Competing Mechanistic Channels in the Oxidation of Aldehydes by Ozone

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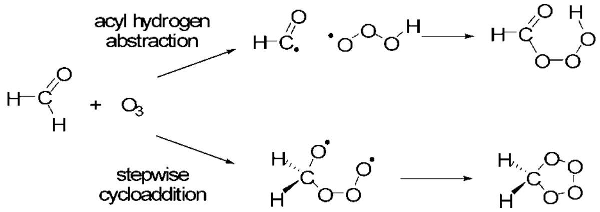
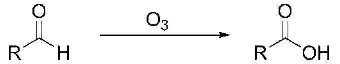


The reaction of ozone with aldehydes has been studied intermittently for over 100 years, but its mechanism remains uncertain. Experimental results support two reaction channels: radical abstraction of the acyl hydrogen and addition to form a five-membered ring tetroxolane. We have studied the aldehyde−ozone reaction by DFT and CCSD(T) calculations. CCSD(T)/6-311+G(d,p)//M05-2X)/6-311+G(d,p) calculations predict two competitive pathways for the oxidation of formaldehyde by ozone. Abstraction of the acyl hydrogen by ozone has a barrier of 16.2 kcal/mol, leading to a radical pair, which can combine to form a hydrotrioxide; this species may subsequently decompose to a carboxylic acid and singlet oxygen. In the second reaction channel, addition of ozone to the carbonyl is stepwise, with barriers of 19.1 and 23.0 kcal/mol, leading to a five-membered ring tetroxolane intermediate. This process may be reversible, consistent with earlier observations of isotopic exchange. The two channels connect by an intramolecular hydrogen abstraction. Ring opening of the tetroxolane by an alternate O−O bond cleavage, followed by spin inversion in the resulting diradical intermediate, can give a carbonyl oxide plus $^3O_2$. It is also possible that reaction of triplet oxygen with carbonyl oxides can produce ozone by the reverse route. These two stepwise reaction channels, hydrogen abstraction and addition to the C═O bond, explain much of what has been observed in the long history of ozone−aldehyde chemistry. Known reaction rates and the substantial barriers to both channels support an earlier conclusion that aldehyde oxidation by ozone is too slow to be of importance in atmospheric chemistry.

Introduction

Ozone (**1**) is a powerful oxidant, most often investigated for its roles in atmospheric chemistry[1] and organic synthesis.[2] Reaction of ozone with alkenes by the Criegee mechanism leads to efficient double bond cleavage.[1b,3] It is not surprising that ozone also oxidizes aldehydes to carboxylic acids (Scheme 1). This fundamental reaction has been studied intermittently[4−22]

SCHEME 1



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(3) For references and disussions, see: (a) Wheeler, S. E.; Ess, D. H.; Houk, K. N. *J. Phys. Chem. A* **2008**, *112*, 1798. (b) Ess, D. H.; Houk, K. N. *J. Phys. Chem. A* **2005**, *109*, 9542. (c) Schank, K. *Helv. Chim. Acta* **2004**, *87*, 2074. (d) Barton, M.; Ebdon, J. R.; Foster, A. B.; Rimmer, S. *J. Org. Chem.* **2004**, *69*, 6967. (e) Chan, W.-T.; Hamilton, I. P. *J. Chem. Phys.* **2003**, *118*, 1688. (f) Kuczkowski, R. L. *Chem. Soc. Rev.* **1992**, *21*, 79. (g) Murray, R. W. *Acc. Chem. Res.* **1968**, *1*, 313. (h) Criegee, R. *Chimia* **1968**, *22*, 392. (i) Criegee, R. *Ozone Chemistry and Technology*; ACS Advances in Chemistry Series No. 21; American Chemical Society: Washington, DC, 1959; p 133.

