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Reactions between microhydrated superoxide anions and formic acid

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Supplementary Information

A note on double collisions

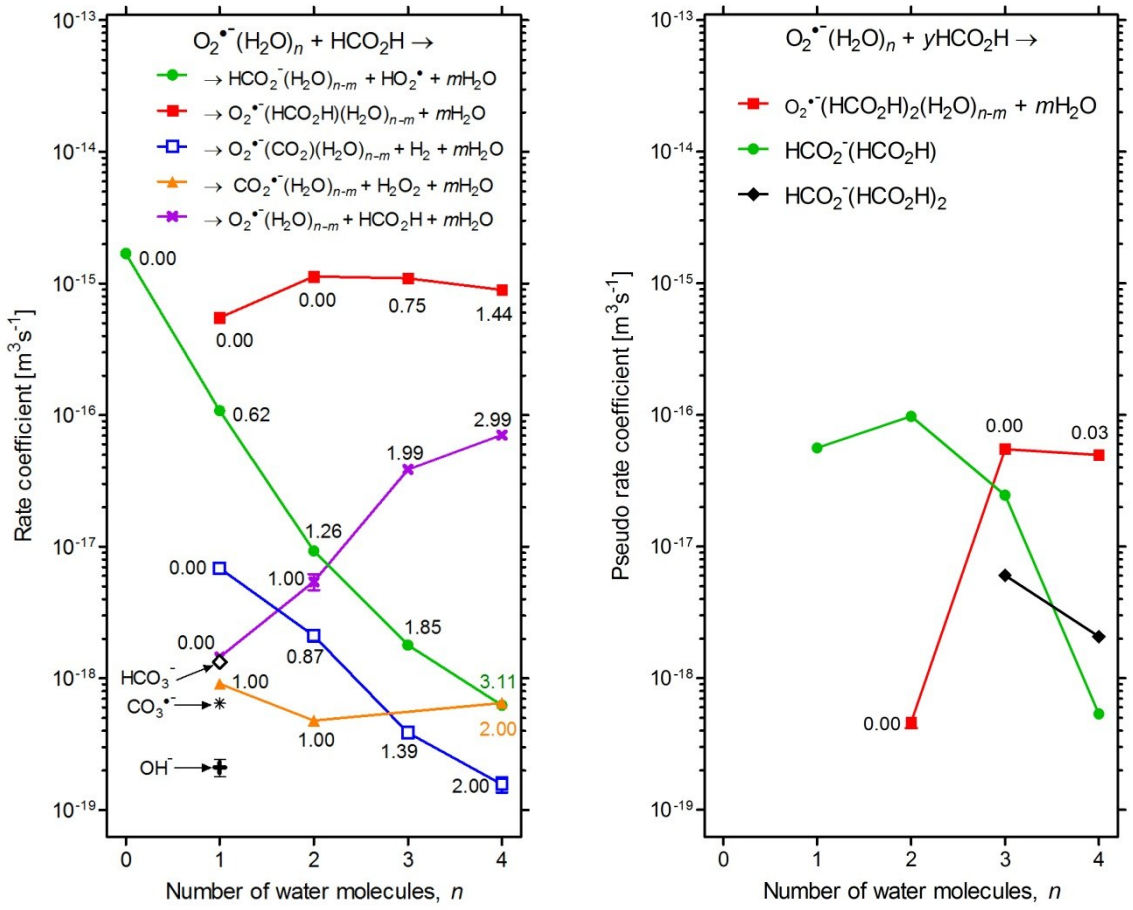

Figure S1. Rate coefficients for the formation of different products in the reaction between $O_2^{\bullet-}(H_2O)_n$ and HCO_2H at 0.6 eV (COM) collision energy. The left panel is identical to Figure 1 in the main text. The right panel shows the detected products originating from double and triple collisions (using a pseudo rate coefficient). The numbers next to the data point indicate the average values of $n-m$. Error bars represent one SD due to count statistics.

Figure S1 shows a comparison between the products of single collisions and the products of double and triple collisions as measured in the experiments (the left panel of Figure S1 is identical to Figure 1 in the main text). The rate coefficients for double and triple collisions are expressed as the respective pseudo rate coefficients $k'_{\text{double}} = k_{\text{double}} \times [HCO_2H]$ and $k'_{\text{triple}} =$

$k_{triple}\times[HCO_2H]^2$; consequently, the rate coefficients in Figure S2 are directly representative of the relative intensity of the different products in the recorded mass spectra. A comparison between the two panels indicates that the total amount of double and triple collisions is lower than the amount of single collisions by about an order of magnitude.

