

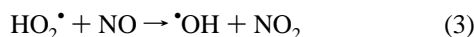
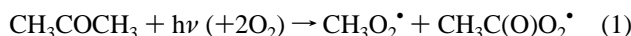
Tropopause Chemistry Revisited: HO₂[•]-Initiated Oxidation as an Efficient Acetone Sink

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Acetone has attracted much attention lately as a key species in the chemistry of the cold and dry Upper Troposphere and Lower Stratosphere (UTLS) as a major source of [•]OH radicals, through its fast photolysis and subsequent reactions with O₂ and NO:¹



Thus, acetone largely controls ozone production in the UTLS by the chain reaction of the resulting [•]OH radicals with (mainly) CO



followed by reaction 3 and fast subsequent NO₂ photolysis



The global source strength of acetone is currently estimated at 95 Tg yr⁻¹, mainly from terrestrial vegetation, ocean emissions, and, in the extratropical Northern Hemisphere, from the oxidation of isoalkanes.² Measured acetone mixing ratios in the UT range from 200 to 2200 ppt and in the LS from 100 to 200 ppt.³ Acetone removal in the UTLS is thought to occur for about 70% of the acetone content by photolysis (1) and for 30% by reaction with [•]OH,^{4,5} which was shown to proceed dominantly through H-abstraction.⁶

Recent flow-reactor studies found *net* removal of HO₂[•] by acetone and several other ketones to be negligibly slow, *k*_{net}(298 K) < 8 × 10⁻¹⁶ cm³ s⁻¹, and relegated such reactions as of no importance in the atmosphere.⁵

In this paper, we present a state-of-the-art quantum chemical (QC) and statistical-rate investigation of the reaction of HO₂[•] with acetone and demonstrate that it is an efficient acetone sink at the low temperatures of the tropopause, *T* ≤ 220 K. All QC calculations were performed using the GAUSSIAN03 program.⁷ The stationary points on the potential energy surface (PES) were characterized at three high levels of theory: a nearly-converged¹² G2M⁸ variant, CBS-QB3,⁹ and G3.¹⁰ The G2M energies, comprising zero-point energies (ZPEs), are defined here as *E*[G2M//DFT] = *E*[CCSD-(T)/6-311G(d,p)//DFT] + {*E*[MP2/6-311++G(3df,3pd)//DFT] - *E*[MP2/6-311G(d,p)//DFT]} + ZPE(DFT), where DFT stands for B3LYP/cc-pVTZ. Rate coefficients for forward and reverse reactions were calculated using multiconformer transition state theory (MC-TST)¹¹ based on the G2M data. Our theoretical methodologies are amply validated¹² by their reproducing the experimental forward and reverse rate coefficients and the equilibrium constant of both the analogous HO₂[•] reactions with CH₂O¹³ and CH₃CHO¹⁴ (*T* ≈ 300 K) within the experimental error of a factor of 2. This implies a G2M accuracy of ≤ 2 kJ/mol for all stationary points involved.

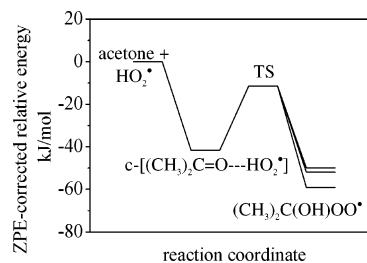
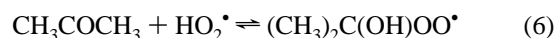


Figure 1. Potential energy profile of the (CH₃)₂CO + HO₂[•] ⇌ (CH₃)₂C(OH)OO[•] reaction at the G2M//B3LYP/cc-pVTZ level.

