Kinetics of the Reactions of OH Radicals with Selected Acetates and Other Esters under Simulated Atmospheric Conditions

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Abstract

The relative hydroxyl radical reaction rate constants from the simulated atmospheric oxidation of selected acetates and other esters have been measured. Reactions were carried out at 297 ± 2 *K* in 100-liter FEP Teflon®-film bags. The OH radicals were generated from the photolysis of methyl nitrite in pure air. Using a rate constant of 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of OH radicals with propene, the principal reference organic compound, the rate constants ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}) obtained for the acetates and esters used in this study are:

n-propyl acetate	3.42 ± 0.87
n-butyl acetate	5.71 ± 0.94
n-pentyl acetate	7.53 ± 0.48
2-ethoxyethyl acetate	10.56 ± 1.31
2-ethoxyethyl isobutyrate	13.56 ± 2.32
2-ethoxyethyl methacrylate	27.22 ± 2.06
4-penten-1-yl acetate	43.40 ± 3.85
3-Ethoxyacrylic acid ethyl ester	33.30 ± 1.22

Error limits represent 2σ from linear least-squares analysis of data.

A linear correlation was observed for a plot of the measured relative rate constants vs. the number of CH_2 groups per molecule of the following acetates: methyl acetate, ethyl acetate, *n*-propyl acetate, butyl acetate, and pentyl acetate. © 1993 John Wiley & Sons, Inc.[‡]

Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere by a number of industrial processes. In combination with sunlight and oxides of

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nitrogen, these VOCs can react photochemically to produce ozone and other toxic products. The predominant process leading to the formation of ozone or other products is the reaction of these VOCs with hydroxyl radicals (OH) [1]. Thus, accurate values for OH reaction rate constants are necessary to assess the tropospheric lifetime and potential adverse impact of VOCs for any given urban airshed.

One class of VOCs which is commonly used in cleaning and painting operations is carbonyl compounds. In this article, we report relative OH radical reaction rate constants for selected acetates and esters: *n*-propyl acetate, butyl acetate, pentyl acetate, 2-ethoxyethyl acetate, 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, 3-ethoxyacrylic acid ethyl ester, and 4-pentene-1-yl-acetate. Propene was used as the principal reference organic compound, while *n*-butane and *trans*-2-butene served as confirming references.

Experimental

Hydroxyl radicals were generated in Teflon®-film bags by the photolysis of methyl nitrite in air [2].

$$CH_3ONO + h\nu\ (300\ \text{to}\ 450\ \text{nm}) \longrightarrow CH_3O + NO$$

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2$$

$$HO_2 + NO \longrightarrow OH + NO_2$$

The methyl nitrite was synthesized by dropwise addition of 50% sulfuric acid into a methanol-saturated solution of sodium nitrite. The methyl nitrite produced was swept out of the reaction flask by a stream of high-purity nitrogen, passed through two saturated sodium hydroxide traps to remove traces of sulfuric acid, dried by passing through a calcium chloride trap, and collected in a trap at 196 *K*. The purity of the methyl nitrite was confirmed by GC/MS and FT-IR analysis. The methyl nitrite was stored in the dark at 193 *K*. All the acetates and esters (Sigma and Aldrich Chemical Co.) were 99% pure. The purity was confirmed by GC analysis. The reference compounds, all research grades, were propene, *trans*-2-butene (M.G. Industries), and *n*-butane (Matheson). Experiments were carried out at 297 ± 2 *K* and at atmospheric pressures of 754 to 766 torr.

