

Role of Quantum Chemistry in Atmospheric Chemical Mechanism Development

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Theoretical

Quantum Chemical Calculations

DFT, Ab initio (MP2, CCSD(T), Multiconfiguration CASSCF, etc.

Kinetic Calculations

Transition Station Theory (TST) or Canonical Variational Transition State Theory (cvTST)

RRKM/Master Equation Formalism

$$\frac{dn_i}{dt} = Rf_i - \omega n_i + \sum_j P_{ij} n_j - \sum_r k_{ri} n_i$$

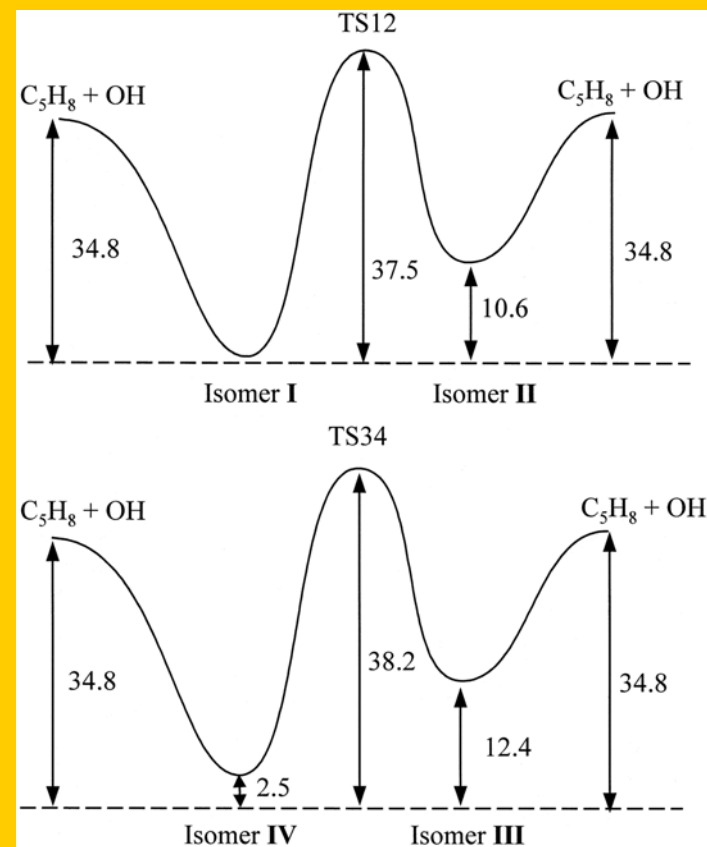
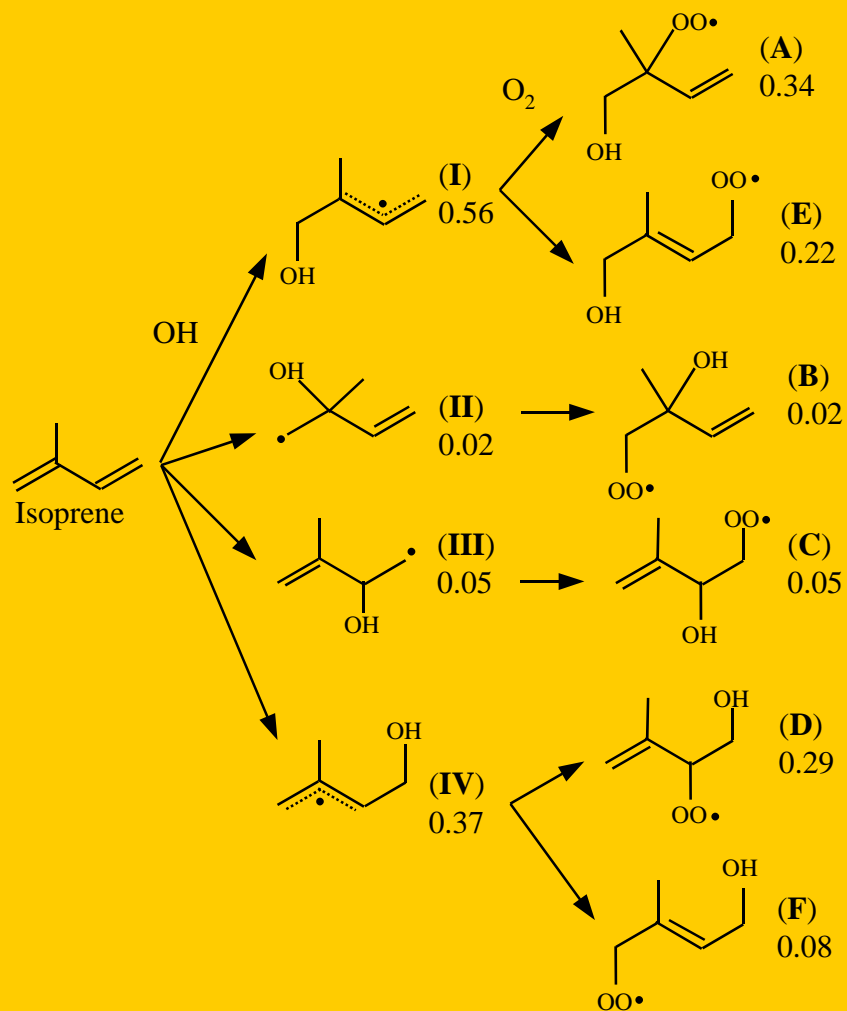
Separate Statistical Ensemble (SSE) Theory

$$P_{RO_i}^{E_{tot}}(E_{RO}) = \frac{N_{RO_i}(E_{RO}) \int_0^{E_{tot}-E_{RO}} [N_{NO_2}(E_{NO_2}) N_{rel.mot.}(E_{tot}-E_{RO}-E_{NO_2})] dE_{NO_2}}{\int_0^{E_{tot}} \left\{ \sum_i N_{RO_i}(E_{RO}) \right\} \int_0^{E_{tot}-E_{RO}} [N_{NO_2}(E_{NO_2}) N_{rel.mot.}(E_{tot}-E_{RO}-E_{NO_2})] dE_{NO_2} } dE_{RO}$$