No products of double collisions were detected for $n = 0$, indicating that the dimer formed upon addition of HCO_2H to HCO_2^- is a transient species under the present experimental conditions. At variance, products of double collisions were observed for $n > 0$ and with abundances of the same order of magnitude as some single collision products. Due to the single collision reactions for $n = 1$–4 being dominated by the adduct formation (Reaction 2), the double collision products can be considered to almost exclusively originate from the encounter of a $O_2^{\bullet-}(HCO_2H)(H_2O)_{n-m}$ type ion with a second HCO_2H. For $n = 1$, 2, the double collision reactant ion is $O_2^{\bullet-}(HCO_2H)$ ($n-m = 0$ as seen in Figure S1, left panel) and collision with a second formic acid molecule is found to active the complex with regards to completing the proton transfer to superoxide:

$$O_2^{\bullet-}(HCO_2H) + HCO_2H \rightarrow HCO_2^-(HCO_2H) + HO_2^{\bullet} \quad \text{(S1)}$$

This activation appears to be quite efficient, seeing as the abundance of its product is on par with the single collision proton transfer product $HCO_2^-(H_2O)_{n-m}$, despite the double collision frequency being at least an order of magnitude lower. For $n = 3$, 4 (especially for $n = 4$), the encounter is instead more likely to result in another ligand switch,

$$O_2^{\bullet-}(HCO_2H)(H_2O)_{n-m} + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H)_2(H_2O)_{n-m-o} + oH_2O. \quad \text{(S2)}$$

The latter effect is enabled by the number of water molecules on the double collision reactant, $n-m$, being larger than zero for $n > 2$. That is, the presence of water molecules enables addition and stabilisation of a second HCO_2H into the cluster.

