Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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The Baeyer Villiger Reaction: Solvent Effects on Reaction Mechanisms

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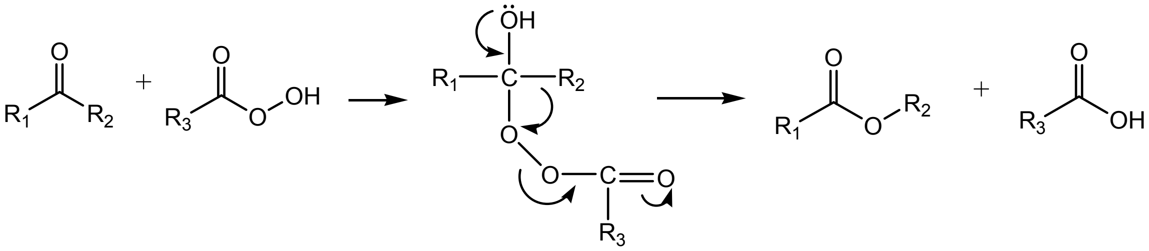
The structures reported in this section were optimized at the MPWB1K/6-311++G(d,p)-IEF-PCM(radii=uahf) level of theory followed by frequency calculations at the same level of theory, unless otherwise indicated.

Appendix 1

Mechanisms for the Baeyer-Villiger reaction that have been reported in textbooks

The different versions of BV reaction mechanisms found in organic textbooks have been split into several groups based on whether or not charges appear, and if they do, where they appear in the mechanism. Below are the mechanisms and the corresponding literature references.

1. No ions are shown in the mechanism and no details regarding the TS structures are provided.

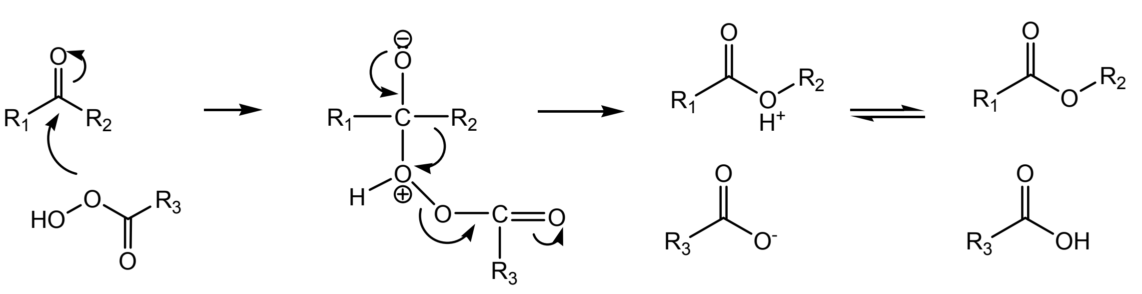


K. P. Vollhardt, N. E. Schore, *Organic Chemistry: Structure and Function*, Freeman: New York, 5th Edition, **2007**, pp. 795-796**.**

M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, Wiley: Weinheim, **1998**, pp. 213-214. In this reference the addition is said to be “proton-catalyzed”.

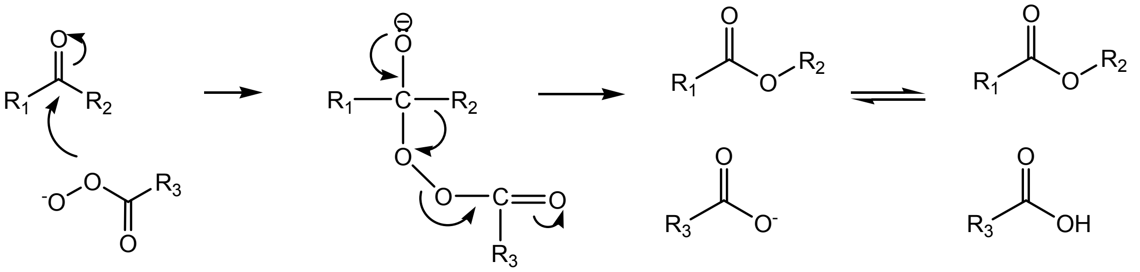
F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, Plenum: New York, 3rd Edition, **1993**, pp. 654-655.

2. Mechanism showing a charge separation pathway.



(18e) D. R. Klein, *Organic Chemistry II As A Second Language*, Wiley, **2006**, pp. 148-151.

3. Mechanism beginning with the attack of the conjugate base of the peroxyacid, forming an anionic Criegee.



(18b) P. Y. Bruice, *Organic Chemistry*, Pearson: Upper Saddle River, NJ, 5th Edition, **2007**, p. 921.

4. The rest of the mechanisms contain slightly different versions of the acid-catalyzed BV addition (A1 to A3) and migration (M1, M2) steps.

A1: Protonation of the ketone by another acid (H^+), attack by neutral peracid, and loss of the proton to form the Criegee.

A2: Protonation of the ketone is achieved by the peracid, and a neutral criegee is formed.

A3: No protonation of the ketone is shown, and neutral products are written in equilibrium with a neutral Criegee.

M1: The neutral Criegee rearranges to produce a protonated ester and a carboxylate anion. These either react with each other, or with an external acid/base to afford the neutral products.

M2: The neutral Criegee is protonated at the carbonyl oxygen of the leaving group, and rearranges to afford a protonated ester and a neutral carboxylic acid. A base in the reaction mixture accepts the proton to produce neutral products.

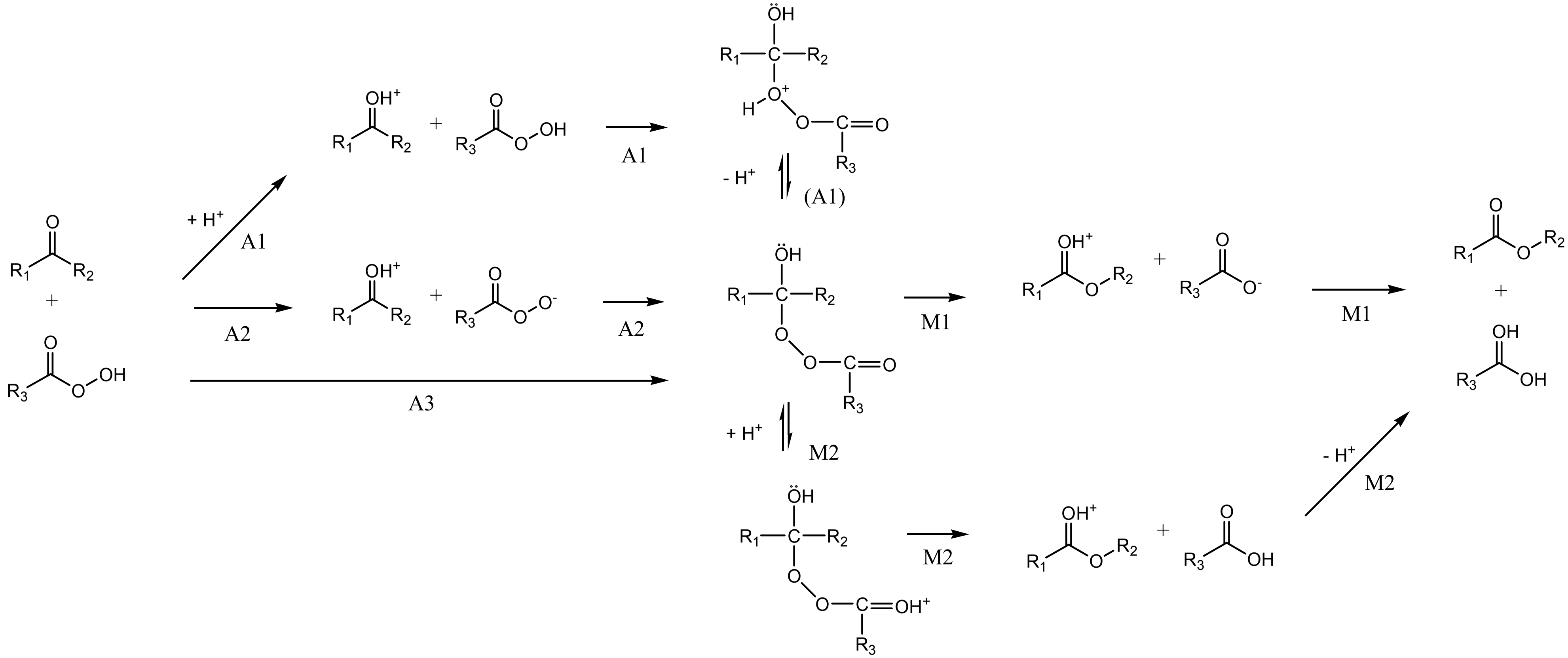
[A1, M1]

(18a) M. B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, Wiley: Hoboken, NJ, 6th Edition, **2007**, pp. 1617-1620.
The charges on the protonated ketone and ester are shown on the carbonyl carbon atom.

(18i) S. N. Eğe, *Organic Chemistry*, D. C. Heath, 2nd Edition, **1989**, pp. 606-608.
This mechanism shows a positively charged Criegee intermediate which then loses the proton.

[A2, M1]

(18f) A. Jacobs, *Understanding Organic Reaction Mechanisms*, Cambridge University Press, **1997**, pp. 195-196.



[A3, M1]
(18d) J. M. Hornback, *Organic Chemistry*, Thomson Brooks/Cole, 2nd Edition, **2006**, p. 998.

(18g) A. Streitwieser, C. H. Heathcock, E. M. Kosower, *Introduction to Organic Chemistry*, MacMillan Publishing: New York, 4th Edition, **1992**, pp. 411-412.

(18j) T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, HarperCollins: New York, 3rd Edition, **1987**, pp. 501-504.

[A3, M2]
(18c) F. A. Carey, *Organic Chemistry*, McGraw-Hill: New York, 6th Edition, **2006**, pp. 763-766.

(18h) T. W. G. Solomons, *Organic Chemistry*, Wiley: New York, 5th Edition, **1992**, p. 713.

(18k) D. S. Kemp, F. Vellaccio, *Organic Chemistry*, Worth Publishers: New York, **1980**, pp. 1134-1135.

Appendix 2

Discussion of solvent effects on the charge distributions of the concerted TSs

The Mulliken charge distributions of the three concerted TSs also undergo slight changes as solvent polarity increases (see Tables S1-S6). The sum of the charges of propanone and formic acid in TS1 (Table S1) show an overall decrease in magnitude with solvent polarity, going from -0.215 in dichloromethane to -0.184 in water. However, the charge separation of the products within TS1 increases with solvent polarity in the two groups of solvents and it is greater in the protic ones. These results are still in agreement with a neutral mechanism for the addition step because the charge separation between reactants and products within TS1 decreases for a given solvent. Since TS1 has an increased product-like resemblance with increased solvent polarity and the charge separation of the product species increases as well, this, as expected, translates to lower G values for TS1 as the polarity of the solvent increases.

