

Rate coefficients for the reactions of OH radicals with the keto/enol tautomers of 2,4-pentanedione and 3-methyl-2,4-pentanedione, allyl alcohol and methyl vinyl ketone using the enols and methyl nitrite as photolytic sources of OH

Anne-Louise Holloway^a, Jack Treacy^b, Howard Sidebottom^{a,*}, Abdelwahid Mellouki^c, Veronique Daële^c, Georges Le Bras^c, Ian Barnes^d

^a Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

^b Department of Chemistry, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland

^c LCSR/CNRS, 1C Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

^d Bergische Universität Wuppertal, Gauss Strasse 20, D-42097 Wuppertal, Germany

Available online 29 September 2005

Abstract

The kinetics of the reaction of OH radicals with 2,4-pentanedione and 3-methyl-2,4-pentanedione have been investigated in the gas-phase using a pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique. Hydroxyl radicals were generated from the parent compounds following pulsed laser photolysis at 248 nm. The rate coefficients were also determined using a conventional relative rate method. Average values of the bimolecular rate coefficients of $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3) = (8.78 \pm 0.58) \times 10^{-11}$, $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3) = (6.06 \pm 0.54) \times 10^{-11}$ and $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3) = (1.16 \pm 0.09) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ were determined at $298 \pm 2 \text{ K}$. Rate coefficients for the reaction of OH radicals with allyl alcohol and methyl vinyl ketone were also determined at $298 \pm 2 \text{ K}$ using the PLP-LIF technique employing the photolysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione as the OH radical sources respectively, $k(\text{OH} + \text{CH}_2=\text{CHCH}_2\text{OH}) = (4.60 \pm 0.19) \times 10^{-11}$ and $k(\text{OH} + \text{CH}_2=\text{CHC}(\text{O})\text{CH}_3) = (1.86 \pm 0.12) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$. The measured rate coefficients are used to derive tropospheric lifetimes for the compounds.

© 2005 Elsevier B.V. All rights reserved.

Keywords: 2,4-Pentanedione; 3-Methyl-2,4-pentanedione; Photolysis; Hydroxyl radical; Atmospheric chemistry

1. Introduction

Ketones are extensively used as solvents and are also produced during the atmospheric oxidation of volatile organic compounds. Although ketones absorb quite strongly in the actinic region, photolysis studies carried out under atmospheric conditions show that except for acetone, photolytic degradation is a minor loss process [1–3]. The available evidence suggests that the oxidation of saturated carbonyl compounds is largely initiated by their reaction with hydroxyl radicals, and the kinetics and mechanisms for these reactions have been comprehensively reviewed [4–6].

It is apparent from the reported kinetic data that a carbonyl group appears to have little effect on the reactivities of $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$ groups in ketones, which are quite similar to their reactivities in alkanes [4–6]. This result may be expected in terms of bond dissociation energies since C–H bond strengths in the α -position of ketones are approximately equal to those for the analogous groups in alkanes [7]. However, the carbonyl group is strongly electron withdrawing, and hence reaction of the electrophilic OH radical with a ketone at the α -position may be expected to be considerably less facile than with the corresponding group in an alkane. Although the $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$ groups in ketones have reactivities similar to those in alkanes, there is considerable enhancement in the reactivity of alkyl groups containing ≥ 3 carbon atoms in carbonyl compounds compared to their reactivities in alkanes [8–11]. In particular, the reactivity of C–H bonds at the β -carbon atom appears to be pronounced. The increase in rate coefficients with chain length

* Corresponding author. Tel.: +353 1 716 2293; fax: +353 1 716 1178.
E-mail address: howard.sidebottom@ucd.ie (H. Sidebottom).

for linear-chain ketones indicates that a $-\text{CH}_2-$ group in the γ -position is also more reactive than expected, although there is a reduction in reactivity along the chain from the β - to the γ -carbon atoms. Smith and Ravishankara [12] have rationalized the enhanced reactivity exhibited by carbonyl compounds in terms of the initial formation of a weakly bound hydrogen-bonded adduct between the OH radical and the carbonyl group, which leads to intramolecular H-atom abstraction from sites in the alkyl group via cyclic transition states. On this basis, the transition state for reaction of OH with acetone is stabilized by hydrogen bonding in a six-membered transition state, and hence the deactivating inductive effect of the carbonyl group is offset to some extent by the stabilizing effect of hydrogen bonding. As the chain length in the carbonyl compound increases, the deactivating inductive effect of the carbonyl group will diminish, while the transition states for H-atom abstraction at sites quite remote from the carbonyl group may be stabilized by hydrogen-bond formation.

Dagaut et al. [13] have reported rate coefficients for the reaction of OH radicals with the diones, 2,3-butanedione, 2,4-pentanedione and 2,5-hexanedione at 298 K using a flash photolysis-resonance fluorescence technique. The rate coefficient for the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3$ ($k_{\text{OH}} = 2.3 \pm 0.2 \times 10^{-13} \text{ cm}^3 (\text{molecule s})^{-1}$ [13]) is similar to that for the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ($k_{\text{OH}} = 2.0 \pm 0.2 \times 10^{-13} \text{ cm}^3 (\text{molecule s})^{-1}$ [7]) indicating that the $-\text{CH}_3$ groups in these compounds have almost the same reactivities. Assuming the α - CH_3 group reactivities in $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ also have similar reactivities to the α - CH_3 groups in acetone and 2,3-butanedione, the reactivities of the bridging $-\text{CH}_2-$ groups in these compounds may be estimated. Dagaut et al. [13] have used the OH radical rate data for reaction with 2,4-pentanedione and 2,5-hexanedione to calculate values of the rate coefficients per $-\text{CH}_2-$ group for reaction of OH with 2,4-pentanedione and 2,5-hexanedione of approximately 0.9×10^{-12} and $3.5 \times 10^{-12} \text{ cm}^3 (\text{molecule s})^{-1}$, respectively. The enhanced reactivity of the $-\text{CH}_2-$ groups in 2,5-hexanedione, which are α to one carbonyl group and β to the other carbonyl group, can be rationalized in terms of the activation of the H atoms by both carbonyl groups as the result of the initial formation of a hydrogen-bonded adduct, followed by formation of a cyclic transition state.

