

Br₂ dissociation in water clusters: the catalytic role of water

J. J. Santoyo-Flores · A. Cedillo ·
M. I. Bernal-Uruchurtu

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Abstract In this work, we explore the effect halogen bonds and hydrogen bonds have on the activation of the chemical bonds modified in the course of the $\text{Br}_2 + (\text{H}_2\text{O})_n \rightarrow \text{HOBr} + \text{HBr}$ reaction and the effect the number of water molecules present in the cluster has on the barrier and the stability of the products formed. Using ab initio MP2 methods, we have analyzed the local electrodonating and electroaccepting power functions that revealed the differentiation between bromine atoms in Br_2 due to interaction with water molecules, thus resulting in an increase in the donor power that stabilizes the proton transfer process from a water molecule in the next step of the reaction. This situation is confirmed by the lowering in the corresponding activation barrier found. Our results show that the catalytic effect of water is already important for clusters with three water molecules and the effect additional molecules have is related to the acid dissociation of the products.

Keywords Halogen bond · Atmospheric chemistry · Halogens · Water clusters · Catalytic effects

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J. J. Santoyo-Flores · M. I. Bernal-Uruchurtu (✉)
Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001,
62209 Cuernavaca, Morelos, México
e-mail: mabel@uaem.mx

A. Cedillo
Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186,
09340 México D. F., México

1 Introduction

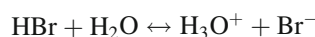
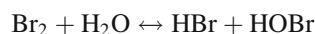
The intermolecular forces acting between halogens and a wide variety of molecules have attracted a significant amount of attention in the recent years. From the nature of the interaction [1–3], passing through their spectroscopic properties [4], to their effect in supramolecular systems and crystal engineering [5], several authors have commented and explored the similarities between hydrogen bonds and halogen bonds [6–8] aimed to design supramolecular systems with tunable forces since the donor, the halogen-containing moiety, might be selected from a vast set of $R-X$ molecules and so the acceptor [9, 10]. However, little has been said about the dihalogens in aqueous environments where the simultaneous and concurrent presence of halogen and hydrogen bonds might be of relevance for understanding water cluster mediated atmospheric chemistry. In contrast, not only the catalytic effects of water but also the hydration of halogenated species and halide ions has been extensively studied with experimental and theoretical methods [11–16].

Some years ago, a DFT study of halogens in water clusters suggested the ionic pair formation as a consequence of the charge separation between the two halogen atoms in aqueous clusters [17]. It is difficult to predict the ionic pair formation from the observed charge separation, however, MP2 calculations confirmed the large polarization occurring in the halogen molecule leading to a partial ionicity in the halogens, thus contributing to the strength of the interactions playing for these structures [2]. The upper limit of this ionicity, the ion pair formation, lies at the bottom of the $\text{H}_2\text{O} + \text{Br}_2 \rightarrow \text{HOBr} + \text{HBr}$ reaction.

The chemistry of hypohalous acids (HOF, HOCl and HOBr) is relevant for atmospheric phenomena where their oxidative properties are involved in stratospheric processes

related to the consumption of ozone in this region [18, 19]. In particular, the bromine-containing systems have been found to be more reactive than the chlorine ones. Voegele et al. have investigated the reverse reactions, that is, $\text{HOX} + \text{HY} + n\text{H}_2\text{O} \rightarrow \text{Br}_2 + (\text{H}_2\text{O})_{n+1}$, with $X = \text{Cl}, \text{Br}$ and $Y = \text{Cl}, \text{Br}$ using DFT and variational transition state theory with tunneling corrections. Their work concludes that barriers for the reaction with $X = Y = \text{Br}$ are consistently smaller than for chlorine and proceed barrierless when at least two water molecules catalyze the reaction [20, 21].

On the other hand, the hypobromous acid formation in liquid water is a process limited by two factors: first, the limited solubility of Br_2 in liquid water, 33.6 g L^{-1} and second, the small equilibrium constant for the reaction, $K = 5.2 \times 10^{-9}$. Nonetheless, the occurrence of this reaction can be easily observed by the spectroscopic absorption signal of the tribromide ion at 267 nm as described by Kerenskaya et al. [22]. The tribromide ion is present in solution as a byproduct of a series of equilibria as follows:



The intensity of the tribromide anion signal is quite large in the early stages of bromine clathrate formation and gets smaller as the amount of Br_2 available in solution decreases when the hydrate is formed. From the small equilibrium constant of the first step in these equilibria, it seems difficult to explain the significant amounts of Br_3^- spectroscopically found. This might suggest that the interaction between water and bromine during the early stages of hydrate formation might be somehow different from the one occurring in liquid solution.

