Free Radical Mechanisms for the Treatment of Methyl *tert*-Butyl Ether (MTBE) *via* Advanced Oxidation/Reductive Processes in Aqueous Solutions

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1. Introduction

Methyl *tert*-butyl ether (MTBE) was manufactured almost exclusively for use as a gasoline additive, and few chemicals were produced in the U.S. in a quantity equal to MTBE. Although it is being phased out as a gasoline additive, its environmental legacy will be with us for some time.[1−3] To date, MTBE has found its way into various environmental compartments, in particular the troposphere, surface and groundwaters, and stormwater.

The interest in MTBE as an environmental contaminant results from the following: (1) A large quantity of it is manufactured annually for use as a fuel oxygenate (up to 15% by volume of gasoline).[4] (2) A number of studies report its presence in the atmosphere.[5,6] (3) Its solubility in water is high, 48 g L^{-1},[7] and therefore, there is practically no MTBE retardation by soil particles in subsurface environments. As a consequence, it is found in surface and subsurface waters[8] and stormwater runoff,[9] and more recently in surface waters in Europe.[10] (4) The results of a recent survey of 954 community water systems show MTBE was the second most frequently detected of the 66 volatile organic compounds analyzed.[1] (5) The slow natural attenuation and/or biodegradability of MTBE in subsurface environments results in plumes in excess of a mile in groundwater. (6) It is not particularly well suited for treatment processes using conventional phase-transfer approaches such as aeration stripping or carbon adsorption. (7) Humans are sensitive to its strong odor when found in water.

The occurrence of MTBE in waters has been reviewed.[1,8,11] In a nationwide survey conducted by the US Geological Survey (USGS), MTBE was found in 5.4 and 14% of the groundwater and surface water sampled, respectively. Its

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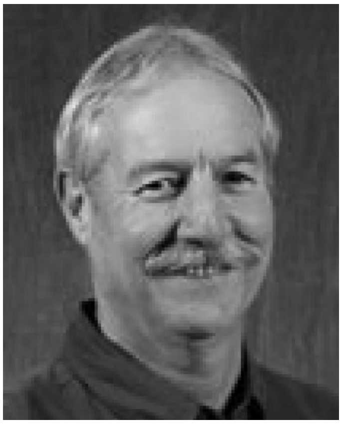
William J. Cooper was born in Rochester, New York, December 1, 1945. He studied chemistry at Allegheny College (B. S. 1968) and then went to The Pennsylvania State University and received his M.S. in Organic Geochemistry in 1971. His studies were interrupted when he was drafted into the U.S. Army, and he progressed from enlisted to officer, and finally, as a civilian doing environmental science, he was program manager for water reuse. His Ph.D. is in Marine and Atmospheric Chemistry at the University of Miami (1987). Concurrently, he was the director of the Drinking Water Research Center at Florida International University (1980−1997), and in 1992 he became Associate Professor in Chemistry. He served three years (1997−2000) as chair of the Department of Chemistry and Biochemistry, University of North Carolina Wilmington, and as Professor until 2006. Presently he is Professor, Department of Civil and Environmental Engineering, and Director, Urban Water Research Center, University of California, Irvine. His fields of interest are environmental chemistry, surface water photochemistry, and radiation chemistry as applied to advanced oxidation processes.

Christopher J. Cramer earned an A.B. in Mathematics and Chemistry from Washington University and a Ph.D. in Chemistry from the University of Illinois. Following 4 years of service as an officer in the U.S. Army, he joined the faculty of the University of Minnesota, where he is currently Distinguished McKnight and University Teaching Professor of Chemistry, Chemical Physics, and Scientific Computation. Author of the textbook *Essentials of Computational Chemistry* and approximately 300 research articles, his interests encompass the development and application of theoretical models to characterize the structure and reactivity of molecules having particular biological, chemical, or environmental interest. His contributions have been recognized by the Arthur S. Flemming award and Alfred P. Sloan and John Simon Guggenheim fellowships.



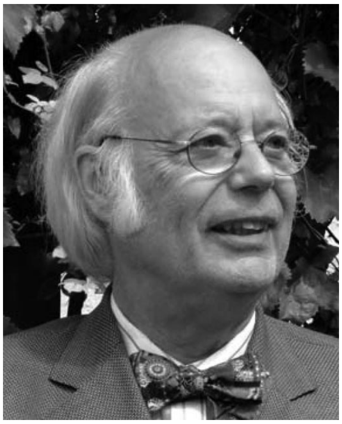
Ned Martin received his A.B. degree with Honors in Chemistry from Denison University in 1967 and a Ph.D. degree in Chemistry from Duke University in 1972. He was a research chemist at the Research Triangle Institute from 1968 to 1970. He was a postdoctoral research associate at the University of Geneva, Switzerland, in 1980−1981. Since 1972 he has been on the faculty of the University of North Carolina Wilmington, where he served as department chair from 1992−1997. He was W. S. DeLoach Professor of Chemistry from 1996 to 2002. He is now Professor of Chemistry and Biochemistry. His research interests include *ab initio* molecular orbital computation remote interactions, including π-stacking effects and through-space magnetic shielding effects.

Stephen P. Mezyk was born in Melbourne, Australia, in 1960 and obtained his B.Sc. degree in Physical Chemistry from the University of Melbourne in 1982, followed by his Ph.D. degree in 1986. He then carried out postdoctoral studies at the University of Calgary, Alberta, Canada, the Radiation Laboratory, and the Department of Chemistry at the University of Notre Dame, Indiana, and the University Saskatchewan, in Saskatoon, Canada. He then joined Atomic Energy of Canada Ltd., first at Pinawa, Manitoba, in the Research Chemistry group and then at Chalk River in Reactor Chemistry. In 2000 he moved to the University of North Carolina at Wilmington, as an Associate Research Professor, before accepting an Assistant Professor faculty position at California State University in Long Beach in 2001. He was promoted to Associate Professor in 2006. His current research interests include the free radical remediation of organic chemical contaminants in waters, as well as the radical mechanisms involved in nitrosamine carcinogenesis and radiation chemistry of nuclear waste reprocessing. He has received the California State University Distinguished Faculty Scholarly and Creative Achievement Award (2008) and Distinguished Faculty Teaching Award (2007), along with multiple concurrent appointments at Department of Energy laboratories in the U.S.

concentration varied from 0.1 to 17,800 μg L^{-1}. Due to its widespread contamination (36 states), there is now a Web site that is maintained by the USGS for MTBE that provides up-to-date information on various aspects (http://sd.water.usgs.gov/nawqa/vocns/mtbe.html). MTBE has also been reported in urban stormwater[9] and waters in other areas in the world, as well,[10,12−16] and more recently in snow.[17]

The presence of MTBE in waters poses a potential health problem.[18,19] It has been shown that MTBE can accumulate in the blood stream and can be detected in breath.[20] The documented effects of MTBE exposure are headaches, vomiting, diarrhea, fever, cough, muscle aches, sleepiness, disorientation, dizziness, and skin and eye irritation.[19] MTBE is a suspect carcinogen; however, it has been concluded that considerable additional work is necessary to better define its health effects.[19,21] A recent study indicated that it was not mutagenic in bacteria, *Salmonella typhimurium*.[22]

Kevin E. O'Shea is currently Professor of Chemistry and Biochemistry at Florida International University. He received his B.S. in Chemistry, with honors, from California State University, Sacramento in 1984. He received a Ph.D. in 1989 from University of California, Los Angeles under the guidance of Prof. Christopher S. Foote. He was a postdoctoral fellow at University of Texas, Austin under the direction of Prof. Marye Anne Fox from 1989 to 1991. His research interests are in the areas of physical and mechanistic organic chemistry. The focus of his research group is on the reactions of reactive oxygen species with organic compounds of biological and environmental importance.



Clemens von Sonntag was born in Stuttgart, Germany, in 1936. He studied Chemistry at the University of Heidelberg (with one semester at Vienna), where he received his Diploma degree on a subject in photochemistry in 1962. He received his Ph.D. degree from the Technical University of Karlsruhe on a subject in radiation chemistry in 1964 and joined the group of F. S. Dainton at Leeds, U.K., as a postdoctoral fellow. In 1965, he became a group leader at the Institute of Radiation Chemistry at the Nuclear Research Center Karlsruhe, passed his Habilitation at the Technical University of Karlsruhe (Professor in 1977), and joined the Max-Planck-Institute for Radiation Chemistry (now Bioinorganic Chemistry) in 1970. His research interests centered on the radiation chemistry of DNA, branching off to fundamental studies on the free radical chemistry of the OH radical; carbon-, nitrogen-, and sulfur-centered radicals; and peroxyl radicals. Related to this were studies on the chemical effects of ultrasound. Other topics were ozone chemistry and photochemistry. The latter led to a multidisciplinary activity that established the feasibility of UV-disinfection of surface waters for the use of drinking water. He received the Weiss Medal and the Marie Sklodowska Curie Medal. After his retirement at the MPI in 2001, he continued to collaborate with various institutions, notably in the area of ozone treatment of wastewater.

Another issue that may be a "driving force" for control of MTBE in water is its organoleptic sensitivity. According to a study,[23] humans can smell MTBE at concentrations between 13.5 and 45.4 μg L^{-1} (0.153−0.515 μM); however, the lowest concentration known to have an adverse health effect on any organism is 145 μg L^{-1}.[24] The EPA suggested limit is 20−40 μg L^{-1} in drinking water,[24,25] and the California Department of Health Services has adopted a secondary maximum concentration level for this chemical of 5 μg L^{-1}.[26]

Because it has been found in many waters that serve as sources for drinking water, there is considerable interest in the removal of MTBE. Remediation technologies for MTBE-contaminated water have been reviewed in depth.[25] Air stripping is not readily applicable due to its high solubility, and this ether only has a moderate affinity for adsorption onto granulated activated carbon.[27] MTBE is not readily biodegraded[28] due to the presence of its *tert*-butyl group; however, some aerobic[29] and anaerobic[30] biodegradation has been reported.

Advanced oxidation processes (AOPs) are now being explored for use in many applications. AOPs are defined as those technologies that utilize the hydroxyl radical ($^\bullet$OH) for oxidation. For water and wastewater treatment of MTBE, several reviews have recently appeared.[31−34] To date, a considerable number of studies have also been reported that explore various AOPs as alternative treatment processes for destroying MTBE in aqueous solution (Table 1). From the data summarized in Table 1, it is also apparent that a number of different reaction byproducts have been identified. However, there is little consistency in the byproducts that have been identified or in the relative proportions measured. Some differentiation of these MTBE byproducts into primary and secondary reaction species has also been reported, as detailed in Table 2.

In addition to $^\bullet$OH, there are AOPs that also produce the hydrogen atom, H$^\bullet$, as well as the hydrated electron, e^-_{aq}. Heterogeneous photocatalytic processes, mostly involving TiO_2,[35] proceed *via* the separation of conductance band electrons, e^-_{CB}, and valence band holes, h^+_{VB}. These two reactive species impart a free radical nature to their reaction processes. In the environmental science and engineering community, there is increased interest in developing kinetic models that describe the destruction of chemicals through various treatment processes. Reaction rate constants and destruction mechanisms are important for the development of kinetic models for AOPs. Once the destruction mechanism is fully elucidated, then that information can be coupled with a detailed description of the kinetics of the reactor to provide a tool which then can be used in process optimization and economic evaluation.

Radiation chemistry provides an excellent tool to study many of the free-radical processes that are of interest in AOPs and other free-radical-mediated processes. To study bimolecular reaction rates, time-resolved electron pulsed radiolysis is typically used. Equation 1 describes the breakdown of water when it is irradiated with high-energy electrons or γ-rays:[36,37]

$$H_2O \rightsquigarrow [0.28]^\bullet\mathbf{OH} + [0.27]\mathbf{e_{aq}}^- + [0.06]\mathbf{H}^\bullet + [0.07]H_2O_2 + [0.27]H_3O^+ + [0.05]H_2 \quad (1)$$

The individual chemical yields (G values in units of μmol J^{-1}) of all species are shown in brackets.

Using the appropriate chemical conditions, a specific radical can be isolated and rate constants determined for its reactions with a substrate. Experimentally, the reactions of the three reactive radical species in eq 1 (in bold) can be studied using electron pulse radiolysis coupled with standard time-resolved detection methods. For example, using pulse radiolysis, the product distributions from the initial radical reactions for a number of environmentally relevant compounds in water have been reviewed.[38]

Table 1. Summary of the Different MTBE Treatment Studies Using Various AOPs in Aqueous Solutions (11.4 μM = 1 mg L^{-1}) Abbreviations used: TBA = tertiary butyl alcohol, TBF = tertiary butyl formate, MA = methyl acetate, MMP = 2-methoxy-2-methylpropanal, FA = formaldehyde

AOP	MTBE conc	reaction byproducts	ref
Aluminum (Bifunctional)			
aluminum	0.16 mM	TBF, TBA, acetone, methyl acetate	*a*−*c*
Carbon Fibers			
Fe/C-fabrics	0.01 μM (in complex mixture of organic compounds)	none identified	*d*
Hydrogen Peroxide (H_2O_2)			
H_2O_2	11.4 μM	no reaction	7
activated carbon/H_2O_2	1.1 mM	none determined	*e*
Fe(II)/H_2O_2	64−80 μM	TBA	*f*
Fenton reaction	22.7 μM	TBF, TBA, MA, acetone	180, *g*, *h*
	1.19 mM	no reaction with H_2O_2 alone TBA, acetone	*i*
	not specified	TBF, TBA, acetone, acetaldehyde (trace), MA, formic acid, acetic acid, propionic acid, CO_2	164
	1 mM	TBF, TBA, MA, acetone	*j*
	1 mM	TBF, TBA, MA, acetone	*k*
	0.38 mM	TBF, TBA, acetone	1
Fenton reaction with zerovalent iron	1.7 mM	acetone	*m*
photo-Fenton reaction		TBF, TBA, MA, acetone, peroxidic material, FA, alkanes (methane, ethane, isobutane), isobutene, acetic and formic acids	*n*
anodic Fenton reaction	0.35−4.5 mM	TBF, TBA, acetone, acetic and formic acids	*o*
UV/H_2O_2	1.14−114 μM	none determined	7
	0.92 mM	TBF, TBA, MMP, MA, acetone, FA, hydroxyl isobutyraldehyde, hydroxyacetone, pyruvaldehyde, hydroxyl isobutyric, formic, pyruvic, acetic, and oxalic acids	27, 97
	10 mM	none determined	*p*
	114 μM	TBF, TBA	*q*
	0.29−2.85 mM	TBF, TBA, acetone, MA, formic acid	*r*
	0.11 mM	none determined	*s*
	0.91 mM	none determined	*t*
Ionizing Radiation			
electron beam	2.7 μM	TBF, TBA	*u*
	26−353 μM	none determined	183
	2.7 μM	TBF, TBA	182
	5.9 mM	TBF, TBA, FA, formic and oxalic acids	143
	2.2−3.0 μM	TBF, TBA	*v*
γ-radiolysis	0.39 mM	none determined	179
	1.14 mM	TBF, TBA, acetone, MA, isobutene, FA	96
	1.05 mM	TBF, TBA, acetone, MA	*w*
Ozone (O_3)			
O_3	100 μM	very slow direct reaction with O_3	98
	20 μM	TBF, TBA, acetone, MA, acetic acid, formic acid	*x*
	0.20−0.88 μM	TBF, FA, acetaldehyde, glyoxal, methylglyoxal	*y*
	2.1−24.2 μM	TBF, TBA, acetone, MA, FA, acetaldehyde, glyoxal, methylglyoxal	*z*
	5.7 μM	none determined	*aa*
	0.09−2 mM	TBF, TBA	141
O_3/UV	1.3 μM	none determined, refinery wastewater	*ab*
	14 μM	TBF, MA, butene, acetone and acetaldehyde	*ac*
	0.84−0.99 mM	TBF, TBA, MA, acetone, hydroxyl isobutyraldehyde, MMP, formaldehyde, pyruvaldehyde; pyruvic, acetic, oxalic and formic acids;	*ad*
pulsed UV/O_3	11.4−22.8 μM	TBF, TBA, acetone, FA, acetaldehyde, glyoxal, methylglyoxal	*ae*, *af*
O_3/H_2O_2	0.09−2 mM	TBF, TBA	*ag*
	100 μM	TBF, TBA, MMP, acetone, MA, FA; hydroxyl isobutyraldehyde	98
	<20 μM−4.0 mM	none determined	*ah*, *ai*
	20 μM	TBF, TBA, acetone, MA, acetic acid, formic acid	*x*
	2.3 μM	TBF, TBA, acetone, MA	*aj*
	0.20−0.88 μM	TBF, FA, acetaldehyde, glyoxal, methylglyoxal	*y*
	2.0−21.8 μM	TBF, TBA, acetone, MA, FA, acetaldehyde, glyoxal, methylglyoxal	*ae*
	0.11 μM	TBF, TBA	*ak*
O_3 and perfluorinated alumina	2.6 μM	TBF, TBA, acetone, FA	*al*, *am*
	25 μM	oxalic, formic and acetic acid	
Permanganate Ion ($KMnO_4$)			
$KMnO_4$	1370 μM	none determined	*an*
	131 μM	none determined	*ao*
	50 mM	none determined	*ap*
Peracids			
acetic peracid	11.4 mM	preliminary study	*aq*
Peroxodisulfate Ion ($Na_2S_2O_8$)			
$Na_2S_2O_8$ thermolysis	60 μM	TBF, TBA, acetone, MA	*ar*
Plasma−Dense Medium			
	1.0 μM	TBF, acetone, FA, CO_2	*as*, *at*
Titanium Dioxide (TiO_2)			
TiO_2/UV	1.0 mM	TBF, TBA, acetone, isobutene, α-hydroperoxymethyl *tert*-butyl ether, acetic acid, formic acid	*au*
	11.4 μM	TBF, TBA, acetone	*av*
	114−570 μM	TBF, acetone, MA	179
	1 mM	TBF, TBA, acetone	*aw*
	1.14		*ax*, *ay*

Table 1. Continued

AOP	MTBE conc	reaction byproducts	ref
$TiO_2/UV/H_2O_2$	14.8−17.1 μM	TBF, TBA, MA	*az*
	1.0 mM	TBF, TBA, acetone	*ba*
TiO_2/solar radiation	2.3 μM	TBF, TBA, acetone	*bb*
TiO_2/xenon lamp	0.91 mM	none determined	*bc*
TiO_2/xenon lamp/H_2O_2	0.91 mM	none determined	*bd*
TiO_2/gold nanoparticles/xenon lamp	2.27 mM	none determined	*be*, *bf*
		Ultrasound	
ultrasound	0.39 mM	TBF, TBA, isobutene, acetone, MA, FA, acetic and formic acids	53
	28.4−284 μM	TBF, acetone	*bg*
ultrasound−O_2 satd	390 μM	TBF, TBA, acetone, MA, isobutylene, formaldehyde, acetic acid, formic acid	*bh*
ultrasound−Ar satd		TBA, acetone, isobutylene, 2-methoxypropene, MA, formaldehyde, acetic and formic acids	
ultrasound/O_3	0.01−1.00 mM	TBF, TBA, MA, acetone	*bi*
	0.01−1.00 mM	MTBE loss only	*bj*
ultrasound/$K_2S_2O_8$	28.4−284 μM	TBF, acetone	*bg*
ultrasound/Fenton reaction	28.4 μM	TBF, acetone	*bg*
	1.14 μM	TBA, acetone	*bk*
ultrasound/photocatalysis	5.5 mM	TBF, TBA, acetone, formic and acetic acid	*bl*
		Ultraviolet Radiation (UV)	
UV (254 nm)	11.4 μM	no reaction	7
UV (254 nm)		no reaction	*r*
pulsed UV	0.55−22.8 μM	TBA, acetone, FA, acetaldehyde, glyoxal, methylglyoxal (TBF not found)	*ae*
		Granualar Activated Carbon−Regeneration	
Fenton reaction	not applicable	no products	*bm*, *bn*

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For studying organic destruction mechanisms, low dose-rate ^{60}Co-γ irradiations provide an equivalent experimental approach where all the reactive species in eq 1 can again be accessed. For γ-irradiations, increasing the exposure

Table 2. Primary and Secondary Reaction Products from the Free Radical-Mediated Destruction of MTBE and of Its Degradation Products[a]

compd (ref)	primary products	secondary products
MTBE[98,99]	TBF, TBA, MMP, acetone, MA	hydroxyisobutyraldehyde, (2-methyl-2-hydroxypropionaldehyde), hydroxyisobutyric acid, (2-methyl-2-hydroxypropionic acid), isobutyraldehyde, pyruvaldehyde, pyruvic acid, oxalic acid, acetic acid, formaldehyde, formic acid
TBF[98]	acetone, formaldehyde, formic acid, hydroxylisobutyraldehyde, TBA	pyruvaldehyde, hydroxyacetone, hydroxyisobutyric acid, pyruvic acid, acetic acid, oxalic acid
TBF[b]	TBA, formic acid, acetone, formaldehyde, acetic acid, isobutylene	
TBA[98,106]	acetone, formaldehyde, hydroxyisobutyraldehyde	pyruvaldehyde, formic acid, hydroxyisobutyric acid, pyruvic acid, acetic acid, oxalic acid
TBA[102]	acetone, formaldehyde, hydroxyisobutyraldehyde, pyruvaldehyde	formic acid, acetic acid, pyruvic acid, oxalic acid
acetone[118−120]	acetic acid, pyruvic acid, oxalic acid, pyruvaldehyde	formic acid, glyoxylic acid, hydroxyacetone, formaldehyde
acetate ion[93,136]	glycolic acid, glyoxylic acid, formaldehyde	

[a] Kim, D. K. Ph.D. Thesis, Florida International University, 2005. [b] Abbreviations used: TBA = tertiary butyl alcohol, TBF = tertiary butyl formate, MA = methyl acetate, MMP = 2-methoxy-2-methylpropanal.

Table 3. Quantitative Distribution of Reaction Byproducts of MTBE and Reaction Byproducts[a]

ref	compd (initial conc)	process	reaction byproduct	conversion (percent of parent)
99	MTBE	O_3/H_2O_2	TBF	42
			TBA	13
			MMP	19
			acetone	18
			MA	8
99	TBF	O_3/H_2O_2	hydroxyisobutyraldehyde	62
			acetone	38
99	TBA	O_3/H_2O_2	hydroxyisobutyraldehyde	60
			acetone	40
98	MTBE (0.92 μM)	UV/H_2O_2	TBF	22
			TBA	11
			MMP	11
			acetone	38
			MA	8
			formaldehyde	18
b	MTBE (1.05 μM)	γ radiolysis	TBF	47
			TBA	11
			acetone	6.4
			MA	9.1
38	*tert*-butanol	radiolysis	acetone	29
			formaldehyde	23
			2-hydroxy-2-methylpropionaldehyde	36
			2-methyl-2,3-propanediol	9
			bis(2-hydroxy-2-methylpropyl)peroxide	12
			H_2O_2	25
119, 120	acetone (1.15 mM)	UV/H_2O_2	pyruvic aldehyde	9
			pyruvate/pyruvic acid	19
			acetate/acetic acid	24
			oxalate/oxalic acid	4
			formaldehyde	2
			formate/formic acid	2
			hydroxyacetone	3
			glyoxylate/glyoxylic acid	4
93	acetate ion	radiolysis (${}^{\bullet}$OH only)	glyoxylic acid	50
			glycolic acid	13
			formaldehyde	26
			carbon dioxide	26
			organic peroxides	13
			H_2O_2	32

[a] Abbreviations used: TBA = tertiary butyl alcohol, TBF = tertiary butyl formate, MA = methyl acetate, MMP = 2-methoxy-2-methylpropanal. [b] Hsieh, L.-L.; Lin, Y.-L.; Wu, C.-H. *Water Res.* **2004**, *38*, 3627.

time increases the delivered dose (the total concentration of the reactive species), and therefore, the progress of the reaction(s) occurring can be followed conveniently.

Table 3 summarizes the quantitative data in the literature on MTBE and its reaction byproducts. For this tabulation, the percent conversion at maximum concentration of the byproduct is provided as a guide for developing the MTBE destruction mechanism.

The characterization of the fate of organic contaminants in the environment, *via* free-radical reactions that can occur in both the gas and condensed phases is of interest for several reasons. Such reactions form an important part of tropospheric chemistry and thus affect the fate and transport of organic compounds. It is also well-known that aquatic (sunlight) photochemical reactions can occur *via* free radical reactions, which in some instances may be catalyzed by metal oxide particles.[39]

There have been several recent reviews that summarize general homogeneous reactions in the troposphere[40−43] and for MTBE in atmospheric droplets.[44] Several reviews of treatment options in water have also appeared,[34,35,45,46] and the effect of MTBE on the movement of petroleum hydrocarbons in soil has also been reviewed.[47]

The focus of this review on reactions leading to the remediation of MTBE is motivated by the widespread extent of environmental contamination by MTBE. Here, we attempt to compile all of the known information on the degradation of MTBE and its reaction byproducts using free-radical processes (AOPs) in order to suggest a complete mechanism for MTBE free-radical chemistry, peroxyl radical formation and decomposition, and the formation and subsequent decomposition of later reaction byproducts. As the reaction byproducts that are formed in the destruction of MTBE are common to many other chemicals in aqueous solution, this review may serve as a reference point for researchers interested in similar processes for the destruction of other organic chemicals. From the mechanism we suggest, it is obvious that the aqueous-phase free-radical-mediated destruction of this relatively simple organic compound is very complex and leads to a variety of products. We complete the review by suggesting areas of further investigation that are necessary to complete this mechanism and to initiate the development of a more complete kinetic model.

2. Aqueous Phase Free Radical Chemistry

2.1. Hydroxyl Radical

The hydroxyl radical ($^{\bullet}OH$) can undergo a number of different reactions with organic compounds, including addition to C=C and C=N double bonds (e.g., reaction 2), H-atom abstraction (e.g., reaction 3), and electron transfer (e.g., reaction 4). These reactions are usually fast, and many rate constants have been documented (for some typical compilations, see www.rcdc.nd.edu).[37,48] Because of its fast reactions with practically all organic substrates, second order radical−radical recombination reactions (e.g., $^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$) can be neglected unless the substrate concentration is very low and high radical concentrations, such as those generated upon intense or prolonged electron beam irradiation or sonication, prevail.

$$^{\bullet}OH + CH_2{=}CH_2 \rightarrow HOCH_2{-}CH_2^{\bullet} \qquad (2)$$

$$^{\bullet}OH + CH_3COCH_3 \rightarrow {}^{\bullet}CH_2COCH_3 + H_2O \qquad (3)$$

$$^{\bullet}OH + NO_2^{-} \rightarrow {}^{\bullet}NO_2 + OH^{-} \qquad (4)$$

2.2. Hydrated Electron

The hydrated or solvated electron, e_{aq}^{-}, is the most powerful reductant in aqueous solution and readily reduces transition metal ions to their lower oxidation states (e.g., reaction 5). It can also attach to solutes, either dissociatively (reaction 6) or associatively (reaction 7). Many hydrated electron reaction rate constants have been published and are summarized in multiple compilations (see www.rcdc.nd.edu).[37,49−52]

$$e_{aq}^{-} + Fe^{3+} \rightarrow Fe^{2+} \qquad (5)$$

$$e_{aq}^{-} + CCl_4 \rightarrow {}^{\bullet}CCl_3 + Cl^{-} \qquad (6)$$

$$e_{aq}^{-} + CH_3COCH_3 \rightarrow (CH_3)_2C(O^{-})^{\bullet} \qquad (7)$$

2.3. Hydrogen Atom

Hydrogen atoms ($H^{\bullet}$) are formed in high yield in sonicated solutions,[53] although their major part undergoes the endothermic (15 kcal mol^{-1}) $^{\bullet}H + H_2O \rightarrow H_2 + {}^{\bullet}OH$ reaction at the high bubble temperatures.[54]

It also accounts for approximately 10% of the total free radicals produced in irradiated water (γ or high energy electrons).[37,55−62] The $H^{\bullet}$ radical undergoes two general types of reactions with organic compounds, addition and hydrogen atom abstraction.

