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Reactions of hydrated electrons $(H_2O)_n^-$ with formic acid

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Abstract

The chemistry of gas phase hydrated electrons $(H_2O)_n^-$ with formic acid is studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Black body infrared radiative dissociation and ligand exchange of water by formic acid molecules take place, accompanied by a small contribution of an intracluster redox reaction. During incorporation of the first formic acid molecule, the electron may recombine with the acidic proton and evaporate as a hydrogen atom, leaving formate as new cluster core. At long time scales, all water molecules are exchanged against formic acid, and three formic acid molecules are sufficient to stabilize the electron. For $m = 3$ and 4, slow formation of $(HCOOH)_{m-1}(HCOO^-)$ is observed. This loss of hydrogen may be activated by collisions with HCOOH, resulting in [HCOOH + H] reaction products of unknown structure.

Keywords: Hydrated electron; Formic acid; Solvation; Hydrogen formation

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1. Introduction

Electrons solvated by water, and less frequently by various other solvents, have been the subject of detailed investigation and research projects in the past [1–7]. Usually, the lifetime of electrons in solution is relatively short (~1 μs) and in pure water mainly limited by the autoionization of water into $H^+ + OH^-$. The reaction $H^+ + e^- \rightarrow H$ leads directly to the formation of atomic hydrogen. In the early 1980s, it has been shown, that solvated electrons can be generated not only in solution, but also in the gas phase [8,9]. Since then the physical and chemical properties of $(H_2O)_n^-$ clusters have been investigated in numerous studies [10–16]. One of the most intriguing properties is the significant increase in lifetime as compared to bulk solution [13,14]. In the absence of impurities and of water autoionization in the cluster, the solvated electrons are stable, and their inherent reactivity with volatile neutral molecules can be investigated in ICR experiments on timescales up to several minutes [10,17].

Solvated electrons, stored in the collision free environment of the ICR-cell, are continuously exposed to room temperature black body radiation, and their temperature is controlled by the interplay of radiative heating and evaporative cooling [18–24]. Mass selected studies revealed an interesting size dependence of their stability, due to two different fragmentation processes [13,14]. Large $(H_2O)_n^-$-species with $n > 32$ exclusively lose water ligands, as observed for most other hydrated species. For clusters $n \leq 32$, this fragmentation competes with electron detachment.

Mass spectrometric studies of the reactions of solvated electrons with various reactant gas molecules [10,17,25–27] have shown, that these clusters exhibit a very interesting, multifaceted chemistry. Collisional activation by neutral gas molecules, ligand exchange reactions, formation of hydrated molecular anions, as well as chemical reactions like hydrogen transfer are possible reaction pathways.

The reactivity of weak organic acids like formic acid or acetic acid is of fundamental interest also from a biochemical point of view. Proton bound formic acid and mixed formic acid/water clusters have been studied by Lifshitz and Feng [28], who observed a competition between formic acid monomer and dimer evaporation if the cluster contains at least six formic acid molecules. The potential energy surface of the formic acid radical cation was studied computationally by Uggerud et al. [29].

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Weak organic acids are not fully dissociated in aqueous solution, and it is not at all obvious whether atomic hydrogen formation can be expected in reactions with gas phase hydrated electrons. The interactions of weak organic acids with free electrons have already been investigated in gas phase [30–34] and condensed phase experiments [35,36]. For formic acid molecules, a dominant reaction channel with a resonance energy of 1.37 ± 0.23 eV, corresponding to the abstraction of a hydrogen radical and the formation of formate ions, was identified in dissociative electron attachment (DEA) experiments by Sailer et al. [33]. In a pulse radiolysis experiment, monitoring the decay of the absorption of the hydrated electron, a rate constant $k = 1.4 \times 10^{8}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ was determined by Gordon et al., without identifying the reaction products [37]. In the present work, experiments of hydrated electrons with formic acid HCOOH and the partly deuterated derivative DCOOH were performed in the gas phase. The FT-ICR experiments allow to determine the reaction products and the effects of solvation upon the reactivity of the electron.

