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Rate and Mechanism of the Reaction of Hydroxyl Radicals with Formic and Deuteriated Formic Acids[†]

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Abstract: Rate constants for the reactions of hydroxyl radicals with the monomer and dimer of formic acid and deuteriated formic acids have been determined in the temperature range 297–445 K by a laser photolysis–resonance absorption technique. Hydroxyl radicals were generated by photolysis of formic acid at 222 nm with a KrCl excimer laser and were monitored by time-resolved resonance absorption. In each case the rate constant of the monomer of formic acid was much larger than that of the dimer, and a large isotope effect was observed when the carboxylic, but not the formyl, hydrogen was substituted by deuterium. A two-channel mechanism is proposed, one involving formation of a hydrogen-bonded adduct followed by transfer of the carboxylic hydrogen to the hydroxyl radical, and the other, direct abstraction of a formyl hydrogen.

Only recently has quantitative information on the mechanism of the reaction of hydroxyl radicals with carboxylic acids been reported. In early work on the photolysis of formic acid by Gorden and Ausloos[1] the mechanism of the reaction OH + HCOOH was considered only in an incidental way, in connection with the secondary chemistry of the photolytically produced OH radicals. Interpretation of these experiments based on the observed stable products (H_2, CO, CO_2) was difficult because it required knowledge of both the primary photolytic process as well as the secondary free-radical chemistry. Gorden and Ausloos concluded that reaction 1 is the most important source of free radicals in

$$\mathrm{HCOOH} + h\nu \rightarrow \mathrm{OH} + \mathrm{HCO} \qquad (1)$$

the direct photolysis of formic acid although quantitative determination of its importance was not possible. For the subsequent reaction of OH with formic acid, reactions 2a and 2b were considered, and qualitative conclusions were attempted about their relative importance. The reaction of OH with the dimer of formic acid, which was also present in the room-temperature experiments, was not considered in the early work.[1]

$$\mathrm{OH} + \mathrm{HCOOH} \rightarrow \mathrm{H_2O} + \mathrm{COOH} \qquad (2a)$$

$$\rightarrow \mathrm{H_2O} + \mathrm{HCOO} \qquad (2b)$$

Recent kinetic studies of reaction 2, prompted by its relevance to atmospheric chemistry, have revealed a number of interesting features regarding its mechanism. Rate constants for the reaction with HCOOH have been reported by Zetzsch and Stuhl[2] and Wine et al.,[3] who used the flash photolysis–resonance fluorescence technique, photolysis of water as the source of OH radicals, and low pressures of formic acid, where essentially only monomeric HCOOH was present, and by Jolly et al.,[4] in this laboratory, who used the flash photolysis–resonance absorption technique, photolysis of formic acid as the source of OH radicals, and higher pressures of formic acid that consisted of equilibrium mixtures of monomer and dimer, $(HCOOH)_2$, to study the reaction of OH with the monomer as well as the dimer of formic acid.

$$\mathrm{OH} + (\mathrm{HCOOH})_2 \rightarrow \text{products} \qquad (3)$$

The rate constants at room temperature reported by Wine et al.[3] and Jolly et al.[4] are in good agreement and are about 40–50% greater than the value of Zetzsch and Stuhl.[2] It was also reported that the rate constants are independent of total pressure (30–300 Torr of He or Ar and 500 Torr of N_2),[2,4] independent of large pressures of added O_2,[4] independent of temperature (298–430 K),[3] and independent of substitution of D for H on carbon.[3] Hydrogen atoms were reported to be formed during the reaction[3,4] with an estimated yield of 0.75 ± 0.25.[3] Furthermore, Jolly et al.[4] found that the dimer was much less reactive than the monomer. Since the dimer has a doubly hydrogen bonded cyclical structure (each acidic OH group forming a hydrogen bond with the carbonyl oxygen of its partner), with two C–H bonds available for interaction with OH, Jolly et al.[4] concluded that hydrogen abstraction from the C–H bonds is only a minor path of the reaction. Although the O–H bond is ~14 kcal/mol stronger than the C–H bond (106.6 and 92.6 kcal/mol, respectively),[5] a bond energy–bond order calculation[4] indicated an activation energy of 1–2 kcal/mol less for abstraction from the acidic O–H bond compared to the C–H bond.