A note on isotopes and isobaric overlaps

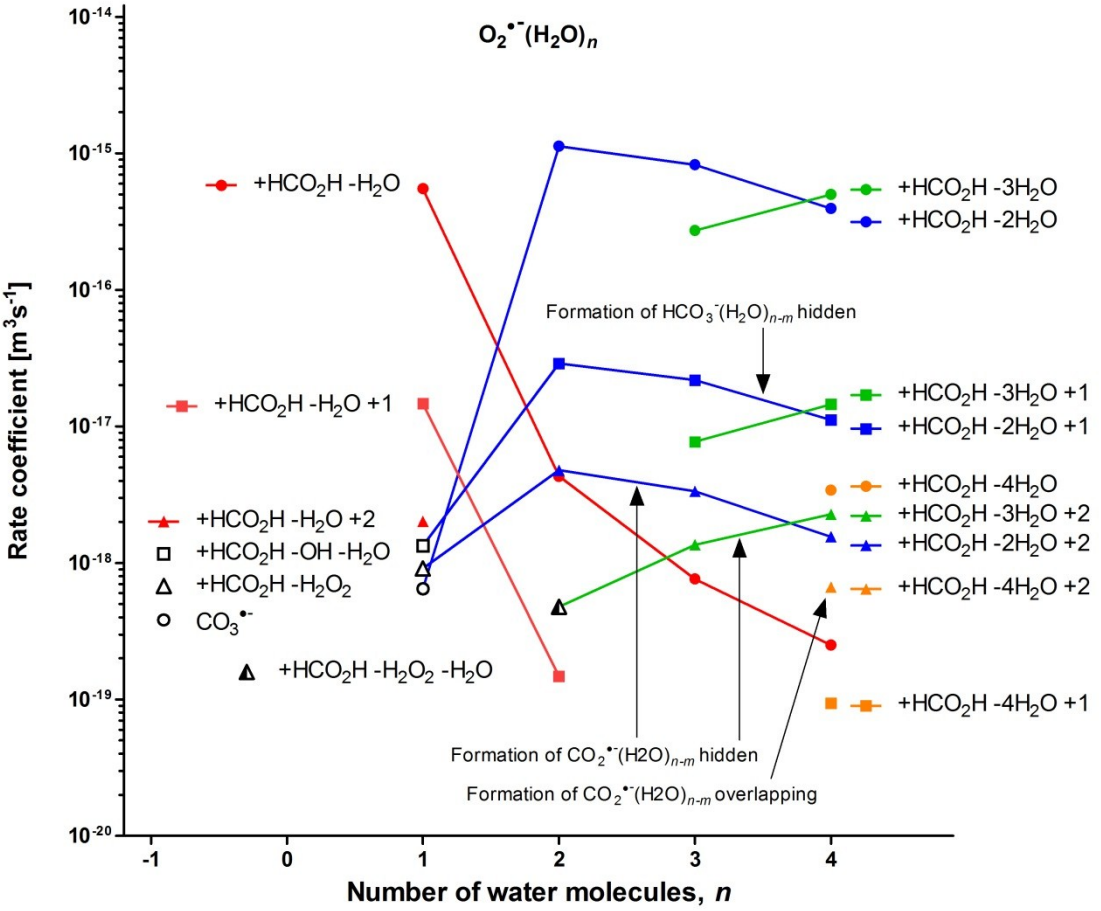

Figure S2. Rate coefficients for the formation of different incorporation products (adding HCO_2H and losing m H_2O) in the reaction between $O_2^{\bullet-}(H_2O)_n$ and HCO_2H at 0.6 eV (COM) collision energy. The reaction channels are shown separated for their respective isotope peaks (monoisotopic, m/z +1 and m/z +2). In addition, the detected instances of the product types $HCO_3^-(H_2O)_{n-m}$ (shown as $+HCO_2H -OH^{\bullet} -H_2O$), $CO_2^{\bullet-}(H_2O)_{n-m}$ (shown as $+HCO_2H -H_2O_2 -mH_2O$) and $CO_3^{\bullet-}$ are shown; a line connects them to the main product isotope which will obscure other instances of them.

The isotope distribution of formic acid results in a distinct pair of mass spectrometric peaks at +1 and +2 Th relative to the monoisotopic peak of all products containing it (at variance, the cluster-ion reactant is monoisotopic from the mass selection). Figure S2 shows the rate coefficients for Reaction 2, *i.e.*, the incorporation reaction $O_2^{\bullet-}(H_2O)_n + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H)(H_2O)_{n-m} + mH_2O$, as a function of cluster starting size, *n*. However, the reaction is now shown with the various degrees of water loss *m* as individual reaction channels; furthermore, the reaction is also shown with separate curves representing the monoisotopic peak, the +1 isotope peak and the +2 isotope peak.

It is easy to show that the intensity of the +1 and +2 isotope peaks relative to the monoisotopic peak should be, respectively, 1.2% and 0.4% for any product containing formic acid (or formate). In our measurements, the results were somewhat different: the numbers, based on the pattern of the HCO_2^- product formed in the reaction of the naked superoxide ion, are 2.4% and 0.4%, respectively. A separate measurement on the isotope pattern of the HCO_2H reagent used in the experiments, using a different mass spectrometer (Maxis II EDT, Bruker), gave the values 1.2% and 0.48%, respectively; this rules out that the discrepancy should be due to an isotopic imbalance in the chemical itself. The relative isotope abundances as detected in these experiments are consistent for all detected formate- and adduct reactions (with one exception in the latter case, as discussed later); that is, the intensity of the +1 and +2 peak relative to the monoisotopic peak is the same for all values of *n* and *m*; on the logarithmic scale of Figure S2 this is observed as a constant distance between the isotope curves and the monoisotopic curve. Two conclusions can be drawn from this. Firstly, the fact that the relative intensity of the +1 isotope peak is consistent for all values of *n* and *m*

regardless of whether the formic acid–containing product is in the form of the adduct (Reaction 2) or the formate (Reaction 1) is a most convincing indication that the peak in question being larger than expected is not due to isobaric overlap with other species. Secondly, any potential isobaric overlaps with the isotope peaks must be so small that it does not significantly alter the ratio of the isotope peaks to the monoisotopic peak.

Let us now address some of the product peaks which have been observed and which likely do overlap with the isotope peaks: $CO_3^{\bullet-}$, $HCO_3^-(H_2O)_{n-m}$ ($+HCO_2H -OH^{\bullet} -H_2O$ in Figure S2) and $CO_2^{\bullet-}(H_2O)_{n-m}$ ($+HCO_2H -H_2O_2 -mH_2O$ in Figure S2).

