

Autoxidation of Formaldehyde with Oxygen—A Comparison of Reaction Channels

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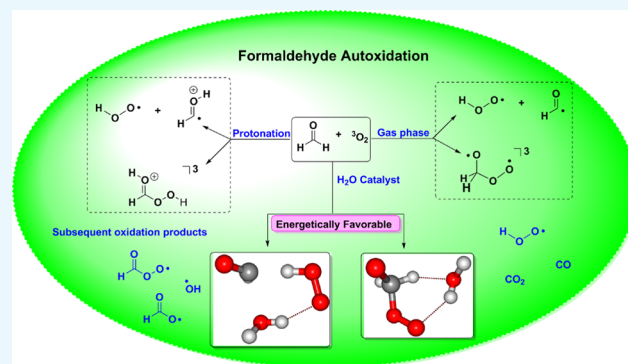


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ABSTRACT: The autoxidation of formaldehyde through initiation by triplet oxygen is studied via two initial steps: (1) H-atom abstraction and (2) $^3\text{O}_2$ addition reaction. The reaction energy profiles show that the reactions are thermodynamically and kinetically demanding. A comparison of the pathways of these initial reactions and the search for a less energy-demanding pathway is presented. The presence of a Brønsted acid has no effect on the energetics of the reaction, while the presence of a single water molecule catalyst enhances the initial reactions. The H-atom abstraction reaction from formaldehyde results in formyl and hydroperoxy radicals. These radicals on further reaction with the second equivalent of $^3\text{O}_2$ lead to a $\text{CO} + 2\text{HO}_2$ product channel. The $^3\text{O}_2$ addition reaction to formaldehyde results in a triplet biradical intermediate which further leads to performic acid, the precursor in the synthesis of carboxylic acids from aldehydes. In the presence of water molecules, performic acid is formed in a single kinetic step, and this leads to a $\text{CO}_2 + \text{OH} + \text{HO}_2$ product channel upon subsequent reaction with $^3\text{O}_2$ in a thermodynamically favorable reaction. The results show that the less established $^3\text{O}_2$ addition reaction to aldehydes is a viable route for autoxidation in the absence of purpose-built initiators, in addition to the well-established H-atom abstraction route.



1. INTRODUCTION

The autoxidation of aldehydes is a well-known reaction that allows the selective generation of acyl radicals by using O_2 as a reagent.^{1,2} This reaction is commonly believed to proceed through a radical chain reaction involving the respective acyl radicals and their hydroperoxy radical analogues as chain-carrying species. The autoxidation of aldehydes in industrial processes is carried out in bulk liquid aldehydes or organic solvents through the introduction of additives into the system.^{3,4} O_2 , being a nonpolar gas, is less soluble in any solvent, and the role of the solvent in the oxidation process is detrimental.² Furthermore, it has been reported that selected aldehydes undergo facile oxidation on stirring their aqueous emulsions in air, leading to carboxylic acids.⁵ How these autoxidation reactions are initiated is much less well known and often attributed to trace impurities present in the substrates or the reaction flask, or external factors such as light. That the mechanisms of initiation are (in the absence of added initiators) unclear is also due to the fact that the direct reaction of (triplet) oxygen with aldehyde substrates is thermochemically quite unfavorable.

Formaldehyde (1) is an important intermediate both in combustion and atmospheric chemistry. It is formed by the partial combustion of alcohols in fossil fuels. In atmospheric chemistry, it is formed by the photo-oxidation of larger organic compounds.⁶ The ambient concentration of O_2 in the air is

about 21%, and for complete combustion to occur, all the fuel molecules require the same amount of oxygen. The solubility of oxygen in water is limited to 5 mL of O_2 L^{-1} water.⁷ Formaldehyde exists usually in the gaseous form and in liquid and vapor states, formaldehyde is very flammable. Hence, the rate of the autoxidation process is determined by the gas phase reaction of formaldehyde with O_2 and depends on the concentration of formaldehyde. Because in the oxidation of several hydrocarbons, formaldehyde is formed as an intermediate. The mechanism by which formaldehyde itself is oxidized in the gas phase is of particular importance in understanding the oxidation of hydrocarbons by O_2 . The oxidation of formaldehyde takes place through a radical chain reaction involving O, H, OH, and HO_2 radicals. The kinetics of these reactions are controlled by the initiation reaction by O_2 and O in the next step, followed by propagation reactions leading to the decomposition of formaldehyde by H and propagation leading to formaldehyde oxidation by OH and H

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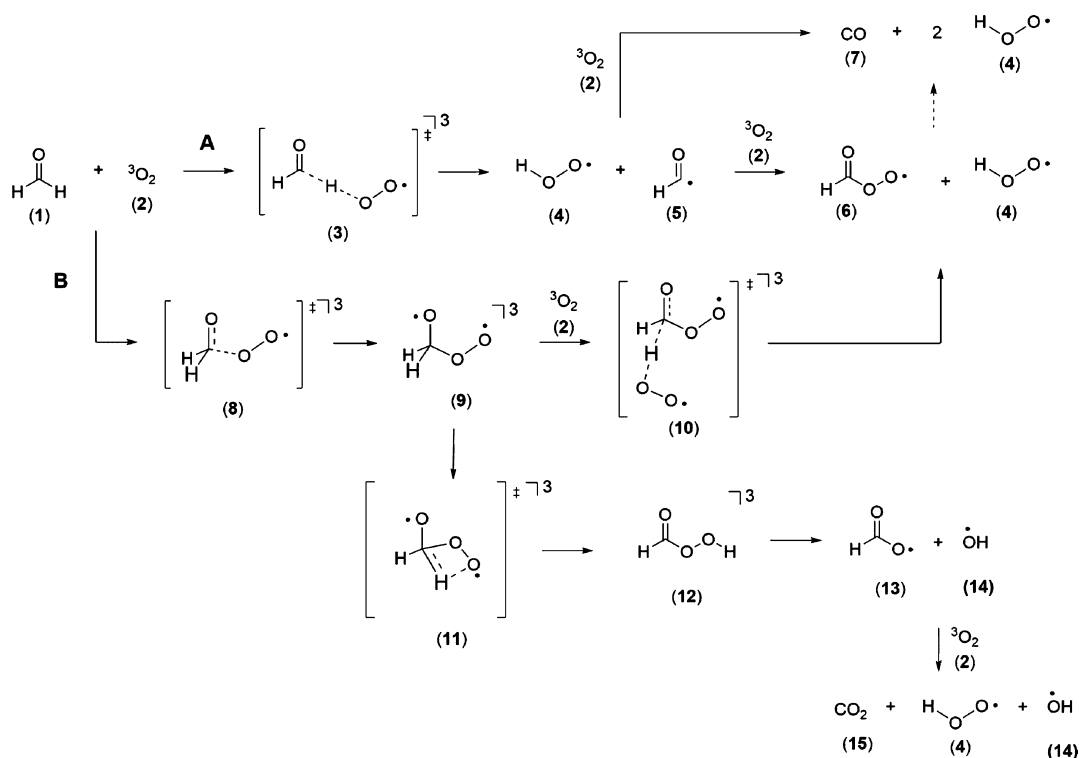


