

Supplemental Information for:

Switching between Proton Vacancy and Excess Proton Transfer Pathways in the Reaction between 7-Hydroxyquinoline and Formate

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1. Acidities and Reactivities as Estimated for 7HQ and Formic Acid in H₂O, CH₃OH and CD₃OD Solution

Table S1 Acidity pK_a -values and derived values for $\Delta pK_a = pK_a(\text{donor}) - pK_a(\text{protonated acceptor})$ and deduced reaction rates/time constants using the BEBO model for Pathway I reactions of 7HQ with formate.

Species / Reaction		H ₂ O	CH ₃ OH	CD ₃ OD
HCOOH/HCOO ⁻	pK_a	3.75	8.77	9.27
7HQ-N	pK_a	8.67	13.02	13.52
$N + HCOO^- \rightleftharpoons A + HCOOH$	ΔpK_a	4.92	4.25	4.25
7HQ-N*	pK_a	0.4	4.1	4.6
$N^* + HCOO^- \rightleftharpoons A^* + HCOOH$	ΔpK_a	-3.35	-4.67	-4.67
	$-\log_{10}[k_r]$	11.26	11.39	11.39
	Time constant τ (ps)	5.5	4.07	4.07
7HQ-Z	pK_a	8.32	9.21	9.72
$A + HCOOH \rightleftharpoons Z + HCOO^-$	ΔpK_a	-4.57	-0.44	-0.45
7HQ-Z*	pK_a	13.4	14.4	14.9
$A^* + HCOOH \rightleftharpoons Z^* + HCOO^-$	ΔpK_a	-9.65	-5.63	-5.63
	$-\log_{10}[k_r]$	11.5	11.44	11.44
	Time constant τ (ps)	3.1	3.6	3.6

We have estimated the acid-base reactivities of the hydroxyl and quinoline nitrogen sites of 7HQ in the S_0 - and S_1 -states for the reaction pathway I of 7HQ + formic acid in H₂O, CH₃OH and CD₃OD solvents. Here we have used reported pK_a -values for 7HQ and formic acid ¹⁻³, well reported empirical relationships for

solvent dependent pK_a -values of acids ⁴⁻⁶, and the Marcus BEBO free-energy-reactivity relationship, that rationalizes proton transfer between acids and bases in protic solvents like water or methanol ⁷⁻¹¹. We note here that within the constraints of the Marcus BEBO free-energy-reactivity framework, proton (deuteron) transfer rates k_r and time constants t indicate solvent-mediated proton transfer in photoacid-base neutralization reactions in protic solvents to occur with the solvent being an essential component in the photoacid-base proton transfer pathways ^{7-9, 12-15}. The derived values for k_r and t are understood as an assessment for the order of magnitude of the reaction time scales as derived from the Marcus BEBO free-energy-reactivity relationship.

2. FT-IR Spectra of Formic Acid in Polar and Non-Polar Solvent Mixtures: HCOOH in DMSO- d_6 :CCl₄

We recall the experimental results presented in **Section 3.2** where we also observed the splitting of the C=O stretching vibration. Since we observed similarities between the C=O stretching vibration of pure HCOOH mixed with polar solvents and of that generated after proton transfer from the 7HQ photoacid to the formate upon electronic excitation of 7HQ, we can say that the observed molecular species of formic acid are the same. We discussed in the previous section the molecular arrangements of formate and methanol solvent around 7HQ chromophore using the force-field molecular mechanics calculations and concluded the proton transfer could be facilitated through a solvent bridge connecting the photoacid and the accepting formate base. Additionally here, we studied the effect of increasing the mole fraction of DMSO- d_6 solvent from 10 % to 100 % in a non-polar environment such as CCl₄ and examined the behavior of C=O stretching vibration of HCOOH through a FT-IR measurement series. We kept the concentration of HCOOH constant at 0.3 M and varied the amount of DMSO- d_6 . The reference in the corresponding spectra was the HCOOH solution in CCl₄ where we see again the single peak that is assigned to formic acid dimers (**Figure S1**). As of now, for a small amount of DMSO- d_6 (10 %) mixed with CCl₄ we remarked significant changes such as splitting of C=O stretching vibration. It can be noticed that for small amounts of DMSO- d_6 , the formic acid molecules occur as monomer species. Increasing the DMSO- d_6 mole fraction led to an increase of the hydrogen bond strength between HCOOH and accepting side of DMSO- d_6 due to solvent-solute interactions and this was depicted by the spectral shifts to lower wavenumbers. The second outcome we acknowledged is the increase in the infrared absorption intensity of the second peak that we assigned to formic acid molecules which are hydrogen-bonded to solvent. We think DMSO- d_6 and CD₃OD can be regarded as hydrogen bond acceptors of similar strengths and thus, we can compare them for our interest to explain the experimental observations. Furthermore, the second component of formic acid that we observed in the transient infrared spectra (**Figure 5**) is located