In this work, we explore the effect halogen bonds and hydrogen bonds have on the activation of the chemical bonds modified in the course of the $\text{Br}_2 + (\text{H}_2\text{O})_n \rightarrow \text{HOBr} + \text{HBr}$ reaction, and the effect the number of water molecules present in the cluster and the hydrogen-bond-halogen-bond network formed have on the barrier and the stability of the products formed.

2 Methodology

The electronic structure calculations reported in this work were obtained using the Gaussian98 suite of programs [23]. The optimized structures of the clusters used as models of the reactants are those reported in a previous work [2] where all structures were optimized at the MP2/aug-cc-pVDZ level. A harmonic frequency analysis was performed confirming that these stationary points correspond to minima or first-order saddle points in the potential

energy surface. In our previous work, the charge transfer and polarization analysis occurring in the clusters was done using the NBO-derived charges. This analysis is used here to understand the modifications on the charge distribution as a consequence of the rupture of the bromine–bromine bond.

In Fig. 1, we present the structure of the clusters selected in this work to study the Br–Br bond dissociation. In a previous work by one of us [2], these structures were fully characterized along several other configurations. A preliminary study on all those structures showed that the Br–Br dissociation depends in a crucial way on the intermolecular network established between the dihalogen and water molecules, that is, the hydrogen-bond-halogen-bond interactions. This behavior has been previously observed for some other proton-coupled activated processes in water clusters [24]. We briefly resume here some of the relevant properties of the clusters where the role of water in the dissociation process was found (See Table 1).

The structure with two water molecules (2W) corresponds to the most stable configuration found for this size of cluster, in it one of the halogen atoms is simultaneously engaged in both a halogen bond (XB) and a hydrogen-halogen (XH) bond with the two ends of a water dimer, a structure favored by the dipole–quadrupole interactions between Br_2 and the water molecules. A quite similar pattern can be observed for the structure with three water molecules (3W) resulting from one of the halogen atoms inserting into the water trimer ring. In this structure, cooperative effects are important; the XB and the XH distances are shorter than the analogous interactions for the 1:1 complex. The cluster with four water molecules used

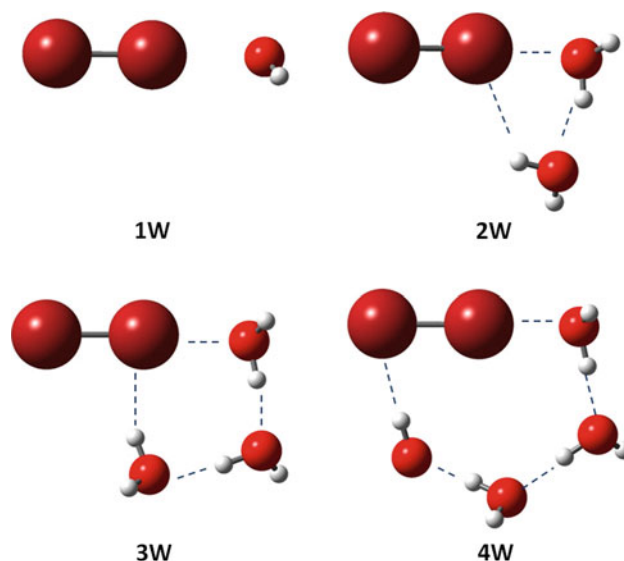


Fig. 1 MP2/aVDZ optimized structures of $\text{Br}_2(\text{H}_2\text{O})_n$ clusters used as reactant geometries (from Ref. [2])

Table 1 Selected properties of the Br₂-water clusters used in this work reported in Ref. [2]

	Cluster	E_{int} (kJ/mol) MP2/aVDZ BSSE corrected	R(Br-Br)	r(Br...O) θ (Br-Br-O)	r(Br...H) θ (Br-Br-H)
1W	Br ₂ -H ₂ O	-15.5	2.338	2.769 (180)	
2W	Br ₂ -(H ₂ O) ₂	-42.3	2.351	2.674 (175)	2.880 (124)
3W	Br ₂ -(H ₂ O) ₃	-77.5	2.364	2.568 (173)	2.570 (155)
4W	Br ₂ -(H ₂ O) ₄	-111.8	2.358	2.470 (179)	2.255 (176)

Distances are in Å and angles are in degrees

here (4W) is 2.1 kcal mol⁻¹ less stable than the structure in which the halogen lies above a cyclic water cluster but results of particular relevance to this study due to the shorter XB interactions leading to a slightly larger charge transfer from the XB water molecule to the halogen as it will be further discussed.

