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Thermochemical and Kinetic Analysis of the H, OH, HO_2, O, and O_2 Association Reactions with Cyclopentadienyl Radical

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Reaction pathways and kinetics for cyclopentadienyl radical association with H, OH, HO_2, O, and O_2 are presented in the temperature range 900−1300 K and atmospheric pressure. Thermochemical data for reactants, intermediate, and product species are evaluated from literature data and from group additivity with hydrogen bond increments. High-pressure limit rate constants for the radical combination reactions and decomposition of the energized adducts are estimated. Pressure-dependent rate constants for each channel in the reaction systems are calculated using bimolecular quantum Rice Ramsperger Kassel, QRRK, for $k(E)$ with a modified strong collision approach for falloff. A submechanism of important cyclopentadienyl radical reactions is assembled and tested in an elementary reaction model for combustion of benzene, where the cyclopentadienyl radical is a key intermediate in the stepwise (C6 → C5 → C4) decomposition. Modeling results are compared with limited literature data on species profiles for appropriate reaction systems, where benzene, cyclopentadiene, and carbon monoxide are the initial fuel, observed intermediate, and major combustion product, respectively. H atom association with cyclopentadienyl radical (CY13PD5$^•$) leads to stabilized cyclopentadiene (CY13PD) as the primary product, with linear pentadienal diradical as a minor product. The hydroxyl association with cyclopentadienyl radical forms an energized adduct, which primarily rearranges to cyclopentadienol isomers, which are stabilized. $O^{(3p)}$ association with cyclopentadienyl radical leads to two main product sets: cyclopentadienone plus H atom or 1,3-butadienyl radical plus carbon monoxide. Hydroperoxy radical combination with cyclopentadienyl radical forms an energized hydroperoxy−cyclopentadiene, which can dissociate to lower energy products cyclopentenoxy radical plus OH, to cyclopentadienone + H_2O, or back to the initial reactants. Oxygen molecule addition to cyclopentadienyl radical forms an energized cyclopentadiene peroxy radical with a very shallow well (ca. 13 kcal/mol), which predominantly dissociates back to reactants. A small, but important, fraction of the energized peroxy adduct undergoes reactions that lead to ring-opening with formation of resonance-stabilized 2-pentenedialdehyde radical or vinyl ketene and formyl radical. These reactions provide paths for cyclopentadienyl radical conversion to linear, unsaturated, oxyhydrocarbons.

Introduction

The use and importance of aromatic compounds in fuels contrasts sharply with the limited elementary reaction kinetic data in the literature regarding their combustion kinetics and reaction pathways. A number of experimental and modeling studies on benzene,[1−6] toluene,[7,8] and phenol[9] oxidation exist in the literature, but it would still be helpful to have more data on species concentration profiles, to understand or evaluate important reaction paths and to validate detailed mechanisms. The above studies show that phenoxy radical is a key intermediate in the gas-phase thermal oxidation of aromatics; it is easily formed via abstraction of the weak phenolic hydrogen atom from phenol. The phenol is formed by rapid addition of hydroxyl to the aromatic carbons and elimination of H atom,[10] which occurs even under atmospheric conditions. Work from the Mackie[11] and Louw[12] research groups has also shown that phenoxy radical is an important intermediate in pyrolysis and oxidation of anisole and probably in other phenyl ethers. The thermal decomposition of phenoxy[1,9,13−16] shows an interesting mechanism in which the bicyclo[3,1,0]hexenone radical is formed and then breaks the cyclic CO−C bond and eliminates carbon monoxide to form the resonance-stabilized cyclopentadienyl radical (see Figure 1).

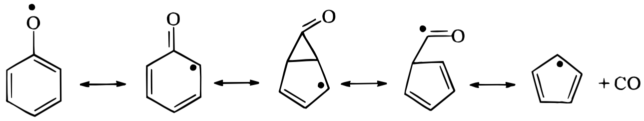

Figure 1. Phenoxy radical degradation reaction pathway.

At higher temperatures this unimolecular C6 → C5 degradation of the stabilized phenoxy radical is the dominant reaction path.

