Quantum mechanical investigation of the reaction CHClBr + O(^{3}P)

Evangelos Drougas, Agnie M. Kosmas *

Department of Chemistry, Physical Chemistry Laboratory, University of Ioannina, GR-45110 Ioannina, Greece

Abstract

The reaction of ground state oxygen atoms with the chlorobromomethyl radical is investigated using high levels of electronic molecular structure theory. The calculations indicate an association–elimination mechanism through the formation of the energy-rich intermediates CHClBrO* and CClBrOH*. The C–Br bond scission and the HBr elimination are the main dissociation pathways of the chlorobromomethoxy radical but Cl release is also shown to be competitive. The hydroxychlorobromomethyl intermediate, CClBrOH, exhibits a much higher stability than CHClBrO with the HBr elimination being the only channel leading to more stable products.
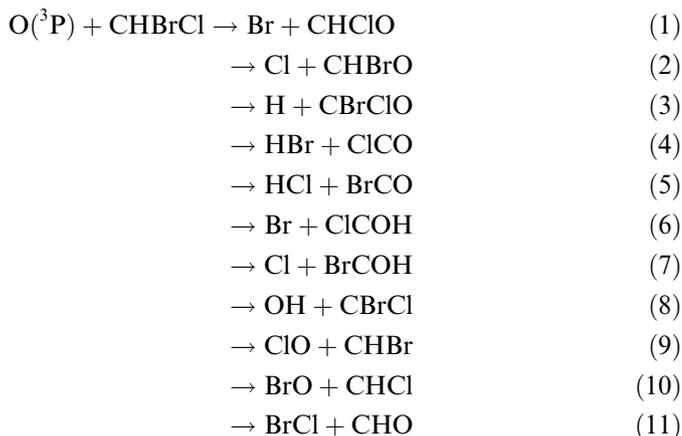© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The investigation of the reactions of halogenated alkyl radicals with oxygen atoms is of significant relevance in hydrocarbon combustion chemistry, in the field of oxidation processes of halogenated wastes containing halogen-bearing polymeric materials [1]. Under typical combustion conditions, a large number of halogenated alkyl radicals are formed with varying thermal stability depending on the halogen atoms coupled directly to the radical center. Several such radicals may live long enough to react to a considerable extent with oxygen atoms, producing highly activated haloalkoxy radicals [2,3]. Thus, due to their significance, several experimental and theoretical investigations of the reactions of halogenated alkyl radicals with O(^{3}P) and the related haloalkoxy intermediates have been carried out [2–6]. Other studies [7–21] have examined directly the reactivity of the relevant haloalkoxy radicals which may also be formed in various steps involved in the atmospheric oxidation of halocarbons, mainly in the reaction of the halogenated alkylperoxy radicals with NO [11–14].

The decomposition studies of halogenated methoxy radicals have revealed interesting correlations for the most probable dissociation pathways, depending on their mode of formation and the corresponding internal energy acquired in comparison with the critical energies to be overcome. The C–F bond scission presents a very high critical energy barrier, much higher than the C–Cl bond scission [7,8], while the chlorinated methoxy radicals present two competing dissociation pathways, the HCl elimination and the C–Cl bond breaking channel [18]. Studies on brominated methoxy radicals reveal that Br release occurs readily while HBr elimination presents a higher critical energy [21]. Particular interest lies on the mixed chlorine and bromine containing alkoxy radicals where the possibilities for both Cl and Br atom elimination are open. Bilde et al. [13,14] have examined in detail the fate of such systems and they have found that both Cl and Br release is often possible, depending on the mode of formation and the amount of internal energy acquired. This behaviour is directly connected to the potential energy surfaces that govern the various steps in the oxidation processes of halocarbons and the subsequent decomposition patterns of haloalkoxy radicals. Therefore, it would be desirable to carry out theoretical investigations of the detailed steps involved in the oxidation mechanism of halocarbons in combustion and atmospheric chemistry.