Figure 1. Reaction pathways for the initiation of formaldehyde autoxidation.

radicals and finally radical termination reactions. In the atmospheric processes, the direct reaction of formaldehyde with the OH radical is a competing reaction with an atmospheric half-life of 7.1–7.3 h. In the industrial processes, in the absence of any radical initiators or catalysts, the autoxidation of formaldehyde is initiated by the reaction with O_2 . In the initiation step, formaldehyde readily reacts with O_2 to form performic acid at low temperatures and at high temperatures, formic acid and O atoms are formed, and they play the role of degenerate chain-branching agent.⁸ Thus, O_2 will consume formaldehyde at temperatures exceeding ~ 450 °C through the radical gas phase reactions. Formaldehyde can alone decompose to CO and H_2O at temperatures above 350 °C.⁹ These products are also formed in subsequent propagation and termination steps. Hence, the lifetime of formaldehyde by O_2 in the air is determined by the respective initiation, propagation, and termination steps.

Taking the oxidation of formaldehyde (1) as an example, the reaction with triplet oxygen (2) is assumed to involve hydrogen atom transfer to yield the hydroperoxy radical (4) and formyl radical (5) (Figure 1). Because singlet oxygen is a high-lying excited state, the autoxidation of hydrocarbons with triplet oxygen is of relevance in the atmospheric and combustion processes. The H-atom abstraction reaction between formaldehyde and singlet oxygen requires energy of 64.6 kJ/mol calculated at UM06-2X/6-311++G(d,p), whereas for H-atom abstraction by triplet oxygen, the energy required is 176.1 kJ/mol. This shows that the singlet oxygen is lying ~ 111 kJ/mol higher than the triplet oxygen, and hence the reaction of formaldehyde with triplet oxygen is more likely to occur. Hence, the reaction of formaldehyde with triplet oxygen is being studied. The fate of the formyl radical (5) is largely determined by the competition between its thermal dissociation and reaction with O_2 . The fate of (5) through the reaction with (2) is important for the oxidation rate of formaldehyde, as

observed in other hydrocarbons.¹⁰ Subsequent reaction of (5) with a second equivalent of oxygen then yields the formylperoxy radical (6). In combustion and tropospheric reactions, the radical (6) represents a short-lived intermediate that undergo bimolecular reaction with (4) leading to carbon monoxide (7) and hydroperoxy radical (4). The same reactants (1) and (2) can, in principle, also react through the initial addition of oxygen to the C–O double bond in (1), yielding triplet biradical (9) as the product. Hydrogen abstraction from this adduct by a second oxygen molecule then yields the same two radicals (6) and (4) as before. Furthermore, a rearrangement of an adduct (9) will also lead to performic acid (12) which will homolytically dissociate, leading to radicals (13) and (14). A second oxygen molecule can abstract a H-atom from the radical (13), leading to CO_2 (15) and hydroperoxy and OH radicals.

The reactions shown in Figure 1 play a certain role in combustion reactions,¹¹ and using readily available heats of formation for some of the species,¹² a reaction enthalpy for the formation of (4) + (5) of $\Delta H_{298} = +163.2$ kJ/mol is obtained. The heat of formation of the formylperoxy radical (6) is less well established.^{13–15} Using the value reported in ref 12, yields a reaction energy of $\Delta H_{298} = +18.4$ kJ/mol for the formation of radicals (6) and (4) with respect to formaldehyde (1) and two equivalents of oxygen (2). The formation of carbon monoxide (7) and two hydroperoxy radicals (4) is similarly endothermic at $\Delta H_{298} = +23.1$ kJ/mol.

With this thermochemical background for the initiation of formaldehyde autoxidation, the key question we address in the present study is whether the formation of these final products from formaldehyde and oxygen can also proceed along an energetically less demanding pathway, for example, through the initial formation of an adduct (9) and the subsequent reaction with a second equivalent of oxygen. Furthermore, how far the solvent or medium effects alter the initiation reactions is

Table 1. Relative Enthalpies (ΔH_{298} , in kJ/mol) for All the Minima Shown in Figure 1

system	exp. ¹²	CBS-QB3	G3B3	WIRO	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)	UM06-2X/6-311++G(d,p)
A						
1 + 2	0.0	0.0	0.0	0.0	0.0	0.0
4 + 5	+163.24 ± 0.16	+166.5	+165.2	+163.0	+169.6	+169.0
4 + 6	+18.4 ± 12	+15.1	+17.2	+15.1	+14.7	+23.9
4 + 4 + 7	+23.1 ± 0.16	+25.4	+25.8	+22.1	+22.2	+34.4
B						
1 + 2	0.0	0.0	0.0	0.0	0.0	0.0
9		+174.7	+174.8	+174.6	+183.3	+160.3
4 + 6	+18.4 ± 12	+15.1	+17.2	+15.1	+14.7	+23.9
4 + 4 + 7	+23.1 ± 0.16	+25.4	+25.8	+22.1	+22.2	+34.4
15 + 4 + 14	-234.6 ± 0.09	-234.3	-239.3	-238.0	-234.7	-232.5

explored by considering two scenarios: (a) protic solvation of the reactants, that is, the reaction in water or at least in the presence of a single water molecule; and (b) Lewis/Bronsted acid activation of the reacting formaldehyde. In the most extreme case, this latter effect can be studied using protonated formaldehyde as the reactant, again following the two alternatives shown in Figure 1 of initial hydrogen abstraction or the addition of triplet oxygen. These questions are explored using a combination of theoretical methods suitable for the description of open-shell species.

