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Evidence for HOOO Radicals in the Formation of Alkyl Hydrotrioxides (ROOOH) and Hydrogen Trioxide (HOOOH) in the Ozonation of C−H Bonds in Hydrocarbons[1]

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Abstract: Low-temperature ozonation of cumene (**1a**) in acetone, methyl acetate, and *tert*-butyl methyl ether at −70° C produced the corresponding hydrotrioxide, $C_6H_5C(CH_3)_2OOOH$ (**2a**), along with hydrogen trioxide, HOOOH. Ozonation of triphenylmethane (**1b**), however, produced only triphenylmethyl hydrotrioxide, $(C_6H_5)_3COOOH$ (**2b**). These observations, together with the previously reported experimental evidence, seem to support the "radical" mechanism for the first step of the ozonation of the C−H bonds in hydrocarbons, i.e., the formation of the caged radical pair ($R^{\bullet}\,{}^{\bullet}OOOH$), which allows both (a) collapse of the radical pair to ROOOH and (b) the abstraction of the hydrogen atom from alkyl radical $R^{\bullet}$ by $HOOO^{\bullet}$ to form HOOOH. The B3LYP/6-311++G(d,p) (ZPE) calculations revealed that HOOO radicals are considerably stabilized by forming intermolecularly hydrogen-bonded complexes with acetone (BE = 8.55 kcal/mol) and dimethyl ether (7.04 kcal/mol). This type of interaction appears to be crucial for the relatively fast reactions (and the formation of the polyoxides in relatively high yields) in these solvents, as compared to the ozonations run in nonbasic solvents. However, HOOO radicals appear to be not stable enough to abstract hydrogen atoms outside the solvent cage, as indicated by the absence of HOOOH among the products in the ozonolysis of triphenylmethane. The decomposition of alkyl hydrotrioxides **2a** and **2b** involves a homolytic cleavage of the RO−OOH bond with subsequent "in cage" reactions of the corresponding radicals, while the decomposition of HOOOH is most likely predominantly a "pericyclic" process involving one or more molecules of water acting as a bifunctional catalyst to produce water and singlet oxygen (Δ^1O_2).

Introduction

The RO_3H species (R = H, alkyl) are believed to be key intermediates in the natural and polluted atmosphere,[2] biological systems,[3] and low-temperature ozonation of various organic substrates.[4]

We have recently reported experimental and theoretical evidence for the "radical" mechanism of the ozonation of isopropyl alcohol and some benzylic alcohols and ethers, involving most likely HOOO radicals.[5] This species[6] was proposed to be formed in the first step of the reaction, that is the abstraction of the hydrogen atom from the R−H bond by ozone, resulting in the formation of the radical pair, $R^{\bullet}\,{}^{\bullet}OOOH$, at a sufficiently large separation after the transition state of the rate-determining step of the reaction thus allowing both the collapse of the radical pair to ROOOH and the abstraction of the hydrogen atom from the carbon radical to form hydrogen trioxide (HOOOH).[5]

In the present work we wish to report that HOOO radicals are most likely involved also in the ozonation of saturated hydrocarbons,[7] i.e., cumene[8] and triphenylmethane.[9] We found

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that in the low-temperature ozonation of cumene, contrary to a previous report,[8] besides the corresponding hydrotrioxide (ROOOH), hydrogen trioxide (HOOOH) is also formed, while triphenylmethyl hydrotrioxide was the only polyoxide detected in the ozonation of triphenylmethane. A considerable stabilization of the HOOO radical in the intermolecularly hydrogen-bonded complex with acetone was found by using unrestricted density functional calculations at the B3LYP/6-311++G(d,p) (ZPE) level.

Experimental Section

Instrumentation. Low-temperature ^1H, ^{13}C, and ^{17}O NMR spectra were recorded on a Bruker Avance 300 DPX (^1H NMR, 300.13 MHz; ^{13}C NMR, 75.48 MHz; ^{17}O NMR, 40.70 MHz) and on Varian Unity Inova-600 spectrometers (^1H NMR, 600.09 MHz; ^{17}O NMR, 81.37 MHz) with TMS (^1H and ^{13}C NMR) and $H_2{}^{17}O$ (^{17}O NMR) as internal standards. GC/MS was performed on a Hewlett-Packard 6890 chromatograph (HP-5MS column).