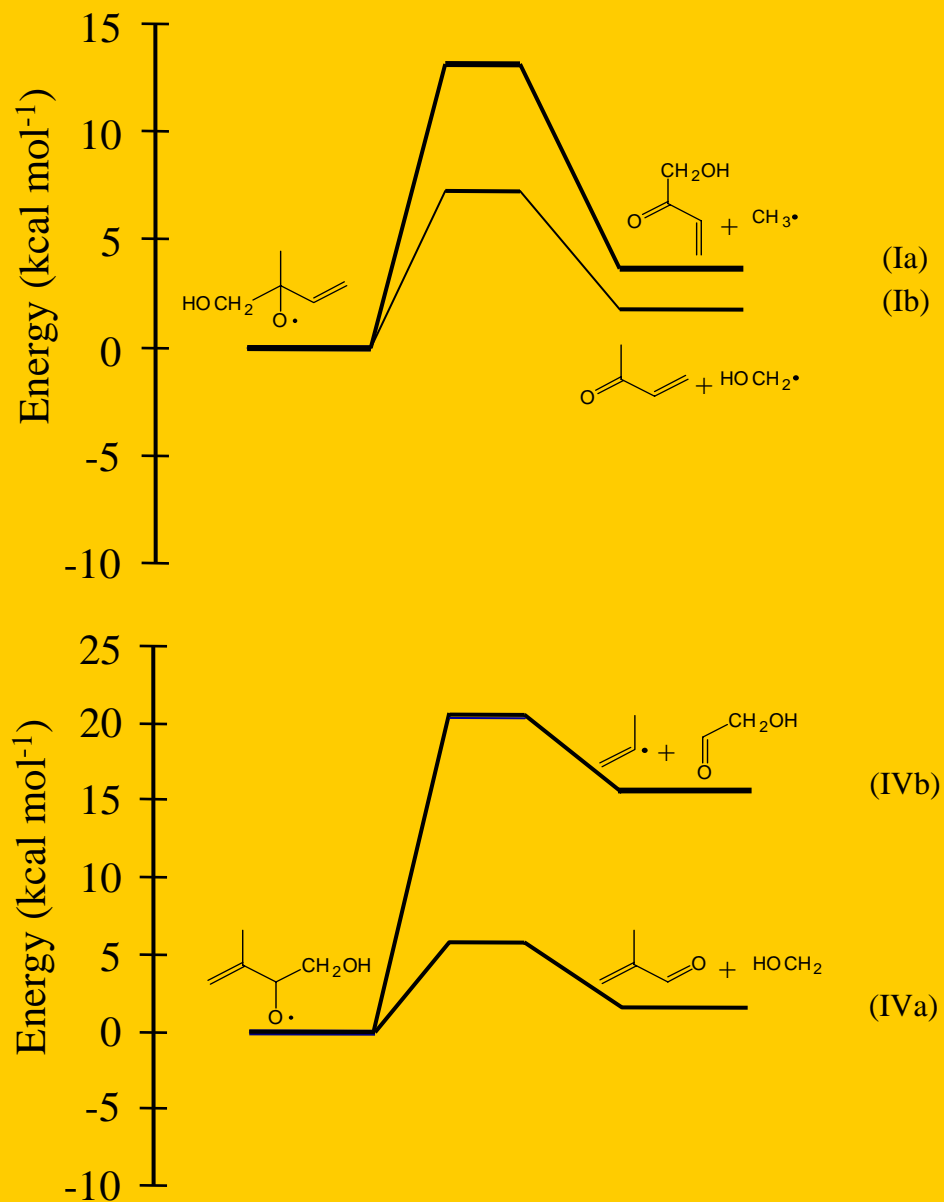
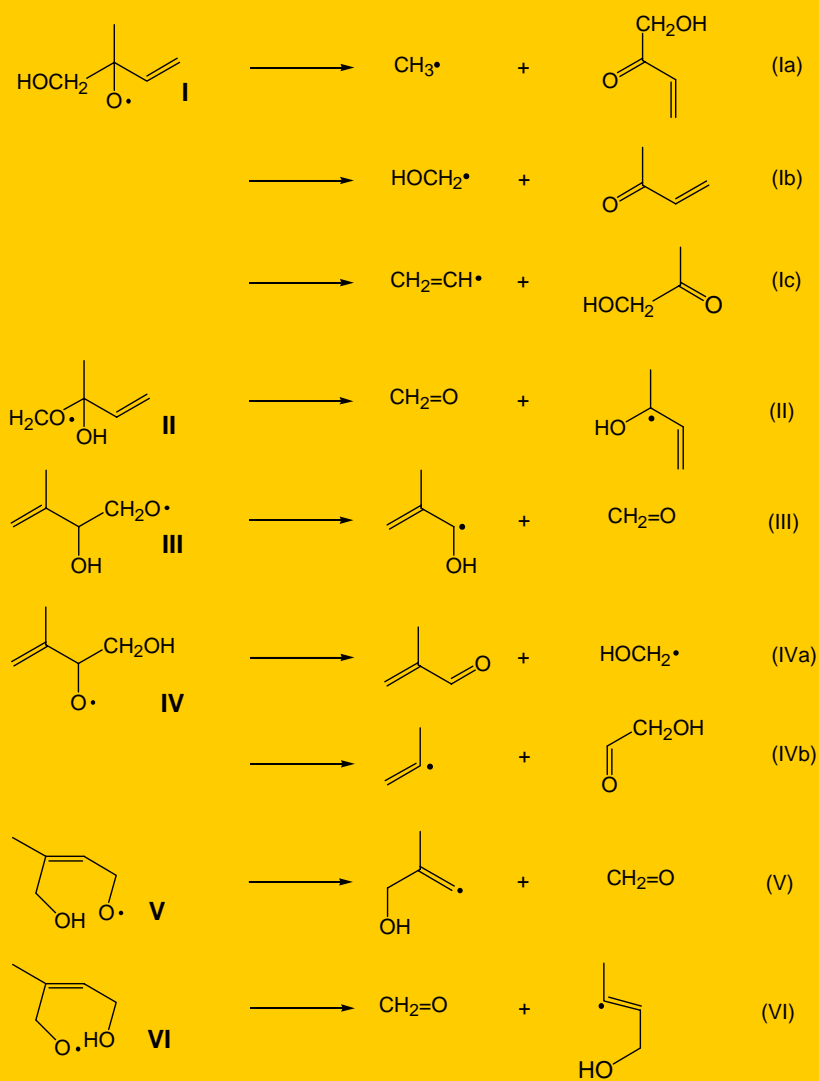
Experimental

Ion Drift-Chemical Ionization Mass Spectrometry (ID-CIMS) for kinetics and mechanism of intermediate radical species and product yields

W. Lei *et al.*, Theoretical study of OH-O₂-isoprene peroxy radicals, *J. Phys. Chem.*, 105, 471 (2001)



W. Lei and R. Zhang, Theoretical study of hydroxy-isoprene alkoxy radicals and their decomposition pathways,
J. Phys. Chem., 105, 3808 (2001)



J. Zhao *et al.*, Oxidation mechanism of δ -hydroxyisoprene alkoxy radicals: hydrogen abstraction versus 1,5 H-shift, *Chem. Phys. Lett.* 369, 204 (2003)