Wine et al.[3] have suggested "a complex rather than a direct mechanism" and a possible intermediate adduct formed by addition of OH to the carbonyl double bond. Jolly et al.[4] have discussed several reaction paths including direct abstraction of the formyl or acidic hydrogen and have suggested a tentative mechanism in which OH forms a hydrogen-bonded complex with formic acid, followed by transfer of the hydroxylic hydrogen in the adduct. The mechanism is analogous to that proposed for the preferential abstraction of hydroxylic hydrogen from alcohols by alkoxy radicals[6] and from phenols by 2,4,6-tri-*tert*-butylphenoxy radicals[7] in solution.

In the present work we have extended our room-temperature measurements on formic acid and determined rate constants for the reactions of OH and OD radicals with the monomer and dimer of formic acid and its deuteriated analogues in the temperature range 297–445 K and over a wide pressure range of reactant. Additional and more precise values of rate parameters were obtained allowing formulation of a more definitive mechanism.

Experimental Section

The measurements were made with the pulsed laser photolysis–resonance absorption technique. The apparatus and experimental procedure

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have been described recently[4,9] and will be mentioned briefly together with modifications made to the apparatus in the present experiments. A 1-m-long cell was surrounded by a jacket in which a thermostatic liquid was circulated to maintain constant temperature. The liquid was also circulated around a spiral preheater located at the entrance of the cell, through which the reactant passed before entering the cell. The temperature of the reactant at the entrance and exit of the cell, measured by thermocouples located at these points, was essentially the same.

OH and OD radicals were generated by photolysis of formic acid vapor or its deuteriated analogues at 222 nm with a KrCl excimer laser. We have established that the photolysis of the monomer of formic acid at 222 nm is an efficient source of hydroxyl radicals.[8] The decay of the hydroxyl concentration with time was followed by time-resolved absorption of resonance radiation (the (0, 0) band of the $A^2\Sigma^+-X^2\Pi$ transition) from a microwave-powered resonance lamp in which H_2O or D_2O in Ar was flowing at low pressure.[4,9] The $Q_1(3)$ (308.2 nm) and $Q_1(5)$ (307.6 nm) rotational lines were used to monitor the OH and OD decays, respectively.

To prevent exchange between the carboxylic H and D atoms on the walls of the reaction cell on changing from one isotope to the other, the reaction cell and attached vacuum line were repeatedly evacuated, filled with the saturation pressure of DNO_3 or HNO_3, and then left overnight with a low pressure of H_2O or D_2O. It was found that nitric acid conditions the walls more efficiently than water or formic acid.

In most experiments the reactant was made to flow slowly (2–20 cm/s) through the reaction cell with automatic flow and pressure controllers. A few experiments in which the cell was filled statically gave the same results. In both cases one aliquot of the reactant was subjected to no more than 10 laser pulses, in order to minimize the effect of depletion of the reactant (0.1–0.2%) or accumulation of reaction products on the measured rates. Signals from a sufficient number of pulses to give a good signal to noise ratio were accumulated in a signal averager and transferred to a computer for further processing.

The values of the pseudo-first-order rate constant, k_1, the intensity at infinite time, I_0, the intensity at zero time (i.e., immediately after the laser pulse), $I_{t=0}$, and their standard deviations were computed by a nonlinear least-squares fit of the transmitted intensity of the resonance radiation, I, to an exponential decay function, $I = I_0(I_{t=0}/I_0)^n$, where $n = \exp(-k_1 t)$.

Although reaction 1 is exothermic by 20 kcal/mol, the OH radicals were formed without significant vibrational or rotational excitation.[10] The translational thermalization of OH is complete within a short time prior to the start of the decay measurements.[4]

Formic acid (Aldrich, 98% in H_2O) and formic-d_1 acid (95% in H_2O, 99.3% D), formic acid-d_1 (95% in D_2O, 98.3% D), formic-d_1 acid-d_1 (95% in D_2O, 99.5% D), purchased from MSD Isotopes, Merck Frosst Canada Inc., were degassed by freeze–pump–thaw cycles. In addition to the water, gas chromatographic analysis of formic acid detected traces of formaldehyde (0.003%) and methanol (0.1%). The water is present to stabilize the acid. If it is removed, the acid decomposes slowly and gives erratic kinetic results. However, it is not necessary to correct the measured pressures of formic acid in the reaction cell for the water impurity because the composition of the vapor is enriched in formic acid,[11] as discussed previously.[4]

