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Journal of Photochemistry and Photobiology A: Chemistry 176 (2005) 183–190

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

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 Universtät Wuppertal, Gauss Strasse 20, D-42097 Wuppertal, Germany*

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 $k(OH + CH_3C(O)CH{=}C(OH)CH_3) = (8.78 \pm 0.58) \times 10^{-11}$, $k(OH + CH_3C(O)C(CH_3){=}C(OH)CH_3) = (6.06 \pm 0.54) \times 10^{-11}$ and $k(OH + CH_3C(O)CH(CH_3)C(O)CH_3) = (1.16 \pm 0.09) \times 10^{-11}$ cm^3 (molecule s)$^{-1}$ were determined at 298 ± 2 K. Rate coefficients for the reaction of OH radicals with allyl alcohol and methyl vinyl ketone were also determined at 298 ± 2 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, $k(OH + CH_2{=}CHCH_2OH) = (4.60 \pm 0.19) \times 10^{-11}$ and $k(OH + CH_2{=}CHC(O)CH_3) = (1.86 \pm 0.12) \times 10^{-11}$ cm^3 (molecule s)$^{-1}$. The measured rate coefficients are used to derive tropospheric lifetimes for the compounds.

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 $-CH_3$ and $-CH_2CH_3$ 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 $-CH_3$ and $-CH_2CH_3$ 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

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

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doi:10.1016/j.jphotochem.2005.08.031

for linear-chain ketones indicates that a $-CH_2-$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 $CH_3C(O)C(O)CH_3$ ($k_{OH} = 2.3 \pm 0.2 \times 10^{-13}$ cm^3 (molecule s)$^{-1}$ [13]) is similar to that for the reaction of OH with $CH_3C(O)CH_3$ ($k_{OH} = 2.0 \pm 0.2 \times 10^{-13}$ cm^3 (molecule s)$^{-1}$ [7]) indicating that the $-CH_3$ groups in these compounds have almost the same reactivities. Assuming the α–CH_3 group reactivities in $CH_3C(O)CH_2C(O)CH_3$ and $CH_3C(O)CH_2CH_2C(O)CH_3$ also have similar reactivities to the α–CH_3 groups in acetone and 2,3-butanedione, the reactivities of the bridging $-CH_2-$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 $-CH_2-$group for reaction of OH with 2,4-pentanedione and 2,5-hexanedione of approximately 0.9×10^{-12} and 3.5×10^{-12} cm^3 (molecule s)$^{-1}$, respectively. The enhanced reactivity of the $-CH_2-$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 $-CH_2-$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 ($CH_3C(O)CH{=}C(OH)CH_3$) 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 π–π* transition [14]. Pulsed laser excitation in the π–π* 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 ± 2 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).

$$\text{2, 4-pentanedione/3-methyl-2, 4-pentanedione} + h\nu\,(\lambda = 248\,\text{nm}) \rightarrow \text{OH} \quad (1)$$

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_11, Q_11^1 and the R_23 lines in the (1,0) of the $(A^2\sum^+, v' = 1) \leftarrow (X^2\Pi, v'' = 0)$ 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 (Standford 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