,5] and to the bromonium ion.[3,6,7] Some questions about these topics are still open: for example, kinetic data are known only for a few cases of complex formation.[4,8] Another question is related to the nature of the bromonium ions,[9] that can be described as π-complexes or as σ-complexes:[10,11] also the reversibility of the reaction of bromonium ion formation is discussed, and some authors indicate this step as irreversible.[9]

Theoretical calculations can provide useful information about (i) the energetics of formation of bromine/alkene complexes and bromonium ions, and the corresponding reaction profiles, thus clarifying also the kinetics of such processes and (ii) the electronic structure of bromonium ions, and the distribution of positive charge on their atoms.

Clearly such information will be much more interesting if they will be able to describe also the effect of the chemical environment (substituents on the alkene, counterions, solvent, etc.).

This paper presents the first results of a theoretical study about the bromination of alkenes in solution. In the first part we explain the method of calculation that we have chosen for this and the

Scheme 1
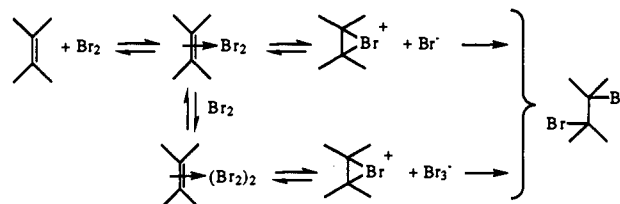
following works on this topic: in particular we present the parameters of the solvation model.

Then the calculated atomic charges in some bromonium ions are reported: both the study of the π- or σ-character of the bromonium ion and the question of the reversibility of its formation, would benefit of the knowledge of the distribution of the ionic charge on the constituent atoms, according to the chemical environment.

Since now, however, there have been only a few attempts to analyze the charge distribution on bromonium ions. Apart from the estimates based on Mulliken's population analysis,[12] whose limits have been underlined by many authors,[13] we know only a work of Cioslowski et al.,[14] based on GAPT (generalized atomic polar tensor) population analysis.[15] This latter paper reports the atomic charges in ethylenebromonium ion and various other organic molecules, calculated from the SCF wave function in vacuo.

The GAPT analysis finds that in ethylenebromonium ion the positive charge is concentrated on carbon atoms, while the bridge bromine atom is almost neutral. Hamilton and Schaefer[10] base also on these results their conclusion that the ethylenebromonium ion can be described as a strong π-complex rather than a σ-complex. Moreover, the lack of positive charge on the bromine atom would support the idea that the formation of bromonium ions is irreversible, except for a few cases of particularly hindered alkenes.[9]

We have evaluated the atomic charges by means of Bader's method,[16] based on the electronic density gradient: this procedure

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I
ethylenebromonium   ion

II
ethylenebromonium   bromide
(completely   optimized)

