

Rates and Mechanism of the Reactions of Hydroxyl Radicals with Acetic, Deuterated Acetic, and Propionic Acids in the Gas Phase[†]

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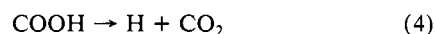
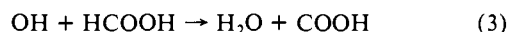
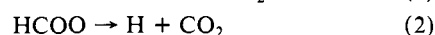
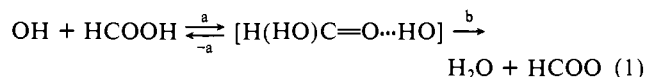
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Abstract: Rate constants for the reactions of hydroxyl radicals with the monomer and dimer of acetic acid, deuterated acetic acids, and propionic acid have been determined by a laser photolysis-resonance absorption technique. Hydroxyl radicals were generated by photolysis of the acids at 222 nm with a KrCl laser and their decay was followed by time-resolved resonance absorption. The monomers of acetic and deuterated acetic acids reacted with OH much faster than the dimers, whereas the monomer and dimer of propionic acid reacted with about equal rate constants. A primary isotope effect was observed when carboxylic but not alkyl hydrogen was substituted by deuterium in acetic acid. The results are entirely consistent with the two-channel mechanism that we proposed for the reaction of OH with formic acid. One channel involves the formation of a hydrogen-bonded adduct followed by transfer of the carboxylic hydrogen to OH, and the other involves direct abstraction of an alkyl hydrogen. The results are interpreted in terms of the variations in C-H bond strengths and in equilibrium constants for adduct formation of the acids studied.

No information was available until recently on the rates and mechanism of the reaction of hydroxyl radicals with aliphatic acids. The atmospheric relevance of the reaction, which is the principal route of oxidation of the acids found in the atmosphere, has prompted recent kinetic studies,¹⁻⁵ which have revealed unexpected and interesting features of the mechanism.

The kinetic measurements were made by using two techniques which operate at different pressure ranges of the acid reactant. In the flash photolysis-resonance fluorescence technique,^{1,2,4} with photolysis of water as the source of OH, low pressures of acids were used where essentially only the monomeric acids were present. In the flash photolysis-resonance absorption technique, employed in this laboratory,^{3,5} the source of OH/OD was photolysis of formic and deuterated formic acids. In this technique, higher pressures of the acids were used, which consisted of equilibrium mixtures of monomer and dimer, so that it was possible to study the reaction of OH/OD with the monomer as well as with the dimer of each acid. The reported rate constants for formic acid monomer from ref 2, 3, and 5 are in good agreement over the whole temperature range whereas the room temperature values from ref 1 and 4 are lower possibly because of absorption of the acid on the cell walls (see the Discussion section).

Regarding the mechanism, little was known prior to the work described in ref 3 and 5. The first piece of significant information was that the dimer was much less reactive than the monomer.³ Given the doubly hydrogen-bonded structure of the dimer, (each acidic OH group forms a hydrogen bond with the carbonyl oxygen of its partner), with two C-H bonds available for interaction with OH, the lack of reactivity of the dimer toward OH indicated that OH interacts mainly with the carboxylic hydrogen of the monomer at room temperature.³ The temperature dependences of the rate constants for reactions of OH/OD with the monomer and dimer of formic and deuterated formic acids⁵ were entirely consistent with the dominant path involving interaction of OH with carboxylic hydrogen at lower temperatures. Also, in each case a large kinetic isotope effect was observed on deuterium substitution of the carboxylic but not the formyl hydrogen. On the basis of these results, we have proposed^{3,5} a two-channel mechanism which is consistent with the above observations and with the stable products of the reaction.^{6,7} One channel involves formation of a hydro-



gen-bonded complex between OH and formic acid followed by transfer of the carboxylic hydrogen in the adduct, in an analogous manner to the preferential abstraction of hydroxylic hydrogen from alcohols by alkoxy radicals in solution.⁸ The other channel involves direct hydrogen abstraction of the formyl hydrogen by OH, which increases in importance with increasing temperature.