Results

The equilibrium constant of the monomer and dimer (eq 4) of formic acid, $K_{eq} = [HCOOH]^2/[(HCOOH)_2]$, and of the deuteriated acids is required for the processing and interpretation of the data. In selecting the values of the equilibrium constant for

$$(HCOOH)_2 \rightleftharpoons 2HCOOH \qquad (4)$$

formic acid at each temperature, the data of Halford,[12] Büttner and Maurer,[13] Barton and Hsu,[14] and Taylor and Bruton[15] were considered. At room temperature, the values of Halford were selected because they were the only ones measured below 318 K. At higher temperatures, the average of the values of Barton and Hsu[14] and of Taylor and Bruton[15] were selected, because their measured values were in good agreement over this temperature range. However, the vapor composition was predominantly monomer at the higher temperatures, and the precise value of the equilibrium constant was of no consequence. In any case, the other data were within 10% of the adopted values. There are no reported values of the equilibrium constants of the deuteriated formic acids. These were calculated at each temperature relative to the corresponding experimental value of the formic acid, by the standard methods of equilibrium statistical mechanics[16] using values of vibrational frequencies[17-20] and rotational constants[20] listed in Table S1 (supplementary material).

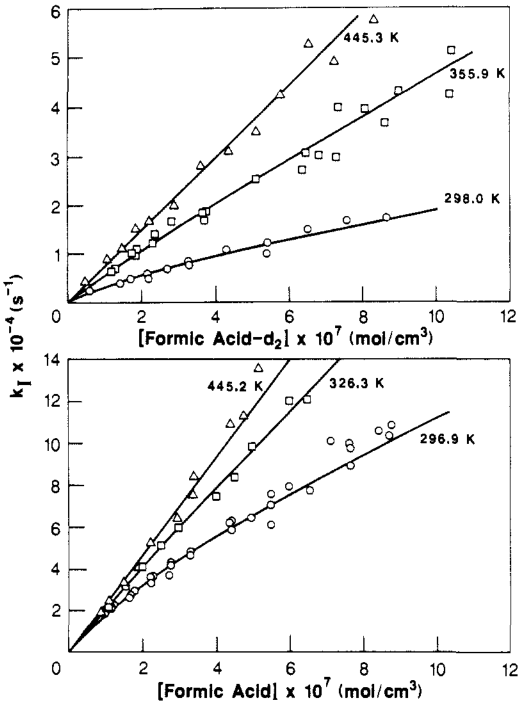

Figure 1. Plots of the pseudo-first-order rate constant, k_1, for the decay of OH or OD against the concentration of formic and fully deuteriated formic acids (monomer + dimer), respectively, at selected temperatures.

As was mentioned in the Experimental Section, we have established that mainly the monomer of formic acid gives OH on photolysis and the same is expected from the photolysis of the deuteriated formic acids. Approximate initial concentrations of OH and OD, $(1.9-3.9) \times 10^{-11}$ and $(0.45-3.5) \times 10^{-11}$ mol/cm^3, respectively, were calculated from the number of 222-nm photons absorbed by monomeric formic acid in the cell measured by a disc calorimeter and taking the quantum yield of OH and OD production to be 1.[8] Experiments were done under pseudo-first-order conditions with the ratio $[\text{monomer}]/[OH] > 10^3$. The first-order decay rates, k_1, defined by $d[OH]/dt = -k_1[OH]$, were obtained as described in the Experimental Section. Values of k_1 for formic acid and formic-d_1 acid-d_1 (DCOOD) and their standard deviations are listed in Table S2 (supplementary material). Representative plots of k_1 against the total concentration [monomer + dimer] at selected temperatures are shown in Figure 1. Rate constants for formic-d_1 acid (DCOOH) and for formic acid-d_1 (HCOOD) were also measured at room temperature and will be discussed below.

