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A theoretical study of abiotic methylation reactions of gaseous elemental mercury by halogen containing molecules

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Abstract

Methylation reactions of gaseous elementary mercury by halogen containing molecules such as halogenomethane species CH_3X (with X=Cl, Br and I) and the dimethylchlorinium ion $CH_3ClCH_3^+$ were investigated at the DFT level. With CH_3X, the reaction is predicted to be almost athermic and kinetically demanding for a thermal reaction. The reaction can proceed photochemically in the visible range; therefore sunlight may increase the reaction rate. These results compare well with the experimental data. Consecutive methylation of the CH_3HgX products (with X=Cl, Br and I) and subsequent formation of CH_3HgCH_3 were also studied. These reactions are predicted to be kinetically inaccessible and thermodynamically unfavorable. With $CH_3ClCH_3^+$, the reaction is predicted to be athermic but kinetically easy. This is due to the suitability of the methyl transfer reagent. Geometrical and electronic data were systematically analyzed in order to rationalize the results.

1 Introduction

Methylmercury (MeHg) is a potent neurotoxin that provokes irreversible damage to the nervous system and can cause death. It is formed through the methylation of mercury (Hg), a toxic element found both naturally and as a human-introduced compound in the environment (Nriagu, 1988, 1989; Fitzgerald et al., 1998). Hg can be transported far from its emission sources, which include mainly fossil fuel combustion, industry and mining (AMAP/UNEP, 2008). It can be deposited after its oxidation to the more water soluble and reactive form divalent mercury (Hg(II)). Then, it has the potential to be converted into organo-metallic forms such as MeHg, which is likely the most ecotoxicologically relevant form. MeHg can bioaccumulate and biomagnify in the ecosystem and is found at high and increasing levels in marine species and freshwater systems all over the world including Arctic fauna (Wagemann et al., 1996). Of particular concern are the high blood Hg concentrations observed in Northern people, whose traditional diet consists of marine organisms.

The mechanisms that produce MeHg are to date unknown, even though many pathways have been suggested (Barkay and Poulain, 2007). The biotic production of MeHg from inorganic mercury in aquatic sediments was first proposed by Jensen and Jernelov (1969). Biotic methylation was shown to be carried out by sulfate-reducing bacteria in anoxic sediments (Gilmour et al., 1992), and more recent evidence suggests that iron-reducing bacteria may methylate mercury as well (Fleming et al., 2006). Recent studies have shown that methylation likely occurs in oxic environments, although the processes are unknown (Cossa et al., 2009; Monperrus et al., 2007).

It has also been shown that the transfer of methyl groups can take place in abiotic conditions without the support of an enzymatic process. Chen et al. (2007) and Hammerschmidt et al. (2007) suggested that this process may be occurring in the aqueous phase in the atmosphere. Abiotic methylation of Hg(II) (Weber, 1993; Siciliano et al., 2005) requires suitable methyl donors and, although available methyl donors may be products of biological processes such as organic compounds (Kawamura et al., 1996), methylation is still considered to be abiotic (Craig, 1986; Falter and Wilken, 1998). Some potential pathways of chemical methylation have been studied, such as the reaction of Hg(II) with fulvic and humic acids (Nagase et al., 1982), acetic acid (Gardfeldt et al., 2003), methylmetals like methyltin or methyllead (Howell et al., 1986; Celo et al., 2006; Woggon et al., 1984; Cerrati et al., 1992), or small molecules such as methyl iodide (Celo et al., 2006; Ebinghaus and Wilken, 1993).

The contribution of abiotic methylation pathways may have been overlooked, in particular methylation involving Hg(0). Since Hg(0) is the dominant mercury specie in the troposphere, abiotic Hg(0) methylation might be an important pathway by which MeHg species are produced and dispersed globally. To the best of our knowledge, only methyl iodide (CH_3I), a well known methylating agent in organometallic chemical synthesis, has been proposed as a possible candidate for Hg(0) methylation (Maynard, 1932; Weber, 1993; Hall et al., 1995; Tokos et al., 1998; Celo et al., 2006).

However, experimental studies have shown important disagreement. Maynard was the first to observe Hg(0) methylation by CH_3I at room temperature in the sunlight (Maynard, 1932), but the yield was found to be low and the reaction rate slow. Weber (1993) also proposed the possible formation of CH_3HgI by the same reaction. In a series of experiments, Hall et al. (1995) reported the absence of Hg(0) methylation in the aqueous phase in the dark, and observed an oxidation of Hg(0) in full sunlight. Direct methylation of Hg(0) by dimethyl sulfide (DMS) was not observed, but slow formation of methylmercury close to the detection limit of the apparatus was observed using Hg(0) and CH_3I (Hall et al., 1995). The authors concluded that Hg(0) methylation by CH_3I was not significant for the cycle of mercury. This was then confirmed by experiments conducted by Tokos et al. (1998). Finally, Celo et al. (2006) found that methylation occurs in the dark at a low rate, but with a yield equivalent to that reported for methylation by sulfate-reducing bacteria.