2. COMPUTATIONAL DETAILS

Quantum mechanical calculations for all the species were performed using a hierarchy of theoretical systems involving hybrid density functional theory (DFT) methods such as B3LYP¹⁶ or M06-2X¹⁷ for geometry optimization and the calculation of thermochemical parameters in combination with 6-31G(d), 6-31+G(d), and 6-311++G(d,p) basis sets. These latter quantities were calculated using the rigid rotor/harmonic oscillator model, but hindered internal rotations required a separate treatment.¹⁸ An unrestricted ansatz was used for the proper treatment of the wave function. Relative energies were subsequently calculated from single point calculations with double hybrid methods such as ROB2-PLYP/cc-pVTZ, coupled-cluster method CCSD(T)/6-311++G(d,p), and compound schemes such as CBS-QB3,¹⁹ G3B3,²⁰ and WIRO.²¹ The results obtained at UM06-2X/6-311++G(d,p) and CCSD(T)//UM06-2X/6-311++G(d,p) levels of theories are discussed in the manuscript, while the results from other levels are given in the Supporting Information. All these calculations were performed using Gaussian 09 program.²²

3. RESULTS AND DISCUSSION

3.1. Thermochemistry and Reaction Mechanism. The reaction pathways shown in Figure 1 involve reactive species with varying degrees of spin character along the potential energy surface (PES) from the reactants to the end products. From the reaction enthalpies collected in Table 1, it is readily seen that calculations with the composite methods CBS-QB3,¹⁹ G3B3,²⁰ and WIRO²¹ reproduce all experimentally known energy data within error limits.^{23,24} According to these results, the thermochemical profile of pathway A is least favorable right at the first step, where the formation of radicals (4) and (5) is endothermic by 166.5 kJ/mol. Starting from the same reactants, the radical adduct (9) is formed in pathway B with a reaction enthalpy of +174.7 kJ/mol, which is 8 kJ/mol less favorable than the maximum in pathway A. The stationary points along the PES of the reaction of formaldehyde with ³O₂

are optimized at the UM06-2X/6-311++G(d,p)¹⁷ level of theory, and single point calculations were performed at the UCCSD(T)/6-311++G(d,p)^{25,26} level on the structures optimized at the UM06-2X/6-311++G(d,p) level. The results obtained at the UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p) level are discussed in the manuscript, and the structural aspects are discussed at the UM06-2X/6-311++G(d,p) level.

The interaction of formaldehyde with ³O₂ initially forms a loosely bound prereactive complex and the H-atom abstraction reaction (path A) proceeds via a high barrier transition state (3) with an energy barrier of 166.5 kJ/mol in a flat PES, resulting in the hydroperoxy radical (4) and formyl radical (5). The addition of a second ³O₂ to (4) + (5) forms CO (7) + 2HO₂ in both concerted and step-wise processes. In the concerted pathway, the H-atom exchange reaction through C–H bond cleavage in (5) forms CO + 2HO₂ through a transition state (16) with an enthalpy barrier of 87.7 kJ/mol. The other pathway involves two steps, where the first step involves the addition of ³O₂ to the formyl radical site, forming the formyl peroxy radical (6) through a tight transition state (17) whose enthalpy barrier is 26.5 kJ/mol higher than the concerted transition state (16). This leads to an intermediate that complexes (6) and (4) with an enthalpy of 20.5 kJ/mol. This complex then undergoes H-atom transfer from the formyl C–H to the peroxy radical site, forming a loosely bound hydroperoxide complex through a transition state (18) with an enthalpy barrier of 92.8 kJ/mol. This hydroperoxide complex undergoes C–O bond cleavage spontaneously forming CO + 2HO₂ products through a product complex (7·4·4), which lies 10 kJ/mol below the isolated products. In (7·4·4), the HO₂ radical pair is strongly bound such that the lifetime of the complex is increased and the radical recombination requires structural changes with a decrease in hydrogen bond strengths. The concerted step is more favorable than the step-wise mechanism for the formation of CO + 2HO₂ products.

The addition of ³O₂ to (1) (path B) occurs through a tight transition state (8), resulting in a triplet biradical (9) with an energy barrier of 24.4 kJ/mol higher than the H-abstraction transition state (3). As shown in Table 1, both the initial steps leading to (4) + (5) and (9) are thermodynamically demanding. The addition of the second ³O₂ to (9) abstracts the H-atom from (9), forming the formyl peroxy radical (6) and HO₂ (4) through a H-abstraction transition state (10). The associated enthalpy barrier with respect to (1) + (2) is 180.2 kJ/mol. The radical pair (6) and (4) then leads to the CO (7) + 2HO₂ product channel as described above.