---
* Corresponding author. Fax: +5109 8798.
  E-mail address: amylona@cc.uoi.gr (A.M. Kosmas).

In the present work, we have studied the reaction of O(^{3}P) atoms with the CHBrCl radicals using ab initio quantum mechanical calculations. The following production channels were considered:

$$O(^3P) + CHBrCl \rightarrow Br + CHClO \qquad (1)$$
$$\rightarrow Cl + CHBrO \qquad (2)$$
$$\rightarrow H + CBrClO \qquad (3)$$
$$\rightarrow HBr + ClCO \qquad (4)$$
$$\rightarrow HCl + BrCO \qquad (5)$$
$$\rightarrow Br + ClCOH \qquad (6)$$
$$\rightarrow Cl + BrCOH \qquad (7)$$
$$\rightarrow OH + CBrCl \qquad (8)$$
$$\rightarrow ClO + CHBr \qquad (9)$$
$$\rightarrow BrO + CHCl \qquad (10)$$
$$\rightarrow BrCl + CHO \qquad (11)$$

The production pathways may take place either through the CHBrClO radical which is the nascent association minimum or the CClBrOH radical formed upon rearrangement of CHBrClO. The two minima as well as the interisomerization process are also examined in detail.

2. Computational details

The geometries of reactants, products and stationary points have been fully optimized at the UMP2/6-311+G(d,p) level of theory. Harmonic vibrational frequencies have been calculated at the same level, in order to determine the nature of the various stationary points as well as the zero-point energy (ZPE) corrections. The number of imaginary frequency (0 or 1) confirms whether a local minimum or a transition state were located. To verify the connection between the transition states and designated reactants and products, intrinsic reaction coordinate (IRC) calculations [22] at the UMP2/6-311+G(d,p) level were also performed. Finally, the energetics was refined by performing single-point CCSD(T)/6-311+G(d,p) [23] calculations at the UMP2 / 6-311+G(d, p) optimized geometries.

All quantum mechanical calculations have been carried out using the GAUSSIAN 98 series of programs [24].

3. Results and discussion

Thirteen structures have been investigated in total, three energy minima and 10 transition states for the isomerization and production pathways. The electronic energies and the relative stabilities at the UMP2 and CCSD(T) levels, are collected in Table 1. It is readily seen that TS10, leading to CHO + BrCl products, is very high located, indicating a negligible contribution of the relevant production channel to the overall reaction mechanism, as it will be discussed in the next section. Thus, TS10 has not been considered in the detailed discussion of the mechanism of the reaction. Also the products BrO + CHCl and ClO + CHBr are much higher located compared to the reactants and are not considered explicitly. Table 2 summarizes the calculated harmonic frequencies at the MP2 level for the energy

Table 1
Total (Hartrees) and relative (kcal mol^{-1}) energies (including ZPE corrections) for species involved in the CHBrCl + (^{3}P)O reaction