Theoretical studies, notably the DFT (Density Functional Theory) method, can be very useful in reconciling experimental inconsistencies since they are able to reliably reproduce the reactivity of organometallic systems (Chemical Review, 2000). These kinds of treatments have already been used for two precedent works involving mercury: its reaction with halogen radicals and anions (Maron et al., 2008) and its reactivity with ozone (Castro et al., 2009). Other theoretical works are present in the literature (e.g., Tossell, 2003; Strömberg et al., 1991; Shepler and Peterson, 2003; Hu et al., 1999; Kaupp et al., 1994), but there is a lack of research in the domain. Indeed, field observations and laboratory experiments can be supported by theoretical studies and insights brought by these methods should not be neglected. In this paper, several reactions that could potentially lead to the methylation of Hg(0) were investigated in the gas phase. Halogenomethane species (CH_3X with X=Cl, Br, I) were selected as potential candidates for mercury methylation not only because they are widely distributed in the marine boundary layer and in the free troposphere (Cox et al., 2003, 2005), but also to enable comparison with the experimental studies involving CH_3I. The different formation reactions of mono-methyl and di-methyl mercury from

Hg(0) and halogenomethane species were studied. In addition, the reaction between Hg(0) and the dimethylchlorinium ion $CH_3ClCH_3^+$, which may potentially lead directly to $HgCH_3^+$, was also examined.

2 Computational details

Mercury (Kuechle et al., 1991) and all the halogen atoms (Bergner et al., 1993) were treated with Stuttgart-Dresden pseudopotentials in combination with their adapted basis set, augmented by a set of polarization functions (f for Hg and d for halogens) (Ehlers et al., 1993). Carbon and hydrogen atoms were described with a 6-31G(d,p) double-ζ basis set (Hehre et al., 1972). Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91 (Perdew and Wang, 1992; Becke, 1993). Geometry optimizations were carried out without any symmetry restrictions, and the nature of the extrema (minima and transition states) was verified with analytical frequency calculations. Gibbs free energies were obtained at $T=298.15$ K within the harmonic approximation. IRC calculations were performed to check the connections of the optimized transition states. DFT calculations were carried out with the Gaussian03 suite of program (Gaussian 03 (Revision D.02) et al., 2004). Finally, the electronic density (at the DFT level) was analyzed using the Natural Bond Orbital (NBO) technique (Reed et al., 1988).

3 Results and discussion

3.1 Reaction of Hg(0) with CH_3X

Reactions between Hg(0) and CH_3X (with X=Cl, Br, I) were computed (Fig. 1). The reaction is an oxidative addition of CH_3X to Hg(0) in order to form the divalent complex $CH_3Hg(II)X$. The geometries are analogous for the three halogens, but bond distances vary because of the increase of the halogen atomic radius with the atomic number. Thus, the C−X bond in CH_3X is longer for X=I (2.17 Å) than for X=Br (1.95 Å) and X=Cl (1.80 Å). The same behaviour is found for the Hg−X bond length in the reaction product (2.66 Å for X=I, 2.47 Å for X=Br and 2.34 Å for X=Cl). The reaction is predicted to be almost athermic for the three halogens. Indeed, even if it is slightly endergonic for X=Cl and X=Br, and slightly exergonic for X=I, it is not possible to conclude since the values are within the systematic error of the DFT method (estimated at 5 kcal mol^{-1}) (Schultz et al., 2008; Zhao and Truhlar, 2008). These thermodynamics are due to the fact that a strong C−X bond is broken during the reaction while two weaker bonds (Hg−C and Hg−X) are formed. The loss and gain of energies reach a balance and induce a globally athermic reaction. Nevertheless, CH_3HgX formation is slightly more favorable when the atomic number of the halogen increases. This is due to the lower C−X bond strength in the CH_3X reactant. Indeed, the electronegativity of X decreases when the atomic number increases, and therefore the C−X bond polarity and strength decrease as well. In any event, these energetic values are characteristic of feasible reactions for the three halogens from a thermodynamic point of view, and even slightly favorable for X=I.

The calculated activation barriers are found to be high (+67.6 kcal mol^{-1} for X=Cl, +64.8 kcal mol^{-1} for X=Br and +60.4 kcal mol^{-1} for X=I), indicating kinetically demanding reactions. The height of the barriers can be explained by geometrical and charge analyses at the transition state level (Fig. 2). The structure is a 3-centered triangle pattern characteristic of oxidative additions, where the methyl group is transferred from X to Hg. Geometrically, it is noteworthy that all the interatomic distances are longer than the corresponding ones in both reactants and products. Indeed, the Hg−C distance is equal to 2.51 Å whereas it is almost equal to 2.09 Å in CH_3HgX. The Hg−X ones are longer too, since the Hg−X bond lengths in CH_3HgX are 2.34 Å, 2.47 Å and 2.66 Å for X=Cl, Br and I, respectively. Finally, the C−X distances in CH_3X are 1.80 Å, 1.95 Å and 2.17 Å for X=Cl, Br and I, respectively, which is shorter than in the transition state structures. Thus, all bonds are not yet fully broken or formed at the transition state.

NBO analysis was performed at the transition state. The charges of the halogen atoms are equivalent to the ones found in the CH_3HgX product. The halogens attract the electronic density from the mercury and from the methyl group in order to be sufficiently charged to form the Hg−X bond. The methyl group is positively charged, which induces an electrostatic repulsion between Hg and CH_3. However, the methyl group is negatively charged in the CH_3HgX product (−0.30 for the three halogens), so an important electronic reorganization is needed.. From the second-order donor-acceptor analysis, it is noteworthy that the 3p (4p) orbitals of Cl (Br) give some electronic density not only to a 6p orbital of Hg, which forms the Hg−Cl (Hg−Br) bond, but also to the antibonding molecular orbital of the Hg−C bond, in order to break it. This is consistent with a slightly late transition state. For X=I, at the second order, a 5p orbital of I gives electronic density to a 6p orbital of Hg, and the 6s orbital of Hg donates to the C−I antibonding molecular orbital. The transition state is no longer late for X=I, thus in total agreement with the Hammond postulate, stating that transition states are late for endergonic reactions (Hammond, 1955). The activation barrier is lower when the atomic number increases. This is also related to the C−X bond strength in the CH_3X reactant. This reaction is difficult from a kinetic point of view, but sunlight irradiation can help the reaction to occur photochemically. Indeed, the absorption radiations needed in order to cross the barrier are equal to 457 nm, 479 nm and 518 nm for X=Cl, Br and I, respectively. These are radiations in the visible range; therefore these reactions may be slightly faster and observable in the presence of sunlight.