Irradiations were carried out in 100-liter, 2-mil FEP Teflon®-film bags, surrounded by six 40-watt black lamps (GE F40 TB BLB) and four 40-watt sun lamps (Westinghouse F40). These lamps provided UV radiation in the 300–450 nm region. The bag and the lamps were housed inside an aluminum box, with a fan at the top to maintain a constant temperature inside the bag. The primary photo-dissociation rate constant for nitrogen dioxide was used as a measure of the intensity of UV radiation in the chamber [3,4]. The actinometric determination of the rate constant k_1 ($NO_2 \xrightarrow{k1} NO + O(^3P)$) was based on the photolysis of NO_2 in nitrogen at one atmosphere. The average value obtained for k_1 was 0.178 ± 0.006 s^{-1}. Reaction mixtures consisted of a reference compound (1 to 3 ppm*v*), sample compound (1 to 5 ppm*v*), and methyl nitrite (0.5 to 20 ppm) diluted in pure air (ozone and nitrogen dioxide less than 1 ppb and 3 ppb, respectively). These components were flushed from a heated Pyrex® "T" (with a silicon rubber septum on one arm) into the Teflon®-film bag by a stream of purified air during the bag loading process. Ozone and oxides of nitrogen were measured with calibrated chemiluminescent instruments (Bendix Model 8002 and Monitor Labs Model 8841). Liquid CH_3ONO was expanded into a vacuum line to give 760 torr of vapor-phase CH_3ONO, from which a measured amount (0.3 to 20 cm^3) was withdrawn through a septum port using an air-tight gas-syringe and injected into the Teflon®-film bag as described above. The contents of the bag were left to mix for periods of time ranging from 1–4 h, after which the initial concentrations of the sample (S_0) and reference (R_0) compounds were determined. These compounds were quantitatively monitored by gas chromatography with flame ionization detection (Hewlett-Packard Model 5890 GC), using a fused silica megabore column (Resteck, RTx-35, 30 m, 0.53 mm ID; Supelco, Spb-5, 15 m, 0.53 mm ID and Spb-10, 15 m, 0.53 mm ID).

The methyl nitrite along with NO (NO/NO_2 ratio of 1.5–4, with an NO maximum concentration of 2.5 ppm) were admitted into the Teflon®-film bag as described above. NO was added to suppress or quench secondary reactions which might occur between the reactants or products and the ozone formed in the photolysis process. The choice of a confirming reference was based on the relative magnitude of the rate constant for the compound of interest based on propene in comparism to the absolute rate constant of the confirming reference organic.

The central assumption in the relative rate technique is that both the sample and reference organics are removed solely by photo-initiated reactions with hydroxyl radicals. To test for possible dark reactions, mixtures of methyl nitrite with both the reference and sample organics were prepared as described above and left in the dark over a typical experimental period. In all cases tested there was no observable evidence of any reaction of the organic compounds with methyl nitrite. In addition, the reference and sample compounds showed no observable photolysis products in the absence of methyl nitrite and NO.

To test for possible overlapping retention times in the GC analyses of primary and secondary irradiation products, separate experiments were carried out in which mixtures of methyl nitrite and either the reference organic or each sample were irradiated. The irradiation time for these tests was longer than the usual experimental photolysis period. No such retention time interferences were observed. Maximum irradiation time for all runs, except interference checks, was 180 s, with an initial 60-s irradiation followed by others at 15-s increments. The total irradiation time was kept to a minimum to avoid possible secondary or competing reactions from primary photolysis products. Typically, each gas mixture was irradiated 5 to 7 separate times so that the decay of the reference and sample organic compound of interest could be monitored over a range of conversion usually less than 35%.

The rate constants for the OH radical reaction with the samples was determined by the relative rate technique [2], which is briefly summarized below. The OH radicals generated by the photolysis of CH_3ONO react with the reference, R, and sample, S, as follows:

$$\text{(1)} \qquad \mathrm{OH} + S \xrightarrow{k_s} \text{Products}$$

$$\text{(2)} \qquad \mathrm{OH} + R \xrightarrow{k_r} \text{Products}$$

Assuming that the reaction with OH is the only significant loss process for both reference and sample, it can be shown mathematically that the following holds for such a competing reaction:

$$\text{(3)} \qquad \ln[S_0/S_t] = k_s/k_r \ln[R_0/R_t]$$

Where the subscripts 0 and t indicate concentrations at the beginning of the experiments and at time, t, respectively. Plots of experimental data for $\ln[S_0/S_t]$ vs. $\ln[R_0/R_t]$ should yield a straight line with a slope of k_s/k_r and an intercept of zero. Thus, knowing k_r, the value of k_s can be calculated from the slope.