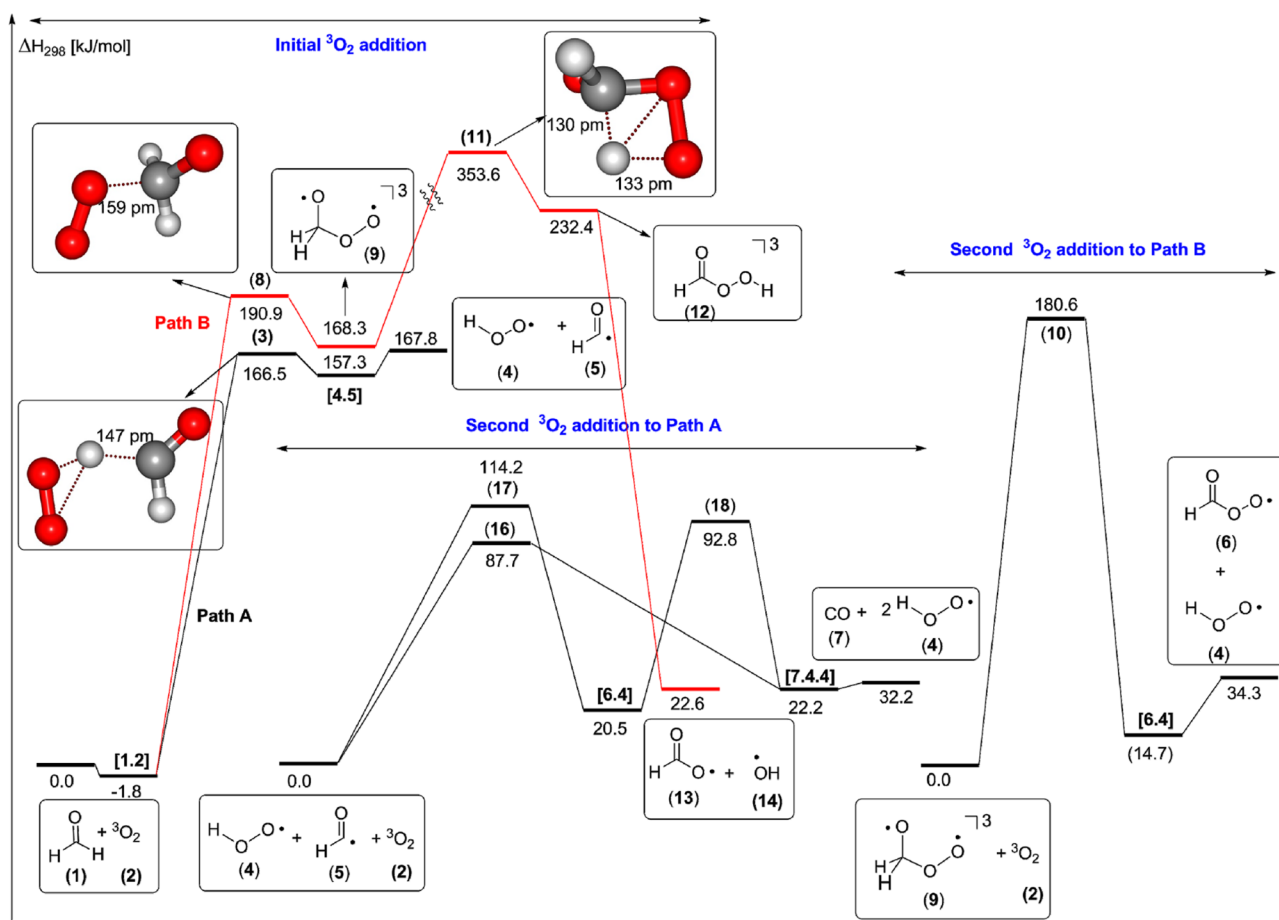


Figure 2. Enthalpy profile of the initial steps of the reaction pathways A (black) and B (red) shown in Figure 1 calculated at the UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p) level.

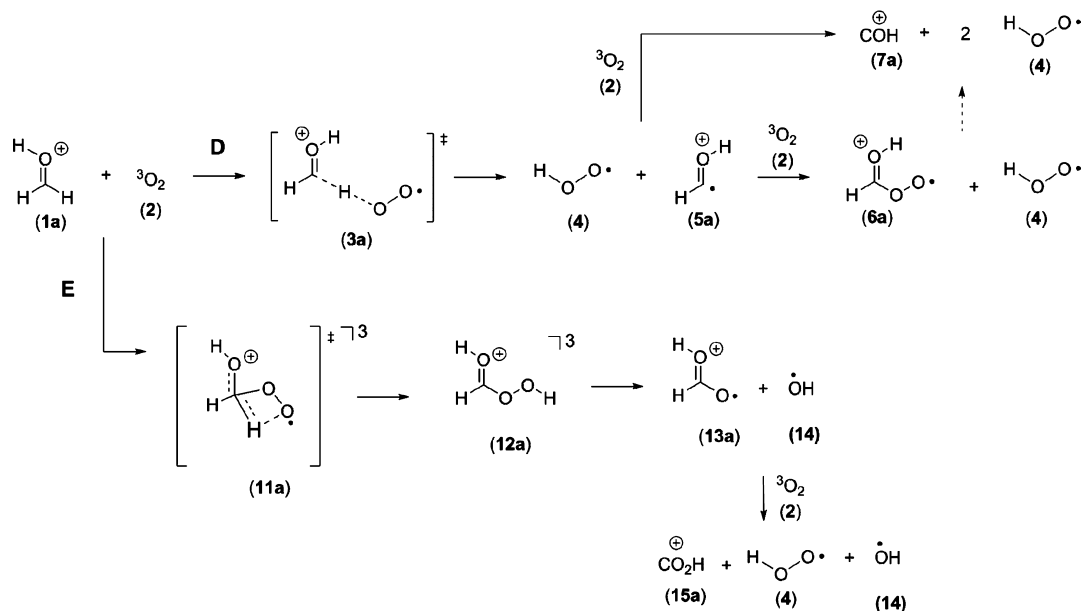


Figure 3. Reaction pathways for the initiation of formaldehyde autoxidation in the presence of Brønsted acids.

The structural aspects of the triplet biradical (9) show that it can also rearrange into performic acid (12). But this reaction is an extremely high barrier reaction that occurs through a transition state (11). The triplet performic acid (12) thus formed is extremely endothermic with $\Delta H_{298} = 240.5$ kJ/mol.