The molecular electrostatic potential was obtained from the electronic density coming from MP2/aug-cc-pVDZ calculations. To better understand, the effect intermolecular forces have on the propensity of donating or receiving fractional amounts of charge on reactive processes as the one we are interested here, the local electroaccepting and electrodonating powers are calculated as $\omega^{\pm}(r) \equiv f^{\pm}(r) (\mu^{\pm})^2/2\eta$, as proposed by Gázquez et al. [25]. Here, $f^{\pm}(r) \equiv \pm[\rho_{N\pm 1}(r) - \rho_N(r)]$ are the acceptor/donor Fukui functions, where ρ_N is the electron density of the electronic system with N electrons; $\eta = \frac{1}{2}(I - A)$ is the chemical hardness, where I and A are the ionization potential and electron affinity, respectively, and μ^{\pm} are the chemical potentials for the process of accepting/donating charge and are given by $\mu^+ \equiv \frac{1}{4}(3A + I)$ and $\mu^- \equiv \frac{1}{4}(3I + A)$, respectively.

3 Results and discussion

3.1 Charge separation and/or polarization as function of the number of water molecules in the cluster

In Table 2, we present the polarization occurring in the bromine calculated with two different methods. There is a reasonable agreement in the trends obtained with these methodologies: charge transfer (CT) from water to the dibromine molecule is small in contrast with the large internal charge transfer occurring in it. From the methods used, it is clear that Mulliken predicts a much larger polarization than NBO. The CT occurring along the Br-Br...O line is small, and it clearly shows the dependence on the Br...O distance as it has been suggested by some experimental studies [4, 26].

3.2 The donor acceptor behavior of molecules in the clusters

To gain a deeper understanding of the role each water molecule in the cluster has on the dibromine dissociation in

Table 2 Molecule polarization calculated as the difference of atomic charges on each atom (δq) and total charge $q(\text{Br}_2)$ for bromine in the Br₂-(H₂O)_{*n*} clusters in a.u. obtained using the density from the MP2/aug-cc-pVDZ level

Cluster	Mulliken		NBO	
	δq^a	$q(\text{Br}_2)$	δq	$q(\text{Br}_2)$
1W				
Br ₂ -H ₂ O	0.137	-0.028	0.078	-0.027
2W				
Br ₂ -(H ₂ O) ₂	0.151	-0.034	0.095	-0.043
3W				
Br ₂ -(H ₂ O) ₃	0.200	-0.063	0.132	-0.054
4W				
Br ₂ -(H ₂ O) ₄	0.408	-0.081	0.082	-0.031

^a All reported values are in a.u.

these clusters, the local electrodonating and electroaccepting powers functions were calculated. In Fig. 2, we present the local indices of the [Br₂(H₂O)_{*n*}] clusters projected onto a molecular surface. For the models 2W, 3W and 4W, one can notice a higher donating capacity on the bromine atom opposite to the oxygen-bromine interaction contact. This activation is due to the intramolecular charge redistribution process resulting from the interaction with the water cluster, which is a consequence of a small, but non-negligible, CT that contributes to the stability of these systems [26]. This differentiated increase in the donor power stabilizes the proton transfer process from a water molecule in the next step of the reaction. This effect is consistent with the lowering in the corresponding activation barrier, as it is shown below. In opposition, the local indices have a negligible value on the water molecules, except for that which interacts with the bromine molecule through its oxygen atom, which presents a marginal contribution.