At the end of each run, the Teflon®-film bag was cleaned by filling it with purified air containing 1 ppm of ozone. Then the bag was evacuated while it was being irradiated. This was followed by a similar process, but this time with 1 ppm of NO. After these irradiations, the bag was filled and flushed twice with purified air then refilled with purified air and sampled by GC for traces of organic compounds. At the end of the above cleaning treatment, no significant quantities of any original compounds or irradiation products were observed. This same cleaning procedure was applied to any newly constructed Teflon®-film bag before being used.

Results and Discussion

The validity of our data was checked by using two different reference organic compounds; a principal reference organic compound and a coreference organic compound. Propene was used as the principal reference compound for all the substrates except 3-ethoxyacrylic acid ethyl ester, and *n*-butane or *trans*-2-butene was used as the coreference. The rate constant for 3-ethoxy acrylic acid ethyl ester, due to GC interferences, was based solely on *trans*-2-butene as the only reference organic. The absolute rate constants (26.3×10^{-12} cm^3 molecule^{-1} s^{-1} for propene, 64.0×10^{-12} cm^3 molecule^{-1} s^{-1} for *trans*-2-butene and 2.54×10^{-12} cm^3 molecule^{-1} s^{-1} for *n*-butane, respectively) for OH reactions were used to place the rate constants of the substrates on absolute basis.

Typical plots of eq. (3) are shown in Figures 1, 2, and 3 for substrates based on propene, *trans*-2-butene, and *n*-butane as reference organics, respectively. Each plot in the figures is an overlay plot of data from five different runs for each substrate/reference pair for propene based reference runs, and overlay plots of data from three runs for those based on *trans*-2-butene and *n*-butene coreferences. The slopes of the fitted lines, obtained by linear least-squares analysis of the data points give the rate constant ratios k_s/k_r. Error limits (2σ) are determined from the average of five reference runs or three for each reference/sample pair. The relative

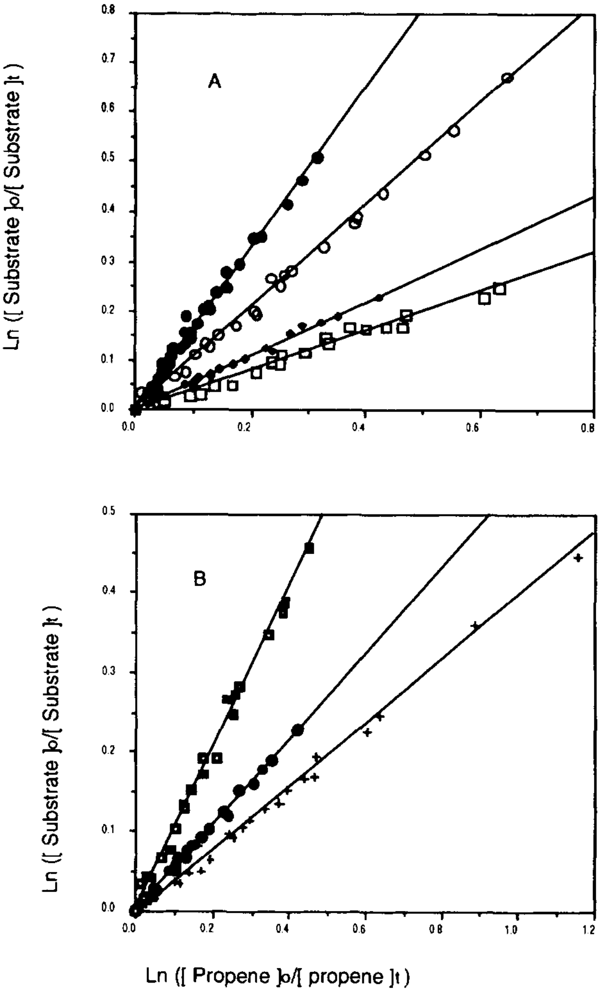

Figure 1. a, b — Plot of eq. (3) for OH reaction with substrates with propene as the reference organic. Each plot in Figure 1(A) is an overlay plot of data from five runs for 2-ethoxyethyl acetate, 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, and 4-penten-1-yl acetate, respectively, with increasing slopes of the least-squares fit. Similarly, Figure 1(B) for propyl acetate, butyl acetate, and pentyl acetate with increasing slopes of the least-squares fit, respectively.