Some interesting links appear between this theoretical study and the experimental ones present in the literature. Indeed, calculations predict a thermodynamically favorable reaction between Hg(0) and CH_3I. This is in agreement with the experimental results by Celo et al. (2006) where MeHg formation was shown to occur in the dark. However, the activation barrier is predicted to be high, which is characteristic of a kinetically difficult reaction. It is for this reason that the formation of methylmercury observed by Celo et al. (2006) is slow. Moreover, Hall et al. (1995) were likely unable to identify any methylation in the dark or in the aqueous phase due to the slowness of the reaction.

On the other hand, the theoretical study shows that the reaction should be faster with the help of solar irradiation. This is in agreement with Hall et al. (1995) who reported the formation of a small amount of methylmercury from gas phase experiments in full sunlight. The reaction was very slow in these conditions, which is consistent with the high activation barrier, but may also be due to other competitive reactions such as the photodissociation of CH_3I.

The products of the reactions are CH_3HgX. We then determined whether it is possible to photodissociate these complexes to form either $HgCH_3$ or $HgCH_3^+$ (Reactions 1 and 2).

$$CH_3HgX \xrightarrow{h\nu} CH_3Hg^+ + X^- \qquad \text{(R1)}$$

$$CH_3HgX \xrightarrow{h\nu} CH_3Hg + X \qquad \text{(R2)}$$

$$CH_3HgX \xrightarrow{h\nu} CH_3 + HgX \qquad \text{(R3)}$$

For dissociation (1), wavelengths of 167 nm, 170 nm and 176 nm are needed for X=Cl, Br and I, respectively. These wavelengths are filtered in the upper atmosphere in the troposphere; therefore the tropospheric formation of $HgCH_3^+$ is not possible. For dissociation (2), radiations of 329 nm, 367 nm and 413 nm are needed for X=Cl, Br and I, respectively. In theory, it is thus possible to form $HgCH_3$ and X from Hg(0) and CH_3X in the presence of sunlight in the troposphere. This photodissociation is however in competition with the photoformation of HgX (3) for which wavelengths of 437 nm, 457 nm and 485 nm are needed for X=Cl, Br and I, respectively. Dissociations (2) and (3) are in competition, thus significantly reducing the formation of $HgCH_3$ from CH_3HgX.

3.2 Reactions of dimethylmercury formation from CH_3HgX

In this section, two possible pathways of dimethylmercury formation from CH_3HgX were studied. First, reactions between CH_3HgX and another molecule of CH_3X to form

CH_3HgCH_3 and X_2 were computed (Fig. 3). The geometries are analogous for the three halogens.

The reactions are found to be very endergonic (+58.4 kcal mol^{-1} for X=Cl, +45.8 kcal mol^{-1} for X=Br and +37.3 kcal mol^{-1} for X=I). This is due to an important bond energy difference between C−X and Hg−X bonds and the formed X−X and Hg−C bonds. CH_3HgCH_3 is not a particularly stable product, in agreement with experimental Hg−C bond dissociation energy (57 kcal mol^{-1}) (Handbook of Chemistry and Physics (89th edition), 2009). The free energy of reaction is higher when the atomic number decreases for the same reason as in the previous reaction. From a kinetic point of view, activation barriers are very high for the three halogens (+82.4 kcal mol^{-1} for X=Cl, +70.0 kcal mol^{-1} for X=Br and +61.2 kcal mol^{-1} for X=I). The structure of the transition state is a metathesis one where a X atom transfers from a methyl group to the X ligand of CH_3HgX. The geometrical configuration is very distorted since the methyl group and both X atoms are almost aligned, which is classical of d^0 metathesis reactions (Maron and Eisenstein, 2001). The electronic pattern of metathesis transition state is introduced (Fig. 4). The B center has to be positively charged in order to stabilize the transition state thanks to the charge alternation (Maron et al., 2003). In the present case, one of the halogen atoms has to be positively charged. Thus, it is natural that the transition states lie at high energies since halogen atoms are rather electronegative.

Geometrically, only the inactive Hg−CH_3 bond is still formed since it remains constant throughout the reaction. The remaining structure does not exhibit any fully formed chemical bond, like in the case of the transition state of the reaction between Hg(0) and CH_3X (Fig. 5). Indeed, X−X bonds are longer than in free molecules (2.04 Å for Cl_2, 2.32 Å for Br_2 and 2.80 Å for I_2), as well as the Hg−C bond (2.11 Å in CH_3HgCH_3) and the C−X bonds (introduced earlier).

From NBO analysis, it is noteworthy that the most negatively charged halogen is the one which is away from the metal. Thus, no electrostatic stabilization is found between this halogen and Hg. For X=Cl and X=Br, electrostatic repulsions are observable

between the two X atoms and between both CH_3X moieties. For X=I, the central halogen is positively charged, which brings slightly more stabilization, as can be seen from the energetic data (the activation barrier is lower for X=I). The C−X strength in CH_3X (as seen previously) is also important for the stabilization of the transition state when the atomic number of X increases.

Therefore, based on our calculations, this reaction is definitively not possible thermically and even photochemically, because thermodynamics push the reaction towards the formation of the reactants instead of the formation of the products.