For example, a typical addition reaction with an organic solute is that of benzene,

$$H^{\bullet} + C_6H_6 \rightarrow C_6H_7^{\bullet} \qquad (8)$$

and a typical H-abstraction reaction is that for methanol,

$$H^{\bullet} + CH_3OH \rightarrow H_2 + {}^{\bullet}CH_2OH \qquad (9)$$

For reactions of the general form shown in eq 9, carbon-centered radical products can be indistinguishable from those from reactions of type (3), and this makes assignment of the overall mechanism more challenging.

2.4. Conduction Band Electrons

Heterogeneous reactions involving TiO_2 (and other photocatalysts) and photons with energy greater than the band gap energy may result in the formation of conductance band electrons, e^{-}_{CB} ($E^{\circ} = -0.2$ V),[63] and valence band holes, h^{+}_{VB} (reaction 10). It is thought that the following reactions occur:[35]

$$TiO_2 + hv \rightarrow e^{-}_{CB} + h^{+}_{VB} \qquad (10)$$

$$h^{+}_{VB} + H_2O_{ads} \rightarrow {}^{\bullet}OH_{ads} + H^{+} \qquad (11)$$

$$h^{+}_{VB} + OH^{-}_{ads} \rightarrow {}^{\bullet}OH_{ads} \qquad (12)$$

$$e^{-}_{CB} + O_{2ads} \rightarrow O_{2ads}^{\bullet-} \qquad (13)$$

The reactions of e^{-}_{CB} are generally selective and usually restricted to the reduction of adsorbed O_2, as the low potential of this electron is not sufficient to initiate electron attachment or dissociation reactions with most organic solutes.

The reactions of $^{\bullet}OH_{ads}$ are similar to those described for $^{\bullet}OH$ above. This assumption appears to be consistent with the data reported for the reaction products from the TiO_2 heterogeneous catalytic destruction of MTBE (Table 1).

The direct comparison of light-initiated, heterogeneous processes and the radiolysis process has been questioned based on reaction byproduct analysis;[64] therefore, caution should be exercised in quantitatively applying the following discussion to an understanding of the TiO_2 and other heterogeneous photocatalytic systems.

2.5. Bimolecular Reaction Rate Constants

A relatively large database of bimolecular reaction rate constants is available in the literature to help understand free-radical processes. Table 4 summarizes all of the known bimolecular reaction rate constants for MTBE and its free-radical-induced decomposition byproduct in aqueous solution. For some of the reaction products that have either been identified or predicted, bimolecular reaction rate constants have not been reported, and these suggest future research topics.

Table 4. Summary of the Relevant Bimolecular Reaction Rate Constants (M^{-1} s^{-1}) and References for the Free Radical Decomposition of Methyl *tert*-Butyl Ether in Aqueous Solution

chemical	reactive species					
	$^{\bullet}$OH	ref	e^{-}_{aq}	ref	H$^{\bullet}$	ref
Five Carbon Molecules						
methyl *tert*-butyl ether (MTBE)	1.6×10^{9}	*a*				
	$(3.9 \pm 0.73) \times 10^{9}$	*b*				
	1.9×10^{9}	101				
	$(1.26 \pm 0.08) \times 10^{9}$	*c*				
	1.71×10^{9}	143	$<8.0 \times 10^{6}$	135	3.49×10^{6}	143
tert-butyl formate (TBF)	$(4.1 \pm 0.2) \times 10^{8}$	*d*				
	$(1.2 \pm 0.40) \times 10^{9}$	*b*				
	7.0×10^{8}	99				
	$(5.23 \pm 0.07) \times 10^{8}$	100	$(5.48 \pm 0.09) \times 10^{8}$	100	$(3.58 \pm 0.07) \times 10^{6}$	100
2-methoxy-2-methylpropanal (MMP)	3.0×10^{9}	99				
	$(3.99 \pm 0.10) \times 10^{9}$	*e*	$(3.11 \pm 0.20) \times 10^{7}$	*e*	$(1.65 \pm 0.05) \times 10^{7}$	*e*
2-methoxy-2-methyl-1-propanol (MMP-OH)	$(8.02 \pm 0.05) \times 10^{8}$	*e*	$(7.83 \pm 1.54) \times 10^{6}$	*e*	$(1.30 \pm 0.10) \times 10^{8}$	*e*
2-methoxy-2-methylpropanoic acid (MMP-COOH)	$(7.73 \pm 0.22) \times 10^{8}$	*e*	$(1.40 \pm 0.05) \times 10^{9}$	*e*	$<1.2 \times 10^{6}$	*e*
Four Carbon Molecules						
tert-butyl alcohol (TBA)	6.0×10^{8}	99	$(4 \pm 1) \times 10^{5}$	*f*	8×10^{4}	*g*
	$(6.0 \pm 0.4) \times 10^{8}$	*h*			1.7×10^{5}	*g*
	$(5.2 \pm 1.0) \times 10^{8}$	*i*			1.5×10^{5}	*j*
	5.5×10^{8}	*f*				
	6.6×10^{8}	*k*				
	$(7.0 \pm 2.0) \times 10^{8}$	*l*				
	4.3×10^{8}	193				
2-methyl-2,3-propanediol	NF		NF		NF	
2-methylpropionaldehyde	NF		NF		NF	
hydroxyisobutyraldehyde(2-hydroxy-2-methyl propanal)	3.0×10^{9}	99	NF		NF	
2-hydroxy-2-methylpropionic acid	NF		NF		NF	
Three Carbon Molecules						
acetone	1.1×10^{8}	37	6.5×10^{9}	37	2.6×10^{6}	*m*
	$(1.3 \pm 0.1) \times 10^{8}$	*h*	5.75×10^{9}	*n*	2.8×10^{6}	*g*
	$(1.0 \pm 0.3) \times 10^{8}$	*i*	$(5.9 \pm 0.2) \times 10^{9}$	*o*	8.1×10^{5}	*p*
	7.7×10^{7}	*q*	5.6×10^{9}	*r*	1.8×10^{6}	*s*
	9.7×10^{7}	*t*	6.5×10^{9}	*u*	$(1.97 \pm 0.10) \times 10^{6}$	*v*
	$(1.1 \pm 0.5) \times 10^{8}$	*l*	$(7.2 \pm 0.5) \times 10^{9}$	*w*		
	2.1×10^{8}	193	8.0×10^{9}	*x*		
hydroxyacetone (acetol)	NF		NF		NF	
methyl acetate	1.2×10^{8}	*t*	8.7×10^{7}	118	NF	
methylglyoxal (pyruvaldehyde)	7.0×10^{8}	37	NF		NF	
	$(5.3 \pm 0.4) \times 10^{8}$	*l*				
	1.1×10^{9}	193				
pyruvic acid (α-ketopropionic acid)	1.2×10^{8}	193	NF		NF	
pyruvate ion	3.1×10^{7}	*y*	6.8×10^{9}	51	NF	
	7.0×10^{8}	193				
Two Carbon Molecules						
acetaldehyde	2.4×10^{9}	92	4.9×10^{9}	37	3.4×10^{7}	*g*
	7.3×10^{8}	*z*	$(4.5 \pm 0.2) \times 10^{9}$	*aa*	3.4×10^{7}	*ab*
	$(2.6 \pm 0.2) \times 10^{9}$	*l*	3.5×10^{9}	*ac*		
acetic acid	1.6×10^{7}	37	2.0×10^{8}	37	9.8×10^{4}	37
	1.41×10^{7}	*q*	$(2.2 \pm 0.3) \times 10^{8}$	*ad*	7.7×10^{4}	*m*
	2.3×10^{7}	*t*	1.76×10^{8}	*ac*	1.2×10^{5}	*g*
	1.7×10^{7}	*ae*				
acetate ion	8.5×10^{7}	37	1.1×10^{6}	*af*	3.5×10^{5}	37
	9.0×10^{7}	*i*	no reaction	*ag*	3.9×10^{5}	*ah*
	7.0×10^{7}	*ae*	$<1 \times 10^{6}$	*ac*	3.5×10^{5}	*p*
			$(1.1 \pm 0.2) \times 10^{6}$	*f*	3.2×10^{5}	149
					2.7×10^{5}	*s*
glyoxal	6.6×10^{6}	*ai*	NF		NF	
	1.1×10^{9}	*aj*				
glycolic acid	6.0×10^{8}	37	4.3×10^{8}	*ak*	1.7×10^{7}	*g*
	5.4×10^{8}	*al*				
	6.6×10^{8}	*z*				
	3.6×10^{8}	193				
glycolate ion	8.6×10^{8}	137	8.2×10^{6}	132	4.0×10^{7}	*m*
	2.6×10^{9}	193			5.5×10^{7}	*am*
					3.7×10^{7}	*ah*
glyoxylic acid	NF		1.3×10^{9}	*ak*	NF	
glyoxylate ion	NF		NF		NF	
oxalic acid	1.4×10^{6}	146	2.5×10^{10}	*an*	3.3×10^{5}	37
					3.0×10^{5}	*m*
					3.8×10^{5}	*g*
hydrogen oxalate ion	4.7×10^{7}	142	3.2×10^{9}	138		
	1.9×10^{8}	195				
oxalate ion	7.7×10^{6}	142	3.1×10^{7}	*ao*	$\leq 4 \times 10^{4}$	*m*
	1.6×10^{8}	193	4.6×10^{7}	*ap*	4×10^{4}	*ah*
			1.7×10^{7}	142		
One Carbon Molecules						
methanol	9.7×10^{8}	37	no reaction	141	2.6×10^{6}	37
	1.9×10^{9}	*h*			3.0×10^{6}	*aq*
	1.01×10^{9}	*ar*			2.5×10^{6}	54
	9.7×10^{8}	*i*			2.4×10^{6}	*as*
	9.5×10^{8}	*at*				

Table 4. Continued

	reactive species					
chemical	$^{\bullet}$OH	ref	e^{-}_{aq}	ref	H$^{\bullet}$	ref
	8.3×10^8	*au*				
	8.8×10^8	101				
	7.8×10^8	101				
	8.0×10^8	*t*				
formaldehyde	1.0×10^9	*z*	$\sim 1 \times 10^7$	*au*	5×10^6	*ab*
(formaldehyde hydrate)	$\sim 1.0 \times 10^9$	129	$<1 \times 10^7$	*ac*	2.1×10^6	*aw*
	2×10^9	51				
	7.8×10^8	*ae*				
formic acid	1.4×10^8	37	1.43×10^8	*ac*	4.4×10^5	37
	1.36×10^8	*q*			7.4×10^5	*g*
	1.4×10^8	*q*			6.8×10^5	*m*
	1.0×10^8	*ae*			1.9×10^5	146
formate ion	3.2×10^9	37	$<1 \times 10^6$	*ac*	2.1×10^8	37
	2.2×10^9	*at*			1.3×10^8	*g*
	3.8×10^9	*k*			1.2×10^8	*ah*
	$(3.5 \pm 0.2) \times 10^9$	*h*			2.8×10^8	*ax*
	$(3.5 \pm 0.5) \times 10^9$	*i*			2.6×10^8	*ax*
	2.45×10^9	*q*			2.4×10^8	*s*
	2.7×10^7	152			2.2×10^8	153
	4.1×10^9	*ay*				
	2.4×10^9	193				

NF = not found

[a] Eibenberger, J. Ph.D. Thesis, University of Vienna, Austria, 1980. [b] Chang, P. B. L.; Young, T. M. *Water Res.* **2000**, *34*, 2233. [c] Mitani, M. M.; Keller, A. A.; Bunton, C. A.; Rinker, R. G.; Sandall, O. C. *J. Hazard. Mater.* **2002**, *89*, 197. [d] Onstein, P.; Stefan, M. I.; Bolton, J. R. *J. Adv. Oxid. Technol.* **1999**, *4*, 231. [e] Mezyk, S. P.; Hardison, D. R.; O'Shea, K. E.; Bartels, D. M.; Song, W.; Cooper, W. J. *J. Phys. Chem. A*, submitted. [f] Gohn, M.; Getoff, N. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1207. [g] Neta, P.; Fessenden, R. W.; Schuler, R. H. *J. Phys. Chem.* **1971**, *75*, 1654. [h] Wolfenden, B. S.; Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1982** 805. [i] Willson, R. L.; Greenstock, C. L.; Adams, G. E.; Wageman, R.; Dorfman, L. M. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 211. [j] Alam, M. S.; Janata, E. *Chem. Phys. Lett.* **2004**, *398*, 557. [k] Elliot, A. J.; Simson, A. S. *Radiat. Phys. Chem.* **1984**, *24*, 229. [l] Monod, A.; Poulain, L.; Grubert, S.; Voisin, D.; Wortham, H. *Atmos. Environ.* **2005**, *39*, 7667. [m] Neta, P.; Holdren, G. R.; Schuler, R. H. *J. Phys. Chem.* **1971**, *75*, 449. [n] Idriss-Ali, K. M.; Freeman, G. R. *Can. J. Chem.* **1984**, *62*, 2217. [o] Anbar, M.; Hart, E. J. *J. Phys. Chem.* **1965**, *69*, 973. [p] Appleby, A.; Scholes, G.; Simic, M. *J. Am. Chem. Soc.* **1963**, *85*, 3891. [q] Thomas, J. K. *Trans. Faraday Soc.* **1965**, *61*, 702. [r] Phillips, G. O.; Wedlock, D. J.; Micic, O. I.; Milosorljevic, B. H.; Thomas, J. K. *Radiat. Phys. Chem.* **1980**, *15*, 187. [s] Nehari, S.; Rabani, J. *J. Phys. Chem.* **1963**, *67*, 1609. [t] Adams, G. E.; Boag, J. W.; Currant, J.; Michael, B. D. In *Pulse Radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: New York, 1965; p 131. [u] Barat, F.; Gilles, L.; Hickel, B.; Lesigne, B. *J. Phys. Chem.* **1973**, *77*, 1711. [v] Mezyk, S. P.; Bartels, D. M. *Can. J. Chem.* **1994**, *72*, 2516. [w] Afanassiev, A. M.; Okazaki, K.; Freeman, G. R. *J. Phys. Chem.* **1979**, *83*, 1244. [x] Maham, Y.; Freeman, G. R. *J. Phys. Chem.* **1985**, *89*, 4347. [y] Kraljic, I. In *The Chemistry of Ionization and Excitation*; Johnson, G. R. A., Scholes, G., Ed.; Taylor and Francis, Ltd.: London, 1967; p 303. [z] Merz, J. H.; Waters, W. A. *J. Chem. Soc.* **1949(V)**, S15. [aa] Duplatre, G.; Jonah, C. D. *Radiat. Phys. Chem.* **1984**, *24*, 557. [ab] Witter, R. A.; Neta, P. *J. Org. Chem.* **1973**, *38*, 484. [ac] Gordon, S.; Hart, E. J.; Matheson, M. S.; Rabani, J.; Thomas, J. K. *Discuss. Faraday Soc.* **1963**, *36*, 193. [ad] Ražem, D.; Hamill, W. H. *J. Phys. Chem.* **1977**, *81*, 1625. [ae] Chin, M.; Wine, P. H. In *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; Lewis Publishers: Boca Raton, FL, 1994; p 85. [af] Köhler, G.; Solar, S.; Getoff, N.; Holzwarth, A. R.; Schaffner, K. *J. Photohem.* **1985**, *28*, 383. [ag] Rabani, J.; Steen, H. B.; Bugge, H.; Brustad, T. *J. Chem. Soc., Chem. Commun.* **1971**, 1353. [ah] Neta, P.; Schuler, R. H. *J. Phys. Chem.* **1972**, *76*, 2673. [ai] Draganic, I.; Marcovic, V. Unpublished Data, in the Radiation Chemistry Data Center, 1968 (www.rcdc.nd.edu). [aj] Buxton, G. V.; Malone, T. N.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (16), 2889. [ak] Mićić, O. I.; Marković, V. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 43. [al] Scholes, G.; Willson, R. L. *Trans. Faraday Soc.* **1967**, *63*, 2983. [am] Shafferman, A.; Stein, G. *Science* **1974**, *183*, 428. [an] Mićić, O. I.; Draganić, I. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 287. [ao] Mulazzani, Q. C.; D'Angelantonio, M.; Venturi, M.; Hoffman, M. Z.; Rodgers, M. A. J. *J. Phys. Chem.* **1986**, *90*, 5347. [ap] Prasad, D. R.; Hoffman, M. Z.; Mulazzani, Q. C.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5135. [aq] Beckert, D.; Mehler, K. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 587. [ar] Elliot, A. J.; McCracken, D. R. *Radiat. Phys. Chem.* **1989**, *33*, 69. [as] Smaller, B.; Avery, E. C.; Remko, J. R. *J. Chem. Phys.* **1971**, *55*, 2414. [at] Baxendale, J. H.; Khan, A. A. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 11. [au] Neta, P.; Dorfman, L. M. *Adv. Chem. Ser.* **1968**, *81*, 222. [av] Marković, V.; Sehested, K. In *Proceedings of the Third Tihany Symposium on Radiation Chemistry*; Dobo, J., Hedvig, Eds.; Akademiai Kiado: Budapest, Hungary, 1972; Vol. 2, p 1243. [aw] Baxendale, J. H.; Smithies, D. H. *Z. Phys. Chem. (Frankfurt Am Main)* **1956**, *7*, 242. [ax] Burchill, C. E.; Dainton, F. S.; Smithies, D. *Trans. Faraday Soc.* **1967**, *63*, 932. [ay] Buxton, G. V. *Trans. Faraday Soc.* **1969**, *65*, 2150.

3. Peroxyl Radical Chemistry

3.1. Radical Reactions with O_2

All of the free-radical-initiated reactions discussed above for organic substrates lead to the formation of carbon-centered radicals. In aerated solution, these carbon-centered species can react with dissolved oxygen to form peroxyl radicals:[65−73]

$$RCH_2^{\bullet} + O_2 \rightarrow RCH_2O_2^{\bullet} \tag{14}$$

Relatively few rate constants for this general reaction have been measured; however, most of the values that have been determined are in the range (2−4) × 10^9 M^{-1} s^{-1},[70] which is just slightly below the diffusion-controlled limit. Table 5 summarizes the rate constants that are relevant to the free-radical-induced degradation of MTBE in aqueous solution. For a detailed treatment of peroxyl radicals in aqueous solution, the reader is referred to von Sonntag and Schuchmann.[38]

Peroxyl radicals formed from carbon-centered radicals are relatively unreactive and usually decay *via* bimolecular self-termination reactions. Mechanistically, the fate of the peroxyl radical in water is very complex.

3.2. Tetroxide Formation

Unless a peroxyl radical can decay unimolecularly (see below), it has to decay bimolecularly; that is, it self-reacts to form a tetroxide as an intermediate (eq 15). Writing a general peroxyl radical as $RCH_2O_2^{\bullet}$, we have

$$2RCH_2O_2^{\bullet} \rightarrow RCH_2{-}O_4{-}CH_2R \tag{15}$$

This tetroxide subsequently decomposes to form a variety of products. For primary and secondary peroxyl radicals, there are four pathways that have been suggested that account for the decomposition of the tetroxide and agree with observed product distributions.[38] These pathways are

$$RH_2C{-}O_4{-}CH_2R \rightarrow RC(O)H + RCH_2OH + O_2 \qquad (16)$$

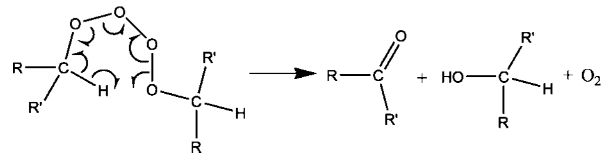
$$\rightarrow 2RCHO + H_2O_2 \qquad (17)$$

$$\rightarrow 2RCH_2CO^{\bullet} + O_2 \qquad (18)$$

$$\rightarrow 2RCH_2COOCH_2R + O_2 \qquad (19)$$

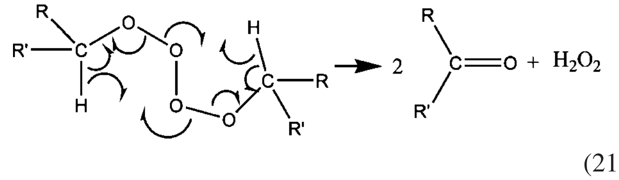
For reactions 16 and 17 to proceed, it is necessary that the α-carbon have a hydrogen (see the discussion on transition states below, i.e., that it is either a primary or secondary carbon).

Reaction 16 leads to the formation of an aldehyde (or ketone) and an alcohol and O_2, and it is referred to as the Russell mechanism.[74] The exact mechanism for the pathway is still the subject of debate; however, based on the product distribution it has been argued that in aqueous solution a concerted process *via* the formation of a cyclic intermediate is favored.[38,74−76] A possible transition state rearrangement for reaction 16 is shown in reaction 20:

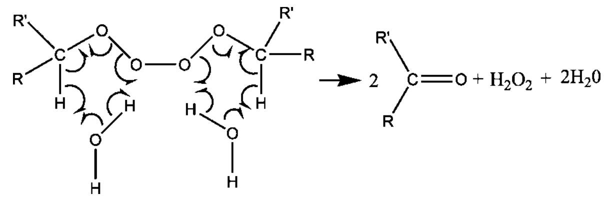


(20)

Reaction 17 leads to the formation of two aldehydes and H_2O_2, and it is referred to as the Bennett reaction.[77,78] For this pathway, two different mechanisms have been suggested, either via unimolecular decomposition, or *via* an alternative transition state with the participation of two water molecules.

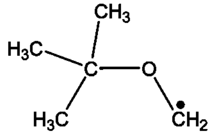
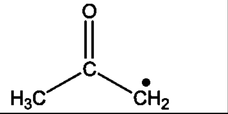
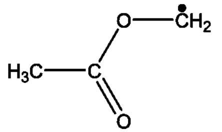
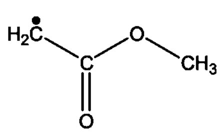
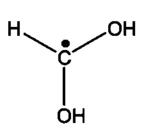


(21)



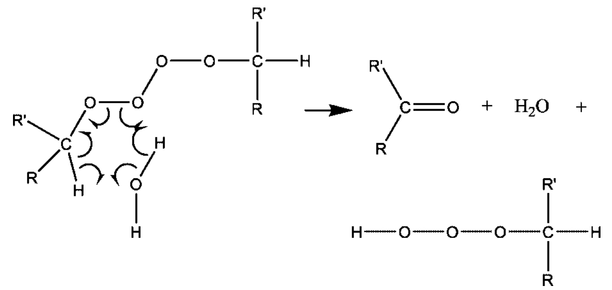
(22)

Table 5. Summary of the Relevant Bimolecular Reaction Rate Constants of Carbon Centered Radicals and O_2 To Form Peroxyl Radicals of Interest in the Decomposition of Methyl *tert*-Butyl Ether in Aqueous Solution

Radical	Rate Constant (M^{-1} s^{-1})	Reference
	(1.23 ± 0.04) x 10^9	143
	3.1 x 10^9	118
	1.4 x 10^9	125
	(1.35±0.15) x 10^{10}	125
	(1.8±0.2) x 10^9	125
$H_2\dot{C}{-}CO_2^-$	1.7 x 10^9	93
	(2.1±0.3) x 10^9	a
	5.0 x 10^8	b
	4.5 x 10^9	132

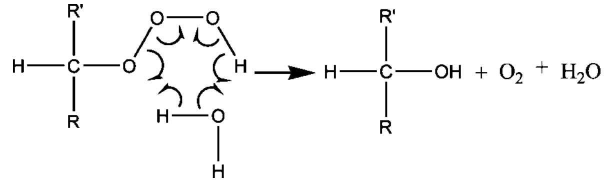
[a] Abramovitch, S. D.; Rabini, J. Pulse radiolysis investigation of peroxy radicals in aqueous solutions of acetate and glycine. *J. Phys. Chem.* **1976**, *80*, 1562−1565. [b] Hayon, E.; Simic, M. Acid−base properties of organic peroxy radicals, OORH, in aqueous solution. *J. Am. Chem. Soc.* **1973**, *95*, 6681−6684.