III
cis   ethylenebromonium   bromide

IV
trans   ethylenebromonium   bromide

V
ethylenebromonium   dibromide

VI
ethylenebromonium   tribromide
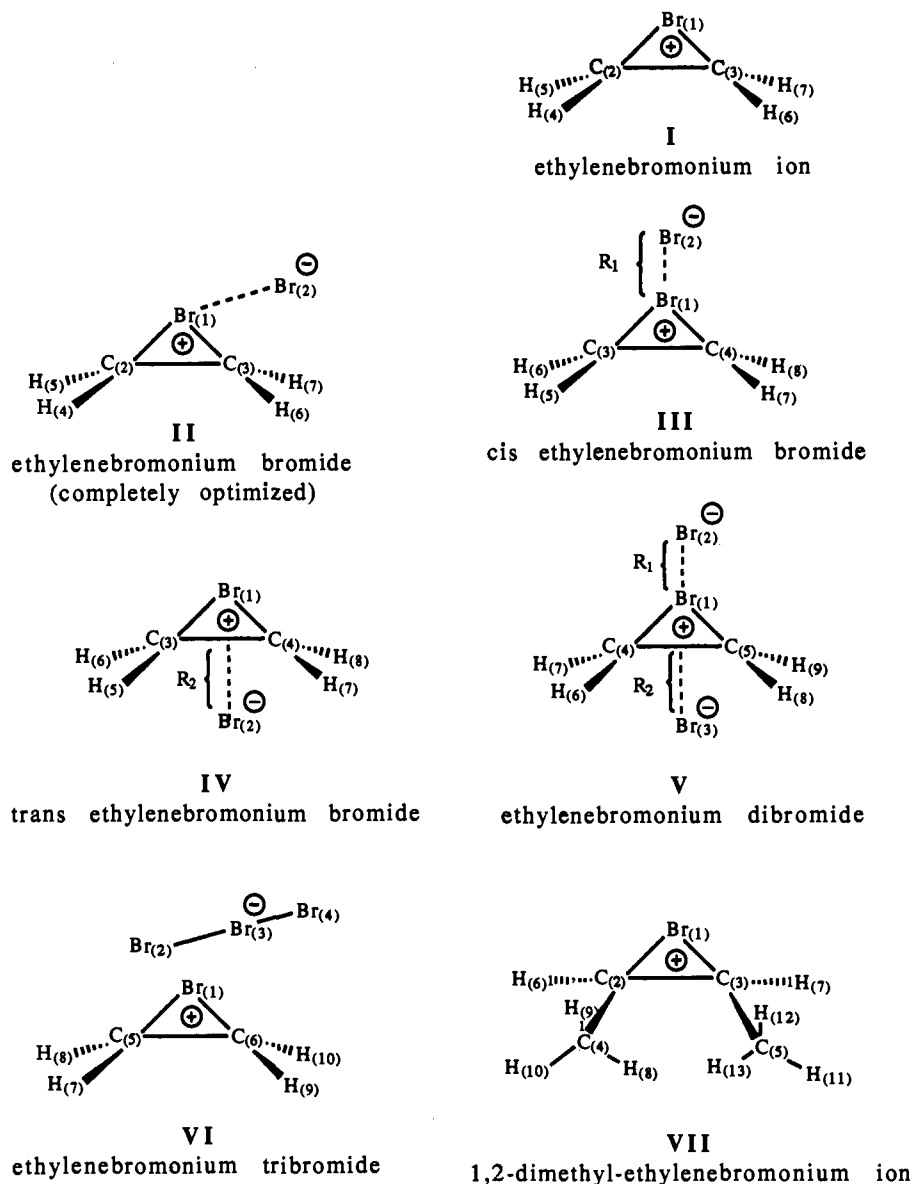

VII
1,2-dimethyl-ethylenebromonium   ion

Figure 1. Structures of the studied chemical systems.

is the most reliable, but until now it had not been applied, because of its computational burden.[14]

Unlike the calculation cited above, our results show that in bromonium ions the bridge bromine atom carries a significant amount of the positive charge, depending on the position of counterions, on the solvent, and on the substituents: these results make more plausible the reversibility of bromonium ions formation.

Studied Systems

We have considered the chemical systems shown in Figure 1. Structure **II** corresponds to a local minimum in the potential energy of the system bromonium ion + bromide ion, though it is higher in energy than the bromine–ethylene complex, as reported in the following section. Structures **III–VI** are not stationary points of the potential energy, as their geometries are based on constrained optimizations: they have been chosen as simple examples to study the influence of approaching counterions on the charge distribution of bromonium ions.

The calculations involving each system have been repeated in vacuo, in 1,2-dichloroethane (DCE) and in methanol,[17] these solvents being representative of low polarity nonprotic and polar protic media, respectively.

Theoretical Methods

The energy and the properties of each molecule have been calculated at the SCF level using the HONDO7 package, distributed by QCPE,[18] adapted by our group to allow calculations in solution with the polarisable continuum model (PCM)[19] procedure. To limit computational efforts, mainly in the atomic charge calculations, and to include gross relativistic effects, we have used effective core potentials (ECP) on the bromine and carbon atoms. The adopted basis set is Br, ECP + 2s2p1d (14 functions);[20] C, ECP + 2s2p1d (14 functions);[21] and H, 2s (2 functions).[21]

In some cases, we have computed the atomic charges also from *all electron* wave functions, using the same basis set as Hamilton and Schaefer:[10] (8s6p3d)[22] for Br, (4s4p1d)[23] for C, and (2s)[23] for H. The

(17) The macroscopic properties used in the PCM solvent model (see below) are as follows: (i) for DCE dielectric constant (ϵ) = 10.36, density = 1.2458 g cm^{-3}, molar volume ($\bar{V}$) = 79.4 cm^3 mol^{-1}, molecular diameter (σ) = 5.01 Å; (ii) for CH$_3$OH ϵ = 32.7, density = 0.7866 g cm^{-3}; $\bar{V}$ = 40.7 cm^3 mol^{-1}; σ = 3.71 Å: as reported by Marcus Y. *Ion Solvation*; Wiley: 1985; pp 133–134.