Another reaction is conceivable in order to form dimethylmercury from CH_3HgX:

$$2CH_3HgX \longrightarrow CH_3HgCH_3 + HgX_2$$

This ligand exchange has already been observed between two CH_3ZnI complexes to form CH_3ZnCH_3 and ZnI_2, so it is interesting to know if this reaction is possible with CH_3HgI, since Hg and Zn are both group 12 transition metals. The reaction was investigated with the three halogens (Fig. 6) and their geometries are analogous.

Thermodynamically, the reaction is endergonic for the three halogens. This is due to the low stability of CH_3HgCH_3. Indeed, the variation of entropy is insignificant in this case and HgX_2 is a very stable molecule. Kinetically, barriers are rather high. Geometrically, the structure is a typical ligand exchange square pattern. The two inactive Hg−X and Hg−C bond lengths remain the same as in CH_3HgCH_3 and HgX_2. The distance between the two Hg atoms is quite small (2.92 Å for X=Cl, 2.90 Å for X=Br and 2.85 Å for X=I) and induces the destabilization of the transition state. Indeed, a strong electrostatic repulsion was found between the two positively charged metals (Table 1). This repulsion is lower when the atomic number of X increases because the electronegativity of X decreases, therefore the Hg atoms are less positively charged (Table 1). The barriers vary in the same way.

The reaction is found to be kinetically difficult and thermodynamically unfavorable. It is thus unexpected that any formation of CH_3HgCH_3 occurs from CH_3HgX.

3.3 Reactions between Hg(0) and the dimethylchlorinium ion

The reaction between Hg(0) and the dimethylchlorinium ion $CH_3ClCH_3^+$ was investigated because it is an interesting way to form $HgCH_3^+$ directly (Fig. 7).

The reaction consists of a CH_3^+ transfer from the ion to the mercury, in order to form CH_3Cl and $HgCH_3^+$. Thermodynamically, the reaction is found to be almost athermic since the systematic error of DFT is 5 kcal mol^{-1}. This is characteristic of a feasible reaction. The transition state structure is typical of a S_N2 nucleophilic substitution where the transferred methyl group is planar (Fig. 8). This is in agreement with the expected transfer of a CH_3^+ group.

The activation barrier is very low, because $CH_3ClCH_3^+$ is a very reactive species, which is known as a good CH_3^+ donor. The difficult oxidation of Hg(0) observed in the previous reactions with CH_3X is counterbalanced by the breaking of the weak Cl−C bond of the dimethylchlorinium ion. From a geometrical point of view, the transition state is intermediate between reactants and products. Indeed, the inactive Cl−C bond length is 1.82 Å, intermediate between the Cl−C ones in $CH_3ClCH_3^+$ (1.85 Å) and in CH_3Cl (1.80 Å). The other Cl−C bond length is elongated up to 2.34 Å. The Hg−C bond length is 2.54 Å whereas in $HgCH_3^+$ it is 2.16 Å. From NBO analysis, the Cl atom is less positively charged in the transition state (+0.19) than in the reactant (+0.50), which is very favorable since Cl is an electronegative element. Moreover, both the CH_3−Cl and Hg−C bonds are already formed. From the second-order donor-acceptor analysis, the 3p orbital of the Cl atom gives electronic density to the antibonding orbital of the Hg−C bond. This reaction is thus possible, even if it is not pushed towards the formation of the products. This is a demonstration of the importance of the nature of the methyl transfer agent. It has to be a reactive molecule that can transfer its methyl group to become more stable, like the dimethylchlorinium ion, in order to compensate for the difficulty of mercury oxidation. This seems easier when the transferred methyl group is planar and positively charged.

4 Conclusions

In this paper, theoretical studies were used for two different purposes. First, experimental results concerning the reaction of Hg(0) with CH_3I were rationalized. This reaction is predicted to be feasible, slightly exergonic, but with a high activation barrier. It is thus kinetically difficult, which is in agreement with its poor observation (Hall et al., 1995) and with the low rate observed experimentally (Celo et al., 2006; Maynard, 1932). Solar irradiation may accelerate the rate of the reaction, as observed by Hall et al. The second approach aims at gaining some insights into the chemical parameters which control the Hg(0) methylation. Some possible reactions of Hg(0) with different substrates in order to form $HgCH_3$ or $HgCH_3^+$ were investigated. The oxidation and methylation of Hg(0) are possible only if the methyl transfer agent is well suited. Indeed, reactions with CH_3X are globally athermic and kinetically difficult because of the high stability of these molecules. Moreover, the transfer of a neutral methyl group seems to be quite difficult. On the other hand, the reaction with the dimethylchlorinium ion $CH_3ClCH_3^+$ is thermodynamically feasible and kinetically easy. This is associated with the reactive nature of this molecule due to the weak Cl−C bond and with the transfer of a positively charged methyl group. Finally, the formation of dimethylmercury is not possible with CH_3X or another molecule of CH_3HgX. This is mainly due to electrostatic repulsions at the transition state level.

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References

AMAP/UNEP: Technical Background Report to the Global Atmospheric Mercury Assessment, Arctic Monitoring and Assessment Programme/UNEP Chemicals Branch, Oslo, 159, 2008.

Barkay, T. and Poulain, A. J.: Mercury (micro)biogeochemistry in polar environments, FEMS Microbiol. Ecol., 59, 232–241, 2007.

Becke, A. D.: A new mixing of Hartree-Fock and local density-functional theories, J. Chem. Phys., 98, 1372–1377, 1993.

Bergner, A., Dolg, M., Kuechle, W., Stoll, H., and Preuss, H.: Ab initio energy-adjusted pseudopotentials for elements of groups 13–17, Mol. Phys., 80, 1431–1441, 1993.