It has recently been suggested that in aqueous solution a hydrotrioxide could also be formed:[38]

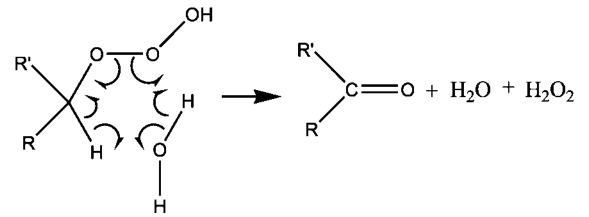


(23)

Subsequent "water-assisted" homolytic fragmentation of a hydrotrioxide (reactions 24 and 25) could occur:



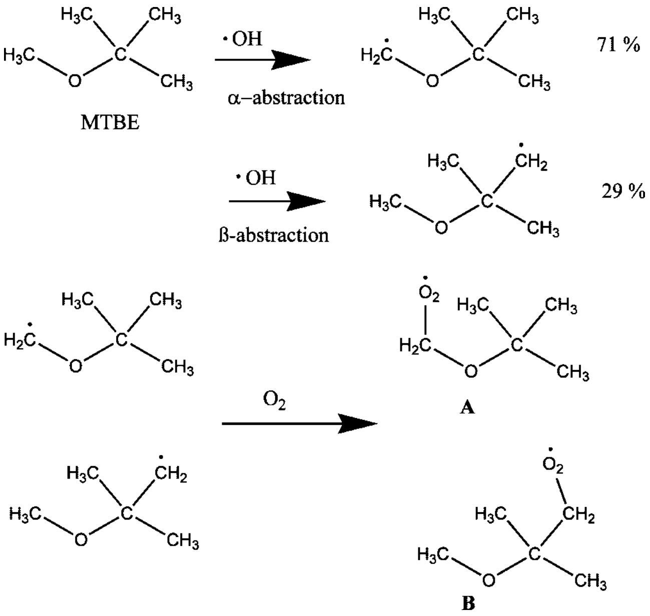
(24)



(25)

The alkoxyl radicals formed in reaction (18) have an α-hydrogen and undergo a rapid 1,2-H-shift (reaction

Scheme 1



26),[79−82] in competition with *β*-fragmentation (reactions 26 and 27):[83,84]

$$RR'CHO^{\bullet} \rightarrow RR'(C^{\bullet})OH \tag{26}$$

$$RR'CHO^{\bullet} \rightarrow {}^{\bullet}R + R'C(O)H \tag{27}$$

Due to these two fast reactions, the recombination of two alkoxyl radicals (reaction 28) can only occur in the solvent cage, and therefore, the yields of organic peroxides are rather low in aqueous solution.

$$2RR'CHO^{\bullet} \rightarrow RR'CHOOCHRR' \tag{28}$$

The α-hydroxyalkyl radical formed from reaction 26 will also add oxygen to give α-hydroxyalkylperoxyl radicals ($RR'C(OH)OO^{\bullet}$). These will undergo spontaneous elimination of $HO_2^{\bullet}$ and/or base assisted elimination of $O_2^{\bullet-}$.[85−88] These reactions can be written in a general form:[86]

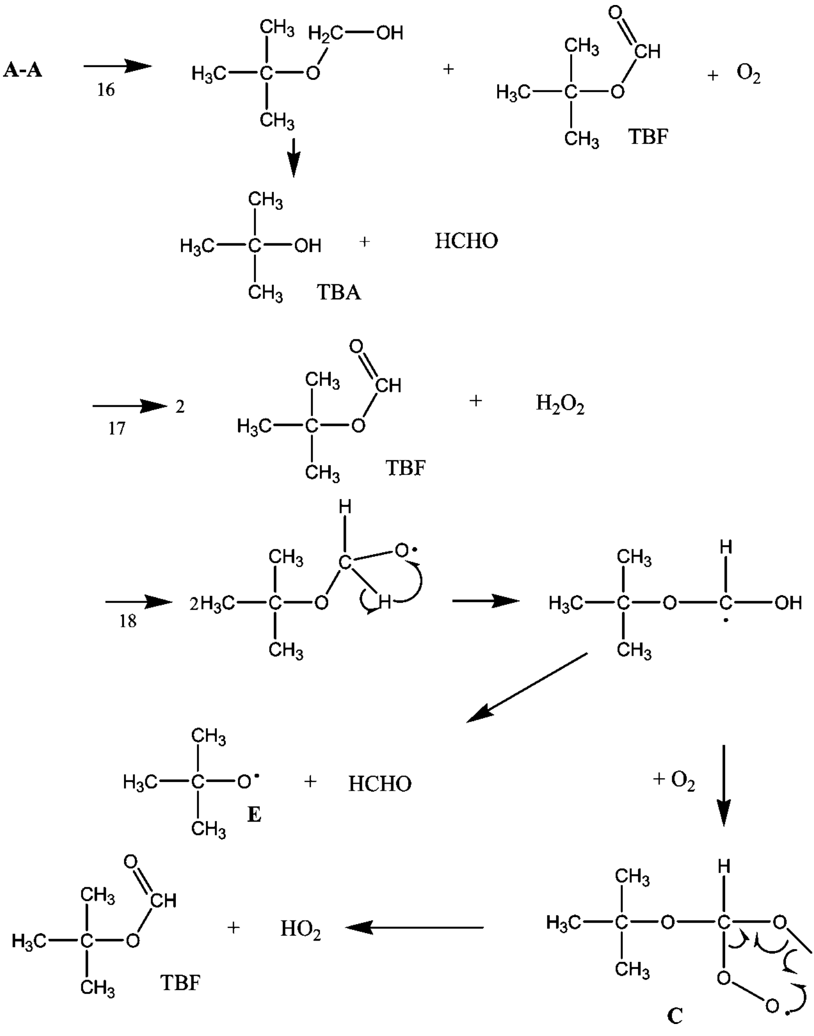
$$RR'C(OH)OO^{\bullet} \rightarrow RR'C{=}O + HO_2^{\bullet} \tag{29}$$

$$RR'C(OH)OO^{\bullet} + OH^- \rightarrow RR'C{=}O + O_2^{\bullet-} + H_2O \tag{30}$$

Due to these reactions, there is always a substantial formation of $HO_2^{\bullet}/O_2^{\bullet-}$ in the decay of organic peroxyl radicals in aqueous solution.

Two other very important reactions that must be considered in irradiated solutions, either as an AOP or in the use of pulse radiolysis or ^{60}Co-*γ*-irradiation, are

Scheme 2



$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet -} \quad (31)$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \quad (32)$$

$HO_2^\bullet$ and $O_2^{\bullet -}$ are in rapid equilibrium, and in neutral solutions, $O_2^{\bullet -}$ dominates.[89−91]

$$HO_2^\bullet \rightleftarrows H^+ + O_2^{\bullet -} \qquad pK_a = 4.8 \quad (33)$$

The rates of $HO_2^\bullet/O_2^{\bullet -}$ bimolecular self-termination reactions are strongly pH dependent. The reaction of $HO_2^\bullet$ with $O_2^{\bullet -}$ is faster than that of $HO_2^\bullet$ with $HO_2^\bullet$, and the self-termination of two $O_2^{\bullet -}$ radicals is almost never practical.[90]

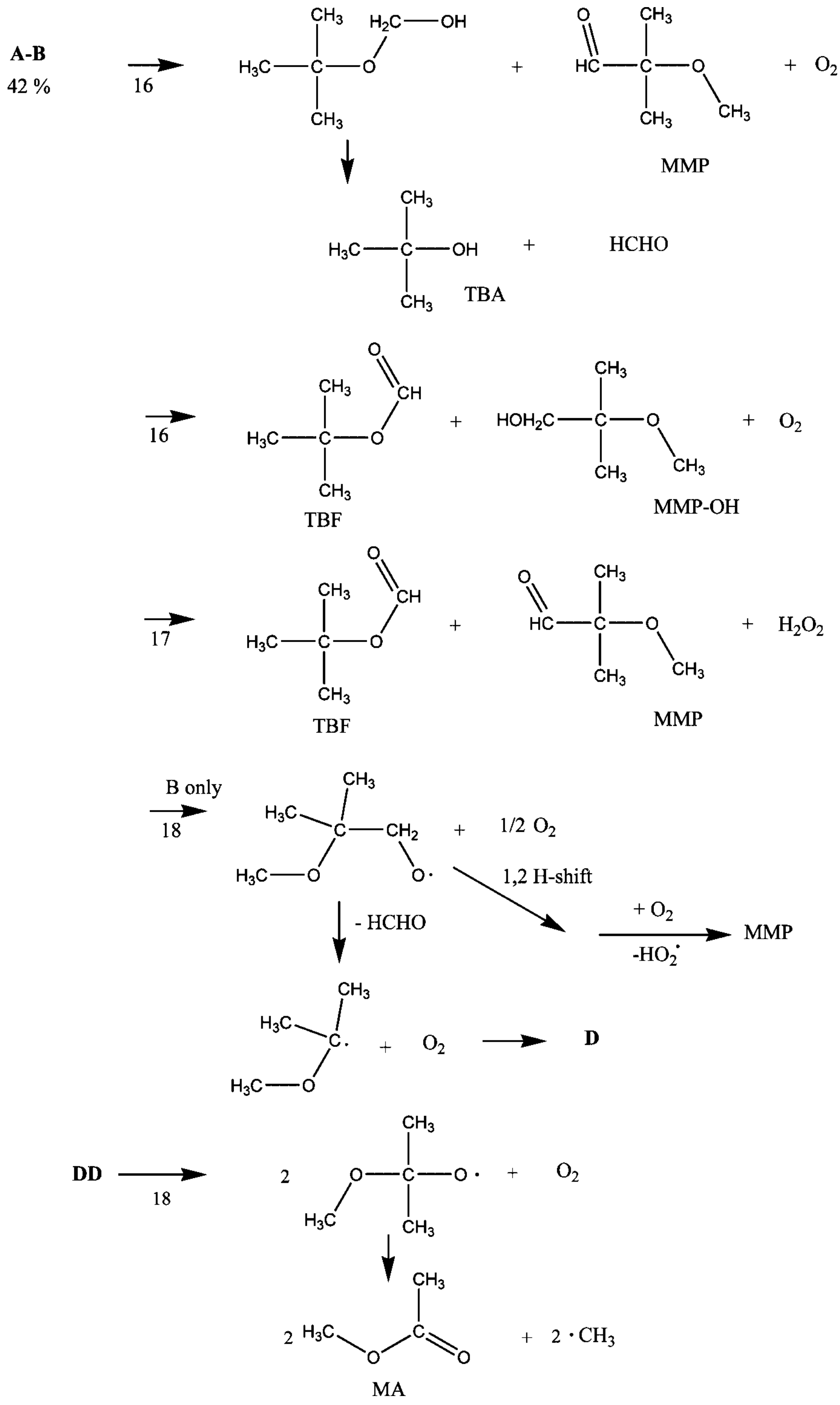
$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_{34} = 8.6 \times 10^5\ M^{-1}\ s^{-1} \quad (34)$$

$$HO_2^\bullet + O_2^{\bullet -} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad k_{35} = 1.0 \times 10^8\ M^{-1}\ s^{-1} \quad (35)$$

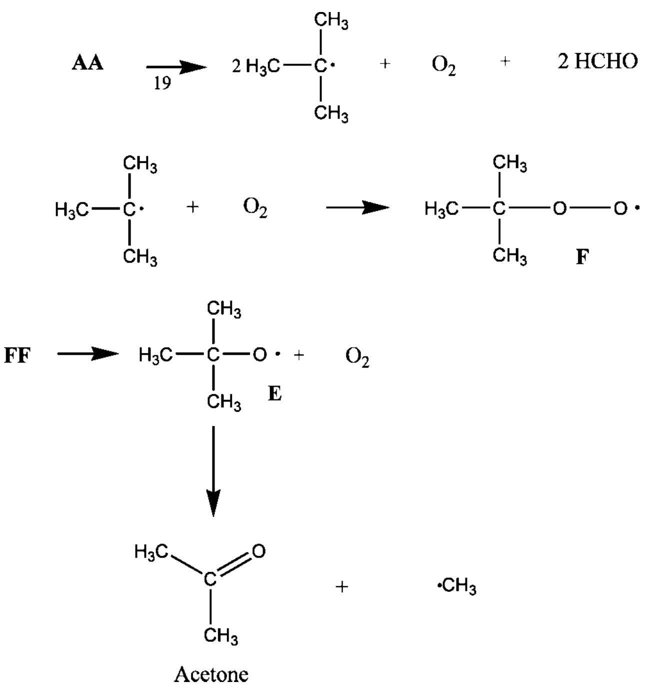
$$2O_2^{\bullet -} \rightarrow O_2^{2-} + O_2 \qquad k_{36} \leq 0.35\ M^{-1}\ s^{-1} \quad (36)$$

However, very little is known about the reactions of $ROO^\bullet$ with $HO_2^\bullet/O_2^{\bullet -}$. Very strongly oxidizing species such as the

Scheme 3



Scheme 4



acetylperoxyl radical react with $O_2^{\bullet -}$ quickly (practically diffusion controlled) largely by electron transfer.[92] The $CH_3CH(OH)OO^{\bullet}$ radical reacts 2 orders of magnitude slower, and the products are not known. The $^{\bullet}OOCH_2C(O)O^-$/$^{\bullet}OOCH_2C(O)OH$ radicals do not react with $HO_2^{\bullet}/O_2^{\bullet -}$ by electron transfer[93,94] to any major extent. For this latter reaction, formaldehyde is one of the products, but no mechanism has yet been elucidated.

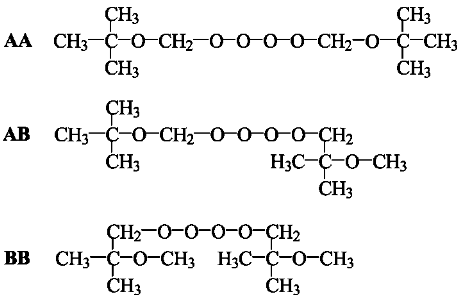
In summary, there are multiple pathways by which the tetroxides decompose. There is no way, *a priori*, to determine the relative contribution of these to the overall decomposition, and therefore, product distributions must be used for mechanistic inference. However, as the products are the same for these different pathways, full elucidation may be difficult in some cases.

4. MTBE Free Radical Degradation Mechanism (tert-Butyl Methyl Ether) [1634-04-4]

Any mechanism for the destruction of a compound must be able to account for all of the major and minor reaction products produced. Initially it was reasoned that MTBE, a relatively simple ether, could easily be degraded by free-radical reactions; however, as we will show, the degradation or mineralization to CO_2 and H_2O is a complex, multistep process. A range of primary and secondary products are involved that themselves undergo free-radical-induced degradation in successive steps. In this review, we detail each of these degradations, organized by decreasing carbon number.

From the reaction rate constants in Table 4, greater than 99.9% of the initial reaction with MTBE is *via* $^{\bullet}OH$. This initial $^{\bullet}OH$ reaction with MTBE results in two carbon-centered radicals. The α-hydrogen (α to the ether carbon) abstraction pathway accounts for 71% while the *β*-hydrogen abstraction is 29%.[95] In oxygenated solutions, the carbon-centered radicals react with O_2 to form two peroxyl radicals (**A** and **B**), respectively (Scheme 1).

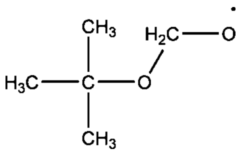
The two peroxyl radicals can then react (*cf.* reaction 15) to form three tetroxides that are designated **AA**, the unsymmetrical **AB**, and **BB**.



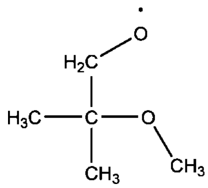
Assuming equal rate constants for **A** + **A**, **A** + **B**, and **B** + **B** and considering the **A**:**B** branching ratio above, the probability of forming **AA**, **AB**, and **BB** will be 50%:42%:8%, respectively. It appears that others have mostly ignored the **AB** tetroxide and focused only on the **AA** and **BB** forms. The inclusion of the **AB** tetroxide results in better explaining the distribution of reaction byproducts that have been reported.

Reaction 16 of the general scheme produces an alcohol and an aldehyde. Applied to the **A** moiety, this results in the formation of the (unstable) *tert*-butyl hemiacetal of formaldehyde and *tert*-butyl formate (TBF) (Scheme 2). The hemiacetal undergoes unimolecular rearrangement to give *tert*-butyl alcohol (TBA) and formaldehyde (FA). The same reaction applied to the **B** moiety gives rise to 2-methoxy-2-methylpropanal (MMP) and 2-methoxy-2-methyl-1-propanol (MMP-OH), as shown in Scheme 3. For the **AB** tetroxide, all four compounds result *via* reaction 16 (Scheme 3).

The reactions for the **A** and **B** moiety that follow reaction 17 of the general scheme give rise to H_2O_2 and the carbonyl compounds TBF and MMP, respectively (Schemes 2 and 3). As far as the formations of oxyl radicals (reaction 18 in the general scheme), **A** gives rise to oxyl radical:



while **B** yields:



A 1,2-H-shift in the oxyl radical (Schemes 2 and 3, general reaction 18) followed by O_2-addition and subsequent $HO_2^{\bullet}$/$O_2^{\bullet -}$ elimination results in the formation of TBF from the **A** moiety and MMP from the **B** moiety. With no α-H atom, these peroxyl radicals form tetroxides, eliminate O_2, and rearrange to give acetone and the methyl radical from moiety **A**, and methyl acetate and methyl radicals from moiety **B**.

It is possible that the oxyl radicals eliminate formaldehyde, giving rise to the *tert*-butoxyl radical (**E**) from the **A** moiety (Scheme 2) and a tertiary radical from the **B** moiety (Scheme 3). For the **B** moiety, the reaction of the carbon-centered radical with O_2 gives rise to the peroxyl radical (**D**). That tetroxide (**DD**) would undergo intramolecular rearrangement, leading to an alkoxyl radical (Scheme 3) which would fragment to give methyl acetate and the methyl radical.

Reaction 19 of the **A** moiety results in the formation of the *tert*-butoxylperoxyl radical (**E**), which dimerizes and decomposes to the *tert*-butoxyl radical (**F**), which then gives rise to acetone and a methyl radical (Scheme 4) with a first order rate constant of between 10^6 and 10^7 s^{-1}.[89−92] The reactions of **BB** are summarized in Scheme 5 and result in the same products as above.

The methyl radical that is formed would react with O_2 to give the methylperoxyl radical (**G**):

$$^{\bullet}CH_3 + O_2 \rightarrow CH_3OO^{\bullet}\ (G) \qquad (37)$$

For the pure methylperoxyl system, that is, in the absence of other peroxyl radicals such as **A**−**F**, it was suggested that the major reaction products formaldehyde, H_2O_2, methanol, methylhydroperoxide, formic acid, and dimethylperoxide were formed from the **GG** tetroxide:[96]

$$\underset{(\mathbf{GG})}{CH_3OOOOCH_3} \xrightarrow{[16]} CH_2O + CH_3OH + O_2 \qquad 56\% \qquad (38)$$

$$\xrightarrow{[17]} 2CH_3O^{\bullet} + O_2 \qquad (39)$$

$$CH_3OOOOCH_3 \xrightarrow{[18]} 2HCHO + H_2O_2 \qquad \leq 19\% \qquad (40)$$

$$CH_3OOOOCH_3 \xrightarrow{[19]} CH_3OOCH_3 + O_2 \qquad 4\% \qquad (41)$$

$$CH_3O^{\bullet} \rightarrow {}^{\bullet}CH_2OH \qquad 6\% \qquad (42)$$

$$^{\bullet}CH_2OH + O_2 \rightarrow HOCH_2OO^{\bullet}\ (\mathbf{H}) \qquad (43)$$

$$2HOCH_2OO^{\bullet} \rightarrow 2HCOOH + H_2O_2 \qquad (44)$$

$$CH_3OO^{\bullet} + HO_2^{\bullet}/(H^+ + O_2^{\bullet -}) \rightarrow CH_3OOH + O_2 \qquad 15\% \qquad (45)$$

In the product studies of MTBE degradation that we have conducted, TBF has been found in approximately a 2-fold excess over TBA,[97] which agrees with the product analysis of others.[98,99] Unfortunately, with the multiple reaction pathways shown in Schemes 1−5 that lead to the formation of these two products, at this time it is not possible to determine the relative importance of the individual reactions.

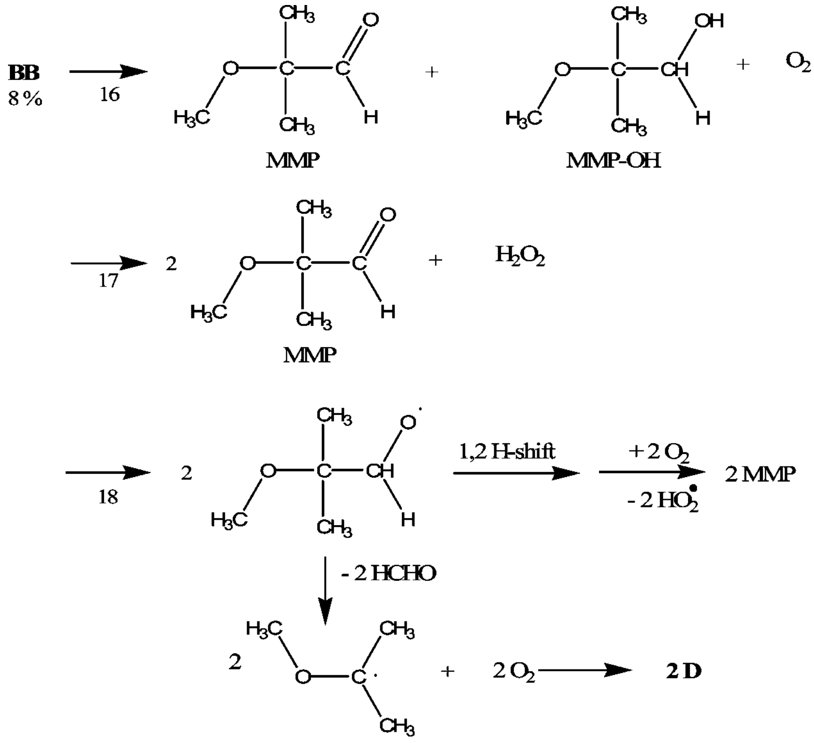
The lack of standards for MMP and its corresponding alcohol, MMP-OH, has hampered their qualitative and quantitative analysis. Although this mechanism predicts the presence of MMP-OH (and later 2-methoxy-2-methylpropanoic acid, MMP-COOH), there have been no reports of either in the literature (Figure 1). It is possible that their polarity prevents extraction into a solvent prior to analysis. These compounds have recently been synthesized,[97] and their free radical chemistry is the subject of an ongoing project.

In summary, the formation and subsequent unimolecular decomposition of **AA**, **AB**, and **BB** lead to the formation of most of the major reaction products that have been reported: TBF, TBA, MMP, MMP-OH, acetone (ACE), methyl acetate (MA), methanol (MeOH), formaldehyde (FA), and formic acid.[7,98,99]

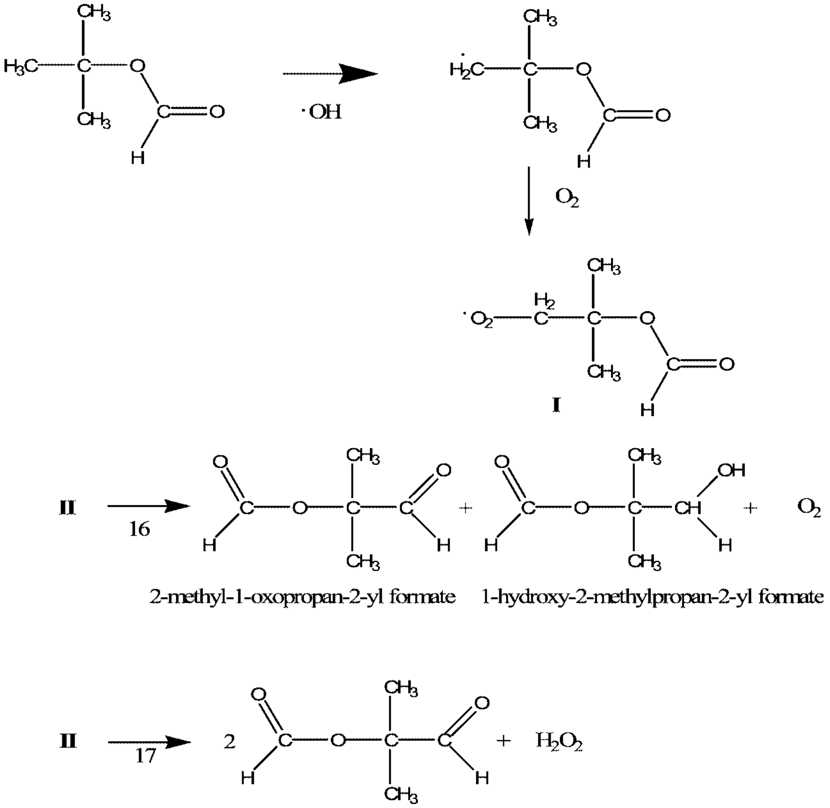
4.1. *tert*-Butyl Formate (TBF) [762-75-4]

One of the major reaction byproducts of the radical-initiated decomposition of MTBE in aqueous solution is TBF. It has been shown that this byproduct initially accumulates and then, with increased reaction time or $^{\bullet}OH$ concentration, decreases. Although initially it was thought that hydrolysis

Scheme 5



Scheme 6



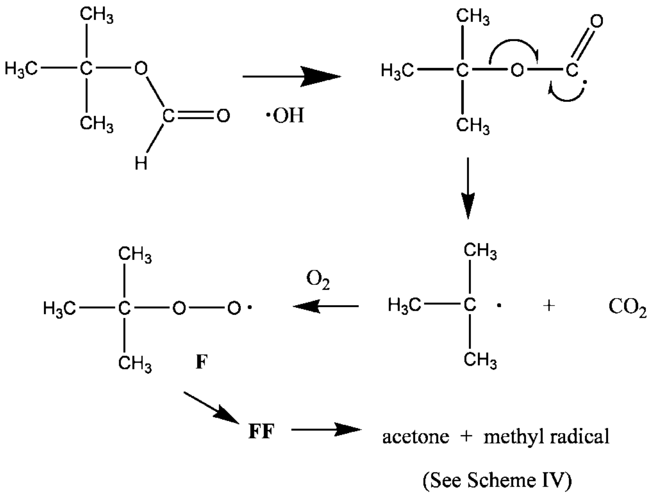
could play an important role in its degradation, it was shown that acid hydrolysis is negligible near pH 4 over short time periods (≤24 h at pH 4).[98] However, base-catalyzed hydrolysis would lead to the formation of TBA and formic acid, two reaction products that have been reported.[98,99]

At near neutral pH under AOP conditions, it appears that radical-mediated processes dominate in TBF destruction. The rate constants for TBF with the three reactive species involved in AOP processes ($^{\bullet}$OH, $^{\bullet}$H, and e^{-}_{aq}) have recently been determined.[100] The rate constant for $^{\bullet}$OH with TBF is considerably slower (approximately 1/5) than the value of MTBE (Table 4). This lower rate constant must be due to the fact that the formyl hydrogen is not as readily abstracted as the hydrogen atom of the methoxy group of MTBE. In agreement with this interpretation is the low $^{\bullet}$OH rate constant with ethyl formate, 3.9×10^{8} M^{-1} s^{-1}.[101] Therefore, H-abstraction from a *tert*-butyl methyl group with subsequent formation of peroxyl radicals (**I**) and subsequent tetroxide formation are likely the initial steps (Scheme 6).

The unimolecular decomposition of **II** leads to two esters, 2-methyl-1-oxopropan-2-yl formate, and 1-hydroxy-2-methylpropan-2-yl formate. If these esters hydrolyze more rapidly than TBF, the formation of the respective aldehyde[98,99] would result. The second product, an as yet unidentified byproduct of MTBE degradation, is the corresponding alcohol. It is also possible that these species undergo H-abstraction followed by the formation of peroxyl radicals and then follow the tetroxide unimolecular decomposition.

The report of acetone as a major primary reaction product of TBF[98,99] suggests that abstraction of the formyl radical-hydrogen may also occur (Scheme 7). The barrier for decarboxylation of *tert*-butyl-OC(O)$^{\bullet}$ radical (to make CO_2 and the *tert*-butyl radical) was predicted to be about 14.5 kcal/mol at a highly correlated level of electronic structure theory.[102] Given that activation energy, transition-state theory predicts a unimolecular rate constant for decomposition on the order of 1.0×10^{3} s^{-1}. If we assume that the alternative reaction of the radical with O_2 occurs at diffusion control rates (see Table 5), then the O_2 concentration need only be 10 μM for the bimolecular reaction to

Scheme 7



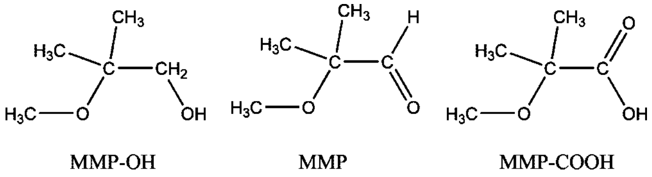
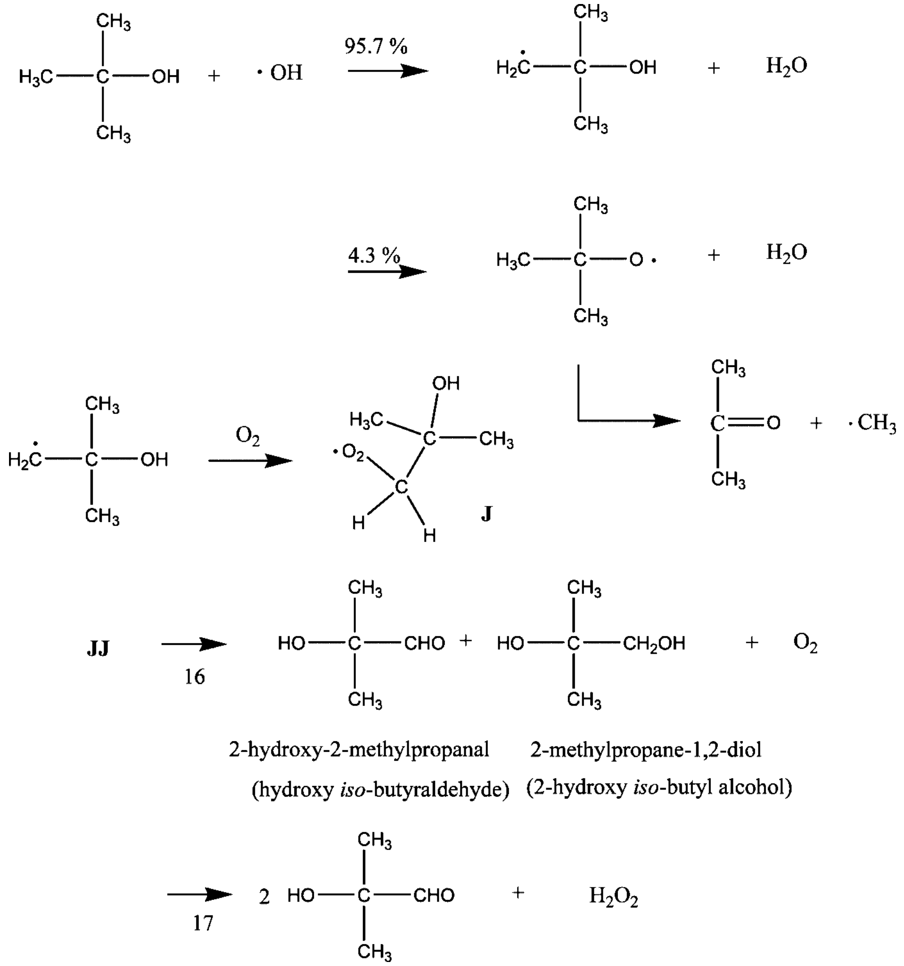


Figure 1. Structures of MMP (2-methyl-2-methoxypropanal); MMP-OH (2-methyl-2-methoxy-1-propanol); and MMP-COOH (2-methyl-2-methoxypropionic acid).

