# Kinetics and Products of the Reactions of Selected Diols with the OH Radical

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ABSTRACT: Using a relative rate method, rate constants have been measured at 296 ± 2 K for the gas-phase reactions of OH radicals with 1,2-butanediol, 2,3-butanediol, 1,3-butanediol, and 2-methyl-2,4-pentanediol, with rate constants (in units of $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) of 27.0 ± 5.6, 23.6 ± 6.3, 33.2 ± 6.8, and 27.7 ± 6.1, respectively, where the error limits include the estimated overall uncertainty of ±20% in the rate constant for the reference compound. Gas chromatographic analyses showed the formation of 1-hydroxy-2-butanone from 1,2-butanediol, 3-hydroxy-2-butanone from 2,3-butanediol, 1-hydroxy-3-butanone from 1,3-butanediol, and 4-hydroxy-4-methyl-2-pentanone from 2-methyl-2,4-pentanediol, with formation yields of 0.66 ± 0.11, 0.89 ± 0.09, 0.50 ± 0.09, and 0.47 ± 0.09, respectively, where the indicated errors are the estimated overall uncertainties. Pathways for the formation of these products are presented, together with a comparison of the measured and estimated rate constants and product yields. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 310–316, 2001

## INTRODUCTION

Volatile organic compounds present in the atmosphere can undergo photolysis and chemical reaction with OH radicals, $NO_3$ radicals, and $O_3$ [1,2], with the OH radical reaction being an important, and often dominant, atmospheric loss process [1,2]. A number of diols are used as solvents [3], and diols can be formed in the atmosphere from the OH radical-initiated reactions of alkenes at sufficiently low NO concentrations that organic peroxy + organic peroxy radical reactions are important [4,5]. It is expected that the dominant atmospheric loss process for diols not containing $>C{=}C<$ bonds is by daytime reaction with the OH radical [1,2]. To date, rate constants for the reactions of the OH radical with diols have been measured only for 1,2-ethanediol [6–9] and 1,2-propanediol [6,7,9].

In this work, we have measured rate constants for the gas-phase reactions of the diols 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, and 2-methyl-2,4-pentanediol with OH radicals at 296 ± 2 K and have investigated selected products formed from these reactions.

## 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 ± 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.

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## Kinetic Studies

Rate constants for the OH radical reactions were determined using a relative rate method in which the relative disappearance rates of the diols and a reference compound, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals [9,10]. Providing that the diols and the reference compound reacted only with OH radicals, then [9,10]

$$\ln\left[\frac{[\text{diol}]_{t_0}}{[\text{diol}]_t}\right] = \frac{k_1}{k_2}\ln\left[\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right] \quad \text{(I)}$$

where $[\text{diol}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the diol and reference compound, respectively, at time $t_0$, $[\text{diol}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time $t$, and $k_1$ and $k_2$ are the rate constants for reactions (1) and (2), respectively.

$$\text{OH} + \text{diol} \longrightarrow \text{products} \quad (1)$$

$$\text{OH} + \text{reference compound} \longrightarrow \text{products} \quad (2)$$

OH radicals were generated by the photolysis of methyl nitrite ($CH_3ONO$) in air at wavelengths >300 nm [11], and NO was added to the reactant mixtures to suppress the formation of $O_3$ and hence of $NO_3$ radicals [11]. The initial reactant concentrations (in molecule $cm^{-3}$ units) were: $CH_3ONO$, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; 1,2-butanediol, $(2.64-3.01) \times 10^{13}$, 1,3-butanediol, $(2.21-2.36) \times 10^{13}$, 2,3-butanediol, $(2.31-4.47) \times 10^{13}$, or 2-methyl-2,4-pentanediol, $(2.28-2.39) \times 10^{13}$; and *n*-octane (the reference compound), $\sim 2.4 \times 10^{13}$. Irradiations were carried out for 5–45 min, resulting in up to 75% consumption of the initially present diol.