The plots of the room-temperature values of k_1 in Figure 1 are not linear, indicating different reaction rates for the monomer and dimer with hydroxyl radicals. At higher temperatures, there is essentially only monomer and the plots are linear. The values of the second-order rate constants for the monomer, k_M, and the dimer, k_D, at low temperatures (298 and 326 K) where both

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Table I. Rate Constants at Various Temperatures for the Reactions of OH and OD with the Monomer, k_M, and Dimer, k_D, of Formic Acid, Formic-d_1 Acid-d_1, and Formic-d_1 Acid[a]

reaction	T, K	K_{eq},[b] mol/cm^3	$k_M \times 10^{-10}$, cm^3/mol·s	$k_D \times 10^{-10}$, cm^3/mol·s
OH + HCOOH	296.9	1.15×10^{-7}	26.9 ± 1.7	4.83 ± 1.24
	326.3	9.39×10^{-7}	22.0 ± 1.8	13.4 ± 6.2
	356.2	5.58×10^{-6}	22.2 ± 1.9	
	396.2	3.64×10^{-5}	22.1 ± 0.7	
	445.2	2.31×10^{-4}	23.5 ± 1.7	
OD + DCOOD	298.0	1.88×10^{-7}	3.83 ± 0.78	0.825 ± 0.815
	324.0	1.18×10^{-6}	4.06 ± 0.31	1.09 ± 0.81
	355.9	8.01×10^{-6}	5.20 ± 0.23	
	396.1	5.11×10^{-5}	5.68 ± 0.27	
	445.3	3.16×10^{-4}	7.39 ± 0.33	
OH + DCOOH	296.0	9.57×10^{-8}	24.1 ± 2.0	−1.22 ± 0.68

[a] The quoted uncertainties are the 95% confidence levels. [b] K_{eq} is the dissociation equilibrium constant for the acids, K_{eq} = [monomer]^2/[dimer].

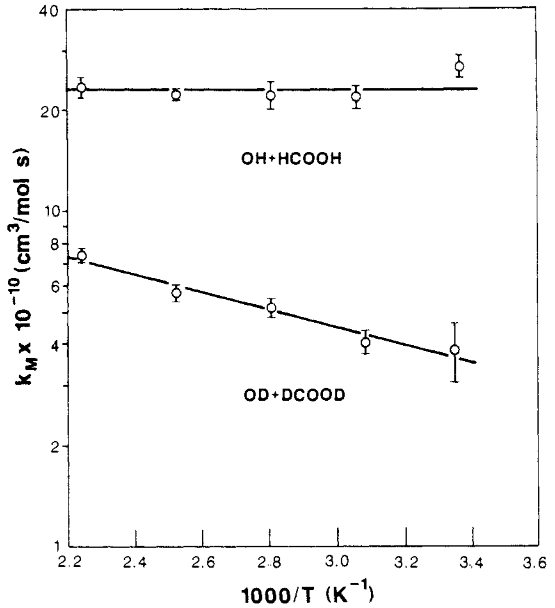

Figure 2. Arrhenius plots of the rate constant, k_M, for reaction of OH and OD with monomeric HCOOH and DCOOD, respectively. The horizontal line is the weighted average of the five values for HCOOH, and the line for DCOOD was calculated by fitting the Arrhenius equation to the points.

monomer and dimer are present were obtained by nonlinear least-squares fits of

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

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

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

to the data. At higher temperatures, where the dimer concentration is insignificant, a one-parameter least-squares fit was made by setting $k_D = 0$. It was not possible to obtain values of k_D at higher temperatures because increasing the formic acid pressure further to increase the dimer concentration would result in a decay rate faster than the measuring capability of the apparatus. The calculated values of k_M and k_D and their 95% confidence levels for OH + HCOOH, OH + DCOOH, and OD + DCOOD and the equilibrium constant K_{eq} at each temperature are given in Table I. A room-temperature value of $k_M \sim 9 \times 10^{10}$ cm^3/mol·s was obtained for OD + HCOOD. However, as discussed below, this value is an upper limit. For OH + HCOOH, the weighted average of our values over the range 296.9–445.2 K gives a temperature-independent value of $k_M = (2.2 \pm 0.2) \times 10^{11}$ cm^3/mol·s, and the weighted least-squares fit of the Arrhenius equation gives $k_M = (1.75 \pm 0.96) \times 10^{11} \exp[(102 \pm 194)/T]$ cm^3/mol·s, where the indicated uncertainties are 2 standard deviations. For OD + DCOOD, the values of k_M increase steadily with increasing temperature and can be described by $k_M(\text{DCOOD}) = (2.69 \pm 1.02) \times 10^{11} \exp[(-(594 \pm 134)/T]$ cm^3/mol·s, by fitting the Arrhenius expression to the data by nonlinear least squares. The indicated uncertainties are 2 standard deviations. Arrhenius plots of the values for HCOOH and DCOOD are given in Figure 2.