Venkat et al.[17] published a general reaction scheme for high-temperature oxidation of aromatic hydrocarbons that included cyclopentadienyl radical. They postulate that benzene decomposes through the sequence

$$\text{C6} \Rightarrow \text{(phenoxy)} \rightarrow \text{C5 (cyclopentadienyl)} \rightarrow (+\text{O2}) \Rightarrow \text{O} + \text{cyclic C5H5O}^\bullet$$

and

$$\text{cyclic C5H5O}^\bullet \Rightarrow \text{linear butadienyl radical } (\text{C}{=}\text{C}{-}\text{C}{=}\text{C}^\bullet) + \text{CO}$$

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TABLE 1: Thermochemical Data

SPECIES	$H_F(298)$	S(298)	C_P300	C_P400	C_P500	C_P600	C_P800	C_P1000	C_P1500	C_P2000	ELEMENTS
H2O	-57.80	43.72	8.17	8.88	9.56	10.20	11.30	12.10	12.98	13.37	H 2 O 1 0
CO	-26.40	47.20	6.71	6.89	7.06	7.23	7.53	7.79	8.29	8.61	C 1 O 1 0
HCO	10.40	53.60	8.37	8.85	9.32	9.78	10.65	11.42	12.80	13.57	H 1 C 1 O 1
CO2	-94.01	51.00	8.90	9.81	10.57	11.20	12.17	12.84	13.77	14.23	C 1 O 2 0
CH2O	-26.00	50.90	8.44	9.48	10.51	11.50	13.30	14.75	16.90	18.06	C 1 H 2 O 1
CY13PD	31.26	65.50	18.23	24.76	30.15	34.59	41.25	45.81	52.50	55.92	C 5 H 6 0
CY13PD5.	57.17	63.58	17.86	24.30	29.47	33.58	39.46	43.26	48.68	51.33	C 5 H 5 0
*H	52.10	27.30	4.90	4.90	4.90	4.90	4.90	4.90	4.90	4.90	H 1 0 0
H2	0.00	31.20	6.89	6.97	7.05	7.12	7.27	7.41	7.69	7.87	H 2 0 0
O2	0.00	49.00	6.86	7.10	7.33	7.54	7.89	8.18	8.70	9.03	O 2 0 0
CPDOOH	6.55	84.87	26.75	34.60	40.98	45.65	52.66	57.34	63.76	66.88	C 5 H 6 O 2
CPDOO.	42.65	83.00	24.72	31.79	37.50	41.63	48.00	52.36	58.61	61.74	C 5 H 5 O 2
C5O2H6221	-3.17	88.34	21.27	29.69	35.96	42.02	53.36	61.15	66.08	69.36	C 5 H 6 O 2
C5O2H5221	28.90	91.02	20.89	29.27	35.37	41.06	51.46	58.35	65.85	67.55	C 5 H 5 O 2
BICYC5O2	17.68	73.89	24.31	32.52	39.23	44.24	53.04	59.35	66.00	69.19	C 5 H 6 O 2
BICYC5.O2	49.75	75.19	23.93	32.10	38.64	43.28	51.14	56.55	61.77	64.27	C 5 H 5 O 2
CYC5O2H6	7.95	75.12	26.01	33.60	39.82	44.27	51.57	58.56	65.20	68.64	C 5 H 6 O 2
CYC5O2H5.	41.45	73.61	25.69	32.92	38.69	42.70	49.29	55.74	60.95	63.73	C 5 H 5 O 2
BOC5OH	-31.21	75.37	23.46	32.51	39.61	44.03	51.71	56.58	63.71	67.21	C 5 H 6 O 2
BOC5O.	20.75	73.72	21.52	30.43	37.35	41.60	48.95	53.50	59.20	62.55	C 5 H 5 O 2
C5H6O2_1	-28.47	84.35	27.13	34.87	40.59	44.71	51.67	56.29	63.18	66.53	C 5 H 6 O 2
C5H5O2_1	14.43	86.10	26.25	33.31	38.55	42.30	48.75	52.99	58.53	61.40	C 5 H 5 O 2
CODC=COH	-48.89	89.64	29.33	35.67	40.70	44.69	50.86	55.29	61.89	65.26	C 5 H 6 O 2
CO.DC=COH	-17.99	90.32	28.19	34.10	38.65	42.20	47.65	51.51	57.22	60.60	C 5 H 5 O 2
CODC=CO.	-12.99	88.58	27.07	33.06	37.80	41.60	47.50	51.72	57.85	60.90	C 5 H 5 O 2
C.OC=CCCO	-19.99	93.53	26.66	32.69	37.55	41.41	47.43	51.48	57.37	60.24	C 5 H 5 O 2
C=OCCKET	-48.47	93.86	30.11	35.75	40.87	44.47	50.60	55.04	62.05	65.35	C 5 H 6 O 2
C=OCC.KET	-14.97	93.73	29.79	35.07	39.74	42.90	48.32	52.22	57.81	60.49	C 5 H 5 O 2
COC=CCCO	-50.89	92.85	27.80	34.26	39.60	43.90	50.64	55.26	62.04	65.39	C 5 H 6 O 2
COC=CC.CO	-17.39	92.72	27.48	33.58	38.47	42.33	48.36	52.44	58.06	60.72	C 5 H 5 O 2
COC=CCC.O	-13.99	93.97	26.97	32.83	37.64	41.48	47.48	51.53	57.39	60.25	C 5 H 5 O 2