	MP2/6-311+G(d,p)	ΔE	CCSD(T)/6-311+G(d,p)	ΔE	ZPE
O(^{3}P) + CHBrCl	−3146.053862	82.9	−3145.636084	80.5	9.3
CHBrClO	−3146.186031	0.0	−3145.764369	0.0	12.8
CBrClOH (cis)	−3146.212276	−16.4	−3145.780533	−10.1	13.0
CBrClOH (trans)	−3146.213495	−17.2	−3145.781554	−10.9	13.1
TS1	−3146.184147	1.2	−3145.762935	0.9	12.1
TS2	−3146.168664	10.8	−3145.753430	6.9	11.9
TS3	−3146.159258	16.7	−3145.730477	21.3	8.8
TS4	−3146.147068	24.5	−3145.719392	28.2	10.0
TS5	−3146.178691	4.6	−3145.759327	3.2	11.6
TS6	−3146.168819	10.8	−3145.749257	9.5	9.9
TS7	−3146.171693	8.9	−3145.741504	14.3	8.9
TS8	−3146.160992	15.7	−3145.732407	20.1	9.1
TS9	−3146.126589	37.3	−3145.695925	42.9	5.3
TS10	−3145.976434	131.5	−3145.571212	121.2	12.3
CHClO + Br	−3146.232044	−28.9	−3145.801497	−23.3	12.2
CHBrO + Cl	−3146.212165	−16.3	−3145.781330	−10.6	11.7
CBrClO + H	−3146.196642	−6.6	−3145.756110	5.2	6.3
CClO + HBr	−3146.227533	−26.0	−3145.797980	−21.1	8.2
CBrO + HCl	−3146.218539	−20.4	−3145.787476	−14.5	7.1
ClCOH + Br	−3146.151027	21.9	−3145.728247	22.7	12.1
BrCOH + Cl	−3146.130043	35.1	−3145.707270	35.8	11.7
OH + CBrCl	−3146.069131	73.3	−3145.653558	69.5	7.9
CHBr + ClO	−3145.985581	125.8	−3145.578123	116.9	8.2
CHCl + BrO	−3145.996431	119.0	−3145.581812	114.5	8.4
CHO + BrCl	−3146.173683	7.7	−3145.739721	15.5	14.7

Table 2
Vibrational harmonic frequencies for various stationary points involved in the $(^3P)O$ + CHBrClO reaction at the MP2/6-311+G(d,p)

Species	Frequencies (cm^{-1})
CHBrClO	206, 272, 423, 576, 766, 1087, 1145, 1324, 3152
CBrClOH (*cis*Br)	237, 313, 356, 466, 571, 822, 1219, 1300, 3833
CBrClOH (*tr*Br)	234, 317, 384, 463, 567, 839, 1222, 1303, 3842
TS1	688i, 201, 293, 457, 746, 940, 1315, 1360, 3142
TS2	892i, 179, 330, 372, 661, 962, 1323, 1382, 3134
TS3	1444i, 230, 335, 512, 581, 663, 703, 775, 2332
TS4	2120i, 244, 339, 473, 576, 694, 836, 1254, 2603
TS5	567i, 68, 239, 466, 702, 999, 1405, 1587, 2630
TS6	1749i, 202, 343, 408, 472, 724, 1026, 1376, 2430
TS7	1668i, 114, 142, 358, 582, 830, 939, 1549, 1741
TS8	1093i, 71, 160, 354, 515, 894, 977, 1540, 2008
TS9	268i, 91, 194, 216, 298, 416, 537, 790, 1204

minima and the nine important transition states. The optimized structures for the 12 stationary points along with the geometrical parameters at the UMP2(full)/6-311+G(d,p) level are presented in Fig. 1. Finally, the reaction energy profile with respect to the CHBrClO isomer, based on the CCSD(T)/6-311+G(d,p) results is depicted in Fig. 2.

3.1. The energy minima

The most important feature of the potential energy surface of the reaction $O(^3P)$ + CHBrCl is the nascent association minimum CHBrClO. The newly formed C–O bond is 1.327 Å and the other three bonds are somewhat longer than those in the CHBrCl radical. CHBrClO is located 82.9 and 80.5 kcal mol^{-1} below the reactants at the MP2 and CCSD(T) levels, respectively. Thus, the association of $O(^3P)$ atoms with the CHBrCl radical produces CHBrClO with enough activation energy to proceed to a variety of dissociation channels and able to survive only for a very short time.