The concentrations of the diols and *n*-octane were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). For the analysis of the diols, hydroxycarbonyl products (see the following) and *n*-octane, 100-$cm^3$ volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~225°C onto a 30-m DB-1701 megabore column held at 0°C and then temperature programmed to 200°C at 8°C $min^{-1}$. Based on replicate analyses in the dark, the GC-FID measurement uncertainties for the diols were in the range 1–5%. GC-FID response factors for the diols and hydroxycarbonyl products were determined by introducing measured amounts of the chemicals into the 7900-liter chamber and conducting several replicate GC-FID analyses [12]. The experimentally measured GC-FID response factors of the four diols, the four hydroxcarbonyl products observed, and *n*-octane agreed with the calculated Effective Carbon Numbers [13] to within ±17%, indicating that the procedures for diol and hydroxycarbonyl introduction into the chamber and the sampling and analysis techniques were quantitative. NO and initial $NO_2$ concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 chemiluminescent NO–$NO_x$ analyzer.

## Product Studies

Products were identified and quantified from the reactions of the OH radical with the four diols studied, both during the kinetic experiments (see above) and from additional irradiated $CH_3ONO$–NO–diol–air mixtures, by GC-FID and by combined gas chromatography–mass spectrometry (GC-MS). The initial $CH_3ONO$ and NO concentrations in the irradiated $CH_3ONO$–NO–diol–air mixtures and GC-FID analysis procedures were similar to those employed in the kinetic experiments described above, and the initial diol concentrations were in the range $(1.51-6.42) \times 10^{13}$ molecule $cm^{-3}$. To verify the product identities, gas samples were collected onto Tenax-TA solid adsorbent for GC-MS analyses, with thermal desorption onto a 30-m DB-1701 fused silica capillary column in a HP 5890 GC interfaced to a HP 5971 Mass Selective Detector operated in the scanning mode.

## Chemicals

The chemicals used, and their stated purities, were: 1,2-butanediol (99%), 1,3-butanediol (99+%), 2,3-butanediol (98%), 1-hydroxy-2-butanone (95%), 3-hydroxy-2-butanone, 4-hydroxy-4-methyl-2-pentanone (99%), 2-methyl-2,4-pentanediol (99%), and *n*-octane (99+%), Aldrich Chemical Company; 1-hydroxy-3-butanone (95+%), TCI America; and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously [11].

# RESULTS

## OH Radical Reaction Rate Constants

A series of $CH_3ONO$–NO–diol–*n*-octane–air irradiations were carried out, and the data obtained are

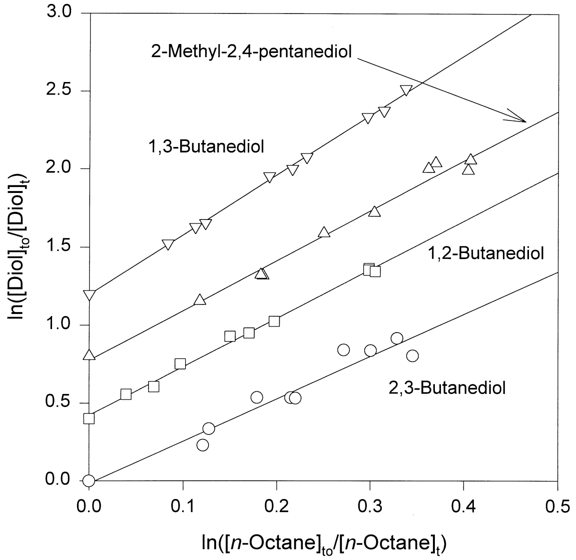

**Figure 1** Plots of eq. (I) for the gas-phase reactions of the OH radical with 2,3-butanediol, 1,2-butanediol, 2-methyl-2,4-pentanediol, and 1,3-butanediol, with *n*-octane as the reference compound. The data for 1,2-butanediol, 2-methyl-2,4-pentanediol, and 1,3-butanediol have been displaced vertically by 0.4, 0.8, and 1.2 units, respectively, for clarity.

plotted in accordance with eq. (I) in Figure 1. Good straight-line plots are observed, and the rate constant ratios $k_1/k_2$ obtained from least-squares analyses of the data are given in Table I. These rate-constant ratios are placed on an absolute basis by use of a rate constant, $k_2$, for reaction of the OH radical with *n*-octane at 296 K of $8.67 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (±20%) [14]. The resulting rate constants $k_1$ are also given in Table I.

