



# Atmospheric reactivity of $\text{CH}_3\text{I}$ and $\text{CH}_2\text{I}_2$ with OH radicals: A comparative study of the H- versus I-abstraction

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## ABSTRACT

Reactants, weak molecular complexes, transition states, and products for the H- and I-abstraction channels in the reactions  $\text{OH} + \text{CH}_3\text{I}$  and  $\text{OH} + \text{CH}_2\text{I}_2$  as well as the energy profiles at 0 and 298 K have been determined using high-level all-electron *ab initio* methods. The results showed that all-electron DK-CCSD(T)/ANO-RCC approach performed very well in predicting the reactivity of iodine. The energy profiles for the I-abstraction, in contrast to the H-abstractions, had the position of the transition states below the products. The H-abstractions were strongly exothermic ( $-80$  to  $-90$   $\text{kJ mol}^{-1}$ ), while the I-abstractions were modestly endothermic ( $20$ – $40$   $\text{kJ mol}^{-1}$ ). Based on our calculations with the ANO-RCC-L(1) basis set, we recommend the following values for the heats of formation at 298 K (in  $\text{kJ mol}^{-1}$ ): 218.6 ( $\text{CH}_2\text{I}$ ), 106.0 ( $\text{CH}_2\text{I}_2$ ), and 298.3 ( $\text{CHI}_2$ ).

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## 1. Introduction

The importance of iodine in the atmosphere is known for more than two decades [1–7]. Among the frequently discussed effects of atmospheric iodine are: (i) the ozone depletion in the lower stratosphere [5,6,8] due to the presence of IO and OIO species, (ii) the role of iodine compounds in new particle formation in marine environments [9–11], (iii) chemistry of halogens in troposphere through the interaction of iodine compounds with bromides and chlorides [12,13], (iv) its relevance to combustion. Iodine substitutes for halon fire extinguishers (like  $\text{CF}_3\text{I}$ ) have shorter atmospheric lifetimes and possess lower ozone depletion potentials for stratospheric ozone than the older fire extinguishing agents (e.g.,  $\text{CF}_3\text{Br}$  or  $\text{CF}_2\text{ClBr}$ ) [14].

Besides iodomethane ( $\text{CH}_3\text{I}$ ), several other organic compounds ( $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{ClI}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{C}_3\text{H}_7\text{I}$ ) have been detected in marine boundary layer in the coastal water or in open ocean [15]. Iodomethane and diiodomethane ( $\text{CH}_2\text{I}_2$ ) are produced by microalgae and phytoplankton in marine boundary layer and belong to the most

abundant and reactive alkyl iodides in the troposphere [13]. They participate in the generation of aerosols in coastal zones. While the former can persist from several hours to several days, the latter has shorter lifetime – from minutes to hours. In both cases, these time windows represent a potential for long distance atmospheric transport of iodine and the potential for chemical reactivity that can affect various atmospheric cycles, including ozone cycle. It is interesting that the possibility for vertical atmospheric transport of compounds produced at low tropospheric altitudes has been shown in the studies of deep convective clouds [16,17] and it demonstrates that alkyl iodides can reach within their lifetimes also lower stratosphere [5].

Alkyl iodides can undergo several decomposition pathways. For instance,  $\text{CH}_3\text{I}$  is easily photolyzed producing iodine atoms that enter ozone cycle or can react with NO,  $\text{HO}_2$ , ClO, BrO, or IO.  $\text{CH}_3\text{I}$  can abstract either H or I under attack of OH radicals, or Cl atoms, provided the concentration of the reactant radicals is high enough to compete with the photolysis. Alternatively, iodomethane can react with atomic oxygen producing IO,  $\text{I}_2\text{O}_2$  and other related compounds [13,18–20]. The abstraction of hydrogen and/or iodine atoms by hydroxyl radicals is conceivable also for  $\text{CH}_2\text{I}_2$ . The kinetics of the reactions involving atmospheric iodine has attracted attention of experimentalists and theoreticians because reliable molecular data serve as input for global geophysical simulation

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models [13,21]. Still holds the quotation of Davis and co-workers from 1996: "...several rate coefficients for gas phase processes need further investigating, as does the efficiency for removal of iodine due to aerosol scavenging processes" [4].

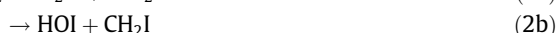
High-level *ab initio* molecular orbital studies offer a viable alternative to provide reliable thermodynamic and kinetic data for the gas-phase chemical reactions. Modelling H- or I-abstraction from alkyl iodides is rather demanding task because for predicting the kinetic parameters one has to reach at least the chemical accuracy of the underlying thermodynamic data (better than  $\pm 4$  kJ mol<sup>-1</sup>). This implies to choose the computational chemistry tools that include all necessary and accurate corrections to molecular energies [22,23] (basis set saturation, valence and core-valence electron correlation, relativistic effects, spin-adaptation, vibration contributions, and tunnelling corrections).