OH radical reaction rate constants for each ester were also calculated from the slopes of the $\ln[S_t]$ vs. time, and $\ln[R_t]$ vs. time, i.e., decay curves. These values were in excellent agreement (within 1%) with corresponding rate constants, k_s, obtained from least-squares fit of eq. (3). All plots had approximately zero intercepts, which indicates that photolysis and/or wall losses were not significant. The relative OH radical rate constants and rate constant ratios obtained in this study are summarized in Table I.

The few literature reports on the kinetics and reaction mechanisms of simple esters [5–8] all seem to agree that the OH radical reacts predominantly with the alkoxy end of the esters rather than the acyl end,

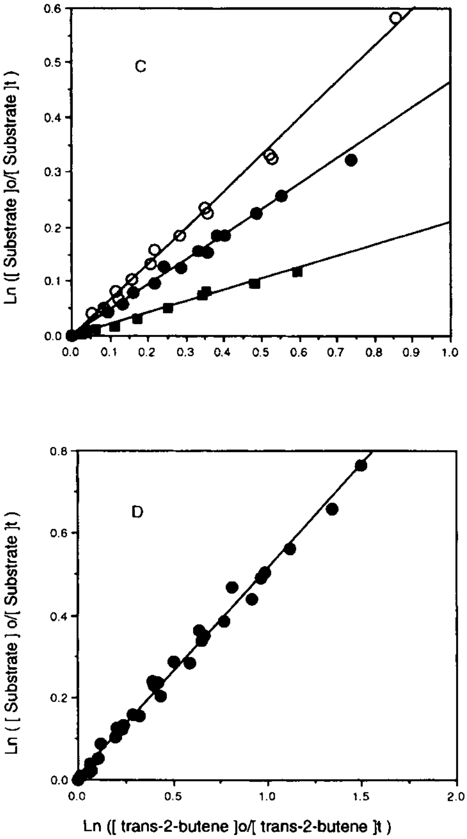

Figure 2. c, d — Plot of eq. (3) for OH reaction with substrates with *trans*-2-butene as the reference organic. Each plot in Figure 2(C) is an overlay plot of data from three runs for 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, and 4-penten-1-yl acetate, respectively, with increasing slopes of the least-squares fit. Figure 2(D) is an overlay plot of data from three runs for 3-ethoxyacrylic acid ethyl ester.

and that there is a general increase in the rate constants with increasing substitution on the alkoxy end of the ester. Figure 4 shows a plot of the number of methylene groups (CH_2) of the simple ester homologous series methyl acetate through pentyl acetate vs. the corresponding relative rate constant obtained in this study. The data of methyl acetate and ethyl acetate are from the relative rate work of Campbell et al. [5]. The rate constant value from Campbell ($1.84 \pm 0.37 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) for ethyl acetate is in good agreement with the absolute technique based value of $1.7 \pm 0.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [1]. The recommended value is 1.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [1]. From methyl acetate we have also used the relative rate data of Campbell (0.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1}), although this value is only about 50% of the absolute technique value reported by Wallington [8] for methyl acetate. A linear correlation was observed for this CH_2 and rate constant plot. This linear relationship further substantiates the above argument that reactions occur at the alkoxy end of the ester molecules. This may also imply that there is an increase in the