A small amount of $CO_3^{\bullet-}$ was observed for $n = 1$ (Reaction 7); this ion was not observed for any other value of n. If this product is formed in its hydrated state it would be indistinguishable from the products of the adduct reaction (Reaction 2). In fact, this product could be arrived at from a Reaction 2 where $m = n + 1$. It could indeed be so that some or all of the adduct reactions observed have $CO_3^{\bullet-}$ as its core ion, but this seems unlikely since the detected intensity of $CO_3^{\bullet-}$ for $n = 1$ should have been larger considering the overall trends in water loss associated with the reaction, and, the $CO_3^{\bullet-}$ ion should have been detected with at least some abundance also for $n > 1$, in particular for $n = 2$. More likely then is the scenario outlined in the main text, that this product represents a fragmentation starting from the **INT3w** intermediate.

Next we have the bicarbonate ion, HCO_3^- which was also observed only for $n = 1$ and only in the non-hydrated state (Reaction 6). The experimentally observed formation is small. If this

product is formed in a hydrated state then its intensity will likely drown in the +1 isotope peak of the $O_2^{\bullet-}(HCO_2H)(H_2O)_{n-m}$ products. We will again stress that the unexpectedly large abundance of this isotope peak cannot be attributed to overlap by other ions.

Finally, the reaction $O_2^{\bullet-}(H_2O)_n + HCO_2H \rightarrow CO_2^{\bullet-}(H_2O)_{n-m} + H_2O_2 + mH_2O$ (Reaction 4) leads to formation of the carbon dioxide radical anion. This product has an isobaric overlap with the +2 isotope peak of the products from the incorporation reaction (Reaction 2), $O_2^{\bullet-}(HCO_2H)(H_2O)_{n-m}$; the first instance of such an isotope peak occurs for $O_2^{\bullet-}(HCO_2H)$ at m/z = 80 in the mass spectrum. For both n = 1 and 2, the monohydrated carbon dioxide radical anion, $CO_2^{\bullet-}(H_2O)$, was observed at m/z = 62 Th. . In addition, the ion $CO_2^{\bullet-}(H_2O)_2$ with mass 80 u could be observed in the case n = 4 because the formation rate of $O_2^{\bullet-}(HCO_2H)$ was in that case very low; the +2 isotope peak of $O_2^{\bullet-}(HCO_2H)$ was estimated (based on being 0.4% of the monoisotopic peak) to be 2.5% of the total intensity in the peak attributed to $CO_2^{\bullet-}(H_2O)_2$. Unfortunately, in all other instances, the abundance of the +2 isotope peak of the incorporation reaction products was approximately 0.4% of the corresponding monoisotopic peak; hence, no estimate of the intensity of a possible $CO_2^{\bullet-}(H_2O)_n$ ion could be made in those cases. The instances of the $CO_2^{\bullet-}(H_2O)_{n-m}$ ion being observed, observed to be absent, or not being observed due to isobaric overlap, are summarized in Table S1.

We mentioned earlier that there was one exception to the consistent isotope pattern for the products shown in Figure S2. This referred to the reaction $O_2^{\bullet-}(H_2O)_4 + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H) + 4H_2O$ where the +2 isotope peak is actually higher than the +1 peak owing to the presence of $CO_2^{\bullet-}(H_2O)_2$.

Table S1. Summary of observations of the reaction $O_2^{\bullet-}(H_2O)_n + HCO_2H \rightarrow CO_2^{\bullet-}(H_2O)_{n-m} + H_2O_2 + mH_2O$.

***n* =**	***m* =**	**$CO_2^{\bullet-}(H_2O)_{n-m}$ mass:**	**Observed**	**Overlap with +2 isotope peak of:**
1	0	62	Yes	None
1	1	44	No (absent)	None
2	0	80	No (overlap)	$O_2^{\bullet-}(H_2O)_2 + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H) + 2H_2O$ (m/z = 78)
2	1	62	Yes	None
2	2	44	No (absent)	None
3	0	98	No (overlap)	$O_2^{\bullet-}(H_2O)_3 + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H)(H_2O) + 2H_2O$ (m/z = 96)
3	1	80	No (overlap)	$O_2^{\bullet-}(H_2O)_3 + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H) + 3H_2O$ (m/z = 78)
3	2	62	No (absent)	None
3	3	44	No (absent)	None