The charge on the carbonyl carbon atom of the ketone (see Table S2) is more positive when in the reactant complex, as expected, and it is negative in TS1 because of the negative charge accepted from the *quasi*-deprotonated peroxide oxygen. The charge on this atom increases with solvent polarity in the ketone and in the reactant complex. However, it becomes less negative in TS1 which could be related to the fact that the C--OO bond distance (see Table 1) increases with solvent polarity. The charges of the leaving hydrogens from PFA and FA increase when in TS1 in a given solvent (see Table S3) because the hydrogen atoms are migrating as “protons” but are close to covalent bond distances to the oxygen atoms. As solvent polarity increases the hydrogen charge in PFA and FA increases and these values are higher in the protic solvents than in the non-protic ones. The opposite is observed for these two hydrogen charges when in TS1. These results are in agreement with the geometrical changes explained above for TS1 since the proton transfers become more product-like the more polar the solvent, hence the protons are more fully transferred to the final host and have lower charges.

The charge on the migrating methyl group increases from the Criegee to TS2 and it increases even more in TS2(cat) (see Table S4). In all cases this charge increases with solvent polarity and it is greater in the protic solvents. In TS2, the sum of the atomic charges of the products increases with solvent polarity; going from (±)0.062 in dichloromethane to (±)0.085 in water (see Table S5). Hence, product charge separation in TS2 (which is slightly greater than in TS1) once again increases with solvent polarity, and is greater in the protic solvents. In TS2(cat), the sum of the atomic charges of the ester is 0.016 in dichloromethane and 0.017 in water, which indicates that the product charge separation in TS2(cat) is much smaller than in TS2 (see Table S6). Charge separation in TS2(cat) increases with solvent polarity, but is lower in the protic solvents. These results translate into lower Gibbs free energy (G) values for TS2 than for TS2(cat) as the polarity of the solvent increases as expected for a neutral mechanism.

Appendix 3

Discussion of solvent effects on the geometry of the concerted non-ionic TSs

Table S7 displays selected bond distances of the concerted non-ionic TSs (TS1, TS2 and TS2(cat)) of the BV reaction of propanone, performic acid and formic acid obtained at the MPWB1K/6-311++G(d,p)-IEM-PCM level of theory.

As solvent polarity increases, the C-OO bond distance (a) in TS1 becomes slightly larger, which would indicate that TS1 more resembles the reactants. However, the addition step is mainly controlled by the two proton-transfer processes (observed in the animation of the transition vector) and the bond distance changes associated with them (b,c,d and e) indicate that TS1 becomes more product-like (resembling more the Criegee intermediate) with increased solvent polarity. The O-H bond distance (c) corresponding to the proton transfer from the acid to the ketone is the TS1 bond distance that changes the most with solvent polarity. In a complex TS, as in the BV reaction, the concept of early or late TS is not a straightforward one because multiple bonds break and form in a synergistic manner. The changes in solvent polarity differently affect the various components of the transition vector, and the protonation of the ketone by the acid catalyst seems to be the process affected (and favoured) the most as solvent polarity increases.

However, the migration TS2(a) and TS2(b) show a trend toward a TS more closely resembling reactants (the Criegee intermediate) as the solvent polarity increases with respect to the three concerted processes: the migration of the methyl group, the cleavage of the CO-O bond and the proton transfer(s). The O--H bond distance (i) in TS2(a) corresponding to the proton transfer from the Criegee to the leaving acid is the bond distance that changes the most with solvent polarity. The other geometrical changes in the protic solvents for TS2(a) are almost negligible. In TS2(b) the changes in bond distance are very similar for the internal coordinates considered, except for the O--H distances labelled (l) and (j) that do not seem to be very sensitive to solvent polarity changes. The relationship between the structural and energetic changes of the different TSs, according to the Hammond postulate, are difficult to establish in these cases because the change in solvent polarity affects the reactants, the TS and the products of each step of this reaction differently.

Appendix 4

Discussion on the effects of acidity and solvent polarity on the mechanism of the BV reaction

As previously discussed, in a strongly acidic aqueous environment, the ionic addition pathway is the least energetic one. However, the concerted uncatalyzed non-ionic migration is the least energetic pathway for the second step. If the ionic pathway in water were to take place in a less acidic medium, the ionic Gibbs free energies of activation would increase by an amount that depends on the pK_a of the acid used ($RT\ln 10 \times pK_a$), to account for the Gibbs free energy required to form H_3O^+ from the chosen acid. If we ignore the practical issues associated with performing a BV reaction in water, and formic acid is to be used, the ionic Gibbs free energy barriers would be increased by 5.1 kcal/mol. This would reduce to 4.3 kcal/mol the energy difference between the ionic and the non-ionic formic acid-catalyzed addition, and it would increase even more (by 7.7 kcal/mol) the energy difference between the ionic migration through TS2(i) and the more favourable route through TS2, the concerted non-ionic uncatalyzed migration.

If a stronger acid (and peracid pair) than formic acid (performic acid) is used instead, *e.g.*, trifluoroacetic acid (TFAA, and trifluoroperacetic acid, TFPAA), the ionic Gibbs free energies of activation would only increase by 0.3 kcal/mol. However, the concerted non-ionic addition and migration $\Delta G^{\neq}$ values for the reaction with the TFAA/TFPAA pair would decrease in comparison to the values obtained with the FA/PFA pair due to the stronger acidity of TFAA and TFPAA. The concerted non-ionic addition $\Delta G^{\neq}$ with the TFPAA/TFAA pair is calculated to be 19.6 kcal/mol (9.0 kcal/mol lower than with the PFA/FA pair) at the same level of theory. Even though this value is very close to the $\Delta G^{\neq}$ of the ionic addition TSs (19.2 kcal/mol), TFAA would be almost totally dissociated and the concentration of hydronium ions would be much greater than that of undissociated TFAA molecules. This will make the catalytic activity of TFAA difficult, as it favours the ionic addition of the peracid to the ketone.

These results seem to indicate that independently of the acid/peracid pair used, the ionic addition of the peracid to the protonated ketone, and the non-ionic uncatalyzed concerted migration (which is the RDS in this and most BV reactions), are the least energetic pathways for the two steps of the BV reaction in water. If the polarity of the solvent decreases, the ionic addition barrier should increase, while the non-ionic addition and migration (RDS) barriers will decrease and, consequently, the rate constant of the reaction will increase. These results are once again in agreement with the experimental work of Hawthorne and Emmons.[8]

When the most favourable reaction pathways in water (in a strong acidic environment) and in dichloromethane (DCM) with a weak acid are compared, we can see that the concerted non-ionic acid-catalyzed addition pathway in DCM is 0.9 kcal/mol more energetic than the ionic addition in water. However, the non-ionic migration in DCM is 5.0 kcal/mol less energetic than in water (see Figure S2). This is not the best comparison for the addition step because the catalytic activity of a strong acid in water is compared to that of a weak acid in DCM. If we use a stronger acid (trifluoroacetic acid, TFAA) than FA instead, the addition reaction of PFA to propanone in DCM becomes 1 kcal/mol less energetic than in water. The change in acid has no effect on the second step in DCM because it is uncatalyzed at the level of theory used (Figure S2). In other words, when the reaction is modelled with strong acids in both solvents, the non-ionic processes in DCM are more favoured than in water. Figure S2 also shows the effect of changing PFA for a more acidic but less nucleophilic peracid, trifluoroperacetic acid (TFPAA), that also leads to the formation of a better leaving acid as by-product of the reaction (TFAA). The addition and migration steps of the reaction of propanone with TFPAA, using TFAA as catalyst, in DCM have barriers that are 1.6 and 8.5 kcal/mol, lower, respectively, than the corresponding barriers of the least energetic pathway in water. Ignoring other factors, this comparison clearly expresses a practical reason why BV reactions with organic peracids and acids are not performed in water.

Table S1 Mulliken atomic charges in TS1.[a]

		Reactant Charges			**Product Charges**	
Solvent	ε^b	*Propanone*	*Formic Acid*	*Performic Acid*	*Criegee*	*Formic Acid*
Dichloromethane	8.93	-0.0397	-0.1750	0.2147	0.0582	-0.0582
Acetone	20.70	-0.0327	-0.1789	0.2116	0.0604	-0.0604
Nitromethane	38.20	-0.0291	-0.1797	0.2088	0.0608	-0.0608
DMSO	46.70	-0.0295	-0.1804	0.2099	0.0611	-0.0611
Ethanol	24.55	-0.0018	-0.1909	0.1927	0.0737	-0.0737
Methanol	32.63	0.0025	-0.1899	0.1875	0.0731	-0.0731
Water	78.39	0.0073	-0.1916	0.1843	0.0749	-0.0749

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S2 Changes of Mulliken atomic charges of the carbonyl carbon of propanone when the reactant complex (RC) and TS1 are formed.[a]

Solvent	ε^b	**Propanone**	**RC**	**TS1**
Dichloromethane	8.93	0.4042	0.5433	-0.2193
Acetone	20.7	0.4071	0.5449	-0.2189
Nitromethane	38.2	0.4083	0.5433	-0.2176
DMSO	46.7	0.4084	0.5435	-0.2188
Ethanol	24.55	0.4497	0.4813	-0.1857
Methanol	32.63	0.4516	0.4874	-0.1804
Water	78.39	0.4547	0.4900	-0.1762

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S3 Mulliken atomic charges of the two protons transferred in TS1.[a]

Solvent	ε^b	**PFA**	**TS1**	**FA**	**TS1**
Dichloromethane	8.93	0.3144	0.5952	0.3119	0.4784
Acetone	20.7	0.3192	0.5951	0.3158	0.4767
Nitromethane	38.2	0.3209	0.5948	0.3172	0.4760
DMSO	46.7	0.3213	0.5950	0.3175	0.4757
Ethanol	24.55	0.3537	0.5899	0.3472	0.4727
Methanol	32.63	0.3554	0.5896	0.3488	0.4727
Water	78.39	0.3583	0.5886	0.3511	0.4720

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S4 Mulliken atomic charges of the methyl groups in the Criegee intermediate and the migrating methyl group in TS2 and TS2(cat).[a]

Solvent	ε [b]	**CH_3(1) in Criegee**	**CH_3(2) in Criegee**	**TS2**	**TS2(cat)**
Dichloromethane	8.93	0.1409	0.2407	0.3166	0.3722
Acetone	20.7	0.1390	0.2419	0.3199	0.3792
Nitromethane	38.2	0.1367	0.2437	0.3213	0.3818
DMSO	46.7	0.1386	0.2417	0.3210	0.3823
Ethanol	24.55	0.1245	0.2391	0.3273	0.3983
Methanol	32.63	0.1274	0.2374	0.3276	0.4001
Water	78.39	0.1265	0.2390	0.3287	0.4014

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S5 Mulliken atomic charges in TS2.[a]