Estimation of Errors. The random errors in k_M and k_D in Table I only indicate how well the nonlinear least squares can fit the data points. A random error in k_1 of ~±7%, indicating the reproducibility of the measurement, was obtained from seven rate measurements at 12.1 Torr of formic acid. The uncertainty associated with the k_D values, in Table I, is fairly large because the random errors of the least-squares fits constitute a large fraction of the small values of k_D.

Potential sources of systematic errors have been discussed in detail in our previous paper.[4] The absorption of formic acid on the walls, its depletion by photolysis and by reaction with OH, and reaction of OH with the formaldehyde and methanol impurities in formic acid were shown to be entirely negligible for our experimental conditions. The small amount of H atom content in the deuteriated formic acids would increase the measured rates by +4% for DCOOD, +7% for HCOOD, and +0.8% for DCOOH.

Another potential source of systematic error is the reaction of OH with the products of photolysis of formic acid. As discussed before,[4] the reaction of OH with the stable products from reaction 5 (which may proceed by a molecular mechanism[21]) as well as

$$(\text{HCOOH})_2 + h\nu \rightarrow \text{H}_2 + \text{CO}_2 + \text{HCOOH} \qquad (5)$$

those from reactions 1 and 2 are negligible and do not contribute significantly to the OH decay rate. Calculated upper limits (for minimum concentration of monomer) for the contribution of reactions of OH with free radicals formed in reactions 1 and 2 (HCO and HCOO) were +10% for the reaction of OH + HCOOH and OD + DCOOD and +41% for that of OD + HCOOD. The contribution of free radicals was based on numerical integration of the appropriate equations, taking the rate constants for reactions of HCOO (recombination and reaction with OH) to be the same as that reported for HCO,[22,23] assuming an isotope effect of 3 for deuterium substitution in DCOO and DCO, and using other rate constants from the literature.[24]

Small variations in the values of the equilibrium constants have minor effects on the calculated values of k_M and k_D. For the low-pressure data of formic acid, repeating the least-squares fit with K_{eq} reduced by 50% results in values of $k_M = 2.94 \times 10^{11}$ (+9%) and $k_D = 5.48 \times 10^{10}$ (+13%), whereas increasing K_{eq} by 50% gives $k_M = 2.50 \times 10^{11}$ (−7%) and $k_D = 0.66 \times 10^{10}$ (−17%). A similar calculation for formic-d_1 acid-d_1 gives +6%, −7% for k_M and +17%, −19% for k_D.

The maximum overall systematic uncertainty in k_M calculated by adding the potential systematic errors itemized above is +19%, +3% for formic acid and +20%, −7% for formic-d_1 acid-d_1. The

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maximum systematic error in k_D is +23%, −7% for formic and +31%, −5% for formic-d_1 acid-d_1. However, for formic acid-d_1 the maximum systematic error in k_M due to secondary reactions alone is +47% because the primary but not the secondary reaction is slowed by deuterium substitution in this case. In addition, a number of tests showed that the first-order rate of this reaction decreased with the number of flashes and to a small extent with the laser power. Also NMR analysis of HCOOD after a number of flashes showed increased content of HCOOH in some experiments. These findings raise the possibility of isotope contamination of HCOOD by exchange with the HCO and HCOO radical products. In view of the large unavoidable interferences occurring in the measurements with formic acid-d_1 we conclude that the measured value of k_M at room temperature is an upper limit.

