**Special Issue**

Journal of Physical Organic Chemistry

Received: 11 December 2007, Revised: 27 March 2008, Accepted: 15 April 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1393

# Low-pressure rate coefficients of the reaction of $O(^3P)$ with $CF_3I$ and $CH_3I$

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**Absolute rate coefficients for the gas-phase reactions of $CF_3I$ and $CH_3I$ with $O(^3P)$ atoms were measured at 298 K by the discharge flow technique coupled to resonance fluorescence to monitor $O(^3P)$ atoms. This is the first kinetic study for these reactions under low-pressure conditions (1.56–3.26 Torr). The overall rate coefficients were $(5.2 \pm 0.7) \times 10^{-12}$ and $(2.3 \pm 0.3) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. The experiments were carried out under pseudo-first-order conditions with $[O(^3P)]_0 \ll [RI]_0$.**

**The results are compared with previous measurements using different experimental techniques at higher pressures. Free energy relationships and atmospheric implications are discussed. Copyright © 2008 John Wiley & Sons, Ltd.**

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**Keywords:** ground state oxygen atom; alkyl iodides; rate coefficients; discharge flow system; gas-phase

## INTRODUCTION

Photolysis of biogenic alkyl iodides is the main source of iodine atoms in the marine boundary layer. Since these compounds have a short life time in respect to photolysis, they can be destroyed through the absorption of visible light, producing I atoms that react fast with $O_3$ to form IO radicals.[1] This reduces the tropospheric ozone budget in some regions of high IO concentration.

On the other hand, the existence of an injection mechanism of hydrocarbons to the upper troposphere and the lower stratosphere by convective transport assisted by clouds has been suggested.[2] The alkyl iodides can be photolysed and generate alkyl radicals and free iodine atoms. The latter can participate in catalytic destructive ozone cycles, which are more effective than those involving bromine and chlorine atoms.[3–4] Due to the strong potential of IO*x* chemistry for destruction of ozone on the troposphere and the lower stratosphere, a better understanding of $I/O_3$ interactions and all other reactions that involve iodine compounds as sources and sinks is necessary in order to evaluate the impact of the emissions on atmospheric chemistry. Therefore, the development and application of modern, more precise and sensitive techniques to determine products and kinetic parameters is required.

The metabolic processes of macroalgae and phytoplankton are the major source of $CH_3I$ released from the ocean to the atmosphere. $CF_3I$ is an anthropogenic alkyl iodide with a potential importance in atmospheric chemistry, since it is used as a replacement for $CF_3Br$ as a fire-extinguishing agent.[5]

The reactions of $O(^3P)$ with alkyl iodides such as $CF_3I$ and $CH_3I$ have been studied in the last years mainly with the pulsed laser photolysis (PLP) method coupled with laser induced fluorescence (LIF) detection of IO nascent radicals, resonance fluorescence (RF) of $O(^3P)$ atoms and cavity ring down (CRD) detection techniques.[6–12] However, there exist no data of the rate constants for these reactions using the discharge flow (DF) method at low-pressure conditions (1–10 Torr).

In this work, rate constants for the reactions $CF_3I + O(^3P)$ and $CH_3I + O(^3P)$ applying the discharge flow–resonance fluorescence technique (DF–RF) are reported. This is the first determination of the rate constant for the reactions cited above at 298 K measured by DF–RF at low-pressure conditions (1.56–3.26 Torr). The present results are in good agreement with previous results obtained by different experimental techniques at higher pressures. Linear free energy relationships and atmospheric implications are discussed.

## EXPERIMENTAL

The experiments were conducted in a newly commissioned discharge flow system with atomic resonance fluorescence (DF–RF) to monitor the oxygen atom concentration.

The schematic diagram of the discharge flow tube apparatus employed in this work is shown in Fig. 1. Briefly, the reactor consisted of a Pyrex tube (95 and 3.2 cm i.d.) coupled with a sliding injector (1.9 cm i.d.).

