# Rate Coefficients for the Reactions $CH_3 + Br_2$ (224–358 K), $CH_3CO + Br_2$ (228 and 298 K), and $Cl + Br_2$ (228 and 298 K)

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ABSTRACT: Rate coefficients for the reactions of CH<sub>3</sub> + Br<sub>2</sub> ( $k_2$ ), CH<sub>3</sub>CO + Br<sub>2</sub> ( $k_3$ ), and Cl + Br<sub>2</sub> ( $k_5$ ) were measured using the laser-pulsed photolysis method combined with detection of the product Br atoms using resonance fluorescence. For the reactions involving organic radicals, the rate coefficients were observed to increase with decreasing temperature and within the temperature range explored, were adequately described by Arrhenius-like expressions:  $k_2$  (224–358 K) = 1.83 × 10<sup>-11</sup> exp(252/T) and  $k_3$  (228–298 K) = 2.92 × 10<sup>-11</sup> exp(361/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>1</sup>. The total, temperature-independent uncertainty for each reaction (including possible systematic errors in Br<sub>2</sub> concentration measurement) was estimated as ~7% for  $k_2$  and 10% for  $k_3$ . Accurate data on  $k_5$  was obtained at 298 K, with a value of 1.88 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained (with an associated error of 6%). A limited data set at 228 K suggests that  $k_5$  is, within experimental uncertainty, independent of temperature. © 2010 Wiley Periodicals, Inc. Int J Chem Kinet 42: 575–585, 2010

## INTRODUCTION

Our major motivation to study the reactions of CH<sub>3</sub> and CH<sub>3</sub>CO radicals and Cl atoms with Br<sub>2</sub> is related to the role of acetone photolysis in atmospheric chemistry. The atmospheric photodissociation of acetone at wavelengths above  $\approx 300$  nm results in formation of CH<sub>3</sub> and CH<sub>3</sub>CO radicals, which react with oxygen to form organic peroxy radicals and eventually HOx (sum of OH and HO<sub>2</sub>) and also stable nitrates (PAN,  $CH_3C(O)O_2NO_2$ ) [1–5]. In a recent publication [6], we presented primary photodissociation quantum yield measurements of acetone based on a scavenging technique, whereby the initially formed organic radicals were converted to Br atoms, which were subsequently detected (R1)–(R3).

 $CH_3C(O)CH_3 + h\nu \rightarrow CH_3 + CH_3CO$  (R1)

 $CH_3 + Br_2 \rightarrow CH_3Br + Br$  (R2)

 $CH_3CO + Br_2 \rightarrow CH_3C(O)Br + Br$  (R3)

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The photolysis of  $Cl_2$  in the presence of  $Br_2$  was used as reference Br atom source for these studies:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (R4)

$$Cl + Br_2 \rightarrow ClBr + Br$$
 (R5)

Based on heats of formation [7,8], (R2) and (R3) are exothermic by  $\approx 105 \text{ kJ mol}^{-1}$  and (R5) is exothermic by 27 kJ mol<sup>-1</sup>.

In the experiments of Khamaganov et al. at 248 and 266 nm [6], detailed kinetic information on reactions (R2) and (R3) was not necessary for the derivation of quantum yields as there were no competing processes for Br formation. At longer wavelengths, however, (e.g., at 308 nm), it was suggested that Br could be formed via reactions of triplet acetone with Br<sub>2</sub>, necessitating a more detailed kinetic analysis of the chemical system and thus accurate rate constants for (R2) and (R3) at temperatures as low as 228 K. As low temperature kinetic data were not available for either (R2) or (R3), a series of experiments was conducted using the pulsed laser photolysis method combined with resonance fluorescence detection of Br, with Br<sub>2</sub>

concentrations measured by long-path UV-absorption spectroscopy. The reaction of Cl with  $Br_2$  (the simplest system analytically) was studied at 298 K as a test of the method.

## **EXPERIMENTAL**

Various features of the pulsed laser photolysis/ resonance fluorescence (PLP/RF) experimental setup (Fig. 1) have been described previously [6,9], and only a brief summary is given here. The central component of the experimental setup is a 500-cm<sup>3</sup>, thermostated (224-358 K), cylindrical photoreactor/RF cell constructed of quartz. Photolysis light was provided by an excimer laser (Lambda-Physik Lextra 50) operated at 193 or 248 nm, a YAG laser (Quantel Brilliant-B) operated with fourth harmonic generation at 266 nm, or a frequency-doubled, YAG-pumped dye-laser tuned to 300 or 308 nm. The laser entrance and exit windows were purged by a small flow of  $N_2$  (<5 sccm each) to keep them clean. Br was detected using resonance fluorescence with photon counting as described by Khamaganov et al. [6] in



Figure 1 Experimental setup. IF = 185 nm interference filter, PD = photodiode, Pen Ray = low pressure "Pen Ray" Hg-lamp, VUV PMT = solar blind photomultiplier tube, FC = gas-mixing and flow control, J = Joule-meter, and MCS = multichannel scaler. The PMT-Box car detection axis (used for laser-induced fluorescence studies) was not operated in this work.

which details of the photomultiplier, optical filters, and electronics are given. At a time resolution of 2 µs, a detection sensitivity of  $\sim 6 \times 10^7$  Br cm<sup>-3</sup> was achieved by coadding 2000-3000 scans, usually at 10 Hz. Precise measurement of the concentration of Br2 was achieved using a monochromator-diode array setup coupled to a multipass absorption cell with 892-cm optical path length. The absorption cell was located upstream of the photolysis reactor and was at room temperature. The concentration of Br<sub>2</sub> was determined by online optical density measurements before and after each experimental run at wavelengths between  $\sim$ 320 and 460 nm and least-squares fitting to reference spectra of Br<sub>2</sub> [10]. With this method, we conservatively estimated the uncertainty in the measured Br<sub>2</sub> concentration to be  $\approx 5\%$ , mostly related to errors in the cross section. The concentration of acetone was monitored by absorption at 185 nm [9].