C=CC.C=O	15.45	76.87	19.45	24.24	28.46	31.96	37.47	41.38	46.93	49.62	C 4 H 5 O 1
C=CC=C=O	1.82	71.96	21.62	26.23	30.23	32.64	36.20	39.20	43.21	45.24	C 4 H 4 O 1
HO2	3.50	54.70	8.28	8.78	9.26	9.71	10.50	11.16	12.24	12.84	H 1 O 2 0
*O	59.51	38.40	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	O 1 0 0
CYC5H5O.	42.94	72.73	20.60	27.20	32.60	36.99	43.44	47.73	53.79	56.74	C 5 H 5 O 1
CYPDONE	7.40	66.71	19.50	25.73	30.87	34.78	40.31	44.27	49.40	51.91	C 5 H 4 O 1
COC=CC=C.	52.34	80.62	26.36	32.27	36.63	39.87	44.67	47.98	52.96	55.52	C 5 H 5 O 1
C2H4	12.52	52.47	10.27	12.79	15.01	16.95	20.13	22.55	26.34	28.38	C 2 H 4 0
C=CC=O	-20.32	67.39	17.01	20.92	24.08	26.62	30.56	33.28	37.42	39.49	C 3 H 4 O 1
C=CC.=O	10.58	68.07	15.87	19.35	22.03	24.13	27.35	29.50	32.72	34.32	C 3 H 3 O 1
C=C.C=O	36.58	68.54	16.52	19.93	22.49	24.50	27.60	29.70	32.84	34.39	C 3 H 3 O 1
C.=CC=O	38.78	69.24	17.44	20.69	23.13	25.03	27.97	29.76	32.54	34.03	C 3 H 3 O 1
C=CC=CCO	-6.76	80.15	25.93	32.50	37.58	41.46	47.26	51.50	57.62	60.73	C 5 H 6 O 1
C.OC=CC=C	24.14	78.76	25.74	31.65	35.99	39.25	44.05	47.61	52.78	55.43	C 5 H 5 O 1
C=CC=C	26.08	66.61	19.23	24.25	28.39	31.81	37.00	40.69	46.53	49.52	C 4 H 6 0
C=CC=C.	83.99	69.05	19.06	23.57	27.22	30.15	34.45	37.38	42.05	44.47	C 4 H 5 0
CYC5ODE.	8.80	66.44	21.34	28.90	35.11	39.40	45.75	51.31	56.02	58.40	C 5 H 5 O 1
BICYC5H6O	7.93	67.20	19.81	28.05	34.66	39.12	46.67	51.65	58.76	62.26	C 5 H 6 O 1
BICYC5H5O	41.43	64.33	19.49	27.37	33.53	37.55	44.39	48.83	54.00	57.08	C 5 H 5 O 1
OH	9.50	43.80	6.79	6.86	6.93	7.00	7.14	7.28	7.61	7.91	H 1 O 1 0
CYC5H5OH	-9.02	75.33	22.08	29.03	34.72	39.34	46.15	50.72	57.40	60.76	C 5 H 6 O 1
CYC5H4OH	16.88	75.23	21.69	28.61	34.08	38.38	44.34	48.04	53.24	55.89	C 5 H 5 O 1
CYPD1OH	-12.20	75.68	21.87	28.72	34.27	38.69	45.42	50.01	56.54	60.29	C 5 H 6 O 1
CYPD1O.	23.70	74.57	20.53	26.73	31.79	35.90	42.29	46.68	52.75	56.04	C 5 H 5 O 1
CYPD2OH	-10.39	77.27	21.57	27.96	33.33	37.77	44.72	49.35	56.07	60.48	C 5 H 6 O 1
CYPD2O.	25.51	76.16	20.23	25.97	30.85	34.98	41.59	46.02	52.28	55.91	C 5 H 5 O 1
CYC5O3H61	-30.78	88.03	30.56	37.71	43.53	48.23	56.61	62.49	69.49	72.84	C 5 H 6 O 3
CYC5O3H51	2.72	84.22	29.02	35.89	41.45	45.91	53.86	59.35	66.78	69.83	C 5 H 5 O 3
LC5O3H62	-27.61	102.72	32.33	40.22	46.10	50.44	57.28	61.81	68.13	71.14	C 5 H 6 O 3
LC5O3H52	9.29	103.84	31.50	38.79	44.14	48.02	54.12	58.08	63.44	65.96	C 5 H 5 O 3
LC5O3H61	-43.26	100.49	32.69	40.23	46.01	50.36	56.62	61.24	67.53	70.69	C 5 H 6 O 3
LC5O3H51	-7.16	100.71	30.64	37.39	42.46	46.27	51.90	56.27	62.43	65.59	C 5 H 5 O 3
C=CC=CC	18.21	76.57	24.37	30.81	36.22	40.63	47.44	52.71	60.57	64.70	C 5 H 8 0
C=CC=CC.	54.31	76.19	23.75	30.25	35.44	39.51	45.60	50.25	57.08	60.34	C 5 H 7 0
C.=CC=CC.	113.41	77.58	23.56	29.50	34.08	37.59	42.78	46.76	52.55	55.26	C 5 H 6 0
CYPD2OOH	11.04	84.53	26.28	33.81	39.57	44.27	51.28	55.90	62.58	65.97	C 5 H 6 O 2
CYPD3OOH	12.85	86.12	25.98	33.05	38.63	43.35	50.58	55.24	62.09	65.58	C 5 H 6 O 2
COC=CKET	-31.02	84.13	28.43	34.43	39.29	42.26	46.62	49.94	54.31	56.40	C 5 H 4 O 2