Materials. All solvents were the purest commercially available products and were (except of acetone-*d*$_6$) rigorously dried and distilled according to the literature methods. The purity was checked by GC/MS. Triphenylmethane (99+%) and 2,6-di-*tert*-butyl-4-methylphenol (BMP, gold label, Janssen) were used as received. Cumene (98%, Fluka) was distilled before use. Commercially available authentic samples of cumyl alcohol, acetophenone, triphenylmethanol, benzophenone, phenol, and phenyl benzoate (Aldrich) were checked by NMR and GS/MS and used as received.

Ozonation Procedure. Ozone−oxygen mixtures were produced by flowing oxygen through a Welsbach T-816 ozonator. Ozone−nitrogen mixtures were obtained as already reported. The concentration of ozone in the gas stream was measured according to the literature procedure. ^{17}O-enriched ozone was generated by flowing ^{17}O-enriched oxygen (58% $^{17}O_2$, ISOTEC) through a semimicro ozonator.[5]

Product Analysis. Decomposition products of alkyl hydrotrioxides **2a** and **2b** were determined by a combination of techniques.[5b] All products, except hydrogen peroxide, were determined by GC/MS, by using calibrated internal standards and known reference materials. All products were also collected and identified by NMR. Hydrogen peroxide was determined by ^1H NMR (and ^{17}O NMR) and by other analytical methods already described previously.[5b]

Kinetic Studies. Kinetics of the decomposition of the alkyl hydrotrioxides and HOOOH were performed by following the decay of the OOOH and CH_3 (for ROOOH) absorptions by ^1H NMR, using TMS as internal standard. Kinetic and activation parameters were obtained by standard procedures.[5]

Methods of Calculation. Ab initio density functional calculations (DFT) were performed by using the unrestricted B3LYP hybrid functional[10] as implemented in GAUSSIAN98[11] with the 6-311++G-(d,p) basis set to fully optimize the molecules under investigation. Frequency calculations were also performed at this level of theory. Zero-point energy (ZPE) corrections were used without scaling. DFT calculations with the B3LYP functional have been shown to be comparable to those of CCSD(T)[12] in cases with some multireference character (for example ozone),[13] and have also produced reliable results for hydrogen-bonded complexes.[14]

Results and Discussion

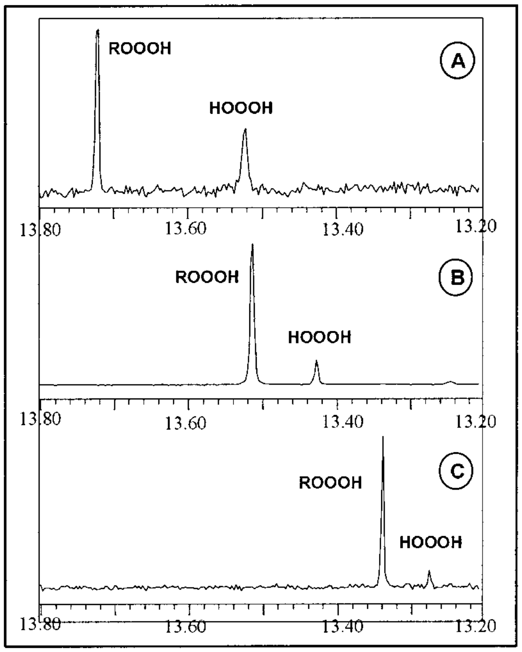

Figure 1. The concentration dependence of the ^1H NMR chemical shift of cumyl hydrotrioxide (**2a**) (**ROOOH**) and hydrogen trioxide (**HOOOH**) formed in the ozonation of (A) 0.10 and (B) 3.6 M solutions of cumene in acetone-*d*$_6$ at −40 °C. (C) ^1H NMR spectrum of polyoxides in 0.05 M solution obtained after diluting the ozonized 3.6 M solution of cumene (acetone-*d*$_6$, −40 °C).

NMR Spectra. Low-temperature ozonation of cumene (**1a**)-(−40 °C) with ozone−oxygen or ozone−nitrogen mixtures in acetone-*d*$_6$, methyl acetate, and *tert*-butyl methyl ether at concentrations (0.1−0.3M) lower than those originally studied by Pryor et al. (3.6M; cca 50 v/v in acetone-*d*$_6$)[8] produced the corresponding alkyl hydrotrioxide, $Ph(Me)_2COOOH$ (**2a**), characterized by the OOOH ^1H NMR absorption at $\delta = 13.10$ (δ $CH_3 = 1.66$) and ^{13}C NMR absorptions at $\delta = 25.0$ (CH_3) and 104.3 (C) downfield from TMS (−10 °C, acetone-*d*$_6$), in yields of 5−10%. Still another absorption at $\delta = 13.03$ was observed in the ^1H NMR spectra. This absorption was, on the basis of ^{17}O NMR spectra of the species, highly enriched with ^{17}O, assigned to hydrogen trioxide, HOOOH[5] (Figure 1). In addition, this absorption was identical with that of HOOOH, generated independently by low-temperature ozonation of hydrazobenzene in various solvents.[5]