It is somewhat surprising that the $-\text{CH}_2-$ group in 2,4-pentanedione which is α to two carbonyl groups appears to be relatively unreactive. However, although 2,4-pentanedione is a β -diketone, it exists predominantly in its enolic form ($\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3$) in the gas-phase [14]. Hence reaction of OH with 2,4-pentanedione is expected to involve mainly addition to the double-bond system rather than a hydrogen abstraction process. The relatively low value reported for the rate coefficient for reaction of OH with 2,4-pentanedione at 298 K appears to be anomalously small for a reaction involving OH addition to a double bond.

A number of studies on the photodissociation dynamics of the enolic form of 2,4-pentanedione in the gas-phase have been reported [15–17]. The UV absorption spectrum of the enolic

form of 2,4-pentanedione shows a broad structureless band with an origin and peak at about 315 and 270 nm, respectively, and has been ascribed to the allowed $\pi-\pi^*$ transition [14]. Pulsed laser excitation in the $\pi-\pi^*$ transition has been found to lead to the rapid production of the OH radical as a result of photodissociation [15–17]. The energy distribution of the nascent OH radicals has been measured using the laser induced fluorescence technique and was found to be vibrationally cold with a Boltzmann type rotational distribution. The aim of this work was to investigate the kinetics of the reaction of OH radicals with 2,4-pentanedione and 3-methyl-2,4-pentanedione using the photolysis of the enolic forms of the parent compounds as the source of OH radicals. Rate coefficients have been determined at room temperature using the technique of pulsed laser photolysis-laser induced fluorescence. The rate data for the reactions were confirmed using a conventional relative rate method and the results have been used to estimate the environmental impact of β -diketones.

2. Experimental

2.1. Absolute rate studies

Absolute rate studies were carried out at $298 \pm 2 \text{ K}$ using a pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique. The experimental set-up employed has been described in detail previously [18,19]. Hydroxyl radicals were produced by the photolysis at 248 nm of 2,4-pentanedione and 3-methyl-2,4-pentanedione using a KrF excimer laser (Lambda Physik LPX 105i).

2, 4-pentanedione/3-methyl-2, 4-pentanedione



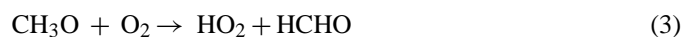
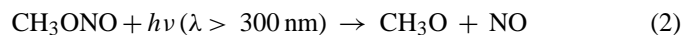
The energy of the photolysis laser was of the order of 2–15 mJ per pulse in the cell and the duration of the pulse was equal to 23 ns, full width at half maximum (fwhm). Hydroxyl radical concentrations were measured by laser induced fluorescence using a Nd:YAG (Continuum) pumped frequency doubled dye laser, which was triggered at a variable delay time after photolysis. The probe laser pulse passed through the reaction cell mutually orthogonal to the photolysis laser beam. The probe pulse excited the $Q_1 1$, $Q_1 1^1$ and the R_{23} lines in the (1,0) of the $(A^2\Sigma^+, v' = 1) \leftarrow (X^2\Pi, v'' = 0)$ transition of the hydroxyl radical at around 282 nm. The probe beam had a pulsewidth of 7 ns (fwhm) and a linewidth of 0.002 nm. Fluorescence from OH radicals was detected with a photomultiplier (Hamamatsu R292) equipped with a narrow bandpass filter (309.4 nm peak transmission, fwhm = 7.6 nm). The signals from 100 probe laser shots were averaged to obtain one datum (concentration, time) point. An OH concentration versus time profile was obtained by averaging signals for delay times from about 10 μs to 30 ms using a delay time generator (Stanford Research Systems DG 535). Typically 6–12 delays were sampled to map out an [OH] profile over at least three lifetimes. Measured amounts of the reactants in the helium bath gas were flowed through the cell with a linear velocity ranging between 5 and

20 cm s⁻¹ so that each photolysis/probe sequence investigated a fresh reaction mixture and reaction products did not accumulate in the cell. The concentration of reactants and the bath gas were calculated from their mass-flow rates, the temperature and the pressure in the reaction cell. The mass-flow meters were calibrated by measuring the rate of pressure increase in a known volume. The cell pressure was measured with a capacitance manometer connected adjacent to the entrance of the cell.

2.2. Relative rate studies

Reactions were carried out at 298 ± 2 K and atmospheric pressure in a collapsible FEP Teflon reaction chamber of volume 50 L. The chamber was surrounded by a bank of fluorescent lamps (Philips TL 20W/08), which supplied radiation over the wavelength range 300–450 nm. The reaction chamber was half-filled with zero-grade air via Teflon tubing using a calibrated flow meter. Measured pressures (MKS Baratron capacitance manometer) of reactants were flushed from calibrated Pyrex bulbs into the reaction chamber using a stream of diluent gas. Due to the low vapour pressure of 3-methyl-2,4-pentanedione, μL volumes of the liquid were injected directly into the diluent gas stream before it entered the chamber. Following addition of all the reactants the chamber was filled to its full capacity with diluent gas. The chamber was kept in the dark and its contents allowed to mix for approximately 30 min. A homogeneous reaction mixture was verified by consistent reproducible gas chromatographic analyses.