Other observations consistent with the suggested mechanism are rate constants independent of total pressure (500 Torr of N₂) and of large pressures of added O₂³ and formation of hydrogen atoms during the reaction^{2,3} with an estimated yield of 0.75 ± 0.25.²

The rate of adduct formation decreases with temperature whereas the rate of direct hydrogen abstraction increases. For a particular acid the relative contributions of the two channels will determine the overall temperature dependence of the rate constant. The contributions in turn will depend on parameters such as the strengths of the C-H and O-H bonds of the acids, and the magnitude of the equilibrium constant of formation of the hydrogen-bonded adduct, the variation of which from one acid to another may be approximated by the variation of the equilibrium constant of dimerization of the corresponding acids.

In the present work, we report rate constants in the temperature range 297-445 K for the reactions of OH radicals with the monomer and dimer of acetic, acetic-2,2,2-d₃, and propionic acids and of OD radicals with acetic acid-d₄. These acids with a range of C-H/C-D bond strengths and equilibrium constants allow

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[†]NRCC No. 29899. Part XVIII of rates of OH radical reactions. For part XVII, see: *J. Am. Chem. Soc.* **1988**, *110*, 7786.

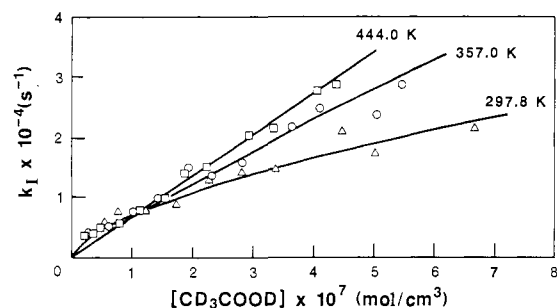


Figure 1. Representative plots of the pseudo-first-order rate constant, k_1 , against the acid concentration, at selected temperatures, for OD + CD₃COOD.

further evaluation of the mechanism.

Experimental Section

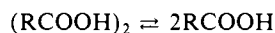
The kinetic measurements were made with the pulsed laser photolysis-resonance absorption technique described in detail recently.^{3,5} OH and OD radicals were generated by photolysis of the vapor of the corresponding acid at 222 nm. Approximate initial concentrations of OH/OD radicals ranging from 1.8×10^{-12} to 3.5×10^{-11} mol/cm³ were calculated from the number of 222-nm photons absorbed by the monomeric acids in the cell, measured by a disk calorimeter and by taking the quantum yield of OH from monomeric acetic and propionic acids to be 0.7 and 0.25, respectively.⁹ These values of the quantum yields and the negligible quantum yields of OH from the dimers of acetic and propionic acids have been determined in separate experiments.⁹ The OH yield from propionic acid at 298.2 and 327.1 K was low because of the large fraction of dimer (which does not give OH on photolysis) at these temperatures and the low OH quantum yield from the monomeric propionic acid.⁹ Experiments were made under pseudo-first-order conditions with the ratio [monomer]/[OH] > 10³. The reactants flowing slowly through the cell were subjected to fewer than 10 pulses in order to avoid the effect on the measured rates of product accumulation. The decay of the hydroxyl concentration was monitored by time resolved resonance absorption of the (0,0) band of the A²Σ⁺-X²Π transition. We used mainly the Q₁(2) and Q₁(3) rotational lines, with lesser amounts of the Q₁(1) and Q₁(4) lines at 308.15 nm for OH and the Q₁(5) line with lesser amounts of the Q₁(4) and Q₁(6) lines at 307.6 nm for OD. Signals were digitized, accumulated in a signal averager, and then transferred to a computer where pseudo-first-order rates, k_1 , were calculated by fitting an exponential decay function to the data as described before.⁵

Anachemia glacial acetic acid (99.7% min) and propionic acid (99.0% min), were found, by gas chromatography, to be free of impurities with the exception of traces of water in the propionic acid. They were subjected to degassing and bulb-to-bulb distillation at 77 K with the top and bottom fractions rejected. MSD Isotopes acetic-2,2,2-d₃ acid (99.2 atom % D) and acetic acid-d₄ (99.5 atom % D), were degassed by freeze-pump-thaw cycles.

