

# ATMOSPHERIC CHEMISTRY OF SELECTED HYDROXYCARBONYLS

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## Introduction

Volatile organic compounds present in the atmosphere can undergo photolysis and chemical reaction with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> [1], with the OH radical reaction being an important, and often dominant, atmospheric loss process [1,2]. Hydroxycarbonyls are formed as atmospheric reaction products of organic compounds; for example, δ-hydroxycarbonyls are formed from the OH radical-initiated reactions of alkanes [1,3] and β-hydroxycarbonyls can be formed from the OH radical-initiated reactions of alkenes [1,3]. Because of difficulties in the analysis of this class of compounds, few data are presently available concerning the atmospheric chemistry of these compounds [1,2]. It is expected that the dominant atmospheric loss process for the hydroxycarbonyls not containing unsaturated >C=C< bonds is by daytime reaction with the OH radical [1], with photolysis also being possible.

In this work, we have measured the rate constants for the gas-phase reactions of the hydroxycarbonyls 1-hydroxy-2-butanone, 3-hydroxy-2-butanone, 1-hydroxy-3-butanone, 1-hydroxy-2-methyl-3-butanone, 3-hydroxy-3-methyl-2-butanone and 4-hydroxy-3-hexanone with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> at 296 ± 2 K. In addition, we have investigated the products formed from the

reactions of the OH radical with the  $\beta$ -hydroxycarbonyls 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone.

## Experimental

Experiments were carried out in a 7900 liter Teflon chamber, equipped with two parallel banks of Sylvania F40/350BL blacklamps for irradiation, at  $296 \pm 2$  K and 740 Torr total pressure of purified air at ~5% relative humidity. This chamber is fitted with a Teflon-coated fan to ensure the rapid mixing of reactants during their introduction into the chamber. Rate constants for the OH radical and  $\text{NO}_3$  radical reactions were determined using relative rate methods in which the relative disappearance rates of the hydroxycarbonyls and a reference compound, whose OH radical or  $\text{NO}_3$  radical reaction rate constant is reliably known, were measured in the presence of OH radicals or  $\text{NO}_3$  radicals [4]. Providing that the hydroxycarbonyls and the reference compound reacted only with OH radicals or  $\text{NO}_3$  radicals, then [4],

$$\ln\left\{\frac{[\text{hydroxycarbonyl}]_{t_0}}{[\text{hydroxycarbonyl}]_t} - D_t\right\} = \quad (I)$$
$$(k_1/k_2)\ln\left\{\frac{[\text{hydroxycarbonyl}]_{t_0}}{[\text{hydroxycarbonyl}]_t} - D_t\right\}$$

where  $[\text{hydroxycarbonyl}]_{t_0}$  and  $[\text{reference compound}]_{t_0}$  are the concentrations of the hydroxycarbonyl and reference compound, respectively, at time  $t_0$ ,  $[\text{hydroxycarbonyl}]_t$  and  $[\text{reference compound}]_t$  are the corresponding concentrations at time  $t$ ,  $D_t$  is a factor to account for any dilution due to additions to the chamber during the reactions, and  $k_1$  and  $k_2$  are the rate constants for reactions (1) and (2), respectively.



OH radicals were generated by the photolysis of methyl nitrite ( $\text{CH}_3\text{ONO}$ ) in air at wavelengths  $>300$  nm, and NO was added to the reactant mixtures to suppress the formation of  $\text{O}_3$  and hence of  $\text{NO}_3$  radicals. The initial reactant concentrations were similar to those used in analogous studies conducted in this laboratory [4]. The hydroxycarbonyls were also photolyzed in air in the presence of cyclohexane (to scavenge any OH radicals present).

$\text{NO}_3$  radicals were generated in the dark by the thermal decomposition of  $\text{N}_2\text{O}_5$  [18], and 1-butene or crotonaldehyde ( $\text{CH}_3\text{CH}=\text{CHCHO}$ ) were used as the reference compounds. Experiments were carried out as described previously [4]. The concentrations of the hydroxycarbonyls and the reference compounds were measured by gas chromatography with flame ionization detection (GC-FID) during the experiments.

Rate constants, or upper limits thereof, for the reactions of the hydroxycarbonyls with  $\text{O}_3$  were determined in the dark by measuring the decay rates of the hydroxycarbonyls in the presence of measured concentrations of  $\text{O}_3$  [4]. Cyclohexane was added to the reactant mixtures to scavenge any OH radicals formed in the reaction systems. Ozone concentrations were measured by ultraviolet absorption using a Dasibi 1003-AH ozone analyzer.

Products were identified and quantified from the reactions of the OH radical with 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone, by GC-FID [4] and by combined gas chromatography-mass spectrometry (GC-MS).

## Results

Photolysis of the hydroxycarbonyls in air at the same light intensity as used in the OH radical rate constant determinations for up to 60 min showed <2% loss of the hydroxycarbonyls. Hence photolysis of the hydroxycarbonyls studied was of no importance during the irradiations employed for the determination of the OH radical reaction rate constants. *OH Radical Reactions*

A series of CH<sub>3</sub>ONO - NO - hydroxycarbonyl - *n*-octane - air irradiations were carried out. The rate constant ratios  $k_1/k_2$  and rate constants  $k_1$  obtained from least-squares analyses of the data are given in Table 1. GC-FID analyses of these irradiated mixtures showed the formation of products from the 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone reactions (but not from the other hydroxycarbonyls). Matching of GC retention times and mass spectra with those of authentic standards showed that the products are 2,3-butanedione (biacetyl) from 3-hydroxy-2-butanone and 3,4-hexanedione from 4-hydroxy-3-hexanone. Least-squares analyses of the data obtained (with corrections to the measured  $\alpha$ -dicarbonyl concentrations to account for minor losses due to photolysis and reaction with OH radicals) lead to formation yields of 2,3-butanedione from 3-hydroxy-2-butanone of  $79 \pm 14\%$  and of 3,4-hexanedione from 4-hydroxy-3-hexanone of  $84 \pm 7\%$ , where the indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the  $\beta$ -hydroxycarbonyls and  $\alpha$ -dicarbonyls of  $\pm 5\%$  each.