## OH Radical Reaction Products

GC-FID analyses of irradiated $CH_3ONO$–NO–diol–*n*-octane–air mixtures showed the formation of one major product from each diol. By comparison of the GC retention times and the mass spectra with those of authentic standards, the products were confirmed to be 1-hydroxy-2-butanone from 1,2-butanediol, 3-hydroxy-2-butanone from 2,3-butanediol, 1-hydroxy-3-butanone from 1,3-butanediol, and 4-hydroxy-4-methyl-2-pentanone from 2-methyl-2,4-pentanediol. These hydroxycarbonyl products also react with the OH radical [10], and their measured concentrations were corrected for secondary reactions with the OH radical as discussed previously [15], using the OH reaction rate constants measured here for the diols and those of Aschmann et al. [10] for the hydroxycarbonyl products. The multiplicative correction factors, *F*, to account for secondary reactions with the OH radical increase with increasing rate constant ratio, *k*(OH + hydroxycarbonyl product)/*k*(OH + diol), and with increasing extent of reaction [15]. The maximum values of *F* were 1.18 for the 1,2-butanediol reaction, 1.33 for the 2,3-butanediol reaction, 1.21 for the 1,3-butanediol reaction, and 1.13 for the 2-methyl-2,4-pentanediol reaction. Plots of the amounts of hydroxycarbonyl formed, corrected for reaction with the OH radical, against the amounts of diol reacted are shown in Figures 2 and 3. Reasonably good straight-line plots are observed, and the hydroxycarbonyl formation yields obtained from least-squares analyses of these data are given in Table II.

## DISCUSSION

Although no literature rate constants for the diols studied here are available for comparison, rate constants for the diols can be calculated using the estimation method proposed by Atkinson [16] and last updated by Kwok and Atkinson [17]. The OH radical reactions with the diols studied here proceed by H-atom abstrac-

**Table I** Rate Constant Ratios $k_1/k_2$ and Rate Constants $k_1$ for the Gas-Phase Reactions of the OH Radical with Diols at 296 ± 2 K

| | | $10^{12} \times k_1$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | |
|---|---|---|---|
| Diol | $k_1/k_2$[a] | This Work[b] | Estimated[c] |
| $CH_3CH_2CH(OH)CH_2OH$ | 3.11 ± 0.15 | 27.0 ± 5.6 | 15.9 (27.9) |
| $CH_3CH(OH)CH(OH)CH_3$ | 2.72 ± 0.48 | 23.6 ± 6.3 | 17.3 (30.2) |
| $CH_3CH(OH)CH_2CH_2OH$ | 3.83 ± 0.12 | 33.2 ± 6.8 | 14.2 (17.2) |
| $(CH_3)_2C(OH)CH_2CH(OH)CH_3$ | 3.20 ± 0.27 | 27.7 ± 6.1 | 10.5 (14.6) |

[a] *n*-Octane used as the reference compound. The indicated errors are 2 least-squares standard deviations.

[b] Placed on an absolute basis by use of a rate constant of $k_2$(*n*-octane) = $8.67 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (±20%) at 296 K [14]. The indicated errors include the estimated overall uncertainty in the rate constant $k_2$.

[c] Calculated using the estimation method of Kwok and Atkinson [17]. The values in parentheses are calculated using revised parameters for F(—OH) and F(—$CH_2OH$) [=F($>$CHOH)=F(—$>$COH)] (see text).

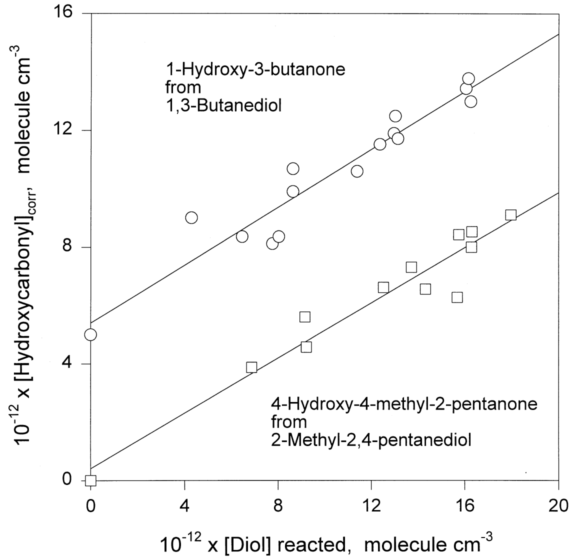

**Figure 2** Plots of the amounts of 4-hydroxy-4-methyl-2-pentanone and 1-hydroxy-3-butanone formed, corrected for secondary reactions (see text), against the amounts of 2-methyl-2,4-pentanediol and 1,3-butanediol reacted with the OH radical, respectively. The data for 1-hydroxy-3-butanone have been displaced vertically by 5.0 × $10^{12}$ molecule cm$^{-3}$ for clarity.