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Table 1. Optimized Geometry for Ethylenebromonium Ion in Vacuo

	R_{Br-C} (Å)	R_{C-C} (Å)	R_{C-H} (Å)	HCH (deg)	$\theta_{out\ of\ plane}$ (H) (deg)
SCF (this work)	2.0627	1.4362	1.074	119.6	16.1
CI (ref 10)	2.025	1.455	1.084	117.8	17.4
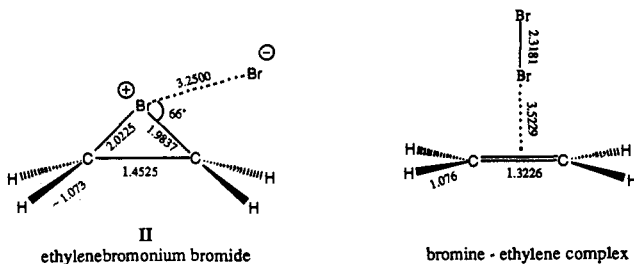
Figure 2. Optimized structures of ethylenebromonium bromide and of bromine–ethylene complex (all distances in Å); in some cases only the relevant parameters are given (see the text).

Table 2. Optimized Distances of Bromide Ion from Ethylenebromonium Ion in Structures III and IV

	vacuum	DCE	CH_3OH
R_1 (Å)	2.77	3.07	3.27
R_2 (Å)	2.70	2.82	3.01

Table 3. Optimized Geometrical Parameters for Ethylenebromonium Tribromide in Vacuo (Structure VI)

	$R_{Br(1)-Br(2)}$ (Å)	$R_{Br(1)-Br(3)}$ (Å)	$R_{Br(2)-Br(3)}$ (Å)	$R_{Br(3)-Br(4)}$ (Å)	Br(2)Br(3)-Br(4) (deg)
this work	2.834	4.414	3.231	2.34	2.87
a	3.097	3.562	2.718	2.412	2.64

a X-ray analysis of adamantylidenadamantane bromonium tribromide (ref 6).

Table 4. Optimized Bond Lengths for the 1,2-Dimethylethylenebromonium Ion in Vacuo (Structure VIII)

R_{Br-C} (Å)	$R_{C(2)-C(3)}$ (Å)	$R_{C(2)-C(4)}$ (Å)	$R_{C(1)-H(6)}$ (Å)	$R_{C(4)-H(8)}$ (Å)
2.115	1.4471	1.4998	1.076	1.08

results, reported in the following sections, are similar to the ECP ones.

The geometry of the ethylenebromonium ion (I) has been optimized at the SCF level in vacuo, with the results listed in Table 1. The partial pyramidalization of ethylene projects the π electrons toward the Br atom, thus lowering the total energy by electrostatic and charge-transfer effects.

The geometry of ethylenebromonium bromide (II), optimized at the SCF level in vacuo, is presented in Figure 2, compared with the optimized structure of the bromine–ethylene complex: In the next step, holding the geometry of the cation fixed, we have optimized in vacuo and in solution the position of the counterion Br⁻ in the molecules III and IV obtaining the distances R listed in Table 2. Notice that, starting the optimization with the bromide ion close to the C_{2v} axis of the ethylenebromonium ion, one finds the minimum on this axis: remember, however, that it is not a real minimum of the potential energy, as we hold the cation fixed. In the dibromide (V) the positions of the two Br⁻ have been taken equal to those of the bromide ions in III and in IV.

In Table 3 we report the geometry of the tribromide ion in the molecule VI, optimized in vacuo with the bromonium fixed and used as such in solution. The slight deviation from linearity of Br₃⁻ agrees with the results of the X-ray analysis of the only alkylbromonium tribromide isolated as a crystal (adamantylidenadamantane bromonium tribromide),[6] while the bond length are more distorted in our case (for the isolated tribromide ion we found a Br–Br distance of 2.61 Å).

Finally, the geometry of molecule VII has been optimized in vacuo and used unchanged in solution: this latter geometry is listed in Table 4.

Parameters of the Solvent Model

The calculations in solution have been carried out in the framework of the polarizable continuum model (see ref 19 for the details of the method).