The greatest yields of HOOOH, i.e., molar ratio **2a**/HOOOH of 1:0.20−0.35, were obtained when dilute solutions of cumene (**1a**, 0.05−0.3 M) were ozonized, while in the ozonation of more concentrated solutions of cumene (>3 M) this ratio was always less than 1:0.10.

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(14) See, for example: Aloisio, S.; Francisco, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9196 and references therein.

A concentration dependence study of ^{1}H NMR chemical shifts of alkyl hydrotrioxide **2a** and HOOOH revealed their strong dependence on the initial concentration of cumene (**1a**). Namely, chemical shifts of both polyoxides obtained during the ozonation of 0.1 M solutions of **1a** were different from chemical shifts of these species generated by ozonizing more concentrated solutions of cumene (3.6 M), with subsequent dilution to 0.05 M solution. These phenomena most probably reflect the difference in both the extent of the intermolecular association of the polyoxides under the investigation, i.e., intermolecularly hydrogen-bonded dimers and/or oligomers, and their solvation.

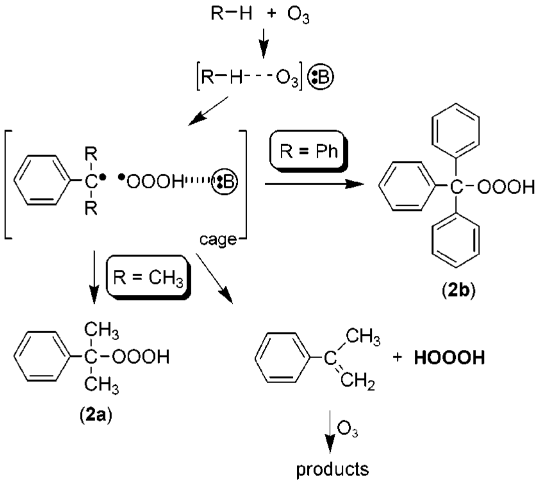
Ozonation of triphenylmethane (**1b**) (0.1−0.2 M) in various solvents at −60 °C, on the other hand, produced only the corresponding triphenylmethyl hydrotrioxide (**2b**) in yields of 30−40%. The hydrotrioxide was characterized by the OOOH ^{1}H NMR absorption at $\delta = 13.38$ and ^{13}C NMR absorption at $\delta = 101.7$ (C), downfield from TMS (−50 °C, acetone-d_6).

All attempts to obtain ^{17}O NMR spectra of highly ^{17}O enriched samples of alkyl hydrotrioxides **2a** and **2b** failed, most likely because of the line broadening caused by the internal asymmetry of the molecules.[15] However, the presence of HOOOH in the ozonized solutions of cumene was confirmed by ^{17}O NMR spectroscopy ($HO_1O_2O_3H$: $\delta = 304$ (O_1 and O_3, $\nu_{1/2} = 490$ Hz), 420 (O_2, $\nu_{1/2} = 490$ Hz); acetone-d_6, −10 °C, $H_2$17O).[5,16]

HOOO Radicals in the Formation of ROOOH and HOOOH. We have already reported theoretical and experimental evidence for the "radical" mechanism of the ozonation of isopropyl alcohol and some benzylic alcohols and ethers.[5] The formation of HOOOH in the ozonation of cumene and its complete absence in the case of triphenylmethane seem to rule out a concerted 1,3-dipolar insertion mechanism, believed previously to be operative in these reactions.[4a] Still another mechanistic proposal involving hydride ion transfer to ozone to form the ion pair, $R^+ \, ^-OOOH$,[17] also appears less likely. Namely, our recent theoretical investigation of the HOOO anion at the CCSD(T)/6-311++G(d,p) level of theory revealed an extraordinarily long HO−OO bond in this species (1.88 Å), indicating a predominantly noncovalent (or a very weak covalent) interaction between HO anion and singlet oxygen.[5,18] Therefore, it appears unlikely that such an assembly could survive as a discrete molecular entity[19] in organic solvents long enough to regenerate HOOOH after protonation.