Oxygen atoms were generated by passing a microwave discharge (30 W, 2.5 GHz) through a dilute flow of $O_2$ in helium and introduced in the flow tube by a sliding Pyrex injector. The

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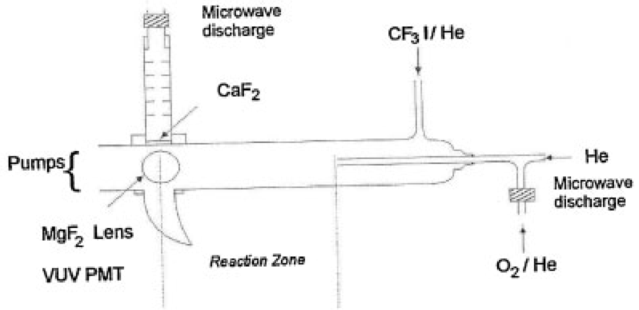

**Figure 1.** Schematic diagram of the discharge flow resonance fluorescence apparatus used in the study of the reaction between O($^3$P) atoms with CF$_3$I and CH$_3$I at 298 K

initial O atom concentration was determined by adding known amounts of I$_2$ or NO$_2$ to the reactor and monitoring the change in O($^3$P) signal, and ranged from 2.6 to 5.1 × 10$^{10}$ atom cm$^{-3}$. This method presumes that the reaction goes to completion (i.e. all I$_2$/NO$_2$ or all O($^3$P) reacted), which is valid for these fast reactions with $k(\mathrm{O}(^3\mathrm{P}) + \mathrm{I}_2) = 1.4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k(\mathrm{O}(^3\mathrm{P}) + \mathrm{NO}_2) = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[13] CF$_3$I and CH$_3$I (diluted in He) were introduced into the flow tube via a fixed side-arm port at the upstream end of the flow tube.

The total pressure (He) from 1.56 to 3.26 Torr was monitored by a 10 Torr capacitance manometer; flow rates of between 1000 and 3000 SCCM were established with calibrated mass flow controllers. Reaction times could be varied by adjusting the distance of the sliding injector with respect to the position of the photomultiplier tube detector (PMT) from 8 to 43 cm in combination with linear velocities of between 13 and 16 m s$^{-1}$ and assuming plug-flow conditions. This resulted in contact times in the range of 6–32 ms.

The laminar flow (with a Reynolds number always <50) and plug-flow conditions thus established in the flow tube allowed us to follow the reaction kinetics of the O($^3$P) in the presence of a known excess of RI, and thus to assume the pseudo-first-order approximation.[14–15]

The concentration of O($^3$P) was monitored by atomic RF. To minimize the detection of H atoms while detecting O, a calcium fluoride window was placed in front of the PMT. The CaF$_2$ window absorbed any Lyman-α radiation at 121.6 nm without significantly changing the detection sensitivity for O. In order to prevent absorption by oxygen, the volume between the resonance lamp, the PMT and the cell, was flushed with N$_2$. The sensitivity for detection of O atoms was better than 2 × 10$^9$ atoms cm$^{-3}$ for 1 s integration time. The output signal *S* of the detector, proportional to the light intensity, was amplified and captured in a boxcar integrator whose output was digitized and recorded by a PC. In all experiments the background signal obtained when [O$_2$] = [RI] = 0, arising from scattered signal light in the reaction tube, was subtracted from *S* before further analysis. In order to assess wall losses of O atoms, several experiments were carried out in which the RF signal in the absence of added RI was determined while O atoms at different contact times were introduced. The measured values of $k_w$ were always <10 s$^{-1}$ indicating therefore that no coating was required.