		Reactant Charges	**Product Charges**	
Solvent	ε [b]	*Criegee*	*Ester*	*Formic Acid*
Dichloromethane	8.93	0.0000	0.0618	-0.0618
Acetone	20.70	0.0000	0.0666	-0.0666
Nitromethane	38.20	0.0000	0.0681	-0.0681
DMSO	46.70	0.0000	0.0682	-0.0682
Ethanol	24.55	0.0000	0.0802	-0.0802
Methanol	32.63	0.0000	0.0828	-0.0828
Water	78.39	0.0000	0.0848	-0.0848

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S6 Mulliken atomic charges in TS2(cat).[a]

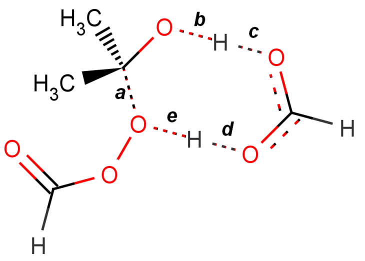
		Reactant Charges		**Product Charges**		
Solvent	ε [b]	*Criegee*	*Formic Acid*	*Ester*	*Formic Acid 1*	*Formic Acid 2*
Dichloromethane	8.93	-0.0660	0.0660	0.0158	0.0247	-0.0406
Acetone	20.70	-0.0663	0.0663	0.0172	0.0218	-0.0390
Nitromethane	38.20	-0.0666	0.0666	0.0175	0.0208	-0.0383
DMSO	46.70	-0.0665	0.0665	0.0177	0.0205	-0.0382
Ethanol	24.55	-0.0684	0.0684	0.0161	0.0142	-0.0303
Methanol	32.63	-0.0688	0.0688	0.0167	0.0128	-0.0295
Water	78.39	-0.0683	0.0683	0.0168	0.0104	-0.0271

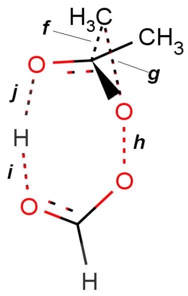
[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.

Table S7 Selected bond distances (in Å) for the TS of the concerted catalyzed addition (TS1), and uncatalyzed (TS2) and catalyzed (TS2(cat)) migration steps of the BV reaction of propanone, performic acid and formic acid.[a]

Solvent	ε [b]	TS1					TS2					TS2(cat)						
		a	b	c	d	e	f	g	h	i	j	f	g	h	k	l	m	j
		C-O	O-H	H-O	O-H	H-O	C-C	C-O	O-O	O-H	H-O	C-C	C-O	O-O	O-H	H-O	O-H	H-O
Dichloromethane	8.93	1.997	1.033	1.449	1.264	1.134	1.736	1.944	1.910	1.600	0.999	1.753	1.942	1.922	1.556	1.002	1.735	0.978
Acetone	20.70	1.998	1.031	1.457	1.263	1.135	1.733	1.947	1.908	1.611	0.997	1.750	1.945	1.919	1.559	1.002	1.738	0.978
Nitromethane	38.20	2.000	1.030	1.460	1.261	1.136	1.732	1.948	1.907	1.613	0.996	1.749	1.946	1.919	1.560	1.001	1.739	0.977
DMSO	46.70	1.999	1.030	1.460	1.261	1.136	1.732	1.948	1.907	1.613	0.996	1.748	1.946	1.918	1.561	1.001	1.739	0.977
Ethanol	24.55	2.003	1.021	1.490	1.251	1.145	1.722	1.959	1.899	1.660	0.989	1.737	1.956	1.909	1.575	0.999	1.752	0.976
Methanol	32.63	2.007	1.020	1.492	1.247	1.148	1.722	1.959	1.899	1.666	0.989	1.736	1.957	1.908	1.577	0.999	1.749	0.976
Water	78.39	2.008	1.019	1.497	1.246	1.149	1.721	1.961	1.897	1.677	0.987	1.734	1.958	1.906	1.580	0.998	1.750	0.976

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40.





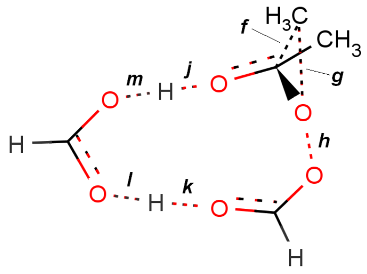


Table S8 Enthalpies and Gibbs free energies (in kcal mol^{-1} at 298.15 K) of the optimized stationary points relative to the isolated reactants for the reaction of propanone with performic acid (PFA) using formic acid (FA) as catalyst.[a]

		RC + PFA		TS1		Criegee + FA		TS2[c] + FA		TS2(cat)		Ester + 2 FA	
Solvent	ε[b]	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
Dichloromethane	8.93	-5.25	-0.90	2.88	18.98	-1.51	7.46	15.78	25.45	9.18	23.88	-68.68	-68.20
Acetone	20.70	-4.93	-0.62	3.69	19.74	-1.21	7.84	16.15	25.79	9.89	24.65	-68.42	-67.95
Nitromethane	38.20	-4.81	-0.50	3.82	19.77	-1.14	7.83	16.30	25.94	10.17	24.90	-68.33	-67.87
DMSO	46.70	-4.79	-0.48	3.91	19.85	-1.06	7.86	16.32	25.95	10.21	24.97	-68.30	-67.85
Ethanol	24.55	-1.00	2.79	11.94	28.10	0.61	10.10	20.08	29.74	18.03	32.81	-67.36	-66.89
Methanol	32.63	-0.92	2.91	12.23	28.40	0.86	10.38	20.24	29.89	18.35	33.37	-67.26	-66.77
Water	78.39	-0.78	3.02	12.81	28.79	1.83	11.18	20.52	30.14	18.78	33.59	-67.10	-66.63

[a] Level of theory: B3LYP/6-311++G(d,p)-IEF-PCM; [b] Relative static permittivities taken from Ref. 40; [c] Uncatalyzed TS.

Table S9 Enthalpy and Gibbs free energy changes (in kcal mol^{-1} at 298.15 K) of the modeled stationary points, relative to the isolated reactants for the BV reaction of propanone with performic acid (PFA) using formic acid (FA) as catalyst.[a]

		RC + PFA		TS1		Criegee + FA		TS2[c] + FA		TS2(cat)		Ester + 2 FA	
Solvent	ε[b]	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
Dichloromethane	8.93	-5.13	-0.08	2.68	19.15	-1.38	7.72	15.48	25.16	8.81	24.11	-68.61	-68.06
Acetone	20.70	-4.82	0.23	3.47	19.94	-1.10	8.01	15.83	25.51	9.44	24.74	-68.35	-67.80
Nitromethane	38.20	-4.68	0.37	3.76	20.23	-0.94	8.16	15.99	25.67	9.67	24.97	-68.25	-67.70
DMSO	46.70	-4.67	0.38	3.83	20.30	-0.95	8.16	15.97	25.65	9.73	25.03	-68.23	-67.68
Ethanol	24.55	-1.41	3.64	10.58	27.05	1.17	10.28	19.02	28.70	16.14	31.44	-67.48	-66.92
Methanol	32.63	-1.29	3.76	10.91	27.38	1.35	10.46	19.14	28.82	16.37	31.67	-67.40	-66.85
Water	78.39	-1.08	3.97	11.38	27.85	1.37	10.48	19.39	29.07	16.79	32.09	-67.26	-66.71

[a] Level of theory: B3LYP/6-311++G(d,p)-IEF-PCM//B3LYP/6-311G(d,p); $G_{solvent} = E_{solvent} + TCG_{gas}$; [b] Relative static permittivities taken from Ref. 40; [c] Uncatalyzed TS.

Table S10 Enthalpy and Gibbs free energy changes (in kcal mol^{-1} at 298.15 K) of the modeled stationary points, relative to the isolated reactants for the BV reaction of propanone with performic acid (PFA) using formic acid (FA) as catalyst.[a]

		RC + PFA		**TS1**		**Criegee + FA**		**TS2^{c} + FA**		**TS2(cat)**		**Ester + 2 FA**	
Solvent	ε^{b}	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
Dichloromethane	8.93	-5.60	-0.39	0.20	17.62	-8.25	1.23	19.29	29.57	11.80	27.64	-74.15	-73.37
Acetone	20.70	-5.27	-0.05	1.01	18.43	-7.97	1.51	19.64	29.92	12.46	28.30	-73.88	-73.10
Nitromethane	38.20	-5.15	0.07	1.29	18.71	-7.85	1.63	19.77	30.05	12.71	28.55	-73.77	-73.00
DMSO	46.70	-5.12	0.10	1.38	18.80	-7.84	1.64	19.80	30.08	12.75	28.59	-73.75	-72.98
Ethanol	24.55	-1.88	3.33	8.06	25.48	-5.53	3.95	22.75	33.03	19.11	34.95	-72.95	-72.17
Methanol	32.63	-1.76	3.45	8.36	25.79	-5.53	3.95	22.89	33.18	19.32	35.16	-72.86	-72.09
Water	78.39	-1.55	3.66	8.81	26.24	-5.56	3.92	23.10	33.39	19.71	35.55	-72.73	-71.96

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM//MPWB1K/6-311G(d,p); $G_{solvent} = E_{solvent} + TCG_{gas}$; [b] Relative static permittivities taken from Ref. 40; [c] Uncatalyzed TS.

Additional calculations with the UFF force field radii (with IEF-PCM and CPCM) are also performed for comparison; in this approach hydrogen atoms are placed in individual solvation spheres.[40] When UFF calculations are performed no distinction is seen between protic and non-protic solvents. Geometry optimizations of ionic species in protic solvents with the UFF radii have shown convergence problems and in general UFF calculations are significantly more time consuming than UAHF calculations. It was not possible to optimize the ionic transition states reported in this paper using the UFF radii in water. Previous calculations in water using continuum solvation models have resulted in better agreement with experiment when using the UAHF atomic radii.

The results obtained (see Table S11) clearly indicate that in the three cases considered the different ΔG of activation values increase with solvent polarity. In all cases the rate-determining step is the migration step. The different scaling parameters, absent in calculations with the UFF radii, reflect the fact that the interaction of protic solvents with polar or ionic species is stronger than that of non-protic solvents. Therefore, the use of UAHF radii produces more realistic results. Nonetheless, the UAHF results are to be understood from a qualitative point of view.