All flows were regulated by mass flow controllers (MKS Instruments) and well mixed in a glass manifold before entering the absorption cell. The pressure in the reactor was measured by a 100-Torr capacitance manometer (MKS Instruments) and adjusted to 60 Torr by throttling the pump downstream. The typical flow rates in the cell were 500–800 cm<sup>3</sup> (STD) min<sup>-1</sup>, which, combined with a laser repetition rate of between 5 and 10 Hz, ensured that a fresh mixture was irradiated with each laser pulse. The approximate laser fluence was monitored using an energy meter placed behind the photoreactor.

Reactions (R2) and (R3) are exothermic by  $\approx 105 \text{ kJ}$  $mol^{-1}$ , which is sufficient to result in population of the spin-excited state of Br, the difference in energy between the Br( ${}^{2}P_{1/2}$ ) and Br( ${}^{2}P_{3/2}$ ) spin states being 44 kJ mol<sup>-1</sup> [11]. For reaction between CH<sub>3</sub> and Br<sub>2</sub>, Kovalenko and Leone [12] suggest that 42% of the available energy is found in vibrations of the alkylhalide fragment. Translational energy has been measured to account for a further 22% [13] or 56% [14] of that available. The energy available for formation of  $Br(^{2}P_{1/2})$  is thus between  $\approx 2$  and 38 kJ mol<sup>-1</sup>, implying that spin-excited Br atoms should not play a significant role. There are no data on the product energy distribution for the  $CH_3CO + Br_2$  reaction, though experiments in which a few Torr of H<sub>2</sub> were added to the usual CH<sub>3</sub>C(O)CH<sub>3</sub>/Br<sub>2</sub> mixture prior to photolysis at 248 nm revealed no difference in the Br atom resonance fluorescence profiles. As H2 is an efficient quencher of  $Br(^{2}P_{1/2})$  [15], this result suggests that  $Br(^{2}P_{1/2})$  need not be further considered in our analysis.

Acetone and Br<sub>2</sub> (both Aldrich, Munich, Germany;  $\geq$ 99.5%) were purified using several freeze-pump-thaw cycles at liquid nitrogen temperature and stored in blackened glass bulbs as mixtures in N<sub>2</sub>. N<sub>2</sub> (Westfalen

AG, Münster, Germany; 99.999%),  $H_2$  (Linde, Pullach, Germany; 99.999%), and  $Cl_2$  (4.76% mixture in  $N_2$ ; Air Liquide, Düsseldorf, Germany) were used straight from the bottles. Gases required for the resonance fluorescence lamp were He (Westfalen AG, 99.999%) and  $CH_4$  (Messer, Sulzbach, Germany; 99.995%).

## **RESULTS AND DISCUSSION**

#### $CH_3 + Br_2(k_2)$

The reaction between CH<sub>3</sub> and Br<sub>2</sub> was initiated by the 193-nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> in the presence of Br<sub>2</sub>. At 193 nm, the CH<sub>3</sub>CO radicals from (R1) are formed in highly excited states and decompose instantaneously to CH<sub>3</sub> + CO, the net result being formation of two CH<sub>3</sub> radicals and one CO per photon absorbed [16–19]. There is also some formation of H atoms (and an organic radical fragment) with a low branching ratio ( $\approx$ 0.04) [18,20].

$$CH_3C(O)CH_3 + h\nu (193 \text{ nm}) \rightarrow 2CH_3 + CO (R1a)$$
  
 $\rightarrow H + CH_3C(O)CH_2$   
(R1b)

As the formation of  $CH_3$  dominates, we initially ignore channel (1b), though we return to this later. In the presence of  $Br_2$ , the instantaneously formed  $CH_3$  radicals react to form Br with the following biexponential rate expression, describing the kinetics of their formation and decay:

$$[Br]_t = 2[CH_3]_0 \times \frac{k'_2}{k'_2 - k_d} \times (e^{-k_d t} - e^{-k'_2 t})$$
(E1)

where

$$k_2' = k_2[Br_2] + c$$
 (E2)

[Br]<sub>t</sub> is the time-dependent Br atom concentration and  $k_2$  is the rate coefficient for reaction of CH<sub>3</sub> with Br<sub>2</sub>. [CH<sub>3</sub>]<sub>0</sub> is the initial radical concentration formed in the 193-nm laser pulse and  $k_d$  is a first-order loss rate constant, representing transport of Br atoms from the viewing zone (the only significant removal process for Br in the system). The term *c* represents first-order losses of CH<sub>3</sub> other than reaction with Br<sub>2</sub>. This expression is valid as long as second-order components (e.g., reactions of CH<sub>3</sub> radicals with each other or reactions of Br with CH<sub>3</sub>) are negligible. This condition is readily fulfilled by keeping the concentration of CH<sub>3</sub> low relative to Br<sub>2</sub>. Typical concentrations of Br<sub>2</sub> were  $\approx (5-50) \times 10^{14}$  molecules cm<sup>-3</sup>, whereas initial radical densities of approximately  $10^{11}$  CH<sub>3</sub> cm<sup>-3</sup> were generated from  $\approx 5 \times 10^{14}$  CH<sub>3</sub>C(O)CH<sub>3</sub> cm<sup>-3</sup> with laser fluences of <1 mJ cm<sup>-2</sup>. Experiments in which the CH<sub>3</sub>C(O)CH<sub>3</sub> and Br<sub>2</sub> concentrations were held constant and the laser fluence was varied between 0.2 and 0.6 mJ cm<sup>-2</sup> resulted in the same decay constant for Br, confirming that secondary chemistry can be neglected at these low radical densities.