4	0	116	No (overlap)	$O_2^{\bullet-}(H_2O)_4 + HCO_2H \rightarrow$ $O_2^{\bullet-}(HCO_2H)(H_2O)_2 + 2H_2O$ (m/z = 114)
4	1	98	No (overlap)	$O_2^{\bullet-}(H_2O)_4 + HCO_2H \rightarrow$ $O_2^{\bullet-}(HCO_2H)(H_2O) + 3H_2O$ (m/z = 96)
4	2	80	Yes (overlap)	$O_2^{\bullet-}(H_2O)_4 + HCO_2H \rightarrow O_2^{\bullet-}(HCO_2H) +$ $4H_2O$ (m/z = 78)
4	3	62	No (absent)	None
4	4	44	No (absent)	None

Structural and energetic data from the quantum chemical computations

Cartesian coordinates (in Å) and energies (in a. u.) of all the stationary points discussed in the text. All calculations have been performed at the M06-2X/6-311+G(d,p) level.

$O_2^{\cdot -}$: H = -150.316146; G = -150.339220

O	0.000000000	0.000000000	0.660942000
O	0.000000000	0.000000000	-0.660942000

$HCO_2H^{\cdot}$: H = -189.714647; G = -189.738709

H	1.051582000	-1.055262000	0.000001000
O	1.110789000	-0.089142000	-0.000002000
C	-0.135237000	0.398871000	0.000007000
O	-1.127115000	-0.264976000	-0.000002000
H	-0.109552000	1.494981000	-0.000013000

INT1: H = -340.099284; G = -340.130325

O	2.107932000	-0.733405000	-0.190273000
O	1.817724000	0.466151000	0.245653000
H	0.702146000	0.627942000	0.022528000
O	-0.528753000	0.797310000	-0.209773000
C	-1.249210000	-0.213143000	0.108430000
O	-2.463836000	-0.314740000	0.005346000
H	-0.671429000	-1.071601000	0.519269000

TS1: H = -340.063529; G = -340.092985 (i = -1013.0 cm-1)

O	1.439873000	-0.892441000	-0.219689000
O	1.870747000	0.335943000	0.262128000
H	1.171226000	0.942095000	-0.074818000
O	-0.630210000	1.142589000	-0.172179000
C	-0.992714000	-0.034216000	0.008330000
O	-2.081289000	-0.582549000	0.127499000
H	-0.007916000	-0.765138000	0.042773000

INT2: H = -340.086592; G = -340.117688

O	1.745365000	-0.865720000	-0.210613000
O	1.920964000	0.465223000	0.283788000
H	1.065231000	0.881588000	0.027332000
O	-0.669419000	1.001171000	-0.240649000
C	-1.200473000	-0.084619000	0.032069000
O	-2.331891000	-0.515402000	0.135857000
H	0.817450000	-1.056052000	0.033194000

INT2′: H = -340.084927; G = -340.117482

C	1.678754000	-0.382570000	-0.043355000
H	-1.177704000	-0.895047000	-0.005477000
O	2.692575000	0.286625000	-0.070826000
O	0.475650000	-0.146309000	0.176315000
H	-1.062059000	0.914377000	0.068473000
O	-2.121264000	-0.643729000	-0.062109000
O	-2.026056000	0.787924000	-0.018737000

TS3: H = -340.054966; G = -340.094079 (i = -791.3 cm-1)

C	-1.317946000	-0.003929000	-0.005421000
H	0.777316000	0.503525000	-0.087362000
O	-2.157890000	-0.868579000	0.021678000
O	-1.183985000	1.207531000	0.023599000
H	2.903716000	-0.372260000	0.809355000
O	1.162897000	-0.383189000	-0.090642000
O	2.707308000	0.030775000	-0.040819000

INT3: H = 340.162747; G = -340.200241

C	-0.771424000	-0.160676000	0.000085000
H	-1.464090000	1.594339000	-0.000197000
O	0.288077000	-0.815496000	0.000639000
O	-1.950067000	-0.529219000	-0.000536000
H	1.798514000	-0.213578000	-0.000061000
O	-0.572764000	1.235777000	0.000249000
O	2.771518000	0.056849000	-0.000383000

HCO_3^-: H = -264.417888; G = -264.448051

C	-0.155272000	0.067502000	-0.000001000
H	1.728890000	-0.129578000	-0.000026000
O	-1.216449000	-0.553384000	-0.000001000
O	0.106649000	1.285584000	0.000001000
O	1.010143000	-0.766629000	0.000004000