2. Experimental details

The experiments were performed on a modified Bruker Spectrospin CMS47X mass spectrometer equipped with an external laser vaporization source described in detail before [14,38,39]. Hydrated electrons were produced by laser vaporization [40,41] of a solid zinc target disk (Aldrich, >99.9%) by a pulsed Nd:YAG laser at a wavelength of 532 nm. The metal plasma was entrained in a 50 μs pulse of helium carrier gas at a backing pressure of 20 bar, which has been seeded with water vapor at a temperature of 20 °C. The supersonic expansion of the hot plasma into high vacuum results in the formation of clusters of the type $(H_2O)_n^-$, with the distribution of n depending on the time-of-flight conditions, and ranging from 15 to 70. The clusters formed in this way were transferred by electrostatic lenses through several stages of differential pumping into the high-field region of the superconducting magnet and stored inside the ICR cell. The reaction gas is introduced to the cell region by a needle valve, raising the pressure from below 10^{-10} mbar to a constant value of 7.1×10^{-9} mbar. Liquid formic acid (Aldrich, >96%) and DCOOH (Aldrich, >98% D) was degassed by three pump-freeze-thaw cycles. The vacuum chamber was kept at a constant temperature of 290 ± 6 K. To monitor the reaction, the ions were accumulated over 20 cycles of laser vaporization and the mass spectra were taken after varying reaction delays.

3. Results and discussion

3.1. Reactivity of hydrated electrons $(H_2O)_n^-$, $n = 30$–70, with formic acid

Hydrated electron clusters $(H_2O)_n^-$ with a starting distribution of $n = 30$–70, which was used in all experiments reported here, were reacted with gaseous HCOOH. The mass spectrum in Fig. 1, recorded after 5 s reaction delay, shows that the dominant primary reaction is ligand exchange, reaction (1). A parallel reaction, with a branching ratio of 15%, results in the formation of a hydrated formate ion and evaporation of atomic hydrogen, reaction (2). Similar experiments with DCOOH confirmed that the acidic proton is lost as a hydrogen atom in reaction (2). Due to the exothermicity of the reaction, the intake of HCOOH is accompanied by the evaporation of water molecules.

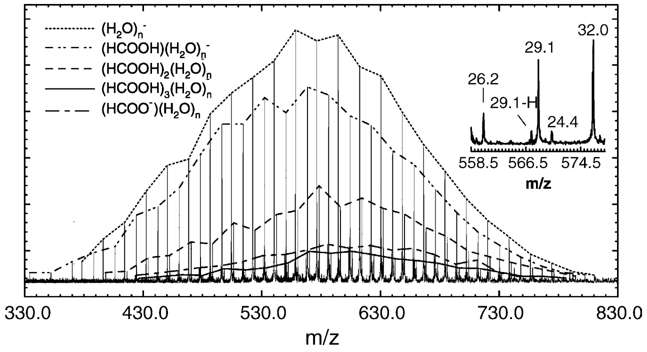

Fig. 1. Mass spectrum for the reaction of solvated electron clusters $(H_2O)_n^-$ with formic acid after 5.0 s reaction delay at a constant pressure of 7.1×10^{-10} mbar. In addition to the initial water cluster distribution, three product distributions for $(HCOOH)_m(H_2O)_n^-$ with $m = 1$–3 and one for the dehydrogenated product $(H_2O)_n(HCOO^-)$ are observed. They result from subsequent exchange of water molecules by formic acid. The inset shows an enlargement of the spectrum, containing all five different species present at this time. The peak label n and m denotes a cluster $(HCOOH)_m(H_2O)_n^-$.

$$(H_2O)_n^- + HCOOH \rightarrow (HCOOH)^-(H_2O)_{n-x} + xH_2O \qquad (1)$$

$$(H_2O)_n^- + HCOOH \rightarrow (HCOO)^-(H_2O)_{n-y} + yH_2O + H \qquad (2)$$

In contrast to reactions with carbon dioxide or molecular oxygen [27], where only a single molecule is taken up by the solvated electron cluster, the reaction with formic acid does not stop with the primary products. Successive uptake of further formic acid molecules can be observed, similar to the reaction with methanol [10]. The primary products react efficiently in consecutive reaction steps to higher product species $(HCOOH)_m^-(H_2O)_n$ with $m = 2$–7, reaction (3). Hydrogen formation is, however, only clearly observed upon uptake of the first HCOOH, although minor contributions from secondary processes cannot be completely ruled out. Also the dehydrogenated primary product $(HCOO^-)(H_2O)_n$ takes up further HCOOH molecules, reaction (4).