The isomeric structure CBrClOH is considerably more stable than CHBrClO and may be formed through the TS4 isomerization transition state. TS4 assumes a triangular geometry and it is formed by the shifting of the H atom from the C atom to the O atom so that the migrating hydrogen is found 1.236 Å away from the migrating origin (C) and 1.235 Å close the migrating end (O). The calculated barrier height is relatively high, 28.2 kcal mol^{-1} at the CCSD(T) level, still much lower than the reactants $O(^3P)$ + CHBrCl, so that the rearrangement process is in principle possible. CBrClOH presents two conformers, shown in Fig. 1, which, depending on the orientation of H atom with respect to Br, are denoted hereafter as CBrClOH (*cis*) and CBrClOH (*trans*). These minima are found to be 10.1 and 10.9 kcal mol^{-1} more stable than CHBrClO, respectively, at the CCSD(T) level, and present interesting structural changes compared to CHBrClO. The C–O bond distance increases from 1.327 Å in CHBrClO to 1.347 Å in the hydroxyl derivative, while the carbon–halogen bond distances decrease considerably. Thus, the C–Br bond distance decreases from 1.956 Å in CHBrClO to 1.924 Å and 1.882 Å in *cis* and *trans* CBrClOH, respectively, and the

C–Cl bond length decreases from 1.783 to 1.714, 1.746 in the same species. It is interesting to note how the C–Br, C–Cl distances decrease further in the CHBrCl radical.

3.2. Reaction pathways

3.2.1. Decomposition of CHBrClO

The energy-rich association complex CHBrClO is immediately subject to dissociation leading to various products through channels (1)–(5) and (9)–(11). The energetically most favorable reaction path is the one that involves the elimination of Br atom through transition state TS1. The transition state configuration is formed by the elongation of the C–Br bond from 1.956 to 2.126 Å, while the C–O and C–Cl bonds are shortened by 0.072 and 0.022 Å, respectively. The corresponding barrier height is negligible, 1.2 and 0.9 kcal mol^{-1} at the MP2 and CCSD(T) levels. The C–Br bond breaking pathway is the most exothermic of all located at 23.3 kcal mol^{-1} below CHBrClO and the overall reaction $O(^3P)$ + CHBrCl → Br + CHBrO is highly exothermic by more than 100 kcal mol^{-1}.

Channels (2) and (3) represent the C–Cl and C–H bond scissions through transition states TS2 and TS3, respectively. In TS2, the breaking C–Cl bond is elongated by 0.350 Å, while the C–O bond is shortened by 0.116 Å. The barrier height is located at 10.8 and 6.9 kcal mol^{-1} at the MP2 and CCSD(T) levels above CHBrClO and the process is exothermic by $\sim$10 kcal mol^{-1}. The overall reaction $O(^3P)$ + CHBrCl → Cl + CHBrO is also highly exothermic by $\sim$91 kcal mol^{-1}. The high exothermicity and the relatively low barrier point out to a non-negligible probability for the C–Cl bond scission channel. TS3 is located at 16.7 and 21.3 kcal mol^{-1} at the MP2 and CCSD(T) levels compared to CHBrClO. The breaking C–H bond is quite elongated from 1.097 Å in CHBrClO to 1.555 Å in TS3 and the C–O bond is shortened considerably by 0.188 Å, becoming 1.159 Å, i.e., close to the double C–O bond in the final product CBrClO. The C–H dissociation is endothermic by $\sim$5 kcal mol^{-1} compared to the intermediate CHBrClO. This endothermicity and the high energy barrier decrease considerably the probability for H removal, although the overall reaction $O(^3P)$ + CHBrCl → H + CBrClO is still highly exothermic by $\sim$75 kcal mol^{-1}.