Castro, L., Dommergue, A., Ferrari, C., and Maron, L.: A DFT study of the reactions of O_3 with Hg° or Br^{-}, Atmos. Environ., 43, 5708–5711, doi:10.1016/j.atmosenv.2009.07.038, 2009.

Celo, V., Lean, D. R. S., and Scott, S. L.: Abiotic methylation of mercury in the aquatic environment, Sci. Total Environ., 368, 126–137, 2006.

Cerrati, G., Bernhard, M., and Weber, J. H.: Model reactions for abiotic mercury(II) methylation: kinetics of methylation of mercury(II) by mono-, di-, and tri-methyltin in seawater, Appl. Organomet. Chem., 6, 587–595, 1992.

Chemical Reviews: entire volume, 100, issue 2, 2000.

Chen, B., Wang, T., Yin, Y., He, B., and Jiang, G.: Methylation of inorganic mercury by methylcobalamin in aquatic systems, Appl. Organomet. Chem., 21, 462–467, 2007.

Cossa, D., Bernard, A., and Pirrone, N.: The origin of methylmercury in open Mediterranean waters, Limnol. Oceanogr., 54(3), 837–844, 2009.

Cox, M. L., Sturrock, G. A., Fraser, P. J., Siems, S. T., Krummel, P. B., and O'Doherty, S.: Regional sources of methyl chloride, chloroform and dichloromethane identified from AGAGE observations at Cape Grim, Tasmania, 1998–2000, J. Atmos. Chem., 45, 79–99, 2003.

Cox, M. L., Sturrock, G. A., Fraser, P. J., Siems, S. T., and Krummel, P. B.: Identification of regional sources of methyl bromide and methyl iodide from AGAGE observations at Cape Grim, Tasmania, J. Atmos. Chem., 50, 59–77, 2005.

Craig, P. J.: Organometallic Compounds in the Environment: Principles and Reactions, edited by: Longman, H., London, ISBN: 0582463610, 1986.

Ebinghaus, R. and Wilken, R. D.: Transformations of mercury species in the presence of Elbe river bacteria, Appl. Organomet. Chem., 7, 127–135, 1993.

Ehlers, A. W., Bohme, M., Dapprich, S., Gobbi, A., Hollwarth, A., Jonas, V., Kohler, K. F.,

Stegmann, R., Veldkamp, A., and Frenking, G.: A Set of F-polarization functions for pseudopotential basis-sets of the transition-metals Sc-Cu, Y-Ag and La-Au, Chem. Phys. Lett., 208, 111–114, 1993.

Falter, R. and Wilken, R.-D.: Isotope experiments for the determination of the abiotic mercury methylation potential of a River Rhine sediment, Vom Wasser, 90, 217–231, 1998.

Fitzgerald, W. F., Engstrom, D. R., Mason, R. P., and Nater, E. A.: The case for atmospheric mercury contamination in remote areas, Environ. Sci. Technol., 32, 1–7, 1998.

Fleming, E. J., Mack, E. E., Green, P. G., and Nelson, D. C.: Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium, Appl. Environ. Microb., 72, 457–464, doi:10.1128/aem.72.1.457-464.2006, 2006.

Gardfeldt, K., Munthe, J., Stromberg, D., and Lindqvist, O.: A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase, Sci. Total Environ., 304, 127–136, doi:10.1016/S0048-9697(02)00562-4, 2003.

Gaussian 03 (Revision D.02), Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. J. A., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J. A.: Gaussian, Inc., Wallingford CT, 2004.

Gilmour, C. C., Henry, E. A., and Mitchell, R.: Sulfate stimulation of mercury methylation in fresh-water sediments, Environ. Sci. Technol., 26, 2281–2287, 1992.

Hall, B., Bloom, N. S., and Munthe, J.: An experimental study of two potential methylation agents of mercury in the atmosphere: CH_3I and DMS, Water Air Soil Poll., 80, 337–341, 1995.

Hammerschmidt, C. R., Lamborg, C. H., and Fitzgerald, W. F.: Aqueous phase methylation as a potential source of methylmercury in wet deposition, Atmos. Environ., 41, 1663–1668, doi:10.1016/j.atomsenv.2006.10.032, 2007.

Hammond, G. S.: A Correlation of reaction rates, J. Am. Chem. Soc., 77, 334–338, doi:10.1021/ja01607a027, 1955.

Handbook of Chemistry and Physics (89th edition), edited by: Lide, D. R., CRC Press Inc., USA, 2009.

Hehre, W. J., Ditchfield, R., and Pople, J. A.: Self-consistent molecular orbital methods. XII. further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules, J. Chem. Phys., 56, 2257–2261, 1972.

Howell, G., Oconnor, M., Bond, A., Hudson, H., Hanna, P., and Strother, S.: Methylmercury generation in seawater by transmethylation reactions of organolead and organotin compounds with inorganic mercury as monitored by multinuclear magnetic-resonance and electrochemical techniques, Aust. J. Chem., 39, 1167–1175, doi:10.1071/CH9861167, 1986.

Hu, A., Otto, P., and Ladik, J.: Relativistic all-electron molecular Hartree-Fock-Dirac- (Gaunt) calculations on HgO, J. Mol. Struc-Theochem., 468, 163–169, 1999.

Jensen, S. and Jernelov, A.: Biological methylation of mercury in aquatic organisms, Nature, 223, 753–754, 1969.

Kaupp, M., Dolg, M., Stoll, H., and von Schnering, H. G.: Oxidation state +IV in Group 12 chemistry. Ab initio study of zinc(IV), cadmium(IV), and mercury(IV) fluorides, Inorg. Chem., 33, 2122–2131, doi:10.1021/ic00088a012, 1994.