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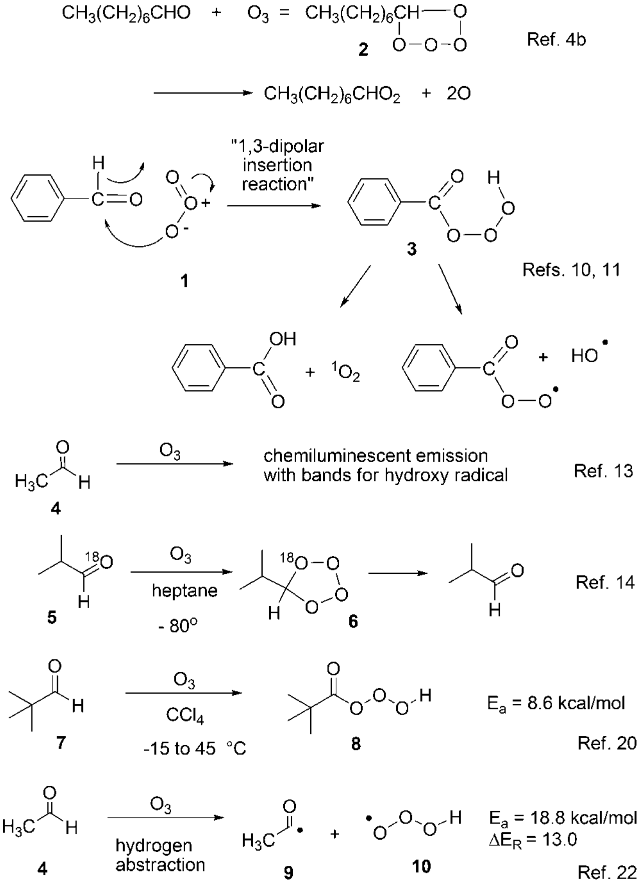
10.1021/jo8026593 CCC: $40.75

since initial reports by Harries and Langheld in 1905,[4] but many aspects of the mechanism have remained poorly understood. Aldehyde oxidation by ozone is nearly absent from the lexicon of synthetic chemistry.[17] Similarly, ozone is believed to play a minor role in the atmospheric oxidation of aldehydes. In a 1984 review of ozone chemistry, Atkinson and Carter concluded that reaction of ozone with aldehydes is slow and thus of "...negligible atmospheric importance."[1g] If ozone is so reactive, why should it easily oxidize alkenes but not aldehydes? What is the mechanism of the ozone−aldehyde reaction?

SCHEME 2. Earlier Studies on Ozone−Aldehyde Reactions



Selected milestones in ozone−aldehyde mechanistic chemistry are presented in Scheme 2. Harries first proposed that oxidation of octanal by ozone proceeds through tetroxolane intermediate **2**, drawn here as in a 1910 paper.[4b] Many experiments have provided evidence that peracids or hydrotrioxides may be intermediates or products of this reaction.[6−12,15,21] For example, Dick and Hanna reported in 1964 that benzaldehyde is efficiently converted to perbenzoic acid by reaction with ozone admixed with oxygen.[9] In 1965, White and Bailey studied the reactions of aromatic aldehydes with ozone and proposed a "1,3-dipolar insertion" leading to a hydrotrioxide intermediate (**3**), which might decompose by several pathways.[10] For benzaldehyde ozonolysis, Erickson and co-workers observed acyl hydrogen kinetic isotope effects (k_H/k_D) ranging from 1.2 to 7.8, depending on oxygen concentration, and aryl ring substituent effects consistent with an "electrophilic mechanism".[11] Their proposed mechanism involved "...either direct insertion of ozone into the carbon hydrogen σ bond, as postulated by White and Bailey, or the formation of a five-membered [tetroxolane] ring which rearranges to the same intermediate." In 1972, Finlayson, Gafney and Pitts showed that reaction of vapor phase acetaldehyde (**4**) with ozone produced chemiluminescent hydroxyl radical, a reaction that could best be explained by the generation of free hydrogen radicals.[13] Klopman and Joiner reported in 1975 that ^{18}O-labeled aldehyde **5** undergoes isotopic exchange when treated with ozone in solution at −80 °C; these results and MINDO/3 calculations supported the reversible formation of a tetroxolane intermediate (**6**).[14] The degree of oxidation was not measured in these experiments. Murray and co-workers observed hydrotrioxide **3** by low temperature ^{1}H NMR spectroscopy (-OOOH resonance at δ 13.1) and measured a barrier of 16.4 kcal/mol for decomposition to benzoic acid plus $^1O_2$.[15] Braslavsky and Heicklen studied the gas-phase reaction of formaldehyde with ozone,[16] reporting a rate constant of 2.1×10^{-24} cm^3/molecule/s. They suggested a chain mechanism with surface effects, noting that "Explosions occur when O_3 and H_2CO are mixed in a fresh vessel...in an aged vessel, the reaction is well behaved." In a rare synthetic application of this chemistry, Djerassi and co-workers reported in 1978 that, in basic methanol, ozone converts aldehydes to methyl esters in one step.[17] In 1981, Atkinson and co-workers studied the gas phase reaction of acetaldehyde with ozone, reporting a rate constant of 6×10^{-21} cm^3/molecule/s.[18] A year later, Martinez reviewed earlier work, underscoring the cycloaddition mechanism and further proposing a connection to Criegee intermediate (carbonyl oxide) chemistry through loss of molecular oxygen from the tetroxolane.[19] In 1986, Pryor and co-workers measured the rate constants for reaction of pivaldehyde (**7**) and 2-phenylethanal with ozone in CCl_4, a reaction presumed to give trioxides such as **8**, reporting an activation energy of 8.6 kcal/mol for **7**.[20] Ozone−aldehyde chemistry lay nearly dormant for another 2 decades[21] until Yang and co-workers recently studied acyl hydrogen abstraction in acetaldehyde by DFT and higher level calculations.[22] Acyl hydrogen abstraction to give radicals **9** and **10** was predicted to be endothermic by 13 kcal/mol with a barrier of 18.8 kcal/mol.