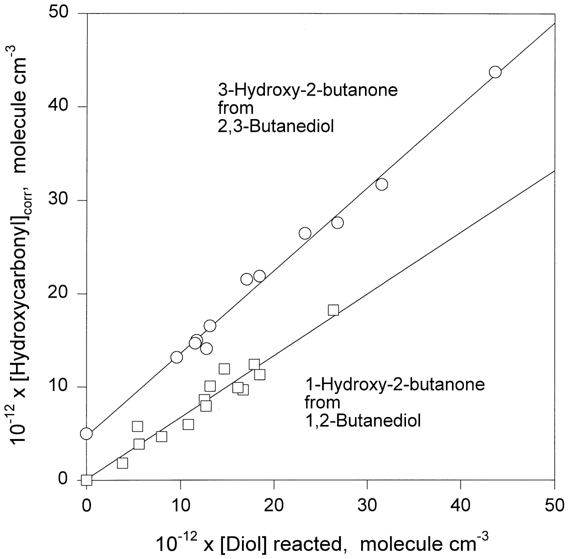

**Figure 3** Plots of the amounts of 1-hydroxy-2-butanone and 3-hydroxy-2-butanone formed, corrected for secondary reactions (see text), against the amounts of 1,2-butanediol and 2,3-butanediol reacted with the OH radical, respectively. The data for 3-hydroxy-2-butanone have been displaced vertically by 5.0 × $10^{12}$ molecule cm$^{-3}$ for clarity.

tion from the various C—H and O—H bonds [1,7,16,17], and the estimation method of Kwok and Atkinson [17] is based on the calculation of rate constants for H-atom abstraction from $CH_3$, $CH_2$, CH, and OH groups. The rate constants for H-atom abstraction from $CH_3$, $CH_2$, and CH groups is assumed to depend on the identity of the substituents attached to these groups, with

$$k(CH_3{-}X) = k_{prim}F(X)$$

$$k(X{-}CH_2{-}Y) = k_{sec}F(X)F(Y)$$

and

$$k(X{-}CH({-}Y){-}Z) = k_{tert}F(X)F(Y)F(Z)$$

where $k_{prim}$, $k_{sec}$, and $k_{tert}$ are the rate constants for H-atom abstraction from $CH_3$, $CH_2$,and CH groups, respectively, for a "standard" substituent, and $F(X)$, $F(Y)$, and $F(Z)$ are the substituent factors for the substituent groups $X$, $Y$, and $Z$, respectively [16,17]. The standard substituent group is chosen to be $X(= Y = Z) = {-}CH_3$, with $F({-}CH_3) = 1.00$ [16,17]. At 298 K, the group rate constants are (in units of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) $k_{prim} = 0.136$, $k_{sec} = 0.934$, $k_{tert} = 1.94$, and $k_{OH} = 0.14$, and the substituent factors are $F({-}CH_2{-}) = F(>CH{-}) = F(>C<) = 1.23$ and $F({-}OH) = 3.5$ [17] .

**Table II** The Formation Yields of Selected Hydroxyketones from the Gas-Phase Reactions of the OH Radical with Diols at 296 ± 2 K, Compared to Estimated Yields

| | | Molar Formation Yield (%) | |
|---|---|---|---|
| Diol | Hydroxyketone | This Work[a] | Estimated[b] |
| $CH_3CH_2CH(OH)CH_2OH$ | $CH_3CH_2C(O)CH_2OH$ | 66 ± 11 | 65 (64) |
| $CH_3CH(OH)CH(OH)CH_3$ | $CH_3C(O)CH(OH)CH_3$ | 89 ± 9 | 96 (97) |
| $CH_3CH(OH)CH_2CH_2OH$ | $CH_3C(O)CH_2CH_2OH$ | 50 ± 9 | 59 (40) |
| $(CH_3)_2C(OH)CH_2CH(OH)CH_3$ | $(CH_3)_2C(OH)CH_2C(O)CH_3$ | 47 ± 9 | 79 (47) |

[a] Indicated errors are 2 least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the diols and hydroxyketones of ±5% each.