Hydroxyl radicals were generated by the photolysis of methyl nitrite.



NO was added to the reaction mixture in order to minimize ozone formation. Typical mixing ratios employed were: [substrate]₀ = [reference]₀ = 20–60 ppm, [CH₃ONO]₀ ~ 90 ppm, [NO]₀ ~ 30 ppm (1 ppm = 2.46 × 10¹³ molecules cm⁻³ at 298 K and 1 atm). Reactions were allowed to proceed until 40–60% depletion of the substrate or reference had occurred, thereby minimizing complications due to secondary reactions. Quantitative analyses of the reaction mixtures were achieved by gas chromatography (Shimadzu GC 8A) with flame ionisation detection. Chromatographic separation was achieved by using a 15 m wide-bore (0.53 mm i.d.) capillary column with SE-30 as the stationary phase and operated over the temperature range 35–55 °C, using N₂ as the carrier gas. The relative change in concentration of substrate and reference compounds was measured from integration of the chromatographic peaks.

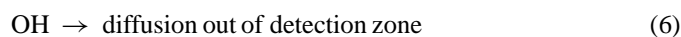
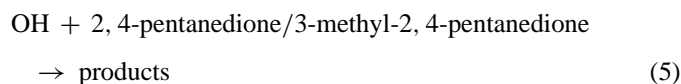
2.3. Materials

Synthetic air (Air Products, zero-grade 21% mol O₂ balance N₂ 99.995%) and helium carrier gas (UHP certified to

>99.995%, Alphagas) were used as received. 2,4-Pentanedione, 3-methyl-2,4-pentanedione, methyl vinyl ketone, 2-propen-1-ol, 2,3-dimethyl-2-butene and *n*-decane were obtained from Sigma–Aldrich and had stated purities of >99%. Methyl nitrite was prepared by the drop-wise addition of 50% sulphuric acid to a saturated solution of sodium nitrite in water and methanol. The products were carried by a stream of nitrogen gas through a saturated solution of sodium hydroxide followed by calcium chloride, to remove excess acid, and water and methanol, respectively. Methyl nitrite was collected and stored at 193 K. All the reactants were stored in evacuated glass vessels and subjected to freeze–thaw–pump cycles prior to use. Ozone was produced by flowing zero-grade air through an ozone generator (Monitor Labs) directly into the Teflon reaction chamber at a flow rate of 1 L min⁻¹ for 10 min.

3. Results

Although 2,4-pentanedione and 3-methyl-2,4-pentanedione are β-diketones, they can also exist in their enolic forms. These α,β-enones, in which there is conjugation between C=C and C=O double-bond systems, have been shown to exhibit rather unusual spectroscopic and photochemical properties [14–17]. Infrared and gas chromatographic analysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione showed that in the gas-phase at 298 K 2,4-pentanedione exists predominantly as the enol CH₃C(O)CH=C(OH)CH₃ (>95%), while for 3-methyl-2,4-pentanedione both the diketone CH₃C(O)CH(CH₃)C(O)CH₃ (40 ± 5%) and enol CH₃C(O)C(CH₃)=C(OH)CH₃ (60 ± 5%) are important. Addition of excess ozone to 3-methyl-2,4-pentanedione in the gas-phase led to the rapid removal of virtually all the enol present in the system. As expected the loss of the diketone was minimal. The system was found to re-equilibrate with a half life of around 10 h, however the rate of reformation of the enol from the diketone was insignificant in comparison with the loss of diketone and enol in relative rate studies on the reaction of OH radicals with 3-methyl-2,4-pentanedione. Pulsed laser photolysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione at 248 nm generated OH radicals which were detected by laser induced fluorescence. The rise in OH radical concentration during the photolysis laser pulse was faster than the experimental resolution of approximately 10⁸ s⁻¹. All absolute rate kinetic experiments were conducted under pseudo-first-order conditions with [substrate]₀ > 100[OH]₀, following OH radical production through photolysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione. Typically, the initial OH concentration, [OH]₀ was estimated at around 1 × 10¹¹ molecules cm⁻³. Following OH formation from the photolysis of the precursor, reaction (1), the radical may be lost through the following processes:



hence

$$\begin{aligned} \frac{d[\text{OH}]}{dt} &= (k_5[2,4\text{-pentanedione}/3\text{-methyl-}2,4\text{-pentanedione}] \\ &+ k_6)[\text{OH}] \end{aligned}$$

The rate of disappearance of OH follows a simple exponential rate law:

$$[\text{OH}]_t = [\text{OH}]_0 e^{-k't}$$

where

$$k' = k_5[2,4\text{-pentanedione}/3\text{-methyl-}2,4\text{-pentanedione}] + k_6$$

(1)

Experiments were conducted at 298 ± 2 K in helium in the pressure range 100–300 Torr. The high $[\text{substrate}]_0/[\text{OH}]_0$ ratios and low OH concentrations ensured that there was a negligible contribution to the reported rate coefficient from secondary reactions involving the reaction products. Values of k' determined at different gas flow rates through the reactor or at various total pressures in the system were indistinguishable. As expected variation in the photolysis laser fluence ($2\text{--}15 \text{ mJ cm}^{-2}$) has no effect on the values of k' . Since 2,4-pentanedione and 3-methyl-2,4-pentanedione were of high purity, the reaction of OH with impurities in the system are likely to be insignificant as the reaction of OH with the substrate compounds is relatively facile. For the conditions employed in these experiments, the decays of OH radicals were found to be exponential over at least two lifetimes. A typical OH radical decay plot is given in Fig. 1 from an experiment in which the concentration of 3-methyl-2,4-pentanedione was $0.509 \times 10^{14} \text{ molecules cm}^{-3}$. Plots of k' versus substrate concentration for the reaction of OH radicals with 2,4-pentanedione and 3-methyl-2,4-pentanedione are given in Fig. 2.