$$\begin{aligned}&(HCOOH)_m(H_2O)_n^- + HCOOH\\&\quad\rightarrow (HCOOH)_{m+1}(H_2O)_{n-z}^- + zH_2O \qquad (3)\end{aligned}$$

$$\begin{aligned}&(HCOOH)_m(HCOO^-)(H_2O)_n + HCOOH\\&\quad\rightarrow (HCOOH)_{m+1}(HCOO^-)(H_2O)_{n-z} + zH_2O \qquad (4)\end{aligned}$$

Reactions (1)–(4) are accompanied by a continuous loss of solvent molecules, induced by the absorption of blackbody radiation and by inelastic collisions with reactant gas molecules.

To get a deeper understanding for the successive loss of water molecules from hydrated electrons during the uptake of a HCOOH molecule and the formation of atomic hydrogen, the

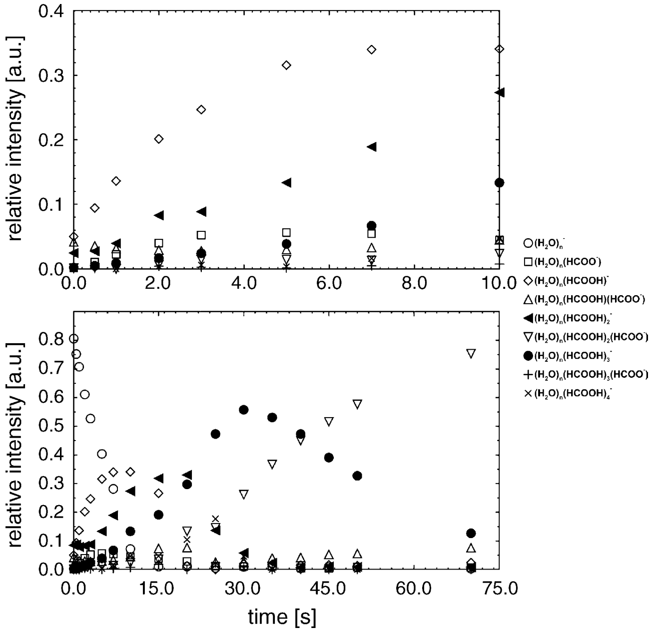

Fig. 2. Intensity–time profile for the reaction of solvated electrons $(H_2O)_n^-$ with gaseous formic acid at a constant pressure of 7.1×10^{-10} mbar in the UHV region. At the beginning of the reaction, pure water clusters are the most abundant species with about 80% of total intensity. Over time, H_2O are exchanged against HCOOH, accompanied by black body radiation induced loss of water molecules. When the first H_2O is exchanged by HCOOH, the electron recombines with the acidic hydrogen of the organic acid and atomic hydrogen is evaporated with a branching ratio of 15%. At long delays above 30 s, the total intensity is spread over two dominant clusters which have lost all H_2O: $(HCOOH)^-{}_3$ and $(HCOOH)_2(HCOO^-)$.

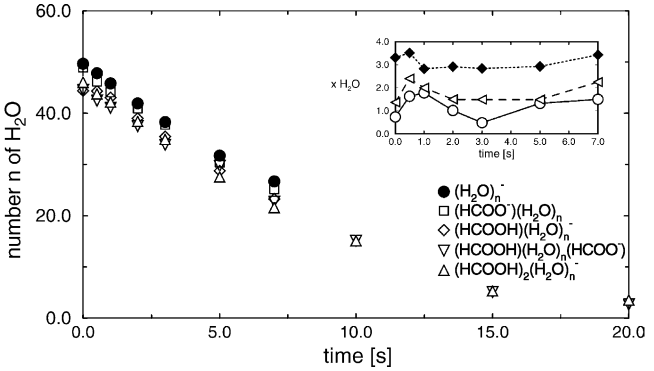

Fig. 3. Average number of water molecules for each cluster type plotted over time. The number of water molecules decreases monotonically with time due to collision and black body radiation induced fragmentation. The inset shows the difference between the reactant $(H_2O)_n^-$ and the product species, which are, on average, independent of time. The data for the uptake of the first HCOOH molecule (filled diamond) and for the formation of atomic hydrogen (open circle) yield average numbers of 3.2 and 1.0 H_2O, while the uptake of the second HCOOH (open triangle left) leads to evaporation of 2.0 H_2O.