Note : See QRRK Analysis input parameter table and reaction portential energy diagram for species ID.
Units; Enthalpy, H_f kcal/mol; Entropy; S and Cp(300) is heat capacity in cal/mol -K of 300 K

These were the only reactions used to describe the formation and oxidation of cyclopentadienyl radical. Wang and Brezinsky[18] recently reported a detailed analysis of cyclopentadienone (C_5H_4O) unimolecular dissociation, which we show is an important product in cyclopentadienyl radical oxidation, where the products were determined to be resonance-stabilized cyclobutadienyl radical + CO.

Lovell et al.[1] reported flow reactor data on benzene combustion at three oxygen concentrations, corresponding to rich, lean, and stoichiometric conditions; they showed initial oxygen concentration significantly affects fuel consumption rates along with formation of carbon monoxide and cyclopentadiene. They suggested that phenoxy degradation is major reaction path for both carbon monoxide formation and benzene consumption. Lovell et al.[1] also reported experimental data on perturbation of benzene oxidation by NO_2 addition. The benzene oxidation rate doubled in the presence of NO_2, and they suggested additional reaction pathways, including hydroxyl radical association with cyclopentadienyl radical.

A number of researchers have recently published benzene or toluene oxidation models and have made modifications to better fit experimental data, but cyclopentadiene reactions were not included in the modifications. Bittker[19] published a mechanism that was based upon previously published reaction paths for ignition delay times plus benzene and toluene loss profiles. Bittker employed a sensitivity code to determine the important reactions and then optimized the fit to the data by adjusting rate constants. Davis et al.[20] modified the Brezinsky groups' mechanism (phenol reactions) to better fit flame speed data. Tan and Frank[21] published a benzene oxidation model and used it for explanation of H and O atom production in their shock tube data. Emdee et al.[22] report an updated mechanism for toluene oxidation based on Brezinsky's model.[1,17,23] They indicated that the branching reaction $C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH_2 + HO_2$ was of major importance. In Emdee et al.'s[22] toluene mechanism the reactions of resonance-stabilized benzyl radical control the reaction at early times.