The plots are linear with close to zero intercepts ($k_6 < 100 \text{ s}^{-1}$) and the slopes provide values of $k(\text{OH} + 2,4\text{-pentanedione}) = (8.80 \pm 0.05) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ and $k(\text{OH} + 3\text{-methyl-}2,4\text{-pentanedione}) = (2.81 \pm 0.16) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ at 298 K. The quoted errors in the rate coefficients are 2σ from the least-squares analysis of the data, and do not include an estimate of systematic errors, which will probably add around 5% due to errors in reactant concentrations.

To verify that photolysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione provides a reliable source of OH radicals in absolute rate experiments, these compounds were employed as OH precursors for the reactions of OH with 2-propen-1-ol (allyl alcohol) and 3-buten-2-one (methyl vinyl ketone). In these systems, the loss of OH radicals following formation from 2,4-pentanedione and 3-methyl-2,4-pentanedione in reaction (1) is governed by the following reactions:

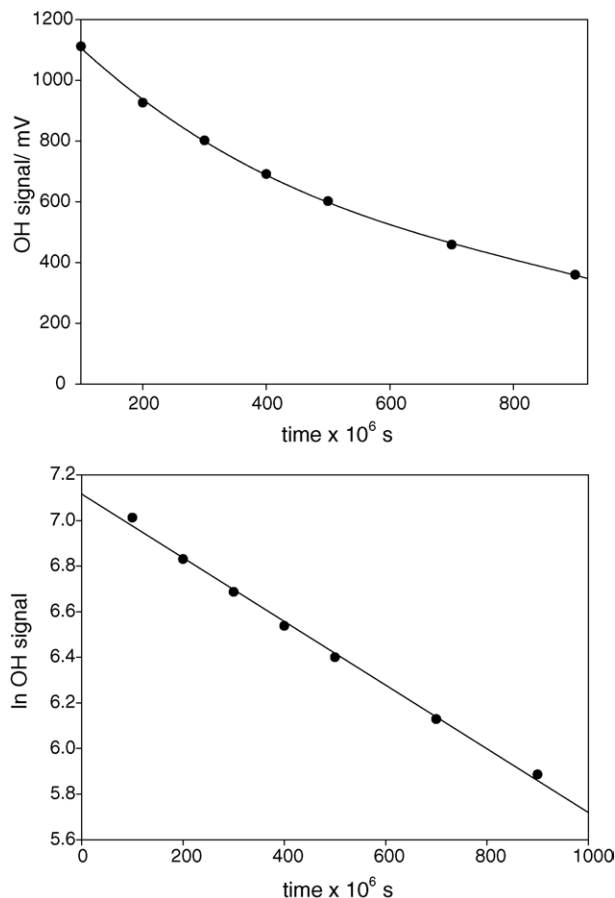
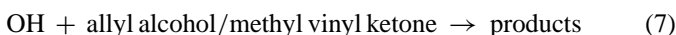
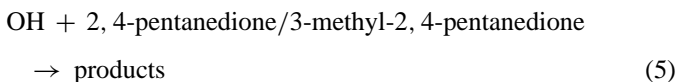


Fig. 1. Plot of OH radical signal versus time for the photolysis of 3-methyl-2,4-pentanedione at 248 nm and 298 K.



hence

$$\begin{aligned} \frac{d[\text{OH}]}{dt} &= (k_5[2,4\text{-pentanedione}/3\text{-methyl-}2,4\text{-pentanedione}] \\ &+ k_7[\text{allyl alcohol}/\text{methyl vinyl ketone}] + k_6)[\text{OH}] \end{aligned}$$

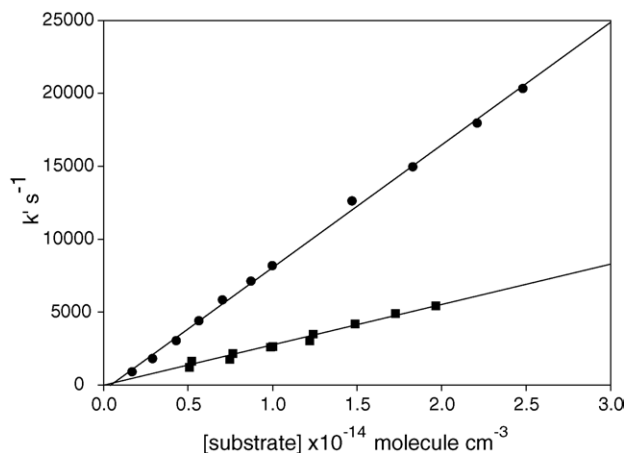


Fig. 2. Plots of k' vs. substrate concentration for the reaction of OH radicals with 2,4-pentanedione (●) and 3-methyl-2,4-pentanedione (■) at 298 K.