Results

Values of the pseudo-first-order decay rates, k_1 , defined by $-d[\text{OH}]/dt = k_1[\text{OH}]$ and obtained as described in the Experimental Section are listed in Table S1 available as supplementary material. Representative plots of k_1 against the total acid concentration [monomer + dimer] at selected temperatures are shown in Figures 1 and 2. At low temperatures where both monomer and dimer are present the plots are nonlinear, indicating different reaction rates of the monomer and dimer. A downward bend of the plot indicates a low rate for the dimer relative to the monomer while the slightly upward bend for propionic acid in Figure 2 indicates a slightly higher relative rate for the dimer of this acid at 327 K.

In order to calculate second-order rate constants from the data we need the equilibrium constant of the monomer and the dimer of the acids, $K_{\text{eq}} = [\text{RCOOH}]^2/[(\text{RCOOH})_2]$.



For acetic acid we used the values derived from the thermodynamic data evaluated by Chao and Zwolinski¹⁰ at each temperature, and

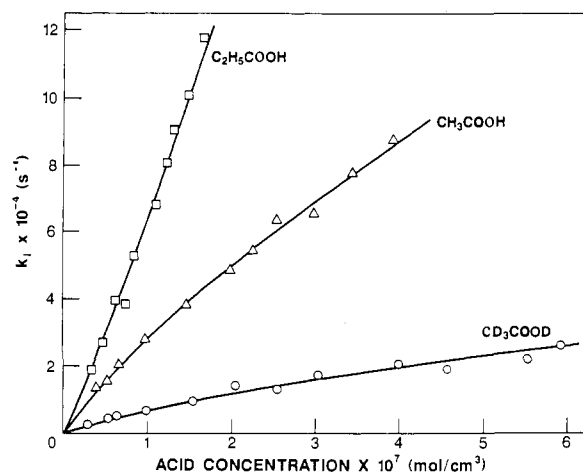


Figure 2. Plots of the pseudo-first-order rate constant, k_1 , against the acid concentration, for the reaction of CH₃COOH, CD₃COOD, and C₂H₅COOH at 326 K. The nonlinearity and the shape of the plots reflect the different reactivities of the monomer and dimer of the acids.

Table I. Rate Constants at Various Temperatures for the Reactions of OH and OD Radicals with the Monomer, k_M , and Dimer, k_D , of Acetic Acid, Acetic-2,2,2-d₃ Acid, Acetic Acid-d₄ and Propionic Acid

reaction	T, K	K_{eq}^a mol/cm ³	$(k_M \pm 2\sigma)$ $\times 10^{-11}$, cm ³ /mol s	$(k_D \pm 2\sigma)$ $\times 10^{-11}$, cm ³ /mol s
OH + CH ₃ COOH	296.8	2.87×10^{-8}	5.22×0.39	0.056 ± 0.160
	326.2	2.59×10^{-7}	3.39×0.26	0.687 ± 0.448
	356.4	1.68×10^{-6}	2.94 ± 0.10	
	396.8	1.30×10^{-5}	2.46 ± 0.08	
	446.2	9.20×10^{-5}	2.38 ± 0.04	
OH + CD ₃ COOH	297.8	3.13×10^{-8}	4.88 ± 0.22^b	-0.138 ± 0.222
	326.9	2.70×10^{-7}	3.90 ± 0.16	
	356.7	1.72×10^{-6}	2.91 ± 0.09	
	374.2	4.38×10^{-6}	2.69 ± 0.04	
	396.8	1.30×10^{-5}	2.49 ± 0.08	
OH + CD ₃ COOD	444.6	8.70×10^{-5}	2.13 ± 0.05	
	297.8	5.02×10^{-8}	1.42 ± 0.10^b	-0.085 ± 0.120
	326.5	3.72×10^{-7}	0.836 ± 0.045	
	357.0	2.18×10^{-6}	0.680 ± 0.052	
	397.0	1.45×10^{-5}	0.647 ± 0.035	
OH + C ₂ H ₅ COOH	444.0	8.63×10^{-5}	0.688 ± 0.039	
	298.2	2.91×10^{-8}	6.16 ± 3.28	6.66 ± 2.66
	327.1	2.14×10^{-7}	5.30 ± 1.16	9.95 ± 3.68
	356.6	1.54×10^{-6}	6.88 ± 0.90	11.3 ± 15.0
	374.9	4.17×10^{-6}	7.23 ± 0.36	
397.1	1.23×10^{-5}	6.59 ± 0.20		
444.7	8.60×10^{-5}	6.25 ± 0.16		