Expression (E1) also assumes that (initially hot) CH<sub>3</sub> radicals formed in the 193-nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> are thermally equilibrated before reacting with Br<sub>2</sub>. Following Kovalenko and Leone [12], and assuming the same vibrational energy transfer rate coefficient for O<sub>2</sub> and N<sub>2</sub>, we estimate that vibrationally hot CH<sub>3</sub> radicals will be quenched in <10  $\mu$ s at pressures of 60 Torr N<sub>2</sub>. This is orders of magnitude smaller than the millisecond time scale for reaction of CH<sub>3</sub> with Br<sub>2</sub> and removing the first 10  $\mu$ s of data from the Br profiles did not change the value of  $k'_2$  returned by the fit of the data to (E1).

Raw data obtained at 358 K and at two different Br<sub>2</sub> concentrations (4.02 × 10<sup>13</sup> and 2.53 × 10<sup>14</sup> molecules cm<sup>-3</sup>) are displayed in Fig. 2 along with least-squares fits using expression (E1). In the absence of CH<sub>3</sub>C(O)CH<sub>3</sub>, no Br signal was observed indicating that Br<sub>2</sub> does not absorb significantly at 193 nm ( $\sigma_{\rm Br_2}^{193 nm} = 6.88 \times 10^{-22} \,{\rm cm}^2$  molecule<sup>-1</sup>) [21].

The values of  $k'_2$  from least-squares fitting expression (E1) to the two data sets displayed are  $1613 \pm 64$  and  $9076 \pm 122 \text{ s}^{-1}$  for the low and high Br<sub>2</sub> concentrations, respectively. The first-order loss term for Br  $(k_d)$  was about 60 s<sup>-1</sup> in both cases, which is consistent with diffusion from the fluorescence-viewing zone



Figure 2 Experimental Br traces obtained at 358 K and at two different concentrations of  $Br_2$ . The solid lines are least-squares fits according to expression (E1).



**Figure 3** Plots of  $k'_2$  versus [Br<sub>2</sub>]. The solid lines are least-squares fits to the data according to expression (E2). The error-bars ( $2\sigma$ ) on each data point are generally smaller than the symbol size.

(essentially the volume of overlap between excimer laser, resonance lamp emission, and focal point of collimiting lens). The uncertainties quoted for  $k'_2$  are  $2\sigma$ as returned by the fit routine. According to (E2), a plot of  $k'_2$  versus [Br<sub>2</sub>] should be a straight line of slope  $k_2$ . Figure 3 displays values of  $k'_2$  obtained at four different temperatures (228, 258, 298, and 358 K) and various Br<sub>2</sub> concentrations. The slopes from these data sets return values of  $k_2 = 5.50 \pm 0.02$ ,  $4.80 \pm 0.04$ ,  $4.20 \pm$ 0.02, and 3.50  $\pm$  0.04 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 228, 258, 298, and 358 K, respectively, indicating a weak, negative dependence on temperature. The uncertainties quoted ( $2\sigma$ , statistical only) are of the order of a percent, underlining the high precision of these data. The intercept of these fit lines (at  $[Br_2] = 0$ ) is not zero but varies from 290  $\pm$  69 s<sup>-1</sup> at 228 K to 185  $\pm$  35 s<sup>-1</sup> at 358 K. This intercept can be partially attributed to diffusive removal of CH<sub>3</sub> from the fluorescence-viewing zone. To a first approximation, the diffusion coefficient varies inversely with the square root of the reduced mass of diffusing molecule and bath gas and we expect that CH<sub>3</sub> should diffuse through N<sub>2</sub> about 50% more rapidly than Br. This would result in losses of  $\approx 100 \text{ s}^{-1}$  for CH<sub>3</sub>, which is less than measured by a factor of about 2. A further possibility for CH<sub>3</sub> loss is reaction with O2 present in the gas mixture (pure N2 at 60 Torr). The rate coefficient for reaction between CH<sub>3</sub> and  $O_2$  (to form  $CH_3O_2$ ) has a room temperature rate coefficient at 60 Torr of  $\approx 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$  $s^{-1}$ . A loss rate of 100  $s^{-1}$  would thus require the presence of impurity O2 at a volume-mixing ratio of 200 ppmv, which exceeds the stated impurity levels in the N<sub>2</sub> cylinder by a factor of 20. In addition, the rate

coefficient for reaction of CH3 with O2 at a total pressure of 60 Torr N<sub>2</sub> increases by a factor of  $\approx$ 4 when the temperature is decreased from 358 to 228 K [22]. As the intercept increased only by  $\sim 50\%$  between 358 and 228 K, it cannot be attributed solely to reaction with O<sub>2</sub>. The possibility that at the lowest [Br<sub>2</sub>], CH<sub>3</sub> may be lost in self-reaction can be evaluated using the known recombination rate coefficient ( $CH_3 + CH_3 \rightarrow$  $C_2H_6$ ) of  $\approx 5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature and 60 Torr [23]. As CH<sub>3</sub> is present at concentrations of less than  $5 \times 10^{11}$  molecules cm<sup>-3</sup>, its loss by self-reaction will be less than  $\approx 20 \text{ s}^{-1}$ . At present, we have no conclusive explanation for the small but statistically significant nonzero intercept, but suggest it arises through a combination of processes including those listed above. As long as second-order components are negligible (i.e., the plots in Fig. 3 are "true" straight lines), the presence of a small intercept should not decrease the accuracy of the rate coefficient.