Scheme 8



dominate over decarboxylation. In most AOPs, especially those employing O_3 or condensed phase reactions in the atmosphere, we would expect the O_2 concentration to be substantially greater than 10 μM. Therefore, additional studies are required to better understand the details of this mechanism.

Based on the relative reaction rates, the reductive pathways appear to be important; however, no studies have been undertaken to elucidate this portion of the mechanism.

4.2. *tert*-Butyl Alcohol (TBA) (2-Methyl-2-propanol) [75-65-0]

The reaction of $^{\bullet}OH$ with TBA is largely by H-abstraction of a carbon-bound hydrogen (95.7%) with a small contribution (4.3%) of H-abstraction at the OH-group (Scheme 8).[103] The major TBA-derived radical reacts with O_2, giving rise to the corresponding peroxyl radical (**J**), while the minor radical, the *tert*-butoxyl radical, decomposes into acetone and $^{\bullet}CH_3$.[104,105]

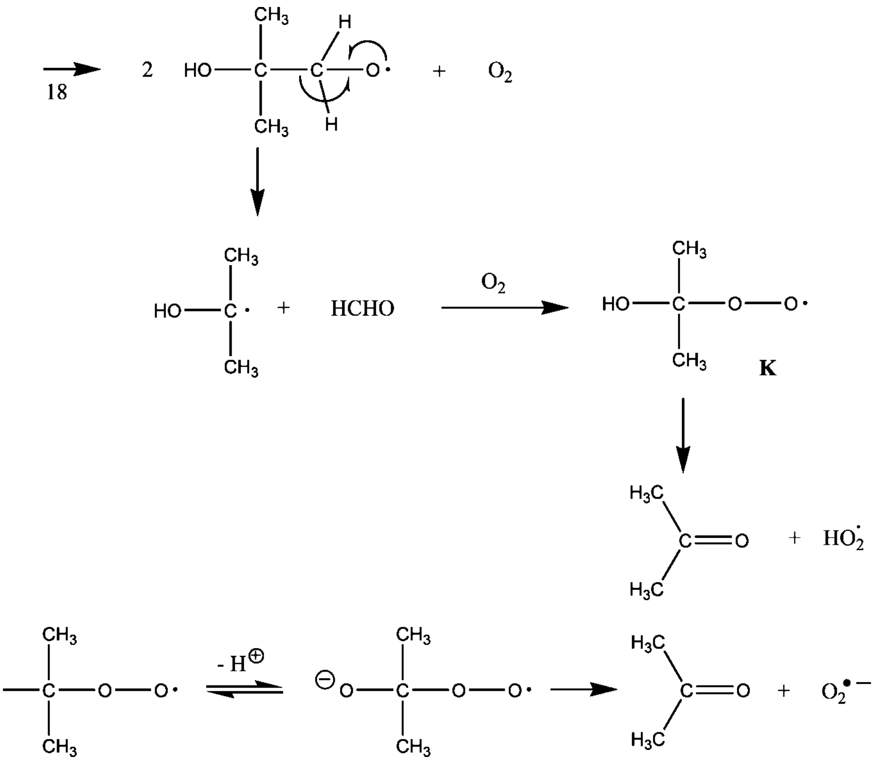
The kinetics and the products of the ensuing reactions have been elucidated by pulse radiolysis and a detailed product study on which Schemes 8 and 9 are based.[106]

The major products that result from the decay of **JJ** are 2-hydroxy-2-methylpropanal (hydroxy isobutyraldehyde), 2-methylpropane-1,2-diol, acetone, formaldehyde, and H_2O_2. En route to acetone and formaldehyde, $HO_2^{\bullet}/O_2^{\bullet-}$ is formed and was detected as an intermediate by pulse radiolysis.[106] An intermediate in this reaction is the peroxyl radical **K**, whose $HO_2^{\bullet}/O_2^{\bullet-}$ elimination reactions were studies in detail.[107] Other AOP studies confirm the formation of these byproducts (Table 3).[38,98,99,108] When O_3 is involved in the formation of $^{\bullet}OH$, such as in O_3/UV, the number of products may increase.[108,109] One of the reasons is that O_3 reacts with carbon-centered radicals as fast as O_2 does.[110] Moreover, the TBA-derived peroxyl radicals also react with O_3 ($k = 2 \times 10^4\ M^{-1}\ s^{-1}$).[111] In this study, it has been concluded that the resulting oxyl radical undergoes an 1,2 H-shift rather than β-fragmentation as depicted in Scheme 10.

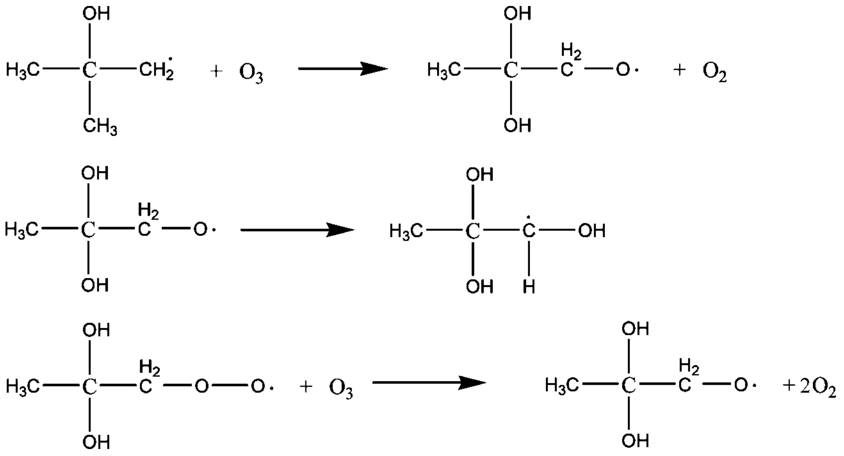
A comprehensive evaluation of the sonolysis of TBA in aqueous solution has been performed.[112] Pyrolysis of the TBA was a significant pathway for its destruction. This study was undertaken in argon-saturated conditions, that is, in the absence of O_2, and thus it is impossible to directly compare the results of that study with those cited above. In another study, TBA was used as probe for $^{\bullet}OH$ in the $h\nu$/Fe^{3+}/H_2O_2/ and Fe^{3+}/H_2O_2 systems to examine the temperature dependence of its formation.[113]

TBA does not react with e^-_{aq} to any appreciable extent, and hence a reductive degradation pathway can be disregarded for this compound.

Scheme 9



Scheme 10



4.3. 2-Methoxy-2-methylpropanal, MMP [36133-35-4]; 2-Methoxy-2-methyl-1-propanol, MMP-OH [22665-67-4]; and 2-Methoxy-2-methylpropionic acid, MMP-COOH [13836-62-9]

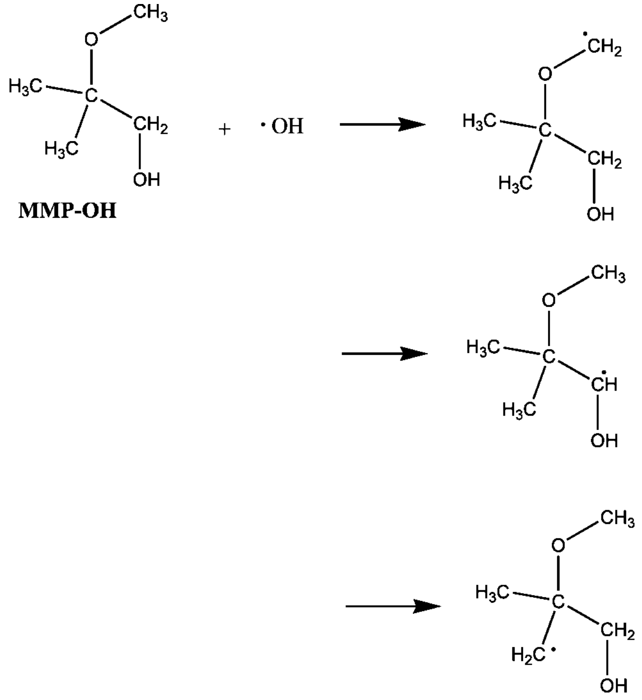
2-Methoxy-2-methylpropanal (MMP) was predicted[98] and has been observed following O_3/H_2O_2 treatment of MTBE.[99] In addition, from the mechanisms that are proposed below, MMP-OH and MMP-COOH should also be formed. There have been no studies reported on the oxidative or reductive degradation mechanisms of these compounds. It appears from the rate data in Table 4 that the oxidative pathways would be favored for the destruction of MMP-OH and MMP. For MMP-COOH, it appears that both the oxidative and reductive pathways would be important in its destruction.

4.3.1. MMP-OH (2-Methoxy-2-methyl-1-propanol)

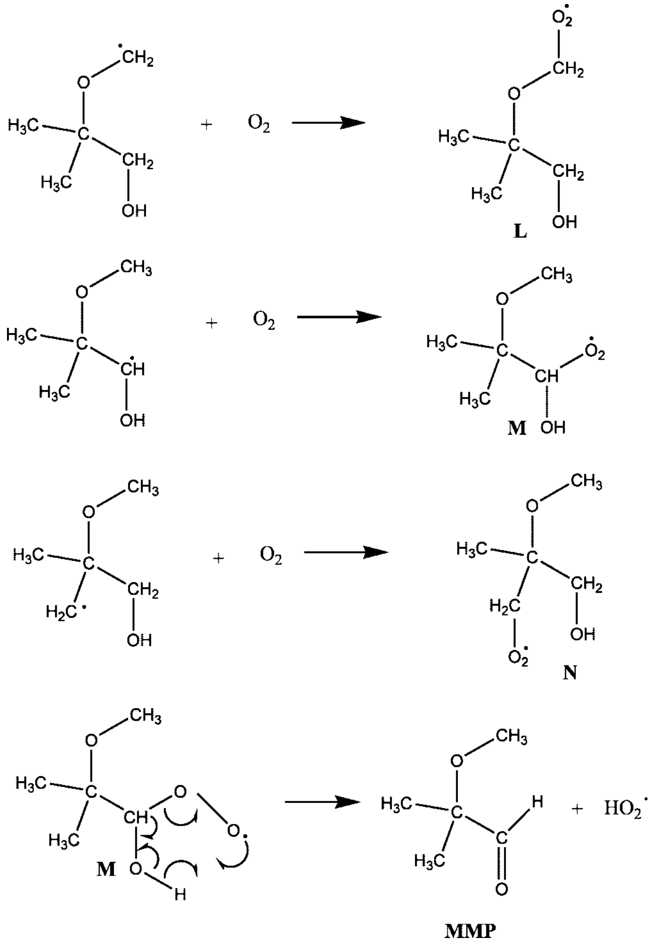
We assume that the initial $^{\bullet}OH$ reaction with MMP-OH would result in three carbon-centered radicals (Scheme 11) and reaction of these radicals with O_2 would result in the formation of peroxyl radicals **L**, **M**, and **N** (Scheme 12). By analogy to MTBE (70:30)[95] we assume that formation of the O-methyl radical is favored over the *tert*-butyl methyl radical. Furthermore, as with ethanol, the α-carbon radical formation is favored 97:3 over H-abstraction from the OH-group.[102,114]

M, an α-hydroxyalkylperoxyl radical, would undergo $HO_2^{\bullet}$ elimination, resulting in the formation of MMP, while **L** and **N** would presumably form tetroxides. **LL** could react *via* reactions 16 and/or 17 to give 1-hydroxy-2-methylpropan-2-yl formate, and also in reaction 16 the corresponding hemiacetal. The hemiacetal would rearrange to give formaldehyde and the corresponding alkoxyl radical, which would

Scheme 11



Scheme 12



further fragment to acetone and a hydroxymethyl radical (Scheme 13).

The formate produced in reaction 16 or 17 of **LL** might further react with •OH. Were the oxyl radical to form (eq 18), it would lead to the formation of hydroxyacetone (Scheme 13). An alternative is that **LL** could proceed through reaction 19 to give the above formate and an alkyl radical that then reacts with O_2 to give peroxyl radical **O** (Scheme 14). **OO** would likely undergo intramolecular rearrangement (reaction 18), eliminating formaldehyde. The resultant alkoxyl radical would then react to give either acetone and a hydroxymethyl radical (major route) or hydroxyacetone and the methyl radical (minor route) (Scheme 14).

The peroxyl radical **N** would likely form a tetroxide **NN** (Scheme 15) and through reactions 16 and 17 undergo rearrangement to give the corresponding aldehyde and alcohol. The fate of these byproducts would likely be *via* •OH reaction and subsequent peroxyl radical chemistry. These further reactions with •OH suggest that the complex nature of the reaction chemistry of MMP-OH and the subsequent 5-carbon systems are significant reaction byproducts of MTBE degradation.

4.3.2. MMP (2-Methoxy-2-methylpropanal)

For MMP it is likely that the aldehyde is partially hydrated (Scheme 16), and based on other aldehydes such as acetaldehyde, we assumed a ratio of 1:1 for the MMP/MMP hydrate. Based on the empirical results for TBF (the observation that acetone is the primary product resulting from abstraction of the formyl-H), we predict that the initial •OH attack of MMP will likely result in four carbon-centered radicals, which will react with O_2 to form the corresponding peroxyl radicals (**P**, **Q**, **R**, and **S**) in Scheme 16. It is likely that the peroxyl radicals **R** and **S** would form hydrates. However, the reactions of these two hydrates were assumed to be the same as those for **R** and **S**, respectively.

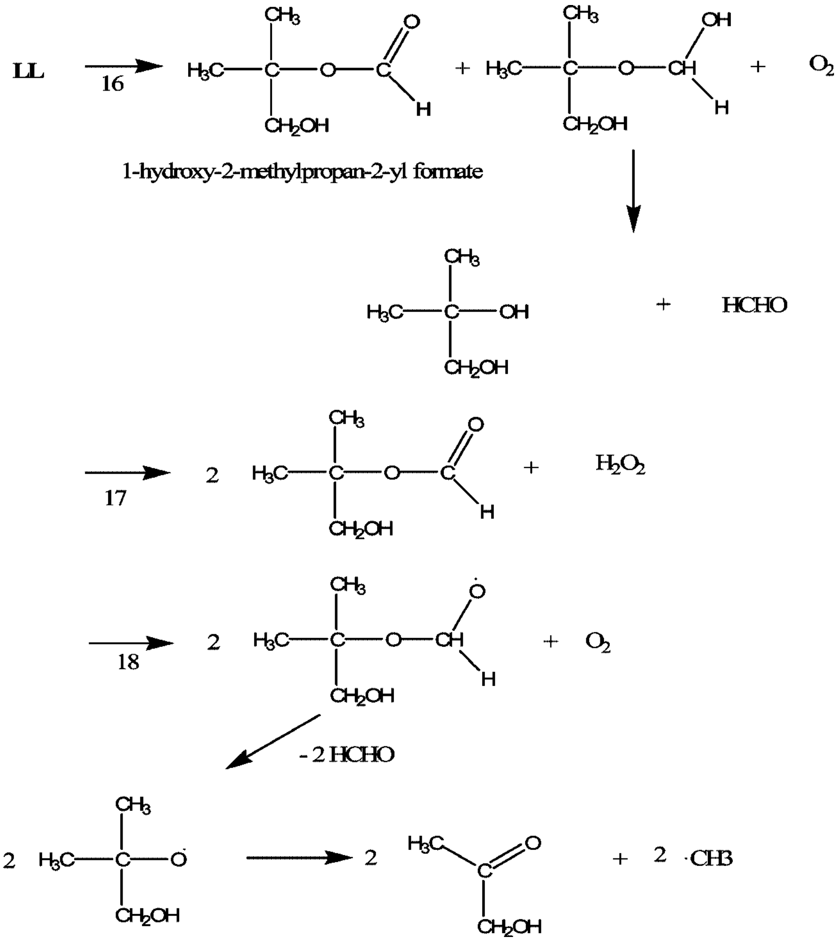
The peroxyl radical **P** would eliminate $HO_2^•/O_2^{•-}$ (Scheme 17) to give MMP-COOH. The tetroxide **QQ** would eliminate O_2 and the ensuing carboxyl radical would decarboxylate. The methoxy-substituted radical that is formed will undergo β-fragmentation only sluggishly and will react with O_2, giving rise to a tertiary alkoxy-substituted peroxyl radical.[115,116]

The decay of such radicals has been studied with diisopropyl ether (Scheme 17).

Presumably, the **RR** tetroxide would react *via* eqs 16 and 17 to give an aldehyde and a hemiacetal (Scheme 18). The hemiacetal would decompose to 2-hydroxy-2-methylpropanal (hydroxyisobutyraldehyde) and formaldehyde. The formate from both reactions 16 and 17 appears to be hydrolytically stable at pH 7. This compound could subsequently react with •OH and lead to additional reaction products or undergo hydrolysis and give 2-hydroxy-2-methylpropanal and formic acid (reaction not shown).

The **SS** tetroxide would react *via* eqs 16 and 17 (Scheme 19) to give a dialdehyde and alcohol. These compounds have not been reported. However, they would further react to give highly oxygenated byproducts. With the methoxy group on this molecule one would expect reactions similar to the initial C-centered radicals of MTBE, where in one case the formate would be formed and in the other a hemiacetal, with subsequent reaction leading to formaldehyde and an alcohol.

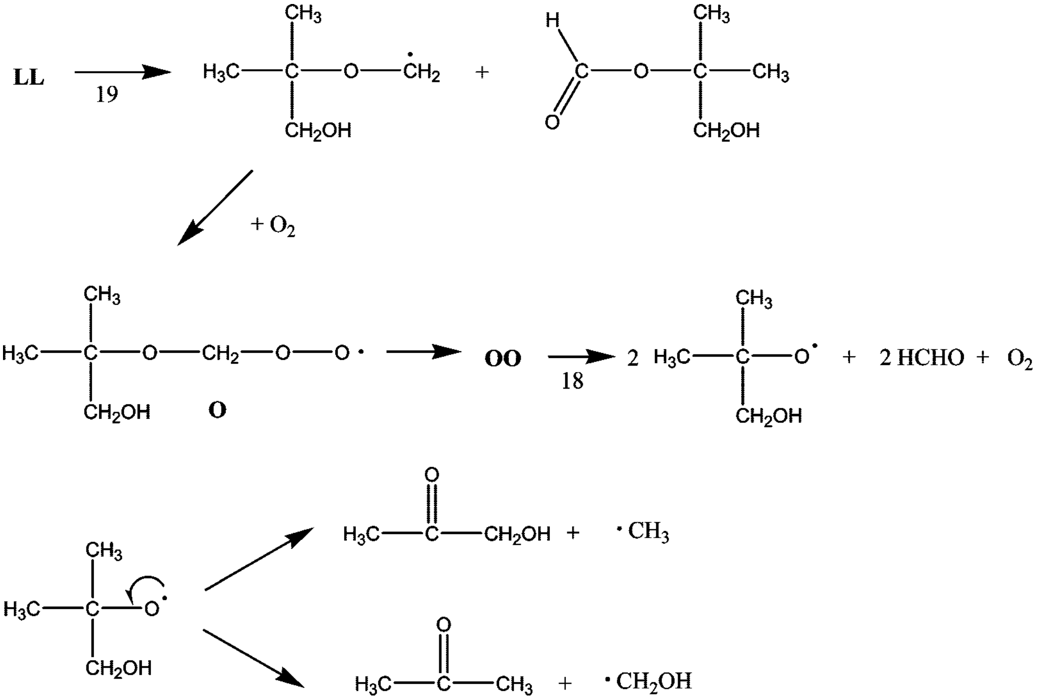
Scheme 13



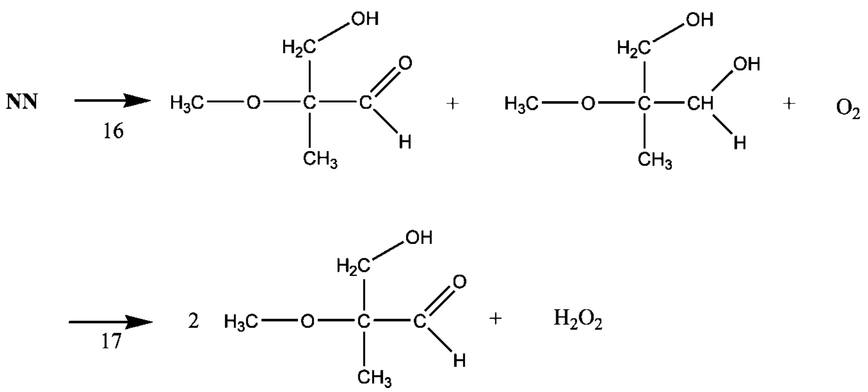
4.3.3. MMP-COOH (2-Methoxy-2-methylpropanoic Acid)

The MMP-COOH would undergo $^{\bullet}$OH oxidation to give two different carbon centered radicals, which upon reaction with O_2 would yield two peroxyl radicals, **T** and **U** (Scheme 20). It is assumed that the tetroxides would form and subsequently decompose *via* reactions 16 and 17. **TT** would give 2-(formyloxy)-2-methylpropanoic acid and a hemiacetal (Scheme 21). The hemiacetal would undergo

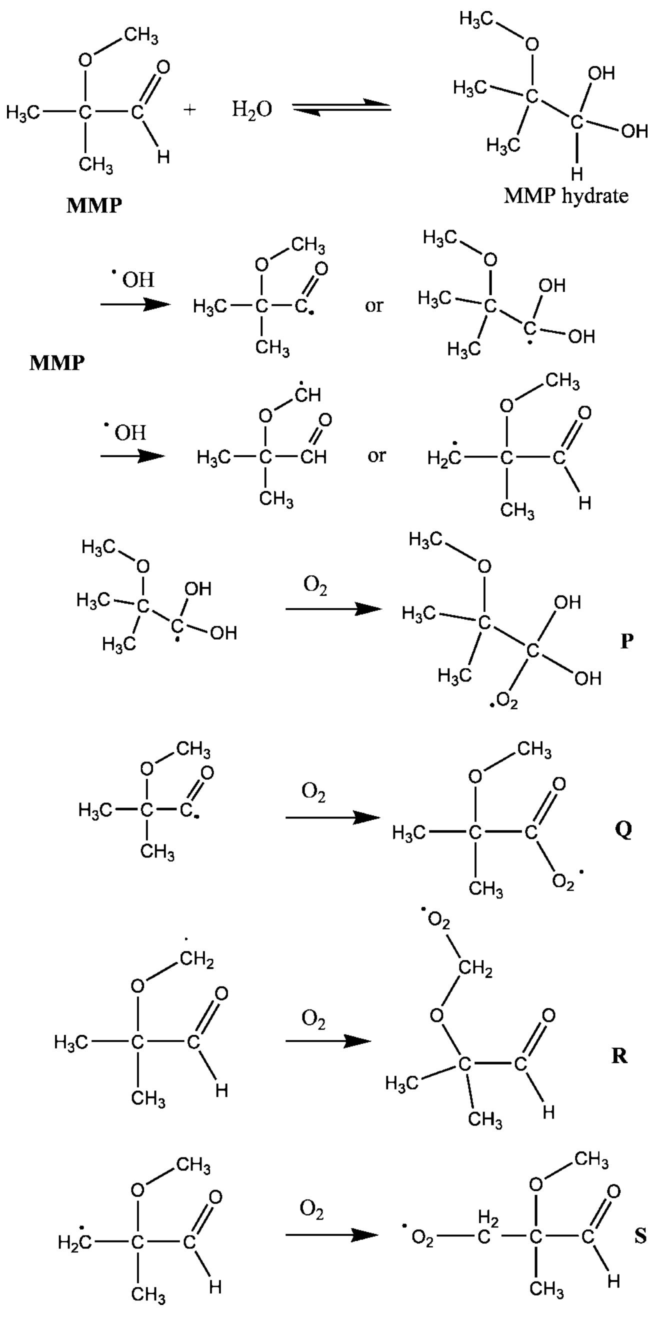
Scheme 14



Scheme 15



Scheme 16



rearrangement to give 2-hydroxy-2-methylpropanoic acid and formaldehyde. In neutral solution, that is, when the oxyl radical formed in the bimolecular decay of **TT** is deprotonated, it may decay into acetone plus $CO_2^{\bullet-}$.

The **UU** tetroxide would lead to the corresponding aldehyde and alcohol *via* reactions 16 and 17 (Scheme 22). It is unclear whether reaction 18 would be operative for these acids. Moreover, the β-fragmentation of the methoxy-substituted radical, as indicated, may be too slow in competition to an O_2 addition.

4.4. Acetone [67-64-1]

In aqueous solution acetone is only about 0.2% hydrated; therefore, the hydrate is not considered in this mechanism.[117] Acetone is known to react *via* both oxidative and reductive pathways. The main features of the $^\bullet$OH mediated decomposition of acetone using γ and pulse radiolysis in oxygenated aqueous solution have been reported (Scheme 23).[118] The major reaction byproducts that were identified were methylglyoxal (α-ketopropionaldehyde, pyruvaldehyde), hydroxyacetone, formaldehyde, and organic acids (primarily acetate ion).