After more than 100 years of research on ozone−aldehyde reactions,[4−22] what may be concluded is that two initial reaction channels are operative: acyl hydrogen abstraction and addition across the carbonyl double bond. Connections between these two channels and links to Criegee intermediate chemistry are likely. It is also clear that mechanistic study of this reaction is

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(6) (a) Briner, E.; Lardon, A. *Helv. Chim. Acta* **1936**, *19*, 850. (b) Briner, E.; Wenger, P. *Helv. Chim. Acta* **1943**, *26*, 30. (c) Briner, E. *Adv. Chem. Ser.* **1959**, *21*, 184.

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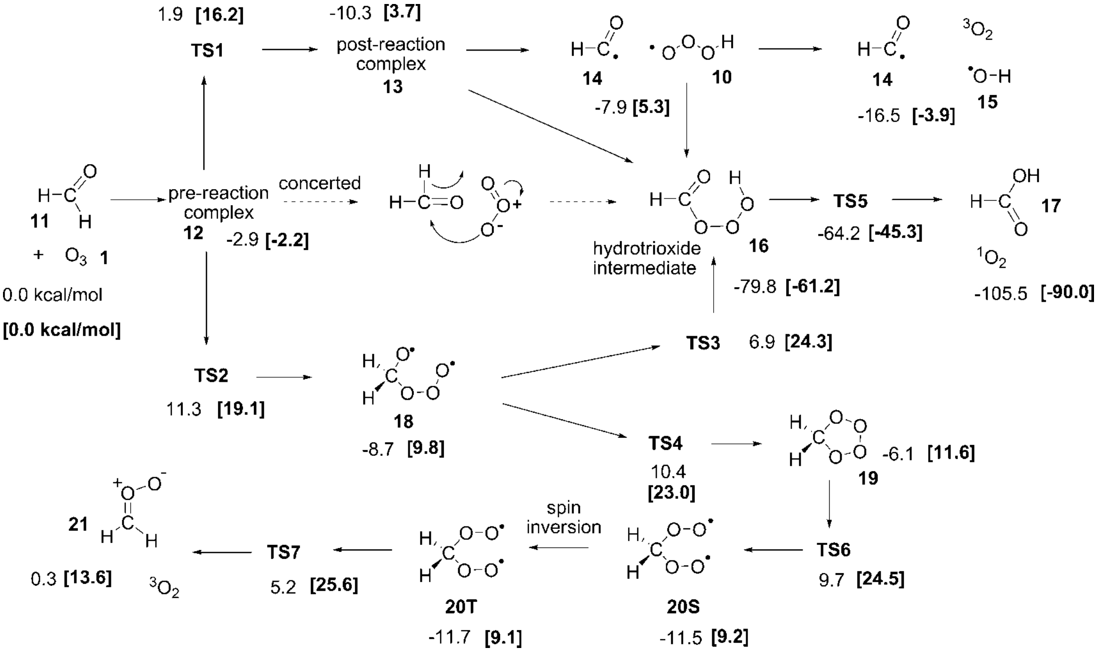
SCHEME 3. Summary of Reaction Energetics UM05-2X/6-311+G(d,p) [CCSD(T)/6-311+G(d,p)//UM05-2X]