The reactivity of OH towards CH<sub>3</sub>I has been studied both experimentally [18–20,24] and theoretically [25] considering both the H- and I-abstraction channels:



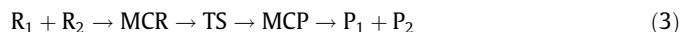
The experimental determinations of the kinetic parameters for the reaction of OH radicals with CH<sub>3</sub>I give unequivocally sound values of the rate constants. Their values are listed in Table 1. The theoretical calculations using Quadratic Configuration Interaction (QCISD(T)) in conjunction with the polarized split-valence basis set by Marshall et al. [25] lead to the rate constant at 298 K for the reaction (1a) of about  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This value is in good agreement with the literature data, as shown in Table 1. The QCISD(T) study also revealed that for the reaction (1b) there is no barrier beyond the endothermicity, i.e., the transition state for I-abstraction lies between the energies of the reactants and products.

The gas-phase reactivity of OH radicals with CH<sub>2</sub>I<sub>2</sub> has been studied very recently using the flash photolysis/resonance fluorescence technique [24]. The measured kinetic parameters are given also in Table 1. In this work, no information is provided concerning the observed products. In analogy with the reaction (1), one can consider the H- and I-abstraction channels for diiodomethane:



In this paper, we will report the results of *ab initio* calculations obtained for the H- and I-abstraction reactions of OH radical with iodomethane and diiodomethane. Typically, the potential energy surface for the bimolecular gas-phase abstraction reaction can be

simplified to the double-well energy profile with two minima corresponding to molecular complexes (MC<sub>R</sub> and MC<sub>P</sub>) separated by the transition state (TS) that can be schematically described as:



Special emphasis must be paid to the choice and validation of efficient theoretical methods that can provide a quantitative and balanced description of each stationary point on the potential energy surface of this process. Our aim is twofold: (i) to define the level of *ab initio* molecular orbital theory suitable for predicting the reactivity of CH<sub>3</sub>I whose kinetics are well known, and (ii) to apply this level of theory for the prediction of the reactivity of CH<sub>2</sub>I<sub>2</sub>. Both the H- and I-abstraction reactions of the OH radical with diiodomethane were not studied yet theoretically.

This article is organized as follows: computational methods are reported in Section 2, while the results are presented and discussed in Section 3.

## 2. Computational methods

In our calculations, we have adopted the following strategy. The stationary points on the reaction profile (reactants, molecular complexes (MC) and transition states (TS)) were determined using gradient optimizations with the second-order perturbation theory employing the Møller–Plesset partitioning of the Hamiltonian (MP2) [26,27]. We have used Dunning's triple-zeta correlation consistent basis set cc-pVTZ for light atoms [28] and Peterson's pseudo potential basis set of the same class on iodine [29] in the geometry optimizations. All optimizations were performed with the Gaussian03 program suite [30]. As usual, the frequency check provides the nature of the stationary point – one imaginary frequency indicating the TS. Special care was taken to determine Minimum Energy Pathways (MEPs), performing Intrinsic Reaction Coordinate analyses (IRC) [31,32] at the MP2/cc-pVTZ level of theory, in order to confirm that specific TS connects the different local minima. Vibrational frequencies and Zero-Point vibrational Energies (ZPE) were determined within the harmonic approximation, at the same level of theory as for geometries. The *ab initio* vibrational frequencies were multiplied by an appropriate scaling factor (0.95) [33].

Single-point energy calculations at all the stationary points of the reaction profile were performed using the Coupled Cluster theory including single, double and non-iterative triple substitutions (CCSD(T)) in the basis of canonical orbitals as implemented in the MOLCAS program package [34]. This very efficient parallel version of the CC-code is based on the Restricted Open-shell Hartree–Fock reference (ROHF). Since the CCSD procedure brings some spin contamination into the final wave function, we have used a simple spin-adaptation scheme of the dominant part of *T*<sub>2</sub> excitation

**Table 1**  
Experimental kinetic parameters for the reactions (1) and (2).

A (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> (kJ mol <sup>-1</sup> )	T (K)	k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Method	Ref.
OH + CH <sub>3</sub> I → products	9.3	298	0.99 × 10 <sup>-13</sup>	DF/RF <sup>a</sup>	[20]
		298	1.2 × 10 <sup>-13</sup>	Data analysis <sup>b</sup>	[19]
		271–423	0.72 × 10 <sup>-13</sup>	EB/RF <sup>c</sup>	[18]
		298			
5.37 × 10 <sup>-12</sup>	11.0	295–390	0.64 × 10 <sup>-13</sup>	FP/RF <sup>d</sup>	[24]
		298			
OH + CH <sub>2</sub> I <sub>2</sub> → products	5.7	295–390	4.5 × 10 <sup>-12</sup>	FP/RF <sup>d</sup>	[24]
		298			

<sup>a</sup> DF/RF = discharge flow/resonance fluorescence.

<sup>b</sup> The yield of OH was measured by laser induced fluorescence and the rate constant was derived from a fit to experimental data.

<sup>c</sup> EB/RF = electron beam/resonance fluorescence.

<sup>d</sup> FP/RF = flash photolysis/resonance fluorescence.

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