The above experimental evidence, together with the previously reported retention of configuration in the ozonation of saturated hydrocarbons,[7a] as well as the log *A* values (7−8) for these reactions,[20] supports the involvement of tight radical pairs, i.e., $[R^\bullet\,^\bullet OOOH]$, in the ozonation of C−H bonds, as suggested previously by Hamilton,[7a] Whiting,[7b] and Pryor,[20] allowing both the collapse of the pair to the ROOOH and the abstraction of the hydrogen atom from the alkyl radical ($R^\bullet$) by HOOO radical to form HOOOH (Scheme 1).[21,22] Namely, it is obvious that $HOOO^\bullet$ cannot abstract the hydrogen atom from the triphenylmethyl radical inside the solvent cage. It is especially noteworthy to point out, however, that the HOOO radical is not stable enough to abstract the hydrogen atom from triphenylmethane outside the solvent cage under the conditions investigated.

Scheme 1



We have long been impressed by the ease with which ozonations of hydrocarbons (and other saturated organic substrates, i.e., ethers,[23] acetals,[23b] and alcohols[5] as well) proceed in organic oxygen bases as solvents. We now wish to report the results of B3LYP/6-311++G(d,p)(ZPE) theoretical studies of the interaction between the HOOO radical and two representative oxygen bases, i.e., acetone and dimethyl ether, which appear to explain these phenomena. The fully optimized structures of the complexes with minimum energies were confirmed to be stable minima by vibrational frequency analysis. Only the global minima energy structures were reported here (Figure 2).

As seen from Table 1, HOOO radical forms relatively strongly bonded complexes with oxygen bases. For comparison, the complex of $HOOO^\bullet$ with water, recently reported by Aloisio and Francisco,[24,25] has also been investigated. The strength of the intermolecular hydrogen bond (the energy difference between the complex and the sum of energies of both components of the complex) decreases in the following order: acetone (AC)-$HOOO^\bullet$ (8.55 kcal/mol) > dimethyl ether (DME)-$HOOO^\bullet$ (7.04 kcal/mol) > HOH-$HOOO^\bullet$ (5.91 kcal/mol).[26] A considerable structural perturbation of the hydrotrioxyl radical[27] was

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[16] Our preliminary results of the ozonation of some other hydrocarbons, for example substituted cumenes, ethylbenzenes, tetralin, and norcaran, showed that besides the corresponding hydrotrioxides (ROOOH), hydrogen trioxide (HOOOH) was formed in these reactions too.

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[18] Koller, J.; Plesničar, B. *J. Am. Chem. Soc.* **1996**, *118*, 2470.

[19] A detailed high-level theoretical investigation on the structure of this unusual molecule is currently underway.

[20] Giamalva, D. H.; Church, D. F.; Pryor, W. A. *J. Org. Chem.* **1988**, *53*, 3429.

[21] We are currently investigating (DFT-IRC) some other possible mechanistic pathways for the reactions of R and OOOH radicals in the cage (ozonolysis of isopropyl alcohol,[5] and some other saturated substrates).

[22] A recent theoretical study on the ozonation of hydrocarbons by using the semiempirical AM1 method supported the involvement of a biradical transition state leading to alkyl and hydrotrioxyl radicals. (Timerghazin, Q. K.; Khursan, S. L.; Shereshovets, V. V. *J. Mol. Struct. (Theochem)* **1999**, *489*, 87.)

[23] (a) Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. Plesničar, B.; Kovac, F.; Schara, M. *J. Am. Chem. Soc.* **1988**, *110*, 214. (b) Kovac, F.; Plesničar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677.

[24] Aloisio, S.; Francisco, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8592.

[25] For some theoretical studies on the HOOO radical, see: (a) Blint, R. J.; Newton, M. D. *J. Chem Phys.* **1973**, *59*, 6220. (b) Mathisen, K. B.; Siegbahn, P. E. M. *Chem. Phys.* **1984**, *90*, 225. (c) Dupuis, M.; Fitzgerald, G.; Hammond, B.; Lester, W. A.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 2691. (d) Vincent, M. A.; Hillier, I. H. *J. Phys. Chem.* **1995**, *99*, 3109. (e) Jungkamp, T. P. W.; Seinfeld, J. H. *Chem. Phys. Lett.* **1996**, *257*, 15. (f) Yu, H. G.; Varandas, A. J. C. *Chem. Phys. Lett.* **2001**, *334*, 173.