complicated by secondary peracid chemistry and the presence of oxygen admixed with ozone, which leads to competitive aldehyde autoxidation.

We became interested in carbonyl−ozone reactions after Wentworth and co-workers posited that ozone might play a role in human immune system chemistry.[23] This theory has been soundly criticized,[24] but it led us to investigate low energy routes for the formation of ozone through cycloreversion of tetroxolanes. As part of a study on the interconnected reaction surfaces, we begin with ozone + formaldehyde; work on more complex aldehydes and ketones is in progress. Our goal in the present work has been to unite disparate results into a more comprehensive mechanistic scheme.

Methodology. All calculations were carried out with Gaussian 03[25] or Spartan 06.[26] Structures were optimized and characterized by frequency analysis at the M05-2X/6-311+G(d,p) level of theory, followed by single point CCSD(T)/6-311+G(d,p) calculation. Unscaled zero point corrections were applied to both DFT and CCSD(T) energies. In addition to the Truhlar M05-2X functional,[27] selected calculations were carried out with B3LYP[28] and BMK[29] functionals.

Results and Discussion

We first located stationary points for abstraction and addition reaction channels. Relative energies from DFT and CCSD(T)//DFT (in brackets) calculations are summarized in Scheme 3. Structures for stationary points are reproduced in Figure 1. The CCSD(T)//M05-2X energetics for each major channel are summarized in Figures 2 and 3. Geometries, energies, and other results are compiled in Supporting Information.

No concerted transition state could be found corresponding to the concerted "dipolar insertion" mechanism proposed by White and Bailey.[10] Trial structures were unstable relative to becoming open shell; depending on initial geometry, these optimized either to **TS1** or **TS2**, which are the stepwise counterparts of White and Bailey's mechanism. Thus, association complex **12**, whose geometry matches the expected polarization of the two reactants, can proceed by two reaction channels: addition or hydrogen atom abstraction. Hydrogen abstraction proceeds through four stages: initial association complex (**12**), transition state (**TS1**), postreaction complex (**13**) and separated radicals (**14** + **10**). As with the recent report on acetaldehyde−ozone reaction by Yang and co-workers,[22] we find a remarkably small DFT barrier (**TS1**) to hydrogen abstraction and a significantly exothermic reaction predicted at this level of theory. The DFT energetics for this abstraction step are clearly wrong: CCSD calculations differ substantially on this portion of the surface, with prediction of a 16.2 kcal/mol barrier and a slightly *endothermic* abstraction step. The origin of this unusually large difference between DFT and CCSD results seems most likely due to spin contamination in the DFT calculations. In our calculations, M05-2X,[27] B3LYP[28] and BMK[29] functionals all gave very similar energetics for this step. Postreaction complex **13** might recombine to **16** (Figure 2) or dissociate to **14** and hydrotrioxy radical (**10**). Radical **10** has a low barrier to dissociation.[30] Thus, **14**, $^3O_2$ and hydroxyl radical (**15**) are likely products along this path.