[b] Calculated using the estimation method of Kwok and Atkinson [17]. The values in parentheses are calculated using revised parameters for $F({-}OH)$ and $F({-}CH_2OH)$ [$=F(>CHOH)=F({-}>COH)$] (see text).

The calculated rate constants for the four diols studied here are given in Table I, and are factors of 1.4–2.6 lower than the measured values. A similar underestimation of rate constants for the reactions of the OH radical with 1-hexanol, 1,2-ethanediol, and 1,2-propanediol was observed previously [9] (and shown in Table III), and our present and previous [9] data suggest that certain parameters in the estimation method of Kwok and Atkinson [17] need to be revised. Accordingly, we have used the literature [1,7,18–22] OH radical reaction rate constants for methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, 2-methylpropan-2-ol (*tert*-butyl alcohol), 2,2-dimethylpropan-1-ol, 1-hexanol, 1,2-ethanediol, and 1,2-propanediol, and for the four diols measured here, to recalculate the substituent group parameters in the Kwok and Atkinson [17] estimation method. In this derivation of revised parameters for the estimation method, the group rate constants $k_{prim}$, $k_{sec}$, $k_{tert}$, and $k_{OH}$ and the substituent factor $F(—CH_2—) = F(>C<) = F(>CH—) = 1.23$ were unchanged from the values of Kwok and Atkinson [17]. In contrast to the Kwok and Atkinson [17] study, effects of the OH substituent(s) on H-atom abstraction at the $\alpha$- and $\beta$-positions were considered (Kwok and Atkinson [17] only considered effects of OH substituents at the $\alpha$-position, in part because of the database then available). Because of the limited database, it was assumed in the present fit that $F(—CH_2OH) = F(>CHOH) = F(—\!>COH)$, and a nonlinear least-squares fit to the rate constants above (minimizing $[(k_{calc} - k_{meas})/k_{meas}]^2$, where $k_{calc}$ and $k_{meas}$ are the calculated and measured rate constants, respectively) resulted in substituent factors of $F(—OH) = 2.9$ and $F(—CH_2OH) = F(>CHOH) = F(—\!>COH) = 2.6$. Use of these revised parameters leads to the calculated rate constants given in parentheses in Table I for the diols studied here, and to the rate constants listed in Table III for the other alcohols and diols used in the derivation of the group substituent factors. As expected, the revised parameters result in closer agreement of the calculated rate constants to the measured values, although discrepancies of up to a factor of 1.9 still occur for 1,3-butanediol and 2-methyl-2,4-pentanediol (Table I). Table IV shows the effect of the revised parameters $F(—OH)$ and $F(—CH_2OH)$ [$= F(>CHOH) = F(—\!>COH)$] on the calculated versus measured [1,10,22] rate constants for the hydroxycarbonyls for which data are available (and which were not used in the derivation of the revised substituent factors). Using the revised substituent factors, the calculated rate constants agree approximately as well with the measured values as do those calculated using the parameters of Kwok and Atkinson [17] for five of the eight hydroxycarbonyls. However, the revised parameters lead to significant disagreements with the measured values for 3-hydroxy-3-methyl-2-butanone (by a factor of 3.2) and glycolaldehyde (by a factor of 4.7, compared to the previous overestimate of a factor of 2.4 [17]), and it appears that rate constants for 1,2-hydroxyaldehydes will be greatly overestimated. Clearly, accurate estimation of OH radical rate constants for hydroxy-containing compounds (to within better than a factor of 2) does not appear possible using the general approach of Atkinson [16].

As noted above, the OH radical reactions proceed by H-atom abstraction from the various C—H and O—H bonds. The hydroxyketones formed arise after H-atom abstraction from the CH(OH) and $CH_2OH$ groups, with the H-atoms on these groups being acti-