Discussion

For the OH + HCOOH reaction, there is good agreement between our present room-temperature value of k_M of $(2.69 \pm 0.17) \times 10^{11}$ cm^3/mol·s, our previously[4] reported value of $(2.95 \pm 0.14) \times 10^{11}$ cm^3/mol·s, and the value reported by Wine et al.[3] of $(2.78 \pm 0.45) \times 10^{11}$ cm^3/mol·s. Very recently Dagaut et al.[25] reported a value, $(2.23 \pm 0.24) \times 10^{11}$ cm^3/mol·s, that is somewhat lower but is in fair agreement with the values above (within the combined errors). At other temperatures there is also agreement with the results of Wine et al.[3] for OH + HCOOH. Over the temperature range 298–430 K, their data could be described by a temperature-independent rate constant, $k_M = (2.78 \pm 0.70) \times 10^{11}$ cm^3/mol·s, or an Arrhenius expression with a slightly negative activation parameter, $k_M = (2.2 \pm 0.5) \times 10^{11} \exp[(77 \pm 75)/T]$ cm^3/mol·s, which is in agreement with our results. For the OH + DCOOH reaction at room temperature, there is also good agreement between our results and those of Wine et al.,[3] 2.8×10^{11} cm^3/mol·s. There is no reported rate data for the reactions of OH with HCOOD and DCOOD, nor for any of the deuteriated dimers.

Consistent with the results of our previous work,[4] the room-temperature rate constant of the dimer is much smaller than that of the monomer for each isotopic acid studied. Within the rather large uncertainty, particularly in k_D, the present room-temperature value of $k_D/k_M = 0.18 \pm 0.06$ is only slightly greater than our previous value, which we estimated could be as large as 0.07 or even larger.

In the subsequent discussion of the mechanism, we suggest that the only reaction path for the dimer involves abstraction by the hydroxyl radical of a hydrogen from the formyl group. Thus, by assuming that the rate constant for the direct abstraction from the C–H bond of the monomer is half that of the dimer, we estimate room-temperature rate constant values of $\sim 2.4 \times 10^{10}$ and $\sim 0.41 \times 10^{10}$ cm^3/mol·s, respectively, for abstraction from H-COOH and D-COOD in the monomers, which correspond to only ~9% and ~11% of the observed total rate constants (k_M), respectively. It should be stressed that these are rough estimates because of the large uncertainties in the values of k_D.

The kinetic isotope effect at room temperature for abstraction from the formyl group can be obtained as the ratio of the values of k_D for $(HCOOH)_2$ and $(DCOOD)_2$, $k_D(H)/k_D(D) \sim 6$. Although, again, this is a rough estimate because of the uncertainties in k_D, it is in line with the range of values observed, 3–5, in hydrogen abstraction reactions by OH from C–H bonds of paraffins and cycloparaffins.[26–30] On the basis of this analysis, the k_D values of $(DCOOH)_2$ and $(DCOOD)_2$ are expected to be the same. However, the k_D value for $(DCOOH)_2$ is a small fraction of the total rate constant and the large uncertainty of the least-squares fit results in a negative value for k_D (Table I). The isotope effect for the reaction with the acidic hydrogen is estimated as ~7, on the basis of the ratio of k_M values for HCOOH and DCOOD and correcting for estimated contributions by abstraction from the formyl group, discussed above.

Mechanism. In the discussion of the mechanism, it is assumed that, at some stage of the reaction, the OH radical abstracts a hydrogen from formic acid to form water, and this is supported by the stable products formed on photolysis of formic acid. In early experiments, Gorin and Taylor[21] showed that at 373 K, where virtually only monomer is present, the product yields $CO_2:H_2:CO:H_2O = 1.0:1.0:1.13:1.13$ are approximately equal. In conjunction with our recent determination that formation of OH is the dominant pathway in the photolysis of the monomer at 222 nm,[8] these results indicate that water is the primary product of the reaction of OH with monomeric formic acid. The same products, but in different proportions, were also formed at lower temperatures where significant quantities of dimer were present.[21]