mass spectra for different reaction delays $t = 0$–90 s were quantitatively analysed. The ion intensities of clusters which differ only in the number of water molecules, e.g., $(HCOOH)(H_2O)_m^-$, were summed over all values of m. These intensities are plotted over time to obtain insight into the kinetics of the different reaction channels. The result of the evaluation for the reactions with formic acid is shown in Fig. 2. It is evident that besides H_2O also HCOOH molecules can be lost from $(HCOOH)_m(H_2O)_n^-$, as product clusters with more than four formic acid molecules show maximum intensity at about 10 s. Whether evaporation of formic acid dimers [28] takes place, cannot be determined from the available data.

In a similar way, the obtained data allow us to calculate the average number of water molecules for each cluster type, and at any reaction delay, and this is summarized graphically in Fig. 3. One can easily see the steady decrease as a function of time for each cluster type. This monotonic decrease in the average number of water ligands, going essentially to zero after about 20 s, is due to cluster fragmentation, induced both by collisions and by the absorption of black body radiation. With some effort, one can also see in the figure that, for instance, the data points for the two primary products, $(HCOOH)(H_2O)_n^-$ and $(HCOO)(H_2O)_n^-$ lie consistently below the corresponding points for the $(H_2O)_n^-$ reactants. A clearer picture of this can be gained by subtracting the two curves, and plotting on an expanded scale the differences, as shown, again for the primary and secondary products in the inset of Fig. 3. The reason for the offset is that the reactions are exothermic, with the heat of the reaction causing the evaporation of water ligands. The cluster thus is a primitive two phase calorimeter, and permits us to estimate crudely the exothermicities for the observed processes.

One finds that on average 3.2 water molecules are lost when the first HCOOH molecule is incorporated into the pure water cluster. The binding energies of water clusters were studied extensively. Arnold et al. [26] suggested that roughly 35.7 kJ/mol are required to eject a water monomer from a $(H_2O)_n^-$ cluster. Shi et al. [42], who studied the stability of protonated water clusters as a function of size, find values around 40 kJ/mol. The average of published values is around 38 kJ/mol, which is also close to the sublimation enthalpy of ice. We can therefore use this value to “calibrate” our “calorimeter”.

The evaporation of 3.2 water molecules would corresponds to an appreciable reaction enthalpy of about $\Delta H_1 = -122$ kJ/mol for dissolving an HCOOH in a pure solvated electron, $(H_2O)_n^-$, cluster, reaction (1). When atomic hydrogen is evaporated in the parallel reaction (2), on the average only about one water molecule is found to be evaporated, suggesting $\Delta H_2 = -38$ kJ/mol. The reaction is thus considerably less exothermic than reaction (1), and the values suggest that roughly 84 kJ/mol are needed for the evaporation of a hydrogen atom from $HCOOH(H_2O)_n^-$.

When a second or third formic acid molecule is incorporated, the average number of water ligands lost is reduced to about 2.0 H_2O, corresponding to $\Delta H_3 = -76$ kJ/mol for each reaction step. The first HCOOH presumably interacts more strongly with the electron inside the hydrated cluster than the second or third HCOOH.

When atomic hydrogen is evaporated, reaction (2), only an average number of 1.0 water molecules, corresponding to $\Delta H_2 = -38.0$ kJ/mol, was found to evaporate. Roughly 84 kJ/mol are needed for the evaporation of a hydrogen atom from $HCOOH(H_2O)_n^-$. This readily explains why the recombination reaction only occurs for the first HCOOH: the uptake of further HCOOH does not release enough energy in the cluster.

The observed $\Delta H_3 = -76.0$ kJ/mol are sufficient to evaporate two water ligands, but not to form and evaporate atomic hydrogen.

After 25 s two dominant species occur in the spectra, the trimeric and tetrameric cluster ions which have lost all water ligands, $(HCOOH)_4^-$ and $(HCOOH)_3^-$. Interestingly, these two pure formic acid solvated electron clusters also show a nominal loss of a hydrogen atom, and fragment further, so that after about 70 s, the $(HCOO)(HCOOH)_2^-$ represents almost 90% of the total ion intensity.