Table S11 Gibbs free energies of activation (in kcal mol^{-1} at 298.15 K) of the concerted non-ionic addition and migration steps, relative to the isolated reactants, for the BV reaction of propanone with performic acid (PFA) using formic acid (FA) as catalyst.[a]

		MPWB1K/CPCM			**MPWB1K/IEF-PCM**			**B3LYP/IEF-PCM**		
Solvent	ε^{b}	**TS1**	**TS2** [c]	**TS2(cat)**	**TS1**	**TS2** [c]	**TS2(cat)**	**TS1**	**TS2** [c]	**TS2(cat)**
Dichloromethane	8.93	19.71	29.65	29.56	20.47	30.61	30.39	21.31	25.61	26.06
Acetone	20.70	20.50	29.89	30.18	21.19	30.68	30.91	22.00	25.68	26.54
Ethanol	24.55	20.57	29.90	30.24	21.25	30.65	30.95	22.03	25.70	26.57
Methanol	32.63	20.64	29.98	30.36	21.30	30.70	31.04	22.15	25.67	26.66
Nitromethane	38.20	20.75	29.96	30.38	21.41	30.68	31.06	22.22	25.73	26.67
DMSO	46.70	20.83	29.98	30.46	21.50	30.69	31.14	22.32	25.72	26.75
Water	78.39	20.77	29.97	30.44	21.42	30.64	31.09	22.26	25.67	26.69

[a] Level of theory: Funtional/6-311++G(d,p)-PCM(radii=uff)//Functional/6-311G(d,p); $G_{solvent} = E_{solvent} + TCG_{gas}$; [b] Relative static permittivities taken from Ref. 40; [c] Uncatalyzed TS.

Table S12 Gibbs free energies changes (in kcal mol^{-1} at 298.15 K) of the optimized stationary points in the reaction of propanone (P) with performic acid (PFA) using formic acid (FA) as catalyst, relative to the values in the least polar solvent (dichloromethane).[a]

Solvent	**P + FA + PFA**	**RC + PFA**	**TS1**	**Criegee + FA**	**$TS2^b$ + FA**	**TS2(cat)**	**Ester + 2FA**
Dichloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetone	-1.36	-1.14	-0.67	-0.78	-1.04	-0.57	-1.14
Nitromethane	-1.84	-1.53	-0.966	-1.10	-1.44	-0.79	-1.57
DMSO	-1.96	-1.70	-0.968	-1.18	-1.52	-0.83	-1.65
Ethanol	-14.78	-11.37	-6.27	-11.42	-10.51	-5.58	-13.30
Methanol	-15.25	-12.10	-6.54	-11.94	-10.89	-5.79	-13.86
Water	-17.08	-12.84	-6.92	-12.89	-11.68	-6.28	-14.59

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Uncatalyzed TS.

Table S13 Gibbs free energies (in au, at 298.15 K) of the stationary points in the reaction of propanone (P) with performic acid (PFA) using formic acid (FA) as catalyst.[a]

Solvent	**P + FA + PFA**	**RC + PFA**	**TS1**	**Criegee + FA**	**$TS2^b$ + FA**	**TS2(cat)**	**Ester + 2FA**
Dichloromethane	-647.61754	-647.61312	-647.57399	-647.60923	-647.56353	-647.55836	-647.73447
Acetone	-647.61970	-647.61493	-647.57506	-647.61048	-647.56519	-647.55926	-647.73629
Nitromethane	-647.62048	-647.61555	-647.57553	-647.61099	-647.56582	-647.55961	-647.73697
DMSO	-647.62066	-647.61583	-647.57553	-647.61112	-647.56596	-647.55968	-647.73711
Ethanol	-647.64109	-647.63123	-647.58397	-647.62742	-647.58028	-647.56725	-647.75566
Methanol	-647.64184	-647.63240	-647.58441	-647.62826	-647.58089	-647.56758	-647.75655
Water	-647.64476	-647.63359	-647.58502	-647.62978	-647.58214	-647.56836	-647.75771

[a] Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM; [b] Uncatalyzed TS.

$G_{aq}(P)$ =-193.054177 au; $G_{aq}(FA)$ = -189.73095 au; $G_{aq}(PFA)$ = -264.85034 au.

Table S14 Change in Gibbs free energy in kcal/mol associated with the hydronium protonation of propanone (P), the Criegee intermediate (C) and the ester (E) in water at 298.15 K (using the data reported in Table S13).

Equilibrium	ΔG_{aq}
P + $H_3O^+ \leftrightarrows$ HP^+ + H_2O	8.4 [a]
C + $H_3O^+ \leftrightarrows$ HC^+ + H_2O	24.5
E + $H_3O^+ \leftrightarrows$ HE^+ + H_2O	20.8

[a] Experimental estimate for a general ketone: 7.2 kcal/mol.

Table S15 Data used for calculating the ΔG_{aq} of the acid-base equilibria of propanone (P), the Criegee intermediate (C) and the ester (E) in water.

Species	G_{aq} [a]	**Species**	G_{gas} [b]	ΔG_{solv} [c]
H_2O	-76.42440	H_2O	-76.40295	-6.4
H_3O^+	-76.85391	H_3O^+	-76.67519	-106.1
C	-457.88953	P	-193.04085	-3.8
HC^+	-458.28007	HP^+	-193.35429	-69.2
E	-268.27722			
HE^+	-268.67359			

[a] MPWB1K/6-311++G(d,p)-IEF-PCM (in au); [b] MPWB1K/6-311G(d,p) (in au); [c] HF/6-31G(d)-IEF-PCM//MPWB1K/6-311G(d,p) (in kcal/mol).

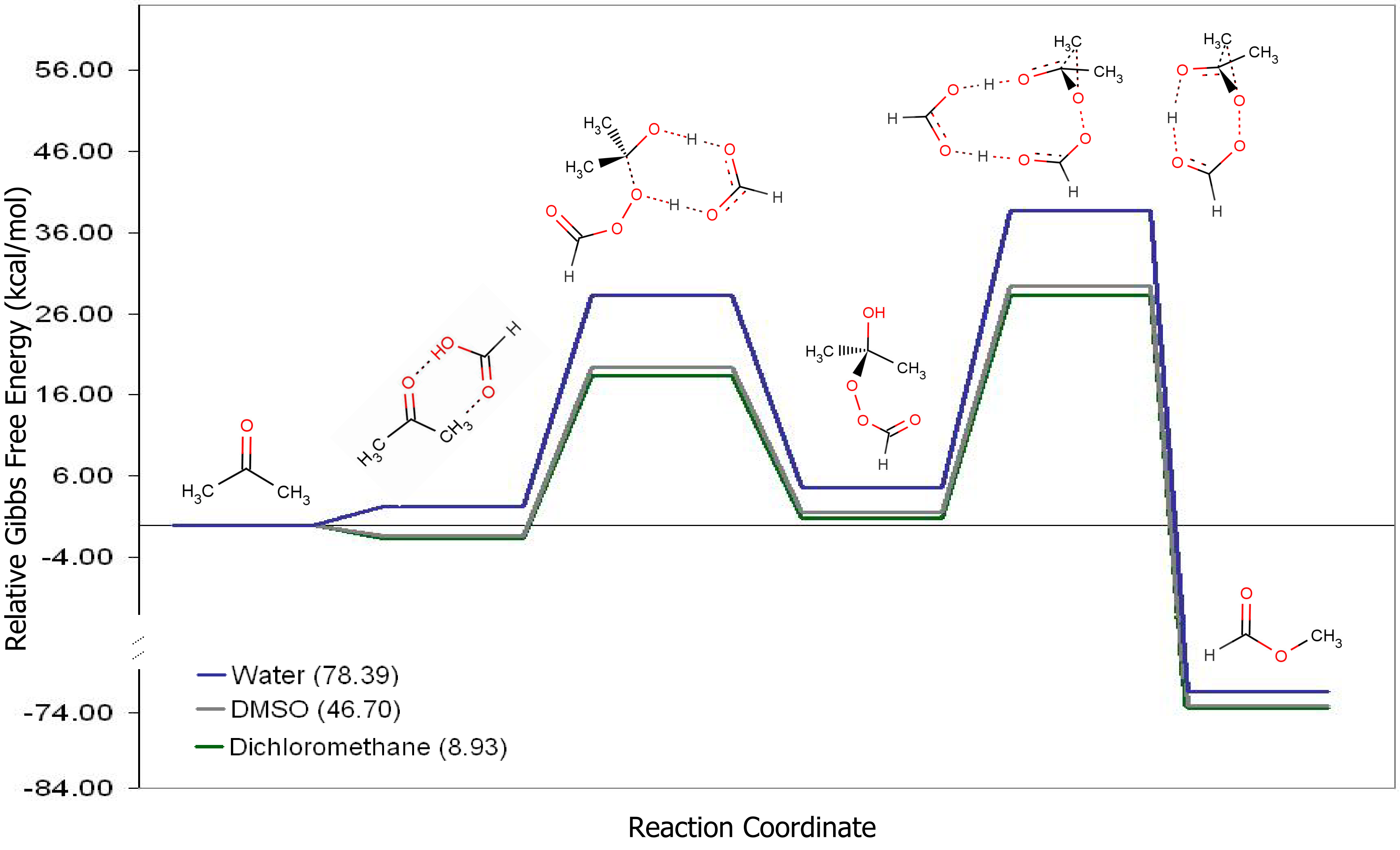


Figure S1 Reaction profile of the concerted BV reaction of propanone with performic acid (catalyzed by formic acid) in water DMSO and dichloromethane at 298.15 K (level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM).