This model represents the solvent as a continuous medium, characterized by its dielectric constant, density, molar volume, and other macroscopic properties and allows the direct calculation of the SCF energy of the solute molecule, and of the electrostatic solute–solvent interaction. The PCM uses apparent surface polarization charges to solve the electrostatic problem of solute–solvent interactions: thus, it does not need solutes of simple shape but is efficient with molecules of arbitrary shape.

The dispersion and repulsion terms of the solute–solvent interaction have been calculated with the method proposed in ref 24, using Caillet's atomic parameters.[25] The cavitation energies[26] have been obtained according to Pierotti's formula,[27a] based on the description of the solvent as a collection of hard spheres.[27b]

The SCF wave functions obtained from PCM can be analyzed with Bader's procedure, in the same way as those obtained in vacuo.

In the PCM procedure the solute molecule is placed in a cavity obtained from an assembly of interlocking spheres, centered on the atoms of the solute: the radii of such spheres are critical parameters, which influence the calculated energies and properties in solution. To choose suitable radii for our systems, we have resorted to a procedure similar to that recently developed by Aguilar and Olivares del Valle,[28] assuming a linear dependence between the actual electronic charge on the solute atoms and the corresponding radii. We mark, however, two differences with ref 28: (i) we compute the atomic charges by means of Bader's approach, instead of Mulliken's population analysis and (ii) we employ a different criterium for the dependence of the radii on the charges, taking also into account the nature of the solvent.

For the bromine atoms in the various molecular systems listed above, a linear relation between the atomic charge in vacuo and the van der Waals radius has been assumed: as the van der Waals radius of Br⁰ is 1.85 Å, and that of Br⁻ is 1.96 Å:[29]

$$r^{vdW}(Br^q) = -0.11q + 1.85\ Å \qquad (1)$$

where q is the net charge on the bromine atom, obtained from the wave function in vacuo. The net charges on the carbon and hydrogen atoms in our systems do not exceed 0.17 au in any case (see Tables 11 and 12); therefore, the size of the spheres around carbon and hydrogen depends directly on the van der Waals radius:

$$r^{vdW}(C) = 1.7\ Å, \qquad r^{vdW}(H) = 1.2\ Å$$

It seems worth to adopt two different definitions of the sphere radii for the calculation of the various contributions to the solution energy.

The cavitation energy, and also the dispersion–repulsion term in the approach of ref 24, directly depends on the physical dimensions of the solute molecule. The van der Waals radii, corrected for the actual atomic charge in the case of bromine, seem suitable for the calculation of this kind of contributions: thus we have obtained the cavitation, dispersion, and repulsion terms using the van der Waals radius of each atom as the radius of the corresponding sphere.

On the other hand, the solute–solvent electrostatic interaction presents more complex aspects: for example, the first solvation

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Table 5. Best Values for κ_{solv} in Several Solvents

	dielectric constant[a]	κ_{solv}	ab initio $\Delta G_{reaction}$ (kcal/mol)	exptl $\Delta G_{reaction}$ (kcal/mol)
water	78.4	1.20	−1.421	~ −1.5[b]
methanol	32.7	1.21	−2.661	~ −2.8[b]
ethanol	24.6	1.22	−3.340	~ −3.5[b]
chloroform	4.9	1.25	−7.29	~ −7.0[c]
dichloroethane	10.4	1.40	−10.422	< −10.0[c]
dichloromethane	8.9	1.40	−10.303	< −10.0[c]

[a] Marcus, Y. *Ion Solvation*; Wiley: 1985. [b] Reference 31b. [c] Reference 31c.

shell, strongly polarized, and the bulk of the solvent should not be treated in the same way. The PCM actually mediates this and other effects, using for the whole continuum the static dielectric constant and representing the solvation with one polarization charge density: it has already been recognized[30] that in calculating the electrostatic terms the van der Waals radii have to be modified to get the sphere radii. On the other hand, the solvation energies, even for ionic solutes, do not depend too steeply on sphere radii [Following one referee's suggestion, we show the dependence of energies on sphere radii with this example: the calculated free energy change of solvation for ethylenebromonium ion (structure I) in methanol is −57.4 kcal/mol with the radii determined as described in the text (Br = 2.18 Å, C = 2.04 Å, H = 1.44 Å for the electrostatic term; Br = 1.82 Å, C = 1.7 Å, H = 1.2 Å for the cavitation and dispersion terms). Increasing the radius of each atom by 5%, we find ΔG(solvation) = −54.7 kcal/mol.]: we can expect that the reaction energies in solution, containing *differences* in solvation energies, will be even less dependent on cavity dimensions.