[26] Binding energies of the $HOOO^\bullet$ -HOH complex: B3LYP/6-311++G(2df,-2p)(ZPE) = 5.0 kcal/mol; CCSD(T)/6-311++G(2df, 2p)//B3LYP/6-311++G(2df,2p) = 6.5 kcal/mol.[24]

Table 1. Corrected and Uncorrected Equilibrium B3LYP/6-311++G(d,p) Energies (au) for the Complexes of the HOOO Radical with Various Oxygen Bases in the Gas Phase and in Oxygen Bases as Solvents

species	$(CH_3)_2CO$-HOOO$^•$	$(CH_3)_2O$-HOOO$^•$	H_2O-HOOO$^•$
solvent	−193.215323 (−193.132438)[a]	−155.077114 (−154.997881)	−76.458531 (−76.437248)
HOOO$^•$ (trans)	−226.134543 (−226.117301)	−226.134543 (−226.117301)	−226.133210[b] (−226.115907)[b]
complex	−419.366028 (−419.263361)	−381.225415 (−381.126397)	−302.604785 (−302.562579)
Δ*E*(BE), kcal/mol	10.14 (8.55)	8.63 (7.04)	8.26 (5.91)
BE[solvent effect], kcal/mol	[7.77][c]	[6.47]	[1.73][b]
Δ*G*, kcal/mol	[−6.64]	[−5.11]	[−1.40][b]

[a] Values in parentheses refer to the ZPE corrected energies. [b] HOOO$^•$ (cis). [c] Values in square brackets refer to the solvent corrected binding energies and Δ*G* values (see Table S1 in the Supporting Information).

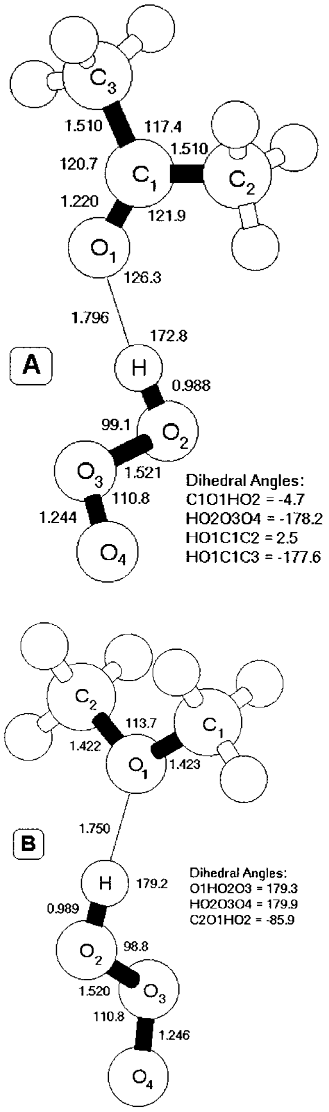

Figure 2. The B3LYP/6-311++G(d,p) optimized structures of (A) acetone (AC)-HOOO$^•$ and (B) dimethyl ether (DME)-HOOO$^•$ complexes. (Acetone (AC): C═O, 1.212 Å; C−C, 1.521 Å; C−O−C, 119.2°. Dimethyl ether (DME): C−O, 1.415 Å; C−O−C, 112.7°. HOOO$^•$ (trans): H−O_1, 0.972 Å; O_1−O_2, 1.565 Å; O_2−O_3, 1.229 Å; H−O_1−O_2, 98.4°; O_1−O_2−O_3, 110.5°; H−O_1−O_2−O_3, 180°. HOOO$^•$ (cis): H−O_1, 0.975 Å; O_1−O_2, 1.519 Å; O_2−O_3, 1.248 Å; H−O_1−O_2, 100.3°; O_1−O_2−O_3, 113.0°; H−O_1−O_2−O_3, 0°).

observed after complexation. For example, the H−O bond is lengthened by 0.017 Å, while the HO−OO and HOO−O bonds are shortened by 0.045 and 0.017 Å, respectively, in the complexes with acetone. The most shifted mode, i.e., the O−H stretch of the HOOO part of the complex, was found to be red-shifted in the following order: DME-HOOO$^•$ (328 cm^{-1}) > AC-HOOO$^•$ (320 cm^{-1}) > HOH-HOOO$^•$ (310 cm^{-1}), thus, indicating relatively strong hydrogen bonds in these complexes (Table 2, and Table S1 in the Supporting Information).