In addition to the above discussed products, two peaks at 90 and 136 amu with minor intensities were found in the spectra of the HCOOH experiment, nominal masses which correspond to $(HCOO)_2(HCOOH)^-$, i.e., loss of two hydrogen atoms or an H_2 molecule. In view of their extreme weakness, we have not investigated these ions further, but believe that they are the result of a ligand exchange reaction with CO_2, which is present in the UHV at a partial pressure below 10^{-10} mbar.

3.2. Mass selected measurements with deuterated formic acid

While it appeared probable that the hydrogen lost from HCOOH is the acidic hydrogen, we have carried out experiments with selectively deuterated DCOOH to verify this. Similarly, the experiment with DCOOH was well suited for establishing, which atom is responsible in the slow, long term loss of hydrogen from the pure $(HCOOH)_n^-$ anions. The experiments clearly confirmed that indeed here both for the initial, fast process, as well as for the last stage reaction in the formic acid trimer anion, it is the acidic, OH proton which is lost. A quantitative evaluation of the data also permitted to extract the rate constants for the competing processes of fragmentation and hydrogen formation.

The experiments with DCOOH were performed under exactly the same experimental conditions used with HCOOH. After the initial reaction delay of 20 s, the tetrameric cluster ions $(DCOOH)_4^-$ with a nominal mass of 188 amu, and in a separate experiment the dehydrogenated product ions $(DCOOH)_3DCOO^-$ with 187 amu were mass selected and observed over a period of additional 70 s. The results of the mass selection of $(DCOOH)_4^-$ are illustrated as a qualitative reaction scheme in Fig. 4. Three reaction channels ((5)–(7)), taking place on significantly different time scales, were identified.

$$(DCOOH)_4^- + DCOOH \rightarrow (DCOOH)_3^- + 2DCOOH \qquad (5)$$

$$(DCOOH)_{3,4}^- + DCOOH \rightarrow (DCOOH)_{2,3}DCOO^- + [DCOOH + H] \qquad (6)$$

$$(DCOOH)_{2,3}DCOO^- + DCOOH \rightarrow (DCOOH)_{1,2}DCOO^- + 2DCOOH \qquad (7)$$

The first process consists of the black body radiation and collision-induced loss of DCOOH from $(DCOOH)_4^-$. This reaction step is relatively fast and completed in less than 7.0 s. The nominal formation of atomic hydrogen on the other hand is much slower for $(DCOOH)_4^-$ ions. The intermediate primary product $(DCOOH)_3DCOO^-$ occurs only in small amounts in the spectra, because reaction (6) is a factor of 30 less efficient than reaction (5), Table 1. In the second process, it takes about 50 s for the primary product $(DCOOH)_3^-$ to loose atomic hydrogen and form $(DCOOH)_2DCOO^-$. This ion appears to be the most stable species and is still present after 90 s total reaction delay. Further fragmentation resulting in $(DCOOH)DCOO^-$ is still observed, but is a factor of about 100 slower.

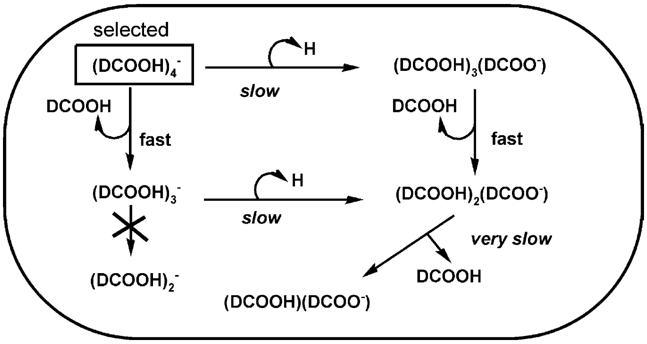

Fig. 4. The scheme shows qualitatively the observed reactions of the mass selected cluster species $(DCOOH)_4^-$ with a nominal mass of 188 amu.