In our case the radius ρ_i of the sphere around the ith atom of the solute has been defined

$$\rho_i = \kappa_{solv}\, r_i^{vdW} \qquad (2)$$

where κ_{solv} depends on solvent.

The values of κ_{solv} have been determined by computing the $\Delta\bar{G}$ of the reaction

$$Br_{2(sol)} + Br^-_{(sol)} \rightleftharpoons Br^-_{3(sol)} \qquad (3)$$
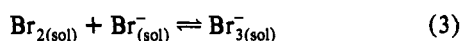
$$\Delta\bar{G}_{(reaction)} = \Delta\bar{G}_{(internal)} + \Delta\bar{G}_{(trasl-rot.-vib)} + \Delta\bar{G}_{(solute-solvent)}$$

in several solvents: this reaction plays an important role in bromination processes, and it has been studied in many solvents.[31]

For each solvent, the PCM yields the values, depending on κ_{solv}, of $\Delta\bar{G}_{(internal)}$ (SCF electronic energy of products minus SCF energy of reagents in solution) and of the $\Delta\bar{G}_{(solute-solvent)}$ (electrostatic, dispersion–repulsion, and cavitation terms); the translational, rotational, and vibrational contributions to $\Delta\bar{G}_{reaction}$ have been also included.[32]

In Table 5 we report the values of κ_{solv}, yielding the best agreement with the experimental data and the corresponding values of $\Delta\bar{G}_{reaction}$. The same values of κ_{solv} have been used in all the following calculations to relate the dimensions of the solvation spheres to the van der Waals radii of the corresponding atoms.

One can see that protic solvents must have smaller values of κ_{solv}: the reason is that, even with the same ϵ, a protic solvent is more effective in solvating an anion, due to the hydrogen bonds: the consequences of this fact on reaction 3 have been underlined

Table 6. Calculated Atomic Charges (au) in Ethylenebromonium Ion

		Br	C	H	total
vacuum	ECP	+0.174	+0.099	+0.162	+1.000
	AE	+0.152	+0.013	+0.206	+1.002
DCE	ECP	+0.140	+0.093	+0.1685	+1.000
	AE	+0.120	+0.021	+0.210	+1.002
CH$_3$OH	ECP	+0.125	+0.096	+0.171	+1.000
	AE	+0.107	+0.019	+0.212	+0.994

Table 7. Electrostatic Potential Due to Ethylenebromonium Ion in Vacuo at the R_1 and R_2 Reported in Table 2

	elec. pot. at R_1	elec. pot. at R_2
ECP basis	0.140 749	0.164 705
AE basis	0.139 078	0.167 93

by Parker.[33] The PCM reproduces this effect putting the polarization charges closer to the solute.

Charge Distribution in Bromonium Ions

In the present work we have resorted to Bader's definition of atomic charges, using the SCF wave functions calculated in vacuo and in solution. We have tested both existing versions of Bader's procedure:[34a] the first (program PROAIMV) defines the atomic regions, where the electronic density has to be integrated, by means of their limiting "zero-flux surfaces"; the other one (program PROMEGA[34b]) uses only local conditions to attribute the electronic charge to the various atoms.

The PROMEGA procedure, though computationally more demanding, has given better results for our molecules. Apparently the program PROAIMV is less accurate when applied to cyclic molecules described with ECPs: the reason may be the spurious maxima in the electronic distribution that appear in this case far from the nuclei. PROMEGA, on the other hand, has proved very reliable, allowing the calculation of the atomic charges in the examined systems, with very interesting results.

In Table 6 the net charges calculated on the atoms of ethylenebromonium ion are shown: the results are obtained both from ECP and from *all electron* (AE) wave functions. With respect to the ECP calculation, the AE positive charge on the bridge bromine is lowered by about 15%, while the carbons become almost neutral: the charge on the hydrogens, on the other hand, is increased.

Such differences, however, are only partially due to actual changes in the electronic distribution. This can be seen, for example, from the dipole moment of the ion, calculated in vacuo: with the ECP basis the absolute value of the dipole moment referred to the center of mass of the molecule is 1.954 au, while with the AE basis it is 2.006 au. From the data reported in Table 6, one could expect a larger variation (about 0.1 au).