3.3 The energetic cost of bromine dissociation in water clusters

The studied isodesmic reaction: Br₂ + H₂O → HOBr + HBr is an endothermic process according to the formation enthalpies differences between the products and the reactants. Accurate predictions of the heat of formation of the compounds involved in this reaction are available in the literature [27] except for HOBr. For this latter, it was only

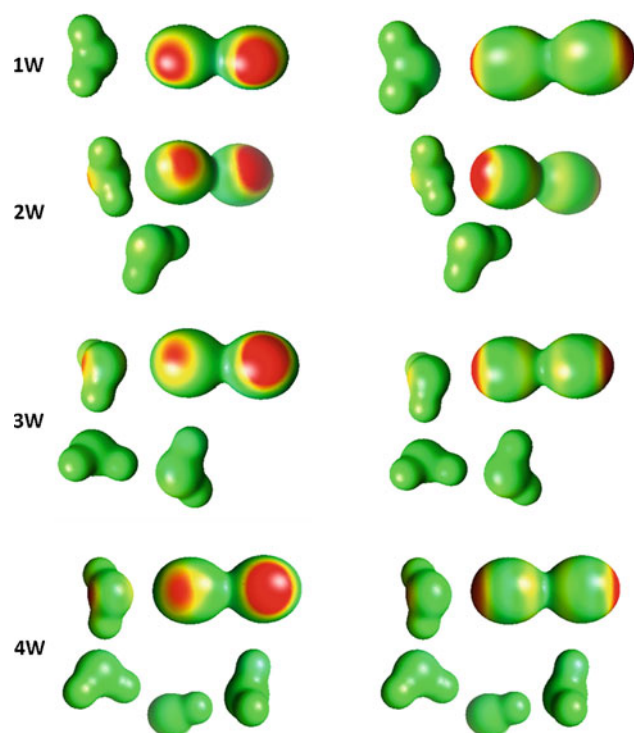


Fig. 2 Electrodonating (*right column*) and electroaccepting (*left column*) power functions projected on the electrostatic potential surface. In all cases, the *red* regions correspond to the maximum values of the analyzed property

few years ago when a refined set of ab initio calculations by Denis [28] converged to the experimentally obtained value of $-259.07 \text{ kJ mol}^{-1}$ that Lock et al. [29] obtained several years ago in photodissociation experiments for the heat of formation of HOBr. Using this value and the corresponding reported values for the other compounds [27], the heat of this reaction is found to be $112.68 \text{ kJ mol}^{-1}$. From the theoretical MP2/aug-cc-pVDZ level predictions of the heat of formation for the participating moieties, the heat of reaction is underestimated by 25 kJ mol^{-1} with respect to the value obtained using experimental data. We found that the energy difference is only 10.5 kJ mol^{-1} if a larger basis set (aug-cc-pVTZ) is used. Considering the computational cost of optimizing cluster geometries and exploring their PES with this latter basis set and the fact that the structure of each molecule, HBr, HOBr and H_2O as well as the interaction energies of the clusters obtained with the aug-cc-pVDZ basis set are in excellent agreement with the ones obtained with the larger basis set, we decided to perform this study with the aug-cc-pVDZ basis set.

To explore the region of the potential energy surface of the clusters involved in the reaction, we performed relaxed scans of the dibromine coordinate, that is, starting from the optimized structure of $[\text{Br}_2(\text{H}_2\text{O})_n]$ with $n = 1-4$, the bromine–bromine distance was stepwise increased from 2.33 to 3.15 Å and fixed, while the others degrees of

freedom were fully relaxed. In Fig. 3, we present the approximate reaction profiles. These profiles do not correspond to the reaction coordinate but are helpful to locate the region of the transition state in processes where several covalent bonds are modified. As it can be seen in Fig. 3, the energetic cost of distorting the Br–Br covalent bond in these conditions is almost unaffected by the number of water molecules present in the cluster. However, it is clear that for the system 4W a different behavior emerges as the Br–Br distance is about 2.90 Å. With this information, we looked for the transition states structures starting from geometries in which this bond was smaller than that value.

a. $[\text{Br}_2-\text{H}_2\text{O}]$:

The TS structure for this system has a single imaginary frequency (ν_i) at -855.5 cm^{-1} and is shown in Fig. 4a. At this level of calculation, the potential energy barrier for the bromine dissociation in presence of a single water molecule is $244.5 \text{ kJ mol}^{-1}$. This structure has a very long Br–Br distance confirming a late TS for the reaction. Furthermore, this structure closely matches the one described by Voegelé et al. [21] for the reverse reaction where they found a $130.2 \text{ kJ mol}^{-1}$ barrier at the MPW1K/6-31+G(d,p) level. The difference between the barriers for the forward and reverse reaction is a good match of the energy difference between reactants and products ($114.3 \text{ kJ mol}^{-1}$), albeit the different methodologies used thus confirming the good performance of both approaches.