The complete data set obtained by 193-nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> is summarized in Table I. The overall uncertainty in the rate coefficient is larger ( $\approx 7\%$ ) and is determined by uncertainty in Br<sub>2</sub> cross sections (see above) and the formation of H atoms (and pre-

Table ISummary of Temperature-Dependent RateCoefficient Data

| Temperature<br>(K) | $[Br_2]^a (10^{14})moleculescm-3)$ | Photolysis<br>Wavelength<br>(nm) | $k (10^{-11} \text{ cm}^3)$<br>molecule <sup>-1</sup><br>s <sup>-1</sup> ) |
|--------------------|------------------------------------|----------------------------------|--|
|                    | $CH_3 + 1$                         | Br <sub>2</sub> (R2)             |  |
| 224                | 0.66-4.09                          | 193                              | $5.56\pm0.02$  |
| 228                | 0.66-4.70                          | 193                              | $5.50\pm0.07$  |
| 228                | 0.68-4.64                          | 193                              | $5.54\pm0.06$  |
| 228                | 0.54-4.10                          | 193                              | $6.05\pm0.07$  |
| 258                | 0.52-3.84                          | 193                              | $4.86\pm0.05$  |
| 258                | 0.59-4.17                          | 193                              | $4.80\pm0.04$  |
| 298                | 0.49-3.57                          | 193                              | $4.20\pm0.02$  |
| 298                | 0.51-3.50                          | 193                              | $4.23\pm0.05$  |
| 298                | 0.40-3.09                          | 193                              | $4.32\pm0.03$  |
| 298                | 0.24-3.14                          | 193                              | $4.44\pm0.03$  |
| 358                | 0.40-2.93                          | 193                              | $3.50\pm0.04$  |
| 358                | 0.33-2.76                          | 193                              | $3.53\pm0.03$  |
|                    | CH <sub>3</sub> CO -               | - Br <sub>2</sub> (R3)           |  |
| 228                | 2.45-3.41                          | 266                              | $14.2\pm0.3$   |
| 298                | 0.10-2.58                          | 266                              | $9.79\pm0.15$  |
| 298                | 0.39–1.71                          | 248                              | $11.0\pm0.50$  |
| $Cl + Br_2 (R5)$   |                                    |                                  |  |
| 298                | 0.12 - 1.74                        | 300/308                          | $19.4\pm0.3$   |
| 228                | 1.17-2.04                          | 300/308                          | $21 \pm 3$   |
|                    |                                    |                                  |  |

<sup>*a*</sup>Range of Br<sub>2</sub> used. Errors are statistical ( $2\sigma$ ) only. The overall uncertainty is expected to be ~7%, 10%, and 6% for (R2) (224–358 K), (R3) (228–298 K), and (R5) (298 K), respectively.

sumably CH<sub>3</sub>C(O)CH<sub>2</sub>) in the 193 nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub>, both of which can react with Br<sub>2</sub>. The rate coefficient for reaction of H with Br<sub>2</sub> has been measured as  $\approx 8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K [24], which is about a factor of 2 more rapid than the rate coefficient measured here for CH<sub>3</sub> + Br<sub>2</sub>. The impact on the rate coefficient  $k_2$  is estimated by assuming that CH<sub>3</sub>C(O)CH<sub>2</sub> also reacts with Br<sub>2</sub> with a rate coefficient of  $8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which results in an overestimation of the rate coefficient for CH<sub>3</sub> + Br<sub>2</sub> by less than 5%.

In Fig. 4, we present the temperature dependence of the rate coefficient in Arrhenius format,  $k = A \exp(-E/RT)$  and compare our results to the two previous direct determinations [12,25]. At room temperature, our result is  $(4.3 \pm 0.3) \times 10^{-11} \text{ cm}^3$  $molecule^{-1} s^{-1}$  (the overall uncertainty quoted takes potential systematic errors into account) which agrees, within error limits, with the value of  $(3.9 \pm 0.8) \times$  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by Timonen et al. [25] who conducted their experiments at low pressures of He (<5 Torr) with detection of CH<sub>3</sub> via photoionization mass spectrometry, following generation by the 193 nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub>. The value of  $k_2 =$  $(2.0 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained by Kovalenko and Leone [12] by detecting infrared emission from the CH<sub>3</sub>Br product is a factor of 2 lower than the present determination. Our temperature-dependent data are well described by the Arrhenius expression  $k_2 = 1.83 \times 10^{-11} \exp(252/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$ which describes the solid line through the 193 nm data set in Fig. 4.

Extended to higher temperatures, this parameterization also accurately reproduces the data of Timonen et al. [25], who derived the expression  $k_2 = 2.0 \times 10^{-11} \exp(196/T) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. Clearly, despite different methodologies and operational pressures and temperatures, these two data sets are in excellent agreement. When combined, the present data set and that of Timonen et al. indicate that the rate coefficient for the reaction between CH<sub>3</sub> and Br<sub>2</sub> is independent of pressure between ~1 Torr He and 60 Torr N<sub>2</sub>.