OH·: H = -75.714622; G = -75.734847

H	0.000000000	0.000000000	-0.864048000
O	0.000000000	0.000000000	0.108006000

H_2O_2: H = -151.503744; G = -151.530087

O	-0.702268000	0.119588000	-0.052682000
O	0.702220000	-0.119563000	-0.052729000
H	1.026498000	0.654448000	0.421682000
H	-1.026113000	-0.654655000	0.421602000

$CO_2^{\cdot-}$: H = -188.540133; G = -188.567970

O	1.141309000	-0.123309000	0.000000000

C	0.000000000	0.328617000	0.000000000
O	-1.141309000	-0.123154000	0.000000000

CO_2: H = -188.559323; G = -188.584198

C	0.000000000	0.000000000	0.000000000
O	0.000000000	0.000000000	-1.154916000
O	0.000000000	0.000000000	1.154916000

TS2: H = -340.032439; G = -340.070753 (i = −989.4 cm-1)

C	1.199429000	0.000310000	0.094897000
H	0.069625000	-0.000242000	1.396274000
O	1.404501000	-1.149338000	-0.070599000
O	1.401865000	1.150200000	-0.072098000
H	-0.813791000	0.000567000	1.108192000
O	-1.630145000	-0.001836000	-0.747158000
O	-1.982772000	0.000701000	0.505624000

$CO_4^{\cdot -}$: H = -338.918058; G = -338.952526

C	-0.658667000	0.102047000	0.000000000
O	-1.524818000	-0.746410000	0.000025000
O	-0.524008000	1.299382000	-0.000013000
O	0.745237000	-0.688697000	-0.000049000
O	1.797590000	0.059191000	0.000037000

HCO_2−: H = -189.167005; G = -189.194703

O	1.131651000	-0.208552000	0.000020000
C	-0.000145000	0.314399000	-0.000076000
O	-1.131801000	-0.208224000	0.000020000
H	0.002073000	1.447815000	0.000144000

$HO_2^{\cdot}$: H = -150.872072; G = -150.898008

O	0.054934000	0.708180000	0.000000000
O	0.054934000	-0.599060000	0.000000000
H	-0.878948000	-0.872962000	0.000000000

$O_2^{\cdot -}(H_2O)$: H = -226.746677; G = -226.779341

O	1.084896000	0.626904000	0.000002000
O	0.874347000	-0.674283000	-0.000003000
H	-0.846902000	-0.517683000	0.000018000
O	-1.692422000	0.002567000	0.000000000
H	-1.287665000	0.876180000	-0.000017000

INT1w: H = -416.508124; G = -416.553682

O	-1.083770000	-0.772054000	0.066602000

O	-0.962168000	0.532752000	-0.002161000
H	0.413483000	0.759992000	0.019403000
O	1.476074000	0.894412000	0.033792000
C	2.102290000	-0.249072000	-0.025677000
O	3.307288000	-0.376955000	-0.027692000
H	1.424838000	-1.119768000	-0.074006000
H	-3.313954000	0.788129000	-0.067122000
O	-3.758076000	-0.064881000	-0.037490000
H	-2.972900000	-0.640105000	0.011371000

TS1w: H = -416.472293; G = -416.515899 (i = −942.3 cm-1)

O	-0.742696000	0.108885000	1.012064000
O	-0.945173000	1.090729000	0.050874000
H	-0.006523000	1.354423000	-0.173695000
O	1.560324000	0.918199000	-0.514757000
C	1.599938000	-0.240163000	-0.052511000
O	2.457847000	-1.105761000	0.005437000
H	0.530769000	-0.500176000	0.468581000
H	-2.633052000	-0.029680000	-0.896306000
O	-2.975055000	-0.822775000	-0.470390000
H	-2.332800000	-0.897812000	0.250664000

INT2w: H = -416.493128; G = -416.539281

O	-0.877693000	-0.891437000	0.369567000
O	-0.976962000	0.476685000	0.783713000
H	-0.163263000	0.872403000	0.367291000
O	1.394927000	1.007145000	-0.220435000
C	1.977941000	-0.082497000	-0.094719000
O	3.101855000	-0.506624000	-0.253282000
H	0.092784000	-1.040082000	0.352381000
H	-2.786230000	0.552397000	-0.078404000
O	-3.408372000	0.024420000	-0.598589000
H	-2.880983000	-0.771244000	-0.720748000