There is a large charge redistribution occurring in the system. If this geometry is considered to be closer to the reactants than to the products, the fragment corresponding to the original Br_2 molecule is negatively charged by 0.18 a.u. A similar analysis, now comparing with the expected products, shows that the fragments

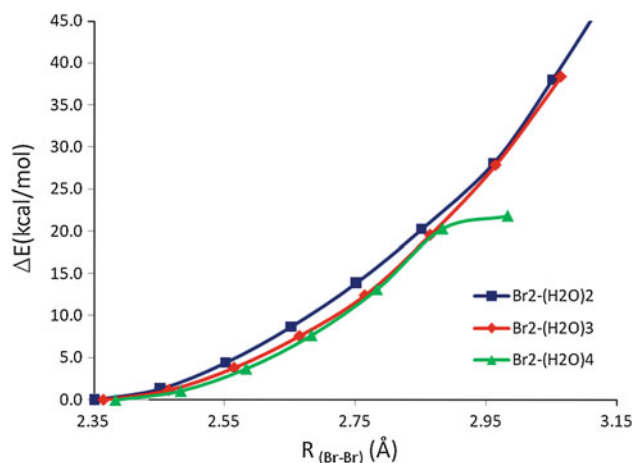
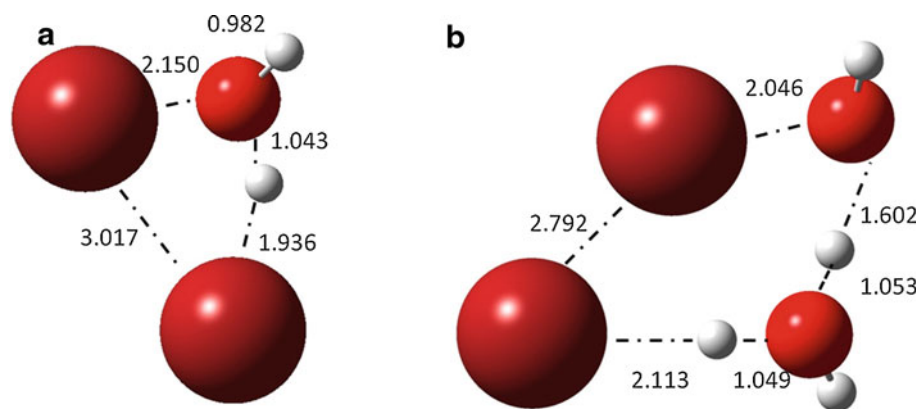


Fig. 3 Energetic profiles of the Br–Br elongation in the clusters. Each symbol corresponds to a value of the Br–Br distance where all other degrees of freedom was optimized

Fig. 4 Transition state structures found for the dissociation of Br_2 in clusters containing one (a) and two water (b) molecules. All distances are in Å



corresponding to HOBr and HBr are far from neutral, c.a. 0.3 a.u. It is possible to relate the high energetic cost of this reaction with the electrostatic work that must accompany the formation of these new moieties.

- b. $[\text{Br}_2(\text{H}_2\text{O})_2]$: The catalytic role of water molecules. The transition state structure identified for the $\text{Br}_2 + 2\text{H}_2\text{O}$ reaction ($\nu_i = -262.2 \text{ cm}^{-1}$) lies $202.2 \text{ kJ mol}^{-1}$ above the structure corresponding to the reactants. In Fig. 4b, it is possible to observe that in this TS structure, the role of one of the water molecules is to mediate the proton transfer between a water molecule and the anionic bromide fragment, a behavior that can be considered as catalytic. It is possible to understand the role of the catalyst as a charge mediator. In a similar way than the TS for the reaction with a single water molecule, in this case the fragments corresponding to the products, HOBr, HBr and H_2O , are all partially charged being the H_2O set the one bearing the largest charge, c.a. 0.4 a.u., whereas HBr and HOBr only 0.2 a.u. Furthermore, the distance between the two bromine atoms is considerably shorter than for the previous cluster thus facilitating the charge redistribution or delocalization.

For the reverse reaction in a previous work [21], two different TS structures were located, one corresponding to a catalyzed process with a barrier of 85 kJ mol^{-1} and another ascribed to an uncatalyzed reaction with a 134 kJ mol^{-1} barrier. The transition state structure found in this work is closer in geometry to the former and the combined barriers match again the change in enthalpy for the reaction. All efforts aimed to locate the so-called, uncatalyzed TS were unsuccessful, thus suggesting that the uncatalyzed channel is not as important as the other one.