The present work provides very clear evidence concerning certain details of the reaction of OH with formic acid and, in particular, which of the two hydrogen atoms is involved in the reaction. One of the striking features of the monomer rate constants, k_M, in Table I for HCOOH, DCOOH, and DCOOD at room temperature is that substitution of the acidic H by D has a very dramatic effect on the reactivity, but a similar substitution at the formyl group has very little effect. These results indicate that the dominant interaction of the OH radical is with the acidic hydrogen of formic acid, rather than with the formyl hydrogen. This conclusion is reinforced by the observation of the very low reactivity of the dimer relative to the monomer for each of the isotopic formic acids studied. In the dimer, each of the acidic hydrogens is hydrogen bonded to a carbonyl group to form a cyclic structure, thus blocking interaction of the OH radical with the acidic hydrogen. The only path available for the dimer, then, would be abstraction of hydrogen from the formyl group, which apparently proceeds at a much slower rate at room temperature than the interaction at the acidic site.

Addition of OH to the carbonyl double bond, suggested by Wine et al.,[3] is not consistent with the dominant role of the acidic hydrogen and with the lack of an effect on the rate constant of added O_2.[4] To rationalize our room-temperature results, a potential mechanism was proposed in our previous paper,[4] which involves reversible formation of a hydrogen-bonded adduct between OH and monomeric formic acid, followed by transfer in the adduct of the carboxylic hydrogen to the hydroxyl radical (eq 6 and 7).

$$\mathrm{OH + HCOOH} \underset{-a}{\overset{a}{\rightleftharpoons}} [\mathrm{adduct}] \xrightarrow{b} \mathrm{H_2O + HCOO} \qquad (6)$$

$$\mathrm{HCOO \rightarrow H + CO_2} \qquad (7)$$

The proposed pathway is consistent with the experimental observations itemized above, including the production of H atoms as a reaction intermediate,[3,4] and with the approximate temperature independence of the rate constant for OH + HCOOH.

The near temperature independence (or slightly negative temperature dependence) of the rate constant near room temperature for the reaction OH + HCOOH, shown in Figure 2, can be interpreted as due to the temperature dependence of the equilibrium constant for adduct formation, k_{6a}/k_{6-a}, offsetting the activation energy for reaction 6b, assuming that $k_{6-a} > k_{6b}$. However, the reaction path involving the direct abstraction of hydrogen from the formyl group of HCOOH must be considered as well, since the experimental results suggest that it could make a small contribution to the overall rate at room temperature, as discussed above. At higher temperatures, abstraction from the formyl group would be expected to make a greater contribution because of its anticipated positive activation energy, and the Arrhenius plot would be expected to curve upward at higher temperatures. The observed temperature independence of the overall rate constant would be the result of the summation of the rate constants for each path, having slightly positive and negative activation energies, respectively. Over the somewhat limited temperature interval of the present work, it is possible to reproduce the observed temperature dependence of the overall rate constant for OH + HCOOH with reasonable values for the Arrhenius

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parameters of each path; furthermore, the experimental Arrhenius plot for OD + DCOOD can be reproduced by applying kinetic isotope effects of about 2 and 9 at 298 K to the C–H abstraction and addition paths, respectively. These kinetic isotope effects are reasonable, as discussed below.

The positive Arrhenius activation energy and lower values of k_M (relative to OH + HCOOH) for the OD + DCOOD reaction can be interpreted in terms of the relative difference in isotope effects for the addition path (i.e., the equilibrium constant k_{6a}/k_{6-a} and the rate constant k_{6b}) and the direct abstraction path involving the formyl group. The equilibrium constant for adduct formation, k_{6a}/k_{6-a}, would be expected to be smaller for the deuteriated formic acid by analogy with the equilibrium constants for the dissociation of hydrogen bonded dimers of the acids in Table I. Also, because the acidic O–H bond is broken in the adduct to form H_2O, k_{6b} is expected to have a kinetic isotope effect. The multiplicative effect of the two steps would therefore likely result in the addition path having a greater kinetic isotope effect than the C–H abstraction path. As a result, direct abstraction of hydrogen from the formyl group would be relatively more important for the OD + DCOOD reaction than for the OH + HCOOH reaction, thus accounting for the positive activation energy for OD + DCOOD. This mechanism would predict that k_D/k_M would be greater for DCOOD than for HCOOH. Although our room-temperature results appear consistent with this prediction, the errors in the k_D values are too large to allow a definite conclusion. Also, tunneling effects could contribute to the observed difference in the temperature dependence of the rate constants for HCOOH and DCOOD if tunneling were more important in reaction 6b than in the abstraction from the formyl group.