Alternatively and more consistent with many solution-phase experiments,[15] the initial radical pair can combine to form hydrotrioxide **16**, which fragments through **TS5** to give formic acid (**17**) and $^1O_2$. Our computations underestimate the

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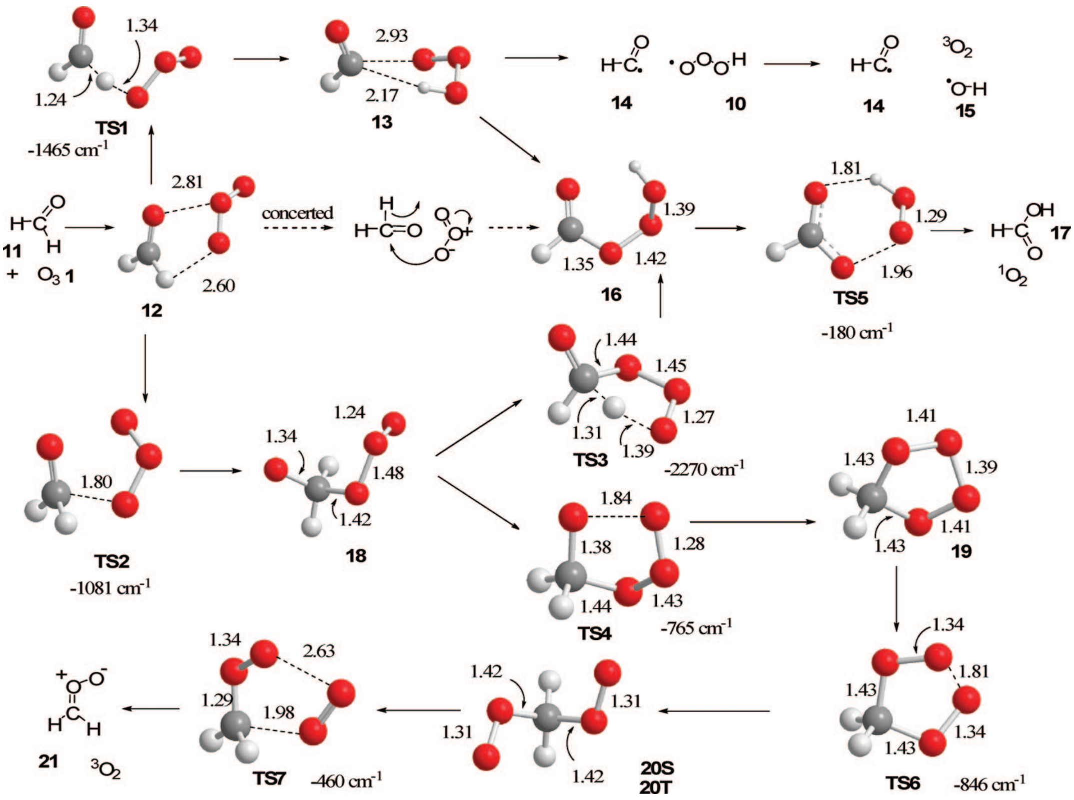

FIGURE 1. Structures for stationary points (distances in Å; imaginary frequencies given).

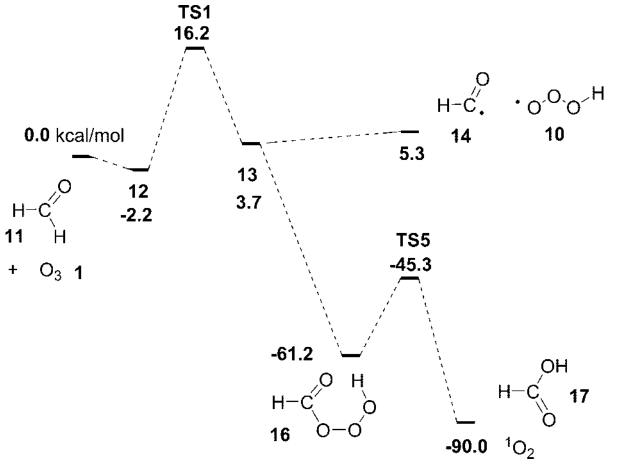

FIGURE 2. CCSD(T)//M05-2X energetics of the hydrogen abstraction channel.

singlet−triplet gap in molecular oxygen; thus, a better estimate for the final energetics of this step might be ca. −80 kcal/mol.