The commercial gases used in this study had the following stated minimum purity: NO$_2$ (Aldrich 99.5%), NO (Matheson 99.5%), O$_2$ (Linde 99.999%), Helium (Linde 99.999%), N$_2$ (99.999%), CF$_3$I (ABCR GmbHg 99%), and CH$_3$I (Aldrich 99%). Nitric oxide was purified by being passed through a trap held at 153 K to remove traces of NO$_2$ and other higher oxides. The true concentration of NO$_2$ was found by correcting for the equilibrium with a N$_2$O$_4$. Helium was flown through a cold trap to remove water. CF$_3$I and CH$_3$I were vacuum distilled before use and their purity was checked optically at 450–610 nm via absorption measurements, especially for I$_2$ impurities (<0.01% for CF$_3$I and <0.001% for CH$_3$I), which react very fast with O atoms (1.4 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).[13] Oxygen was used as a supplier.

## RESULTS

With the DF–RF technique, the rate constants for the following reactions at 298 K were obtained:

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{CF_3I} \rightarrow \text{products} \tag{1}$$

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{CH_3I} \rightarrow \text{products} \tag{2}$$

Absolute reaction rate coefficients for the reactions (1) and (2) were determined as described below. All experiments were carried out under pseudo-first-order conditions with a ratio, [RI]$_o$/[O($^3$P)]$_o$, >30–300, with RI = CF$_3$I or CH$_3$I. Therefore, under these conditions and in the absence of secondary reactions that significantly deplete the transient O($^3$P) atoms, [O($^3$P)] should obey the following expressions:

$$[\mathrm{O}(^3\mathrm{P})]_t = [\mathrm{O}(^3\mathrm{P})]_o \exp[-(k[\mathrm{RI}]_o + k_x)t] \tag{I}$$

$$\ln[\mathrm{O}(^3\mathrm{P})]_t = -k't + \ln[\mathrm{O}(^3\mathrm{P})]_0 \tag{II}$$

where [O($^3$P)]$_o$ is the concentration in the absence of RI and [O($^3$P)]$_t$ is the concentration after reaction with RI over time *t*, $k'$ is the measured pseudo-first-order rate coefficient and $k_x$ is the first-order rate coefficient for O($^3$P) atoms disappearance by diffusion out of the detection zone, reaction with background impurities or wall losses.

It can be shown that the intensity *S* of the O RF signal is proportional to the O concentration; therefore the intensity of the RF signal at selected points down the tube is a relative measure of [O($^3$P)].

The first-order kinetic analysis is based on the ratio ln($S_o$/$S_t$), which is applicable to our system. $S_o$ is the signal without reactant and $S_t$ is the signal after addition of reactant at a fixed contact time.

Taking into account the above considerations and Eqn (II), it is possible to write:

$$\ln S_t = -k[\mathrm{RI}]_0 t + \ln S_0 \tag{III}$$

The pseudo-first-order decay rate coefficient $k'$ was computed from the slope of a plot of ln $S_t$ *vs.* time of contact which was linear for approximately three lifetimes (Figs. 2 and 3). The second-order rate coefficient for reactions (1) and (2), $k_1$ and $k_2$ were obtained from the slope of the line of a plot of $k'$ *vs.* [RI] (Figs. 4 and 5). A linear least-squares fit to the data points yield a value of $k_1 = (5.2 \pm 0.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_1 = (2.3 \pm 0.3) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. These values of the rate constant for reactions (1) and (2) were further corrected for axial and radial diffusion through the following approximate expression:[14]

$$k_{\mathrm{corr}} = k_{\mathrm{exp}}(1 + k_{\mathrm{exp}} D/v^2 + k_{\mathrm{exp}} R^2/48D) \tag{IV}$$