Kawamura, K., Yanase, A., Eguchi, T., Mikami, T., and Barrie, L. A.: Enhanced atmospheric transport of soil derived organic matter in spring over the high Arctic, Geophys. Res. Lett., 23, 3735–3738, 1996.

Kuechle, W., Dolg, M., Stoll, H., and Preuss, H.: Ab initio pseudopotentials for mercury through radon. I. Parameter sets and atomic calculations, Mol. Phys., 74, 1245–1263, 1991.

Maron, L. and Eisenstein, O.: DFT Study of H−H Activation by Cp_2 LnH d^0 Complexes, J. Am. Chem. Soc., 123, 1036–1039, doi:10.1021/ja0033483, 2001.

Maron, L., Perrin, L., and Eisenstein, O.: CF_4 defluorination by Cp_2Ln−H: a DFT study, Dalton T., 4313–4318, doi:10.1039/b308433g, 2003.

Maron, L., Dommergue, A., Ferrari, C. P., Delacour-Larose, M., and Faïn, X.: How elementary mercury react in presence of halogen radicals and/or halogen anions: a DFT investigation, Chem.-Eur. J., 14, 8322–8329, 2008.

Maynard, J. L.: The action of mercury on organic iodides. I. the formation of

methylmercuric iodide and benzylmercuric iodide, J. Am. Chem. Soc., 54, 2108–2112, doi:10.1021/ja01344a065, 1932.

Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., and Donard, O. F. X.: Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea, Mar. Chem., 107, 49–63, 2007.

Nagase, H., Ose, Y., Sato, T., and Ishikawa, T.: Methylation of mercury by humic substances in an aquatic environment, Sci. Total Environ., 25, 133–142, 1982.

Nriagu, J. O.: A global assessment of natural sources of atmospheric trace metals, Nature, 338, 47–49, 1989.

Nriagu, J. O. and Pacyna, J. M. : Quantitative assessment of worldwide contamination of air, water and soils with trace metals, Nature, 333, 134–139, 1988.

Perdew, J. P. and Wang, Y.: Accurate and simple analytic representation of the electron-gas correlation-energy, Phys. Rev. B, 45, 13244–13249, 1992.

Reed, A. E., Curtiss, L. A., and Weinhold, F.: Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, Chem. Rev., 88, 899–926, 1988.

Schultz, N. E., Zhao, Y., and Truhlar, D. G.: Benchmarking approximate density functional theory for s/d excitation energies in 3d transition metal cations, J. Comput. Chem., 29, 185–189, 2008.

Shepler, B. C. and Peterson, K.: Mercury monoxide: a systematic investigation of its ground electronic state, J. Phys. Chem. A, 107, 1783–1787, 2003.

Siciliano, S. D., O'Driscoll, N. J., Tordon, R., Hill, J., Beauchamp, S., and Lean, D. R. S.: Abiotic production of methylmercury by solar radiation, Environ. Sci. Technol., 39, 1071–1077, doi:10.1021/es048707z, 2005.

Strömberg, D., Strömberg, A., and Wahlgren, U.: Relativistic quantum calculations on some mercury sulfide molecules, Water Air Soil Poll., 56, 681–695, 1991.

Tokos, J. J. S., Hall, B., Calhoun, J. A., and Prestbo, E. M.: Homogeneous gas–phase reaction of Hg° with H_2O_2, O_3, CH_3I, and $(CH_3)_2S$: implications for atmospheric Hg cycling, Atmos. Environ., 32, 823–827, 1998.

Tossell, J. A.: Calculation of the energetics for oxidation of gas-phase elemental Hg by Br and BrO, J. Phys. Chem. A, 107, 7804–7808, 2003.

Wagemann, R., Innes, S., and Richard, P. R.: Overview and regional and temporal differences of heavy metals in Arctic whales and ringed seals in the Canadian Arctic, Sci. Total Environ., 186, 41–66, 1996.

Weber, J. H.: Review of possible paths for abiotic methylation of mercury(II) in the aquatic environment, Chemosphere, 26, 2063–2077, 1993.

Woggon, H., Klein, S., Jehle, D., and Zydek, G.: Transformationsreaktionen ausgewählter Metalle in Organismen und in der Umwelt. 2. Mitt. Abiotische Methylierungsreaktionen von Quecksilber, insbesondere durch Methylzinn-Verbindungen und Humin- und Fulvinsäuren, Nahrung-Food, 28, 851–862, 1984.

Zhao, Y. and Truhlar, D. G.: Density functionals with broad applicability in chemistry, Accounts Chem. Res., 41, 157–167, doi:10.1021/ar700111a, 2008.

Table 1. Charges of mercury atoms in the transition state structures of the reaction between two CH_3HgX complexes, from a NBO analysis. Hg_1 is the Hg−X inactive bond, Hg_2 is the Hg−C inactive bond.

	Cl	Br	I
Hg_1	+0.79	+0.64	+0.42
Hg_2	+0.82	+0.79	+0.75

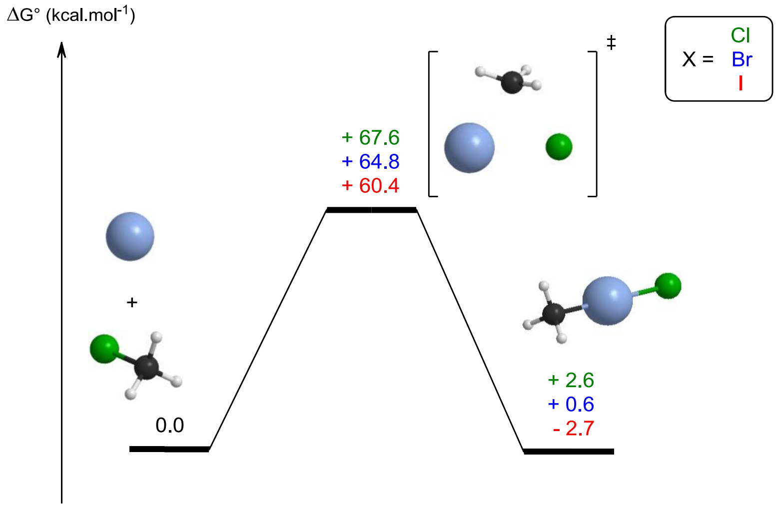

Fig. 1. Calculated Gibbs free energy profiles for the reaction of Hg(0) with CH_3X. The 3-D structures are the optimized structures for X=Cl.