INT2w': H = -416.490497; G = -416.539497

C	-2.471684000	-0.018258000	0.409779000
H	0.251205000	0.689084000	0.699952000
O	-3.471743000	-0.387609000	-0.167218000
O	-1.248500000	-0.060659000	0.158997000
H	0.193875000	0.004252000	-0.974250000
O	1.162492000	0.886658000	0.385951000
O	1.117663000	0.326750000	-0.935452000
H	2.989325000	-0.783689000	-0.556240000
O	3.499896000	-0.722362000	0.258531000
H	2.917233000	-0.142319000	0.765395000

TS3w: H = -416.471204; G = -416.517571 (i = −828.9 cm-1)

C	-1.903885000	-0.155447000	-0.001656000
H	-0.042092000	0.841246000	-0.191811000

O	-2.598166000	-1.035265000	0.437459000
O	-1.935022000	0.841234000	-0.704948000
H	1.942481000	1.619977000	1.057017000
O	0.588926000	0.374244000	0.380374000
O	1.868443000	1.280055000	0.160278000
H	2.763481000	-0.442958000	-0.267887000
O	2.700763000	-1.406404000	-0.327909000
H	1.759888000	-1.516488000	-0.149419000

INT3w: H = -416.581477; G = -416.625994

C	1.320986000	0.073789000	-0.010490000
H	1.102744000	-1.800735000	0.242197000
O	0.686635000	1.144095000	-0.070700000
O	2.520716000	-0.167871000	-0.112136000
H	-0.854262000	1.381717000	0.043083000
O	0.493304000	-1.057462000	0.221908000
O	-1.854200000	1.575362000	0.093739000
H	-2.511091000	-0.331623000	-0.087274000
O	-2.377420000	-1.287388000	-0.143330000
H	-1.415586000	-1.345981000	-0.050914000

$HCO_3^-(H_2O)$: H = -340.840894; G = -340.878821

C	0.822543000	-0.162898000	-0.000103000
H	0.875051000	1.743103000	-0.000029000
O	0.044613000	-1.124219000	-0.000827000
O	2.055813000	-0.086994000	0.000978000
O	0.155804000	1.106463000	-0.000792000
H	-1.742279000	-0.621718000	0.000040000
O	-2.510397000	-0.015865000	0.000669000
H	-2.034693000	0.820922000	0.000377000

$OH\cdot(H_2O)$: H = -152.119469; G = -152.150714

H	0.634160000	0.000462000	-0.024354000
O	1.612214000	-0.000023000	0.006289000
H	-1.803321000	0.769301000	0.087075000
O	-1.240747000	0.000018000	-0.025005000
H	-1.802574000	-0.769725000	0.087006000

$H_2O_2(H_2O)$: H = -227.905739; G = -227.941378

O	-0.945667000	-0.705488000	0.095602000
O	-0.945364000	0.705448000	-0.095532000
H	-1.413603000	1.007692000	0.692363000
H	-1.411944000	-1.007617000	-0.693484000
H	1.312608000	0.714846000	-0.221362000
O	1.915923000	0.000063000	-0.000141000
H	1.313811000	-0.715100000	0.223055000

$CO_2\cdot^-(H_2O)$: H = -264.962432; G = -264.997811

O	0.701010000	-1.137122000	0.000018000
C	1.171320000	0.000629000	-0.000059000
O	0.698855000	1.137524000	0.000047000
H	-1.317512000	-0.736399000	-0.000035000
O	-1.949059000	-0.000643000	0.000032000
H	-1.316859000	0.734555000	-0.000384000

TS2w: H = -416.450778; G = -416.497014 (i = −589.8 cm-1)

C	1.945881000	-0.140868000	-0.001629000
H	0.285864000	-0.656447000	-0.067317000
O	2.519959000	-1.162099000	0.053473000
O	1.809843000	1.027241000	-0.041027000
H	-0.527757000	-1.040148000	-0.074711000
O	-2.559629000	-0.452817000	0.065454000
O	-1.809462000	-1.507816000	-0.068121000
H	-0.235107000	1.761738000	-0.029493000
O	-1.154388000	2.042712000	0.008100000
H	-1.648873000	1.202297000	0.038255000