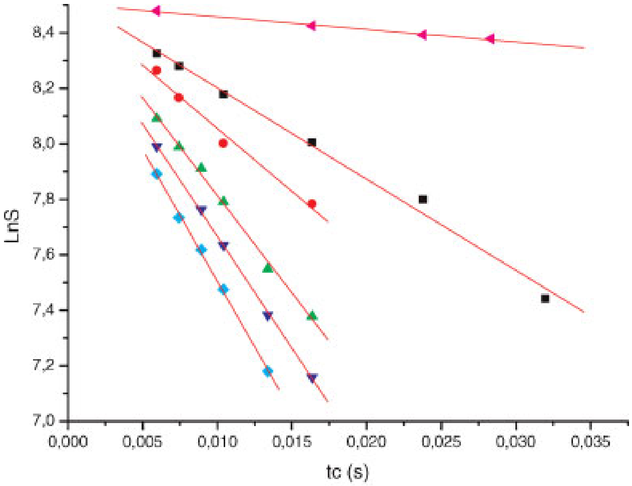

**Figure 2.** Typical pseudo-first-order plot for the reaction of O($^3$P) with $CH_3I$ at 298 K at different concentrations of $CH_3I$

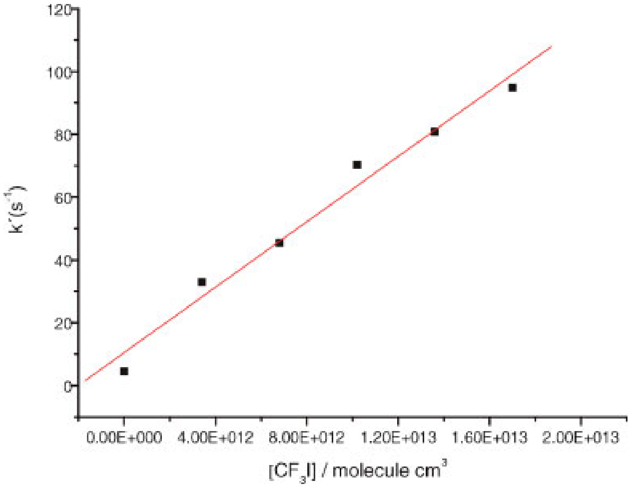

**Figure 4.** Second-order plot for the reaction of O($^3$P) with $CF_3I$ at 298 K

where *D* is the diffusion coefficient (in units of $cm^2 s^{-1}$) of O($^3$P) in He, *v* is the linear flow velocity ($cm s^{-1}$), and *R* is tube radius (cm). Correction values calculated for our experimental conditions of linear flow velocities and pressures were $<0.08\%$ for axial diffusion, and $<3\%$ for radial diffusion. Hence, we can assume that there are no concentration gradients and that the flow velocity is the transport velocity of the reactants.

The influence of secondary reactions should be considered for the reactions (1) and (2) in a flow tube due to the high reactivity of O($^3$P) atoms with the major reaction product, IO radical. This could be overcome by using considerable high $CF_3I$/O($^3$P) and $CH_3I$/O($^3$P) ratios. However, in the discharge flow tube, the lowest usable O($^3$P) concentrations were restricted by the detection limit, whereas maximum observable decay rates (e.g. maximum rates that allow mixing and sufficient spatial resolution) restricted the maximum value of [RI]. Initial experiments of reaction (1) revealed a significantly higher value ($>6 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$) of the rate coefficient $k_1$ than those obtained in the literature, and also a dependence on the concentration of O($^3$P), providing strong indications of secondary processes removing O($^3$P). For this reason, $\sim 4 \times 10^{13}$ molecules $cm^{-3}$ of NO was added through a side-arm port to the flow tube. NO undergoes rapid reaction ($\tau_{1/2} \sim 1$ ms) with IO to convert it to $NO_2$, but does not react significantly with O($^3$P) at the low pressures of these experiments. The lifetime $\tau$ was calculated from the evaluated rate coefficient for the reaction of IO with NO[13] and, under typical experimental conditions, it is at least 10 times shorter than that of O($^3$P) due to reaction with $CF_3I$.

$$IO + NO \rightarrow NO_2 + I \tag{3}$$

Although the product of this reaction, $NO_2$, can also react with O($^3$P), the ratio $k(O(^3P) + NO_2/k(O(^3P) + IO)$ is about 0.1,[13] implying that addition of NO should reduce the overall rate coefficient if O($^3$P) + IO reaction.