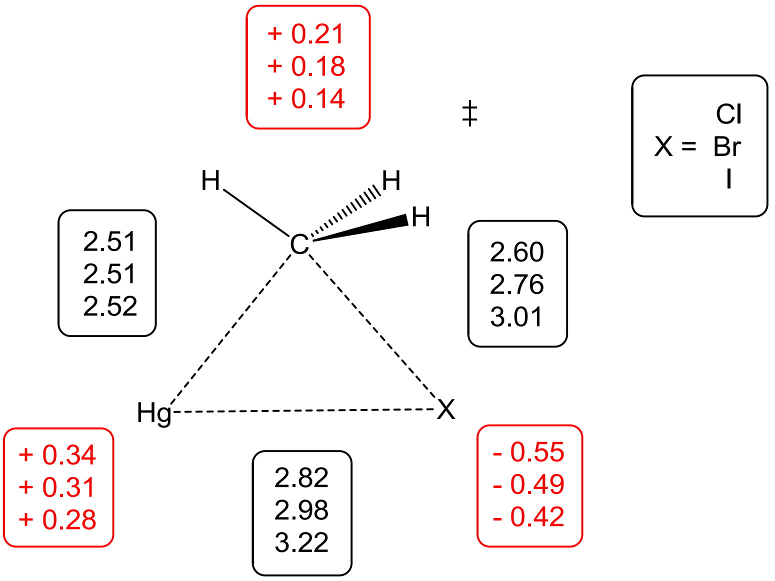

Fig. 2. Bond distances (black values) and charges (red values) at the transition state level of the reaction of Hg(0) with CH_3X.

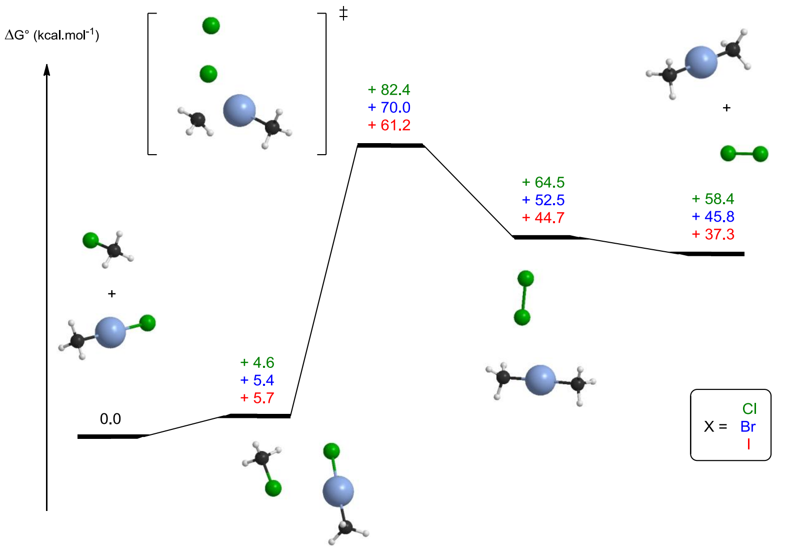

Fig. 3. Calculated Gibbs free energy profiles of the reaction of CH_3HgX with CH_3X. The 3-D structures are the optimized structures for X=Cl.

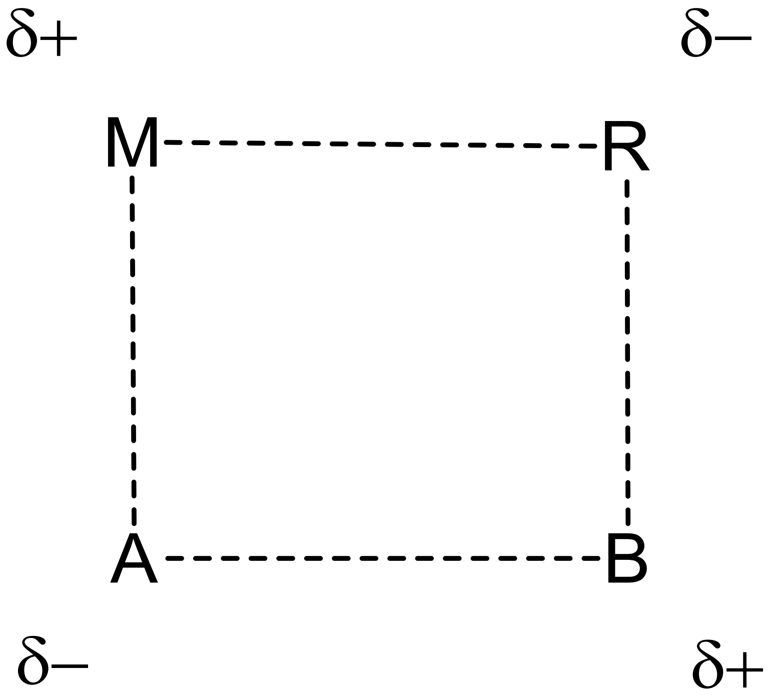

Fig. 4. Metathesis transition state pattern.