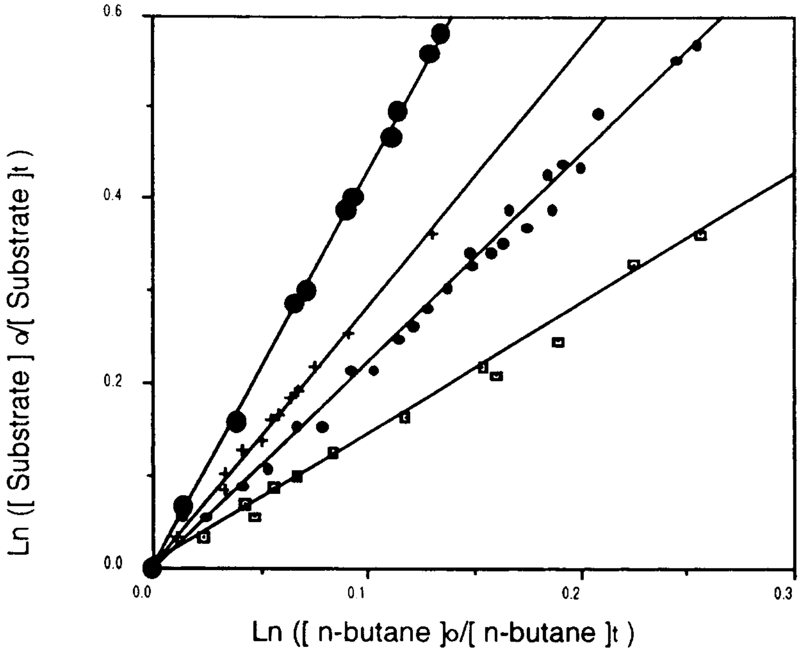

Figure 3. Plot of eq. (3) for OH reaction with substrates with butane as the reference organic. Each plot is an overlay plot of data from three runs for propyl acetate, butyl acetate, pentyl acetate, and 2-ethoxy ethyl acetate, respectively, with increasing slopes of least-squares fit.

rate of hydrogen abstraction by OH radicals with increase in the number of methylene groups per molecule. Based on Figure 4 the rate constant contribution per methylene group is about 1.86 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

Except for *n*-propyl acetate there are no previously reported rate constants measured in relative rate studies for the reaction of OH radicals with the esters in Table I. Our values for *n*-propyl acetate are 3.42 ± 0.87 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 3.56 ± 0.85 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} based on propene and *n*-butane references, respectively. These values are in excellent agreement with the absolute technique based value of 3.45 ± 0.34 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} reported by Wallington [8]. Winer [1] reports a relative rate based technique value of 4.2 ± 0.9 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, while Ker and Stocker report a value of 2.5 ± 0.25 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [1]. Overall, these last two literature reports for *n*-propyl acetate rate constant are not in fair agreement with our data, however, the value reported by Winer is the upper limit of our propene based value, i.e., $3.42 + 2\sigma$ (4.29 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), while Ker and Stocker's value is the lower limit, i.e., $3.42 - 2\sigma$ (2.55 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}). The recommended value by Atkinson [6], which is in excellent agreement with our value, is 3.4 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. For *n*-butyl acetate, Wallington et al. [8] and Hartman et al. [9] have reported on OH degradation rate constant based on absolute techniques and their values are 4.3 ± 0.8 and 4.15 ± 0.30 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. With propene and *n*-butane as references for the reaction of butyl acetate with OH radicals, we obtained

TABLE I. Relative rate constants and rate constant ratios for the reactions of hydroxyl radicals with acetates and other esters.