# $CH_3CO + Br_2(k_3)$

**266-nm Photolysis of CH**<sub>3</sub>C(O)CH<sub>3</sub>. To measure the rate coefficient for the reaction of CH<sub>3</sub>CO with Br<sub>2</sub>, we made use of the fact that acetone photolysis at 266 nm (R1) results in formation of one CH<sub>3</sub> and one CH<sub>3</sub>CO radical. Our previous studies [6,26] have showed that at 60 Torr of N<sub>2</sub>, both the overall CH<sub>3</sub>C(O)CH<sub>3</sub> photodissociation quantum yield and the yield of CH<sub>3</sub> are close to unity, and that negligible amounts of the CH<sub>3</sub>CO formed decompose thermally to CH<sub>3</sub> + CO. The rate



Figure 4 Temperature dependence of  $k_2$  (CH<sub>3</sub> + Br<sub>2</sub>) and  $k_3$  (CH<sub>3</sub>CO + Br<sub>2</sub>). The error bars on the present data set for  $k_2$  include an estimate of uncertainty related to the Br<sub>2</sub> absorption cross sections and the fact that a small fraction of acetone is dissociated to H + CH<sub>3</sub>C(O)CH<sub>2</sub> at 193 nm.

expression for Br atom formation is then

$$[Br]_{t} = [R] \times \left( e^{-k_{d}t} \left( \frac{k_{2}'}{k_{2}' - k_{d}} + \frac{k_{3}'}{k_{3}' - k_{d}} \right) - e^{-k_{2}'t} \frac{k_{2}'}{k_{2}' - k_{d}} - e^{-k_{3}'t} \frac{k_{3}'}{k_{3}' - k_{d}} \right)$$
(E3)

and

$$k'_3 = k_3[Br_2] + c$$
 (E4)

where  $[R] = [CH_3] + [CH_3CO]$ . The other terms have the same meaning as for expressions (E1) and (E2). A typical data set (obtained at 228 K) is displayed in Fig. 5. A small, prompt Br signal due to Br<sub>2</sub> photolysis was observed at this wavelength ( $\sigma_{Br_2}^{266 \text{ nm}} = 1.78 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ ) [21]. The prompt signal was close to the detection limit (~1% of that obtained in the presence of acetone), and its subtraction had no significant impact on the kinetic analysis.

There are two options for analyzing the raw data obtained: least-squares fitting using expression (E3) to derive first-order loss constants  $k'_2$  and  $k'_3$  for both reactions leading to Br formation, or by constraining expression (E3) with the rate constant  $k_2$  derived above and the known Br<sub>2</sub> concentration. The second method was preferred as an unconstrained, multiexponential

analysis of a single rise and decay profile was not expected to yield uniquely assignable kinetic parameters. The results of the analysis are plotted as the inset to Fig. 5 and yield rate coefficients of  $k_3 = (9.79 \pm$ 



**Figure 5** Photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub>/Br<sub>2</sub>/N<sub>2</sub> mixtures at 266 nm and 228 K. The raw Br signal is analyzed according to Eq. (E3) to generate values of  $k'_3$  at various concentrations of Br<sub>2</sub>. The inset shows the dependence of  $k'_3$  on [Br<sub>2</sub>] at 228 and 298 K, which can be used to derive the rate coefficient  $k_3$ .

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 $(0.15) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and a larger value of  $(1.41 \pm 0.03) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 228 K. The total uncertainty (including errors in [Br<sub>2</sub>] measurement) is estimated as 10%.

Somewhat surprisingly, unconstrained fits to the data gave consistent results, with values of  $k_3$  that were just 4% and 6% larger at 228 and 298 K, respectively. This method also generates values of  $k_2$ , which were lower than those presented in the  $CH_3$  + Br<sub>2</sub> section by only 6% (at 228 K) and 10% (at 298 K). The fact that the data analysis using the unconstrained fit returned consistent values for two rate coefficients separated only by  $\approx 50\%$  in value, is a reflection of the high quality (low noise levels) of the data set including precise optical measurement of the Br<sub>2</sub> concentration. This good agreement in different methods to obtain  $k_3$  may also be taken as evidence that the formation of radical fragments other than CH<sub>3</sub> in the 193nm photolysis did not have a significant impact on its determination.

As already stated, our analysis uses our previous result [26] that the ratio of  $CH_3$  to  $CH_3CO$  is unity when  $CH_3C(O)CH_3$  is photolyzed at 266 nm. This diverges from the results of Blitz et al. [27], who suggest that the quantum yield of  $CH_3CO$  radicals is 0.61 at this pressure and wavelength, with an overall quantum yield of 0.98, inferring a  $CH_3$  to  $CH_3CO$  ratio of 2.21. Our data analysis was therefore repeated with Eq. (3) modified to take this into account, so that

$$[Br]_{t} = [R] \times \left( e^{-k_{d}t} \left( \frac{\Phi_{CH_{3}}^{266 \text{ nm}} \cdot k_{2}'}{k_{2}' - k_{d}} + \frac{\Phi_{CH_{3}CO}^{266 \text{ nm}} \cdot k_{3}'}{k_{3}' - k_{d}} \right) - e^{-k_{2}'t} \frac{\Phi_{CH_{3}}^{266 \text{ nm}} \cdot k_{2}'}{k_{2}' - k_{d}} - e^{-k_{3}'t} \frac{\Phi_{CH_{3}CO}^{266 \text{ nm}} \cdot k_{3}'}{k_{3}' - k_{d}} \right)$$
(E5)