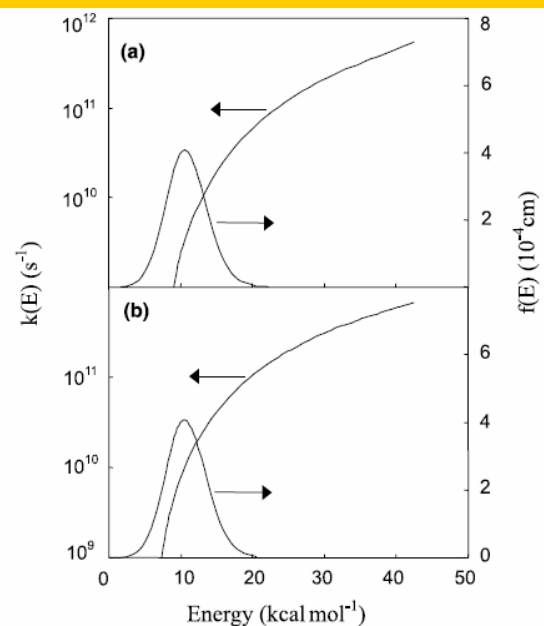
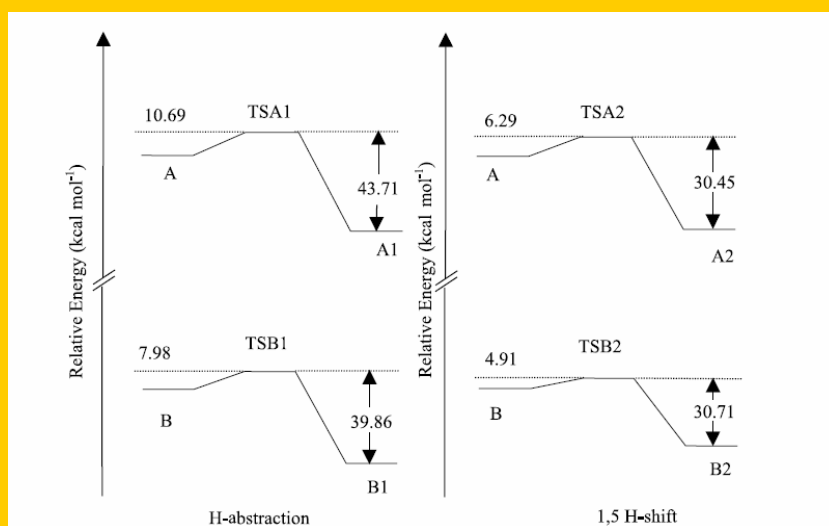
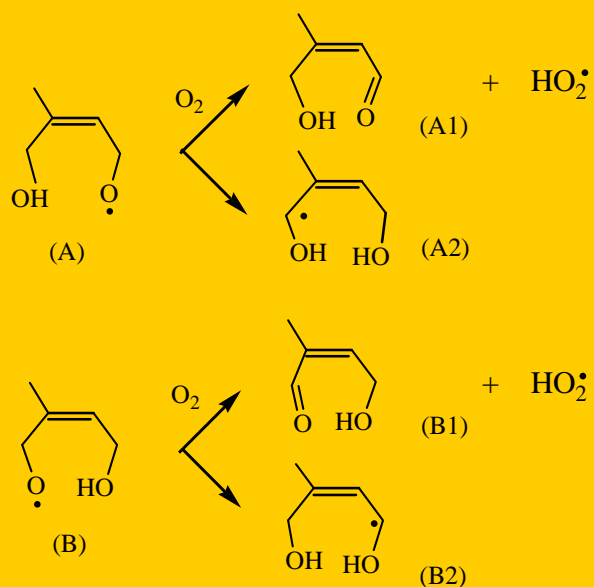
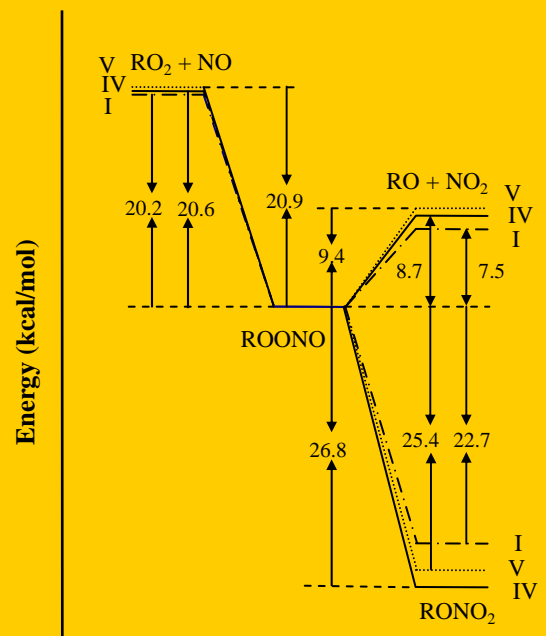
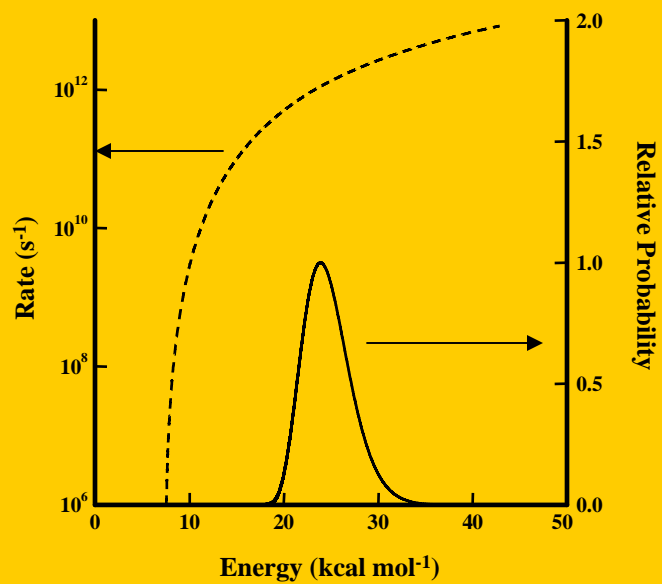
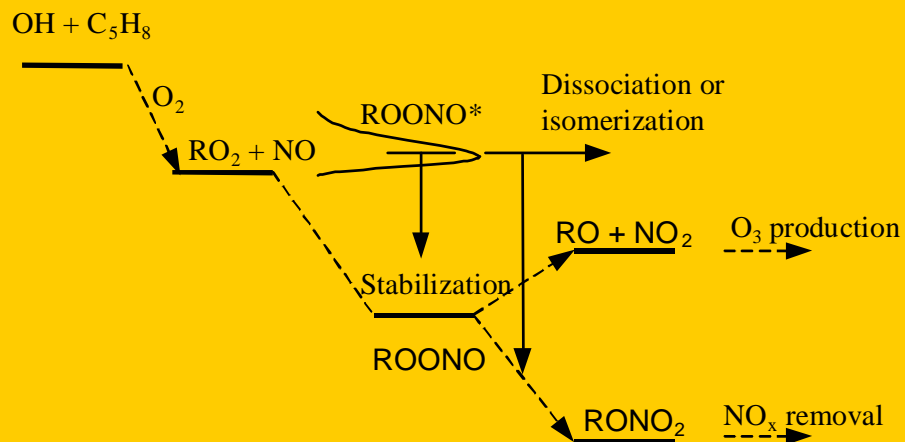
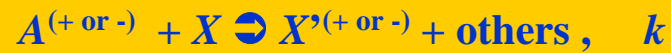
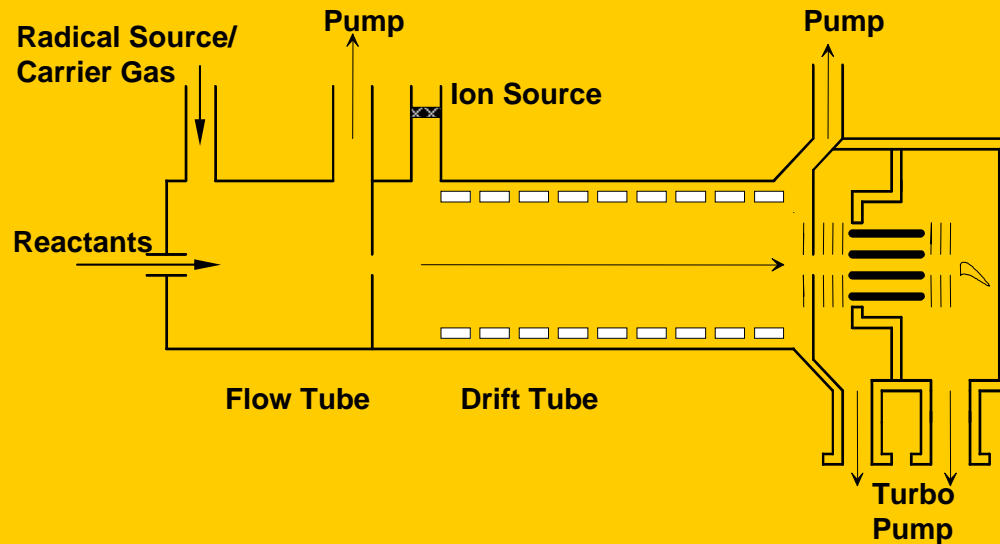


Fig. 5. RRKM rates for 1,5 H-shift of the alkoxy radicals A and B as a function of microcanonical energy. For comparison, the collision rate is $1.3 \times 10^{10} \text{ s}^{-1}$ at 760 Torr and 298 K. Also shown is the energy distribution of the excited alkoxy radicals A* and B* calculated according to the SSE theory.

D. Zhang *et al.*, Hydroperoxy nitrites and nitrates from OH initiated reactions of isoprene, *J. Am. Chem. Soc.*, 124, 9600 (2002)



E. Fortner *et al.*, Development of ion drift-chemical ionization mass spectrometry, *Anal. Chem.* 76, 5436 (2004)



$$[X'] = k [A][X] dt$$

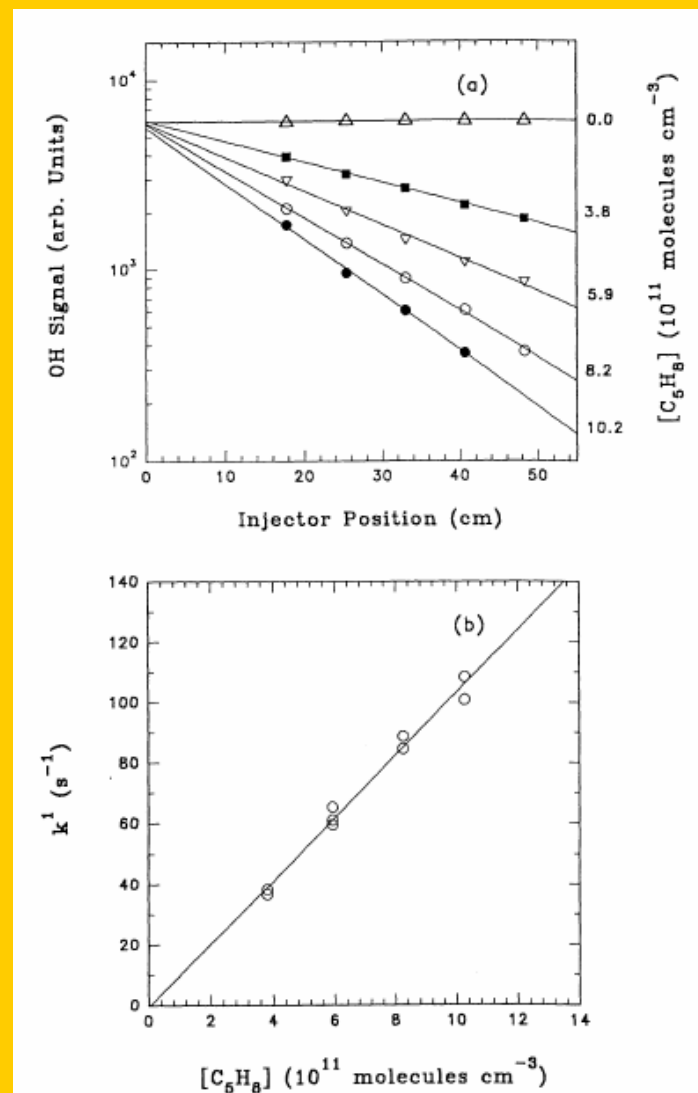
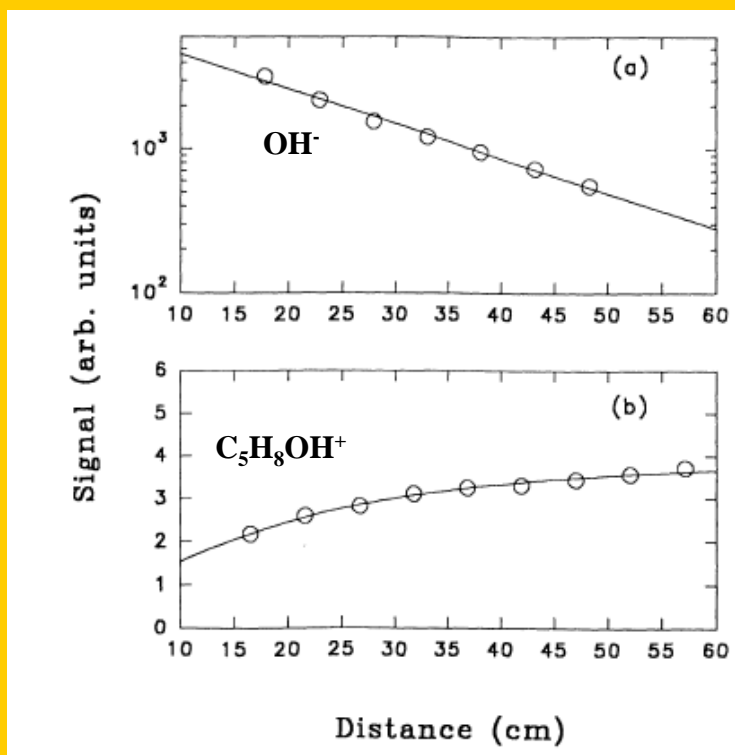
$$dt = l/U$$