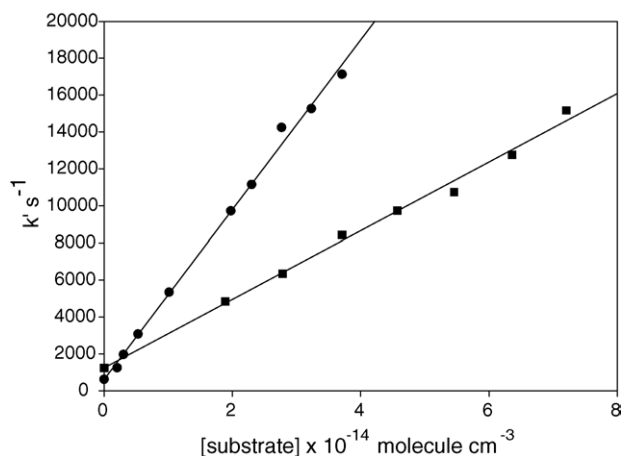


Fig. 3. Plot of k' vs. substrate concentration for the reaction of OH radicals with allyl alcohol (●) and methyl vinyl ketone (■) at 298 K using 2,4-pentanedione and 3-methyl-2,4-pentanedione as the OH precursor, respectively.

and the pseudo-first-order rate coefficient, k' , is given by:

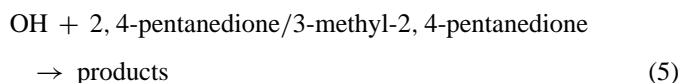
$$k' = k_5[2,4\text{-pentanedione}/3\text{-methyl-2,4-pentanedione}] + k_7[\text{allyl alcohol}/\text{methyl vinyl ketone}] + k_6 \quad (\text{II})$$

The reaction of OH radicals with allyl alcohol was carried out with 2,4-pentanedione as the OH source, with $[2,4\text{-pentanedione}]_0 = 1.57 \times 10^{13} \text{ molecules cm}^{-3}$ for which $(k_5[2,4\text{-pentanedione}] + k_6) = 1.4 \times 10^3 \text{ s}^{-1}$. A plot of k' against $[\text{allyl alcohol}]$ is shown in Fig. 3 and the slope provides a value $k_7(\text{OH} + \text{allyl alcohol}) = (4.60 \pm 0.19) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$.

In a similar series of experiments, 3-methyl-2,4-pentanedione was used to generate OH radicals in an investigation of the reaction of methyl vinyl ketone with OH. Fig. 3 shows the data from reactions in which $[3\text{-methyl-2,4-pentanedione}] = 5.15 \times 10^{13} \text{ molecules cm}^{-3}$ and $(k_5[3\text{-methyl-2,4-pentanedione}] + k_6) = 1.5 \times 10^3 \text{ s}^{-1}$ giving $k(\text{OH} + \text{methyl vinyl ketone}) = (1.86 \pm 0.12) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$.

3.1. Relative rate studies

Relative rate coefficients for the reaction of OH radicals with 2,4-pentanedione and 3-methyl-2,4-pentanedione were determined by comparing the loss of the substrate to that of a reference compound whose rate coefficient for reaction with OH is accurately known.



Assuming both reactant and reference compounds are lost only due to reaction with OH and dilution due to sampling is negligible, it can be shown that:

$$\ln \left\{ \frac{[\text{substrate}]_0}{[\text{substrate}]_t} \right\} = \frac{k_5}{k_8} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (\text{III})$$

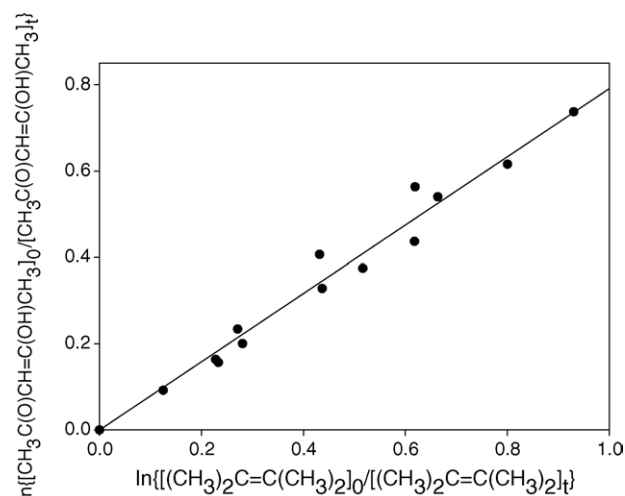


Fig. 4. Concentration–time data for the reaction of OH radicals with the enol tautomer of 2,4-pentanedione and 2,3-dimethyl-2-butene as the reference compound at $298 \pm 2 \text{ K}$.

The subscripts 0 and t indicate the concentration of reactants at the beginning and at time t of the experiment, respectively. The substrate and reference compounds used were shown to be stable in the dark. Photochemical loss of the reference compounds, 2,3-dimethyl-2-butene and n -decane and the enol tautomer of 2,4-pentanedione were shown to be negligible over the time period of the relative rate studies. 3-Methyl-2,4-pentanedione (both tautomers) was found to photolyse slowly under the experimental conditions employed, however, photolysis was shown not to lead to tautomerisation in the system. The following correction was made to Eq. (III) in order to account for this photolysis:

$$\ln \left\{ \frac{[\text{substrate}]_0}{[\text{substrate}]_t} \right\} - k_p t = \frac{k_5}{k_8} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (\text{IV})$$

where k_p is the measured photolysis rate. Values of the experimental photolytic rate coefficients were $k_p(\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3) = 4.8 \times 10^{-5} \text{ s}^{-1}$ and $k_p(\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3) = 1.2 \times 10^{-4} \text{ s}^{-1}$. At least three different experiments were carried out for each compound. Concentrations of substrate and reference compounds were measured as a function of time and plots in the form of Eqs. (III) and (IV) were used to determine k_5 . Since both the diketone and enol tautomers of 3-methyl-2,4-pentanedione were present in the system, it was possible to monitor the loss of both of these species. Preliminary experiments showed that the rate of interconversion of the diketone and enol forms of 3-methyl-2,4-pentanedione was insignificant compared to the loss of the tautomers due to reaction in the OH radical kinetic experiments. Hence, rate coefficients for reaction of OH radicals with both tautomers could be determined separately in relative rate experiments. The concentration–time plots for the reaction of OH radicals with 2,4-pentanedione and 3-methyl-2,4-pentanedione are given in Figs. 4 and 5, respectively, and exhibit excellent linearity with near zero intercepts.

