Computational studies of the reactions of CH₃I with H and OH

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Abstract

Transition states for attack by H and OH at the C-H and C-I bonds of CH₃I have been characterized at the Gaussian-2 level of theory. The results are employed in transition state theory analyses to obtain *ab initio* rate constants and product branching ratios. For the H reaction the major pathway is predicted to be I-atom abstraction, while for OH attack H-atom abstraction is faster than HOI formation. The rate constants agree well with measurements at around room temperature and are extrapolated to combustion conditions. The contributions of the title reactions to the flame chemistry of CH₃I are assessed.

Introduction

Interest has recently focused on the reaction kinetics of iodine-containing molecules in two contexts. Solomon et al. [1] proposed that tropical storms rapidly transport CH_3I to the lower stratosphere and argued for a role for iodine in catalytic ozone destruction at altitudes around 20 km in mid-latitudes. The major sources of CH_3I are suggested to be natural emissions from marine plankton and burning of terrestrial biomass [1]. Iodine chemistry is also relevant to combustion. Halon production is banned under the Montreal Protocols on Substances that Deplete the Ozone Layer and therefore there is a search for substitutes for the halon fire extinguishing agents CF_3Br and CF_2ClBr [2]. Potential candidates for some applications are compounds such as CF_3I , whose ozone depletion and global warming potentials are small because it possesses a short atmospheric lifetime [3]. A barrier to detailed understanding of the chemistry of iodine-mediated flame suppression is a lack of kinetic and product branching information for iodine reactions, especially at elevated temperatures. The present work describes the first *ab initio* analysis of the kinetics of the reactions

We focus on CH_3I , which is the simplest prototype compound containing a C-I bond. CH_3I formation in flames via $\text{CH}_3 + \text{I}$ recombination, followed by reaction 1b, contributes to the radical inhibition chemistry of CF_3I [4]. The transition state for 1b has been characterized previously by Schiesser et al. [5]. Our results are employed to derive high-temperature rate constants via transition state theory (TST) and branching ratios for H vs I abstraction. The data help clarify the contributions of channels 2a and 2b to the kinetic measurements of Brown et al. [6]. The potential energy surfaces (PES) for reactions 1 and 2 were analyzed with the Gaussian-2 theory of Pople and coworkers [7], which has been extended to iodine compounds by Glukhovtsev et al. [8]. The present kinetic results show good accord with the available data for reactions 1 and 2 near room temperature, and are employed to assess the relative contributions of possible pathways for CH_3I destruction in a stoichiometric CH_4/air flame.

Methodology

The general quantum chemistry methods are outlined elsewhere [9][10], and have been implemented with the GAUSSIAN 92 and 94 codes [11][12]. Computations were carried out on a SGI Power Challenge computer. The geometries and vibrational frequencies (scaled by a standard factor of 0.893 [13]) of the stationary points on the PES were initially obtained at the self-consistent field (Hartree-Fock) level using the 6-31G(d) atomic basis set. Minima and transition states were distinguished by the number of imaginary frequencies, 0 or 1, respectively. The stability of the wavefunction with respect to relaxation of internal constraints [14] was verified for each stationary point. Next, the geometries were refined with a partial correction for the effects of electron correlation by means of MP2/6-31G(d) theory. The moments of inertia and frequencies were employed to calculate the rate constant k via canonical TST as implemented in the POLYRATE program [15]:

$$k = \Gamma \frac{k_B T}{h} \frac{Q_{TS}}{Q_{\text{reactants}}} \exp\left(-\frac{E_0^\ddagger}{RT}\right) \quad (4)$$

Γ is a one-dimensional zero-curvature tunneling correction, the Q s are the partition functions, and $E_0^\ddagger$ is the enthalpy of the transition state (TS) relative to the reactants at 0 K. The latter term is derived from the G2 energies, which approximate QCISD(T)/6-311+G(3df,2p) results by a series of additive approximations [7] based on the MP4/6-311G(d,p) energy. These high-level energy calculations were carried out for iodine-containing species as detailed by Glukhovtsev et al. [8], and are all-electron frozen-core computations without effective core potentials.

Results and discussion

$\text{CH}_3\text{I} + \text{H}$

As a check on the accuracy of the G2 methodology we have computed $\Delta_f H_0$ for the C-H and C-I bond breaking reactions 1a and 1b. The results are -9.0 and -61.7 kJ mol⁻¹, in excellent accord with the experimental values of -5.3 ± 6.7 and -62.2 ± 0.9 kJ mol⁻¹ [16], and thus the thermochemistry of the C-H and C-I bonds is well-described at the G2 level.