$$[X_{fr}] = P/\Delta p [X]$$

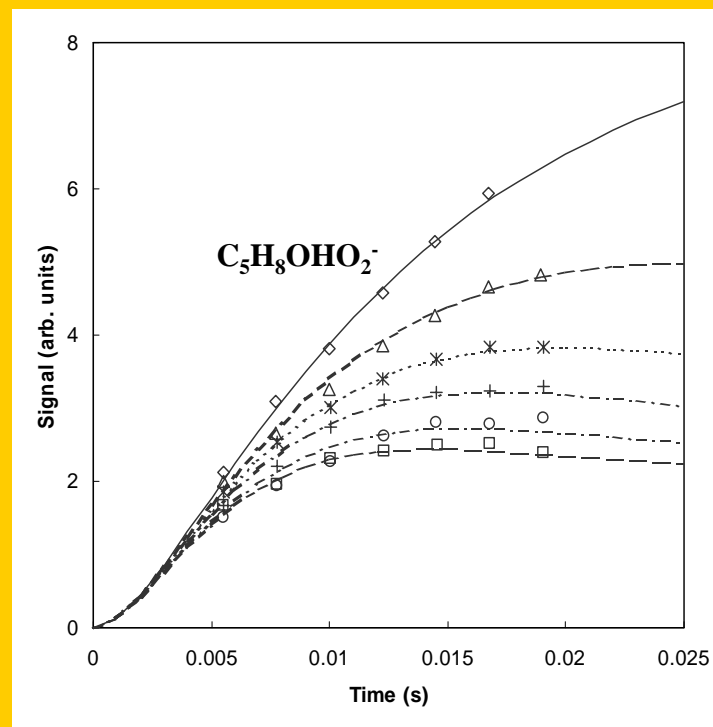
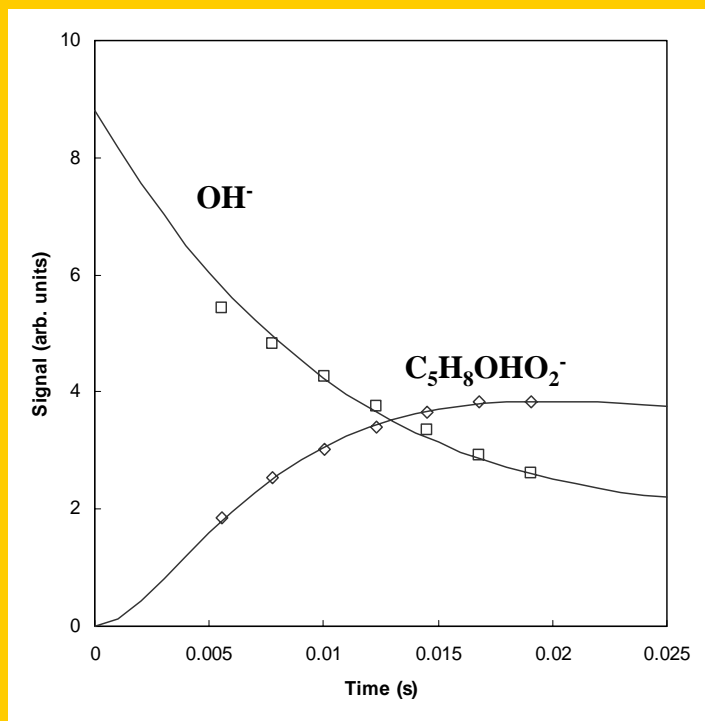
$A = \text{H}_3\text{O}^+$, Proton-transfer reaction MS, PTR-MS

k determined using the average-dipole-orientation (ADO) theory

R. Zhang et al., Kinetic studies of OH-initiated reactions of isoprene,
J. Geophys. Res., 105, 24627 (2000)

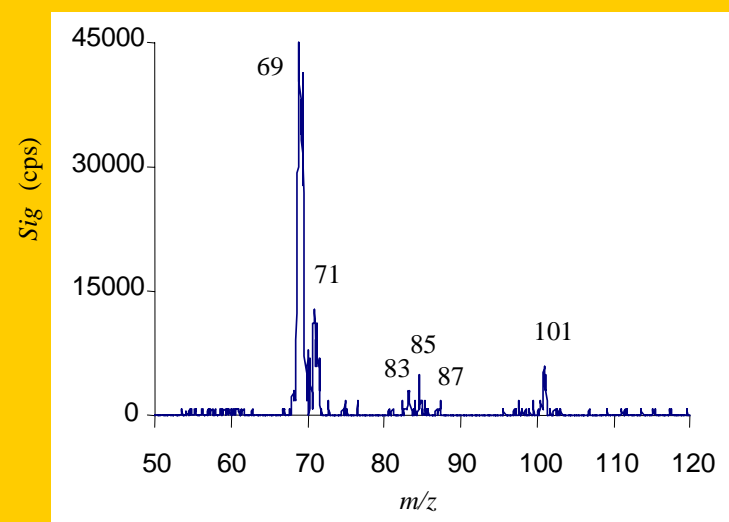
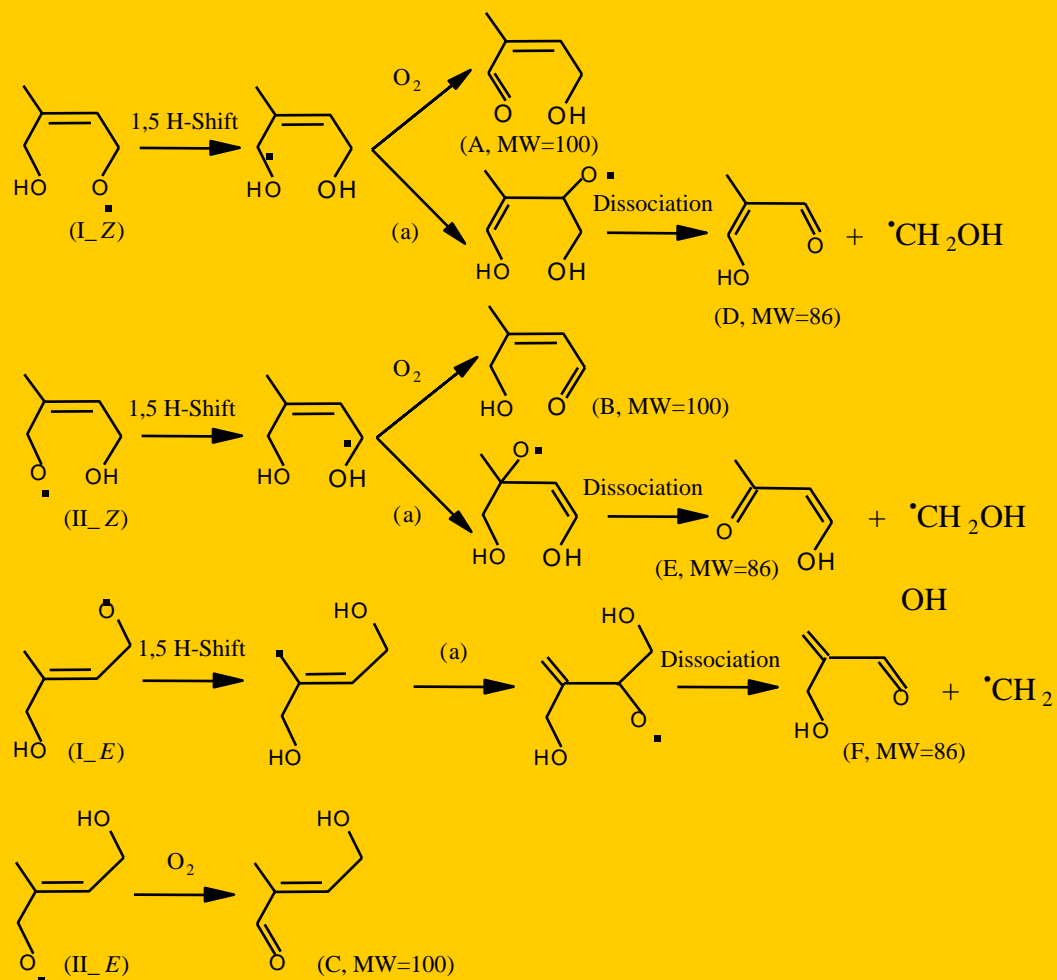