- c. $[\text{Br}_2(\text{H}_2\text{O})_3]$: A stable products cluster is found. The potential energy barrier for bromine dissociation in a three water molecule cluster was found to be $103.4 \text{ kJ mol}^{-1}$; this is at least 96 kJ mol^{-1} smaller than for the cluster with two water molecules. The transition state structure ($\nu_i = -214.7 \text{ cm}^{-1}$), shown in Fig. 5a, is only 5.9 kJ mol^{-1} less stable than the cluster containing the products (Fig. 5b), in line with the idea advanced by Voegelé et al., of a barrierless process in the reverse sense. There is an interesting modification in the cluster as the reaction proceeds to products. As it is previously

Fig. 5 Transition state structure found for the dissociation of Br_2 in clusters containing three water molecules (a) and stable structure of the reaction products (b). All distances are in Å

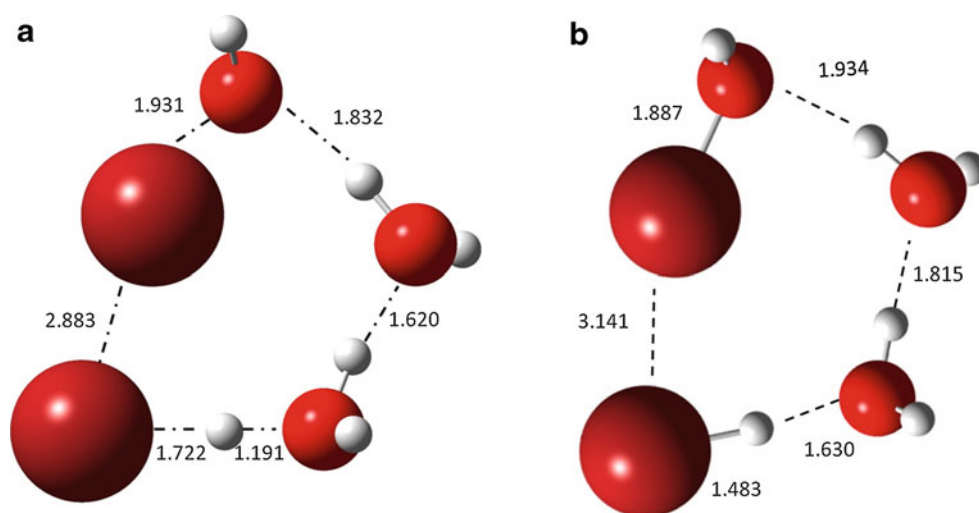
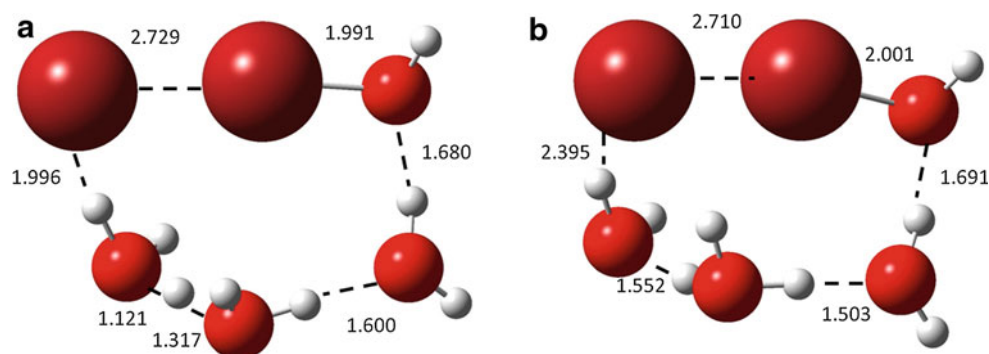


Fig. 6 Transition state structure found for the dissociation of Br₂ in clusters containing four water molecules (a) and stable structure of the reaction products (b). All distances are in Å



mentioned on the reactants structure, it is possible to see the same halogen atom involved in a XB and a XH interaction. This latter interaction breaks as soon as the bromine–bromine bond is slightly larger than the equilibrium distance. The proton formerly engaged in the XH interactions points to the anionic side of the halogen molecule forming a new XH interaction, thus enabling the concerted proton transfer. Again, the catalytic role of water molecules is due to their ability to separate the charges through their proton donor/acceptor properties and, in this case, the combined effect with their halogen acceptor ability. From the charge distribution of the TS structure, it is possible to see that the HBr and the HOBr fragments bear a small fractional charge, ~ 0.1 a.u.