Table 2. B3LYP/6-311++G(d,p) Calculated Frequencies and IR Intensities of the Complexes of HOOO$^•$ with Acetone (AC) and Dimethyl Ether (DME)

species	freq in cm^{-1} (IR intensities in km/mol)
AC-HOOO$^•$	3423 (1246), 3146 (6), 3141 (4), 3091 (10), 3084 (2), 3034 (4), 3027 (0), 1759 (311), 1488 (25), 1473 (25), 1462 (11), 1461 (4), 1449 (26), 1395 (57), 1391 (32), 1277 (164), 1251 (77), 119 (4), 1089 (0), 906 (6), 888 (0), 795 (0), 689 (92), 671 (160), 552 (22), 496 (37), 491 (22), 388 (6), 176 (16), 130 (1), 95 (5), 79 (0), 60 (1), 40 (3), 34 (0), 12 (2)
HOOO$^•$ (trans)	3743 (76), 1381 (40), 1225 (137), 626 (49), 430 (87), 164 (129)
DME-HOOO$^•$	3415 (1175), 3130 (14), 3129 (16), 3052 (0), 3048 (89), 2999 (87), 2992 (44), 1513 (2), 1496 (15), 1492 (19), 1487 (2), 1482 (0), 1460 (1), 1439 (8), 1272 (13), 1271 (125), 1187 (9), 1185 (82), 1157 (0), 1107 (73), 923 (81), 769 (67), 676 (101), 500 (42), 417 (16), 238 (6), 194 (0), 168 (9), 80 (3), 76 (0), 52 (2), 26.7 (1), 26.6 (2)

Since the strength of the interaction was obtained as the energy difference between species with very different dipole moments, the solvent effect has also been studied by using the polarized continuum model, developed by Tomasi and co-workers.[28] Although the calculated binding energies were somewhat lower in acetone (BE = 7.77 kcal/mol, Δ*G* = −6.64 kcal/mol) and diethyl ether (BE = 6.47 kcal/mol) as compared to the values in the gas phase, the trend of the strengths of the hydrogen bonds remained the same (see Table 1, and Table S1 in the Supporting Information). A dramatic lowering of the binding energy in water as a solvent (BE = 1.73 kcal/mol), together with a much less favorable Δ*G* (−1.40 kcal/mol), indicates that the stabilization of the HOH-HOOO$^•$ complex is not particularly favorable in the liquid phase.

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(27) For comparison, our CCSD(T)/6-311++G(d,p) calculations showed that the trans form of HOOO$^•$ was also slightly more stable (Δ*E* = 0.25 kcal/mol) than the cis isomer: (trans), H−O_1= 0.970, O_1−O_2 = 1.535, O_2−O_3 = 1, 244, H−O_1−O_2 = 98.1°, O_1−O_2−O_3 = 109.6°, H−O−O−O = 180°, *E* = −225.63351 au; (cis), H−O_1 = 0.974, O_1−O_2 = 1.497, O_2−O_3 = 1.261, H−O_1−O_2 = 99.2°, O_1−O_2−O_3 = 111.8°, H−O−O−O = −9.9°, *E* = −225.63311 au.

(28) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (b) See also: Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161.

Table 3. Kinetic and Activation Parameters for the Decomposition of Cumyl Hydrotrioxide (**2a**), Hydrogen Trioxide (**HOOOH**) Formed in the Ozonation of Cumene (**1a**), and Triphenylmethyl Hydrotrioxide (**2b**) in Various Solvents[a]

		ROOOH					HOOOH			
			$10^4k(T)$, s^{-1}							
solvent	T, °C	δ_{OOOH}, ppm	OOOH[b]	CH_3[c]	E_a, kcal mol^{-1}	log A	δ_{OOOH}, ppm	$10^4k(T)$, s^{-1}	E_a, kcal mol^{-1}	log A
2a acetone-d_6	−10	13.10	0.95 (0.71)[d]	0.86 (0.66)[d]	22.9[b] (24.4)[b,d]	14.9[b] (16.6)[b,d]	13.03	1.09 (0.67)[d]		
	5	12.95	10.4 (10.0)[d]	9.32 (9.16)[d]	23.3[c] (25.7)[c,d]	15.4[c] (17.1)[c,d]	12.88	6.06 (4.71)[d]	15.2 (19.0)[d]	9.5 (11.6)[d]
methyl acetate	−10	12.59	0.84 (0.82)[d]	0.76 (1.01)[d]	19.9[b] (23.1)[b,d]	12.6[b] (15.1)[b,d]	12.52	1.65 (1.46)[d]		
	5	12.44	8.35 (8.11)[d]	7.76 (6.78)[d]	21.6[c] (24.1)[c,d]	13.8[c] (15.8)[c,d]	12.39	9.85 (6.61)[d]	16.7 (17.2)[d]	10.2 (10.3)[d]
tert-butyl methyl ether	−10	12.84	0.61 (0.52)[d]		23.6[b] (24.1)[b,d]	15.4[b] (15.7)[b,d]	12.63	0.69 (0.65)[d]	17.1 (18.4)[d]	10.1 (11.1)[d]
	5	12.75	7.24 (6.05)[d]				12.53	5.38 (4.12)[d]		
2b acetone-d_6	−40	13.29[e]	1.05 (1.01)[d]		23.9 (24.8)[b,d]	18.4 (19.3)[b,d]				
	−30	13.19	7.99 (8.31)[d]							
methyl acetate	−40	12.83	0.63 (0.63)[d]		24.1 (23.2)[b,d]	18.4 (17.6)[b,d]				
	−30	12.67	5.22 (5.75)[d]							