Figure 1 depicts the PES of the reaction



at the G2M level. Similar to HO₂[•] + CH₂O¹⁵ and HO₂[•] + CH₃CHO,¹² reaction 6 proceeds through a cyclic H-bonded pre-reaction complex, while the critical transition state (TS) to the products involves concerted addition of the terminal O of HO₂[•] to the carbonyl C and H-transfer from HO₂[•] to the carbonyl O.^{15a} A variational treatment¹² shows that the precomplex redissociates much more rapidly than it overcomes the barrier of the tight TS to yield the products such that the overall rate constant *k*₆ is essentially determined by the relative energies and partition functions of the TS and the initial reactants only.¹²

Three enantiomer pairs of (CH₃)₂C(OH)OO[•] conformers and one enantiomer pair of the rate-determining TS were identified and characterized. Table 1 demonstrates the excellent agreement of the relative energies at the different levels of theory.¹²

The two lowest-frequency vibrational modes of acetone were duly treated as hindered internal rotations (see Supporting Information). The MC-TST-calculated *k*₆(*T*) for *T* = 200–600 K can be expressed as 5.1 × 10⁻¹⁵ cm³ s⁻¹ × exp(11.1 kJ mol⁻¹/RT). The *k*₆(300 K) result of 4.4 × 10⁻¹³ cm³ s⁻¹ is somewhat higher than the rate coefficients of the analogous HO₂[•] reactions with CH₂O and CH₃CHO,^{12–14} showing that HO₂[•] reacts with ketones at least as fast as with aldehydes, contrary to currently held views.⁵ However, α-hydroxy-alkylperoxy radicals formed from ketones are found to be 5 kJ/mol less stable than those from the aldehydes,¹² and our MC-TST results show that (CH₃)₂C(OH)OO[•] redissociation (−6) is very rapid, e.g., *k*_{−6}(300 K) = 2.3 × 10⁴ s⁻¹, i.e., 1 or 2 orders of magnitude faster than the analogous reverses for the aldehydes.^{12–14} In the atmosphere, this rapid redissociation will result in an equilibrium of reactions 6 and −6. Therefore, the equilibrium constant *K*₆ ≡ [(CH₃)₂C(OH)OO[•]]/{[(CH₃)₂C=O] × [HO₂[•]]} is the crucial quantity here. It is determined by the relative energy (+ZPE) of the lowest-energy product conformer, for which the three levels of theory agree within 0.3 kJ/mol, and by the (*T*-dependent) product/reactants partition function ratio. The G2M-based calculated *K*₆(*T*) can be fitted by *K*₆ = 7.8 × 10⁻²⁸ exp(59.7 kJ mol⁻¹/RT) cm³ (200–600 K). Around 300 K, the equilibrium is shifted far to the left, *K*₆(300 K) = 1.9 × 10⁻¹⁷ cm³, such that reaction 6 is of no conse-

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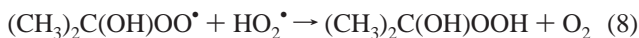
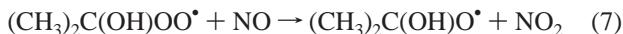
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Table 1. Relative Energies (Including ZPE), in kJ/mol, of Stationary Points on the Acetone + HO₂^{*} PES at Various Levels of Theory

species	G3	CBS-QB3	G2M ^b
(CH ₃) ₂ C=O + HO ₂ [*]	0.0	0.0	0.0
<i>c</i> -[(CH ₃) ₂ C=O...HO ₂ [*]]	-41.2	-39.9	-41.6
TS	-10.7	-10.7	-11.4
(CH ₃) ₂ C(OH)OO [*] _a	-58.5	-58.8	-59.1
(CH ₃) ₂ C(OH)OO [*] _b	-52.2	-51.6	-51.9
(CH ₃) ₂ C(OH)OO [*] _c	-49.7	-49.3	-49.9

^a a, b, and c denote the different (CH₃)₂C(OH)OO^{*} conformers. ^b Frequencies for CH₃-group torsions in acetone corrected (see Supporting Information).

quence and should escape experimental observation, in full accord with ref 5. However, at $T \leq 210$ K, as frequently found near the tropopause, k_{-6} drops very sharply such that the (CH₃)₂C(OH)OO^{*} equilibrium concentration becomes high, entailing fast acetone removal via the subsequent reactions:



The effective acetone removal rate through (CH₃)₂C(OH)OO^{*} can be expressed by $k_{\text{eff}} = K_6 \times [\text{HO}_2^*] \times \{k_7[\text{NO}] + k_8[\text{HO}_2^*]\}$. The rate coefficient k_7 (200 K) for a whole series of peroxy radicals is known to be $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.¹⁶ From known data for similar RO₂^{*} + HO₂^{*} reactions,¹⁶ one roughly estimates k_8 (200 K) $\approx 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, within a factor of 3.

Typical concentrations in the tropopause at temperate latitudes (altitude 10 km) are $[\text{HO}_2^*] \approx 2.5 \times 10^7$, $[\text{OH}] \approx 6 \times 10^5$, and $[\text{NO}] \approx 4 \times 10^8 \text{ cm}^{-3}$.¹⁷ At 210 K, we thus expect an HO₂^{*}-initiated acetone removal rate $k_{\text{eff}} \approx 8 \times 10^{-8} \text{ s}^{-1}$, with the bulk due to the (CH₃)₂C(OH)OO^{*} + NO reaction. This nearly equals the $9 \times 10^{-8} \text{ s}^{-1}$ rate of acetone removal by ^{*}OH in the given conditions ($k = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at $\approx 200 \text{ K}$ ⁴). At 200 and 190 K, we predict even higher HO₂^{*}-initiated acetone loss rates of $k_{\text{eff}} \approx 6 \times 10^{-7}$ and $5 \times 10^{-6} \text{ s}^{-1}$, respectively, the latter besting the $4 \times 10^{-7} \text{ s}^{-1}$ acetone photolysis¹⁸ rate by an order of magnitude.

Thus, even allowing for a factor of 3 error on the calculated rates, the newly proposed mechanism is shown to be an efficient acetone sink at $T \leq 210$ K. It may also be an important source of acetic acid in the UTLS where CH₃COOH is found in mixing ratios up to 1 ppb.¹⁹ The origins of acetic acid in the UTLS are still far from known.²⁰ Addition of ^{*}OH to acetone as a source of acetic acid⁴ was shown to be entirely negligible.⁶ Yet, the UTLS measurement of Arnold et al. at $\sim 50^\circ \text{ N}$, above Germany, not only reveals a close correlation between acetic acid and acetone but also shows the acetic acid mixing ratio to maximize around 9 km altitude,²¹ i.e., close to the altitude where the efficiency of our HO₂^{*}-initiated acetone oxidation path is expected to be highest. Our mechanism readily rationalizes these observations: the exclusive fate of the (CH₃)₂C(OH)-O^{*} oxy radical from reaction 7 is decomposition into CH₃COOH plus CH₃^{*}, which faces a barrier of only $\sim 32 \text{ kJ mol}^{-1}$ ⁶ and hence even at temperatures of 200 K should proceed at a rate $\geq 10^5 \text{ s}^{-1}$.

Our data¹² on the analogous HO₂^{*}-initiated oxidation of formaldehyde¹³ give k_{eff} values at 210–190 K in the 10^{-5} to 10^{-4} s^{-1} range, approaching the CH₂O photolysis rate; thus, the reaction of the resulting CH₂(OH)O^{*} radical with O₂ may be the principal source of formic acid in the tropopause. Similar HO₂^{*}-initiated degradation routes can also be invoked for ring-strained cyclic ketones such as cyclohexanone and nopinone (major oxidation product of β -pinene). Preliminary results¹² indicate that the ring-strain relaxation following the HO₂^{*} reaction to form the unstrained α -hydroxy-cyclohexylperoxy radical shifts the equilibrium toward the latter to such an extent that it more than offsets the faster reactions of these cyclic ketones with ^{*}OH.

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Supporting Information Available: Geometries, energies, ZPE, rotational constants, vibration frequencies, and hindered-internal-rotation data of discussed structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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