The HBr and HCl 1,1 eliminations take place via the triangular transition states TS5 and TS6. The C–H bond distance is elongated to 1.145 and 1.153 Å in TS5 and TS6, respectively, while the H–C–Br and H–C–Cl bond angles decrease significantly to 78.9° and 73.5° from $\sim$110° in CHBrClO. The energy barriers are relatively low, especially for HBr removal where the barrier height is located at 4.6 and 3.2 kcal mol^{-1} above CHBrClO at the MP2 and CCSD(T) levels. The products HBr + ClCO and HCl + BrCO are located at 21.1 kcal mol^{-1} and 14.5 kcal mol^{-1} below CHBrClO. The low barriers and the high exothermicities of the elimination channels make these dissociation routes quite probable, particularly the HBr elimination.
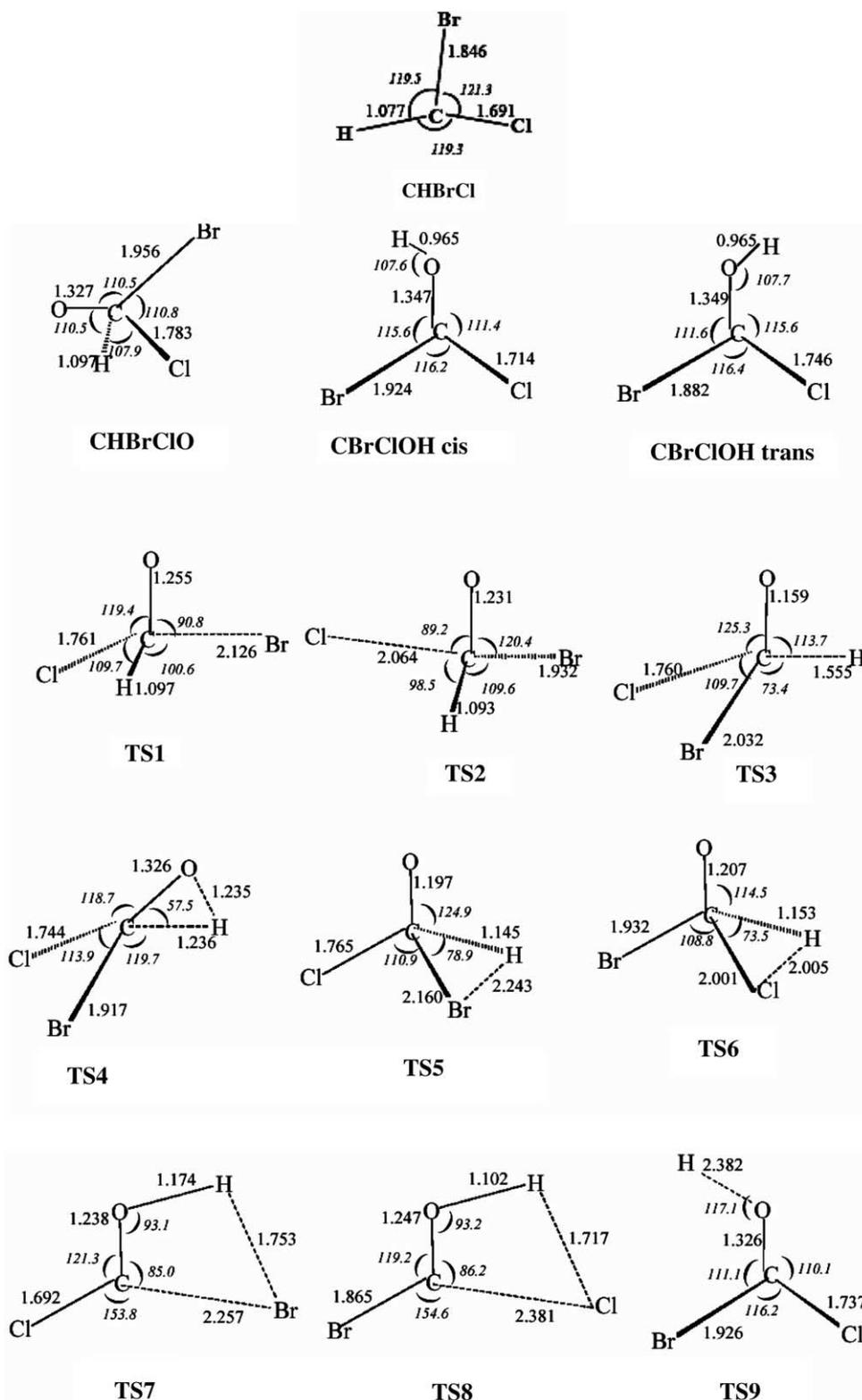
Fig. 1. Structures of the most important stationary points on the potential energy surface of the reaction O(3P) + CHBrClO at the MP2/6-311+G(d,p) level.