D. Zhang *et al.*, Experimental study of NO reaction with hydroxyalkyl peroxy radicals from OH-initiated reaction of isoprene, *J. Phys. Chem.* 107, 11013 (2003)



NO
↓

J. Zhao *et al.*, Quantification of hydroxycarbonyls from OH-isoprene reactions, *J. Am. Chem. Soc.* 126, 2686 (2004)



Zhao et al., J. Am. Chem. Soc. 126, 2686 (2004)

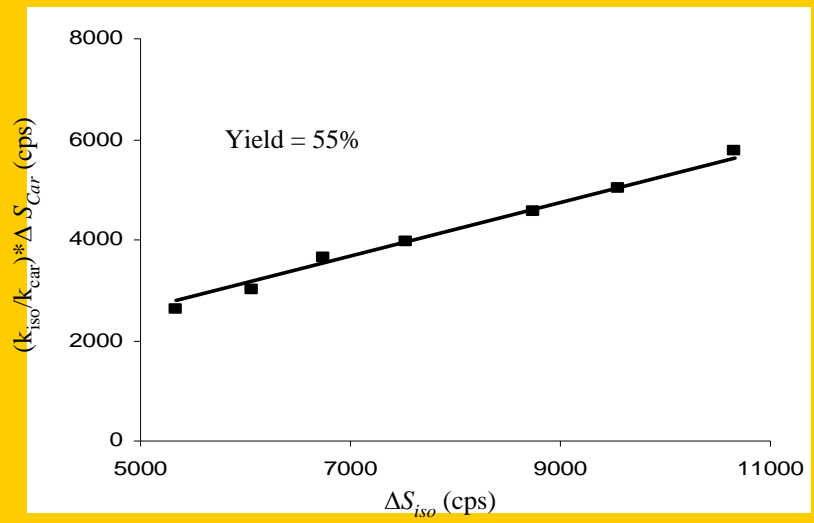
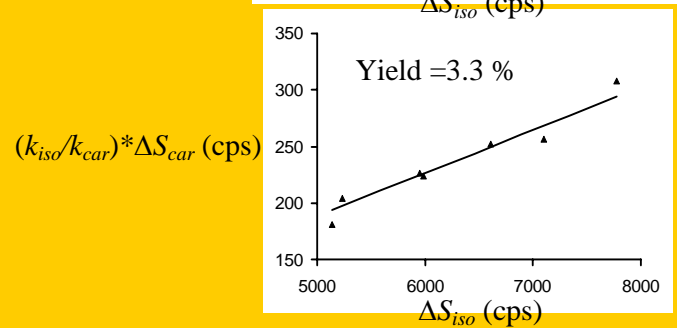
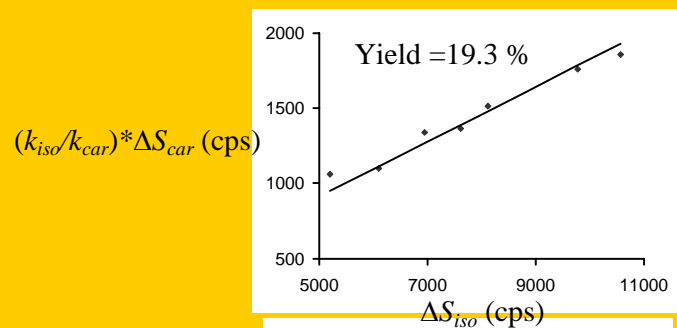
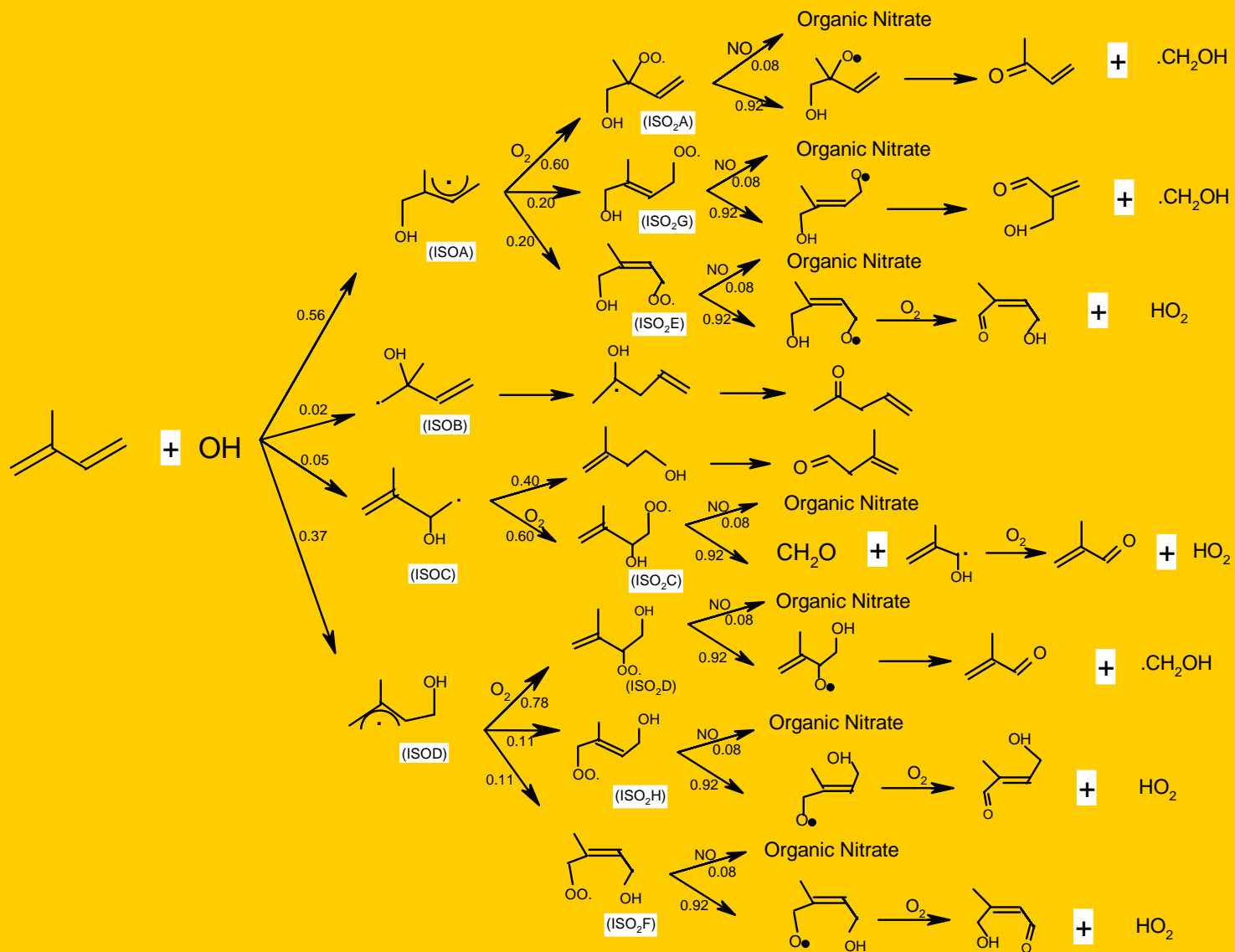