$CO_4^{\cdot -}(H_2O)$: H = -415.332741; G = -415.374825

C	1.439148000	0.173922000	-0.000021000
O	1.667581000	1.354845000	0.000058000
O	1.934729000	-0.914081000	-0.000143000
O	-0.246811000	0.065249000	0.000078000
O	-0.719337000	-1.136188000	0.000120000
H	-2.398377000	1.076902000	-0.000104000
O	-3.096095000	0.414170000	-0.000116000
H	-2.557057000	-0.392403000	0.000260000

$HCO_2^-(H_2O)$: H = -265.593721; G = -265.628613

O	-0.603008000	-1.128622000	-0.000018000
C	-1.139449000	0.000002000	0.000006000
O	-0.603000000	1.128622000	0.000142000
H	1.358946000	-0.726928000	-0.000066000
O	2.003685000	-0.000002000	-0.000105000
H	1.358940000	0.726920000	-0.000014000
H	-2.262606000	0.000006000	-0.000105000

Kinetic analysis of O_2•−(H_2O) + HCO_2H

Rate coefficients were calculated for various steps of the reaction paths of O_2•−(H_2O) + HCO_2H as given in Figure 3; the rate coefficients are shown in Table S2. The rate coefficients were calculated using the Mechanism-Based Kinetics Simulator as implemented at http://www.stolaf.edu/depts/chemistry/courses/toolkits/126/js/kinetics/. The relative amount of each species as a function of time is displayed in Figure S3.

Table S2. Computed transition state theory thermal rate coefficients k^{TST} (in s^{-1}) at 298 K for each of the processes of Figure 3.

Number	Reaction	k^{TST}
1	INT1w → $CO_4^{\bullet-}$ + H_2	1.39×10^{-11}
2	INT1w → HCO_2^-(H_2O) + $HO_2^\bullet$	2.26
3	INT1w → INT1 + H_2O	1.24×10^{10}
3	INT1w → INT2w	2.81×10^{-5}
4	INT2w → INT1w	12.8×10^{1}
5	INT2w → INT3w	42.9×10^{1}
6	INT3w → INT2w	7.30×10^{-38}
7	INT3w → HCO_3^-(H_2O) + $HO^\bullet$	1.53×10^{7}
8	INT2w → $H_2O_2^-$ + $CO_2^{\bullet-}$(H_2O)	3.44×10^{7}

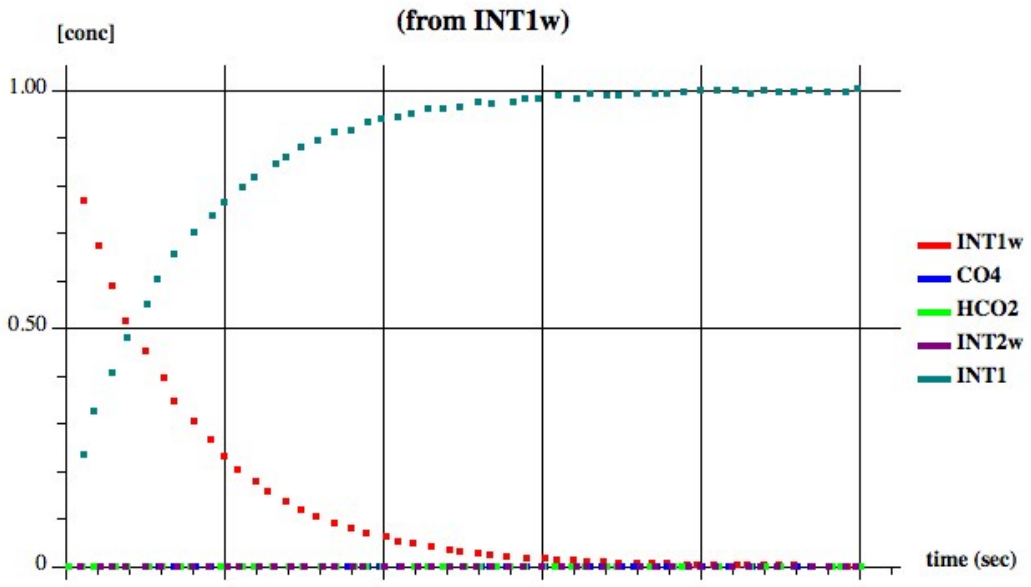

Figure S3. Time evolution of the relative amount of each of the species involved in the reaction between monohydrated superoxide and formic acid.