Figure 1 illustrates the computed geometries of the TSs for reactions 1a and 1b at the HF/6-31G(d) and MP2/6-31G(d) levels of theory. The parameters for TS 1b are similar to those obtained by Schiesser et al. [5] who employed effective core potentials, except that they obtained a bent H-I-C group upon inclusion of electron correlation. Table 1 lists the TS frequencies and Table 2 lists the components of the G2 energies and the energy barriers for the two reaction pathways. The degree of spin contamination is indicated by deviations of $\langle S^2 \rangle$ from the ideal value of 0.75 for a pure doublet, and is largest for TS 1b and TS 2b. However, the QCI-based energies used here are only slightly affected by spin contamination. TST rate constants have been computed in two ways, first using HF frequencies and second using MP2 frequencies. Because MP2 overestimates the electron correlation effects neglected at the HF level the two rate constant calculations illustrate the range of uncertainty introduced via the frequencies. Both calculations employ the same fundamental classical barrier and MP2 geometries, but different vibrational partition functions and zero-point vibrational energies. The rate constants are plotted in Arrhenius form in Fig. 2. The results are consistent with the known bond strengths DH_{298} [16], where the weaker C-I bond ($DH_{298} = 239 \text{ kJ mol}^{-1}$) is much more reactive than the C-H bond ($DH_{298} = 431 \text{ kJ mol}^{-1}$). This is in accord with previous experimental studies which concluded or assumed that HI was the dominant product [17][18][19][20]. Figure 2 reveals good agreement between the *ab initio* and experimental k_{1b} values at room temperature, where the HF and MP2 rate constants bracket the experimental values. Most of the difference between the two sets of results arises from the different frequencies computed for the doubly-degenerate loose C-I-H bending mode in the TS. The geometric mean of the two TST approaches is a compromise between neglect and overestimation of the influence of electron correlation on the vibrational frequencies and yields a rate expression which fits the experimental data well. A key piece of information for combustion modeling is this first TST extrapolation of k_{1b} to elevated temperatures, which is summarized in Table 3 along with the estimated branching ratio for the minor CH_2I production channel.

CH₃I + OH

The TS structures for attack by the OH radical at the H and I atoms are shown in Fig. 1. In the latter case no barrier beyond the endothermicity was discernable on the HF/6-31G(d) PES

and a TS could be located only at the MP2/6-31G(d) level of theory. G2 analysis revealed that the energy of this apparent TS in fact lies *between* the energies of the reagents and products, which is consistent with the idea that there is no barrier to reaction 2b beyond the endothermicity. This is confirmed by the QCISD(T)/6-311G(d,p) energies calculated at selected points along the MP2/6-31G(d) intrinsic reaction coordinate (IRC), and plotted in Fig. 3. The energy is below that of HOI + CH₃ at all points. A distinct TS therefore cannot be localized and canonical TST cannot be applied. For this channel k_{2b} was roughly estimated via the relation $k = A \exp(-E_a/RT)$ by assuming a preexponential factor $A = 1 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, equal to that measured for CF₃I + OH [21], and an activation energy $E_a = 23 \text{ kJ mol}^{-1}$. This is equal to the endothermicity at 298 K based on $\text{DH}_{298}(\text{HO-I}) = 216 \text{ kJ mol}^{-1}$ [21]. Strictly this is an upper bound and any variational effects on the fairly flat IRC of Fig. 3 would tend to lower k_{2b} .

Visualization of the normal modes of the H-abstraction TS, 2a, showed that the lowest frequency mode is predominantly internal rotation of the OH group. Analysis by the method of Truhlar [22] using HF and MP2 data yielded reduced moments of inertia of 4.33 and $9.77 \times 10^{-46} \text{ kg m}^2$, respectively, which were employed in the TST calculations. Figure 4 shows that, unlike in the previous system, the more reactive bond is the stronger C-H bond and that CH₂I + H₂O formation, the more exothermic channel, is expected to dominate at all temperatures. A check on the reliability of the kinetic calculations is the comparison with the measurements of the total removal rate constant $k_2 = k_{2a} + k_{2b}$ by Brown et al. [6]. They are seen to be in excellent agreement, as is the room temperature k_2 value obtained by Gilles et al. [20]. Again, the geometric mean of the HF and MP2-based TST results gives the best accord with experiment and provides a TST extrapolation of these measurements to combustion conditions (Table 3). This extrapolation at 2000 K is about 25 times greater than the value obtained from a simple linear Arrhenius extrapolation of the data of Brown et al. [6], which reflects the significant curvature of the TST Arrhenius plot. This predicted curvature is similar to that measured for the analogous reaction of OH with CH₄ [23]. The TST analysis also indicates that HOI formation by OH attack on CH₃I is of only minor importance in both flames and the atmosphere.