The addition of NO at concentrations listed above did indeed result in a decrease in the decay rate of O($^3$P) for a given concentration of $CF_3I$, confirming the presence of secondary loss processes for O($^3$P). We note that the addition of NO reduces the contribution of secondary reactions of O($^3$P), but does not remove them completely as O($^3$P) also reacts with $NO_2$ formed in

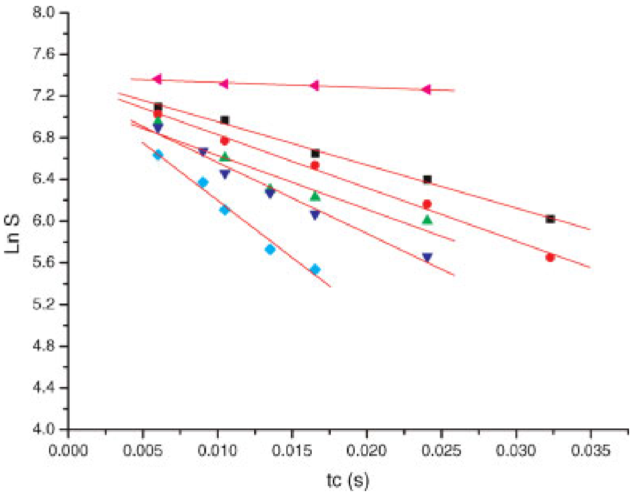

**Figure 3.** Typical pseudo-first-order plot for the reaction of O($^3$P) with $CF_3I$ at 298 K at different concentrations of $CF_3I$

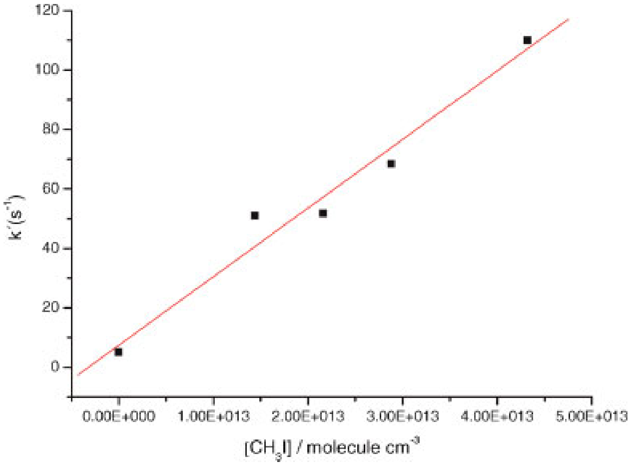

**Figure 5.** Second-order plot for the reaction of O($^3$P) with $CH_3I$ at 298 K

reaction (3). The rate coefficients obtained by this method should be regarded as an upper limit.

The precision of the individually measured second-order rate coefficient $k_1$ may be derived from the standard propagation of random error analysis of the various flow tube parameters that determine $k_1$.[14] Using the estimated percentage errors for the measurements of the He gas flow rate (<0.2%), $[\mathrm{RI}]_o$ (<2%), temperature (<0.1%), pressure (<0.02%), flow tube radius (1.6%) and the slope of the pseudo-first-order decay plot (<3.8%), we arrive at lower than 13% the resulting uncertainty in the values of $k_1$ and $k_2$. Consideration of possible systematic errors in calibration and measurements gives an estimated accuracy in the range 13–20%.

The pressure of the reactor for the $CF_3I + O(^3P)$ experiments was changed from 1.6 to 3.2 Torr and no variation in the global rate constant was observed.