^a K_{eq} is the dissociation equilibrium constant for the acids, $K_{\text{eq}} = [\text{monomer}]^2/[\text{dimer}]$. ^b This value was obtained by setting $k_D = 0$ in the least-squares fitting.

the value of the equilibrium constant for CD₃COOH was taken to be the same as for CH₃COOH because of the absence of experimental data. Substitution by deuterium of the methyl hydrogens in CH₃COOH is not expected to change significantly the equilibrium constant. For CD₃COOD we used the values reported by Potter, Bender, and Ritter.¹¹ In selecting the values for propionic acid the data of MacDougall,¹² Taylor and Bruton,¹³ and Guilleme and Wojtkowiak¹⁴ were considered. Values of the second-order rate constant for the monomer, k_M , and the dimer, k_D , at low temperatures, where both are present, were obtained by nonlinear least-squares fits of the equation below to the data.

$$k_1 = k_M[\text{monomer}] + k_D[\text{dimer}]$$

$$[\text{monomer}] = -0.5K_{\text{eq}} + 0.5(K_{\text{eq}}^2 + 4K_{\text{eq}}P)^{1/2}$$

$$P = [\text{monomer}] + [\text{dimer}]$$

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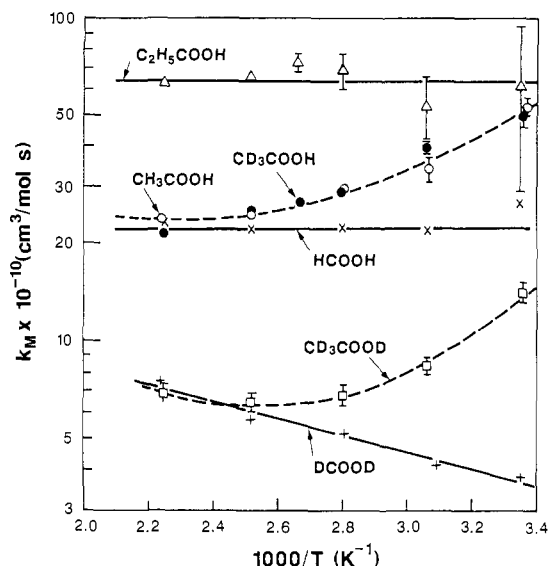


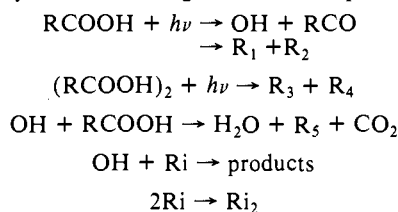
Figure 3. Arrhenius plots of the rate constant k_M for the reactions of OH or OD with all monomeric acids studied. The plots for formic acid were taken from our previous work.⁵ The dashed lines are visual fits. The horizontal lines are the weighted averages of the values. The line for DCOOD was obtained by fitting the Arrhenius equation to the points by nonlinear least squares.⁵