Combustion implications

Comparison of the rate constants for reactions 1, 2 and

for which $k_3 = 1.0 \times 10^{-11} \exp(+170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [20] shows that, even in low-temperature regions of a flame, attack by H and O atoms on CH_3I is rapid with rate constants that are close to gas kinetic. The major pathway for both processes involves C-I bond cleavage. At higher temperatures OH attack also becomes rapid.

In order to assess the importance of these processes more quantitatively we compare the effective first-order loss rates of CH_3I (the reciprocal of the lifetimes) via reactions 1-3 and unimolecular decomposition in the low-pressure limit

for which $k_4 = 4.2 \times 10^{-9} \exp(-21420/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24]. An adiabatic premixed stoichiometric CH_4/air flame at atmospheric pressure was modeled with CHEMKIN [25] using the GRI-Mech mechanism [26]. The results apply to trace quantities of CH_3I (i.e. the C/H/O chemistry was assumed to be unaffected). Of course at fixed pressure the rate of unimolecular decomposition depends only on the temperature, while the rates of the bimolecular steps depend both on the temperature and the radical concentrations. To evaluate k_4 we set $[\text{Ar}]$ equal to the total density; this neglects the effects of alternative collision partners which may be more effective than Ar so that the rate of reaction 4 is slightly underestimated for the flame. As may be seen from Fig. 5, the dominant removal pathway is via H-atom attack, because $[\text{H}] > [\text{O}]$. The next most important removal pathway, about an order of magnitude less effective than reaction 1, is attack by OH. Thus CH_2I will be a minor product of CH_3I decay, with HI as the dominant product. Above 900 K, unimolecular decay and O-atom attack are of comparable importance, although both are slower than reaction 2.

Conclusions

Ab initio data have been employed to derive rate expressions for the reactions of CH_3I with H and OH radicals, and to show that major products of H-atom attack are $\text{HI} + \text{CH}_3$, whereas OH attack yields predominantly $\text{H}_2\text{O} + \text{CH}_2\text{I}$. Where the rate expressions can be

compared with experimental results, theory is in good accord and provides a means to extrapolate limited-temperature information over wider temperature ranges. This shows that *ab initio* calculation of rate constants is sufficiently accurate to survey a wide range of possible steps in combustion mechanisms, in order to help limit the number of processes to be included in combustion models and to aid in the identification of key reactions that merit more detailed laboratory study. For example, in a stoichiometric CH₄/air flame the fastest path for CH₃I destruction is shown to be via H-atom attack, followed by OH attack, with lesser roles for O-atom attack and unimolecular decomposition.

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Table 1. Transition state frequencies, in cm^{-1} .^a

TS for reaction 1a		TS for reaction 1b		TS for reaction 2a		TS for reaction 2b
HF	MP2	HF	MP2	HF	MP2	MP2 ^b
2100 i	1822 i	790 i	916 i	3011 i	2348 i	268 i
287	293	196	67	59	49	40
523	544	196	67	97	130	142
526	568	405	608	316	306	173
889	930	738	777	454	514	575
922	951	738	777	555	633	593
1169	1195	1144	1201	688	796	714
1181	1196	1414	1453	858	941	984
1336	1393	1414	1453	1046	1036	1069
1384	1773	2933	3060	1092	1257	1425
2967	3091	3062	3203	1356	1402	1443
3069	3208	3062	3203	1429	1449	3067
				2969	3089	3222
				3070	3190	3244
				3605	3591	3614

^aHF/6-31G(d) values scaled by 0.8929 and MP2=FULL/6-31G(d) values scaled by 0.9646.

^bNo TS at the HF/6-31G(d) level of theory.

Table 2. Absolute G2 energies of transition states for CH₃I reactions.