Using a heat of formation of 6.1 kcal/mol for radical **10**[30f] and standard NIST values for other species, we calculate an enthalpy change of 5.5 kcal/mol for the reaction **1** + **11** → **14** + **10**. This agrees well with our predicted CCSD(T) value of 5.3 kcal/mol.

The abstraction channel almost certainly leads to a complex collection of free radical and peroxy chemistry. Acyl radicals such as **14** will react with molecular oxygen to give acylperoxy radicals. Thus, an array of carboxylic acid, peracid, and hydrotrioxy chemistry may be initiated by atom abstraction from aldehydes by ozone. The connection between ozone reactions and autoxidation was shown in earlier experiments by Briner and co-workers.[6]

Ozone has long been recognized as having some diradical character,[31a] although this has recently been disputed.[31b] There is, however, ample precedent for hydrogen abstraction by ozone.[20,32,33] The best studied example is hydrogen abstraction from acetals, which leads to hydrotrioxides.[32,33] Cremer and co-workers recently argued for an ionic reaction mechanism proceeding through hydride abstraction by ozone.[32a] Scheme 4 presents an isodesmic comparison of ionic and radical dissociation processes for acetals and aldehydes. Ionic chemistry heavily favors the acetal because of stability of the dialkoxycarbenium ion **22**, whereas radical chemistry favors the acyl species. Thus, while an ionic hydrogen abstraction mechanism might apply to acetals, we conclude that it is highly unlikely for aldehydes.

Klopman's ^{18}O exchange results provide evidence for a second general mechanism (Figure 3), which passes through a tetroxolane (**19**).[14] In principle, this cyclic tetroxide might be formed by a concerted $\pi 2s + \pi 4s$ process, similar to the reaction of ozone with alkenes.[3] We find that closed-shell solutions to this concerted transition state are easily located, but the wave function is unstable; allowing open shell character leads to **TS2**

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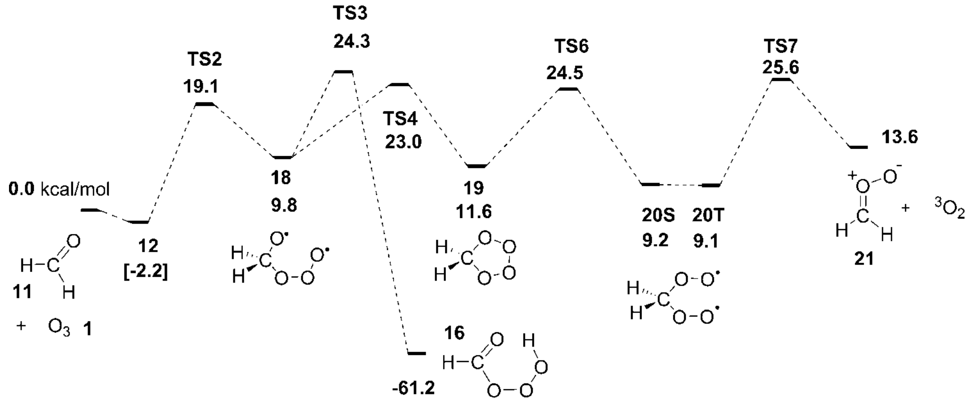
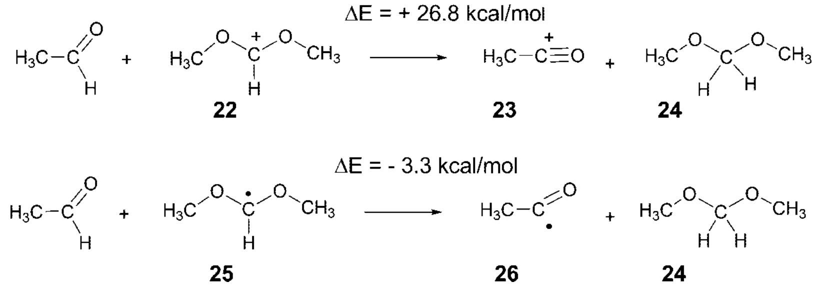


FIGURE 3. CCSD(T)//M05-2X energetics of the ozone addition channel.