The performic acid (12) in triplet state further dissociates by O–O bond homolysis, forming the formyl (13) and hydroxyl (14) radical pair in a less thermodynamically demanding reaction. This dissociation proceeds along a continuous downhill path lacking any transition states. The second

Table 2. Relative Enthalpies (ΔH_{298} , in kJ/mol) for All the Minima Shown in Figure 3

system	CBS-QB3	G3B3	WIRO	UM06-2X/6-311++G(d,p)	UCCSD(T)//UM06-2X//6-311++G(d,p)
C					
1a + 2	0.0	0.0	0.0	0.0	0.0
4 + 5a	+272.2	+271.9	+270.2	+269.9	+272.6
4 + 6a	+66.4	+66.3	+64.5	+74.6	+67.0
4 + 4 + 7a	+302.3	+305.6	+302.7	+309.7	+305.7
D					
1a + 2	0.0	0.0	0.0	0.0	0.0
12a	+172.9	+170.1	+171.7	+172.0	+168.5
13a + 14	+48.3	+40.6	+43.3	+40.5	+41.3
15a + 4 + 14	-62.2	-67.5	-65.5	-52.6	-57.3

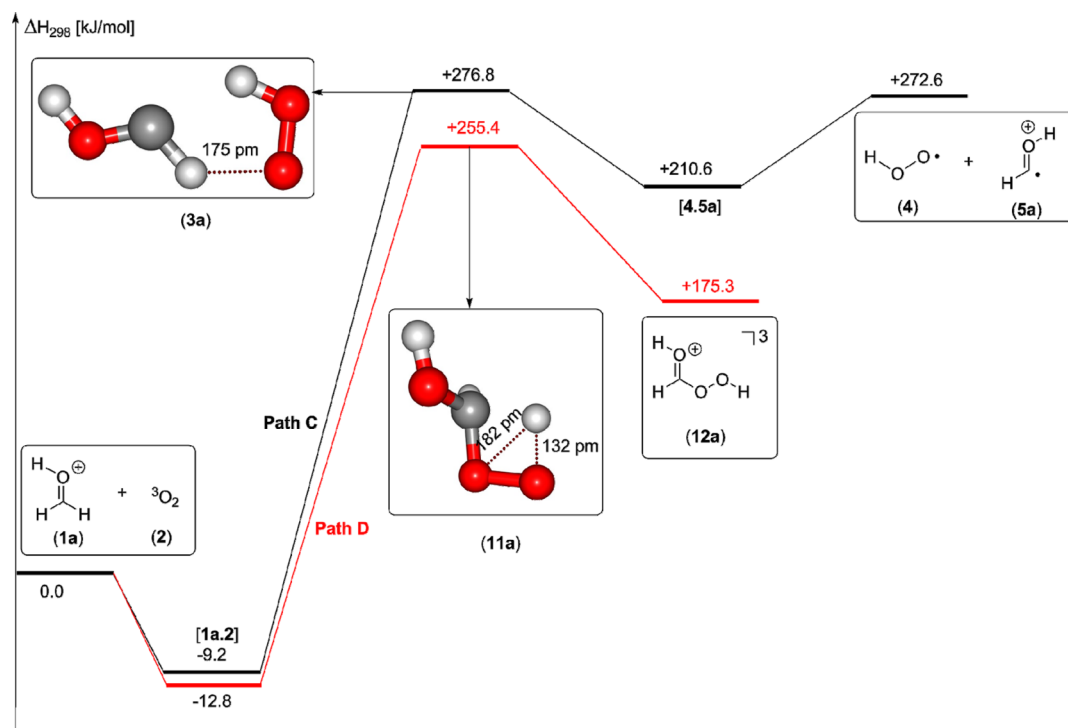


Figure 4. Enthalpy profile of the initial steps of the reaction pathways C (black) and D (red) shown in Figure 3 calculated at the UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p) level.

addition of $^3\text{O}_2$ to the (13) + (14) radical pair abstracts the H-atom from (13), forming CO_2 (15) + HO_2 (4) and OH (14) as products. The formation of these products occurs in a highly exothermic reaction with a reaction enthalpy of -234.3 , -239.3 , and -238.0 kJ/mol calculated at CBS-QB3, G3B3, and WIRO methods, respectively. Thus, CO_2 + HO_2 + OH products are formed more thermodynamically feasible than the CO + 2HO_2 products, revealing that CO_2 + HO_2 + OH is the most favorable product channel in the autoxidation of formaldehyde.

3.2. Effect of Brønsted Acid in the Initial Step of Autoxidation. The initial H-atom abstraction reaction from protonated formaldehyde (Figure 3), resulting in (4) and (5a), is a highly endothermic reaction with a reaction enthalpy of 272.2 kJ/mol at the CBS-QB3 level. On the other hand, interestingly, the $^3\text{O}_2$ addition to protonated formaldehyde is about 100 kJ/mol less endothermic than the H-atom abstraction reaction. The addition of the second $^3\text{O}_2$ to the protonated formyl radical (5a), forming a protonated formyl peroxy radical (6a) and a hydroperoxy radical (4), is somewhat energetically accessible with an enthalpy of 66.4 kJ/mol at the

CBS-QB3 level. In contrary to this, the alternative reaction of second $^3\text{O}_2$ with the products (4) and (5a) through H-atom abstraction from the (5a) forming protonated CO and two hydroperoxy radicals results in an extremely energy-demanding reaction with a reaction enthalpy of 302.3 kJ/mol. The protonated performic acid (12a) resulting from the addition reaction leads to the radical products (13a) and (14) with a reaction enthalpy of 48.3 kJ/mol. On reacting the second $^3\text{O}_2$ with the radical products (13a) and (14), the protonated CO_2 and HO_2 and OH radicals are formed exothermically with a reaction enthalpy of -62.2 kJ/mol, showing the feasibility of the reaction. The thermodynamic results for the reactions shown in Figure 3 calculated at various levels of theory are summarized in Table 2. The thermodynamic results obtained with the compound methods are in good agreement with each other, and the DFT-M06-2X results are in closer agreement with the results of compound methods and those of the coupled-cluster method.