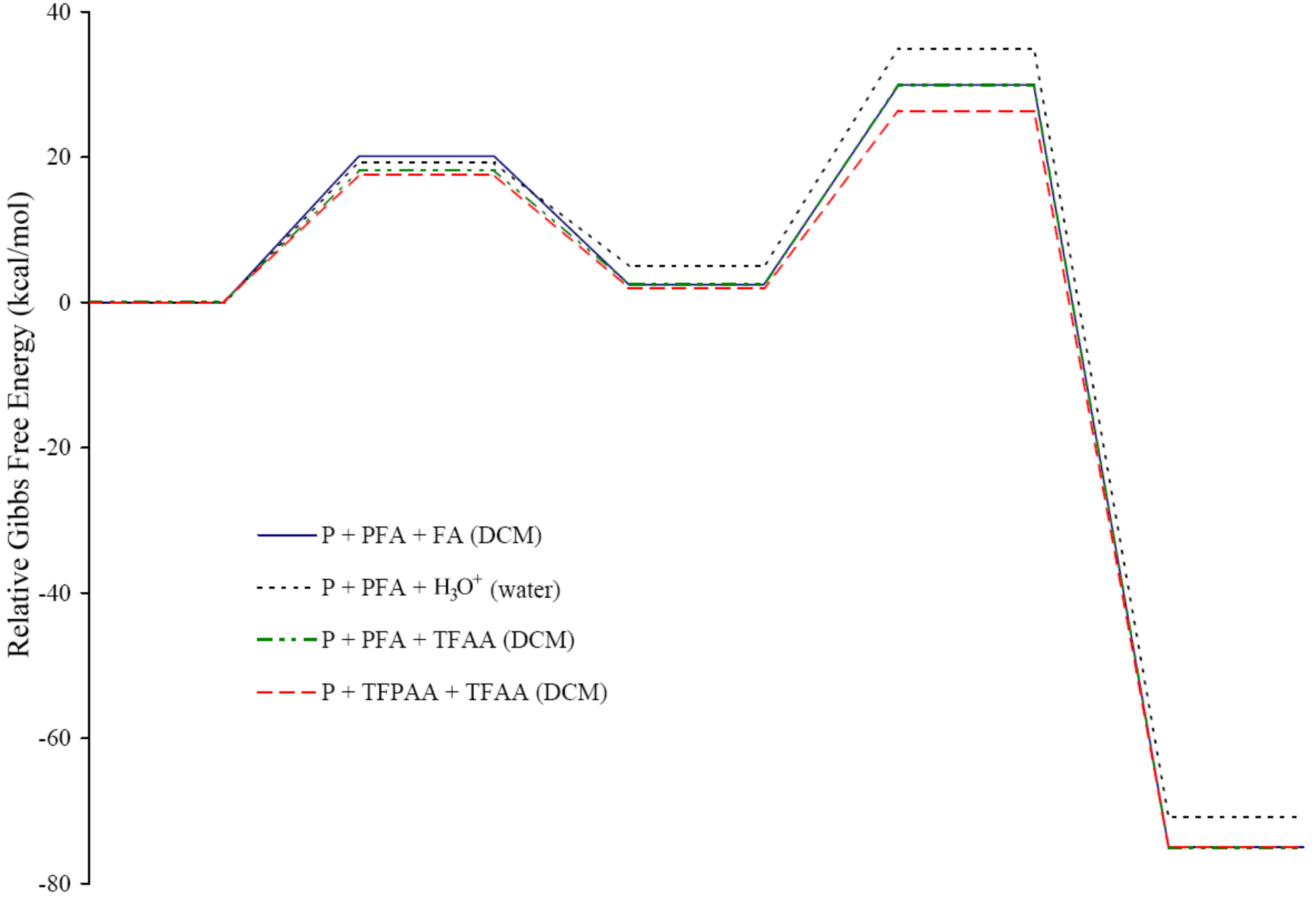
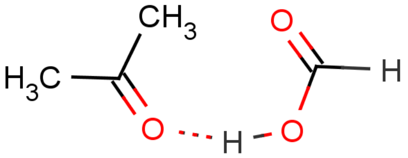


Figure S2 Reaction profile comparison of several BV reactions involving propanone (P), performic acid (PFA), formic acid (FA), trifluoroacetic acid (TFAA) and trifluoroperacetic acid (TFPAA) in dichloromethane (DCM) and water (strong acidic environment). The least energetic reactions pathways are shown relative to the lowest Gibbs free energy starting point in each case. Level of theory: MPWB1K/6-311++G(d,p)-IEF-PCM.

Cartesian coordinates of some stationary points at the MPWB1K/6-311++g(d,p)-IEF-PCM (radii=uahf) level of theory.

(a) **RC** (reactant complex) in dichloromethane (DCM) and water.

RC – DCM



6	-1.570528	-0.059516	0.014649
6	-1.230309	1.374096	0.235021
6	-3.009710	-0.403783	-0.160903
8	-0.720505	-0.920031	-0.016701
1	-1.503235	1.633229	1.257214
1	-0.170802	1.543578	0.091924
1	-1.816101	2.013107	-0.419121
1	-3.614070	0.086357	0.597293
1	-3.343084	-0.023527	-1.124888
1	-3.152391	-1.475882	-0.127591
1	0.996362	-0.924922	0.101951
8	1.955442	-1.113013	0.184802
6	2.666051	-0.034754	-0.020910
8	2.232215	1.050656	-0.274842
1	3.733081	-0.249085	0.070001

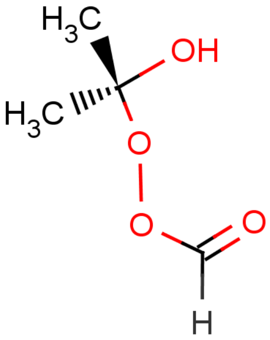
RC – Water

6	1.654631	1.342453	0.479373
6	1.625534	-0.048847	-0.049582
8	0.611547	-0.545622	-0.491825
6	2.900079	-0.815246	-0.016054
8	-1.822098	0.538094	-0.789760
6	-2.760038	0.078723	-0.002339
8	-2.610223	-0.755266	0.844448
1	2.232641	1.958976	-0.208402
1	0.656097	1.751249	0.574840
1	2.168395	1.370354	1.437002
1	3.717308	-0.209051	-0.399096
1	3.136164	-1.045376	1.022529
1	2.809737	-1.735525	-0.579596
1	-0.955539	0.111105	-0.605880
1	-3.719845	0.558120	-0.212687

(b) Criegee intermediate in dichloromethane (DCM) and water.

Criegee – DCM

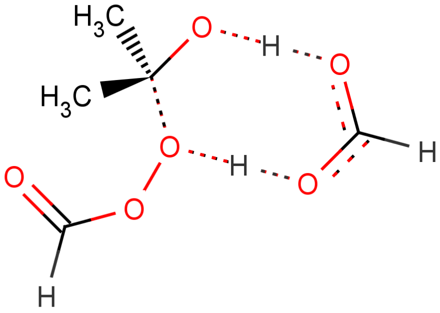
6	-1.073317	-0.060691	0.058277
6	-1.882455	-1.256522	-0.360768
6	-1.670642	1.253234	-0.379536
8	0.174334	-0.285234	-0.607901
8	-0.892144	-0.116770	1.425420
1	-1.408399	-2.161531	0.001704
1	-2.873445	-1.177469	0.071362
1	-1.966663	-1.299627	-1.440497
1	-1.759455	1.284867	-1.459830
1	-2.655854	1.364572	0.060492
1	-1.049198	2.084295	-0.059355
1	-0.593539	0.733450	1.744739
8	1.033494	0.761573	-0.240488
6	2.260497	0.316294	0.039717
1	2.856423	1.195571	0.299404
8	2.640019	-0.801820	0.002449



Criegee – Water

6	-1.045759	-0.064519	0.066035
6	-1.881643	-1.212622	-0.428152
6	-1.685811	1.282028	-0.151986
8	0.141377	-0.184962	-0.737989
8	-0.731567	-0.286807	1.389778
1	-1.373994	-2.150261	-0.226712
1	-2.831495	-1.203327	0.095856
1	-2.064124	-1.120293	-1.493387
1	-1.883101	1.438006	-1.207505
1	-2.623128	1.324040	0.393743
1	-1.037703	2.077222	0.205895
1	-0.438944	0.531718	1.809405
8	1.037005	0.813719	-0.330389
6	2.216133	0.308843	0.037771
1	2.849871	1.157565	0.315808
8	2.526323	-0.834081	0.049211

(c) **TS1** in dichloromethane (DCM), DMSO, ethanol and water.



TS1 – DCM

6	-1.371691	1.915845	-0.281550
6	-0.009718	1.390916	-0.057869
8	0.678565	1.179740	-1.103442
6	0.659482	1.646116	1.241799
8	-0.497297	-0.469018	0.482251
8	-1.126086	-1.102177	-0.586043
6	-2.440547	-1.225414	-0.390628
8	-3.059386	-0.826156	0.534563
8	1.619425	-1.589566	0.596623
6	2.647311	-1.142110	0.034706
8	2.747266	-0.085459	-0.599658
1	3.544119	-1.759535	0.134638
1	1.583254	0.725988	-0.895231
1	0.506351	-0.995162	0.514967
1	-2.007233	1.725623	0.572917
1	-1.284407	2.991251	-0.428972
1	-1.794828	1.484261	-1.180841
1	-0.019384	1.463571	2.064620
1	1.559140	1.053460	1.352224
1	0.941641	2.698035	1.250704
1	-2.837558	-1.758519	-1.258113

TS1 – DMSO

6	-1.375602	1.917167	-0.278514
6	-0.012540	1.395397	-0.056932
8	0.673853	1.183561	-1.104583
6	0.659411	1.652750	1.240237
8	-0.495131	-0.468099	0.481897
8	-1.123388	-1.096911	-0.589505
6	-2.436862	-1.227189	-0.393099
8	-3.054059	-0.841300	0.539332
8	1.618470	-1.592681	0.596387
6	2.647480	-1.144234	0.035460
8	2.746327	-0.088470	-0.599474
1	3.544273	-1.761391	0.137644
1	1.576543	0.733055	-0.898016
1	0.510457	-0.995707	0.513765
1	-2.008766	1.725849	0.577528
1	-1.290470	2.992995	-0.424900
1	-1.799876	1.485427	-1.177260
1	-0.017349	1.471439	2.065081
1	1.560611	1.062192	1.349805
1	0.939439	2.705408	1.246555
1	-2.834761	-1.751420	-1.265558

TS1 – Ethanol

6	-1.342480	1.973244	-0.271438
6	0.007877	1.423792	-0.050108
8	0.689187	1.198289	-1.101857
6	0.686599	1.666172	1.244172
8	-0.505856	-0.439927	0.475367
8	-1.133437	-1.042290	-0.612188
6	-2.438486	-1.224785	-0.405727
8	-3.049823	-0.911679	0.559526
8	1.572331	-1.624462	0.591726
6	2.617169	-1.199549	0.035505
8	2.740379	-0.142763	-0.591817
1	3.496778	-1.842860	0.137032
1	1.575401	0.735577	-0.895595
1	0.495672	-0.993153	0.510335
1	-1.966179	1.837738	0.602599
1	-1.224682	3.041342	-0.456654
1	-1.794194	1.526316	-1.149962
1	0.010906	1.485523	2.071255
1	1.586516	1.072324	1.347872
1	0.970671	2.719092	1.253521
1	-2.837195	-1.712486	-1.300887

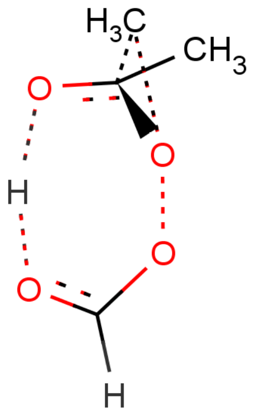
TS1 – Water

6	-1.344898	1.976993	-0.268313
6	0.006571	1.429870	-0.050383
8	0.683662	1.199547	-1.104037
6	0.689870	1.675207	1.240406
8	-0.504713	-0.437534	0.480130
8	-1.127955	-1.040960	-0.609645
6	-2.432390	-1.229631	-0.407886
8	-3.047849	-0.922633	0.557137
8	1.570766	-1.624772	0.597344
6	2.614370	-1.202976	0.034813
8	2.735601	-0.149050	-0.596768
1	3.493116	-1.847707	0.135392
1	1.569047	0.738338	-0.899385
1	0.500477	-0.992126	0.516765
1	-1.964751	1.843031	0.608890
1	-1.228567	3.044960	-0.455967
1	-1.799893	1.527268	-1.143966
1	0.016956	1.496906	2.070322
1	1.591078	1.082898	1.342890
1	0.972354	2.728748	1.245707
1	-2.827062	-1.715878	-1.305759

(d) **TS2** in DCM, DMSO, ethanol and water.