**Table III** Comparison of Calculated and Experimentally Measured Room-Temperature Rate Constants for Reaction of the OH Radical with a Series of Alcohols and Diols

| | $10^{12} \times k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | | | |
|---|---|---|---|---|
| Hydroxy Compound | Calc. [17] | Calc. (revised) | Measured | Reference |
| $CH_3OH$ | 0.62 | 0.53 | 0.944 | [1,18] |
| $CH_3CH_2OH$ | 3.58 | 3.20 | 3.27 | [1,7,18] |
| $CH_3CH_2CH_2OH$ | 5.48 | 6.07 | 5.53 | [1,18] |
| $CH_3CH(OH)CH_3$ | 7.27 | 6.47 | 5.07 | [18,19] |
| $CH_3CH_2CH_2CH_2OH$ | 6.89 | 7.78 | 8.57 | [1,18] |
| $CH_3CH(OH)CH_2CH_3$ | 9.98 | 10.0 | 8.89[a] | [20] |
| $(CH_3)_3COH$ | 0.64 | 1.20 | 1.08 | [21] |
| $(CH_3)_3CCH_2OH$ | 4.66 | 3.97 | 5.53 | [22] |
| $CH_3(CH_2)_4CH_2OH$ | 9.72 | 10.6 | 15.8 | [9] |
| $HOCH_2CH_2OH$ | 8.32 | 14.4 | 14.7 | [9] |
| $CH_3CH(OH)CH_2OH$ | 12.8 | 22.3 | 21.5 | [9] |

[a] Reevaluated to be consistent with the most recent recommendation [14] for the cyclohexane reference compound used.

**Table IV** Comparison of Calculated and Experimentally Measured Room-Temperature Rate Constants for Reaction of the OH Radical with a Series of Hydroxycarbonyls

| | $10^{12} \times k$ ($cm^3$ $molecule^{-1}$ $s^{-1}$) | | | |
|---|---|---|---|---|
| Hydroxycarbonyl | Calc. [17] | Calc. (revised) | Measured | Reference |
| $HOCH_2CHO$ | 23.4 | 46.1 | 9.9 | [1] |
| $CH_3C(O)CH_2OH$ | 2.69 | 2.27 | 3.0 | [1,23] |
| $CH_3CH_2C(O)CH_2OH$ | 3.82 | 3.40 | 7.7 | [10] |
| $CH_3C(O)CH(OH)CH_3$ | 5.86 | 5.84 | 10.3 | [10] |
| $CH_3C(O)CH_2CH_2OH$ | 13.9 | 12.6 | 8.1 | [10] |
| $C_2H_5C(O)CH(OH)C_2H_5$ | 11.4 | 16.2 | 15.1 | [10] |
| $(CH_3)_2C(OH)C(O)CH_3$ | 1.30 | 3.00 | 0.94 | [10] |
| $CH_3C(O)CH(CH_3)CH_2OH$ | 15.3 | 15.1 | 16.2 | [10] |

vated by the presence of the OH substituent group, as shown, for example, for the 1,2-butanediol reaction.

$$OH + CH_3CH_2CH(OH)CH_2OH \longrightarrow H_2O + CH_3CH_2\dot{C}(OH)CH_2OH \quad (3)$$

followed by reaction of the $\alpha$-hydroxyalkyl radical with $O_2$ [1].

$$CH_3CH_2\dot{C}(OH)CH_2OH + O_2 \longrightarrow CH_3CH_2C(O)CH_2OH + HO_2 \quad (4)$$

Note that the hydroxy-aldehyde $CH_3CH_2CH(OH)CHO$ will be formed by an analogous reaction at the 1-position $CH_2OH$ group, but hydroxyaldehydes do not appear to be amenable to analysis by gas chromatography without derivatization [24], and hence we only observe (because of analytical limitations) hydroxyketones. Our observed hydroxyketone formation yields given in Table II can be compared with the yields calculated using the estimation method of Kwok and Atkinson [17] and using the revised parameters (by calculating the fraction of the overall calculated OH radical reaction rate constant that is due to H-atom abstraction from the CH(OH) or $CH_2OH$ group leading to formation of the hydroxyketone observed). Our measured formation yields agree well with the yields calculated using the revised substituent group factors, with a significantly improved agreement between the estimated and measured formation yield of 4-hydroxy-4-methyl-2-pentanone from 2-methyl-2,4-pentanediol (Table II).

Finally, our measured room-temperature rate constants can be combined with an assumed ambient concentration of OH radicals to calculate the tropospheric lifetimes of the diols studied here. Using a 12-h average daytime OH radical concentration of $2.0 \times 10^6$ molecule $cm^{-3}$ [25,26], the calculated lifetimes of the four diols studied here are in the range 4–6 h.

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