and by  $\Phi_{CH_3}^{266 \text{ nm}} = 1.38$  and  $\Phi_{CH_3CO}^{266 \text{ nm}} = 0.62$ . The use of this expression (again, with  $k'_2$  constrained as above) resulted in slightly poorer fits to the Br profiles, and the plot of  $k'_3$  versus [Br<sub>2</sub>] was not a good straight line. The value of  $k_3$  obtained was  $1.75 \times 10^{-10} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, an increase of 80% compared to our preferred analysis using CH<sub>3</sub> to CH<sub>3</sub>CO ratios of unity. The apparent increase in  $k_3$  is simply compensation of the fact that less of the (faster reacting) CH<sub>3</sub>CO radical is available to react with Br<sub>2</sub> to form Br.

As we show below, this large value of  $k_3$  is not consistent with the literature data, giving us independent (albeit indirect) confirmation that our previous work showing that CH<sub>3</sub> and CH<sub>3</sub>CO are formed in equal amounts at the 266-nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub>

is correct and appropriate for analysis of the present data set.

The rate coefficients obtained for  $k_3$  at 228 and 298 K are plotted along with the data for  $k_2$  in Fig. 4 and are listed in Table I. Similar to  $k_2$ ,  $k_3$  also displays a slight negative dependence on temperature, and can be parameterized with  $k_3 = 2.92 \times 10^{-11} \exp(361/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Our results for  $k_3$  can be compared so the single, room temperature value reported by Nicovich et al. [28], who derived  $k_3 = (1.08 \pm 0.38) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> by photolyzing Br<sub>2</sub> in the presence of CH<sub>3</sub>CHO and monitoring Br (by resonance fluorescence) formed in the chain propagation reaction of CH<sub>3</sub>CO with Br<sub>2</sub>. The results, obtained in 150 Torr N<sub>2</sub>, agree with those presented here to  $\approx 10\%$ , which is much less than the combined experimental errors. The 298 K data point of Nicovich et al. is also plotted in Fig. 4.

**248-nm Photolysis of CH**<sub>3</sub>C(O)CH<sub>3</sub>. A further set of experiments (also at 60 Torr N<sub>2</sub>) were conducted using the 248-nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> to generate the CH<sub>3</sub> and CH<sub>3</sub>CO radicals. At 248 nm, the Br<sub>2</sub> cross section increases to  $\sigma_{Br_2}^{248 \text{ nm}} = 5.79 \times 10^{-21} \text{ cm}^2$  molecule<sup>-1</sup> [21] and prompt Br formation was observed from its photolysis. This amounted to a few percent of the signal in the presence of acetone and was subtracted.

At a total pressure of 60 Torr of N<sub>2</sub>, the thermal decomposition of vibrationally excited CH<sub>3</sub>CO to CH<sub>3</sub> and CO radicals leads to an inequality in the CH<sub>3</sub> and CH<sub>3</sub>CO concentrations available for reaction with Br<sub>2</sub>. In our previous study at 248 nm, we determined that at 298 K the yields of CH<sub>3</sub> and CH<sub>3</sub>CO are given by  $\Phi_{CH_3}^{248 \text{ nm}} = 1.37$  and  $\Phi_{CH_3CO}^{248 \text{ nm}} = 0.63$ , respectively, in 60 Torr N<sub>2</sub>. Expression (E5) with modified (relative) CH<sub>3</sub> and CH<sub>3</sub>CO yields is thus appropriate for the analysis.

As described above for the data obtained at 266 nm, the least-squares fits to the expression were constrained using values of  $k_2$  from this study. At room temperature, the quality of the fit to the raw data was similar to that observed when working at 266 nm, and the plot of  $k'_3$  versus [Br<sub>2</sub>] was a straight line with slope,  $k_3 =$  $(1.10 \pm 0.05) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This value, also listed in Table I, is within 10% of that derived from experiments at 266 nm. In contrast, at 228 K the quality of the fits to the raw data was reduced, the qualitative observation being an underpredicted initial rate of Br formation. As a result, the plot of  $k'_3$  versus [Br<sub>2</sub>] was no longer a good straight line. This "low-temperature" problem was not encountered when working at 266 nm, and we hypothesize that it is a result of using the wrong initial (relative) concentrations of  $CH_3$  and  $CH_3CO$  to constrain the fit. Note the density change in going from 298 to 228 K at 60 Torr N<sub>2</sub> is insufficient to change the initial  $CH_3:CH_3CO$  ratio significantly [26].