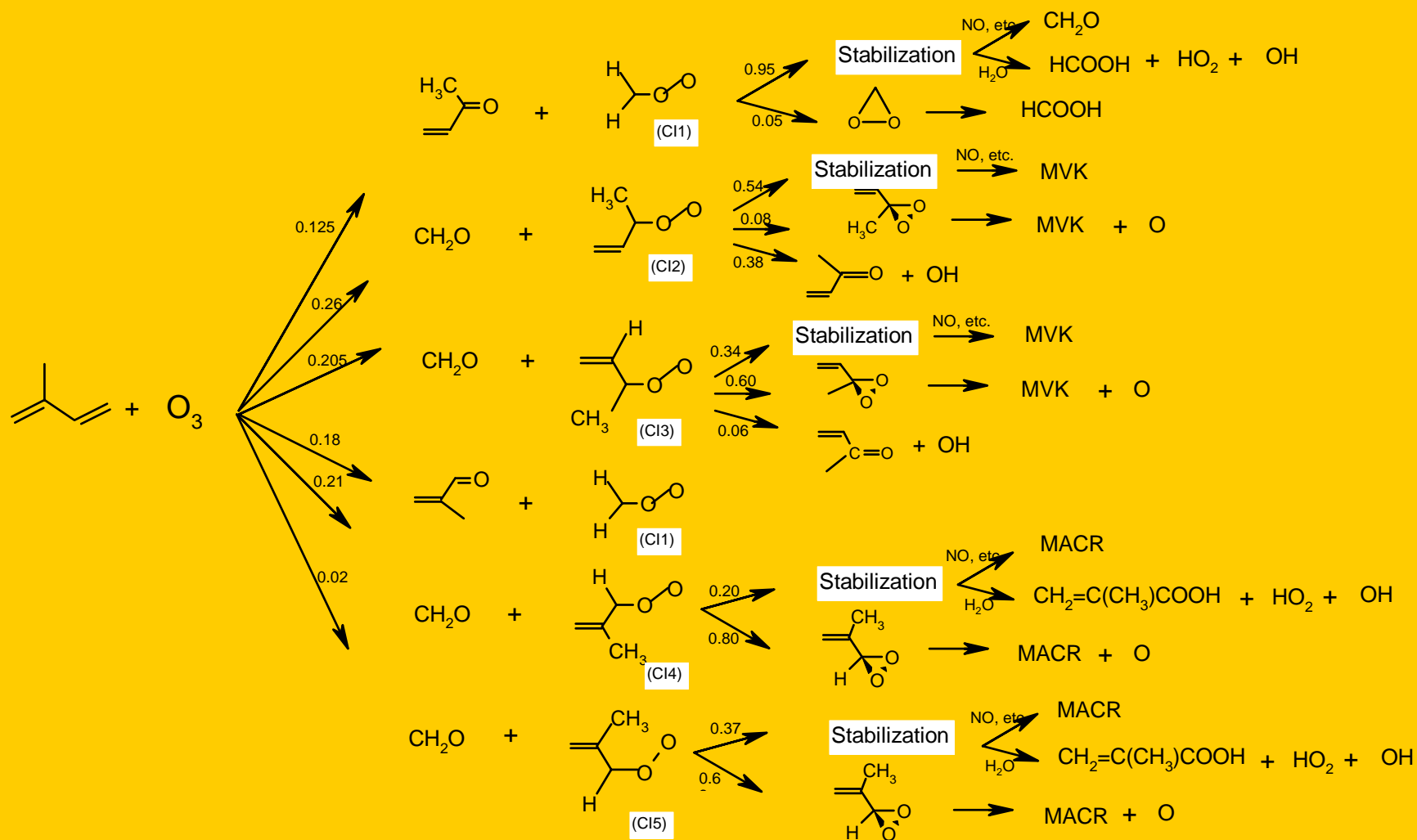
Table 1. Product Yields (%) from OH-Initiated Oxidation of Isoprene in the Presence of NO

product	previous work	this work ^a
MVK	29 ± 7, ^b 36 ± 4, ^c 32 ± 5 ^d , 44 ± 6 ^e	55 ± 6
MACR	21 ± 5, ^b 25 ± 3, ^c 22 ± 2 ^d , 28 ± 4 ^e	
organic nitrate	8–14, ^b 8–12, ^e 4.4 ± 0.8 ^f	
3-methyl furan	<2, ^e 4.4 ± 0.6 ^g	
C5-hydroxycarbonyl		19.3 ± 6.1
C4-hydroxycarbonyl		3.3 ± 1.6
C5-carbonyl		8.4 ± 2.4

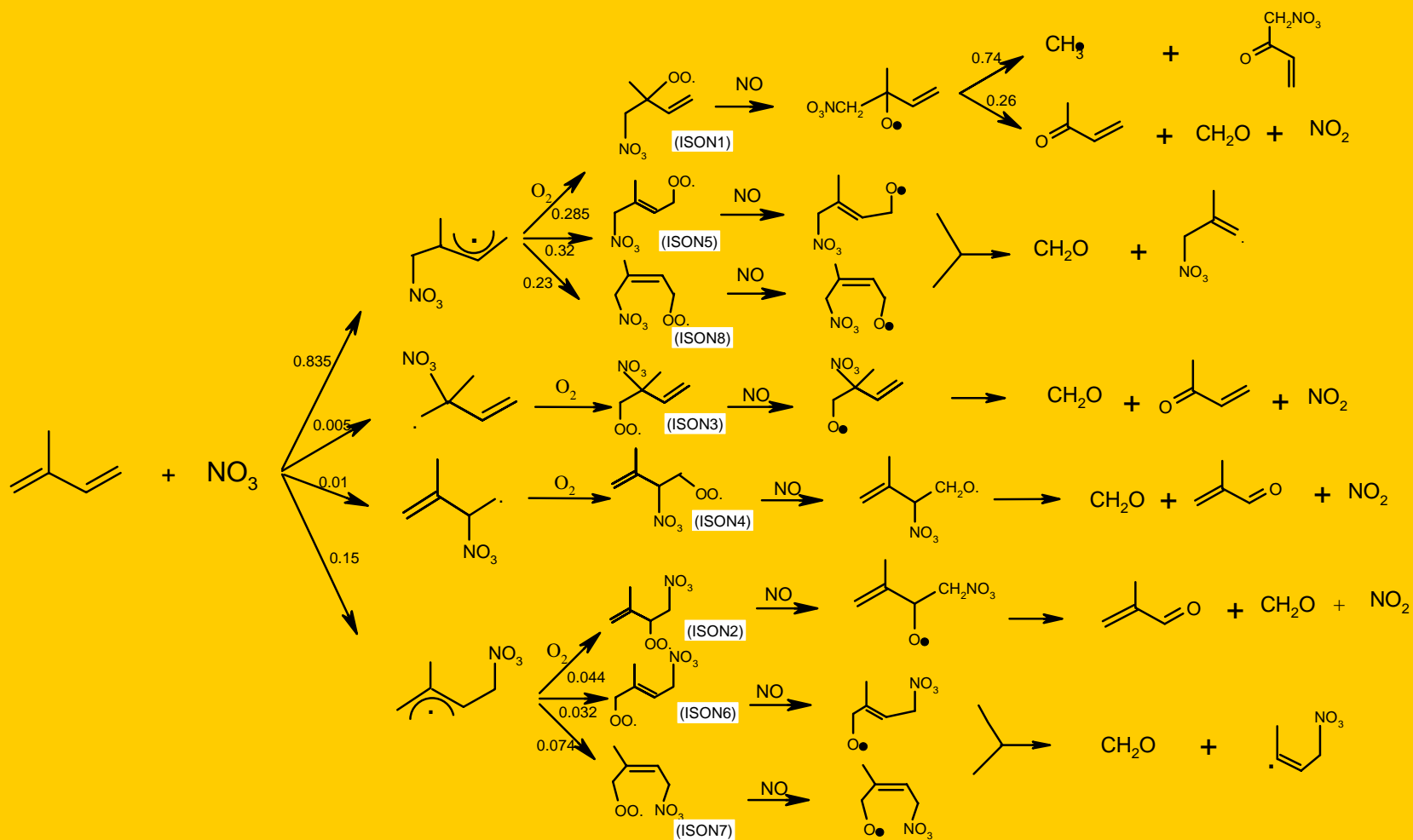
J. Fan and R. Zhang, Atmospheric oxidation mechanism of isoprene, *Environ. Chem.* 1, 140-149 (2004)



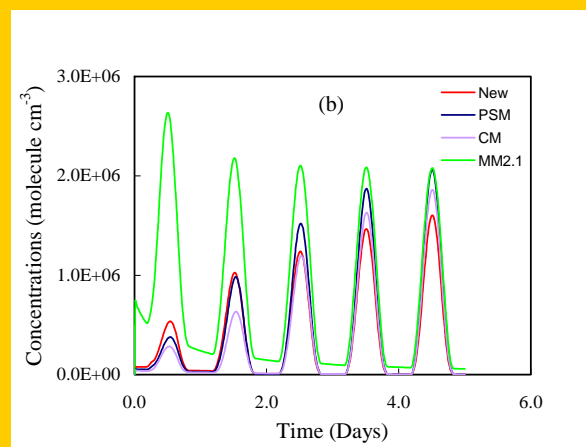
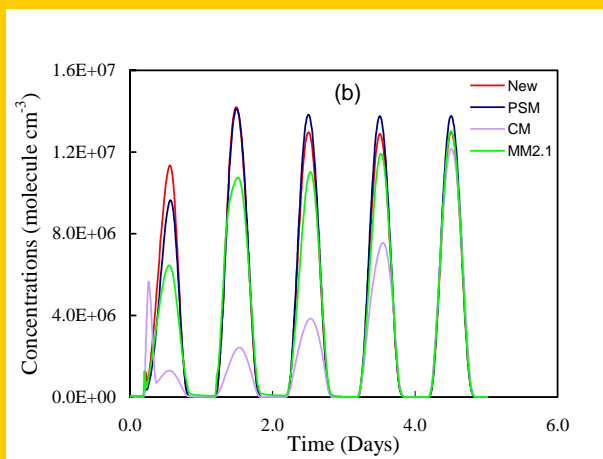
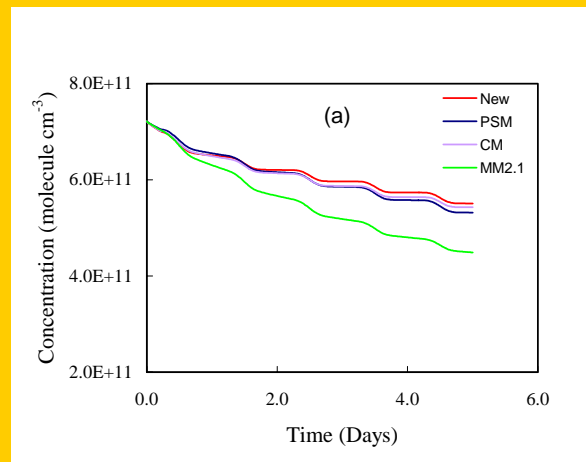
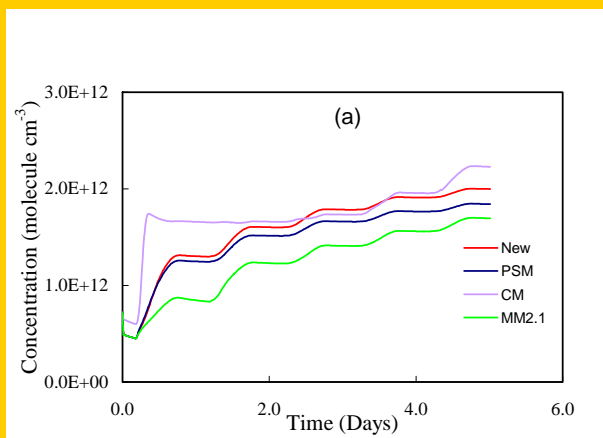
Fan and Zhang, *Environ. Chem.* 1, 140-149 (2004)