Reaction	MP4/6-311G(d,p) ^a	$\langle S^2 \rangle^b$	$\Delta E(+)^c$	$\Delta E(2df)^c$	$\Delta E(QCI)^c$	$\Delta E(ZPE)^{c,d}$	Δ°	$E_0(G2)^a$	$E_0^\ddagger{}^e$
1a	-6957.21128	0.792	-1.42	-65.06	-3.05	+32.47	-27.39	-6957.31092	50.1
1b	-6957.22601	0.874	-1.56	-66.99	-5.46	+34.85	-28.13	-6957.32847	4.0
2a	-7032.30952	0.785	-9.64	-102.74	-4.27	+40.08	-31.72	-7032.46799	15.5
2b	-7032.29596	0.886	-11.89	-114.23	-5.93	+46.26 ^f	-32.21	-7032.46415	25.6

^aIn au. 1 au $\approx$ 2625 kJ mol⁻¹. The G2 energy is $E_0(G2) = E(\text{MP4/6-311G(d,p)}) + \Delta E(+) + \Delta E(2df) + \Delta E(QCI) + \Delta E(\text{HLC}) + \Delta E(\text{ZPE}) + \Delta + 0.00114 \eta_{\text{pair}}$ au, where the individual terms are defined in ref. 7.

^bFor the HF/6-311G(d,p) wavefunction.

^cComponent of G2 energy in 10⁻³ au.

^dBased on HF/6-311G(d) frequencies.

^eG2 enthalpy relative to reagents at 0 K, in kJ mol⁻¹.

^fMP2/6-31G(d) frequencies used.

Table 3: Computed rate constants and product branching ratios for CH₃I reactions.

Reactants	Major products	Minor products	Overall rate constant, cm ³ molecule ⁻¹ s ⁻¹ ^a			Minor product branching ratio		
			A	n	B	A	n	B
H + CH ₃ I	CH ₃ + HI	CH ₂ I + H ₂	2.14e-15	1.66	300	5.86e-02	0.24	5210 ^b
OH + CH ₃ I	CH ₂ I + H ₂ O	CH ₃ + HOI	2.72e-24	3.97	-450	3.68e+12	-3.97	3220

^aIn the form $A T^n \exp(-B/T)$ for $T = 250$ - 2500 K.

^bFor $T = 400$ - 2500 K.

Figure captions

Fig. 1 Geometries of transition states computed at the HF/6-31G(d) and in parentheses MP2/6-31G(d) levels of theory. Distances in Å and angles in degrees. (1a) $\text{CH}_3\text{I} + \text{H} \rightarrow \text{CH}_2\text{I} + \text{H}_2$; (1b) $\text{CH}_3\text{I} + \text{H} \rightarrow \text{CH}_3 + \text{HI}$; (2a) $\text{CH}_3\text{I} + \text{OH} \rightarrow \text{CH}_2\text{I} + \text{H}_2\text{O}$; (2b) $\text{CH}_3\text{I} + \text{OH} \rightarrow \text{CH}_3 + \text{HOI}$.

Fig. 2 Comparison of rate constants for $\text{H} + \text{CH}_3\text{I}$. For the two product channels TST with MP2 frequencies yields the solid line and HF frequencies yield the dashed line. The points are experimental data: ($\blacktriangle$) Leipunskii et al. [17], ($\bullet$) Levy et al. [18], ($\square$) Sillesen et al. [19] and ($\circ$) Gilles et al. [20].

Fig. 3 Evaluation of QCISD(T)/6-311G(d,p) energies along the MP2/6-31G(d) reaction coordinate for $\text{OH} + \text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{HOI}$.

Fig. 4 Comparison of rate constants for $\text{OH} + \text{CH}_3\text{I}$. For $\text{CH}_2\text{I} + \text{H}_2\text{O}$ formation TST with MP2 frequencies yields the solid line and HF frequencies yield the dashed line. The solid line for $\text{CH}_3 + \text{HOI}$ shows an empirical estimate. The points are measurements of total OH loss: ($\blacksquare$) Brown et al. [6] and ($\bullet$) Gilles et al. [20].

Fig. 5 Reciprocal lifetimes for traces of CH_3I in an adiabatic premixed stoichiometric CH_4/air flame at atmospheric pressure with respect to unimolecular decomposition and attack by H, O and OH (solid lines, left axis), and the temperature profile (dashed line, right axis).