at the same frequency position (i.e. 1736 cm^{-1}) as for pure formic acid in DMSO-d_6 . This means we observed a formic acid molecule, generated after proton transfer through a hydrogen-bond from 7HQ to HCOO^- via a CD_3OD solvent molecule, following the decay on hundreds of picoseconds timescale related to breaking of this hydrogen bond. This correlates well with our observations regarding the existence of a hydrogen-bonded complex such as $\text{R-OD} \cdots \text{CD}_3\text{OD} \cdots \text{HCOO}^-$.

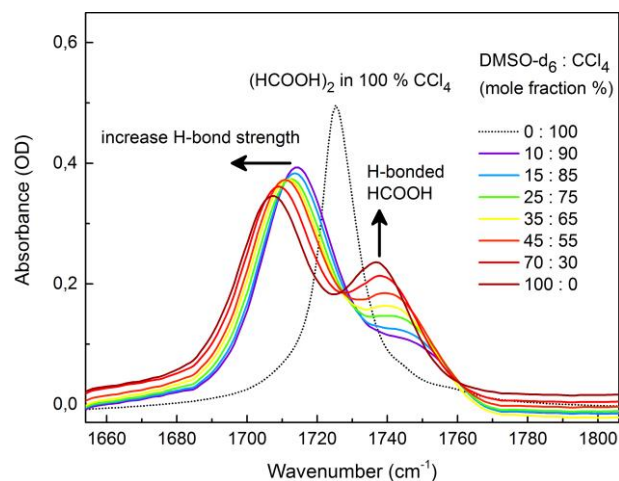


Figure S1 Comparative FT-IR spectra of the C=O stretching vibration of 0.3 M HCOOH dissolved in CCl_4 and DMSO-d_6 showing the hydrogen bonding between HCOOH and DMSO-d_6 by increasing the solvent concentration

3. Average Distances and Angles and Lifetimes of Hydrogen Bonds between 7HQ and Formate Anion

Figure S2 presents the average distances and angles where the hydrogen bonds are formed between 7HQ-OH and HCOO^- . The highest probabilities were found at distances from 150 to 200 pm and at angles between 135° and 180° . Table S2 provides an overview of the hydrogen bond lifetimes as derived from the classical molecular dynamics simulations.

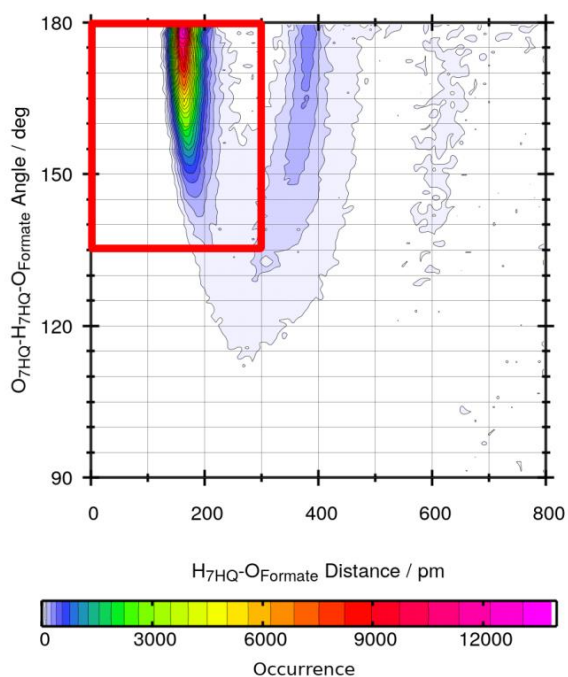


Figure S2 Combined distance/angle histograms of the hydrogen bond geometry between 7HQ-OH and HCOO^- . The red rectangle shows the geometric criterion .

Table S2 Hydrogen bond lifetimes in picoseconds

HCOO^- Concentration (M)	7HQ-OH and HCOO^-	CH_3OH and N- atom of 7HQ	7HQ-OH and CH_3OH	HCOO^- and CH_3OH
0	-	10	146	-
0.5	286	10	103	64
1	476	10	100	66
2	484	10	93	70
4	475	10	91	76

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