Rate coefficients for the reaction of OH with substrates were determined from the slopes of the plots, k_5/k_8 , using $k(\text{OH} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 (\text{molecule s})^{-1}$ and $k(\text{OH} + n\text{-decane}) = 1.12 \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ based on

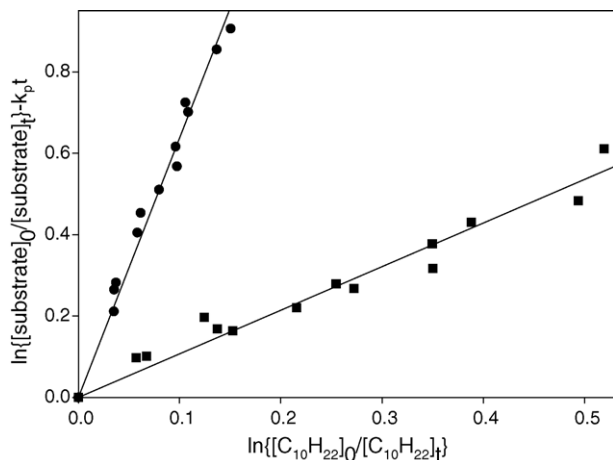


Fig. 5. Concentration–time data for the reaction of OH radicals with the keto (■) and enol (●) tautomers of 3-methyl-2,4-pentanedione and *n*-decane as the reference compound at 298 ± 2 K.

the evaluation of Atkinson [20]. The values of the slopes of the plots were $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3)/k_8(\text{OH} + (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2) = 0.796 \pm 0.052$, $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{C}(\text{C}\text{H}_3)=\text{C}(\text{OH})\text{CH}_3)/k_8(\text{OH} + \text{C}_{10}\text{H}_{22}) = 6.24 \pm 0.29$ and $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3)/k_8(\text{OH} + \text{C}_{10}\text{H}_{22}) = 1.04 \pm 0.08$. The derived rate coefficients were $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3) = (8.76 \pm 0.57) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$, $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3) = (6.99 \pm 0.32) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ and $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3) = (1.16 \pm 0.09) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$. The quoted errors are twice the standard deviation arising from the least-squares fit of the data and do not include an estimate of the error in the reference rate coefficient, k_8 . The errors in k_8 probably add a further 20% to the uncertainty of the rate coefficients reported in these relative rate studies.

4. Discussion

Absolute rate coefficient data have been determined in this work for the reactions of OH radicals with $\text{CH}_2=\text{CHCH}_2\text{OH}$ and $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$ using the photolysis of the enolic tautomers of 2,4-pentanedione and 3-methyl-2,4-pentanedione, respectively, as the OH radical source. The values determined for $k_7(\text{OH} + \text{CH}_2=\text{CHCH}_2\text{OH}) = (4.60 \pm 0.19) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ and $k_7(\text{OH} + \text{CH}_2=\text{CHC}(\text{O})\text{CH}_3) = (1.86 \pm 0.12) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ are in excellent agreement with previously reported rate data for these compounds. Papagni et al. [21] reported a rate coefficient for the reaction of OH radicals with allyl alcohol of $(5.46 \pm 0.35) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ and Orlando et al. [22] have determined a similar rate coefficient of $(4.5 \pm 0.6) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$. For the reaction of OH radicals with methyl vinyl ketone, Chuong and Stevens [23] have reported a rate coefficient of $(1.73 \pm 0.21) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$. These results demonstrate that the photolysis of 2,4-pentanedione and 3-methyl-2,4-pentanedione provides a reliable source of thermalized OH radicals in PLP-LIF studies of OH radical

kinetics. It is interesting to note that Upadhyaya et al. [24] have recently determined the rate coefficient for the reaction of OH with allyl alcohol using a pulsed laser photolysis-laser induced fluorescence technique in which the OH radical was generated by the laser photolysis of the alcohol at 193 nm. The experiments were carried out in 10–20 Torr of argon and the rate coefficient is slightly below that reported in the present work and the atmospheric pressure rate coefficient determined by Papagni et al. [21] and Orlando et al. [22]. It is possible that addition of OH to the double-bond system in $\text{CH}_2=\text{CHCH}_2\text{OH}$ is in the fall-off region at the low pressures employed by Upadhyaya et al. [24].

2,4-Pentanedione exists predominantly as the enol tautomer in the gas-phase and hence the value of $k_5 = (8.80 \pm 0.05) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ measured in the present absolute rate study is for the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3$. The rate coefficient is in excellent agreement with the value of $k_5 = (8.76 \pm 0.57) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ derived from the relative rate studies on this reaction. The PLP-LIF and relative rate data provide an average value of $k_5(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3) = (8.78 \pm 0.58) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$. The rate coefficient determined in the present work is almost two orders of magnitude higher than the value previously reported by Dagaut et al. [13]. In the flash photolysis technique employed by Dagaut et al. [13], in which OH was generated by vacuum UV photolysis of H_2O at $\lambda \geq 165 \text{ nm}$, significant amounts of OH would also be formed from the photolysis of 2,4-pentanedione. This additional source of OH in the system may have caused problems in the analysis of the OH decays and since the reaction was carried out at relatively low pressures (25–50 Torr argon diluent) the reaction may be in the fall-off region with the initial OH-enol adduct decomposing back to the reactants.