By completely constraining the terms  $k'_2$  and  $k'_3$  by using the values of k2 (228 K) and k3 (228 K) measured at 193 and 266 nm, respectively, and by the known Br<sub>2</sub> concentration, we can inverse the problem and optimize the fit by allowing the initial relative concentrations of CH<sub>3</sub> and CH<sub>3</sub>CO to vary. For all the data at 228 K, the best fit was obtained when the CH<sub>3</sub> yield,  $\Phi_{CH_2}^{248 \text{ nm}}$ , was reduced from 1.37 (the room temperature value) to between 1.06 and 1.16 (average value from four experiments of  $1.10 \pm 0.05$ ). Although this appears to be only a small effect, it propagates through to a large change in the initial CH<sub>3</sub> to CH<sub>3</sub>CO ratio from 2.17 to 1.22. As the rate coefficient at 228 K for CH<sub>3</sub> and CH<sub>3</sub>CO reactions with Br<sub>2</sub> differ by a factor of  $\approx 2.6$ , the data set is quite sensitive to changes in the relative amounts of these two radicals. This is illustrated in Fig. 6, where we display the Br signal generated from the 248 nm photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> at 248 nm and 228 K. The solid lines are simulations of the data using expression (E3). In both cases, the simulation is constrained by the rate coefficients for  $CH_3$  +  $Br_2(k_2)$  and  $CH_3CO + Br_2(k_3)$  at 228 determined in experiments at 193 and 266 nm, respectively. The lower simulation line uses the yields of  $CH_3$  (1.37) and CH<sub>3</sub>CO (0.63) formation as derived previously by Khamaganov et al. and also used to successfully



**Figure 6** Br signal generated from the 248 nm photolysis of  $CH_3C(O)CH_3$  at 248 nm and 228 K. The solid lines are simulations of the data using expression (E3) with different initial  $CH_3:CH_3CO$  ratios.

analyze the room temperature data. The data are clearly not well reproduced, and the simulation underestimates the initial rate of Br formation. The upper curve is the result of a simulation whereby the yield of CH<sub>3</sub> radicals is reduced to 1.1 (and thus that of CH<sub>3</sub>CO increased to 0.9). Increasing the concentration of CH<sub>3</sub>CO relative to CH<sub>3</sub> results in a more rapid formation of Br as  $k_3$  is larger than  $k_2$  and reproduces the experimental profile well.

The fits to the data could also be improved by increasing the rate constants  $k_2$  and  $k_3$  to reproduce the faster rise in the Br kinetic profile. The rate coefficients required were, however, unrealistically large (by 20% for  $k_2$  and by 60% for  $k_3$  when changed individually) and thus incompatible with the 193- and 266-nm derived rate coefficients and also with literature values.

Although recognizing that this method is indirect, the implication is that the relative yield of  $CH_3$  and  $CH_3CO$  obtained by photolyzing acetone at 248 nm is not only both pressure but also temperature dependent. This observation is in accord (regarding the pressure effect) with our previous work on acetone photolysis quantum yields [6,26]. The literature concerning the thermal dissociation of  $CH_3CO$  was reviewed in our previous publication [26] and is not repeated here.

# $Cl + Br_2(k_5)$

The reaction between Cl and Br<sub>2</sub> was initiated by the photolysis of Cl<sub>2</sub> at either 300 or 308 nm (R4) using the frequency-doubled dye laser. Typical Cl<sub>2</sub> concentrations were  $1.5 \times 10^{14}$  molecules cm<sup>-3</sup> with  $\sim 10^{11}$  Cl cm<sup>-3</sup> generated in the  $\sim 10$  mJ cm<sup>-2</sup> pulse. At 298 K, the raw data obtained were qualitatively similar to those for reaction (R2) and are not displayed. The Br<sub>2</sub> cross section is small close to 300 nm ( $\sigma_{Br_2}^{300 \text{ nm}} = 1.1 \times 10^{-22} \text{ cm}^2$  molecule<sup>-1</sup>) [21], and no Br signal was observed in the absence of Cl<sub>2</sub>. In addition, at the low concentrations used, the low rate coefficient ( $\sim 10^{-22} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>) [29] ensures that the reaction of Br<sub>2</sub> with Cl<sub>2</sub> does not lead to significant BrCl formation (or loss of Br<sub>2</sub>) during mixing of these gases.

The kinetic analysis was also identical to that performed for the 193-nm photolysis of acetone, with Cl substituting for CH<sub>3</sub> and  $k_5$  for  $k_2$  in Eqs. (E1) and (E2). A combined data set, showing all results at 298 K, is given in Fig. 7.

The average rate coefficient obtained at room temperature was  $(1.94 \pm 0.12) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, where the errors include potential systematic error in Br<sub>2</sub> measurements as well as propagated statistical error. No systematic study of the reaction of Cl with Br<sub>2</sub> at other temperatures was made as part of this



**Figure 7** Reaction of Cl with Br<sub>2</sub> at 298 and 228 K. The solid line is a least-squares fit through the 298 K data. Data at 228 K were not collected with systematic variation of Br<sub>2</sub> (see the text for details), and the dashed line is the result of a calculation with  $k_5 = 2.1 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 228 K and the intercept forced through zero. The dotted lines represent values of 1.8 (lower) and  $2.4 \times 10^{-10}$  (upper) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

work, although a number of data points were gathered at 228 K as part of our ongoing study of the photodissociation of  $CH_3C(O)CH_3$  at low temperatures. In this case, the  $Br_2$  concentration was not varied systematically and the experiments were not carried out at constant pressure. Nonetheless, as an accurate  $Br_2$ concentration was recorded our data do provide constraint on  $k_5$  which we report as  $2.1 \pm 0.3 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> where the errors take into account the scatter in the data at this temperature and also the potential systematic error in Br<sub>2</sub> cross sections. Our rate coefficients for  $k_5$  are plotted in Arrhenius format in Fig. 8, along with previous determinations, of which there are several. Although all the previous



Figure 8 Temperature dependence of the reaction of Cl with Br<sub>2</sub>.