The enthalpy profile for the initial steps of the formaldehyde autoxidation in the presence of Brønsted acids calculated at the UCCSD(T)//UM06-2X/6-311++G(d,p) level is shown in

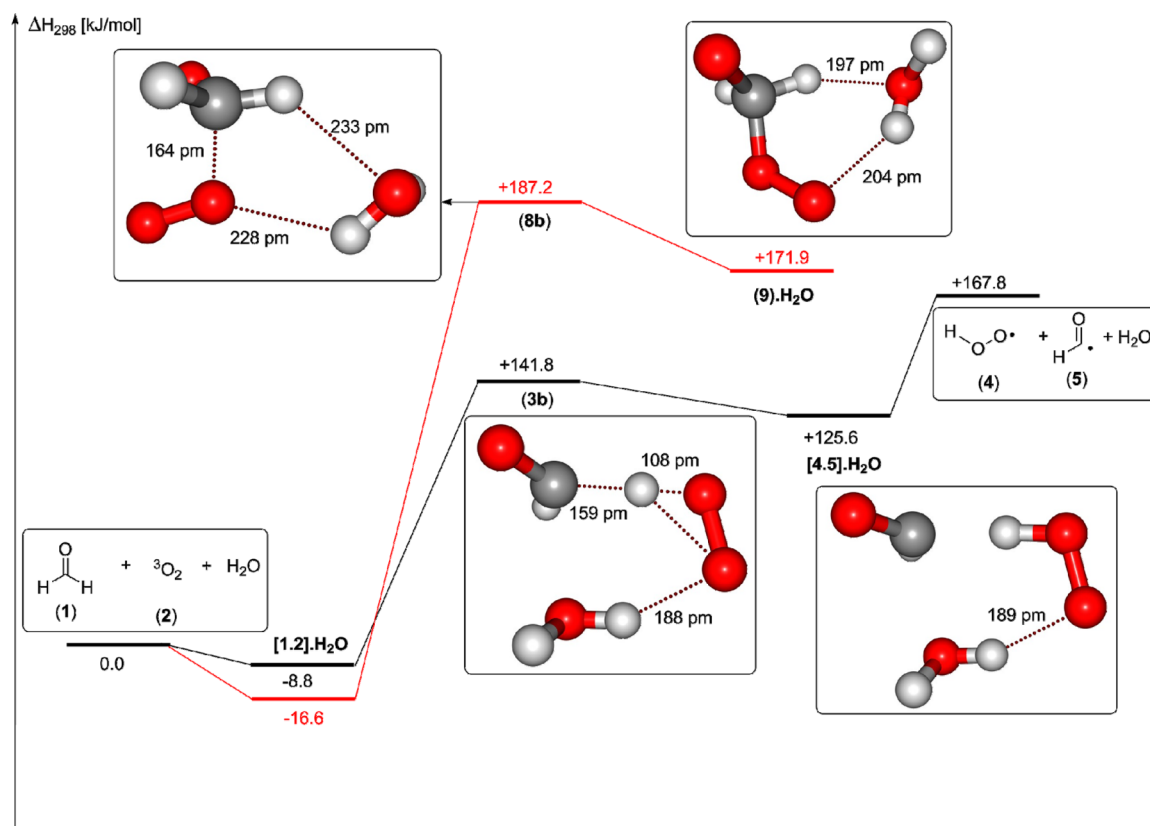


Figure 5. Enthalpy profile of the initial steps of the reaction pathways A (black) and B (red) in the presence of H₂O calculated at the UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p) level.

Figure 4. The protonated formaldehyde and ³O₂ initially form a strongly bound prereactive complex where a hydrogen-bonding interaction exists between the protonation site of (1a) and O of (2) and the complex is stable by 9.2 kJ/mol than the isolated reactants. The H-atom abstraction transition state (3a) is a late transition state with a fully broken C–H bond and a partially formed O–H bond with distances of 192 and 102 pm, respectively. The enthalpy barrier for this process is 276.8 kJ/mol. The transition state (3a) leads to a deep potential well which is 66.2 kJ/mol below the reactants and requires almost 62 kJ/mol to break into separated products (4) and (5a). Unlike the H-atom abstraction reaction leading to (4) + (5a) in the gas phase, the protonation results in a more stable product complex (4)·(5a) with a longer lifetime.

The ³O₂ addition to protonated formaldehyde leads to performic acid (12a) in a concerted reaction where the O₂ addition is accompanied by the transfer of the CH₂ H-atom of protonated formaldehyde to the O-radical site. The energy barrier for this process associated with the transition state (11a) is also high, but almost 21 kJ/mol less when compared with the H-atom abstraction reaction. This concerted C–H bond cleavage and the formation of C–O and O–H bonds is dependent on the alignment of the reacting partners. In (11a), the reacting O₂ is aligned parallelly with the –C–H– bond of (1a), resulting in a tight four-membered complex. The transition state (11a) leads to protonated performic acid (12a), which lies 175.3 kJ/mol below the separated reactants. The protonated performic acid is 65.2 kJ/mol more stable than the performic acid in the gas phase. The Brønsted acid acts as a hydrogen bond donor and promotes the ³O₂ addition by stabilizing performic acid not via the formation of a biradical

(9), but directly. The abovementioned results show that the H-atom abstraction by ³O₂ in the presence of Brønsted acids has no effect on the activation energy and the reaction enthalpy. The Brønsted acids do activate the ³O₂ addition to formaldehyde in a concerted mechanism and also drive the reaction enthalpically when compared to the abstraction reaction. Furthermore, the formation of performic acid directly rather than involving the biradical intermediate (9) implies that the autoxidation of formaldehyde in the presence of Brønsted acids may lead favorably to the CO₂ + HO₂ + OH product channel.