SCHEME 4. M05-2X/6-311+G(d,p) Isodesmic Comparision for Ionic and Radical Reactions



and onward to singlet diradical **18**. *Thus, in contrast to alkene−ozone reactions, cycloaddition of ozone to carbonyl compounds is stepwise.* Diradical **18** can proceed to hydrotrioxide **16** by intramolecular hydrogen abstraction (**TS3**), thus providing a straightforward connection to the abstraction reaction channel. This mechanistic bridge was noted earlier by Martinez.[19] However, closure to tetroxolane **19** is slightly more favorable. The tetroxolane lies in an energy minimum with two options for O−O bond cleavage. Reversal to diradical **18** and ozone dissociation provide an explanation for the observed isotopic label exchange (Scheme 1).[14]

A mechanistic detour of some importance arises with cleavage of the tetroxolane O2−O3 bond to give a different 1,5-diradical (**20S**), a route proposed in some detail by Martinez.[19] Not surprisingly, we find the singlet (**20S**) and triplet (**20T**) states of this species to be nearly identical in energy and geometry. Under these conditions, spin inversion may proceed at a rate competitive with other processes. Thus, **20S** can lead through spin inversion to **20T** and onward to carbonyl oxide **21** plus $^3O_2$. The net reaction is very similar to alkene ozonolysis. The reverse process, i.e., reaction of carbonyl oxide **21** with $^3O_2$, offers an eventual route *to* ozone through the tetroxolane. Ozone is believed to be generated in some oxygenated matrix studies on carbonyl oxides, but this is attributed to photochemical generation of oxygen atoms from carbonyl oxide photolysis.[34] Sawaki and co-workers have suggested that carbonyl oxide + $^3O_2$ → tetroxolane chemistry might explain the formation of esters in the photosensitized oxidation of diazomethanes.[35]

Although we have not estimated rate constants, the slow reaction of formaldehyde measured by Braslavsky and Heicklen[16] is consistent with a significant activation barrier. More problematic by comparison to our computational results is the 8.6 kcal/mol barrier reported by Pryor's group for aldehyde **7** (Scheme 3) and similar results for 2-phenylethanal.[20] In Pryor's work, kinetics were measured by UV observation of ozone loss. It is possible that an alternate mechanism or effect of the solution phase leads to a much lower energy process. However, we think it more likely that observed rates[20] are too high because they do not account for ozone loss by other mechanisms.[36]

Although many fascinating cyclic oxygen species have been described,[37] little is known about the chemistry of tetroxolanes. These fragile structures were first proposed as intermediates by Harries and Langheld in 1910[4b] but aside from one study on their conformation[37c] have not been studied. Parenthetically, we note that related 1,5-diradicals such as **23** have been suggested as late-stage intermediates in the thermal decomposition of the explosive TATP (**22**).[38]

Atmospheric Ozone−Aldehyde Chemistry. Formaldehyde and acetaldehyde have long been recognized as significant

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[34] For a discussion and leading references, see: (a) Tomioka, H. *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M. , Jr., Eds.; John Wiley & Sons, Inc.: New York, 2004; Chapter 9, pp 375−461. Reviews on carbonyl oxide chemistry: (b) Schwartz, C.; Raible, J.; Mott, K.; Dussault, P. H. *Tetrahedron* **2006**, *62*, 10747. (c) Block, K.; Kappert, W.; Kirschfeld, A.; Muthusamy, S.; Schroeder, K.; Sander, W.; Kraka, E.; Sosa, C.; Cremer, D. *Peroxide Chem.* **2000**, 139. (d) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (e) Sander, W. *Angew. Chem.* **1990**, *102*, 362.

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[36] In our experience, dilute ozone solutions lose their color quickly (<30 min), even at 0° C. Ozone self-decomposition has been well documented in aqueous solutions: Tomiyasu, H.; Fukutomi, H.; Gordon, G. *Inorg. Chem.* **1985**, *24*, 2962.

[37] For example: (a) Greer, A. *Science* **2003**, *302*, 235. (b) Korshin, E. E.; Bachi, M. D. *Chem. Peroxides* **2006**, *2* (1), 189. (c) Cremer, D. *Israel J. Chem.* **1983**, *23*, 72.