At higher temperatures, where the dimer concentration is insignificant, a one-parameter fit was made by setting $k_D = 0$. The calculated values of k_M and k_D and the equilibrium constant K_{eq} at each temperature are listed in Table I. Arrhenius plots of the rate constants are given in Figure 3, where the values for HCOOH and DCOOD from our previous measurements⁵ have also been plotted for comparison. The rate constants of acetic and deuterated acetic acids decrease initially with temperature and then level off to about half their initial values. For propionic acid, the rate constant in the range 298–445 K can be expressed by the temperature independent value $k_M = (6.47 \pm 0.30) \times 10^{11} \text{ cm}^3/\text{mol s}$, where the uncertainty is two standard deviations.

Estimation of Errors. The uncertainty associated with the k_M values of propionic acid at 298.2 and 327.1 K and with all the k_D values, in Table I, is fairly large. As noted in the Experimental Section, the initial OH concentration from monomeric propionic acid is low and, in addition, it is rapidly depleted before the start of the measurement due to the high reactivity of the dimer, thus resulting in large uncertainties in k_M at these temperatures. In the case of k_D , the random errors of the fits constitute a large fraction of the very small k_D values.

It has been shown before, in connection with the reaction of OH with formic acid,^{3,5} that absorption of the acid on the cell walls and its depletion by photolysis and reaction make an entirely negligible contribution to the OH decay, for our experimental conditions. The small amount of H atom content in acetic acid- d_4 will increase the rate constant by at most 2%. More important potential sources of systematic errors are (a) reactions of OH with radical products of the photolysis of the acids and of their reaction with OH and (b) uncertainties in the values of the equilibrium constants.

There is little information on the identity and quantum yields of products other than OH from the photolysis of the monomers and dimers of acids. We have estimated an upper limit to the contributions of reactions of OH with free radicals generated in the system by numerical integration of the equations below



with the following assumptions: (a) all the absorbed photons, the number of which has been measured as described in the Experimental Section, generate two radicals and (b) all radicals (R_i) in the system either react with OH or recombine with rates close to collision ($\sim 10^{14} \text{ cm}^3/\text{mol s}$). The calculated upper limits for the worst case (lowest reactant pressure and rate constant) are +9% and +11% for acetic and propionic acids, respectively. The effect on the rate constants of variations of K_{eq} were calculated by repeating the least-squares fit with K_{eq} values reduced and increased by 50%. The resulting changes in the k_M values are as follows: CH_3COOH +25%, -11%; CD_3COOH +33%, -14%; $\text{C}_2\text{H}_5\text{COOH}$ +1.7%, -3.5%. The estimated overall maximum values of the potential systematic error, obtained by adding the individual values, is +34%, -11% (CH_3COOH), +42%, -14% (CD_3COOH), and +12.7%, -3.5% ($\text{C}_2\text{H}_5\text{COOH}$). These values are for exaggerated worst case conditions and are intended to show the significance in differences in reactivity for the purpose of mechanistic interpretation of the data. A more refined analysis would include the observation that acetic acid has photolytic paths that give stable molecules (CO_2 , CH_4)¹⁵ that do not react or react very slowly with OH and that many radicals react with OH with less than the collision rate. Moreover, the equilibrium constants in most cases are known to better than $\pm 20\%$, so that a more realistic estimate of the maximum potential systematic errors in the reported rate constants are $\sim 15\%$ for CH_3COOH and $\sim 5\%$ for $\text{C}_2\text{H}_5\text{COOH}$.