3.3. Effect of H₂O in the Initial Step of Autoxidation.

The impact of water on a radical oxidation reaction is chemically interesting. The PES for the initial step in the autoxidation of formaldehyde in the presence of H₂O is calculated and shown in Figure 5. The best conformation of H₂O complexing formaldehyde and O₂ [1·2]·H₂O lies 13.3 and 20.6 kJ/mol below the isolated reactants, for H-abstraction and O₂ addition reactions, respectively. The prereactive complex [1·2]·H₂O through which the H-atom abstraction takes place possess a H-bonding interaction between O₂ and H₂O in a bent structure, with H₂O acting as a bridge between (1) and (2). In the O₂ addition reaction, the OH group of H₂O is oriented more toward the O-atom of (1) than the O-atom of (2) in the prereactive complex. The hydrogen bond distance between the O-atom of (1) and the H-atom of H₂O is 200.6 pm and that between the O-atom of (2) and the H-atom of H₂O is 252.0 pm. Unlike the reactions discussed above, the H-atom abstraction reaction possesses an energetically lower barrier than the addition reaction. The barrier for H-abstraction from formaldehyde in the presence of H₂O is

~40 kJ/mol less than that of the reaction without any catalyst and 155 kJ/mol less than the autoxidation in the presence of Brønsted acids. The enthalpy of the product complexes [4·5]·H₂O and 9·H₂O are 115.2 and 120.8 kJ/mol, which form a penalty in the barrier for the formation of final products. The products are thus eluted by H₂O, disfavoring the final product formation through the large endothermicity required to break the product complexes.

In the transition state (3b) associated with the H-atom abstraction reaction, the water OH bond is oriented toward molecular O₂ and interacts strongly through H-bonding with a 188.6 pm bond distance, and the reacting C–H and O–H are arranged in a linear fashion. In the case of the O₂ addition transition state (8b), H₂O interacts with both O₂ and the H-atom of (1) via H-bonding. The H-bond formed between the water and O₂ is slightly longer (206.9 pm) than that formed between O₂ and H₂O in the transition state (3b). The biradical character of (9) is reflected in the O–O and C–O bond distances of (8b), which are 128.4 and 127.4 pm, respectively, whereas the C–O bond distance in (8b) is 118.8 pm. In the product complex [4·5]·H₂O, the water OH group is oriented toward the carbon radical site and the O-atom of H₂O forms an H-bond with the H-atom of HO₂. The complex HO₂·H₂O has been well studied using theoretical approaches, and here HO₂ acts as a hydrogen donor and H₂O acts as a hydrogen acceptor.^{27–29} The intermolecular bond distance between H₂O and HO₂ is 172.8 pm, in good agreement with the earlier studies.³⁰ The HO₂·H₂O complex is in equilibrium with the monomers and, hence, they do not react with each other. Furthermore, the peroxy functionality of HO₂ forms a sterically stable H-bond with the formyl radical (5), which can promote H-atom transfer reactions.^{31,32} This leads to the possibility of the formation of CO (7) and HO₂ upon the addition of the second O₂ molecule. The binding energy of the HO₂·H₂O complex is 6.9 kcal/mol and 30% of free HO₂ is complexed with H₂O.²⁸ Even though the H-atom abstraction reaction takes place on the flat PES, the strong binding of HO₂·H₂O in the [4·5]·H₂O complex prevents back reaction. Given the large enthalpy barrier for the formation of isolated (4), (5), and H₂O products, from the abovementioned discussions, it is well predicted that the second O₂ addition reaction from [4·5]·H₂O is more favorable than the formation of (4) + (5) + H₂O. The product complexing (9) and H₂O shows strong binding with H₂O through O–H interactions between the H-atom of (9) and the O-atom of H₂O and the H-atom of H₂O and the peroxy radical site of (9). This is a double hydrogen-bonded complex in a six-membered ring structure. The carbonyl radical site of (9) shows no interaction with H₂O. The high O–H bond energy (+497.1 kJ/mol) in water compensates for the energetic demand for the binding of O₂ in (9), rather than the formation of two separate open shell species (4 + 5). Besides the H-atom abstraction and O₂ addition reactions, other reactions are conceivable in the presence of water, where H-shift reactions³³ between water and (1) and (2) can take place. However, the relevance of this reaction is dependent on the hydrogen-bonding interactions of H₂O with the radical and biradical.^{34–36}

4. COMPARISON OF REACTION CHANNELS

In the absence of radical initiators/catalysts, the autoxidation of aldehydes proceeds by H-atom abstraction by O₂ or O₂ addition reactions. However, as shown in Figures 2, 4, and 5, these reactions are energy demanding both kinetically and

thermodynamically. The comparison of these initial steps can be discussed in terms of the activation enthalpies and activation free energies given in Table 3. On comparing the

Table 3. Activation Enthalpies and Free Energies of Initial Reactions

medium	reaction	ΔH_{298}^\ddagger (kJ/mol)	ΔG_{298}^\ddagger (kJ/mol)
gas phase	H-atom abstraction	+166.5	+201.6
	O ₂ addition	+190.9	+241.3
protonation	H-atom abstraction	+276.8	+315.2
	O ₂ addition	+255.4	+299.6
H ₂ O catalyst	H-atom abstraction	+141.8	+219.9
	O ₂ addition	+187.2	+267.5