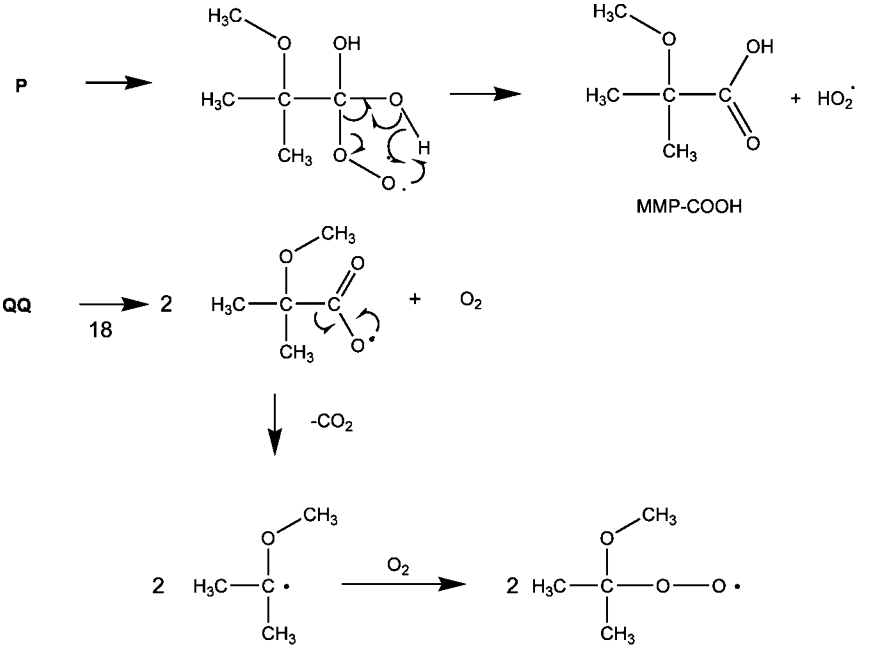
Two detailed studies have been conducted for the $^\bullet$OH mediated decomposition of acetone using UV/H_2O_2.[119,120] The disappearance of acetone and the appearance and disappearance of the reaction byproducts were measured. The total organic carbon was also monitored to assess the extent of mineralization of the process. The major reaction byproducts identified, at an initial acetone concentration of 1.1 mM, included pyruvaldedyde (methylglyoxal or α-ketopropanal), acetic acid, pyruvic acid, and oxalic acid. Minor reaction byproducts were hydroxyacetone, formaldehyde, and formic and glyoxylic acids (Table 3).

The initial formation of acetic acid/acetate ion implies that it is a primary reaction byproducts.[118,120] It has been suggested that the formation of acetic acid results from a cross-termination reaction of the acetylperoxyl radical (**W**) and peroxyl radical (**V**) from the reaction of O_2 with $^\bullet C(O)-CH_3$ and $CH_3C(O)CH_2^\bullet$, respectively (Scheme 23).[118]

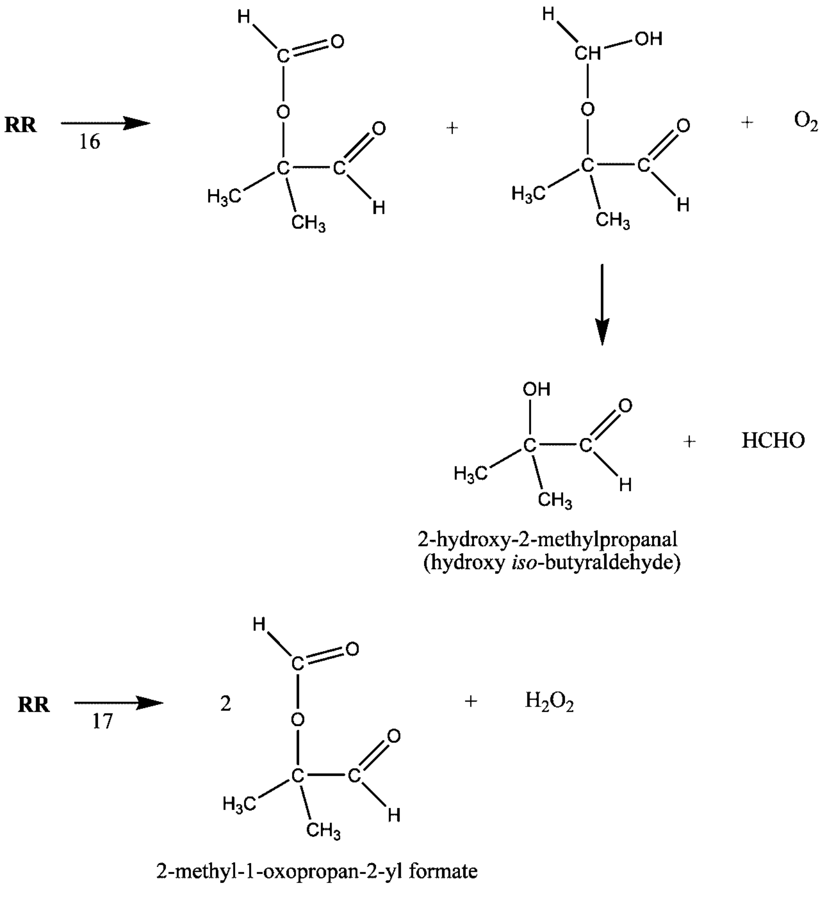
The reaction of the methylperoxyl radical, **G**, with **W** might lead to the formation of acetic acid/acetate ion (Scheme 24). However, in solutions of acetone because of the relatively low concentrations of the methylperoxyl radical, it is likely a minor pathway.[120] Yet, in the overall degradation of MTBE, methylperoxyl radical may be formed from other pathways (e.g., see Schemes 3, 5, 11, 12, and 14), and so this additional pathway may be important.

The reaction of acetone with e^-_{aq} in oxygenated solutions results in the formation of the 2-hydroxy-2-

Scheme 17



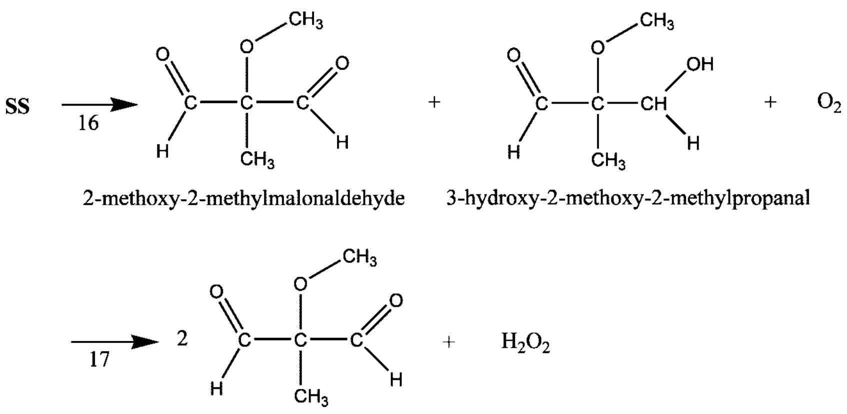
Scheme 18



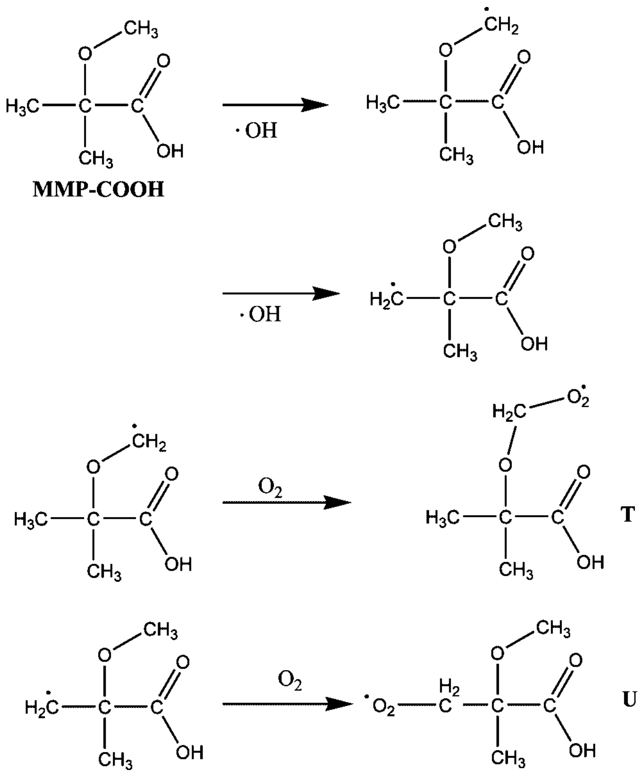
propyl radical and subsequently the corresponding peroxyl radical. It does not decay bimolecularly at low rates of $^•OH$ formation but rather eliminates $HO_2^•$ (650 s^{-1} at pH 7) and reforms acetone (Scheme 25).[106] Thus, this reductive pathway for acetone is not important in the removal of this chemical.

Acetone removal has been used to evaluate the efficiency of several AOPs.[121] It was found that under oxidizing conditions all of the AOPs were able to degrade acetone; however, there were differences in the rate of removal and the completion of the destruction. That study did not attempt to determine any reaction byproducts.[121]

Scheme 19

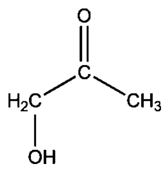


Scheme 20



4.5. Hydroxyacetone (Acetol) [116-09-6]

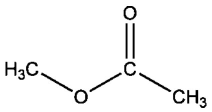
The free-radical chemistry (oxidation or reduction) of hydroxyacetone (acetol) has not been reported. However, by analogy with the •OH initiated reaction mechanisms for acetone,[118] ethanol,[122] and methanol and 2-propanol,[124] it may be possible to predict some of the chemistry. H-abstraction from the α-carbon is favored 97:3,[103,117] and therefore, we estimate that >95% of the H-abstraction will also occur in the α-position to the OH group. For this discussion, we do not consider H-abstraction occurring from the methyl group.



The ensuing α-hydroxyalkylperoxyl radical may eliminate $HO_2^•$ (cf. reactions 29 and 30). The rate of spontaneous $HO_2^•$ elimination varies dramatically with the substituents at that carbon and cannot be predicted at present. If it were as fast as the $HO_2^•$ elimination from $HOC(CH_3)_2OO^•$ (650 s^{-1}),[107] the unimolecular decay yielding pyruvaldehyde (Scheme 26) would dominate. Otherwise, bimolecular processes would also have to be envisaged.

4.6. Methyl Acetate [79-20-9]

The initial reactions for both the oxidative and reductive pathways have been studied for methyl acetate.[124,125]



4.6.1. Oxidative Pathways

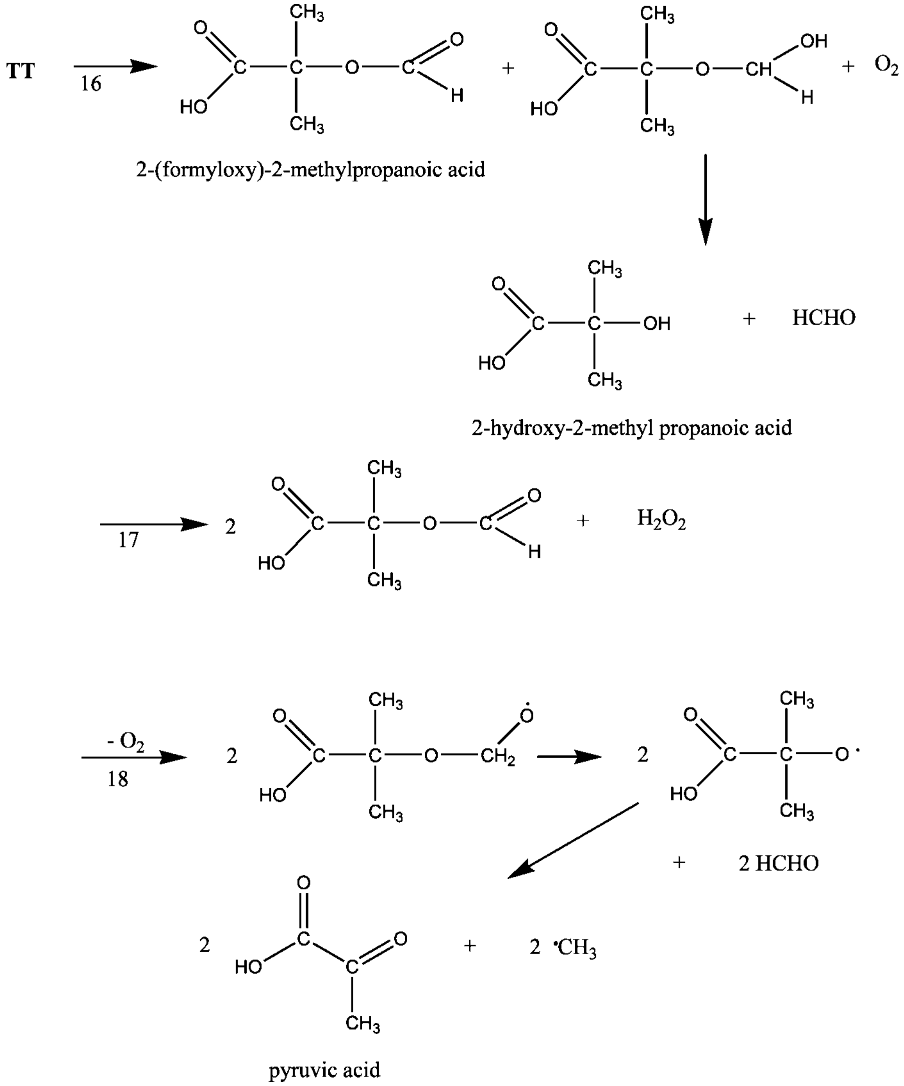
The initial •OH reaction can abstract hydrogen from either the alkoxyl or the acyl groups, and subsequent reaction with O_2 leads to the formation of peroxyl radicals as shown in Scheme 27. The rates for these reactions are found in Table 4.[125]

Two peroxyl radicals would be formed (**Y** and **Z**) that would subsequently form two major tetroxides, **YY** and **YZ**, and one minor tetroxide, **ZZ**, in a ratio of 64%:32%:4%. The tetroxides would likely decompose *via* reactions 16 and 17, leading to the formation of several highly oxygenated three-carbon aldehydes, an alcohol and esters. From the decomposition of the hemiacetal, acetic acid/acetate ion and formaldehyde are produced (Schemes 28 and 29). Tetroxide **ZZ** would lead to the same reaction byproduct as those of **YY** and **YZ**.

4.6.2. Reductive Pathways

The reaction of methyl acetate and the hydrated electron has been studied in some detail.[124,125] Electron attachment results in the formation of a radical anion[126] that rapidly ($k = 5.5 \times 10^5$ s^{-1}) decays into acetyl radical and a methoxide ion and/or acetate ion plus a methyl radical.[125] This reaction is fast enough to compete with O_2 addition at moderate O_2 concentrations. To what extent the reaction with O_2 (formation of **A1**) and subsequent bimolecular decay of **A1** can contribute to product formation at elevated O_2 concentrations (Scheme 30) remains to be studied.

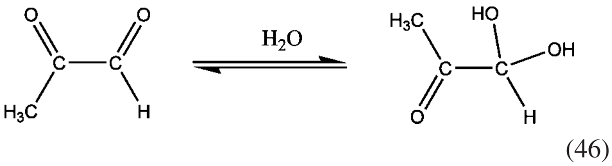
Scheme 21



Acetic acid (acetate anion) was identified and quantified as a byproduct from the reductive reaction pathway in about 50% yield (Scheme 30).[124]

4.7. Methyl Glyoxal (Pyruvaldehyde) (α-Ketopropionaldehyde) [78-98-8]

Acetone is a significant byproduct of the •OH initiated destruction of MTBE.[98,99] One of the major reaction byproducts of the degradation of acetone is methylglyoxal (pyruvaldehyde or α-ketopropanal), found mostly in the hydrated form in aqueous solution.[127] (The equilibrium constant of eq 46 has not been evaluated.)



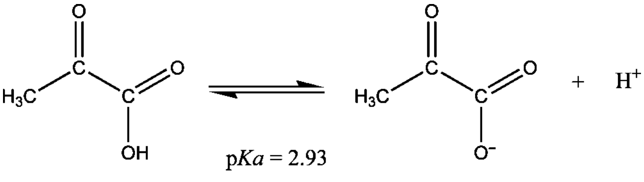
(46)

The •OH reaction would abstract a methine H atom (gem-diol carbon),[120] leading to the formation of a peroxyl radical (**A2**). The subsequent elimination of $HO_2^•$ gives pyruvic acid/pyruvate ion as the major product (Scheme 31).

No reaction rates or studies of the reductive processes of methylglyoxal have been reported.

4.8. Pyruvic Acid (α-Ketopropionic Acid) [127-17-3]

The pK_a of pyruvic acid has been reported to be 2.93.[128] Near neutral pH, the pyruvate ion would be the dominant species in solution. Therefore, only the reaction rate between the •OH and the pyruvate ion has been reported (Table 4). The •OH radical reaction would occur at the methyl group (Scheme 32).

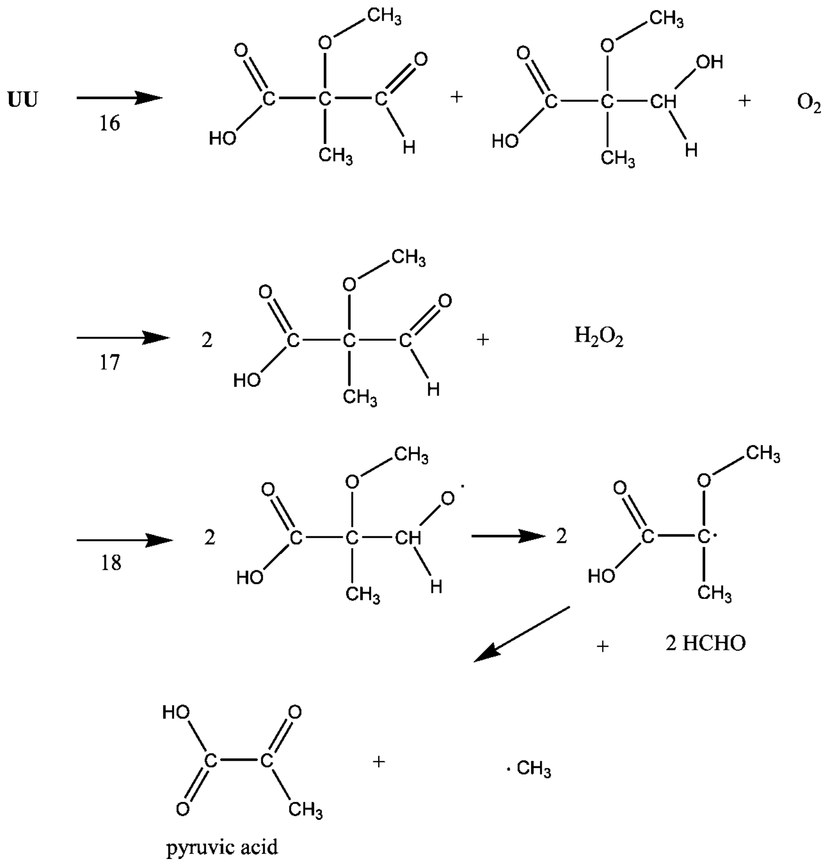


It was suggested that β-scission leading to the ketene and $CO_2^{•-}$ was the major degradation pathway.[120] The ketene would then react with water to give acetic acid/acetate ion. The reaction (eq 47) would complete the chemistry associated with the carboxylate fragment.

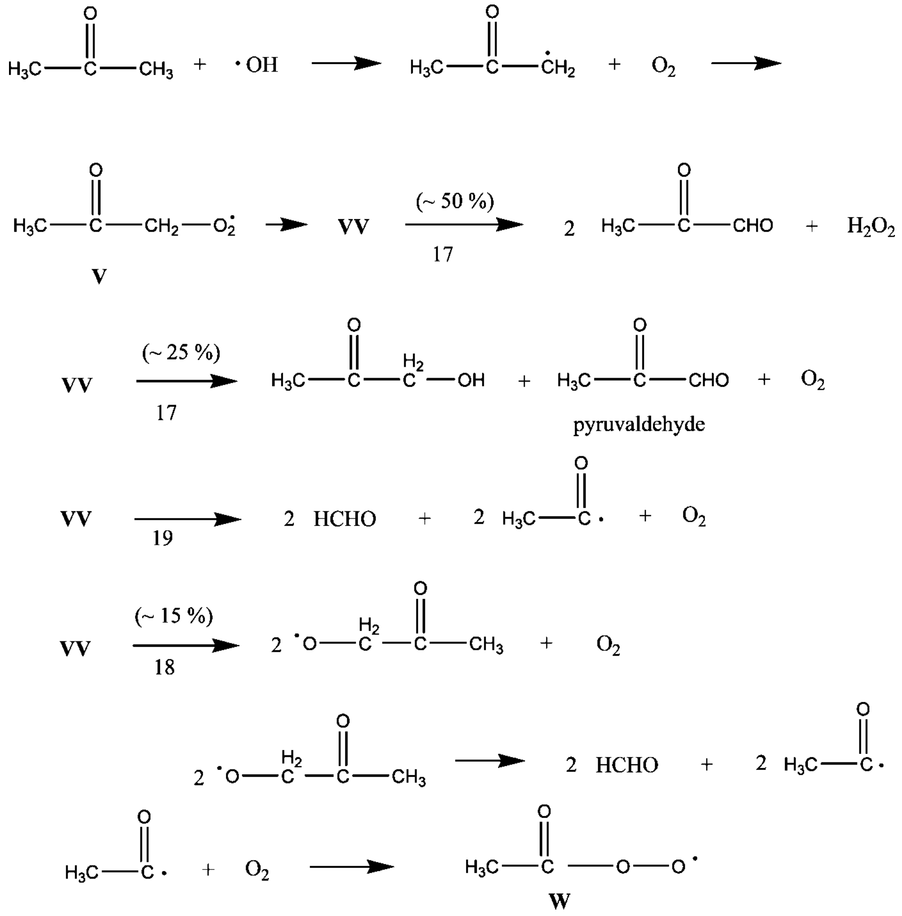
$$CO_2^{•-} + O_2 \rightarrow CO_2 + O_2^{•-} \tag{47}$$

They argued that the ketene route was the principle route, as neither 2,3-dioxopropanoic acid nor 3-hydroxy-2-

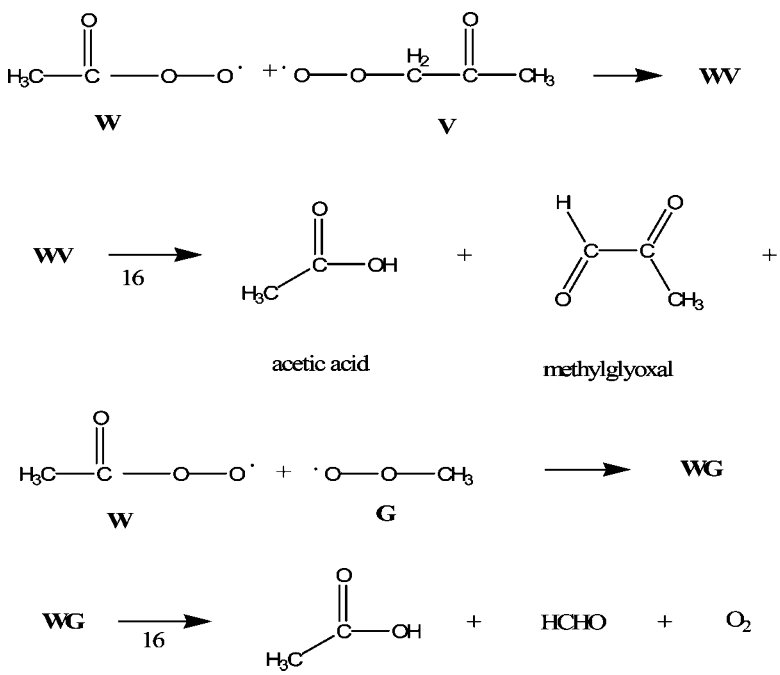
Scheme 22



Scheme 23



Scheme 24



oxopropanoic acid were detected. Nonetheless, we have proposed a pathway *via* the peroxyl radical (**A3**) and the subsequent tetroxide (**A3A3**) leading to highly oxygenated 2,3-dioxopropanoic acid and 3-hydroxy-2-oxopropanoic acid that might compete with the formation of the ketene.

There is still a considerable amount of work necessary to complete the radical chemistry of pyruvic acid/pyruvate ion. One study has reported the reaction rate of the e^-_{aq} with pyruvate ion;[129] however, there was no attempt to determine the reaction mechanism.

4.9. Acetaldehyde [75-07-0]

Acetaldehyde in aqueous solution rapidly hydrates with a ratio of the aldehyde/hydrate of 0.8:1.0 ($K = 1.246$ at 20 °C):[130,131]

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2 \qquad (48)$$

Thus, the free radical reactions of acetaldehyde are somewhat more complicated than would appear at first.

The initial steps in the free radical reactions of acetaldehyde and its hydrate have been reported:[92]

$$^{\bullet}OH + CH_3CHO\ (65\%) \rightarrow CH_3C^{\bullet}O + H_2O$$
$$k_{49} = 3.6 \times 10^9\ M^{-1}\ s^{-1} \qquad (49)$$

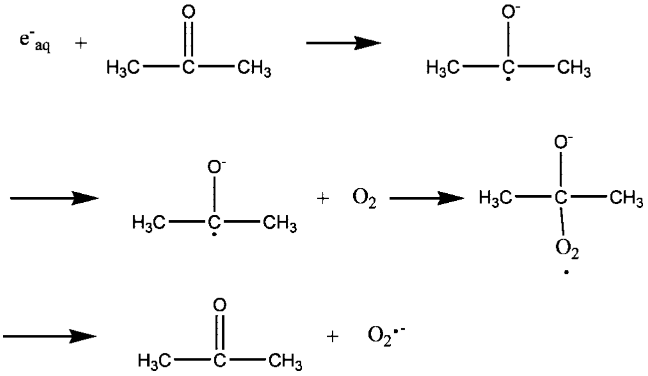
$$^{\bullet}OH + CH_3CH(OH)_2\ (26\%) \rightarrow CH_3C^{\bullet}(OH)_2 + H_2O$$
$$k_{50} = 1.2 \times 10^9\ M^{-1}\ s^{-1} \qquad (50)$$

$$^{\bullet}OH + CH_3CHO \rightarrow {}^{\bullet}CH_2CHO + H_2O$$
$$k \approx 10^8\ M^{-1}\ s^{-1} \qquad (51)$$

$$^{\bullet}OH + CH_3CH(OH)_2 \rightarrow {}^{\bullet}CH_2CH(OH)_2 + H_2O$$
$$k \approx 10^8\ M^{-1}\ s^{-1} \qquad (52)$$

where reactions 51 and 52 contribute approximately 5–10% to the initial $^{\bullet}OH$ reaction with acetaldehyde.