### *NO<sub>3</sub> Radical Reactions*

A series of reacting NO<sub>3</sub> - N<sub>2</sub>O<sub>5</sub> - NO<sub>2</sub> - hydroxycarbonyl - 1-butene (and/or crotonaldehyde) - air mixtures were carried out. While no significant ( $\leq 2\%$ ) consumption of 3-hydroxy-3-methyl-2-butanone occurred under conditions where 78% of the initial 1-butene had reacted, losses of the other hydroxycarbonyls were observed. Plots of Equation (I) showed distinct curvature, with the slope of

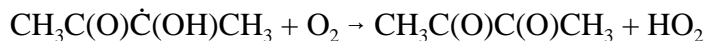
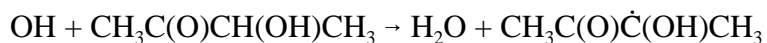
the curves decreasing with the extent of reaction to close to zero towards the end of the reactions (irrespective of whether 1-butene or crotonaldehyde was used as the reference compound and of the initial NO<sub>2</sub> concentration). While the reasons for this behavior are not presently understood, we used the final values of  $\{\ln([\text{hydroxycarbonyl}]_t/[\text{hydroxycarbonyl}]_0) - D\}$  and  $\{\ln([\text{reference compound}]_t/[\text{reference compound}]_0) - D\}$  to obtain upper limits to the rate constant ratios  $k_1/k_2$  and hence to the rate constants  $k_1$  (which are given in Table 2).

### *O<sub>3</sub> Rate Constants*

The measured maximum losses of gas-phase hydroxycarbonyls in the presence of  $3.44 \times 10^{13}$  molecule cm<sup>-3</sup> of O<sub>3</sub> over a period of 3.8 hr were <2-3% in each case, and within the analytical uncertainties. Assuming maximum hydroxycarbonyl losses due to reaction with O<sub>3</sub> of 5% leads to upper limits to the rate constants at  $296 \pm 2$  K of  $k_3 < 1.1 \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for each of these hydroxycarbonyls.

### **Discussion**

The lack of observed reaction of the hydroxycarbonyls studied with O<sub>3</sub>, and the slow reactions with the NO<sub>3</sub> radical, are consistent with literature data for aliphatic alcohols and ketones [1,5]. As is the case for the reactions of the OH radical with aliphatic alcohols and ketones, the OH radical reactions proceed by H-atom abstraction from the various C-H bonds and (generally to a minor extent) from the O-H bond [1,2]. The α-dicarbonyl products observed from 3-hydroxy-2-butanone and 4-hydroxy-3-hexanone clearly arise after H-atom abstraction from the activated tertiary H-atom of the CH(OH) group:



Combining our measured room temperature rate constants with a 24-hr average tropospheric OH radical concentration of  $1.0 \times 10^6$  molecule  $\text{cm}^{-3}$  [6,7] leads to calculated lifetimes of: 1-hydroxy-2-butanone, 1.5 day; 3-hydroxy-2-butanone, 1.1 day; 1-hydroxy-3-butanone, 1.4 day; 1-hydroxy-2-methyl-3-butanone, 0.7 day; 3-hydroxy-3-methyl-2-butanone, 12 days; and 4-hydroxy-3-hexanone, 0.8 day.

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Table 1. Rate constant ratios  $k_1/k_2$  and rate constants  $k_1$  for the gas-phase reactions of the OH radical with hydroxycarbonyls at  $296 \pm 2$  K.

hydroxycarbonyl	$k_1/k_2$ <sup>a</sup>	$10^{12} \times k_1$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) <sup>b</sup>
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$	$0.893 \pm 0.083$	$7.7 \pm 1.7$
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$	$1.19 \pm 0.05$	$10.3 \pm 2.2$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$	$0.940 \pm 0.082$	$8.1 \pm 1.8$
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	$1.87 \pm 0.09$	$16.2 \pm 3.4$
$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O})\text{CH}_3$	$0.108 \pm 0.036$	$0.94 \pm 0.37$
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	$1.74 \pm 0.07$	$15.1 \pm 3.1$

<sup>a</sup>Indicated errors are two least-squares standard deviations.

<sup>b</sup>Placed on an absolute basis by use of a rate constant of  $k_2(n\text{-octane}) = 8.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\pm 20\%$ ) at 296 K [3]. The indicated errors include the estimated overall uncertainty in the rate constant  $k_2$ .



Table 2. Rate constants  $k$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the gas-phase reactions of the hydroxycarbonyls studied with OH and  $\text{NO}_3$  radicals and  $\text{O}_3$  at  $296 \pm 2$  K.

hydroxycarbonyl	$10^{19} \times k_{\text{O}_3}$	$10^{16} \times k_{\text{NO}_3}$	$10^{12} \times k_{\text{OH}}$
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$	<1.1	$\leq 3$	$7.7 \pm 1.7$
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$	<1.1	$\leq 9$	$10.3 \pm 2.2$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$	<1.1	$\leq 18$	$8.1 \pm 1.8$
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	<1.1	$\leq 16$	$16.2 \pm 3.4$
$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{O})\text{CH}_3$	<1.1	$\leq 3$	$0.94 \pm 0.37$
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	<1.1	$\leq 13$	$15.1 \pm 3.1$