TS2 – DCM

6	1.940877	-0.783382	-0.959785
6	0.913679	-0.001956	0.200740
8	0.245107	0.164264	-0.894558
6	1.640946	1.155047	0.800854
8	0.440031	-0.873898	1.073731
8	-1.385737	1.069627	-0.482480
6	-2.228038	0.210673	-0.110813
8	-2.012268	-0.914954	0.328701
1	0.890398	1.777943	1.279958
1	2.153470	1.733895	0.043277
1	2.339479	0.809439	1.553247
1	-0.490165	-1.096616	0.786819
1	1.454217	-1.634472	-1.407255
1	2.379173	-0.094035	-1.661623
1	2.641297	-1.090957	-0.187474
1	-3.269719	0.552198	-0.196084



TS2 – DMSO

6	1.944856	-0.776864	-0.960294
6	0.916143	-0.003473	0.198337
8	0.241992	0.166490	-0.893293
6	1.640074	1.152849	0.803944
8	0.443490	-0.880171	1.070165
8	-1.385074	1.070138	-0.477844
6	-2.230391	0.212602	-0.108186
8	-2.018007	-0.916725	0.322731
1	0.889269	1.769661	1.290494
1	2.148216	1.737990	0.048204
1	2.343468	0.804696	1.550665
1	-0.483031	-1.105619	0.781493
1	1.460688	-1.625299	-1.415733
1	2.383796	-0.081245	-1.655648
1	2.644709	-1.089575	-0.189215
1	-3.270413	0.560852	-0.187136

TS2 – Ethanol

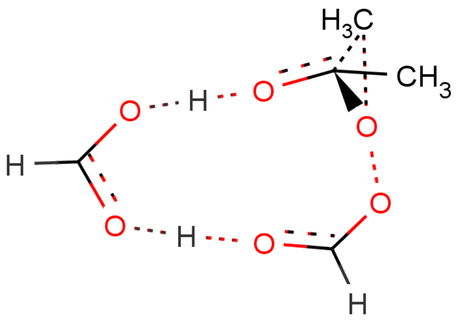
6	1.953319	-0.768466	-0.957873
6	0.923520	-0.004882	0.192078
8	0.231403	0.163063	-0.889133
6	1.638518	1.156040	0.798893
8	0.457823	-0.886586	1.071359
8	-1.384233	1.068534	-0.470008
6	-2.239066	0.217104	-0.100593
8	-2.032561	-0.920771	0.308763
1	0.887728	1.760158	1.303074
1	2.129670	1.752219	0.039463
1	2.358418	0.808726	1.531440
1	-0.454593	-1.133717	0.779438
1	1.472794	-1.615419	-1.423083
1	2.389737	-0.062372	-1.645911
1	2.654186	-1.086609	-0.187572
1	-3.275140	0.584320	-0.159720

TS2 – Water

6	1.952659	-0.777465	-0.951842
6	0.925145	-0.003280	0.191108
8	0.228257	0.154286	-0.888759
6	1.640473	1.163628	0.785793
8	0.461209	-0.876203	1.081341
8	-1.383326	1.065663	-0.473790
6	-2.240504	0.218212	-0.099070
8	-2.036746	-0.920450	0.308546
1	0.891065	1.771027	1.288218
1	2.128172	1.753503	0.019163
1	2.364127	0.822943	1.517822
1	-0.444756	-1.137896	0.787529
1	1.471834	-1.630023	-1.406605
1	2.386122	-0.077984	-1.648604
1	2.656525	-1.086099	-0.180136
1	-3.274879	0.591594	-0.152031

(e) **TS2(cat)** in DCM, DMSO, ethanol and water.

TS2(cat) – DCM



6	1.166699	-1.846060	-0.956312
6	1.434707	-0.506924	0.143183
8	0.797875	0.056184	-0.829567
6	2.900752	-0.283000	0.287570
8	0.816439	-0.686540	1.295315
8	0.897770	1.937475	-0.449892
6	-0.131514	2.408736	0.089651
8	-1.192407	1.851377	0.348535
8	-2.705020	0.022755	-0.569354
6	-2.566614	-1.138887	-0.030317
8	-1.676217	-1.476477	0.713928
1	3.021858	0.689227	0.755498
1	3.384833	-0.270773	-0.680037
1	3.338184	-1.041593	0.924683
1	-0.145922	-0.785485	1.152172
1	0.124382	-2.034721	-1.149719
1	-2.012231	0.670434	-0.245876
1	1.780380	-1.761171	-1.836628
1	1.561020	-2.550602	-0.228360
1	-3.358702	-1.828818	-0.323929
1	-0.025511	3.472118	0.357838

TS2(cat) – DMSO

6	1.161602	-1.849220	-0.949917
6	1.432751	-0.509306	0.140189
8	0.792765	0.057875	-0.828969
6	2.899537	-0.286937	0.281085
8	0.816788	-0.683725	1.296171
8	0.895620	1.936193	-0.452827
6	-0.129566	2.409490	0.093094
8	-1.191156	1.854101	0.354656
8	-2.689700	0.019410	-0.585046
6	-2.562241	-1.138957	-0.034190
8	-1.685432	-1.468562	0.729298
1	3.024294	0.683265	0.752257
1	3.380862	-0.273558	-0.687941
1	3.337571	-1.048877	0.913863
1	-0.145370	-0.783076	1.155552
1	0.118501	-2.037555	-1.140018
1	-2.002259	0.667097	-0.252723
1	1.772239	-1.767015	-1.832730
1	1.558083	-2.553682	-0.222733
1	-3.348873	-1.831045	-0.336917
1	-0.018630	3.471689	0.363546

TS2(cat) – Ethanol

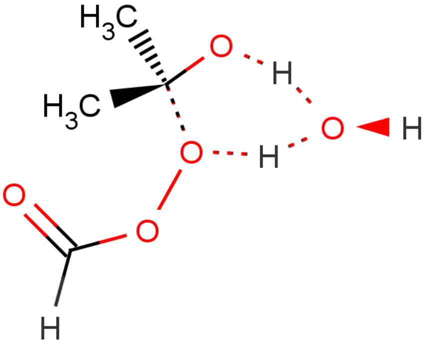
6	1.126705	-1.855352	-0.940166
6	1.421784	-0.522422	0.133451
8	0.776102	0.064924	-0.822016
6	2.893505	-0.322373	0.259285
8	0.816194	-0.677793	1.302711
8	0.905897	1.933745	-0.453132
6	-0.111974	2.418211	0.100615
8	-1.175649	1.867025	0.365132
8	-2.645782	0.018011	-0.622435
6	-2.553922	-1.131778	-0.041799
8	-1.710802	-1.445786	0.765436
1	3.041359	0.631188	0.759096
1	3.360397	-0.289845	-0.717221
1	3.328760	-1.110807	0.862439
1	-0.147442	-0.769751	1.176027
1	0.084673	-2.012730	-1.165781
1	-1.970268	0.664303	-0.270042
1	1.765336	-1.791481	-1.805927
1	1.476343	-2.574434	-0.200874
1	-3.333946	-1.824854	-0.363379
1	0.010515	3.479694	0.371786

TS2(cat) – Water

6	1.134782	-1.856185	-0.940241
6	1.422176	-0.525127	0.132890
8	0.780304	0.066132	-0.823580
6	2.892888	-0.322585	0.267581
8	0.810098	-0.681244	1.299740
8	0.907929	1.932717	-0.457491
6	-0.107511	2.418968	0.099792
8	-1.170069	1.868384	0.370165
8	-2.652826	0.024164	-0.617123
6	-2.560945	-1.129872	-0.044001
8	-1.715168	-1.448937	0.758443
1	3.036978	0.629858	0.770754
1	3.365065	-0.287872	-0.706388
1	3.325672	-1.112363	0.870857
1	-0.152238	-0.776024	1.166630
1	0.093526	-2.015030	-1.170304
1	-1.973436	0.665440	-0.265221
1	1.777040	-1.790303	-1.803322
1	1.483164	-2.575973	-0.200745
1	-3.343161	-1.819822	-0.367043
1	0.016910	3.481170	0.367429

(f) **TS1(H_2O)**, **TS2(cat)(H_2O)** and **TS2(cat)($2H_2O$)** in water.

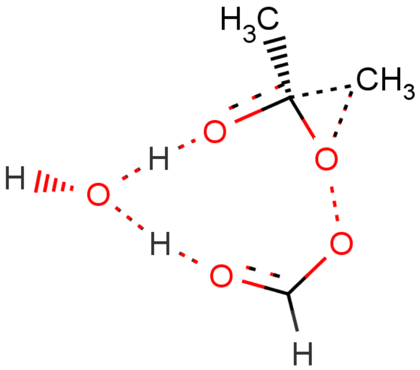
TS1(H_2O)



6	1.107015	0.864371	-0.177607
6	1.675046	0.939817	1.186332
6	0.172693	1.914129	-0.624708
8	1.604816	0.114809	-1.046331
8	-0.377644	-0.669808	0.642993
8	-1.281369	-0.930403	-0.397614
6	-2.430609	-0.307596	-0.274526
8	-2.762494	0.432206	0.601982
1	-3.054417	-0.584403	-1.131389
1	-0.468456	2.239647	0.184295
1	-0.408273	1.562282	-1.469620
1	0.772638	2.764507	-0.953837
1	0.913752	1.203460	1.909254
1	2.420132	1.738096	1.164848
1	2.175578	0.022253	1.473139
1	0.675112	-1.630522	0.353427
1	1.832642	-0.929791	-0.602497
8	1.548063	-2.009888	-0.073924
1	2.145455	-2.345177	0.598582

G_{aq} = -534.255842 au

TS2(cat)(H_2O)

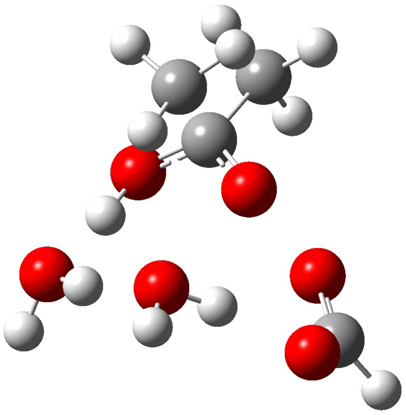


6	1.789791	0.805455	1.183964
6	1.211748	-0.133672	-0.157148
8	0.258227	-0.300950	0.705448
6	2.146086	-1.260149	-0.436263
8	0.986568	0.644505	-1.205306
8	-0.974010	-1.545333	-0.029429
6	-2.150959	-1.092156	0.001860
8	-2.522504	0.043228	0.266119
8	-0.912474	2.164439	-0.249767
1	1.622627	-1.951977	-1.091439
1	2.413428	-1.771111	0.480677
1	3.034156	-0.896540	-0.940087
1	0.275487	1.292895	-0.979621
1	1.143264	1.649518	1.367965
1	2.021195	0.210737	2.052928
1	2.682897	1.098697	0.633894
1	-2.905442	-1.856744	-0.250661
1	-1.524548	1.456370	0.019650
1	-1.429514	2.804179	-0.744302