- d. [Br₂(H₂O)₄]: HBr is a strong acid in aqueous clusters. In Fig. 6, the structure of the transition state ($\nu_i = -125.6$ cm⁻¹) and products for the reaction are shown. In contrast to the structures for smaller clusters, the transition state is not very close in geometry to the products; the relative planarity of the initial reactant cluster is not conserved. This TS structure is -0.96 kJ mol⁻¹ below the energy of the initial cluster, and the products lay 19.9 kJ mol⁻¹ below this value. This is the only case in the series where the TS lies lower in energy than the reactant structure. It is possible that besides pointing toward a barrierless dissociation of dibromine, this barrier is more closely related with the acid/base equilibrium established between HBr and the water molecules than with the bromine dissociation itself. Several attempts to locate a precedent TS structure and/or possibly some intermediary structures were not successful possibly due to the flatness of the PES in that region, that is, the hydrogen bonds stabilizing this structure are very short thus promoting the proton delocalization between them. The TS structure (6a) is possible to observe that HBr dissociates in a bromide anion and a proton forming a hydronium, that is, a contact ion pair. This structure

evolves to a solvent separated ionic pair product structure through a proton migration to a neighbor water molecule. Goursot et al. [30] studied the behavior of HBr in 4 and 5 water molecule clusters finding that in all cases, four water molecules were needed to dissociate HBr and that contact ionic pair structures evolve to solvent separated ones being these latter slightly more stable for the cases with four and five water molecules. Our observations match not only qualitatively their results but also the energy difference between both ionic structures although our system only has three water molecules. This might be due to the presence of HOBr in the cluster and the role it plays in the charge redistribution.

The delocalization of the electronic density leads to a very polarized cluster, in which all fragments bear a partial charge being negatively charged Br⁻, HOBr and one water molecule and positively charged the hydronium ion and one water molecule. This situation is similar to what has been described for the dissociation of HCl in water clusters [31], there is a significant charge transfer within the cluster that prevents its breaking apart thus enabling the reverse reaction to readily take place.

4 Conclusions

In this work, we have looked into the effect local interactions have on the reactivity of bromine. Our results confirm that the combined effect of strong intermolecular interactions like halogen bonds and hydrogen bonds is behind the catalytic role of water molecules in this dissociation process. These interactions favor the process balancing the polarization of Br₂ in the reactant cluster and the charge transfer from water to it and later on act as mediators promoting the charge delocalization that favors the bond breaking of Br₂. Depending on the size of the cluster, the role of water molecules as proton donors and proton

acceptors are reinforced by the halogen bond and the hydrogen–halogen interactions presents in the cluster. The double catalytic role of water molecules has already been described for some other reactive processes in the gas phase [24, 32] and in the liquid [16].

In particular, the analysis of the local electrodonating and electroaccepting powers made evident that the interactions between the dihalogens and water molecules do not have a strong effect on the halogen. However, this interaction stabilizes the proton transfer process involved in the chemical reaction through an enhancement of the electrodonating power of the halogen-bonded water molecule.

An interesting finding is the dissociation of HBr in the presence of only three water molecules. Probably, this is due to the possibility of forming a H_3O^+ ion with a triple coordination to strongly polarized and partially charged water molecules. As found for some other reactive systems, the extent of formation of the acid, HBr in this case, depends sensitively on the arrangement of water molecules in the network. Furthermore, the charge transfer between the protonated water molecule and its first solvation shell might be a phenomenon closely related to the lack of barrier on the reverse sense, thus explaining the small equilibrium constant of this reaction. However, on the feasibility of this reaction occurring in the atmosphere, several considerations must be taken into account: first, the occurrence of this structures in the atmosphere is not entropically favored; second, photochemical processes might be relevant, either conducting to molecular water evaporation thus impeding the reaction to take place or by modifying the quantum tunneling rates in these clusters, situations that deserve to be carefully analyzed. The fact that this process is characterized by a very small equilibrium constant in liquid solution might point to a different environment around bromine. Work is in progress to address the hydration structure of bromine in condensed phases.

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