The normalized ion intensities were fitted with a genetic algorithm following pseudo-first-order kinetics. The result is shown in Fig. 5, and relative rate constants are listed in Table 1. It has to be noted that cluster species with 91 and 138 amu do not appear. This is in agreement with the assignment of the 90 and 136 amu peaks in the HCOOH experiment to reactions with a CO_2 impurity. The kinetics also shows unambiguously that an invisible reaction channel such as electron detachment does not occur.

The neutral product of reaction (6), [DCOOH + H], may of course be simply H + DCOOH. However, recent calculations by Hou and Wang of the $O + CH_2OH$ potential energy surface [43] reveal that several other possibilities are up to 40 kJ/mol lower in energy, with $DC(OH)_2$ and $DCO + H_2O$ being the energetically most favourable exit channels. We have written reaction (6) as being collisionally activated, because we believe this to be the most likely process, since the clusters are relatively small, and black body radiation induced processes become increasingly less probable, although they cannot be completely ruled out on the basis of the present results.

Table 1
Results of the kinetic evaluation of the mass selection of $(DCOOH)_4^-$

Reaction	k_{rel} (s^{-1})
$(DCOOH)_4^- \rightarrow (DCOOH)_3^- + DCOOH$	0.3393
$(DCOOH)_4^- \rightarrow (DCOOH)_3(HCOO^-) + H$	0.0105
$(DCOOH)_3(HCOO^-) \rightarrow (DCOOH)_2(HCOO^-) + DCOOH$	0.3774
$(DCOOH)_3^- \rightarrow (DCOOH)_2(HCOO^-) + H$	0.0327
$(DCOOH)_2(HCOO^-) \rightarrow (DCOOH)(DCOO^-) + DCOOH$	0.0032

The relative rate constants for the observed reactions and cluster species are shown.

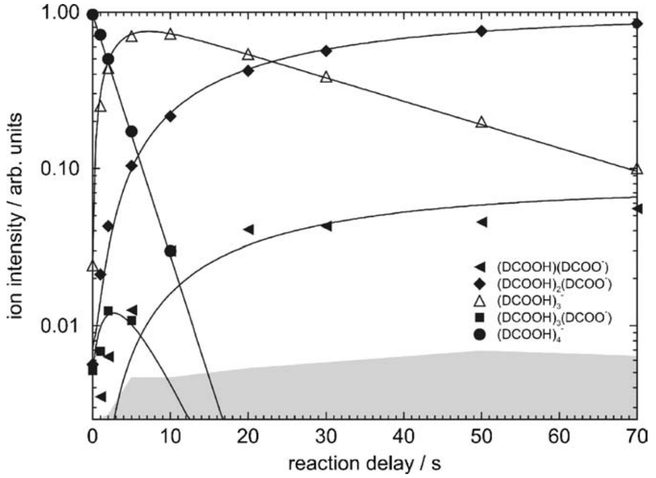

Fig. 5. The experimental data (symbols) for the mass selection experiment with DCOOH at a constant reaction gas pressure of 7.1×10^{-10} mbar in the UHV region are plotted over time. All the fit functions (solid lines) were calculated assuming (pseudo)-first-order reaction kinetics. The grey shaded area denotes the noise level. The initial intensities of each species were treated as fit parameters.

4. Conclusion

Formic acid reacts efficiently with gas phase solvated electrons via ligand exchange, until all water molecules are replaced by HCOOH or lost due to black body radiation or collision induced dissociation. In the first step, HCOOH uptake is strongly exothermic, with an estimated enthalpy of −122 kJ/mol, leading to the evaporation of on average 3.2 water molecules. Species with up to seven HCOOH were found. Uptake of further HCOOH is less exothermic, as evidenced by the smaller number of water molecules evaporating. This is probably the reason why formation of atomic hydrogen, a process endothermic by +84 kJ/mol as estimated from the number of water molecules evaporating, is observed only upon uptake of the first HCOOH, which releases enough energy to make this reaction thermochemically possible in the cluster. Further spectroscopic and theoretical studies are desirable to identify the nature of the interaction of HCOOH with the electron, whether the electron is solvated by HCOOH or enters its LUMO. The loss of a hydrogen atom from $(HCOOH)_m^-$ after very long reaction delays, possibly upon collision with neutral HCOOH yielding products [HCOOH + H], also deserves further attention.

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