Both tautomers of 3-methyl-2,4-pentanedione are present in the gas-phase and hence the value of $k_5 = (2.81 \pm 0.16) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ determined from the slope of a plot of k' where $k' = k_5[3\text{-methyl-2,4-pentanedione}] + k_6$, Eq. (I) against the concentration of 3-methyl-2,4-pentanedione, Fig. 2, gives the overall rate coefficient for the loss of OH radicals by reaction with 3-methyl-2,4-pentanedione. However, since OH is lost by reaction with both tautomers:

$$k(3\text{-methyl-2, 4-pentanedione}) = k_5(\text{diketone})[\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3] + k_5(\text{enol})[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3] \quad (\text{V})$$

combining Eqs. (I) and (V) gives:

$$k' = k_5(\text{diketone})[\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3] + k_5(\text{eno1})[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3] + k_6 \quad (\text{VI})$$

and

$$k' - k_5(\text{diketone})[\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3] = k_5(\text{enol})[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3] + k_6 \quad (\text{VII})$$

A value of $k_5(\text{diketone}) = (1.16 \pm 0.09) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ was determined from the relative rate studies

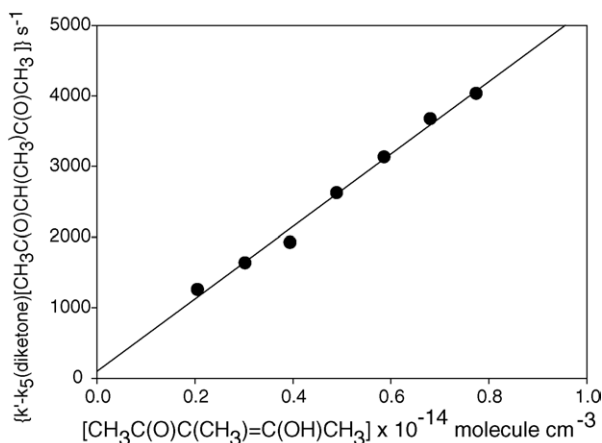


Fig. 6. Plot of $k' - k_5(\text{diketone})[\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3]$ vs. $[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3]$.

on the reaction of OH with 3-methyl-2,4-pentanedione and the concentrations of the diketone and enol tautomers were obtained from the total substrate concentration taking the ratio $[\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3]:[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3] = 60:40$. A plot of $k' - k_5(\text{diketone}) [\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3]$ against $[\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3]$, Fig. 6, yields a value of $k_5(\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3) = (5.13 \pm 0.44) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$.

The quoted error is twice the standard deviation arising from the least-squares fit of the data plotted in Fig. 6, but does not include the errors in the value of $k_5(\text{diketone})$ and in the relative concentrations of the diketone and enol. The value of $k_5 = (5.12 \pm 0.44) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ for the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3$ derived from the overall rate coefficient for the reaction of OH with 3-methyl-2,4-pentanedione determined from PLP-LIF experiments combined with the rate coefficient for the reaction of OH with the diketone tautomer from relative rate studies is in reasonable agreement with the value of $k_5 = (6.99 \pm 0.32) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ obtained directly from relative rate experiments. The average value of the two determinations for the reaction of OH with $\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3$ is $(6.06 \pm 0.54) \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$.

The rate coefficients determined in this work for the reaction of OH radicals with the enols tautomers of 2,4-pentanedione and 3-methyl-2,4-pentanedione show that the reactions are relatively facile suggesting that the reactions probably involve addition to the carbon–carbon double-bond system. Since the measured rate coefficients were found to be independent of the He pressure over the range 100–300 Torr it appears that the reactions are at the high pressure limit. The available kinetic data for the addition of OH radicals to carbon–carbon unsaturated bonds shows that the reactivity depends on the number, identity and position of substituent groups around the carbon–carbon double bond [25]. Substitution of the hydrogen atoms in ethene with methyl groups leads to a progressive increase in the rate coefficients for reaction: $k(\text{OH} + \text{CH}_2=\text{CH}_2) = 0.852$, $k(\text{OH} + \text{CH}_2=\text{CHCH}_3) = 2.63$, $k(\text{OH} + E/Z \text{ CH}_3\text{CH}=\text{CHCH}_3)$

$= 6.0$, $k(\text{OH} + \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2) = 8.69$ and $k(\text{OH} + (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2) = 11.0$, [20], in units of $10^{11} \text{ cm}^3 (\text{molecule s})^{-1}$. The rate coefficient for reaction of OH with $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$, $k_{\text{OH}} = 1.8 \times 10^{-11} \text{ cm}^3 (\text{molecule s})^{-1}$ [[23], this work] is only slightly smaller than for the reaction of OH with propene showing that the $-\text{C}(\text{O})\text{CH}_3$ group has a similar activating effect to that of a $-\text{CH}_3$ group. No kinetic data is available for the reaction of OH with an alkene in which an $-\text{OH}$ group is directly bonded to a carbon atom of a double bond, however, rate coefficient data for the reaction of OH with allyl alcohol [21,22] and vinyl ethers [26,27] show that the activating effect of both $-\text{CH}_2\text{OH}$ and $-\text{OR}$ (R is an alkyl group) is about a factor of two greater than that shown by a $-\text{CH}_3$. It is possible that the activating effects of $-\text{C}(\text{O})\text{CH}_3$, $-\text{CH}_2\text{OH}$ and $-\text{OR}$ groups is at least partly due to the possibility of the formation of a hydrogen-bonded adduct between the attacking OH radical and the oxygenated substituent group leading to the stabilization of the transition state for the reaction [6]. Thus, it seems likely that a $-\text{OH}$ group bonded directly to the double-bond site will also lead to enhancement of the rate for the reaction of OH with an alkene. The rate coefficients obtained for the reaction of OH radicals with the enols, $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{OH})\text{CH}_3$ and $\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{C}(\text{OH})\text{CH}_3$ are similar, and are in line with the rate data for the reactions of OH with $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$. The rate coefficient reported for the diketone tautomer of 3-methyl-2,4-pentanedione, $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$, is considerably smaller than the value for reaction of OH with the enols and is consistent with a reaction involving H-atom abstraction from a tertiary carbon atom, which is α to two $-\text{C}(\text{O})\text{CH}_3$ groups.