Another reference quantity is the electrostatic potential around the ion, that is an approximated measure of the attraction exerted by the ion itself on the nucleophiles. In Table 7 we report the values of electrostatic potential, calculated with the two basis sets in the positions occupied by the counterions in the molecules **III** and **IV**: in this case too the AE and ECP results differ negligibly.

In fact, the calculated atomic charges depend also on the definition of "atoms"; in Bader's approach the spatial limits of an atom are related to the gradient of the electronic density: a measure of such spatial extension is the distance from the nucleus of the nearest saddle point of the electronic density.[34a] Such distances, referred to the atoms of the molecule **I**, are listed in Table 8: with the AE wave function the bromine atom results a

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(32) The following quantities have been used in calculating the canonical partition functions: mass of Br = 80 g mol⁻¹, interatomic distances = 4.372 au for Br$_2$ and 4.938 au for Br$_3$⁻, vibrational frequencies (from HONDO7 calculation) = 341 cm⁻¹ for Br$_2$ and 98, 133, and 169 cm⁻¹ for Br$_3$⁻.

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Table 8. Ethylenebromonium Ion: Distances of the Nuclei from the Nearest Saddle Point in the Electronic Density

	vacuum (Å)		DCE (Å)		CH₃OH (Å)	
	ECP	AE	ECP	AE	ECP	AE
Br	1.149	1.152	1.153	1.154	1.154	1.155
C	0.708	0.719	0.709	0.723	0.710	0.724
H	0.366	0.341	0.365	0.343	0.363	0.344

bit larger, and the carbons markedly larger, while the hydrogens appear smaller. These variations may depend on the different quality of the valence parts of the two basis sets (in fact, the valence p functions on C in the AE set are more expanded).

The above considerations convince us that the ECP basis set describes adequately the electronic structure of the molecules under study and that the atomic charges are well approximated with the adopted method: all the following results have been obtained with the ECP basis.

Tables 9–12 show the net charges (in au) calculated on the bridge bromine, on the counterion, when present, on the carbons and on the hydrogens in molecules I–VII.

One can see that our results differ considerably from those obtained with the GAPT method: in the ethylenebromonium ion in vacuo the bromine atom bears a positive charge of 0.174 au, while the carbon atoms share a minor part of the total molecular charge.

It is of interest the analysis of the influence of the chemical environment on the charge distribution. In the presence of a counterion on the cis side (molecules II, III, and VI) the bridge bromine gains a much greater positive charge. One can expect

two opposite effects due to the bromide ion: it polarizes the bromonium ion, thus increasing the positive charge of bridge Br, but at the same time it loses a not negligible fraction of its negative charge (Table 10), thus lowering the total charge of the bromonium ion. The data listed in Table 9 show that the former effect prevails and confirm that there exists a significant electrostatic attraction between the *cis*-bromide ion and the bridge bromine.

On the other hand, the Br⁻ in trans position (**IV**) moves more charge to the carbon atoms, while system **V** stays in an intermediate situation. It is worth noting the effect of the two methyl substituents, that are able to attract most of the charge, leaving the bridge bromine almost neutral.

When the solvent is present, it has the general effect of moving the positive charge from the bromine atom to the ethylenic skeleton: this effect is greater in more polar solvents. In the presence of counterions, the solvent tends to polarize the ionic couple, and also this effect is enhanced in more polar liquids: thus in molecules **II–VI** a greater amount of positive charge is found on the cation in methanol than in DCE. Notice that the position of counterions in molecules **II–VI** has been optimized also in solution: we argue that other geometrical changes would have a minor effect on the charge distribution.