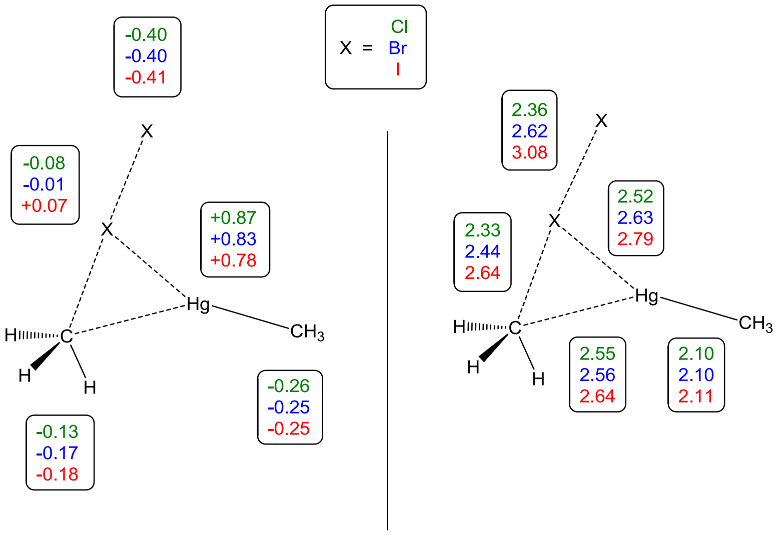

Fig. 5. Bond distances (right) and charges (left) at the transition state level of the reaction of CH_3HgX with CH_3X.

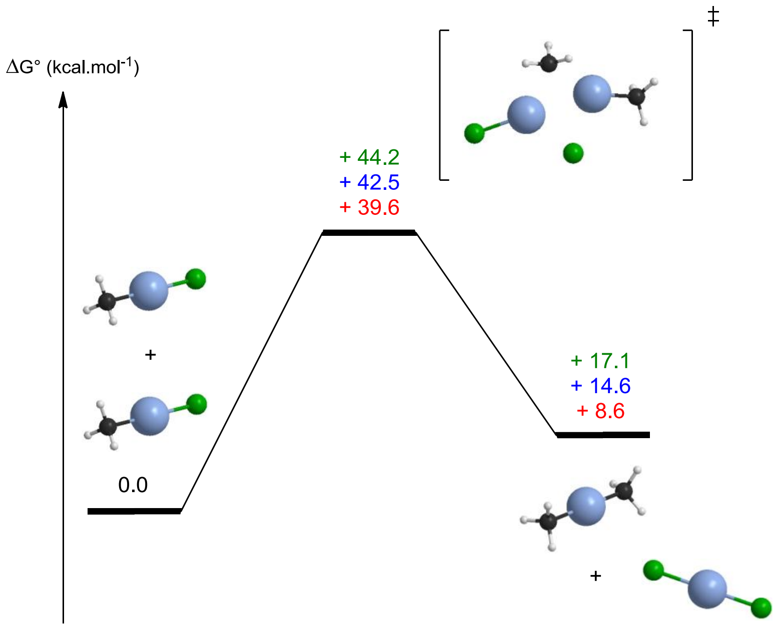

Fig. 6. Calculated Gibbs free energy profiles of the reaction between two CH_3HgX complexes. The 3-D structures are the optimized structures for X=Cl.

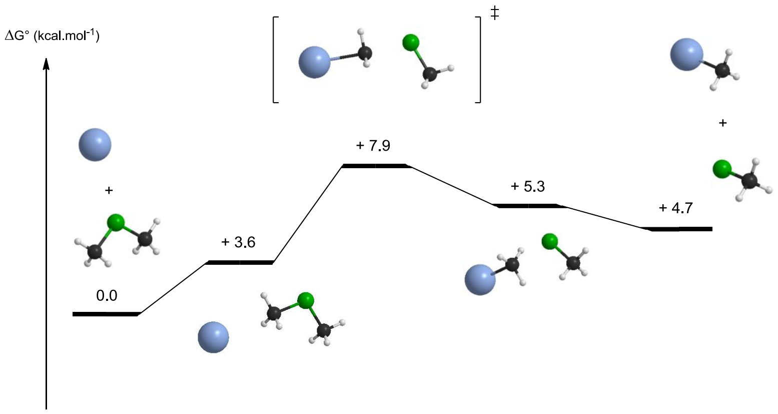

Fig. 7. Calculated Gibbs free energy profile of the reaction of Hg(0) with $CH_3ClCH_3^+$.

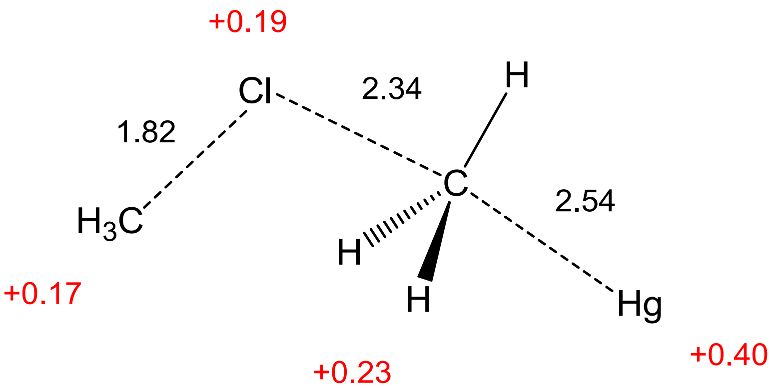

Fig. 8. Bond distances (black values) and charges (red values) at the transition state level of the reaction between Hg(0) and $CH_3ClCH_3^+$.