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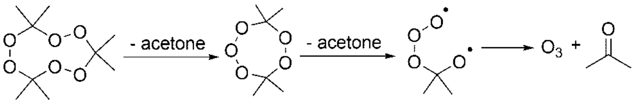
SCHEME 5. Thermal Decomposition of TATP



22 "TATP" **23**

atmospheric species.[1f,39] In addition to localized anthropogenic sources, their formation in the atmosphere is usually attributed to reaction of ozone with isoprene and other alkenes by the Criegee mechanism or oxidation of alkanes proceeding through reaction of alkoxy radicals with oxygen.[40] Formation of atmospheric carboxylic acids is generally attributed to reactions other than aldehyde−ozone chemistry.[41] Rate constants for gas phase reaction of both aldehydes with ozone have been measured:[16,18] for **11**, $k = 2.1 \times 10^{-24}$ cm^3/molecule/s; for **4**, $k = 6 \times 10^{-21}$ cm^3/molecule/s. The difference in rates is consistent with relative acyl bond dissociation energies, reported to be 88.2 kcal/mol for **11** and 84.5 kcal/mol for **4**.[42] As a comparison, the rate for reaction of ethylene with ozone is much faster: $k = 1.6 \times 10^{-18}$ cm^3/molecule/s.[1f] We conclude that ozone−aldehyde reactions might play a minor role in localized atmospheric regions where the concentration of both species is high but are unlikely to be significant elsewhere.

Conclusions

The reaction of ozone with aldehydes has been studied for over 100 years.[4−22] Our computations on reactions of ozone with formaldehyde support the existence of two competing reaction channels: acyl hydrogen abstraction and stepwise cycloaddition to the carbonyl group. Both processes have significant predicted activation barriers: 16.2 kcal/mol for abstraction and 19.1 and 23.0 for the two steps in cycloaddition. Acyl hydrogen abstraction (Scheme 3, **TS1**) and subsequent radical combination leads to a hydrotrioxide (**16**), which can decompose by a cyclic transition state (**TS5**) to give formic acid and singlet oxygen. Other O−O bond cleavage paths and oxygen atom transfer reactions exist for hydrotrioxides. Addition of ozone to the carbonyl carbon (**TS2**) leads to a 1,5-diradical (**18**) that can close to a tetroxolane (**19**). This process is reversible, consistent with Klopman's observation of isotopic exchange for a simple aldehyde.[14] The two channels connect by a second intramolecular atom abstraction (**TS3**). These two reaction channels explain much of what has been observed in the long history of ozone−aldehyde chemistry.[4−22] Ring opening of the tetroxolane by an alternate bond cleavage (**TS6**) can lead to a carbonyl oxide plus $^3O_2$, although the energetics for this route are not very favorable. As we had initially surmised, reversal of this sequence might provide a low energy route to ozone from Criegee intermediates.

Known reaction rates[16,18] and the substantial barriers to both channels support Atkinson's earlier conclusion[1g] that aldehyde oxidation by ozone is too slow to be of great importance in atmospheric chemistry.

We should finally answer the question posed earlier: Why are reactions of alkenes and aldehydes with ozone so different? One obvious answer lies in simple thermochemistry. Cycloaddition of alkenes with ozone is *exothermic* by ca. 50 kcal/mol.[3] In the reaction of formaldehyde with ozone, both abstraction and cycloaddition channels are modestly *endothermic* and thus have significant barriers. For the addition channel, this conclusion was first reached by Nangia and Benson in 1980 on the basis of estimates of the tetroxolane heat of formation.[43] Thus, in contrast to the rapid, concerted and unidirectional cycloaddition to ethylene,[3] cycloaddition of ozone to the formaldehyde carbonyl group is slow, stepwise, and reversible. Our preliminary calculations on other carbonyl compounds show similar mechanisms.

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Note Added in Proof. As this work was in review, another paper has appeared on reaction of ozone with benzaldehyde: Cerkovnik, J.; Plesničar, B.; Koller, J.; Tuttle, T. *J. Org. Chem.* **2009**, *74*, 96.

Supporting Information Available: Tables of energies, Cartesian coordinates and summary energetics for stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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