Three additional dissociation channels (9)–(11) were examined. Channels (9) and (10) lead to halogen monoxide XO, X = Cl, Br and CHY, Y = Br, Cl. These decomposition products are located higher than the reactants and consequently they do not contribute to the reaction. A final decomposition channel examined is the fragmentation of CHBrClO to BrCl + CHO which are located at 65 kcal mol⁻¹ below reactants. However, the transition state TS10 leading to these products is very high located making this dissociation route also unimportant.
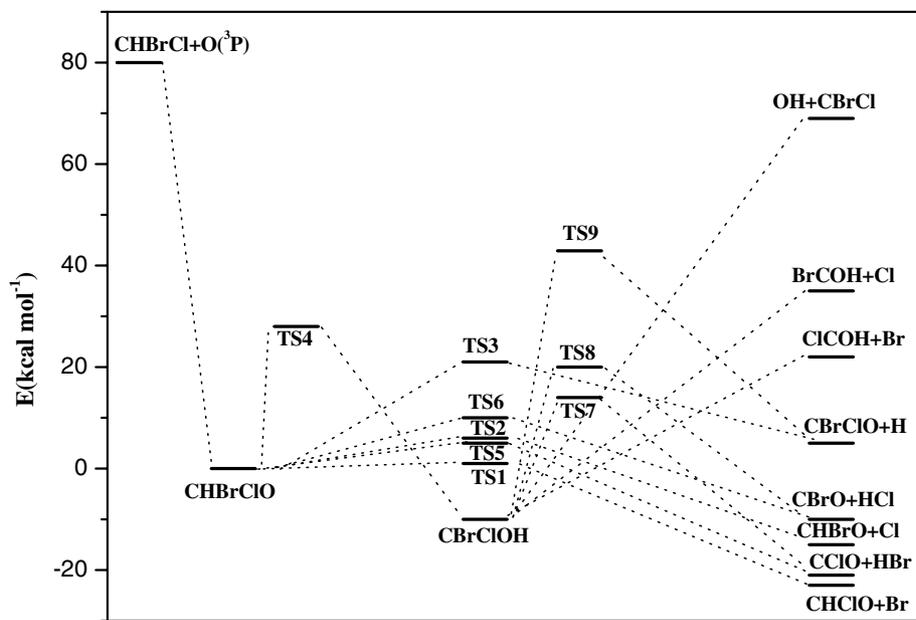
Fig. 2. Relative energy profile with respect to the CHBrClO species at the CCSD(T)/6-311+G(d,p) level of theory.

3.2.2. Decomposition of CBrClOH

HBr and HCl 1, 2 eliminations may also result from CBrClOH (*cis*) and CBrClOH (*trans*) conformers, respectively, via the four-center transition states TS7 and TS8, located relatively high at 24.4 kcal mol^{-1} and 30.2 kcal mol^{-1} compared to CBrClOH (*trans*) at the CCSD(T) level. In TS7, the breaking C–Br and O–H bonds are elongated to 2.257 and 1.174 Å and the forming H–Br distance is shortened to 1.753 Å. Formation of HCl may occur from the CBrClOH (*trans*) conformer, where the Cl and H atoms present a *cis* geometry. The breaking bonds C–Cl and O–H in TS8 expand to 2.381 and 1.102 Å, respectively, and the H and Cl atoms approach to 1.717 Å to form the H–Cl bond. Finally, O–H bond fission is possible through transition state TS9. The corresponding barrier height is even higher than TS7 and TS8, making this process even more improbable. The last three possible dissociation channels for CBrClOH are simple bond fission processes taking place without well defined energy barriers. The C–Br, C–Cl, and C–O bond scissions produce Br + ClCOH, Cl + BrCOH, and OH + CBrCl. They are very endothermic relative to CBrClOH but still lower than the reaction energy and thus, they may present some contribution to the mechanism of the reaction.