In order to check the performance of our flow system to achieve reliable results, we also measured the overall rate constant for the reaction of $NO_2$ with $O(^3P)$, in which a value of $(9.7 \pm 0.2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was obtained in excellent agreement with the present evaluations $(1.0 \pm 0.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[13]

## DISCUSSION

The results presented in this work are compared in Table 1 with values previously reported.

It is shown that the rate constants for the reactions (1) and (2) determined in this work at 298 K are in good agreement, within the experimental error, with most of the previous values from the literature.[6–12]

### $CF_3I + O(^3P) \rightarrow$ products

In a previous study, we determined the rate constants of the reactions of $O(^3P)$ atoms with selected alkyl iodides, including $CF_3I$ and $CH_3I$. For this, we used the PLP–RF method between 223 and 363 K.[9]

The value obtained in the present work of $k_1 = (5.2 \pm 0.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is around 20% high than that reported value using the PLP–RF method of $(4.25 \pm 0.26) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The same difference can be observed when comparing our results with the rate constant determined by Gilles *et al.*[7] by PLP–RF and PLP–LIF systems.

However, Hölscher *et al.* using a PLP system coupled with LIF of the nascent IO radicals formed,[6] obtained a value of $(5.30 \pm 0.25) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in excellent agreement with the rate constant reported here.

Dillon and Heard[8] determined the rate constant of the reaction of O atoms with $CF_3I$ through the PLP system monitoring the LIF signal of IO radicals formed between 223 and 523 K. They found a weak dependence of the IO yield with pressure at 223 K which suggested the existence of an association channel. The rate constant of $(4.6 \pm 0.3) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ reported is in a good agreement, within the experimental error, with the kinetic results at low pressures of this work.

Good agreement can also be observed by comparing the value obtained in the present work with that reported by Atkinson *et al.*[10] of $(5.8 \pm 1.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ or the older room temperature studies by Watson *et al.*[11] and Addison *et al.*[12] of $(11 \pm 3)$ and $(6.5 \pm 1.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

Gilles *et al.* proposed the following favourable thermodynamic channels for the reaction of $O + CF_3I$:

$$O(^3P) + CF_3I \rightarrow IO + CF_3 \tag{1a}$$

$$O(^3P) + CF_3I \rightarrow IF + CF_2O \tag{1b}$$

$$O(^3P) + CF_3I \rightarrow I + F + CF_2O \tag{1c}$$

$$O(^3P) + CF_3I \rightarrow I^* + CF_3O \tag{1d}$$

$$O(^3P) + CF_3I \rightarrow I + CF_3O \tag{1e}$$

$$O(^3P) + CF_3I + M \rightarrow M + CF_3IO \tag{1f}$$

The authors determined a yield of less than one at 298 K for the formation of IO radical $(0.83 \pm 0.09)$ and less than 0.01 for the $CF_3O$ reaction, even though only IO radical was identified as a reaction product.[7] They postulated the possible existence of an

**Table 1.** Summary of the rate constants obtained in this work and those from previous determinations

| Reaction | $k_{298K}/10^{-12}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | $T$ range (K) | Method | Reference |
|---|---|---|---|---|
| $O + CH_3I$ | $23 \pm 0.3$ | 298 | DF–RF | This work |
| | $20.1 \pm 1.5$ | 223–363 | PLP–RF | 9 |
| | $17.4 \pm 1.6$ | 213–364 | PLP–RF | 7 |
| | $19 \pm 2$ | 238–310 | PLP–LIF | 6 |
| $O + CF_3I$ | $5.2 \pm 0.7$ | 298 | DF–RF | This work |
| | $4.251 \pm 0.26$ | 223–363 | PLP–RF | 9 |
| | $4.34 \pm 0.38$ | 213–364 | PLP–RF | 7 |
| | $5.30 \pm 0.25$ | 230–310 | PLP–LIF | 6 |
| | $5.8 \pm 1.5$ | | PLP–CRD | 10 |
| | $11 \pm 3$ | | FP–RA | 12 |
| | $6.5 \pm 1.5$ | | PLP–LIF | 11 |
| | $4.6 \pm 0.3$ | 223–523 | PLP–LIF | 8 |