Fan and Zhang, *Environ. Chem.* 1, 140-149 (2004)



Fan and Zhang, *Environ. Chem.* 1, 140-149 (2004)



Comparisons of O_3 (a) and OH (b) concentrations at high (right) and low (left) NO_x conditions predicted by the various mechanisms

Conclusions

Quantum chemical and kinetic rate calculations provide important energetic data to evaluate the reaction pathways and isomeric branching

Combined experimental and theoretical studies improve the understanding of complex hydrocarbon oxidation reactions.

Section: Aerosol Cloud-Precipitation Interaction: Facts and Fiction

Monday afternoon MCW Level 2

A13C-0925

**Simulations of Effects of Aerosols and Relative Humidity on
Cumulus Clouds Using Cloud-Resolving Models**

Presented by Jiwen Fan

Section: Tropospheric Heterogeneous Chemistry and Aerosol Phase Transitions

Wednesday Afternoon MCW Level 2

A33A-0962

Heterogeneous Chemistry of Carbonyls and Alcohols With Sulfuric Acid: Implications for Secondary Organic Aerosol Formation

A33A-0966

Aging of soot by interaction with organic compounds

Both presented by Jun Zhao

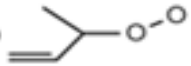
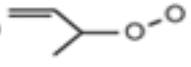
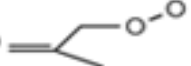

Thank you for your attention !

Question?

C₅ Compounds

ISOP	isoprene	ISN1	CH ₂ =CHC(CH ₃)(O [•])CH ₂ (ONO ₂)
ISOA	CH ₂ =CHC [•] (CH ₃)CH ₂ OH	ISN3	CH ₂ =CHC(CH ₃)(ONO ₂)CH ₂ (O [•])
ISOB	CH ₂ =CHC(CH ₃)OHCH ₂ [•]	ISN5	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (O [•]) (<i>Z</i>)
ISOC	CH ₂ =C(CH ₃)CH(OH)CH ₂ [•]	ISN6	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (O [•]) (<i>Z</i>)
ISOD	CH ₂ =C(CH ₃)CH [•] CH ₂ OH	ISN7	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (O [•]) (<i>E</i>)
ISO ₂ A	CH ₂ =CHC(CH ₃)(OO [•])CH ₂ OH	ISN8	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (O [•]) (<i>E</i>)
ISO ₂ C	CH ₂ =C(CH ₃)CH(OH)CH ₂ OO [•]	ISOC11	CH ₂ =CHC(CH ₃)(OO [•])CH ₂ Cl
ISO ₂ D	CH ₂ =C(CH ₃)CH(OO [•])CH ₂ OH	ISOC12	CH ₂ =CHC(CH ₃)ClCH ₂ OO [•]
ISO ₂ E	[•] OOCH ₂ CH=C(CH ₃)CH ₂ OH (<i>Z</i>)	ISOC13	CH ₂ =C(CH ₃)CH(Cl)CH ₂ OO [•]
ISO ₂ F	HOCH ₂ CH=C(CH ₃)CH ₂ OO [•] (<i>Z</i>)	ISOC14	CH ₂ =C(CH ₃)CH(OO [•])CH ₂ Cl
ISO ₂ G	[•] OOCH ₂ CH=C(CH ₃)CH ₂ OH (<i>E</i>)	ISOC15	[•] OOCH ₂ CH=C(CH ₃)CH ₂ Cl
ISO ₂ H	HOCH ₂ CH=C(CH ₃)CH ₂ OO [•] (<i>E</i>)	ISOC16	ClCH ₂ CH=C(CH ₃)CH ₂ OO [•]
ISON1	CH ₂ =CHC(CH ₃)(OO [•])CH ₂ (ONO ₂)	ISC11	CH ₂ =CHC(CH ₃)(O [•])CH ₂ Cl
ISON2	CH ₂ =C(CH ₃)CH(OO [•])CH ₂ (ONO ₂)	ISC12	CH ₂ =CHC(CH ₃)ClCH ₂ O [•]
ISON3	CH ₂ =CHC(CH ₃)(ONO ₂)CH ₂ (OO [•])	ISC13	CH ₂ =C(CH ₃)CH(Cl)CH ₂ O [•]
ISON4	CH ₂ =C(CH ₃)CH(ONO ₂)CH ₂ (OO [•])	ISC14	CH ₂ =C(CH ₃)CH(O [•])CH ₂ Cl
ISON5	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (OO [•]) (<i>Z</i>)	ISC15	[•] OCH ₂ CH=C(CH ₃)CH ₂ Cl
ISON6	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (OO [•]) (<i>Z</i>)	ISC16	ClCH ₂ CH=C(CH ₃)CH ₂ O [•]
ISON7	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (OO [•]) (<i>E</i>)	ISON	Hydroxyalkylnitrates and alkyl nitrates
ISON8	CH ₂ (ONO ₂)C(CH ₃)=CHCH ₂ (OO [•]) (<i>E</i>)	IALD1	C ₅ hydroxycarbonyls, e.g. CHOC(CH ₃)=CHCH ₂ OH
		CO51	C ₅ carbonyls

C₄ Compounds

CHC	C ₄ hydroxycarbonyls and dihydroxy carbonyls
MACR	methacrolein
MVK	methyl vinyl ketone
CI2	CH ₂ =CHC(CH ₃)(-O-O) 
CI3	CH ₂ =CHC(CH ₃)(-O-O) 
CI4	CH ₂ =C(CH ₃)CH(-O-O) 
CI5	CH ₂ =C(CH ₃)CH(-O-O) 