[a] c(ROOOH) = 0.001−0.01 M. Molar ratio **2a**/HOOOH approximately 1:0.15−0.25. Standard deviations ±10%. Temperature range studied, −45 to +10 °C. [b] By following the decay of the ROOOH absorption. [c] By following the decay of the CH_3 absorption of the hydrotrioxide **2a**. [d] Runs in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BMP) (molar ratio, BMP/hydrotrioxide = 3:1). [e] Triphenylmethyl hydroperoxide: ^{1}H NMR δ_{OOH} = 11.10 ppm; ^{13}C NMR δ_{COOH} = 93.2 ppm (acetone-d_6, −40 °C, TMS). Prepared by following the procedure in: Hägel, E.; Kropf, H.; Munke, S. In *Organische Peroxo-Verbindungen;* Kropf, H., Ed.; Houben-Weyl Methoden der Organischen Chemie, Vol. E13; George Thieme Verlag: Stuttgart and New York, 1988; pp 140−141.

Product and Kinetic Studies of the Decomposition of ROOOH and HOOOH. An investigation of the products in the decomposition mixture, after warming the ozonized solutions of **1a** in acetone-d_6 (0.1−0.5M), by GC/MS and NMR spectroscopy indicated the presence of cumyl alcohol (81 ± 5%), acetophenone (19 ± 3%), hydrogen peroxide, and oxygen (Σ^3O_2/Δ^1O_2). Product analysis of the decomposition mixture after warming the ozonized solutions of **1b** in acetone-d_6 (0.1−0.2 M) revealed benzophenone (84 ± 5%), triphenylmethanol (4 ± 2%), phenyl benzoate (7 ± 2%), phenol (5 ± 2%), and oxygen (Σ^3O_2/Δ^1O_2). These data are similar to those already reported previously for the ozonolysis of triphenylmethane.[9]

The kinetics of decomposition of alkyl hydrotrioxides **2a** and **2b** were measured by following the decay of the OOOH and CH_3 absorptions, and in all cases they were found to obey cleanly first-order kinetics over at least 3−4 half-lives in all solvents investigated. Kinetic and activation parameters for the decomposition of **2a** and **2b** are typical of homolytic processes involving the cleavage of the RO−OOH bond as the first decomposition step (E_a = 23.0 ± 2.0 kcal/mol, log A = 16.0 ± 2.0) (Table 3 and Figure 3; for complete kinetic data see Table S2 in the Supporting Information.) The addition of radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (BMP), has a relatively small effect on the rates and activation parameters for the decomposition of **2a** and **2b**, indicating predominantly the "in cage" reaction pathways (Scheme 2a). This is in contrast with observations made by Pryor et al.,[8] working with more highly concentrated solutions of cumene in acetone-d_6 (3.6 M), that alkoxyl radicals participate significantly in the induced decomposition of cumyl hydrotioxide. However, the activation parameters for the decomposition of **2a** are in excellent agreement with those reported by these workers in the presence of the inhibitor. *It thus appears that higher initial concentrations of cumene lead to a lower polarity and/or smaller hydrogen bond-acceptor capability of the medium, which significantly affects the outcome of the reaction.*