Scheme 25



The acetyl radical formed in reaction 49 rapidly reacts with oxygen to form the corresponding peroxyl radical (**A4**), which was shown to be a strongly oxidizing radical. Subsequently, this peroxyl radical reacts with the reducing $O_2^{\bullet -}$, forming a peracetic acid/anion (reaction 53).[92] The peracetic acid acts as an oxidant in aqueous solutions that contain alkenes and other easily oxidized compounds.

$$\underset{(\mathbf{A4})}{CH_3C(O)O_2^{\bullet}} + O_2^{\bullet -} \rightarrow CH_3C(O)O_{2^-} + O_2$$
$$k \approx 10^9\ M^{-1}\ s^{-1} \qquad (53)$$

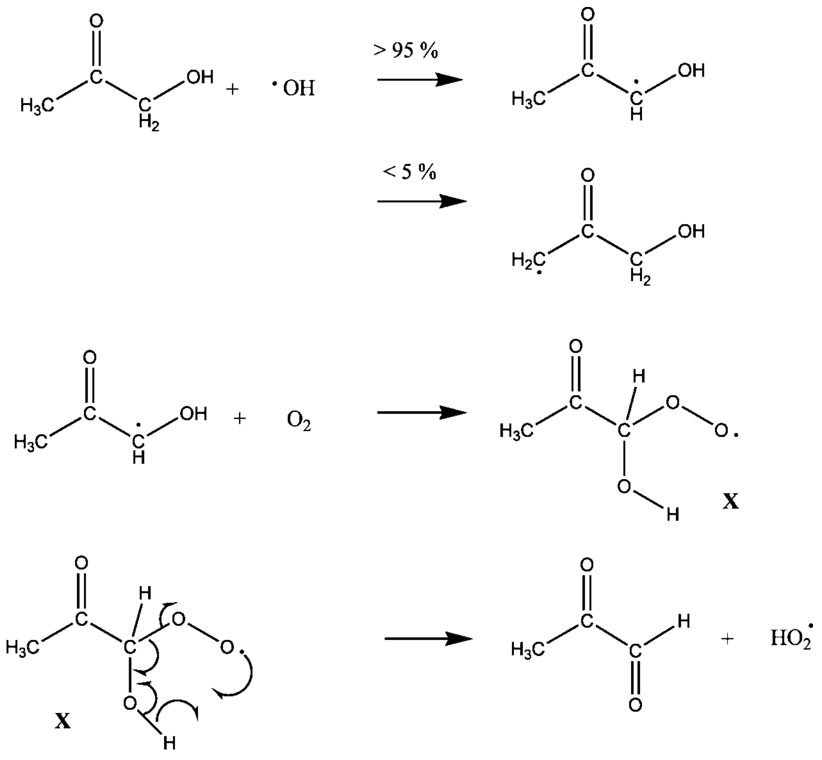
Consistent with the rapid elimination of $HO_2^{\bullet}$ from α-hydroxyalkylperoxyl radicals,[78,90,132] the hydrated acetyl radical (formed in reaction 50) forms a peroxyl radical (**A5**), which then eliminates $O_2^{\bullet -}$ to give the acetate ion:[92]

$$\underset{(\mathbf{A5})}{CH_3C(OH)_2O_2^{\bullet}} \rightarrow 2H^+ + CH_3CO_2^- + O_2^{\bullet -} \qquad (54)$$

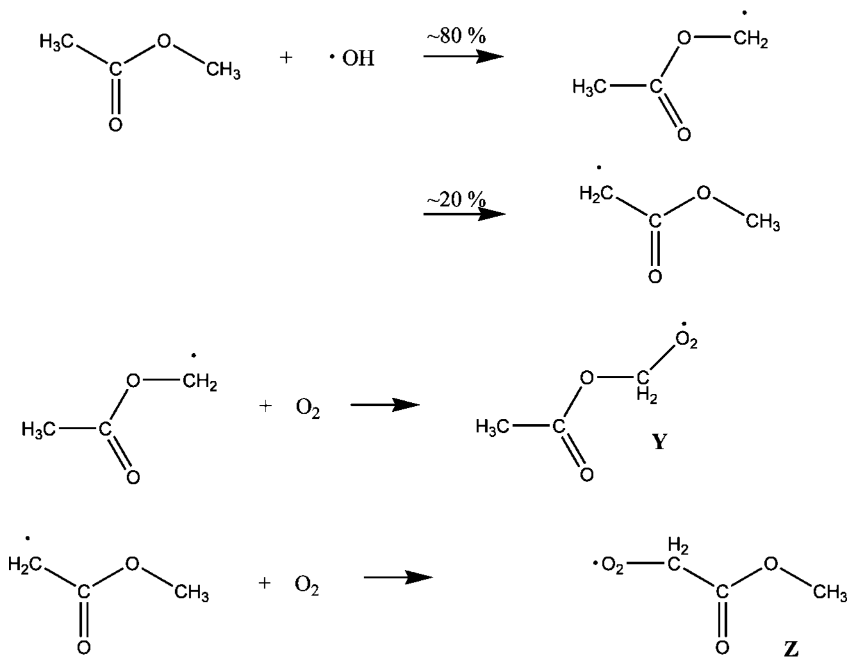
4.10. Glycolic Acid (Glycolate Ion) [79-14-1]

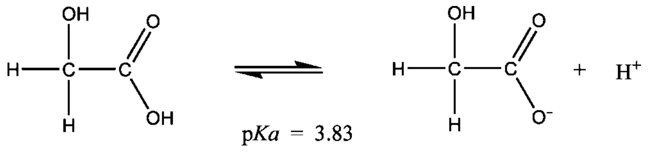
Glycolic acid and its conjugate base are reaction byproducts of the reaction of acetic acid with $^{\bullet}OH$.

Scheme 26



Scheme 27

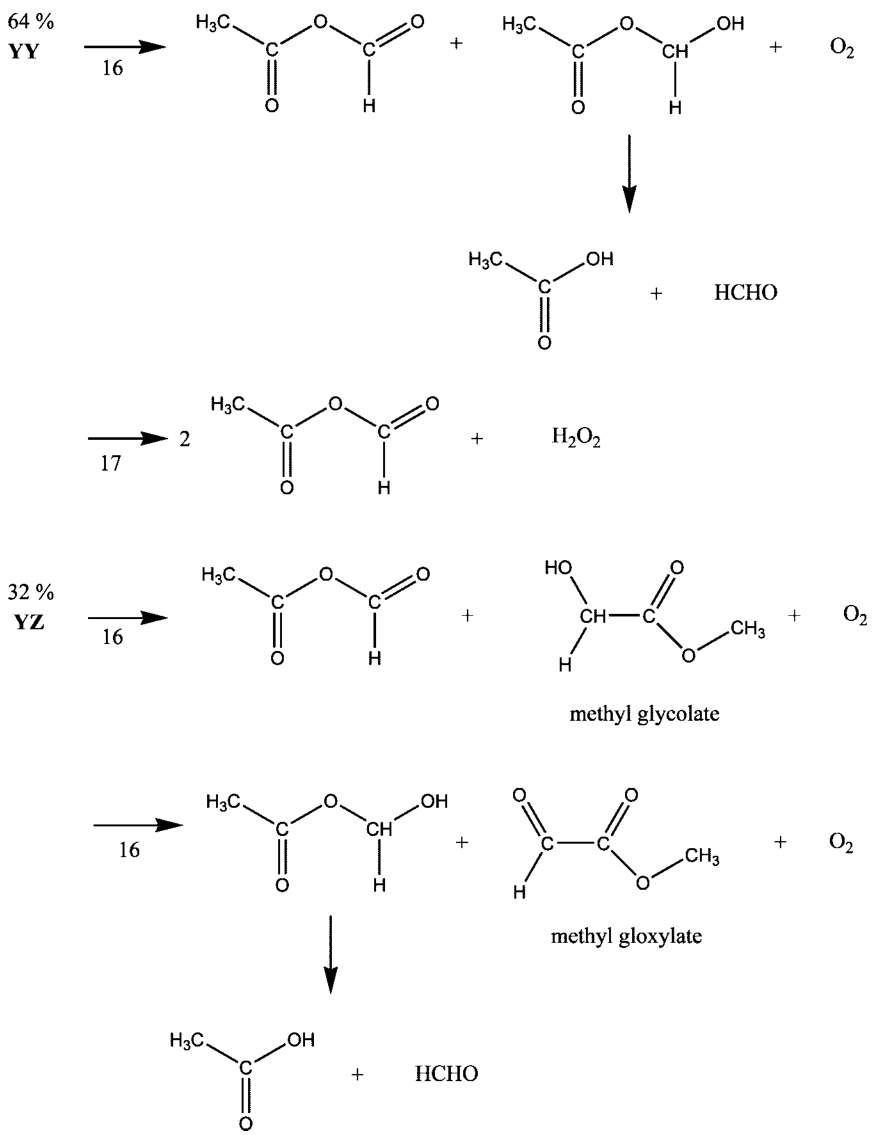




The mechanism for the $^{\bullet}OH$ mediated decomposition of glycolic acid using UV/H_2O_2 has been reported.[133] It was proposed that the initial $^{\bullet}OH$ reaction resulted in H-abstraction from the α-carbon, and the resulting radical trapped O_2 to form (**A6**), which rapidly eliminated $HO_2^{\bullet}$ to form glyoxylic acid/glyoxylate ion (Scheme 33).

Oxidation of the alcohol functional group to the aldehyde gave a glyoxylic acid/glyoxylate ion intermediate, which reached a steady state concentration of approximately 33% of the parent. The aldehyde was then further oxidized to oxalic acid/oxalate ion and approached a concentration of approximately 60% of the initial glyoxylic acid concentration. The apparent higher conversion of glycolate ion to oxalate ion (Scheme 34) is due to the stability of the oxalate ion under the reaction conditions. Formic acid, as a reaction product, was also shown to be present when the starting concentration of the glyoxylic acid was reduced from 1 to 0.5 mM. However, it never reached a concentration of greater than 10% of the parent

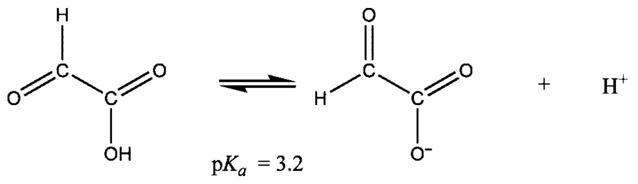
Scheme 28



and disappeared relatively rapidly upon further oxidation. This suggests that mineralization (the formation of CO_2) occurs at this stage in dilute solutions.

4.11. Glyoxylic Acid (Gloxylate Ion) [298-12-4]

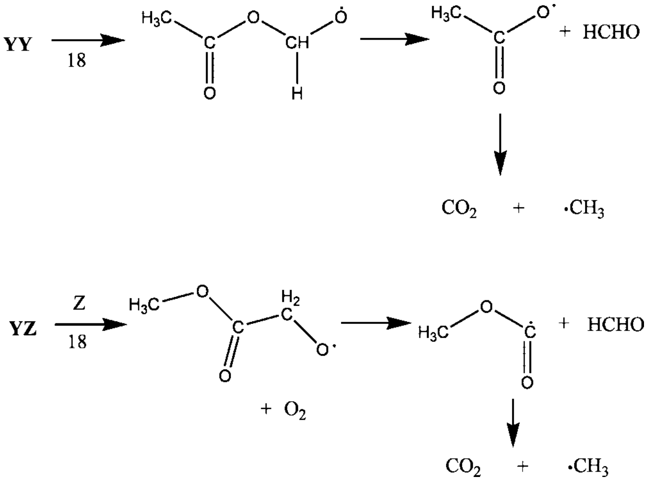
The hydroxyl radical induced oxidation of glycolic acid (glycolate ion) according to Scheme 33 above results in the formation of glyoxylic acid/glyoxylate ion):



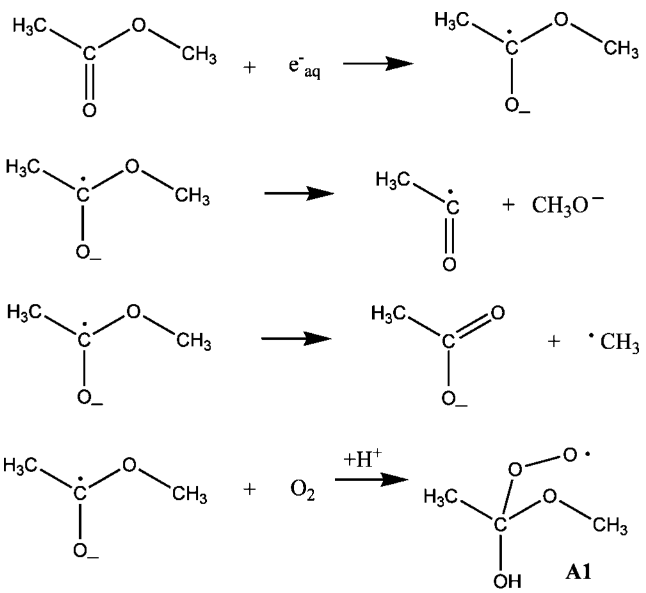
It appears that the dominant oxidation byproduct of glyoxylic acid is oxalic acid, which was formed rapidly and in high yield (~70% of the starting glyoxylic acid concentration) in less than 100 min of UV/H_2O_2 irradiation.[133]

One has to consider that a large proportion of the glyoxylate is present as its hydrate. $^{\bullet}OH$ attack at this hydrate, O_2 addition, and subsequent $O_2^{\bullet -}/H^+$ release will directly lead to the formation of oxalic acid. The $^{\bullet}OH$ attack at the aldehyde form with subsequent O_2 addition gives rise to a peroxyl radical that can only decay *via* the oxyl radical route (reaction 18). This would eventually lead to complete mineralization (Scheme 34).

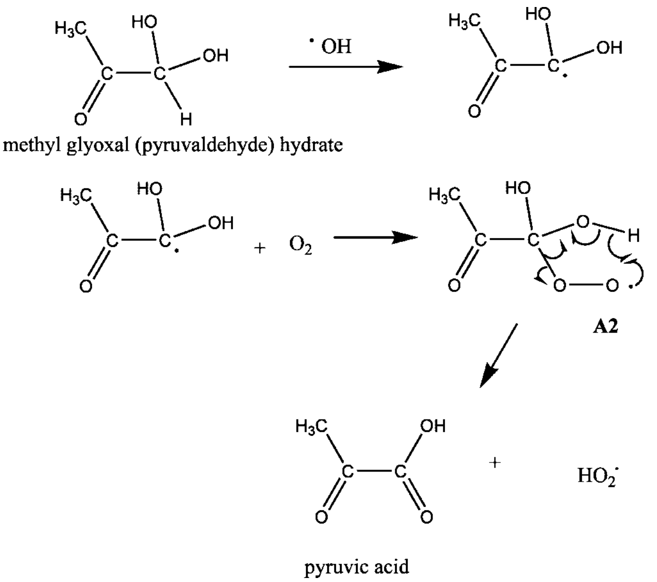
Scheme 29



Scheme 30

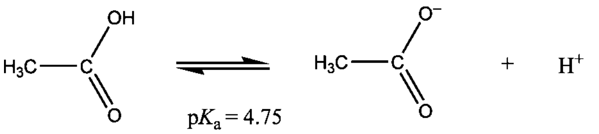


Scheme 31



4.12. Acetic Acid (Acetate Ion) [64-19-7]

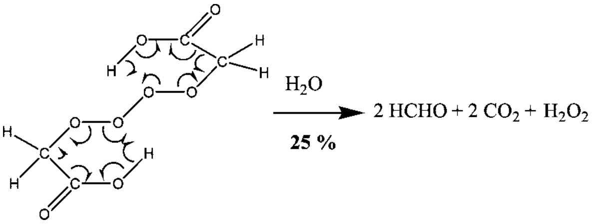
Acetic acid/acetate ion is a common radiolysis product of many environmentally relevant compounds, and its free radical chemistry is reasonably well-known. The pK_a of this acid suggests that under natural water conditions the acetate anion is the principal reactant:



The hydroxyl radical reaction with the acetate anion is relatively slow compared to that of other compounds in the degradation scheme of MTBE (Table 4). Early studies of the reaction of $^\bullet$OH with acetic acid/acetate ion established that H-atom abstraction occurred preferentially at the methyl C−H and that the pK_a of the resultant radical was 4.5.[134] The preference for the hydrogen abstraction route was confirmed in UV/H_2O_2 studies.[135] They also showed that acetic acid was more refractory to UV/H_2O_2 than were either glycolic or formic acids.

Quantitative estimates for several of the branching ratios have been provided for the initial degradation of the acetate ion (Scheme 35).[93,94] It has been reported that the pK_a of the acetate peroxyl radical was 2.1 ± 0.2, significantly more acidic than that of acetic acid.[94]

The free radical induced acetate ion degradation byproducts and their distribution are summarized in Table 3. Reactions 16 and 18 (Scheme 35) account for approximately 25% of the tetroxide decomposition.[93] In the tetroxide decomposition, the major reaction byproducts observed were glyoxylic acid, glycolic acid, formaldehyde (confirming earlier work[136]), and organic (hydro)peroxide. Very little $O_2^{\bullet -}$ was formed under these conditions. To account for the distribution of reaction byproduct, the following intramolecular tetroxide (**A8A8**) decomposition was proposed:



(55)

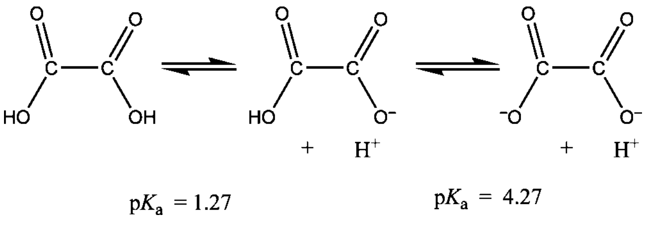
The irradiation of acetate ion, or more generally its peroxyl radical mediated decomposition, leads to a substantial amount of CO_2, 26%. This means that some mineralization does occur at this stage in the decomposition of MTBE.

The decomposition of acetic acid at pH = 3.8 was studied by UV/H_2O_2 and showed that the major byproduct was oxalic acid.[133] It appears that oxalic acid was formed up to approximately 15% of the initial concentration. The oxalic acid was not substantially degraded in these solutions after 425 min of UV/H_2O_2 treatment.

Thus, oxalic acid appears to be one of the most common two-carbon byproducts in the radical-induced degradation of MTBE under some AOP conditions and is a relatively recalcitrant reaction product.

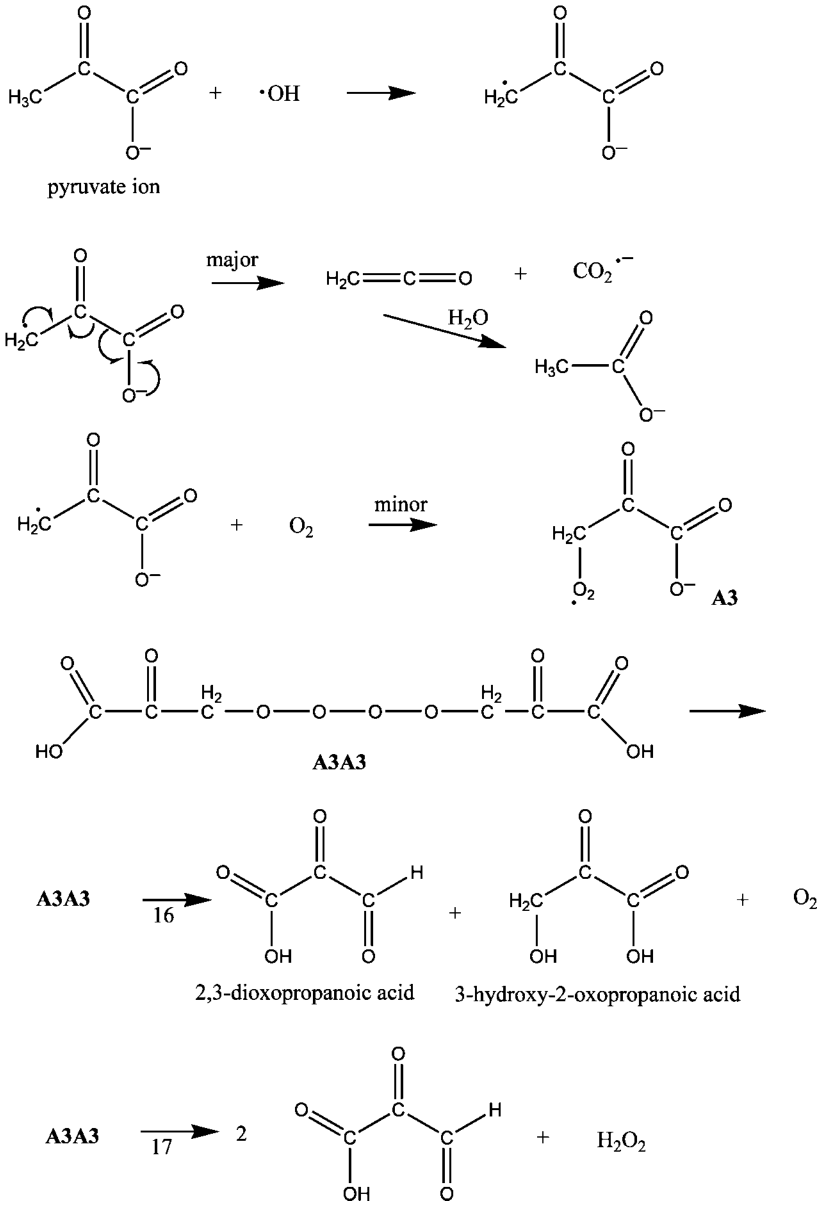
4.13. Oxalic Acid

Oxalic acid is one of the most highly oxidized compounds in the route to ultimate mineralization of many organic compounds:



The radiation chemistry of oxalic acid and its deprotonated (ionic) forms has been studied.[137,138] The rate of reaction of $^\bullet$OH with the monoanion is 1.4 × 10^6 M^{-1} s^{-1}, and that with the dianion is not much faster, 7.7 × 10^6 M^{-1} s^{-1}.[138] This is why oxalic acid is such a persistent byproduct. The recalcitrant nature of oxalic acid to free-radical decomposition has recently been confirmed in high dose irradiation

Scheme 32



studies of MTBE degradation.[139] The reason for this slowness of this reaction may be that it can only proceed by electron transfer, a reaction that is reluctantly undergone by the •OH radical. The product of this reaction is an acyloxyl radical. If other acyloxyl radicals are a good guide, it must decay at a rate near 10^9 s^{-1}.[140] From this it follows that the major decomposition pathway should be as depicted in Scheme 36.

The decomposition of oxalic acid using H_2O_2/UV and O_3/H_2O_2 has been reported.[133,141,142] AOPs using O_3 and/or H_2O_2 as a component to generate •OH cannot be very effective, as these reagents react much faster or at least equally fast with •OH than with oxalic acid.

In the UV/H_2O_2 studies, the removal of >90% of the oxalic acid required 225 min at a pH = 2.9 either in the presence or absence of O_2. Based on the analysis of total organic carbon (TOC), the authors reported that these processes lead to mineralization with a minimum of oxygen consumption.[133] However, at a pH = 5.9 in the absence of O_2, less than 20% decomposition of the oxalate ion was obtained after 225 min of UV/H_2O_2 treatment (note that oxalate is regenerated by the recombination of $CO_2^{\bullet -}$).

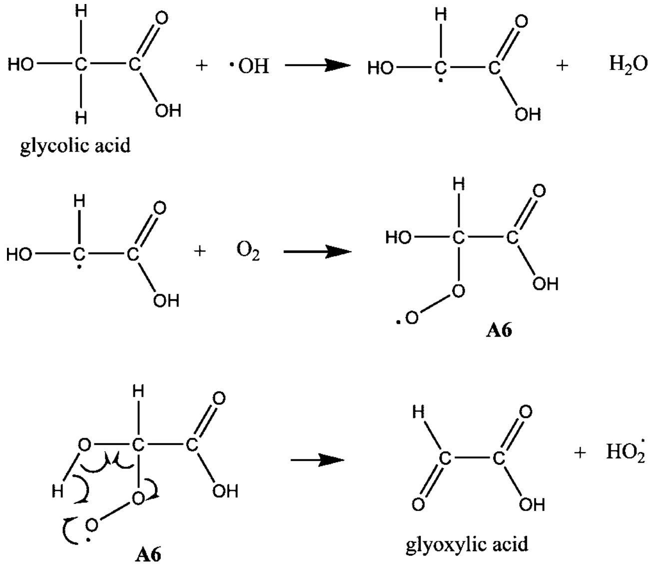
A recent study utilized oxalic acid as a probe chemical for examining the removal efficiency for the O_3/UV process.[143] Oxalic acid was removed; however, the primary purpose for using oxalic acid was to differentiate direct reactions of O_3 and the reactions of •OH.

Silver doped TiO_2 has been studied for the decomposition of oxalic acid. The studies conducted were at pH 2.5−3.5 with different initial concentrations of Ag(I) in solution.[144] Initially, oxalic acid decomposition was slow; however, as the deposition of silver was completed, the decomposition of oxalate increased. There was no indication of the oxalic acid decomposition pathway, as the study was focused more on the mechanism of Ag doped TiO_2. These are the only studies that have been reported on the reductive pathway of oxalic acid removal.

4.14. Methanol

Methanol has been shown to be a major reaction product of the methyl radical with O_2 (reactions 38 and 45 and Schemes 3, 13, 14, and 17). The reactions of •OH with

Scheme 33



methanol will result in H-abstraction. A comprehensive study reported the initial reactions of •OH with a series of aliphatic alcohols[103] that included the branching ratio for the initial reaction (Scheme 37).

The hydroxymethyl radical (93%) reacts with O_2 to give the peroxyl radical **A10**. This peroxyl radical eliminates $HO_2^•$ and leads to formaldehyde. The spontaneous $HO_2^•$ elimination is slow ($<10\ s^{-1}$), and at high radical concentrations such as generated by an electron beam, these peroxyl radicals would decay bimolecularly. The alkoxy radical also undergoes a rapid 1,2-H shift and follows the same path as above, leading to formaldehyde. It appears that •OH with methanol quantitatively gives formaldehyde (reactions 37 and 45).

No reaction between e^-_{aq} and methanol at concentrations of 10−20% methanol in aqueous solution was observed.[145]

4.15. Formaldehyde

Formaldehyde in aqueous solution establishes an equilibrium between the aldehyde and its hydrate with a K_d at 25 °C of (4.5−5.5) × 10^{-4}:[117]

$$CH_2(OH)_2 \rightleftharpoons CH_2O + H_2O \qquad (56)$$

Therefore, the radiation chemistry of interest is that of the formaldehyde hydrate, $CH_2(OH)_2$. From the data summary in Table 4, it is obvious that the major pathway for the destruction of formaldehyde hydrate is *via* •OH mediated reactions. The following equations show the reaction with •OH followed by the reaction with O_2 to form the dihydroxymethylperoxyl radical:

$$CH_2(OH)_2 + {}^•OH \rightarrow {}^•CH(OH)_2 + H_2O \qquad (57)$$

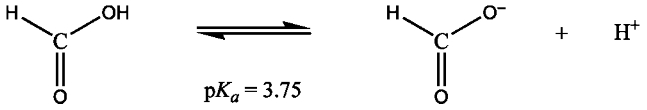
$${}^•CH(OH)_2 + O_2 \rightarrow \underset{\mathbf{(A11)}}{HC(OH)_2OO^•} \qquad (58)$$

$$\underset{\mathbf{(A11)}}{HC(OH)_2OO^•} \rightarrow HCOOH + HO_2^• \qquad (59)$$

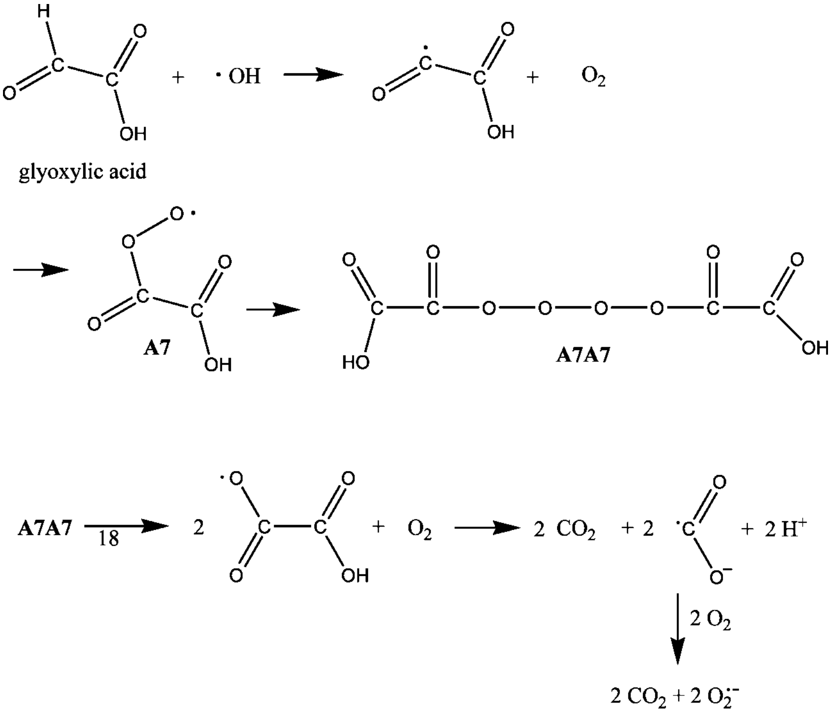
The reaction of $^•CH(OH)_2$ (pK_a($^•CH(OH)_2$) = 9.5)[146] with O_2 (eq 58) gives rapid rise to $O_2^{•-}/HO_2^•$ (eq 59), preventing any bimolecular decay of the peroxyl radical.[132] The major byproducts are formic acid/formate ion, almost quantitatively formed in N_2O saturated solutions.