In summary, the complete study of all possible production channels indicates that the outcome of the reaction between chlorobromethyl radicals and ground state oxygen atoms in combustion chemistry may contain traces of a large variety of fragments. Certainly, the most probable production channel is the release of active bromine atoms. However, the detailed examination of the reaction energy profile indicates that Cl release and HBr, HCl formation also present low barriers and thus, a good probability for these species to be found among the products. This conclusion is consistent with the experimental studies of Bilde et al. [14] on the atmospheric fate of mixed chlorobrominated methoxy radicals, which demonstrated that apart from Br elimination which is the dominant decomposition pathway, they may also release chlorine atoms, depending on their route of formation and the energy content acquired during this process.

4. Summary

The most important stationary points on the potential energy surface for the reaction O(^{3}P) + CHBrCl are investigated at the CCSD(T)/6-311+G(d,p) level of theory based on the initial optimization of reactants, products and transition states performed at the MP2(full)/6-311+G(d,p) level. The calculations reveal a capture-limited association–elimination mechanism and show that the release of Br atoms dominates the reaction. Release of Cl atoms and formation of HBr and HCl are also shown to be possible reaction pathways.

References

[1] S.M. Senkan, Environ. Sci. Technol. 22 (1988) 2368.
[2] J.A. Seetula, I.R. Slagle, D. Gutman, S.M. Senkan, Chem. Phys. Lett. 252 (1996) 299.
[3] J.A. Seetula, I.R. Slagle, Chem. Phys. Lett. 277 (1997) 381.
[4] H. Hou, B. Wang, Y. Gu, J. Phys. Chem. A 103 (1999) 5075.
[5] B. Wang, H. Hou, Y. Gu, J. Phys. Chem. A 103 (1999) 2060.
[6] H. Hou, B. Wang, Y. Gu, J. Phys. Chem. A 103 (1999) 8075.
[7] Z. Li, J.S. Francisco, J. Am. Chem. Soc. 111 (1989) 5660.
[8] F. Wu, R.W. Carr, J. Phys. Chem. 96 (1992) 1743.
[9] M.R. Zachariah, W. Tsang, P.R. Westmoreland, D.F.R. Burgess Jr., J. Phys. Chem. 99 (1995) 12512.
[10] J. Chen, V. Catoire, H. Niki, Chem. Phys. Lett. 245 (1995) 519.
[11] J.J. Orlando, G.S. Tyndall, T.J. Wallington, J. Phys. Chem. 100 (1996) 7026.

[12] J.J. Orlando, G.S. Tyndall, T.J. Wallington, M. Dill, Int. J. Chem. Kinet. 28 (1996) 433.

[13] M. Bilde, J. Sehested, O.J. Nielsen, T.J. Wallington, J. Phys. Chem. A 101 (1997) 5477.

[14] M. Bilde, T.J. Wallington, C. Ferronato, J.J. Orlando, G.S. Tyndall, E. Estupiñan, S. Haberkorn, J. Phys. Chem. A 102 (1998) 1976.

[15] F. Wu, R.W. Carr, J. Phys. Chem. A 105 (2001) 1423.

[16] H. Somnitz, R. Zellner, PCCP 3 (2001) 2352.

[17] A. Kukui, G. Le Bras, PCCP 3 (2001) 175.

[18] F. Wu, R.W. Carr, J. Phys. Chem. A 106 (2002) 5832.

[19] F. Wu, R.W. Carr, J. Phys. Chem. A 107 (2003) 10733.

[20] E. Drougas, A.M. Kosmas, J. Phys. Chem. A 108 (2004) 5972.

[21] E. Drougas, A.M. Kosmas, Chem. Phys. 300 (2004) 233.

[22] C. Gonzalez, H.B. Schlegel, J. Chem. Phys. 90 (1989) 2154.

[23] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.

[24] M.J. Frisch et al., GAUSSIAN 98, Gaussian, Inc., Pittsburgh, PA, 1998.