Sample	Ref.	*ks*/*kr*	*ks* × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}	Literature *ks*
propyl acetate	propene	0.130 ± 0.033	3.42 ± 0.87	4.2 ± 0.9[6a]
	n-butane	1.408 ± 0.335	3.58 ± 0.85	3.45 ± 0.34[8b]
n-butyl acetate	propene	0.217 ± 0.036	5.71 ± 0.94	4.3 ± 0.8[9c]
	n-butane	2.184 ± 0.339	5.55 ± 0.86	4.15 ± 0.30[8d]
n-pentyl actetate	propene	0.286 ± 0.018	7.53 ± 0.48	
	n-butane	2.970 ± 0.022	7.54 ± 0.56	
2-EE acetate	propene	0.402 ± 0.050	10.56 ± 1.31	13 ± 2[9e]
	n-butane	4.198 ± 0.248	10.66 ± 0.63	
2-EE isobutyrate	propene	0.513 ± 0.088	13.56 ± 2.32	
	n-butane	5.130 ± 0.414	13.69 ± 1.05	
	trans-2-butene	0.213 ± 0.260	13.65 ± 1.70	
2-EE methacrylate	propene	1.035 ± 0.078	27.22 ± 2.06	
	trans-2-butene	0.438 ± 0.053	28.03 ± 3.38	
4-penten-1-yl acetate	propene	1.648 ± 0.146	43.40 ± 3.85	
	trans-2-butene	0.669 ± 0.045	42.90 ± 2.88	
3-EAA-ethyl ester	*trans*-2-butene	0.515 ± 0.019	33.30 ± 1.22	

ks = Relative rate constant and *ks*/*kr* = rate constant ratio.
2-EE = 2-ethoxyethyl and 3-EAA = 3-ethoxyacrylic acid.
[a] Relative to methyl propene (4.94 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}).
[b–e] Based on absolute techniques.

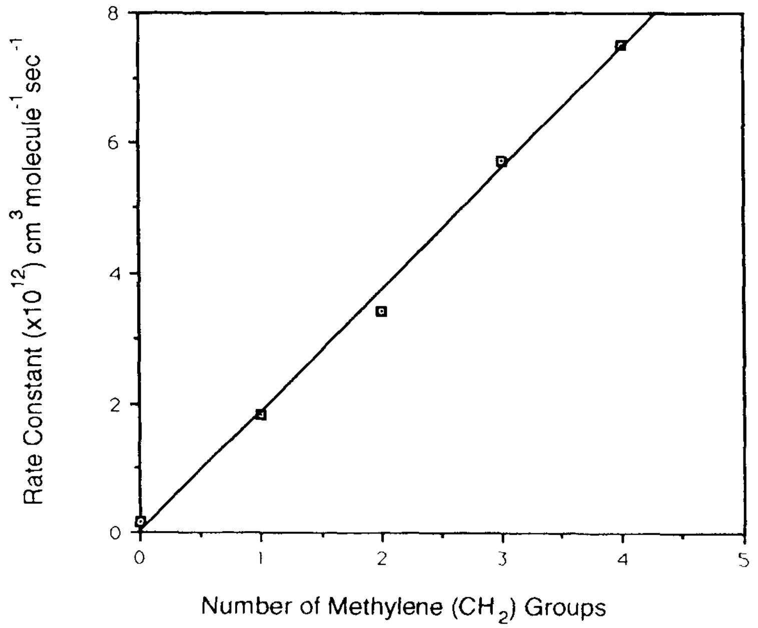

Figure 4. Plot of the number of methylene groups (CH_2) per molecule of methyl, ethyl, propyl, butyl, and pentyl acetates vs. their corresponding rate constants based on propene reference. (Methyl acetate and ethyl acetate data are from ref. [5]).

rate constants of 5.71 ± 0.94 and 5.55 ± 0.86 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. These values are on the high side of the rate constants obtained by absolute techniques, but based on our findings summarized in Figure 4, and comparing the relative rate constant of butyl acetate with other members of its homologous series, we conclude that the relative rate constants can not be greater than 6.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} or less than 4.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. It is also worth noting that the work of Wallington and Hartman were carried out at extremely low pressures; 25 to 50 torr as in the work of Wallington. In addition, reasonable amounts of dilutent gases are often employed. In the relative rate technique work is normally carried out in atmospheric conditions (760 torr) in the presence of synthetic air. The absolute rate data reported by these authors were not extrapolated to atmospheric pressure. We, therefore, recommend a value of 5.71 ± 0.94 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for *n*-butyl acetate, based on propene as the reference organic. Our rate constants for OH reactions with pentyl acetate are 7.53 ± 0.84 and 7.54 ± 0.56 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, with respect to propene and *n*-butane. For OH radical reactions with pentyl acetate, no previous relative or absolute reaction rate constants have been reported in the literature. Therefore, we recommend a value of 7.53 ± 0.48 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} as the rate constant for the reaction of pentyl acetate with OH radicals.