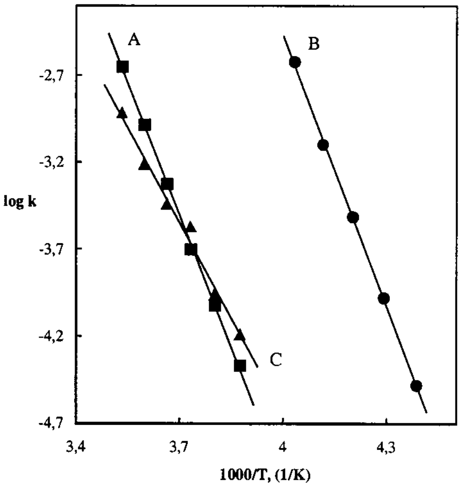

Figure 3. The Arrhenius plot for the decomposition of (A) cumyl hydrotrioxide (**2a**), (B) hydrotrioxide of triphenylmethane (**2b**), and (C) HOOOH formed in the low-temperature ozonation of cumene in acetone-d_6.

Kinetic and activation parameters for the decomposition of HOOOH, generated in the ozonation of hydrocarbons (E_a = 16.5 ± 1.5 kcal/mol, log A = 10 ± 0.5), are very similar to those already reported previously for the decomposition of samples of HOOOH, prepared independently by other methods.[5,29] They are in accord with the involvement of water (one or more molecules) as a bifunctional catalyst in a "pericyclic" decomposition pathway for this simplest of polyoxides to produce water and singlet oxygen (Δ^1O_2) (Scheme 2b). However, as indicated by the not completely negligible effect of the

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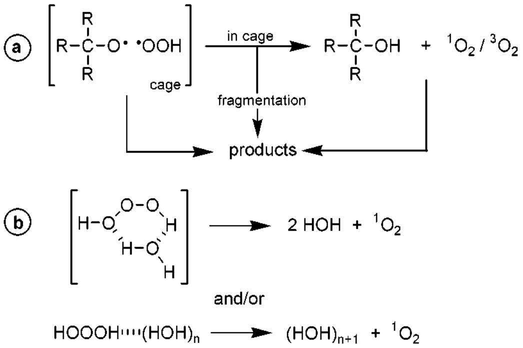
(29) Plesničar, B.; Cerkovnik, J.; Koller, J.; Kovac, F. *J. Am. Chem. Soc.* **1991**, *113*, 4946. Cerkovnik, J.; Plesničar, B. *J. Am. Chem. Soc.* **1993**, *115*, 12169.

Scheme 2



inhibitor, some radical contributions to the decomposition pathways of HOOOH cannot be completely ruled out under conditions investigated.

Conclusions

We have demonstrated that low-temperature ozonation of C−H bonds in saturated hydrocarbons with abstractable β-hydrogen atoms produced the corresponding alkyl hydrotrioxides (ROOOH) and hydrogen trioxide (HOOOH). The proposed "radical" mechanism for the first step of ozonation most probably involves radical pairs in a rather tight solvent cage, i.e., $R^{\bullet}\,{}^{\bullet}OOOH$, allowing both collapse of the pair to ROOOH and the abstraction of the hydrogen atom from alkyl radical ($R^{\bullet}$) by HOOO radical to form HOOOH. Hydrotrioxyl radical is considerably stabilized by forming intermolecularly hydrogen-bonded complexes with acetone and dimethyl ether as model oxygen bases, as determined by B3LYP/6-311++G(d,p) calculations. The formation of these complexes in a rather tight solvent cage seems to explain the previously observed retention of configuration, as well as a rather small polar solvent effect. Namely, we believe that relatively fast ozonations of hydrocarbons (as well as ethers, alcohols, and acetals) in oxygen bases as solvents are not predominantly due to their polarity, but are rather caused by their hydrogen-bond acceptor ability (basicity) to form complexes with HOOO radicals. The absence of HOOOH in the reaction mixture after the ozonation of triphenylmethane indicates that HOOO radical is most likely not stable enough to abstract the hydrogen atom outside the solvent cage. Kinetic and activation parameters for the decomposition of alkyl hydrotrioxides **2a** and **2b** are compatible with a homolytic cleavage of the RO−OOH bond as the first step of the decomposition with subsequent "in cage" reactions of radicals, while a "pericyclic" mechanism, involving the participation of one or more molecules of water acting as a bifunctional catalyst, is most likely operative in the decomposition of HOOOH.

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Supporting Information Available: Table S1, containing the solvent-corrected B3LYP/6-311++G(d,p) energies, free energies, and binding energies for the complexes of HOOO radical, Table S2, containing a complete set of kinetic and activation data, and Figure S1, containing the B3LYP/6-311++G(d,p) optimized structure for the HOH−HOOO$^{\bullet}$ complex (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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