DF–RF, discharge flow–resonance fluorescence; PLP–RF, pulsed laser photolysis–resonance fluorescence; PLP–LIF, pulsed laser photolysis–laser induced fluorescence; PLP–CRD, pulsed laser photolysis–cavity ring down; FP–RA, flash photolysis–resonance absorption.

association channel leading to the formation of an $[O–CF_3I]$ adduct.

From the previous studies, only Dillon *et al.* have reported a considerable pressure dependence of *k* at 223 K, but they did not find pressure dependence of the rate coefficients at room temperature in the range from 20 to 200 Torr using nitrogen as bath gas. However, they informed a reduction of 40% in the intensity of the IO LIF signal at 223 K compared to that at 294 K and in contrast to Gilles *et al.* who observed no fluorescence reduction below 254 K. Bloss *et al.*[16] reported a dependence of the IO yield at 220 K, with a 20% reduction in the yield between 100 and 760 Torr. Nevertheless, they did not show pressure dependence of the yield at 295 K.

In our previous work, we did not find pressure dependence of *k* even at 223 K studying the reaction in $N_2$ or He and at range of 20–310 Torr.[9] This does not agree with the weak dependence of *k* with total pressure at 223 K, found by Dillon and Heard, consistent with the existence of an association channel. The pressure independence of the rate constant of the reaction between O atoms and $CF_3I$ could be interpreted to mean that the reaction mechanism does not involve a reversible adduct formation. Due to that, and to the positive activation energy determined in the experiments, the last channel for the formation of $CF_3IO$ appears as a less probable reaction channel. Furthermore, more experiments should be done to measure products and yields of this reaction in order to shed light on the reaction mechanism.

### $CH_3I + O(^3P) \rightarrow$ products

The rate constant for the reaction $O(^3P) + CH_3I$ obtained in this work of $(2.3 \pm 0.3) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ is in a fairly good agreement with the value reported previously by the PLP–RF system $(19.8 \pm 0.6)\ 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$.

The same agreement is possible to be observed when the value is compared with the previous reported by Gilles *et al.* of $(17.4 \pm 1.6) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ using the PLP–RF, and the value by Hölscher *et al.* of $(19 \pm 2) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ by the PLP–LIF method.

### Free-energy relationships and atmospheric implications

The comparison between the reactivities of $O(^3P)$ atoms with the corresponding for other tropospheric oxidants, like OH radicals or Cl atoms, towards hydrogenated alkyl iodides in terms of a relationship of the rate constants shows a poor correlation. These results can be rationalized since different reactions mechanisms operate for these reactions. Namely, OH radicals and Cl atoms react with hydrogenated alkyl iodides involving mainly direct H-atom abstraction channel, whereas for the for $O(^3P) + RI$ reactions the existence of an association complex R–I–O that can be stabilized and rearranged to lead to multiple reaction products has been suggested.[7,9]

Concerning the atmospheric implications of the reactions studied, although it is well know that the OH-initiated oxidation is the main homogeneous fate of the majority of the organics in the troposphere, the reaction with $O(^3P)$ atoms can contribute to the calculation of the residence times of alkyl iodides in the atmosphere. $CF_3I$ and $CH_3I$ have unusual higher reactivities with $O(^3P)$ atoms (about 200 times) than with OH radical[13] that can equilibrate the lower (around $10^3$ times)concentration of $O(^3P)$ in the troposphere.

## Acknowledgements

The author wish to acknowledge the BMBF (AFO 2000-AFOHAL) and the EU(Thaloz) for financial support to the research and the Max-Planck Institute for Chemie, Mainz and Max-Planck Gesellschaft, Germany for a postdoctoral fellowship.

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