Discussion

Our results show that the bridge Br atom in the bromonium ions **I** and **VII** shares a positive charge about equal or larger than the olefinic carbons, in vacuo as well as in polar solvents. This indicates that the basic character of π-complex of the bromonium

**Table 9.** Calculated Charges (au) on the Bridge Bromine Atom

	ethylene-bromonium ion	equilibrium ethylenebrom. bromide	*cis*-ethylene-bromonium bromide	*trans*-ethylene-bromonium bromide	ethylene-bromonium dibromide	ethylene-bromonium tribromide	dimethyl-ethylenebromonium
vacuum	+0.174	+0.249	+0.309	–0.119	+0.107	+0.306	+0.065
DCE	+0.140	+0.197	+0.223	–0.041	+0.066	+0.240	+0.031
CH₃OH	+0.125	+0.179	+0.165	+0.020	+0.069	+0.202	+0.037

Table 10. Calculated Charges (au) on the Counterions

	bromide ion in structure II	*cis*-bromide ion in structure III	*trans*-bromide ion in structure IV	*cis*-bromide ion in structure V	*trans*-bromide ion in structure V	tribromide ion in structure VI
vacuum	–0.915	–0.703	–0.774	–0.841	–0.881	–0.760
DCE	–0.953	–0.884	–0.865	–0.922	–0.901	–0.845
CH₃OH	–0.963	–0.941	–0.927	–0.953	–0.938	–0.874

Table 11. Calculated Charges (au) on the Carbon Atoms
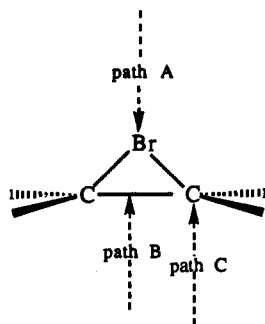
	ethylene-bromonium ion	equilibrium ethylenebrom. bromide[a]	*cis*-ethylene-bromonium bromide	*trans*-ethylene-bromonium bromide	ethylene-bromonium dibromide	ethylene-bromonium tribromide	dimethyl-ethylenebromonium[b]
vacuum	+0.089	+0.156 +0.040	+0.0205	+0.159	+0.125	+0.030	+0.0115
DCE	+0.093	+0.105 +0.087	+0.059	+0.147	+0.128	+0.0465	+0.0175
CH₃OH	+0.0955	+0.099 +0.102	+0.0775	+0.1315	+0.1185	+0.0565	+0.015

[a] Carbon (3) and carbon (4) in structure II, respectively. [b] Only the carbons directly bound to Br.

Table 12. Calculated Charges (au) on the Hydrogen Atoms

	ethylene-bromonium ion	equilibrium ethylenebrom. bromide[a]	*cis*-ethylene-bromonium bromide	*trans*-ethylene-bromonium bromide	ethylene-bromonium dibromide	ethylene-bromonium tribromide	dimethyl-ethylenebromonium[b]
vacuum	+0.162	+0.167 +0.067	+0.088	+0.144	+0.092	+0.099	+0.126
DCE	+0.1685	+0.156 +0.126	+0.136	+0.153	+0.126	+0.128	+0.1485
CH₃OH	+0.171	+0.153 +0.138	+0.155	+0.161	+0.147	+0.140	+0.141

[a] Hydrogens (5), (6) and hydrogens (7), (8) in structure II, respectively. [b] Only the hydrogens (6) and (7) of structure VI.

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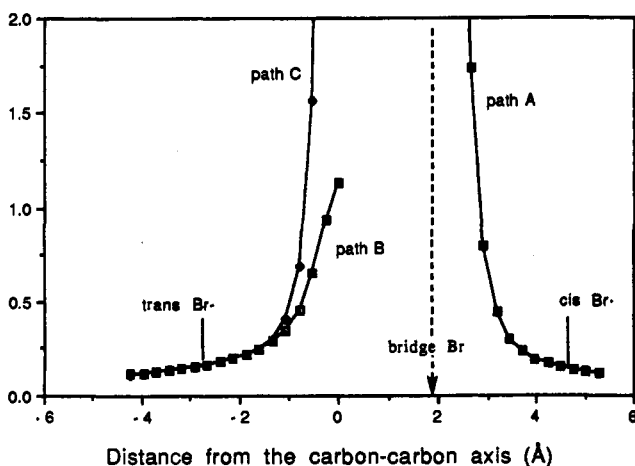
Figure 3. Ethylenebromonium ion in vacuo: electrostatic potential (au). The positions occupied by the bridge bromine atom and by the trans and cis counterions are shown.

ion does not imply a complete electron transfer from ethylene to Br^+ and that a partial character of σ-complex is present. This view is confirmed by the inspection of the SCF wave functions: for example, Mulliken population analysis of ethylenebromonium ion in vacuo shows that the p_x orbital of bromine (same symmetry of the π^* orbital of ethylene, responsible for the σ-like bond[10]) and the p_z and s orbitals of bromine (symmetry of the π orbital of ethylene, responsible for the π-like bond) have almost the same weight in the bromine–alkene bond.