G_{aq} = -534.257443 au

TS2(cat)(2H_2O)

6	1.387464	0.922114	1.389970
6	1.452697	-0.133056	0.006034
8	0.281487	-0.397569	0.493837
6	2.560248	-1.114757	0.185083
8	1.534197	0.547982	-1.125419
8	-0.432670	-1.819550	-0.543180
6	-1.681618	-1.867198	-0.379339
8	-2.395260	-1.104373	0.257339
1	2.444472	-1.872711	-0.585490
1	2.502474	-1.583678	1.159458
1	3.519365	-0.626249	0.056474
1	0.765115	1.161300	-1.221536
1	0.525149	1.572778	1.397160
1	1.527590	0.363334	2.301125
1	2.284479	1.451030	1.072043
1	-2.143700	-2.727015	-0.894784
8	-1.930753	1.525123	0.888894
1	-2.795999	1.885724	1.090907
1	-2.060970	0.575147	0.731714
8	-0.418735	2.300977	-1.199064
1	-1.061027	2.103663	-0.493690
1	-0.925808	2.433341	-2.003114

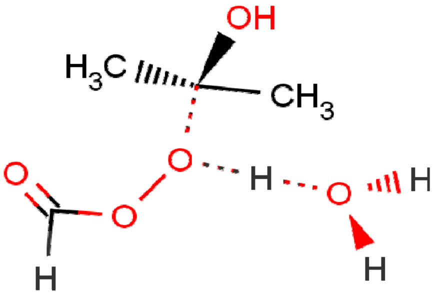


G_{aq} = -610.670418 au

(g) **TS1(H_2O-i)**, **TS1($2H_2O$-i), TS2(i)** and **TS2(H_2O-i)** in water.

TS1(H_2O-i)

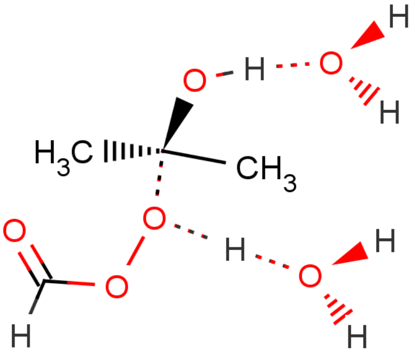
6	-1.314644	-0.711284	0.085786
6	-0.761966	-1.954179	-0.493248
8	-1.324018	-0.714238	1.380013
6	-2.363037	0.029748	-0.651239
8	0.084360	0.424671	-0.351426
8	1.188712	0.109223	0.432908
6	2.213106	-0.286266	-0.360267
8	3.235665	-0.604403	0.135238
1	1.959001	-0.261794	-1.424271
1	0.091626	-2.296380	0.082092
1	-1.542646	-2.710283	-0.419297
1	-0.505303	-1.818286	-1.536895
1	-2.060456	0.206884	-1.677210
1	-2.612659	0.965607	-0.158697
1	-3.250297	-0.602763	-0.658969
1	-0.067405	1.483806	-0.181676
8	-0.149580	2.797319	-0.003352
1	-0.675797	3.127332	0.755163
1	-1.846014	0.012664	1.773649
1	-0.411920	3.324521	-0.787115



G_{aq} = -534.708161 au

TS1(2H$_2$O-i)

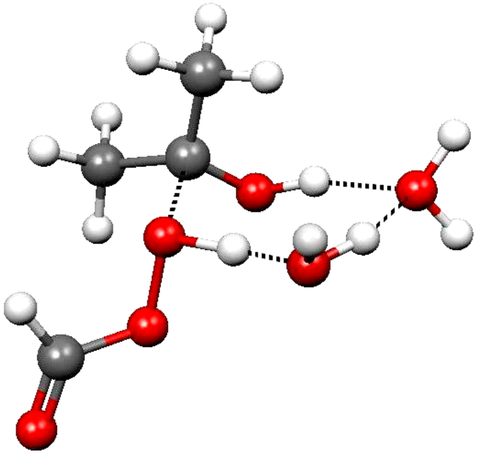
6	0.576241	-1.132512	0.146872
6	-0.423877	-2.225776	0.154132
8	1.010440	-0.835049	-1.035605
6	1.499868	-1.002656	1.303938
8	-0.504655	0.248994	0.603316
8	-1.399394	0.495064	-0.434034
6	-2.665457	0.296958	0.000899
8	-3.564156	0.453388	-0.748328
1	-2.711069	0.000381	1.052994
1	-1.110117	-2.119141	-0.679366
1	0.122238	-3.158309	0.023133
1	-0.957090	-2.264208	1.096908
1	0.952815	-1.054135	2.238492
1	2.076952	-0.086009	1.249253
1	2.186991	-1.846281	1.259715
1	0.053907	1.202735	0.706466
8	0.752534	2.276697	0.831831
1	0.608757	2.735631	1.688602
1	1.816203	-0.258176	-1.028703
1	0.596244	2.944657	0.128759
8	3.132695	0.668351	-1.038213
1	3.078454	1.547398	-1.425587
1	3.945357	0.279805	-1.377447



E_{aq} = -611.068180 au; H_{aq} = -611.067236 au; G_{aq} = -611.124727 au

TS1(2H$_2$O-i) – Another version that is less favoured

6	0.734753	2.167331	-0.190903
1	1.338727	2.228654	0.706980
1	1.326294	1.846676	-1.041413
1	0.333936	3.155678	-0.409777
6	-0.422794	1.266355	0.004294
6	-1.254736	1.429447	1.224005
1	-1.993138	0.640017	1.320940
1	-0.633838	1.471055	2.111525
1	-1.779700	2.378343	1.123591
8	-0.999111	0.917634	-1.104262
1	-1.835396	0.425219	-0.961554
1	-0.263901	-1.046606	0.713345
8	0.445446	-0.231748	0.550336
8	1.246747	-0.696119	-0.489343
6	2.540529	-0.725550	-0.086886
1	2.670739	-0.396117	0.948196
8	3.369435	-1.085402	-0.845267
8	-1.131551	-2.030097	0.835079
1	-1.996942	-1.830717	0.453235
1	-1.270367	-2.373933	1.743852
8	-3.059196	-0.733038	-0.685677
1	-3.905045	-0.428534	-0.333496
1	-3.276228	-1.212425	-1.495757

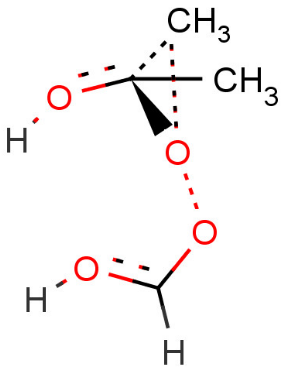


E_{aq} = -611.062498 au; H_{aq} = -611.061554 au; G_{aq} = -611.117302 au

TS2(i)

6	-1.722419	1.463573	-0.233405
6	-1.181465	-0.065832	0.063349
8	0.022030	0.460976	-0.038815
6	-1.626604	-0.999994	-1.016418
8	-1.546363	-0.504948	1.278733
8	1.198564	-0.869700	0.081674
6	2.345912	-0.447541	0.020372
8	2.618893	0.789495	-0.109089
1	-1.107680	-1.943633	-0.872939
1	-1.382767	-0.595300	-1.991247
1	-2.694860	-1.166379	-0.938195
1	-1.136295	0.029117	1.981672
1	-1.369019	2.171404	0.504383
1	-1.517952	1.768697	-1.248191
1	-2.779280	1.248427	-0.076936
1	3.162290	-1.173853	0.079727
1	3.588022	0.953695	-0.141686

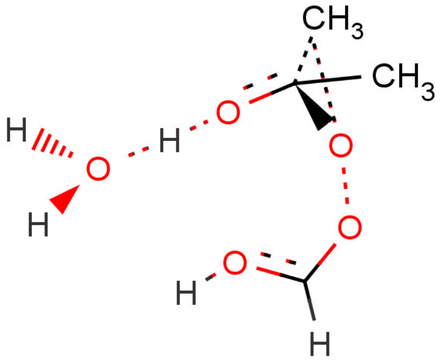
G_{aq} = -458.261784 au



TS2(H_2O-i)

6	1.500614	-0.493679	1.461579
6	0.884079	-0.742773	-0.043024
8	-0.211302	-0.169909	0.435815
6	0.803956	-2.203407	-0.354437
8	1.556330	-0.061461	-0.976895
8	-1.446366	-0.233958	-0.830384
6	-2.524903	0.168401	-0.413368
8	-2.694076	0.573118	0.781943
8	1.628443	2.477883	-0.180609
1	0.234311	-2.316725	-1.272776
1	0.308132	-2.737244	0.447561
1	1.801350	-2.600213	-0.505020
1	1.572005	0.893584	-0.759800
1	1.530853	0.558111	1.707706
1	1.007595	-1.095159	2.210005
1	2.503022	-0.863311	1.246798
1	-3.370866	0.175284	-1.107288
1	2.452190	2.970136	-0.241366
1	0.935046	3.100218	-0.417843
1	-3.620351	0.858691	0.948555

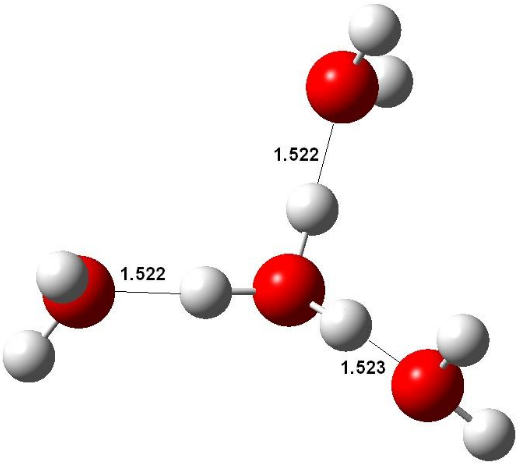
G_{aq} = -534.676929 au



(h) Solvated hydronium cluster $H_3O^+(H_2O)_3$

8	0.003917	-0.012027	-0.531741
1	-0.731317	-0.636138	-0.242317
1	0.916428	-0.323366	-0.240590
1	-0.177145	0.940961	-0.261144
8	2.332120	-0.728912	0.145259
1	2.489814	-1.119087	1.011235
1	2.842630	-1.248584	-0.484467
8	-1.903153	-1.530489	0.138750
1	-1.917698	-1.943082	1.008751
1	-2.174974	-2.208725	-0.488485
8	-0.389410	2.392541	0.145772
1	-0.804901	2.987071	-0.487610
1	-0.790622	2.582044	1.000305