4.16. Formic Acid

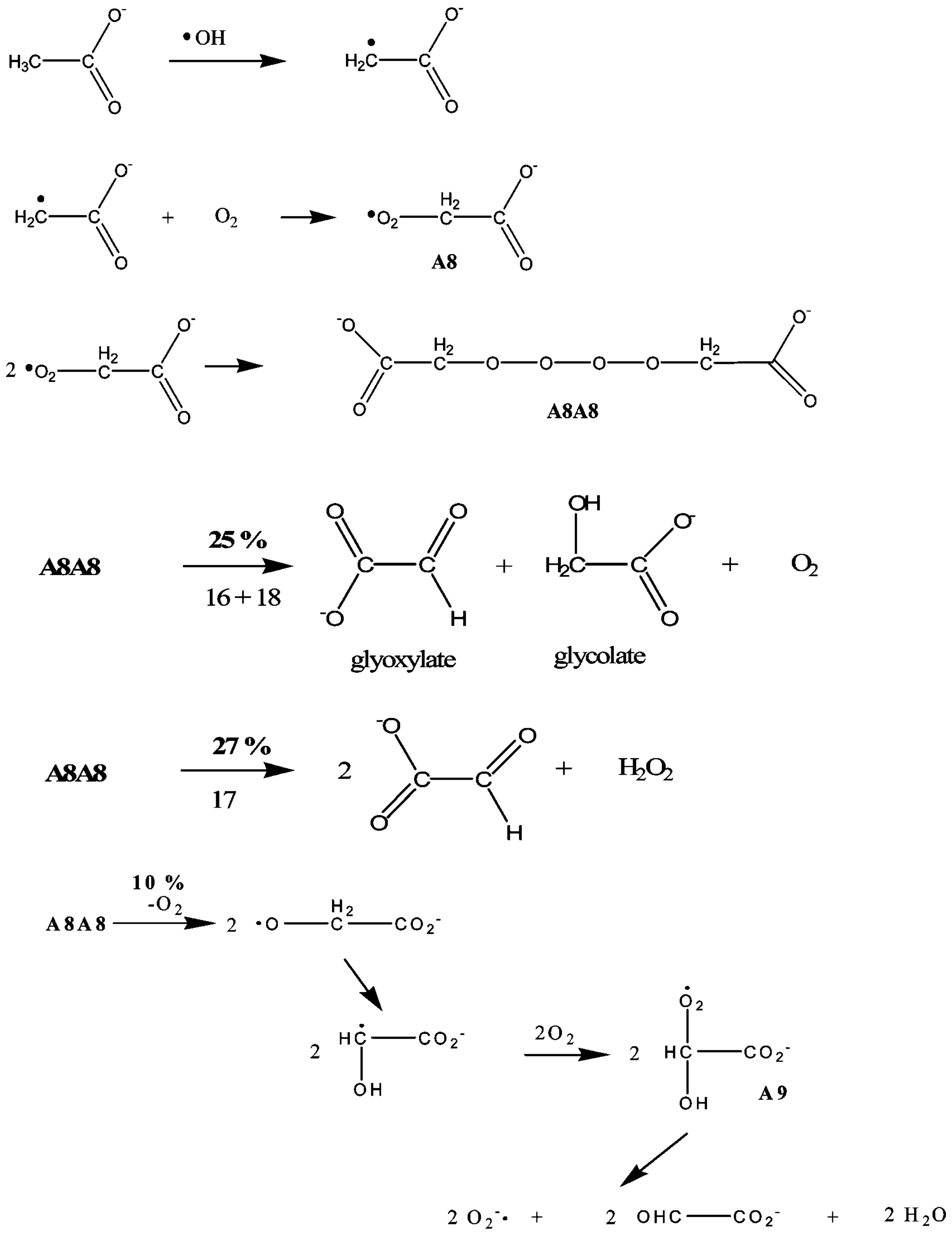
One of the last series of steps in the mineralization of MTBE (or for that matter *any* organic compound) involves formic acid (pK_a = 3.75) or the formate ion:



Scheme 34



Scheme 35



The oxidative and reductive radical chemistry of formic acid/formate ion has been studied for many years.[134,147−150]

$$HCOO^- + {}^\bullet OH \rightarrow {}^\bullet COO^- + H_2O \qquad (60)$$

By examining the initial absorption spectra of $CO_2^{\bullet-}$ it was shown that the decay rates were invariant with pH.[151] This observation established the equivalence of the carboxyl radical formed and its associated acid form. It was established in other studies that reactions of both ${}^\bullet OH$ and ${}^\bullet H$ with formate give the carboxyl radical:[134,152−154]

$$HCOO^- + {}^\bullet OH/H^\bullet \rightarrow CO_2^{\bullet-} + H_2O/H_2 \qquad (61)$$

The equilibrium of the carboxyl radical was studied and the pK_a initially determined[155] as 1.4. However, more recently it was reevaluated as 2.3:[156]

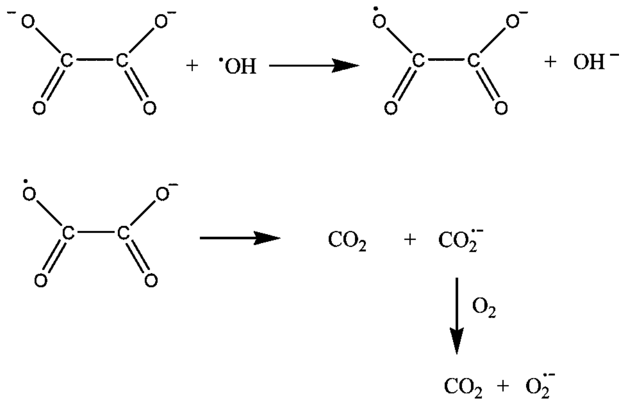
$$ {}^\bullet COOH \underset{pK_a = 2.3}{\rightleftharpoons} {}^\bullet COO^- + H^+$$

$CO_2^{\bullet-}$ rapidly transfers an electron to O_2, resulting in the formation of CO_2:[157]

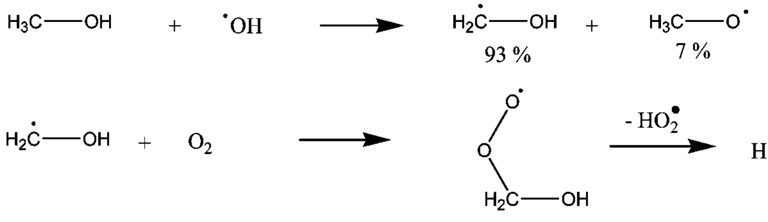
$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^{\bullet-} \qquad (62)$$

In the absence of O_2, $CO_2^{\bullet-}$ recombines, giving rise to oxalic acid at pH > 3, but it also disproportionates in acid solution

Scheme 36



Scheme 37



A10

to form CO_2.[134,158] A rather complex mechanism has been postulated to account for these observations (Scheme 38).[156]

An asymmetric dimer of $^{\bullet}CO_2^-$ has also been observed in the acetate system and in both cases appears to be an intermediate in the disproportionation reactions.[159] The pH dependence of this reaction scheme[156] confirmed the earlier work that showed that at pH > 3 the dimerization of the carboxyl radical results in the formation of oxalic acid,[34] or the oxalate anion (k_{64}[151,155]).

$$^{\bullet}CO_2H + {}^{\bullet}CO_2H \rightarrow HOOC{-}COOH \qquad k_{63} = (1.7 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1} \quad (63)$$

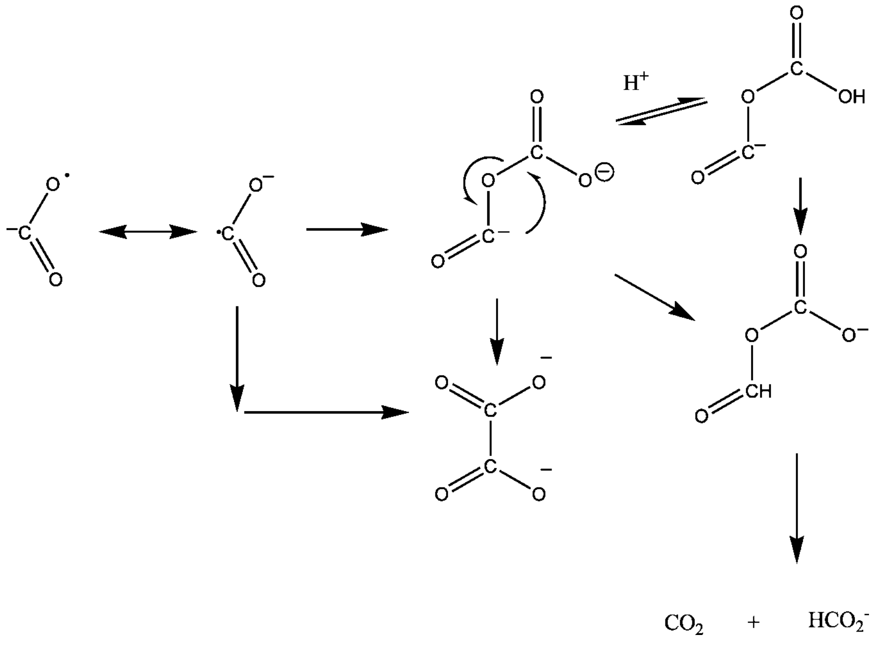
$$^{\bullet}CO_2^- + {}^{\bullet}CO_2^- \rightarrow {}^-OOC{-}COO^- \qquad k_{64} = 1.0 \times 10^9\ M^{-1}\ s^{-1} \quad (64)$$

The decomposition of oxalic acid was discussed previously. The formation of oxalic acid/oxalate is the one case in the degradation of MTBE that leads to the formation of a byproduct that has an additional carbon in the structure. The importance of this radical—radical recombination will depend upon the concentration of those byproducts that leads to the formation of the carboxyl radical. At low concentrations, the dimerization is likely to be of little importance; however, it must not be eliminated from consideration.[98]

More recently, a study examined the Fenton-mediated oxidation of formic acid in the presence and absence of oxygen.[160] This study also presents a kinetic model that decribes the observed destruction of formic acid, and they verifed the reaction rate of $^{\bullet}OH$ with formic acid as 1.3×10^8. The absence of O_2 in the reaction scheme allowed verification of the details of the mechanism and allowed an accurate kinetic model to be developed.

A study using UV/H_2O_2 in the presence and absence of O_2 confirmed the above reactions.[142] In another study, using electron beam irradiation, the decomposition of formic acid was studied and a kinectic model was developed using literature data that adequately described the decomposition in aqueous solution.[161] Formic acid was also used as a model

Scheme 38



reactant to evaluate several different sonochemical reactors to evaluate the energy efficiency of those reactors.[162]

Thus, once the decomposition has reached the formic acid/formate ion stage, there are several routes to the formation of CO_2. With the exception of the reformation of oxalic acid/oxalate ion, this is a terminal step. The formation of CO_2 represents the final mineralization of the carbon in MTBE.

5. Kinetic Computer Modeling

Kinetic modeling has long been used to try to better understand the atmospheric chemistry of global climate change and other areas of science. The atmospheric models are extremely complex and continue to evolve as additional information is obtained. In general, atmospheric models for the fate of organic chemicals are limited to compounds that have fewer than three carbon atoms.[40]

In natural water fate and transport models, there has not been an equivalent effort to parallel that of atmospheric science. However, an emerging trend in the application of environmental chemistry to engineering applications for treating pollutants of concern is the use of kinetic models that incorporate a mechanistic description of the organic contaminant destruction and the kinetics of the reactions that define these processes.[163]

A full kinetic model is divided into three separate components using coupled differential equations to provide the overall description. These components provide a description of the following:
(1) formation of reactive species in the individual process,
(2) the destruction mechanism including reaction rates, and
(3) the formulation of the reactor design to include fluid mechanics.

These models are useful for different reasons, for example:
(1) as a guide for experimental studies (by formulating a kinetic model and running sensitivity analyses, it is possible to determine the important reaction rate constants that need to be evaluated and what further mechanistic studies are required.),
(2) to evaluate processes for potential application,[163−167]
(3) to evaluate the economics of potential treatment processes,
(4) to develop information that can be used in environmental fate and transport models,
(5) and, in the present study, to identify future research topics associated with the free radical destruction of MTBE.

There are numerous reports of the development of kinetic models for various advanced oxidation processes, for example, the H_2O_2/UV process has been modeled.[162,166,167] The O_3/H_2O_2 process was modeled for hazardous materials;[168−170] the O_3/UV process was modeled for *tert*-butyl alcohol;[102] and then oxalic acid was used as a probe chemical.[143] Fenton's chemistry has also been used for the oxidation of atrazine[171] and *p*-hydroxybenzoic acid,[172] and kinetic models were developed for both compounds. A kinetic model has been proposed for another advanced oxidation process, γ-radiolysis, of 2-butanone.[173]

The electron beam advanced oxidation process has been modeled for a number of different contaminants,[174−180] and ^{60}Co-γ-irradiation[97,181] and studies modeling the heterogeneous TiO_2 process have been initiated.[182,183] Once models are developed, it is possible to evaluate or to calibrate various treatment processes for use in pollution control by adding reactor fluid dynamics.

Several papers have reported a partial kinetic model for the destruction of MTBE.[98,99,181,184−188] The model proposed in this review is built on those initial studies and, based on the proposed mechanisms reported above, has resulted in a more comprehensive summary of the free radical chemistry involved in the treatment of MTBE contaminated waters. Table 6 is a linearization of the detailed mechanisms outlined in this review. This linearization is the beginning of a model and includes both oxidative and reductive pathways; however, much more information is known of the oxidative pathways than the reductive pathways.

The formulation of an MTBE model based on the mechanism outlined above also serves to indicate where there is need for additional mechanistic and reaction kinetic data. It is somewhat surprising that for many of the lower molecular weight reaction products there are significant gaps in our detailed understanding of reaction kinetics and mechanisms. Nonetheless, we have proposed a working model that should be helpful in guiding future studies in this area.

We envision future studies that will elucidate the details of the reaction byproducts that have been identified in this proposed mechanism. These might then be "plug-in" modules in a kinetic model that would start with the lower carbon byproduct and work up to the more complex five-carbon MTBE system. Because many of the lower carbon compounds that have been identified as reaction byproducts of MTBE might also be found in degradations of other compounds, this approach would be more generalizable. For example, the destruction of formic and oxalic acids at several pH values using ^{60}Co-γ-irradiation has been studied.[189] Proposing a simple model, it was possible to duplicate the experimental data to a close approximation.[189] However, this points out that there is still work to be done for many of even the simplest of organic compounds.

In summary, kinetic models are developed in a stepwise manner and as more information about the destruction mechasnism is developed, improvements are made.[190] It is fair to say that now computing power is usually not the limiting part of aqueous destruction models; rather, it is a combination of reaction rate constants and destruction mechanistic considerations.

6. Conclusions and Future Research

A quantitative, mechanistically based understanding of the free radical-induced destruction mechanism of MTBE in aqueous systems will clearly assist in the development of better models for application in treatment process design and optimization and complement studies using physical methods such as fugacity.[191] It appears that similar mechanisms are operative in atmospheric droplets; therefore, this study will extend our understanding of the fate and transport of MTBE in the troposphere.[44,192] It is also likely that a better understanding of the factors affecting the gas-phase destruction of MTBE would benefit from these studies.[193]

A major area not addressed in this paper or to any great extent in the literature is the likely cross-termination reactions which would occur under certain circumstances. For example, as MTBE is destroyed and reaction byproducts appear, it is entirely likely that, in the formation of tetroxides, a peroxyl radical of TBA or TBF might encounter one from MTBE. These tetroxides would ultimately result in the same byproduct as noncross termination reactions; however, incorporation of these may be necessary to account for the product distributions observed in some studies or even in actual remediation situations, were AOPs to be employed. This

Table 6. Reactions and Associated Rate Constants That Describe Water Radiolysis (10^{-7} s after Electron Injection) in Distilled Water, Natural Water Constituents, The Disinfectant Monochloramine, and MTBE and Reaction Byproducts[a]

no.	reaction									rate constant (M^{-1} s^{-1}) unless specified	notes
1	OH	+	H_2	→	H	+	H_2O			4.20×10^7	radiolysis of water
2	OH	+	H_2O_2	→	HO_2	+	H_2O			2.70×10^7	radiolysis of water
3	OH	+	$O_2^{\bullet -}$	→	O_2	+	OH^-			8.00×10^9	radiolysis of water
4	OH	+	$HO_2^{\bullet}$	→	H_2O	+	O_2			6.00×10^9	radiolysis of water
5	OH	+	OH	→	H_2O_2					5.50×10^9	radiolysis of water
6	OH	+	O^-	→	HO_2^-					2.00×10^{10}	radiolysis of water
7	OH	+	OH^-	→	H_2O	+	O^-			1.30×10^{10}	radiolysis of water
8	OH	+	HO_2^-	→	OH^-	+	HO_2			7.50×10^9	radiolysis of water
9	OH	+	$H_2O_2^+$	→	H_3O^+	+	O_2			1.20×10^{10}	radiolysis of water
10	O^-	+	H_2O	→	OH^-		OH			1.80×10^6	radiolysis of water
11	O^-	+	H_2	→	H	+	OH^-			8.00×10^7	radiolysis of water
12	O^-	+	H_2O_2	→	O_2^-	+	H_2O			5.00×10^8	radiolysis of water
13	O^-	+	HO_2^-	→	O_2^-	+	OH^-			4.00×10^8	radiolysis of water
14	O^-	+	O_2^-	→	OH^-	+	OH^-	+	O_2	6.00×10^8	radiolysis of water
15	e^-_{aq}	+	H	→	H_2	+	OH^-			2.50×10^{10}	radiolysis of water
16	e^-_{aq}	+	e^-_{aq}	→	OH^-	+	OH^-	+	H_2	5.00×10^9	radiolysis of water
17	e^-_{aq}	+	O_2	→	O_2^-					1.90×10^{10}	radiolysis of water
18	e^-_{aq}	+	H_2O_2	→	OH	+	OH^-			1.10×10^{10}	radiolysis of water
19	e^-_{aq}	+	O_2^-	→	O_2^{2-}					1.30×10^{10}	radiolysis of water
20	e^-_{aq}	+	H^+	→	H					2.30×10^{10}	radiolysis of water
21	e^-_{aq}	+	H_2O	→	H	+	OH^-			1.90×10^1	radiolysis of water
22	e^-_{aq}	+	HO_2^-	→	OH	+	OH^-	+	OH^-	3.50×10^9	radiolysis of water
23	e^-_{aq}	+	OH	→	OH^-					3.00×10^{10}	radiolysis of water
24	e^-_{aq}	+	O^-	→	OH^-	+	OH^-			2.20×10^{10}	radiolysis of water
25	H	+	O_2	→	HO_2					2.10×10^{10}	radiolysis of water
26	H	+	H	→	H_2					7.80×10^9	radiolysis of water
27	H	+	OH	→	H_2O					7.00×10^9	radiolysis of water
28	H	+	HO_2	→	H_2O_2					1.00×10^{10}	radiolysis of water
29	H	+	H_2O_2	→	H_2O	+	OH			9.00×10^7	radiolysis of water
30	H	+	OH^-	→	e^-_{aq}					2.20×10^7	radiolysis of water
31	H	+	H_2O	→	H_2	+	OH			1.00×10^1	radiolysis of water
32	H	+	O_2^-	→	HO_2^-					2.00×10^{10}	radiolysis of water
33	HO_2	+	O_2^-	→	O_2	+	H_2O	+	OH^-	8.90×10^7	radiolysis of water
34	HO_2	+	HO_2	→	H_2O_2	+	O_2			8.30×10^5	radiolysis of water
35	H^+	+	O_2^-	→	HO_2					4.50×10^{10}	radiolysis of water
36	HO_2			→	H^+	+	O_2^-			8.00×10^5	radiolysis of water
37	H^+	+	HO_2^-	→	H_2O_2					2.00×10^{10}	radiolysis of water
38	H_2O_2			→	H^+	+	HO_2			3.60×10^2	radiolysis of water
39	H^+	+	OH^-	→	H_2O					1.43×10^{11}	radiolysis of water
40	H_2O			→	OH^-	+	H^+			2.60×10^5	radiolysis of water
41	HCO_3	+	OH	→	RCO_3	+	H_2O			8.50×10^6	carbonate system
42	HCO_3	+	e^-_{aq}	→	PDTS					1.00×10^6	carbonate system
43	HCO_3	+	H	→	PDTS					4.40×10^4	carbonate system
44	CO_3	+	OH	→	RCO_3	+	OH^-			3.90×10^8	carbonate system
45	CO_3	+	e^-_{aq}	→	PDTS					3.90×10^5	carbonate system
46	RCO_3	+	OH	→	PDTS					3.00×10^9	carbonate system
47	RCO_3	+	O_2^-	→	O_2	+	CO_3			6.50×10^8	carbonate system
48	RCO_3	+	H_2O_2	→	HCO_3	+	HO_2			8.00×10^5	carbonate system
49	RCO_3	+	HO_2^-	→	HCO_3	+	O_2^-			5.60×10^7	carbonate system
50	DOC	+	e^-_{aq}	→	PDTS						natural organic matter[a]
51	DOC	+	H	→	PDTS						natural organic matter[b]
52	DOC	+	OH	→	PDTS					$(1.60 \pm 0.24) \times 10^8$	natural organic matter[b]
53	NH_2Cl	+	e^-_{aq}	→	PDTS					2.20×10^{10}	typical disinfectant
54	NH_2Cl	+	OH	→	PDTS					5.20×10^8	typical disinfectant
55	NH_2Cl	+	H	→	PDTS					1.20×10^9	typical disinfectant
56	MTBE	+	OH	→	MTB1					1.20×10^9	Scheme 1
57	MTBE	+	OH	→	MTB2					5.10×10^8	Scheme 1
58	MTBE	+	H	→	MTB1					3.49×10^6	
59	MTBE	+	e^-_{aq}	→	PDTS					$<8.00 \times 10^6$	
60	MTB1	+	O_2	→	**A***					8.73×10^8	Scheme 1
61	MTB2	+	O_2	→	**B**					3.57×10^8	Scheme 1
62	**A**	+	**A**	→	**AA****						Scheme 2
63	**AA**			→ 16	TBF	+	hemiacetal of A	+	O_2		Scheme 2
64	hemiacetal of **A**	+	H_2O	→	TBA	+	HCHO				Scheme 2
65	**AA**			→ 17	2TBF	+	H_2O_2				Scheme 2
66	**A**-alkoxy			→ 18	1,2-H shift **A**						Scheme 2
67	1,2 H shift **A**	+	O_2	→	**C**						Scheme 2
68	**C**			→	TBF	+	HO_2				Scheme 2
	1,2-H shift **A**			→	*tert*-butoxy	+	HCHO				Scheme 2
69	**A**	+	**B**	→	**AB**						Scheme 3
70	**AB**			→ 16	hemiacetal of **A**	+	MMP	+	O_2		Scheme 3

Table 6. Continued

no.	reaction									rate constant (M^{-1} s^{-1}) unless specified	notes
71	**AB**			$\underset{16}{\rightarrow}$	TBF	+	MMP-OH	+	O_2		Scheme 3
72	**AB**			$\underset{17}{\rightarrow}$	TBF	+	MMP	+	H_2O_2		Scheme 3
73	**AB**			→	**B**-alkoxy	+	O_2				Scheme 3
74	**B**-alkoxy			→	1,2-H shift **B**						Scheme 3
75	1,2-H shift **B**	+	O_2	→	MMP	+	HO_2				Scheme 3
76	**B**-alkoxy			→	alkyl radical **B**						Scheme 3
77	alkyl radical **B**	+	O_2	→	**D**						Scheme 3
78	**D**	+	**D**	→	**DD**						Scheme 3
79	**DD**			$\underset{18}{\rightarrow}$	2-alkoxy radicals	+	O_2				Scheme 3
80	2-alkoxy radicals			→	2 methyl acetate	+	2 Me radicals			10^6-10^7 s^{-1}	Scheme 3[81]
81	**AA**			$\underset{19}{\rightarrow}$	2 *tert*-butyl alkyl	+	O_2	+	2HCHO		Scheme 4
82	*tert*-butyl alkyl	+	O_2	→	**F**						Scheme 4
83	**F**	+	**F**	→	**FF**						Scheme 4
84	**FF**			→	2 *tert*-butoxy (**E**)	+	O_2				Scheme 4
85	**E**			→	ACE	+	Me radical			10^6-10^7 s^{-1}	Scheme 4[81]
86	**B**	+	**B**	→	**BB**						Scheme 5
87	**BB**			$\underset{16}{\rightarrow}$	MMP	+	MMP−OH	+	O_2		Scheme 5
88	**BB**			$\underset{17}{\rightarrow}$	2 MMP	+	H_2O_2				Scheme 5
89	**BB**			$\underset{18}{\rightarrow}$	**B**-alkoxy	+	O_2				Scheme 5
90	Me radical	+	O_2	→	**G**						eq 37
91	**G**	+	**G**	→	**GG**						
92	**GG**			$\underset{16}{\rightarrow}$	HCHO	+	MeOH	+	O_2		eq 38
93	**GG**			$\underset{17}{\rightarrow}$	2HCHO	+	H_2O_2				eq 40
94	**GG**			→	Di-Me peroxide	+	O_2				eq 41
95	**GG**			→	2Meoxy	+	O_2				eq 39
96	Meoxy			→	**G**-1,2-H shift ($^{\bullet}CH_2OH$)						eq 42
97	1,2-H shift	+	O_2	→	**H**						eq 43
98	2 **H**			→	2 HCOOH	+	H_2O_2				eq 44
99	Meoxy	+	HO_2	→	Me peroxide	+	O_2				eq 45
100	TBF	+	OH	→	TBF1					5.23×10^8	Scheme 6
101	TBF	+	e^-_{aq}	→	PDTS					5.48×10^8	Scheme 6
102	TBF	+	H	→	TBF1					3.58×10^6	
103	TBF1	+	O_2	→	**I**						Scheme 6
104	**I**	+	**I**	→	**II**						Scheme 6
105	**II**			$\underset{16}{\rightarrow}$	2-methyl-1-oxopropan -2-yl formate	+	1-hydroxy -2-methlypropan -2-yl formate	+	O_2		Scheme 6
106	**II**		$\underset{16}{\rightarrow}$ $\underset{16}{\rightarrow}$	$\underset{17}{\rightarrow}$	2-methyl-1-oxopropan -2-yl formate	+	H_2O_2				Scheme 6
107	TBF	+	OH	→	TBF2						Scheme 7
108	TBF2			→	*tert*-butyl alkyl	+	CO_2				Scheme 7
109	*tert*-butyl alkyl	+	O_2	→	**F**						Scheme 7
110	TBA	+	OH	→	TBA1					5.76×10^8	Scheme 8