H-atom abstraction channels, the activation enthalpy in the presence of Brønsted acid is actually higher than that of the gas phase and water catalyst reactions. In the presence of H₂O, the H-atom abstraction TS possesses two H-bonds, which thereby reduces the energy barrier for the H-atom abstraction reaction, unlike the reaction in the gas phase and in the presence of Brønsted acids. The presence of Brønsted acids enhances the addition reaction in a single kinetic step, whereas the presence of a single water molecule activates both abstraction and addition reactions. We may thus conclude that the water molecule has an enormous effect in driving the H-atom abstraction and O₂ addition reactions by reducing the energy barriers. Moreover, O₂, being a nonpolar gas, is less soluble in any solvent and, hence, the effect of the solvent is unfavorable for the oxidation.² Hence, the presence of a single water molecule is able to quantify the role of the water catalyst in the autoxidation of formaldehyde to some extent. On comparing the activation enthalpies and activation free energies, we note that these reactions are entropically disfavored. At a temperature of 298.15 K, the entropic penalty for the initial reactions in the gas phase and in the presence of Brønsted acid is ~40–50 kJ/mol, whereas the water catalyzed initial reactions possess an entropic penalty of ~80 kJ/mol. This reveals that the reaction is likely to show a large dependence on the reaction temperature and, as shown in a very earlier study,¹ formaldehyde readily reacts with O₂ to form performic acid at low temperatures, and at high temperatures, formic acid is formed, which compares to the entropic penalty for O₂ addition reactions leading to performic acid.

The formation of performic acid via the O₂ addition reaction in a rate-determining step is in good agreement with the earlier study¹ that showed that the first product formed during oxidation is peracid in a very slow reaction. As obtained in the current calculations, CO₂ is the major product formed from performic acid decomposition.¹ Aside from undergoing O–O bond homolysis, performic acid can react with formaldehyde, leading to formic acid,^{2,37} which is a prototype of the “molecule-induced radical formation (MIRF)” reactions.³⁸ This reaction leads to two molecules of formic acid² in an extremely exothermic reaction with a reaction enthalpy of –359.0 kJ/mol.¹² This reaction, however, involves either a step-wise/concerted process where the O–O bond homolysis of performic acid occurs at the first and the radical intermediate couples with the second reaction partner (formaldehyde) and results in the formation of radical/nonradical products. As observed in benzyl hydroperoxide dissociation induced by a second reaction partner,³⁸ the radicals (13) and (14) will be the major intermediates

participating in the reaction, and the formation of carboxylic acids from aldehydes should follow the route from (12) to (13) + (14).

The autoxidation of aldehydes has been shown to proceed through the acyl radical, which on subsequent reaction with O₂ forms the peracyl radical and delivers carboxylic acid.^{39,40} The proposed mechanism in the current study demonstrates that the acyl and peracyl radicals are formed through the H-atom abstraction process and CO and HO₂ are the major products. As discussed above, the more feasible route for carboxylic acid formation from aldehyde autoxidation is through performic acid, which is most likely formed by the less established ³O₂ addition reaction to aldehydes.

5. CONCLUSIONS

The autoxidation of formaldehyde through the initiation by triplet oxygen proceeds through two initial steps: (1) H-atom abstraction and (2) ³O₂ addition reaction. The reactions are studied in the gas phase and also in the presence of a Brønsted acid and a water molecule. From the results obtained, we arrive at the following conclusions:

1. The H-atom abstraction and O₂ addition reactions in the gas phase proceed through high energy barriers in highly endothermic reactions. The H-atom abstraction reaction results in formyl and hydroperoxyl radicals, which on subsequent oxidation by triplet oxygen lead to CO and HO₂ as the major products. The ³O₂ addition reaction to formaldehyde results in a triplet biradical intermediate, which further rearranges to performic acid and, upon subsequent ³O₂ reaction, forms CO₂, OH, and HO₂ as the major products.
2. The presence of a Brønsted acid does not enhance the reaction, but reduced the energy barrier and endothermicity for the ³O₂ addition reaction by ~21 and ~100 kJ/mol, respectively, when compared with the H-atom abstraction reaction.
3. The presence of a single water molecule catalyst reduces the energy barriers of the initial reactions considerably. In the presence of a water catalyst, the ³O₂ addition reaction leads to performic acid in a single kinetic step without involving biradical intermediates, favoring the formation of the CO₂ + OH + HO₂ product channel. This shows that the less established/less documented ³O₂ addition reaction to aldehydes in the presence of a water catalyst can serve as a better initiation reaction in the autoxidation of aldehydes.
4. Furthermore, the present study demonstrated that the “classical synthesis” of carboxylic acids from aldehydes may follow the proposed ³O₂ addition route, where homolysis/MIRF of performic acid leads to carboxylic acids in a thermodynamically accessible reaction. The higher oxygen solubility in organic solvents can act as a driving force for such reactions, with a maximum oxygen concentration in the solution of about 250 μmol L⁻¹ oxygen.⁴⁰ Oxygen is highly soluble in many organic solvents compared with water, where the solubility is limited to 5 mL of O₂ L⁻¹ water.⁴¹ Hence, studying these oxidation reactions in organic solvents may lead to thermodynamically and kinetically favorable reaction pathways.

Much more work needs to be done to understand the kinetic feasibility of such reactions. It is hoped that the comparison of

plausible initial reactions as presented in the current study is the first step in apprehending this task.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06375>.

Structures and energetics of the reactive species studied in the present work calculated at various levels of theory (PDF)

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Notes

The authors declare no competing financial interest.

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http://atct.anl.gov/Thermochemical%20Data/version_1.118/: $\Delta_f H^\circ(\text{CH}_2\text{O}, 1) = -109.15 \pm 0.11$ kJ/mol; $\Delta_f H^\circ(^3\text{O}_2, 2) = 0.0$ kJ/mol; $\Delta_f H^\circ(\text{HOO}^\bullet, 4) = +12.25 \pm 0.16$ kJ/mol; $\Delta_f H^\circ(\text{H}(\text{O})\text{C}^\bullet, 5) = +41.84 \pm 0.11$ kJ/mol; $\Delta_f H^\circ(\text{CO}, 7) = -110.52 \pm 0.03$ kJ/mol; $\Delta_f H^\circ(\text{CO}_2, 15) = -393.474 \pm 0.015$ kJ/mol; $\Delta_f H^\circ(\text{OH}, 14) = 37.488 \pm 0.026$ kJ/mol.

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