	Rate constant ^A	Ref.
OH-Isoprene Reactions		
ISOP + OH = 0.56 ISOA + 0.02 ISOB + 0.05 ISOC + 0.37 ISOD	1.00×10^{-10}	[9,17]
ISOA + O ₂ = 0.60 ISO ₂ A + 0.20 ISO ₂ E + 0.20 ISO ₂ G	2.20×10^{-12}	[18,21]
ISOB + O ₂ = CO51 + HO ₂	2.50×10^{-11}	[23]
ISOC + O ₂ = 0.40 CO51 + 0.40 HO ₂ + 0.60 ISO ₂ C	1.40×10^{-12}	[18,23]
ISOD + O ₂ = 0.78 ISO ₂ D + 0.11 ISO ₂ F + 0.11 ISO ₂ H	5.90×10^{-13}	[18,23]
ISO ₂ A + NO = 0.08 ISON + 0.92 MVK + 0.92 CH ₂ O + 0.92 HO ₂ + 0.92 NO ₂	1.00×10^{-11}	[5,19,40,41]
ISO ₂ C + NO = 0.08 ISON + 0.92 MACR + 0.92 CH ₂ O + 0.92 HO ₂ + 0.88 NO ₂	1.00×10^{-11}	[5,19,40,41]
ISO ₂ D + NO = 0.08 ISON + 0.92 MACR + 0.92 CH ₂ O + 0.92 HO ₂ + 0.88 NO ₂	1.00×10^{-11}	[5,19,40,41]
ISO ₂ E + NO = 0.08 ISON + 0.92 CHC + 0.92 CH ₂ O + 0.92 HO ₂ + 0.92 NO ₂	1.00×10^{-11}	[15,21,40,41]
ISO ₂ F + NO = 0.08 ISON + 0.92 IALD1 + 0.92 HO ₂ + 0.92 NO ₂	1.00×10^{-11}	[15,21,40,41]
ISO ₂ G + NO = 0.08 ISON + 0.92 IALD1 + 0.92 HO ₂ + 0.92 NO ₂	1.00×10^{-11}	[15,21,40,41]
ISO ₂ H + NO = 0.08 ISON + 0.92 IALD1 + 0.92 HO ₂ + 0.92 NO ₂	1.00×10^{-11}	[15,21,40,41]
ISO ₂ A + ISO ₂ E = 0.9 MVK + 1.1 CHC + 1.8 CH ₂ O + 1.8 HO ₂	2.50×10^{-12}	[26,39]
ISO ₂ A + ISO ₂ F = 0.9 MVK + 1.1 CHC + 1.8 CH ₂ O + 1.8 HO ₂	4.70×10^{-12}	[26,39]
ISO ₂ C + ISO ₂ A = 0.9 MACR + 0.2 CHC + 1.8 CH ₂ O + 1.8 HO ₂ + 0.9 MVK	2.60×10^{-12}	[26,39]
ISO ₂ C + ISO ₂ C = 1.2 MACR + 0.8 CHC + 1.2 CH ₂ O + 1.2 HO ₂	4.80×10^{-12}	[26,39]
ISO ₂ C + ISO ₂ D = 1.2 MACR + 0.8 CHC + 1.2 CH ₂ O + 1.2 HO ₂	5.20×10^{-12}	[26,39]
ISO ₂ C + ISO ₂ E = 0.6 MACR + 1.4 CHC + 0.6 CH ₂ O + 1.2 HO ₂	4.70×10^{-12}	[26,39]
ISO ₂ C + ISO ₂ F = 0.6 MACR + 1.4 CHC + 0.6 CH ₂ O + 1.2 HO ₂	3.70×10^{-12}	[26,39]
ISO ₂ D + ISO ₂ A = 0.9 MACR + 0.3 CHC + 1.8 CH ₂ O + 1.8 HO ₂ + 0.9 MVK	3.90×10^{-12}	[26,39]
ISO ₂ E + ISO ₂ E = 2 CHC + 1.2 CH ₂ O + 1.2 HO ₂	3.90×10^{-12}	[26,39]
ISO ₂ F + ISO ₂ F = 2 CHC + 1.2 CH ₂ O + 1.2 HO ₂	2.80×10^{-12}	[26,39]
O₃-Isoprene Reactions		
ISOP + O ₃ = 0.26 CI2 + 0.205 CI3 + 0.21 CI4 + 0.02 CI5 + 0.12 MVK + 0.21 MACR + 0.33 CH ₂ -O-O + 0.67 CH ₂ O	1.60×10^{-7}	[27,28]
CH ₂ -O-O = 0.05 CH ₂ (OO*) + 0.95 CH ₂ -O-O ^B	9.62	[27,28]
CH ₂ -O-O [†] + H ₂ O = HCOOH + HO ₂ + OH	4.00×10^{-16}	[39]
CH ₂ -O-O [†] + NO (NO ₂) = CH ₂ O + NO ₂ (NO ₃)	4.00×10^{-16}	[39]
CH ₂ (OO*) = HCOOH	2.00×10^{-1}	[42,43]
CI2 = 0.08 CH ₂ =CHC*(CH ₃)(OO*) + 0.38 MVK + 0.38 OH + 0.54 CI2 [†]	1.50×10^{-1}	[27,28]
CI2 [†] + NO (NO ₂ , etc.) = MVK + NO ₂ (NO ₃ , etc.)	4.00×10^{-16}	[39]
CI3 = 0.60 CH ₂ =CHC*(CH ₃)(OO*) + 0.06 MVK + 0.06 OH + 0.34 CI3 [†]	9.40×10^{-1}	[27,28]
CI3 [†] + NO (NO ₂ , etc.) = MVK + NO ₂ (NO ₃ , etc.)	4.00×10^{-16}	[39]
CHC*(CH ₃)(OO*) = MVK + O	2.00×10^{-1}	[42,43]
CI4 = 0.80 CH ₂ =C(CH ₃)CH*(OO*) + 0.20 CI4 [†]	4.5	[27,28]
CI4 [†] + H ₂ O = CH ₂ =C(CH ₃)COOH + HO ₂ + OH	4.00×10^{-16}	[39]
CI4 [†] + NO (NO ₂ , etc.) = MACR + NO ₂ (NO ₃ , etc.)	4.00×10^{-16}	[39]
CI5 = 0.63 CH ₂ =C(CH ₃)CH*(OO*) + 0.37 CI5 [†]	3.5	[27,28]
CI5 [†] + H ₂ O = CH ₂ =C(CH ₃)COOH + HO ₂ + OH	4.00×10^{-16}	[39]
CI5 [†] + NO (NO ₂ , etc.) = MACR + NO ₂ (NO ₃ , etc.)	4.00×10^{-16}	[39]
CH ₂ =C(CH ₃)CH*(OO*) = MACR + O	2.00×10^{-1}	[42,43]
NO₃-Isoprene Reactions		
ISOP + NO ₃ = 0.285 ISON1 + 0.044 ISON2 + 0.005 ISON3 + 0.01 ISON4 + 0.32 ISON5 + 0.032 ISON6 + 0.074 ISON7 + 0.23 ISON8	7.20×10^{-13}	[29-31]
ISON1 + NO = ISN1 + NO ₂	6.80×10^{-12}	[39]
ISON2 + NO = ISN2 + NO ₂	6.80×10^{-12}	[39]
ISON3 + NO = ISN3 + NO ₂	6.80×10^{-12}	[39]
ISON4 + NO = ISN4 + NO ₂	6.80×10^{-12}	[39]
ISON5 + NO = ISN5 + NO ₂	6.80×10^{-12}	[39]
ISON6 + NO = ISN6 + NO ₂	6.80×10^{-12}	[39]
ISON7 + NO = ISN7 + NO ₂	6.80×10^{-12}	[39]
ISON8 + NO = ISN8 + NO ₂	6.80×10^{-12}	[39]
ISN1 = 0.74 CH ₂ + 0.74 CH ₂ =CHCOCH ₂ (ONO ₂) + 0.26 MVK + 0.26 CH ₂ O + 0.26 NO ₂	2.80×10^6	[31]
ISN2 = MACR + CH ₂ O + NO ₂	8.00×10^6	[31]
ISN3 = MVK + CH ₂ O + NO ₂	0.14	[31]
ISN4 = MACR + CH ₂ O + NO ₂	6.10×10^7	[31]
ISN5 = CH ₂ (ONO ₂)C(CH ₃)=CH* + CH ₂ O	1.46	[31]
ISN6 = CH ₂ (ONO ₂)CH=C*(CH ₃) + CH ₂ O	16.60	[31]
ISN7 = CH ₂ (ONO ₂)CH=C*(CH ₃) + CH ₂ O	32.90	[31]
ISN8 = CH ₂ (ONO ₂)C(CH ₃)=CH* + CH ₂ O	7.00×10^{-3}	[31]
Cl-Isoprene Reactions		
ISOP + Cl = 0.15 ISOC11 + 0.02 ISOC12 + 0.07 ISOC13 + 0.25 ISOC14 + 0.19 ISOC15 + 0.17 ISOC16 + 0.15 CH ₂ =C(CH ₂)CH=CH ₂ + 0.15 HCl	4.27×10^{-10}	[32-34,38]
CH ₂ =C(CH ₂)CH=CH ₂ + O ₂ = CH ₂ =C(CHO)CH=CH ₂ + HO ₂	2.50×10^{-13}	[32,38]
ISOC1 <i>n</i> + NO = ISCl <i>n</i> + NO ₂ (<i>n</i> = 1-6)	6.80×10^{-12}	[39]
ISCl11 = 0.02 CH ₂ + 0.15 CH ₂ =CHCOCH ₂ Cl + 0.98 MVK + 0.98 ClCH ₂	9.00×10^3	[32,37]
ISCl12 + O ₂ = HO ₂ + CH ₂ =CHC(CH ₃)(Cl)CHO	1.00×10^{-15}	[32,37]
ISCl13 + O ₂ = HO ₂ + CH ₂ =C(CH ₃)CH(Cl)CHO	1.00×10^{-15}	[32,37]
ISCl14 + O ₂ = HO ₂ + CH ₂ =C(CH ₃)COCH ₂ (Cl)	1.00×10^{-15}	[32,37]
ISCl15 + O ₂ = HO ₂ + CH ₂ (Cl)C(CH ₃)=CCH ₂ O	1.00×10^{-15}	[32,37]
ISCl16 + O ₂ = HO ₂ + CH ₂ (Cl)CH=C*CH ₃	1.00×10^{-15}	[32,37]

^A At 300 K. Units are s⁻¹ for unimolecular reactions and cm³ molec⁻¹ s⁻¹ for bimolecular reactions.

^B The dagger (†) represents the stabilized state.