Gas-phase reaction with hydroxyl radicals is expected to be an important loss process for β -diketones in the troposphere. Since the enol tautomers of β -diketones in the gas-phase are important and contain carbon–carbon double-bond systems, reaction with O_3 and NO_3 radicals may also contribute to their degradation processes. The atmospheric lifetimes (τ) of β -diketones with respect to reaction with OH radicals may be calculated by using the following expression $\tau = 1/k_{\text{OH}}[\text{OH}]$, where k_{OH} is the bimolecular rate coefficient and $[\text{OH}]$ is the tropospheric concentration of OH radicals. Using the values of k_{OH} obtained in this work for reaction with 2,4-pentanedione and 3-methyl-2,4-pentanedione and an average concentration of $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ [28], the lifetimes of these β -diketones are around 4 h. Lifetimes of around 6 and 15 h are estimated for allyl alcohol and methyl vinyl ketone, respectively, from the rate data obtained in this work. The relatively short lifetimes indicate that these unsaturated oxygenated compounds will be oxidized rapidly by reaction with OH (and probably also by O_3 and NO_3) near their anthropogenic origin.

Acknowledgement

Financial support for this work was provided by the European Commission through the research project MOST, Contract No. EVR2-CT-2001-00114.

References

- [1] R.D. Martinez, A.A. Buitrago, W.W. Howel, C.H. Hearn, J.A. Joens, *Atmos. Environ.* 26A (1992) 785.
- [2] M. Yujing, A. Mellouki, *J. Photochem. Photobiol. A: Chem.* 134 (2000) 31.
- [3] T. Gierczak, J.B. Buckholder, S. Bauerle, A.R. Ravishankara, *Chem. Phys. Lett.* 213 (1998) 229.
- [4] R. Atkinson, *J. Phys. Chem. Ref. Data Monogr.* 1 (1989).
- [5] R. Atkinson, *J. Phys. Chem. Ref. Data Monogr.* 2 (1994).
- [6] A. Mellouki, G. Le Bras, H. Sidebottom, *Chem. Rev.* 103 (2003) 5077.
- [7] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson Jr., J.A. Kerr, M.J. Rossi, J. Troe, *J. Phys. Chem. Ref. Data* 28 (1999) 191.
- [8] R. Atkinson, S.M. Aschmann, W.P.L. Carter, J.N. Pitts Jr., *Int. J. Chem. Kinet.* 14 (1982) 839.
- [9] T.J. Wallington, M.J. Kurylo, *J. Phys. Chem.* 91 (1987) 5050.
- [10] R. Atkinson, S.M. Aschmann, *J. Phys. Chem.* 102 (1988) 4008.
- [11] S. Le Calvé, D. Hitlier, G. Le Bras, A. Mellouki, *J. Phys. Chem. A* 102 (1998) 4579.
- [12] I.W.M. Smith, A.R. Ravishankara, *J. Phys. Chem. A* 106 (2002) 4798.
- [13] P. Dagaut, T.J. Wallington, R. Liu, M.J. Kurylo, *J. Phys. Chem.* 92 (1988) 4375.
- [14] H. Nakanishi, H. Morita, S. Nagakura, *Bull. Chem. Soc. Jpn.* 50 (1977) 2255.
- [15] M.C. Yoon, Y.S. Choi, S.K. Kim, *Chem. Phys. Lett.* 300 (1999) 207.
- [16] M.C. Yoon, Y.S. Choi, S.K. Kim, *Chem. Phys. Lett.* 110 (1999) 11850.
- [17] H.P. Upadhyaya, A. Kumar, P.D. Naik, *J. Chem. Phys.* 118 (2003) 2590.
- [18] A. Mellouki, S. Téton, G. Laverdet, A. Quilgars, G. Le Bras, *J. Chim. Phys.* 91 (1994) 473.
- [19] A. Mellouki, S. Téton, G. Le Bras, *Int. J. Chem. Kinet.* 27 (1995) 791.
- [20] R. Atkinson, *J. Phys. Chem. Ref. Data* 26 (1997) 215.
- [21] C. Papagni, J. Arey, R. Atkinson, *Int. J. Chem. Kinet.* 33 (2001) 142.
- [22] J.J. Orlando, G.S. Tyndall, N. Ceazan, *J. Phys. Chem. A* 105 (2001) 3364.
- [23] B. Chuong, P.S. Stevens, *J. Phys. Chem. A* 107 (2003) 2185.
- [24] H.P. Upadhyaya, A. Kumar, P.D. Naik, A.V. Sapre, J.P. Mittal, *Chem. Phys. Lett.* 349 (2001) 279.
- [25] E.S.C. Kwok, R. Atkinson, *Atmos. Environ.* 29 (1995) 1685.
- [26] R.A. Perry, R. Atkinson, J.N. Pitts Jr., *J. Chem. Phys.* 67 (1977) 611.
- [27] G. Thiault, R. Thévenet, A. Mellouki, G. Le Bras, *Phys. Chem. Chem. Phys.* 4 (2002) 613.
- [28] R.G. Prinn, R.F. Weiss, B.R. Miller, F.N. Huang, J. Algea, D. Cunnold, P.J. Fraser, D.E. Hartley, P.J. Simmonds, *Science* 269 (1995) 187.