Discussion

There are no previously reported rate measurements for the deuterated acids. Our room-temperature values of the rate constants for acetic acid are slightly higher (by 14% and 30%, respectively) than reported values.^{1,4} For propionic acid the large uncertainty at room temperature overlaps the literature values.^{1,4} Also, the temperature independence of the rate constant for propionic acid found in the present work is in agreement with the results of Dagaut et al.⁴ However, our results for the temperature dependence of the rate constant for acetic acid differ from those of Dagaut et al.,⁴ ours decreasing by 54% and theirs increasing by 12% from room temperature to about 440 K. In the measurements of Dagaut et al.,⁴ the reactant in the cell (in the millitorr range) was taken from stock mixtures prepared in a bulb. Carboxylic acids are strongly absorbed on the reactor walls and this affects the concentration measurement, as observed before,^{1,5} particularly at 240 K. In our experiments, in which the acid concentration was measured directly in the cell and was 1–2 orders of magnitude greater, wall absorption represented a much smaller loss. In addition, Dagaut et al.⁴ calculated rate constants at 240 K (where mainly dimeric acids are present) by taking the acid concentration as that of the monomer plus twice that of the dimer (i.e., assuming equal rates of hydrogen abstraction from C–H bonds of monomers and dimers). Our previous⁵ and present experiments (see below) show conclusively that OH reacts much slower with the dimer than with the monomer of formic and acetic acids at low temperatures; therefore, the calculation of Dagaut et al.⁴ would give an apparent low rate constant for CH_3COOH and particularly so at 240 K. Their values for $\text{C}_2\text{H}_5\text{COOH}$, which are affected less by the assumption because there is appreciable reaction with the dimer via abstraction of the secondary alkyl hydrogens (see below), are in better agreement with ours.

Mechanism. As is the case with formic acid,^{3,5} the important feature of the acetic acid results is the lack of reactivity of OH toward the dimer and the large isotope effect observed when the carboxylic but not the alkyl hydrogen is substituted by deuterium. On the other hand, OH reacts with the monomer and the dimer of propionic acid with about equal rates. The results, which are entirely consistent with the two-channel mechanism outlined in the introduction, will be interpreted in terms of two parameters: the bond-dissociation energy of the O–H and C–H bonds of the acids and the equilibrium constant of the formation of the hydrogen-bonded adduct between OH and the acid, k_{1a}/k_{-1a} , which

is assumed to parallel that of the acid dimerization, $[(\text{RCOOH})_2]/[\text{RCOOH}]^2$.

The bond-dissociation energies of the carboxylic hydrogen are about the same for all acids $D(\text{RCOO-H}) = 106 \pm 2$ kcal/mol, i.e., $D(\text{HCOO-H}) = 106.6 \pm 2$,¹⁶ $D(\text{CH}_3\text{COO-H}) = 105.8 \pm 2$,¹⁷ $D(\text{C}_2\text{H}_5\text{COO-H}) = 106.4 \pm 2$ ¹⁷ kcal/mol. The deuterated O-D and C-D bonds should be about 1-2 kcal stronger, due to zero-point energy differences. The C-H bond strength for formic acid, $D(\text{H-COOH})$, is 92.6 kcal/mol.¹⁶ The strengths of the H-CH₂COOH and H-CH(CH₃)COOH bonds, for which there are no reported values, are assumed to be 98 ± 2 and 93 ± 2 kcal/mol, respectively, which are in line with $D(\text{H-CH}_2\text{COCH}_3) = 98.3 \pm 1.8$ and $D(\text{H-CH(CH}_3)\text{COCH}_3) = 92.3 \pm 1.4$ kcal/mol¹⁷ and with the strengths of primary and secondary bonds in alkanes (98.2 and 95.1 kcal/mol, respectively).¹⁷ The equilibrium constant of the dimerization of the acids and by analogy that of the [OH+acid] adduct formation increases with increasing chain length, i.e., $\text{C}_2\text{H}_5\text{COOH} > \text{CH}_3\text{COOH} > \text{HCOOH}$ and decreases with deuterium substitution of the carboxylic hydrogen, i.e., $\text{RCOOH} > \text{RCOOD}$, but it does not change significantly with deuterium substitution of the hydrogen attached to carbon, i.e., $\text{HCOOH} = \text{DCOOH}$.⁵ We also assume that the rate constants for direct hydrogen abstraction by OH and OD would be essentially the same, as has been shown to be the case for the direct-abstraction reactions from alkanes.¹⁸ However, an isotope effect for OH and OD radicals would be expected for the path involving a hydrogen-bonded adduct.