The only literature value for the reaction of OH radicals with 2-ethoxyethyl acetate is 13 ± 2 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, based on an absolute techniques [9]. Our values are 10.56 ± 1.31 and 10.66 ± 0.63 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} with propene and *n*-butane references, respectively. These values agree quite well with the value from the absolute technique. We recommend a value of 10.56 ± 1.31 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the reaction of 2-ethoxyethyl acetate with OH radicals. The comparatively large rate constants obtained for *n*-propyl acetate, *n*-butyl acetate, pentyl acetate, and 2-ethoxyethyl acetate indicate that they will be quite reactive in the troposphere, with estimated lifetimes of 81 h, 49 h, 37 h, and 26 h, respectively, (based on 10^6 OH radicals per cm^3 [10]).

For other esters in Table I, no previous relative rate constants for their reactions with OH radicals have been reported in the literature. Our recommended values are 13.56 ± 2.32, 27.22 ± 2.06 and 43.40 ± 3.85 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate and 4-penten-1-yl acetate, respectively. These values are based on propene and corresponding values based on *trans*-2-butene are in good agreement with these propene values, as shown in Table I. The rate constant for OH degradation of 3-ethoxyacrylic acid ethyl ester was based solely on *trans*-2-butene, and this value is 33.30 ± 1.22 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

Based on the rate constants used to put the sample rate constants on absolute basis (26.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, 64.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, and 2.54 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for propene, *trans*-2-butene, and *n*-butane, respectively), the propene/*n*-butane and propene/*trans*-2-butene rate constant ratios are 10.354 and 0.411, respectively. From the respective sample/reference rate constant ratios, Table I, these same propene/*n*-butane and propene/*trans*-2-butene rate constant ratios can be calculated, and the values are 10.345 ± 0.089 and 0.415 ± 0.000, respectively. These values are therefore in excellent agreement, less than 1% difference, with values based directly on the absolute rate constants for the individual references as outlined above.

The atmospheric lifetimes of the last four esters in Table I due to loss by reaction with OH radicals estimated from the rate constants reported here are respectively, 20 h, 10 h, 6 h, and 8 h.

Conclusions

The relative rate constants for the reactions of OH radicals with a series of acetates and esters have been determined. Where corresponding literature values for these rate constants exist, most of them are in good agreement with the values obtained in this study. In the simple acetate homologous series methyl acetate through pentyl acetate, there is a linear correlation between the number of methylene groups and the observed OH reaction rate constant. This supports the argument that OH reactions occur at the alkoxy end of ester molecules. The relative rate values determined in this study will provide additional data for use in atmospheric photochemical models.

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Bibliography

[1] R. Atkinson and Alan C. Lloyd, *J. Phys. Chem. Ref. Data,* **13,** 2 (1984).
[2] R. Atkinson, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Air Pol. Control,* **31,** 1090 (1981).
[3] J. R. Holmes, R. J. O'Brien, J. H. Crabtree, T. A. Hecht, and J. H. Seinfeld, *Environ. Sci. Technol.,* **7,** 519 (1973).
[4] C. H. Wu and H. Niki, *Environ. Sci. Technol.,* **9,** 46 (1975).
[5] I. M. Campbell and P. E. Parkinson, *Chem. Phys. Lett.,* **53,** 385 (1978).
[6] A. M. Winer, A. C. Lloyd, K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., *Chem. Phys. Lett.,* **51,** 221 (1977).
[7] J. A. Kerr and D. W. Stocker, *J. Atmos. Chem.,* **4,** 253 (1986).
[8] T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.,* **20,** 177 (1988).
[9] D. Hartmann, A. Gedra, D. Rhasa, and R. Zeller, *Proc. 4th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants,* 1986, Riedel, Dordrecht, Holland, 1987.
[10] J. G. Anderson, *Geophysics Res. Lett.,* **3,** 165 (1976).

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