Table 6. Continued

no.	reaction						rate constant (M^{-1} s^{-1}) unless specified	notes
111	TBA	+ OH	→	TBA2			4.00 × 10^6	Scheme 8
112	TBA	+ H	→	TBA1			1.70 × 10^5	
113	TBA	+ e^-_{aq}	→	PDTS			4.00 × 10^5	
114	TBA1	+ O_2	→	**J**				Scheme 8
115	TBA2	+ O_2	→	*tert*-butoxy				Scheme 8
116	**J**	+ **J**	→	**JJ**				Scheme 8
117	**JJ**		$\underset{16}{\rightarrow}$	2-OH-2-methylpropanal (hydroxy isobutyraldehyde)	+ 2-methylpropane -1,2-diol	+ O_2		Scheme 8
118	**JJ**		$\underset{17}{\rightarrow}$	2-OH-2-methylpropanal	+ H_2O_2			Scheme 8
119	**JJ**		$\underset{18}{\rightarrow}$	2 **J**-alkoxy				Scheme 9
120	**J**-alkoxy		→	J-1,2-H-shift				Scheme 9
121	**J**-1,2-H-shift		→	*sec*-but alkyl	+ HCHO			Scheme 9
122	*sec*-but alkyl	+ O_2	→	**K**				Scheme 9
123	**K**		↔	**K**-anion-rad				Scheme 9
124	**K**-anion-rad		→	ACE	+ HO_2			Scheme 9
125	**JJ**		$\underset{19}{\rightarrow}$	*sec*-propanol radical	+ O_2	+ 2HCHO		Scheme 10
126	2 *sec*-but alkyl radical	+ O_2	→	**K**				Scheme 10
127	**KK**		→	2 ace	+ $2HO_2$			Scheme 10
128	MMP-OH	+ OH	→	MMPH1			8.02 × 10^8	Scheme 10
129	MMP-OH	+ OH	→	MMPH2				Scheme 11
130	MMP-OH	+ OH	→	MMPH3				Scheme 11
131	MMP-OH	+ e^-_{aq}	→	PDTS			7.83 × 10^6	
132	MMP-OH	+ H	→	PDTS			1.30 × 10^8	
133	MMPH1	+ O_2	→	**L**				Scheme 12
134	MMPH2	+ O_2	→	**M**				Scheme 12
135	MMPH3	+ O_2	→	**N**				Scheme 12
136	**M**		→	MMP	+ HO_2			Scheme 12
137	**L**	+ **L**	→	**LL**				
138	**LL**		$\underset{16}{\rightarrow}$	**L**-formate	+ **L**-hemiacetal			Scheme 13
139	**L**-hemiacetal		→	2-alkoxy 1-propanol	+ HCHO			Scheme 13
140	2-alkoxy 1-propanol		→	HO-ACE	+ Me radical			Scheme 13
141	**LL**		$\underset{17}{\rightarrow}$	2 **L**-formate	+ H_2O_2			Scheme 13
142	**LL**		$\underset{18}{\rightarrow}$	2 **L** oxyl radicals	+ O_2			Scheme 13
143	**L** oxyl radical		→	**L** alkoxy radical	+ HCHO			Scheme 13
144	**L** alkoxy radical		→	HO-ACE	+ Me radical			Scheme 13
145	**LL**		$\underset{19}{\rightarrow}$	**L**-alkyl	**L**-formate			Scheme 14
146	**L**-alkyl	+ O_2	→	**O**				Scheme 14
147	**O**	+ **O**	→	**OO**				Scheme 14
148	**OO**		$\underset{18}{\rightarrow}$	2 1-OH-2-alkoxy	+ HCHO			Scheme 14
149	1-OH-2-alkoxy		→	HO-ACE	+ Me radical			Scheme 14
150	1-OH-2-alkoxy		→	ACE	+ ($^{\bullet}CH_2OH$) **G**-1,2-H shift			Scheme 14
151	**L**-formate	+ H_2O	→	2-methyl-1,2-propanediol	+ formic acid			
152	**N**	+ **N**	→	**NN**				
153	**NN**		→	N-aldehyde	+ N-alcohol	+ O_2		Scheme 15
154	**NN**		→	2N-aldehyde	+ H_2O_2			Scheme 15
155	MMP	+ H_2O	↔	MMP-hydrate				Scheme 16
156	MMP	+ OH	→	MMP1/MMP-hyd			3.99 × 10^9	Scheme 16
157	MMP	+ OH	→	MMP2				Scheme 16
158	MMP	+ OH	→	MMP3				Scheme 16

Table 6. Continued

no.	reaction									rate constant (M^{-1} s^{-1}) unless specified	notes
159	MMP	+	OH	→	MMP4						Scheme 16
160	MMP	+	e^{-}_{aq}	→	PDTS					3.11×10^{7}	
161	MMP	+	H	→	PDTS					1.65×10^{7}	
162	MMP-hydrate	+	O_2	→	**P**						Scheme 16
163	MMP2	+	O_2	→	**Q**						Scheme 16
164	MMP3	+	O_2	→	**R**						Scheme 16
165	MMP4	+	O_2	→	**S**						Scheme 16
166	**P**			→	MMP-COOH	+	HO_2				Scheme 17
167	**QQ**			$\underset{18}{\rightarrow}$	**Q**-alkoxy						Scheme 17
168	**Q**-alkoxy			→	**Q**-alkyl	+	CO_2				Scheme 17
169	**Q** -alkyl			→	2 ACE	+	2Me radical				Scheme 17
170	**RR**			$\underset{16}{\rightarrow}$	**R**-aldehyde	+	**R**-hemiacetal	+	O_2		Scheme 18
171	**R**-hemiacetal			→	2- hydroxy-2-methylpropanal	+	HCHO				Scheme 18
172	**RR**			$\underset{17}{\rightarrow}$	2-methyl-1-oxopropan-2-yl formate	+	H_2O_2				Scheme 18
173	**SS**			$\underset{16}{\rightarrow}$	2-methoxy-2-methylmalonaldehyde	+	3-hydroxy-2-methoxy-2-methylpropanal	+	O_2		Scheme 19
174	**SS**			$\underset{17}{\rightarrow}$	2 2-methoxy-2-methylmalonaldehyde	+	H_2O_2				Scheme 19
175	MMP-COOH	+	OH	→	MMP-COOH 1					7.73×10^{8}	Scheme 20
176	MMP-COOH	+	OH	→	MMP-COOH 2						Scheme 20
177	MMP-COOH	+	e^{-}_{aq}	→						1.40×10^{9}	
178	MMP-COOH	+	H	→						$<1.2 \times 10^{6}$	
179	MMP-COOH 1	+	O_2	→	**T**						Scheme 20
180	MMP-COOH 2	+	O_2	→	**U**						Scheme 20
181	**T**	+	**T**	→	**TT**						
182	**U**	+	**U**	→	**UU**						
183	**TT**			$\underset{16}{\rightarrow}$	**T**-aldehyde	+	**T**-hemiacetal	+	O_2		Scheme 21
184	**T**-hemiacetal			→	2-hydroxymethyl propionic acid	+	HCHO				Scheme 21
185	**TT**			$\underset{17}{\rightarrow}$	2 **T**-aldehyde	+	H_2O_2				Scheme 21
186	**TT**			$\underset{18}{\rightarrow}$	2 **T**-oxyl radicals						Scheme 21
187	**T**-oxyl radical			→	**T**-alkoxy radical	+	HCHO				Scheme 21
188	**T**-alkoxy radical			→	pyruvic acid	+	Me radical				Scheme 21
189	**UU**			$\underset{16}{\rightarrow}$	**U**-aldehyde	+	**U**-alcohol	+	O_2		Scheme 22
190	**UU**			$\underset{17}{\rightarrow}$	**U**-aldehyde	+	H_2O_2				Scheme 22
191	ACE	+	OH	→	ACEtyl radical					2.00×10^{6}	Scheme 23
192	ACEtyl radical	+	O_2	→	**V**						Scheme 23
193	**V**	+	**V**	→	**VV**						Scheme 23
194	**VV**			$\underset{17}{\rightarrow}$	2Me glyoxal	+	H_2O_2				Scheme 23
195	**VV**			$\underset{17}{\rightarrow}$	HO-ACE	+	Me glyoxal	+	O_2		Scheme 23

Table 6. Continued

no.	reaction						rate constant (M^{-1} s^{-1}) unless specified	notes
196	**VV**		→ 19	2FOR	+ 2 ethyl radical	+ O_2		Scheme 23
197	**VV**		→ 18	2ACEtyl alkoxy	+ O_2			Scheme 23
198	2ACEtyl alkoxy		→	2HCHO	+ 2 ethyl radical			Scheme 23
199	ethyl radical	+ O_2	→	**W**				Scheme 23
200	**W**	+ **V**	→	**WV**				Scheme 24
201	**WV**		→ 16	HAc	+ Me glyoxal	+ O_2		Scheme 24
204	ACE	+ e^-_{aq}	→	ACE	+ O_2^-		6.50×10^9	Scheme 25
205	HO-ACE	+ OH	→	HO-ACE1				Scheme 26
206	HO-ACE	+ OH	→	HO-ACE2				Scheme 26
207	HO-ACE1	+ O_2	→	**X**				Scheme 26
208	**X**		→	Me glyoxal	+ HO_2			Scheme 26
209	MeAC	+ OH	→	MeAC1			9.60×10^7	Scheme 27
210	MeAC	+ OH	→	MeAC2			2.40×10^7	Scheme 27
211	MeAC	+ H	→	MeAC1			1.00×10^5	
212	MeAC1	+ O_2	→	**Y**				Scheme 27
213	MeAC2	+ O_2	→	**Z**				Scheme 27
214	**Y**	+ **Y**	→	**YY**				
215	**Z**	+ **Z**	→	**YZ**				
216	**YY**		→ 16	**Y**-formate	+ **Y**-hemiacetal			Scheme 28
217	**Y**-hemiacetal		→	HAc	+ HCHO			Scheme 28
218	**YY**		→ 17	**Y**-formate	+ H_2O_2			Scheme 28
219	**YZ**		→ 16	**Y**-formate	+ Me glycolate	+ O_2		Scheme 28
220	**YZ**		→ 16	**Y**-hemiacetal	+ Me gloxylate	+ O_2		Scheme 28
221	**YY**		→ 18	**Y**-alkoxy radical				Scheme 29
222	**Y**-alkoxy radical		→	**Y**-oxyl radical	+ HCHO			Scheme 29
223	**Y**-oxyl radical		→	CO_2	+ Me radical			Scheme 29
224	**YZ**		→ 18	**Z**-alkoxy radical				Scheme 29
225	**Z**-alkoxy radical		→	**Z**-oxyl radical	+ HCHO			Scheme 29
226	**Z**-oxyl radical		→	CO_2	+ Me radical			Scheme 29
227	MeAC	+ e^-_{aq}	→	MeAC anion rad			8.70×10^7	Scheme 30
228	MeAC anion rad	+ O_2	→	**A1**				Scheme 30
229	**A1A1**		→ 19	2HAc	+ 2Meoxy	+ O_2		Scheme 30
230	Me glyoxal	+ H_2O	↔	Me glyoxal hyd				
231	Me glyoxal hyd	+ OH	→	Me glyoxal rad			$(5.3 \pm 0.4) \times 10^8$	Scheme 31
232	Me glyoxal rad	+ O_2	→	**A2**				Scheme 31
233	**A2**		→	pyruvic acid	+ HO_2			Scheme 31
234	pyruvate	+ OH	→	pyruvate rad			3.1×10^7	Scheme 32
235	pyruvate rad		→	ketene	+ $CO_2^{\bullet -}$			Scheme 32
236	$CO_2^{\bullet -}$	+ H^+/ O_2	→	CO_2	+ HO_2			eq 47
237	ketene	+ H_2O	→	HAc				Scheme 32
238	pyruvate rad	+ O_2	→	**A3**				Scheme 32
239	**A3**	+ **A3**	→	**A3A3**				Scheme 32
240	**A3A3**		→ 16	2,3-dioxopropanoic acid	+ 3-hydroxy-2-oxopropanoic adic	+ O_2		Scheme 32

Table 6. Continued

no.	reaction									rate constant (M^{-1} s^{-1}) unless specified	notes
241	**A3A3**			$\xrightarrow[17]{}$	2,3-dioxopropanoic acid	+	H_2O_2				Scheme 32
242	acetal (0.8)	+	H_2O	$\leftrightarrow$	acetal hydrate (1.0)						eq 48
243	acetal	+	OH	→	acetal rad					3.6×10^9	eq 49
244	acetal hyd	+	OH	→	acetal hyd rad					1.2×10^9	eq 50
245	acetal	+	OH	→	C center rad						eq 51
246	acetal hyd	+	OH	→	C center hyd rad						eq 52
247	acetal rad	+	O_2	→	**A4**						
248	**A4**	+	O_2^-	→	peracetic acid						eq 53
249	ACETal hyd rad	+	O_2	→	**A5**						
250	**A5**			→	HAc	+	O_2^-				eq 54
251	glycolic acid	+	OH	→	glyco rad					6.0×10^8	Scheme 33
252	glyco rad	+	O_2	→	**A6**						Scheme 33
253	**A6**			→	glyoxylic acid	+	HO_2				Scheme 33
254	glyoxylic acid	+	OH	→	glyoxylic rad						Scheme 34
255	glyoxylic rad	+	O_2	→	**A7**						Scheme 34
256	**A7**	+	**A7**	→	**A7A7**						Scheme 34
257	**A7A7**	+	H_2O	→	2oxalic acid	+	O_2				Scheme 34
258	HAc	+	OH	→	HAcR					1.6×10^7	Scheme 35
259	HAcR	+	O_2	→	**A8**						Scheme 35
260	**A8**	+	**A8**	→	**A8A8**						Scheme 35
261	**A8A8**			$\xrightarrow[16+18]{}$	glyoxylate	+	glycolate	+	O_2		Scheme 35
262	**A8A8**			$\xrightarrow[17]{}$	2glyoxylate	+	H_2O_2				Scheme 35
263	**A8A8**			$\xrightarrow[18]{}$	2HAc-alkoxy	+	O_2				Scheme 35
264	**A8A8**			→	2HCHO	+	$2CO_2$	+	H_2O_2		eq 55
265	HAc-alkoxy			→	glyoxylate	+	glycolate				Scheme 35
266	HAc-alkoxy			→	1,2-H shift						Scheme 35
267	1,2-H shift	+	O_2	→	**A9**						Scheme 35
268	**A9**			→	glyoxylate	+	O_2^-	+	H_2O		Scheme 35
269	oxal	+	OH	→	oxal rad	+	H_2O			1.4×10^6	Scheme 36
270	oxal	+	H	→	oxal rad	+	H_2			3.3×10^5	
271	2oxal rad.			→	oxalic rad cage					1.0×10^9	
272	oxalic rad cage			→	oxal	+	2 CO_2			1.0×10^6	Scheme 36
273	oxal	+	e^-_{aq}	→	$HOOC-C^{\bullet}(OH)-O^-$					2.5×10^{10}	
274	MeOH	+	OH	→	Me alkyl rad	+	methoxy rad				Scheme 37
275	Me alkyl rad	+	O_2	→	**A10**						Scheme 37
276	**A10**			→	HCHO	+	HO_2				Scheme 37
277	HCHO	+	H_2O	$\leftrightarrow$	$HCH(OH)_2$						eq 56
278	$HCH(OH)_2$	+	OH	→	$CH(OH)_2$					1.00×10^9	eq 57
279	$CH(OH)_2$	+	O_2	→	**A11**						eq 58
280	**A11**			→	HCOOH	+	HO_2				eq 59
281	$HCOO^-$	+	OH	→	COO	+	H_2O			3.2×10^9	eq 60
282	$HCOO^-$	+	H	→	COO	+	H_2			2.1×10^8	
283	HCOOH	+	OH	→	COOH	+	H_2O			1.4×10^8	
284	COO	+	O_2	→	CO_2	+	O_2^-				eq 61
285	HCOOH	+	H	→	COO	+	H_2			4.4×10^5	
286	HCOOH	+	e^-_{aq}	→	H•	+	$H-COO^-$			1.4×10^8	
287	COOH	+	COOH	→	oxalic acid					1.7×10^9	eq 62
289	COO	+	COO	→	oxalate ion					1.0×10^9	eq 63

[a] Bolded letters refer to peroxyl radicals identified in the reaction schemes. Bolded double letters are tetroxides. PDTS = unidentified products. [b] Westerhoff, P.; Mezyk, S. P.; Cooper, W. J.; Minakata, D. *Environ. Sci. Technol.* **2007**, *41*, 4640.

would be best studied under controlled conditions and would be a very interesting study with potentially important conclusions.

Another area for which there is no data is the extension to "natural waters", where in many cases there would be the uncharacterized fraction known as "dissolved organic matter". It is known that this fraction does react with both $^{\bullet}OH$ and e^-_{aq}. However, what is not known is the effect of this on the destruction of organic chemicals in these waters. This is a major research area that should be undertaken if the concept of kinetic modeling is to be extended to "real world" applications.

In addition, this full mechanistic understanding may be helpful toward a better understanding of MTBE biochemistry. Recent investigations[194,195] suggest that the human liver cytochrome P450 system, known to be free radically based, and specifically cytochrome P450 2A6, which is 5−10% of the total microsomal system, is the major enzyme responsible for metabolism of MTBE.[196] Like the initial $^{\bullet}OH$ reaction in aqueous solution, this metabolism is not a very specific reaction, and by better understanding the free radical chemistry of MTBE in an aqueous system, it may be possible to better understand the basis of its health effects.[195]

Our proposed condensed-phase, free radical-mediated mechanism, and hence the proposed kinetic model, for the destruction of MTBE is far from complete. However, it can be used as a framework to identify unanswered questions with respect to reaction byproducts, additional research, and a way to focus the future studies on the highest priority questions. MTBE serves as a good example of this overall approach because of its widespread occurrence in the environment. The degradation of MTBE forms chemicals of lower carbon number that are also of interest in environmental chemistry[197] and are reaction products of other chemicals, e.g. aromatic compounds,[198] amino acids,[199] and complex mixtures of pollutants.[200]

It is clear that additional kinetic studies under carefully controlled reaction conditions need to be performed. As an example, the reaction rate constant for the oxalate dianion has been evaluated twice, with the two values differing by over an order of magnitude. The reactions of the hydroxyl radical are relatively easily studied using methods established for radiation chemistry, as the addition of N_2O quantitatively converts hydrated electrons and hydrogen atoms to this radical, and flash photolysis.[197] Therefore, in general, many of the oxidative pathways for simple compounds have been established. In contrast, very few of the reducing pathways have been studied and future work should emphasize this area. While not important for MTBE itself, many of the lower molecular weight compounds produced in its free radical-induced degradation reduce quickly, and this chemistry also needs to be included in the model.

No studies, other than bimolecular reaction rate studies,[100] have been reported for *tert*-butyl formate, a commercially available chemical and one of the primary reaction products from MTBE. The initial question to be studied is the initial reaction pathway and the branching ratio for hydrogen abstraction, formyl hydrogen *vs* methyl hydrogen abstraction. It is known that many oxygen-centered radicals undergo facile β-fragmentation, and for example, acyloxyl radicals, intermediates in the electrolytic oxidation of acids (Kolbe electrolysis), rapidly decompose into alkyl radicals and carbon dioxide, reaction eq 65. The rate of these reactions is on the order of 10^9 s^{-1} and increases with increasing branching of the alkyl substituent, i.e. decreasing $C-CO_2^{\bullet}$ bond energy.[201]

$$R-C(O)O^{\bullet} \rightarrow R^{\bullet} + CO_2 \qquad (65)$$

How this affects the branching ratio is not clear.

We have recently synthesized MMP and MMP-OH in quantities which will allow us to intiate some studies on the destruction mechanisms. One of the problems associated with studies of this type is identification of the highly oxygenated polar byproducts. Recently, a series of derivatizing reagents have been developed specifically for highly polar chemicals such as those that are byproducts in the degradation of MTBE.[202−204] Such advances may provide important new tools for mechanistic studies regarding the byproducts yet to be carefully elucidated.

An alternative approach which may be logistically easier would be to start detailed mechanistic studies with the lower carbon number compounds, for which little data exists, and work up in carbon number to more complex molecules. For example, there are limited reports for many of the lower carbon-number reaction byproducts, methylglyoxal (pyruvaldehyde), pyruvic acid (pyruvate ion), glyoxal, and glyoxylic acid (glyoxylate ion).

The hydrated electron can be observed directly using absorption spectroscopy at 700 nm. However, in order to isolate these reactions from those of the hydroxyl radical and hydrogen atom, it is necessary to add a chemical that scavenges these latter two species. Usually, a low molecular weight alcohol is added. While this does not interfere with the kinetic measurements, the presence of a large amount of alcohol makes it very difficult to study the associated reaction mechanisms with the reductive pathways(s) using steady-state radiolysis.

There is still a dearth of kinetic information for the formation and decomposition of the peroxyl radicals and tetroxide species involved in the degradation process. For some species, the absorption coefficient for the peroxyl radical in the far UV portion of the spectrum is sufficiently different from the carbon-centered radical to allow peroxyl radical formation kinetics to be elucidated. However, for many low-molecular-weight species, this difference is not large enough to provide quantitative data. Moreover, there can also be significant interference from other species, such as $O_2^{\bullet -}$. The superoxide radical also absorbs strongly in the far UV, and the involvement of $O_2{\bullet}^-$ in chain reactions in oxygenated aqueous solutions has been demonstrated.[82,205] Unfortunately, there have only been very limited studies of this nature reported, and so these reactions have not been considered to the fullest extent in this paper, mainly because of the lack of understanding of the mechanistic implications.

Studies under carefully controlled reaction conditions with the quantitative determination of reaction byproducts need to be carried out where as many of the byproducts as possible are quantitatively identified through the course of the reaction. It is possible that the use of stable isotope labeled compound(s), using ^2H, ^{13}C, and ^{18}O, could provide valuable information on reaction byproducts and be extremely useful in elucidating or confirming reaction pathways.[206,207] These studies will be extremely useful in evaluating some of the branching ratios of competing reactions in the degradation mechanisms of MTBE.

Another potential use of ^{13}C-labeled compounds, and direct, time-resolved, electron paramagnetic resonance spectroscopy, would be in monitoring these reactions. This approach would allow a direct method for evaluating the decay of the peroxyl radicals to form tetroxides, as well as elucidating the importance of the reactions of peroxyl radicals with $O_2^{\bullet -}$:

$$RO_2^{\bullet} + O_2^{\bullet -} \rightarrow \text{products} \qquad (66)$$

Also, this approach could be used to establish the kinetics of cross-termination reactions of peroxy radicals of different parent compounds:

$$R'O_2^{\bullet} + RO_2^{\bullet} \rightarrow \text{products} \qquad (67)$$

In the early stages of MTBE decomposition in AOPs where the hydroxyl radical is continuously formed, such combination reactions could be important and, therefore, need to be included in the kinetic model. These cross-reactions would influence the distribution of reaction products but would not likely result in new products that have not been proposed in this scheme.

One other approach to explore the formation and fate of peroxyl radicals formed in free radical reactions in oxygenated aqueous solution is from stable product analyses. Recently, an example of alkyl nitrate formation in aqueous solutions according to reactions 67 and 69 has been reported.[208]

$$\mathrm{ROO^{\bullet} + NO^{\bullet} \rightarrow RONO_2} \quad (68)$$

$$\mathrm{\rightarrow RO^{\bullet} + NO_2^{\bullet}} \quad (69)$$

The branching ratio ($k_{67}/(k_{67} + k_{68})$) increases with carbon number for C1−C3 compounds. This suggests that, under controlled pulse radiolysis conditions, the branching ratio of multisite reactions could be determined by HPLC analysis of the stable alkyl nitrates. With more information on this reaction pathway, this may provide a convenient probe for the formation of peroxyl radicals and assist in mechanistic studies.[209]

The above kinetic experiments will need to be complemented by quantitative determination of reaction byproducts under different conditions. Based upon our mechanism, we believe that there are additional stable products formed in the free radical-induced degradation of MTBE in solution, for example MMP-OH, which still needs to be identified and quantified. Techniques such as LC/MS are now readily available for this purpose. In addition, these techniques can be used to help establish the individual pathways of tetroxide decompositions. Again utilizing labeled compounds, both ^{13}C- and perhaps perfluorinated moieties that will eliminate specific pathways, the contributions for each individual tetroxide degradation pathway can be determined.[202,203]

As stated previously, degradation induced by hydrated electron reactions will also need to be elucidated, but in the absence of the alcohol typically used for kinetics measurements. It is possible that for very soluble organic compounds that the carbonate ion could be added to scavenge the hydroxyl radicals (where the pH of the solution is maintained at or around 9), as the resultant carbonate radical is a rather unreactive species. Unfortunately, the use of the carbonate ion will not work for those organic compounds that are marginally soluble in water and would be "salted out" in such solutions. Additional studies to identify noninterfering $^{\bullet}$OH scavengers may also have to be performed.

Concomitant with these experimental studies should be kinetic model development. Sensitivity analyses for individual reactions, or groups of reactions, can be performed, based upon the available library of experimental kinetic data and measured product distributions under different conditions. This will allow the most important reactions and mechanistic pathways to be identified, which will help focus and optimize future experimental efforts. These analyses will also help eliminate reactions in the model that are of minimal importance.

Once the most important reactions are identified, through both experiment and modeling, it will also be important to establish their temperature-dependence. At this time, there is no data available for any of the kinetics other than at room temperature, which may not correspond to real-world treatment conditions. Moreover, measurement of stable-product distributions at different temperatures may also provide insight into the important degradation mechanisms.

Finally, it seems apparent that, within available resources and time, the experimental determination of the necessary rate constants and destruction mechanisms for all of the compounds that are of environmental importance is a particularly daunting task. Therefore, we suggest that computational chemistry methods should be developed to assist in constructing robust kinetic models.[210] The two areas of particular interest are characterization of reactive intermediates to predict the energetic likelihood of various possible reaction pathways (e.g., what might be the relative likelihoods of different bond homolyses in a given radical anion) and prediction of rate constants for various uni- and bimolecular reactions taking place in solution. Further, we suggest that computational chemistry techniques should be developed to fully characterize low-energy destruction pathways and compute spectral signatures of likely key intermediates, as well as compute rate constants for as yet uncharacterized reactions. Each computational step would take advantage of synergy with experiment. Prediction of low-energy pathways and intermediate properties will be useful in designing experiments to measure the kinetics for specific steps, as opposed to phenomenological rate constants for potentially many steps. And, as experimental data become increasingly available for comparison with theoretical predictions, we will likely be able to refine the theory to improve its accuracy. Computation of rate constants will also help to prioritize which reactions should be experimentally measured next, because of their importance to the overall kinetic model. It will also help to build reasonably complete initial models for testing while experiment is refining a subset of the rate constants. In addition, when experimental rates become available, it should prove possible to refine the theory in such a way as to improve its accuracy without adding prohibitively to computational cost.

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8. References

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