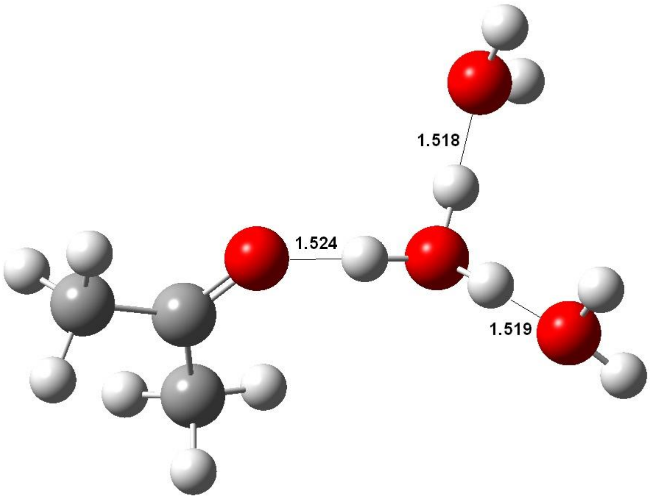
G_{aq} = -306.100415 au



(i) Solvated complex between the hydronium ion and propanone H_3O^+(Propanone)$(H_2O)_2$

6	-2.009805	-0.036911	-0.075808
6	-2.095768	0.218441	1.384708
1	-2.439489	1.242948	1.527973
1	-2.841122	-0.430861	1.836511
1	-1.136923	0.090551	1.872602
6	-3.280660	-0.164131	-0.829483
1	-3.750094	-1.106387	-0.546659
1	-3.968937	0.628402	-0.546638
1	-3.098873	-0.155009	-1.896741
8	-0.940701	-0.138616	-0.650024
8	1.369401	0.006861	0.377911
1	1.845559	0.850747	0.099227
1	1.916200	-0.820515	0.195411
1	0.443752	-0.053083	-0.018991
8	2.684864	-2.110836	-0.028148
1	3.142552	-2.242284	-0.865272
1	3.289178	-2.404721	0.661731
8	2.498269	2.173258	-0.262876
1	2.979570	2.242994	-1.094196
1	3.041375	2.607476	0.403633

G_{aq} = -422.725843 au



(j) Protonated Criegee intermediate in water.

6	1.881171	1.309413	-0.328760
6	1.152786	0.055863	0.069298
8	1.059581	-0.004107	1.431012
6	1.699584	-1.197822	-0.553742
8	-0.176236	0.339282	-0.480281
8	-0.996413	-0.761884	-0.171667
6	-2.196110	-0.434359	0.028922
8	-2.570212	0.752637	-0.037030
1	1.428575	2.170251	0.152224
1	2.909991	1.218394	0.003720
1	1.866110	1.438573	-1.405406
1	1.688007	-1.118379	-1.635490
1	2.723126	-1.333786	-0.219070
1	1.118903	-2.066183	-0.253350
1	0.906596	-0.909419	1.735062
1	-2.858242	-1.271970	0.251020
1	-3.541409	0.866520	0.140697

G_{aq} = -458.280070 au

(k) Protonated ester in water.

6	-0.453113	0.050456	-0.009266
8	-0.419446	1.315912	-0.002725
8	0.559253	-0.698593	-0.010070
6	1.906164	-0.187461	0.006327
1	2.535541	-1.064565	0.003486
1	2.071704	0.407267	-0.886882
1	2.056771	0.390952	0.912813
6	-1.773419	-0.580569	0.001198
1	-2.419427	-0.072256	-0.707880
1	-1.688573	-1.635698	-0.220271
1	-2.193859	-0.442844	0.997600
1	0.441593	1.784047	0.013944

G_{aq} =-268.673593 au

(l) Protonated propanone in the gas phase (MPWB1K/6-311G(d,p))

6	-1.335693	-0.529635	-0.008408
6	-0.005290	0.062156	-0.000389
6	1.212487	-0.743958	0.006881
8	0.038128	1.322200	-0.005246
1	-1.348458	-1.450705	-0.581304
1	-1.556847	-0.803961	1.027644
1	-2.084972	0.174071	-0.346299
1	1.081408	-1.623103	0.629931
1	1.351903	-1.110187	-1.013894
1	2.094738	-0.188019	0.303855
1	0.928183	1.692932	0.033526

G_{gas} =-193.354292 au

Cartesian coordinates of some stationary points calculated in water at the MPWB1K/ 6-311++G(d,p)-CPCM (radii=uahf) level of theory.

(a) Solvated hydronium cluster $H_3O^+(H_2O)_3$

O	-0.00477200	-0.00504900	-0.52055100
H	-0.92821000	-0.28882500	-0.23678000
H	0.70691400	-0.65899700	-0.23707600
H	0.21120000	0.93703000	-0.23630400
O	1.84301800	-1.59831500	0.14315500
H	1.79893600	-2.06966600	0.98189000
H	2.13744500	-2.23850800	-0.51338700
O	-2.35792400	-0.65633100	0.13924200
H	-2.52549400	-1.06657000	0.99431500
H	-2.88186500	-1.14546600	-0.50399800
O	0.60696200	2.35698400	0.13994100
H	0.39562400	3.06343300	-0.47965500
H	0.38718600	2.68926700	1.01670300

G_{aq} = -306.100195 au

(b) TS1

C	-1.34749700	1.97555300	-0.26725700
C	0.00464000	1.42969200	-0.05065700
O	0.68042100	1.19877700	-1.10501800
C	0.68942600	1.67652000	1.23899700
O	-0.50398700	-0.43834200	0.48177500
O	-1.12561300	-1.04344100	-0.60800900
C	-2.43034800	-1.23152700	-0.40802800
O	-3.04711900	-0.92261400	0.55560000
O	1.57317300	-1.62240200	0.59967800
C	2.61555200	-1.20053200	0.03475500
O	2.73447500	-0.14780000	-0.59917600
H	3.49519300	-1.84403800	0.13545600
H	1.56642600	0.73880200	-0.90111100
H	0.50236700	-0.99138400	0.51880100
H	-1.96603100	1.84202700	0.61093200
H	-1.23199900	3.04345800	-0.45594700
H	-1.80342800	1.52485700	-1.14194100
H	0.01774800	1.49822000	2.06993000
H	1.59139000	1.08522700	1.34071100
H	0.97076200	2.73039900	1.24316000
H	-2.82386700	-1.71923100	-1.30564100

G_{aq} = -647.584768 au

(c) TS1(H_2O-i)

C	-1.31537500	-0.71184900	0.08587200
C	-0.76353800	-1.95366700	-0.49611800
O	-1.32223700	-0.71641100	1.37989500
C	-2.36400500	0.03131800	-0.64850900
O	0.08503500	0.42532000	-0.35201000
O	1.18908100	0.10950100	0.43263900
C	2.21353500	-0.28621500	-0.35998000
O	3.23590000	-0.60469000	0.13601300
H	1.95997500	-0.26167400	-1.42412500
H	0.09107300	-2.29670000	0.07720800
H	-1.54408200	-2.70994600	-0.42211500
H	-0.50858300	-1.81593400	-1.53994900
H	-2.06193000	0.21104900	-1.67417800
H	-2.61314000	0.96584900	-0.15314900
H	-3.25132500	-0.60113900	-0.65734700
H	-0.06657600	1.48532100	-0.18201300
O	-0.14910800	2.79748700	-0.00221000
H	-0.69102300	3.12219300	0.74801800
H	-1.84252000	0.01117600	1.77543800
H	-0.40494000	3.32263400	-0.78999400

G_{aq} = -534.708702 au

(d) TS1(2H_2O-i)

C	0.57897400	-1.13386200	0.14723100
C	-0.41849600	-2.22936700	0.15684400
O	1.01019000	-0.83545200	-1.03591400
C	1.50339900	-0.99951400	1.30301900
O	-0.50615300	0.24636800	0.60459000
O	-1.39913400	0.49236100	-0.43424900
C	-2.66607500	0.29806800	-0.00056200
O	-3.56341000	0.45421400	-0.75163200
H	-2.71392200	0.00465500	1.05234400
H	-1.10712800	-2.12408000	-0.67486300
H	0.12957500	-3.16057200	0.02426700
H	-0.94921200	-2.26906900	1.10094500
H	0.95753100	-1.05279800	2.23818100
H	2.07591900	-0.08010400	1.24710200
H	2.19412400	-1.84019200	1.25836400
H	0.05173400	1.19994900	0.71038900
O	0.75122300	2.27312700	0.84113300
H	0.59024400	2.73864200	1.69160700
H	1.81411100	-0.25578800	-1.03071100
H	0.60900400	2.93605000	0.13002300
O	3.12655600	0.67562900	-1.04465500
H	3.06693300	1.55235000	-1.43678900
H	3.94008900	0.28903200	-1.38424000

G_{aq} = -611.125127 au

(e) TS2

C	1.95265900	-0.77746500	-0.95184200
C	0.92514500	-0.00328000	0.19110800
O	0.22825700	0.15428600	-0.88875900
C	1.64047300	1.16362800	0.78579300
O	0.46120900	-0.87620300	1.08134100
O	-1.38332600	1.06566300	-0.47379000
C	-2.24050400	0.21821200	-0.09907000
O	-2.03674600	-0.92045000	0.30854600
H	0.89106500	1.77102700	1.28821800
H	2.12817200	1.75350300	0.01916300
H	2.36412700	0.82294300	1.51782200
H	-0.44475600	-1.13789600	0.78752900
H	1.47183400	-1.63002300	-1.40660500
H	2.38612200	-0.07798400	-1.64860400
H	2.65652500	-1.08609900	-0.18013600
H	-3.27487900	0.59159400	-0.15203100

G_{aq} = -457.841915 au

(f) TS2(i)

C	-1.72279200	1.46320800	-0.23506200
C	-1.18140900	-0.06569200	0.06381600
O	0.02190400	0.46073900	-0.04203200
C	-1.62904800	-1.00202500	-1.01305100
O	-1.54375400	-0.50203000	1.28095600
O	1.19851000	-0.86990300	0.07958000
C	2.34596800	-0.44762200	0.02029100
O	2.61915000	0.78937000	-0.10883700
H	-1.10993200	-1.94546700	-0.86890400
H	-1.38734500	-0.59930400	-1.98924300
H	-2.69717800	-1.16805200	-0.93212800
H	-1.13175800	0.03379300	1.98176700
H	-1.36847900	2.17210600	0.50127100
H	-1.51967600	1.76664700	-1.25064200
H	-2.77945200	1.24814700	-0.07699800
H	3.16237000	-1.17383800	0.08110300
H	3.58866800	0.95335500	-0.13952600

G_{aq} = -458.262048 au