The charge distribution we have found shows that a nucleophilic attack of Br^- or Br_3^- to the bridge Br should not be excluded a priori. In the structures III and VI, although the counterion transfers negative charge to the bromonium ion, the bridge Br increases its positive charge, as an effect of electrostatic polarization. In this way, the pair $Br_{(1)}$–$Br_{(2)}$ approaches the electroneutrality, that is the condition of a leaving Br_2 molecule.

In addition to the atomic charges, one can resort to the electrostatic potential to compare the attraction exerted by the ion on the nucleophiles in the trans and cis positions. The values in Table 7 show that the electrostatic potential due to the ion in vacuo is a bit larger in the trans equilibrium position than in the cis one: the repulsion of the core electrons of the bridge bromine prevents Br^- from coming closer to the ion.

In Figure 3 the electrostatic potential along three approaching directions to the ion is shown: one can see that the electrostatic attraction on the line pointing to the bridge bromine is comparable with that on the path toward the carbon atoms.

Table 13. Calculated Free Energies of Reaction (kcal/mol)

	vacuum	DCE	CH_3OH
$C_2H_6 + Br_2 = C_2H_4 \rightarrow Br_2$ (complex)	−1.4	−9.1	−3.8
$C_2H_6 + Br_2 = C_2H_4Br^+(I) + Br^-$	+142.9	+37.1	+15.7
$C_2H_6 + Br_2 = C_2H_4Br^{\cdot+}Br^-$ (II)	+54.7	+28.4	+20.7
$C_2H_6 + Br_2 = cis\ C_2H_4Br^{\cdot+}Br^-$ (III)	+43.4	+21.5	+12.7
$C_2H_6 + Br_2 = trans\ C_2H_4Br^{\cdot+}Br^-$ (IV)	+31.4	+15.9	+9.8
$C_2H_6 + Br_2 + Br^- = C_2H_4Br^{\cdot+}2Br^-$ (V)	+14.8	+12.0	+9.4
$C_2H_6 + 2Br_2 = C_2H_4Br^{\cdot+}Br_3^-$ (VI)	+38.8	+17.5	+15.1
$C_4H_8 + Br_2 = C_4H_8Br^+$ (VII) + Br^-	+135.7	+33.1	+13.2

Of course one needs quantitative information about the reaction profiles, before concluding whether a Br^- is likely to attack the bridge bromine rather than the carbon atoms in a bromonium ion: in other words, before evaluating the actual reversibility of the formation of bromonium ions.

The local minimum in the potential energy that we have found for the ionic couple (structure II) has an energy markedly higher than its precursor complex: in vacuo the bromide II is 56.1 kcal/ mol higher than the complex, while in dichloroethane and in methanol the free energy difference lowers to 37.5 and 24.5 kcal/ mol, respectively (Table 13).

If we try to completely optimize the structure III, with the bromide ion near the C_{2v} axis (releasing the constraints on the bromonium ion), we reach the ethylene–bromine complex without potential energy barriers. Thus it is crucial that the accurate knowledge of the potential energy map around the local minimum II, and in particular of the transition state leading to the complex, should be compared with the reaction profile leading from a structure similar to IV or V to the dibromoalkane.

This complex task will be addressed in a further work: at present, we report the computed free energy changes for the various processes of interest: in Table 13 the reaction ΔG's (geometries of ethylene, 2-butene, and Br_2 optimized in vacuo) are listed.

In vacuo, *trans*-ethylenebromonium bromide (IV) is more stable than the cis complex (III), by 12 kcal/mol, showing that the attack to carbon is favored over that to bromine, in the preparatory step. However, the energy difference is greatly reduced in polar solvents (down to 2.9 kcal/mol in CH_3OH).

From the point of view of computational methods, the presented results show the adaptability and the utility of the combined use of PCM and Bader's procedure, to get very accurate measures of the atomic charges of organic molecules, according to the chemical environments. Our data strengthen the hypothesis that the formation of bromonium ions is generally reversible and not only in the particular cases of highly encumbered alkenes.

Supplementary Material Available: Tables of calculated atomic charges in equilibrium, cis- and *trans*-ethylenebromonium bromide, ethylenebromonium dibromide and tribromide, and 1,2-dimethylethylenebromonium ion and calculated solvation free energies (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.