studies agree that the rate coefficient is very large, there are significant deviations in the values reported. The room temperature, discharge-flow studies of Clyne and co-workers used resonance fluorescence detection of both Cl and Br atoms to derive values of  $(1.2 \pm 0.15) \times$  $10^{-10}~{\rm cm^3}$  molecule^{-1}  ${\rm s^{-1}}$  [30] and (1.9  $\pm$  0.2)  $\times$ 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [31]. Accurate control of the Br<sub>2</sub> concentration was difficult at the low partial pressure demanded by a fast reaction in a flow system and the requirement of a simple pseudo-first-order kinetic analysis and was suggested to be the source of the difference in the rate coefficient in these two studies. A discharge-flow tube experiment, with mass spectrometric detection of the BrCl product of reaction (R5) to derive kinetic parameters, was conducted as part of a study of the reaction of Cl with isoprene [32]. Data were obtained at five temperatures between 233 and 320 K, with no systematic dependence of the rate constant on temperature; data at 320, 298, 273, and 248 K giving (within error limits) the same value, close to  $1.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The rate constant obtained at 233 K was  $\approx 10\%$  lower, though there was no convincing evidence for a temperature dependence within this data set. Pseudo-firstorder conditions were not easy to achieve, and the authors reported depletion of Br2 (the excess reagent) of between 5 and 25%, with maximum Br<sub>2</sub> concentrations of  $\approx 5 \times 10^{12}$  molecules cm<sup>-3</sup> determined manometrically. Temperature-dependent rate coefficients (298-401 K) have been reported by Nicovich and Wine [33], who used a pulsed laser photolysis system with resonance fluorescence detection of Cl atoms. The concentration of Br2 was measured optically using an literature absorption cross section of  $5.87 \times 10^{-19} \text{ cm}^2$ molecule<sup>-1</sup> at 415.8 nm [34]. Although the data could be represented with an Arrhenius expression  $k_5 =$  $(2.40 \pm 1.25) \times 10^{-10} \exp[-144 \pm 176)/T] \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup>, the authors suggest that a temperatureindependent value of (1.58  $\pm$  0.22)  $\times$   $10^{-10}~{\rm cm^3}$ molecule $^{-1}$  s $^{-1}$  describes the data equally well. The overall uncertainty at all temperatures was suggested to be 20%. Since this study, improved absorption cross sections for Br<sub>2</sub> have become available [10] and the preferred value [35] at 415.8 nm is now  $6.55 \times 10^{-19}$ cm<sup>2</sup> molecule<sup>-1</sup>. The rate coefficients of Nicovich and Wine plotted in Fig. 8 have therefore been adjusted upward by  $\approx 12\%$ . An approximate value of  $(0.9 - 1.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  has been reported by Chesnokov [36], though this was derived from a complex system involving chain formation of radicals in the photolysis of Cl<sub>2</sub> in the presence of SiH<sub>2</sub>Cl<sub>2</sub> and is not expected to be accurate.

As can be seen from Fig. 8, the two pulsed photolysis experiments, which were carried out under strictly pseudo-first-order conditions and which were not limited by time resolution considerations to use of low Br2 concentrations, are in good agreement. The use of in situ optical absorption measurement of the Br2 concentration makes these the most reliable determinations. Together the results of Nicovich and Wine [33] and the present study indicate that the rate coefficient is independent of temperature between  $\sim$ 200 and 400 K. Although Bedjanian et al. [32] combined their data with that of Nicovich and Wine to derive a parameterization of the rate coefficient with a positive temperature dependence, this appears to be the result of combining rate coefficient data at different temperatures which were separated in the absolute values by systematic errors. The data of Nicovich and Wine and the present study can be combined to derive a value of  $k_5 = (1.81 \pm$  $(0.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature from 200 to 400 K.

# SUMMARY AND CONCLUSIONS

We have investigated the reactions of alkyl radical fragments (CH3 and CH3CO) and Cl atoms with molecular bromine. For  $CH_3$  ( $k_2$ ) and  $CH_3CO$  ( $k_3$ ), the large rate coefficients increase with decreasing temperature, indicating that the reaction proceeds with no significant barrier, in line with the conclusions of molecular beam experiments of reaction (R2) [14,37,38]. The data for CH<sub>3</sub> confirm and extend the data set of Timonen at al. [25] As discussed by Timonen et al., the rates of reactions of radical fragments with Br<sub>2</sub> are controlled by long-range attractive forces rather than reaction thermochemistry, with the reactions with larger (more polarizable) radicals being more rapid. This conclusion extends also to the reaction of Cl atoms with Br<sub>2</sub> (the least exothermic studied here), for which the largest rate coefficient was obtained. By improving the accuracy of the rate constants for the reaction of Cl +  $Br_2$  and extending the temperature range covered, we have shown that the previous description of this reaction with a positive activation energy is most likely erroneous.

Given a well-defined set of rate constants,  $k_2$  and  $k_3$ , the detection of Br formed in the photolysis of CH<sub>3</sub>C(O)CH<sub>3</sub> in the presence of Br<sub>2</sub> allows us to make an estimation of the initial relative concentration of CH<sub>3</sub> and CH<sub>3</sub>CO. The data sets obtained at 248 nm and 298 or 228 K revealed that the ratio changes with temperature in a manner consistent with reduced thermal decomposition of CH<sub>3</sub>CO at low temperatures. Finally, the new, accurate rate coefficient data from this work will be used in the kinetic analysis of Br atoms resulting from the back-to-back photolysis of

acetone and  $Cl_2$  at wavelengths greater than 280 nm in experiments to determine acetone photodissociation quantum yields.

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