With reference to Figure 3, the near temperature independence of the rate constant of HCOOH at room temperature was interpreted⁵ as due to the negative temperature dependence of the equilibrium constant of adduct formation, k_{1a}/k_{-1a} , offsetting the positive temperature dependence of reaction 1b and that of abstraction of the formyl hydrogen. The O-H bond strength in CH₃COOH and CD₃COOH is equal to that in HCOOH whereas the equilibrium constant for adduct formation is expected to be larger. Therefore, the rate constants of the reactions OH + CH₃COOH and OH + CD₃COOH, at room temperature, are expected to be greater than that for OH + HCOOH, as observed.

The contribution of direct hydrogen abstraction from the alkyl group in CH₃COOH is expected to be even less than that in HCOOH, due to the larger bond strengths of the three primary C-H and C-D bonds. The low reactivity of the dimer relative to the monomer of acetic acid confirms that abstraction from the C-H bond is very slow at low temperatures. Accordingly, the rate constants of the OH + CH₃COOH and OH + CD₃COOH reactions are approximately equal and are observed to decrease with temperature, because at low temperatures the rate is determined mainly by the temperature dependence of the equilibrium constant for adduct formation. At higher temperatures (> 370

K) direct hydrogen abstraction is expected to become appreciable and the rate constants appear to level off more so for CH₃COOH than for CD₃COOH. A primary isotope effect, $k(\text{H})/k(\text{D}) \sim 4$, is observed for the adduct channel, by comparing the rate constants of CD₃COOH and CD₃COOD.

The temperature dependence of the rate constant of the OD + CD₃COOD reaction parallels that of OH+CH₃COOH, but the values appear to level off earlier and to start increasing at 444 K. The equilibrium constant for adduct formation, k_{1a}/k_{-1a} , is expected to be smaller for the deuterated acid whereas the isotope effect for breaking the O-H and C-H bonds may be approximately equal. As a result, direct abstraction of hydrogen from the alkyl group would become significant at a lower temperature for OD + CD₃COOD than for OH + CH₃COOH. Hydrogen abstraction from the alkyl group is even more important for the reaction with propionic acid, which has two weak secondary C-H bonds, thus accounting for the reactivity of the dimer and the temperature independence of the rate constant. We were able to reproduce the temperature dependence of the rate constants of all acids, over the limited temperature range of the present work, by using reasonable values of Arrhenius parameters for each path and isotope effects of 4 for paths 1b and 3.

The structure of the adduct is presumed to involve hydrogen bonding between the carbonyl oxygen of the acid and the hydrogen of the hydroxyl radical. Such a structure has been suggested to account for the low quantum yield of OH from photolysis of the dimer of formic acid^{9,19} as well as acetic and propionic acids.⁹ Specifically, because of the hydrogen-bonded structure of the dimer, any OH formed in the initial photolytic step of the dimer would find itself hydrogen bonded to a carbonyl oxygen and continue along the reaction path indicated by reaction 1b. On the basis of kinetic isotope effects, reaction 1b is evidently the dominant decomposition pathway of the adduct in the case of formic,⁵ acetic, and propionic acids. However, with increasing size of the alkyl chain, an alternative decomposition path of the adduct involving formally abstraction of H from the relatively weaker secondary C-H bonds may occur to some extent.

Our previous⁵ and present results for reactions of OH and OD with monomeric and dimeric formic, acetic, and propionic acids and their deuterated analogues provide a comprehensive set of kinetic data which exhibit a range of reactivities and temperature dependences. Trends in reactivity with expected association equilibrium constants and with C-H bond strengths are consistent with a two-channel mechanism. Further evaluation of the mechanism may be obtained by theoretical calculations of the structures and potential energies of the intermediates in the two channels.

Supplementary Material Available: Table S1 of measured pseudo-first-order decay rates at each temperature for all the reactions studied (6 pages). Ordering information is given on any current masthead page.

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