In the discussion of isotope effects, we assume that the rate constants for the direct abstraction reactions of OH and OD with formic acid would be essentially the same. This is a reasonable assumption because it has been shown in previous work that OH and OD radicals do not have a significant isotope effect in the direct abstraction reactions with alkanes.[26] However, an isotope effect for OH and OD radicals would be expected for the proposed reaction path involving a hydrogen-bonded adduct. It will be difficult to determine experimentally such an isotope effect because of the ease of isotopic scrambling between the source of the hydroxyl radical and the acidic hydrogen of formic acid.

Fluorine atoms, which are isoelectronic with OH, also react with HCOOH by two paths. Macdonald and Sloan[31] found that, under their conditions, abstraction by F of the acidic hydrogen is favored by a 2:1 margin over the formyl hydrogen. Furthermore, the distribution of energy in the HF product indicated that the reaction at the acidic site involves a long-lived complex, whereas direct abstraction occurs at the formyl group.

Further experiments with other acids with varying strengths of C–H and O–H bonds may help to clarify the mechanism further. More important however would be theoretical calculations of the structures of the adducts and the potential energies of the reaction channels.

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Supplementary Material Available: Table S1 of vibrational frequencies and rotational constants used to calculate the dimerization equilibrium constants of formic acid and its deuteriated analogues and Table S2 of measured first-order decay rates at each temperature for the reaction of OH with formic acid and OD with formic-d_1 acid-d_1 (6 pages). Ordering information is given on any current masthead page.

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Divalent Metal Ion Catalysis in the Hydrolysis of Phosphomonoesters. Hydrolysis of 2-(1,10-Phenanthrolyl) Phosphate

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Abstract: Rate constants have been determined for hydrolysis of 2-(1,10-phenanthrolyl) phosphate in water at 85 °C and $\mu = 0.1$ M with KCl. The plot of k_{obsd} vs pH is bell-shaped, which shows that the monoanion and the neutral species are the maximally reactive species. Divalent metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}) exert a pronounced catalytic effect on the hydrolysis reaction of the phosphate dianion species (a dianion reaction cannot be observed in the absence of metal ion). The Cu(II) complex of the 2-(1,10-phenanthrolyl) phosphate dianion hydrolyzes at 40 °C more than 10^8-fold faster than the phenyl phosphate dianion and 60 000-fold faster than *p*-nitrophenyl phosphate dianion. Binding of the metal ions produces an absorbance change near 270 nm, as is the case with 1,10-phenanthroline, and the measured rate constants for metal ion binding are also similar to those of 1,10-phenanthroline. Thus, the metal ions are chelating the phenanthroline nitrogens. Binding of the metal ions is very strong; saturation effects occur at low metal ion concentration (<0.005 M). The plots of k_{obsd} vs pH in the hydrolytic reactions are then pH independent at pH >6. The value of ΔS^* for the pH-independent reaction at pH >6 in the presence of a saturating concentration of Cu^{2+} is –46.8 eu, but ΔH^* is only 8 kcal/mol. The reaction very likely involves nucleophilic attack of H_2O on phosphorus or a kinetic equivalent. There is an accelerating effect of pyridine and imidazole in the reaction of the Ni(II) complex of the 2-(1,10-phenanthrolyl) phosphate dianion. This reaction is highly dependent on the presence of the metal ion; catalysis could not be detected in the absence of metal ion. A metal ion will not favorably chelate the leaving-group oxygen of 2-(1,10-phenanthrolyl) phosphate in a 1:1 complex because of the steric situation; complexation of the other phosphate oxygens will retard the metaphosphate elimination but will enhance nucleophilic attack at phosphorus. Thus, a strongly bound metal ion will produce large rate enhancements in the hydrolysis reactions of such phosphomonoesters and can lead to catalytic processes that proceed most likely by nucleophilic pathways.

Phosphate esters are among the most important of biologically active compounds.[2] There has been considerable effort made to understand the chemistry of their hydrolytic reactions.[3] Phosphomonoesters, e.g., methyl phosphate, exhibit bell-shaped plots

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