Zhang and Mckinnon et al.[4] published an elementary reaction model of high-temperature benzene combustion under fuel-rich conditions, near sooting environment. They report that the flame speeds for benzene could not be matched by their model and suggested that some important reaction paths may be missing. Shandross et al.[2] reported data from molecular beam experiments on benzene flames and showed that current models strongly overpredicted destruction of phenol at high temperatures. Shandross et al. modified the phenol reaction chemistry of Emdee and Brezinsky, of Linstedt and Skevis,[3] and of Zhang and Mckinnon to obtain improved results, but did not report on data or analysis of cyclopentadienyl radical in their early publication.

Cyclopentadiene is also important in fulvene and naphthalene formation. Moskaleva et al.[24] report the methyl radical association with cyclopentadienyl radical as a possible reaction pathway to benzene through fulvene. Melius et al.[25] show cyclopentadienyl radicals can combine to form nathphalene along with fulvene and benzene in reactions catalyzed by H atom, under "near sooting" conditions.

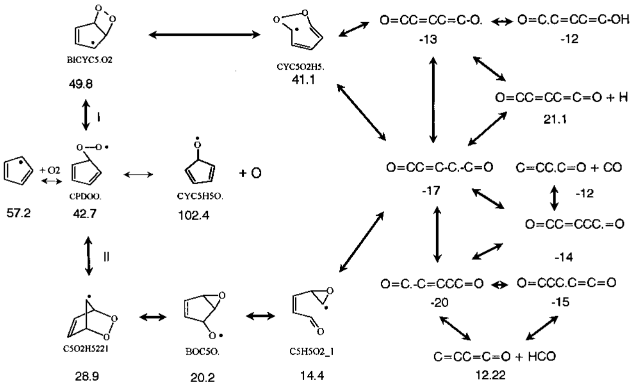

Figure 2. Reaction scheme of cyclopentadienyl radical with oxygen molecule. 2,4-Cyclopentadienyl peroxy addition, then isomerization (cyclidation) to both the 2 and 3 positions results in formation of stabilized intermediates and identical final products. Major products are 2-pentenedialdehyde radicals and vinyl ketene plus formyl radical.

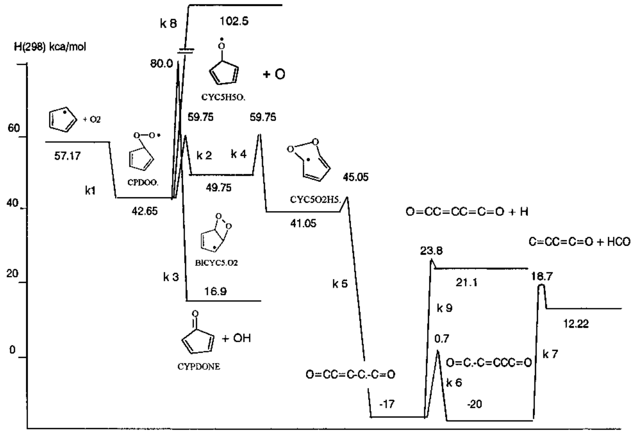

Figure 3. Potential energy diagram for cyclopentadienyl radical association with oxygen molecule (channel I). The intermediates are cyclopentene-3,4-cycloperoxy-5-yl radical (BICYC5•O2), 1,3-cycloperoxyheptadiene-5-yl radical (CYC5O2H5•), and 2-pentenedialdehyde radicals. Important products are vinyl ketene (C=CC=C=O) plus formyl radical.

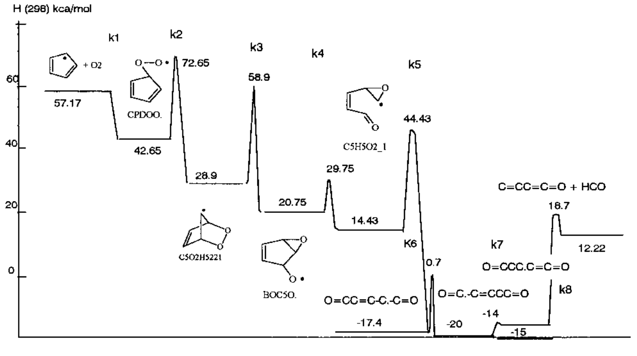

Figure 4. Potential energy diagram for cyclopentadienyl radical association with oxygen molecule (channel II). The intermediates are bicyclo[2.2.1.]hexene peroxy radical (C5O2H5221), cyclopenten-3,4-epoxy-5-oxy radical, (BOC5O•), 4,5-epoxy-2-pentenal-5-yl radical, (C5H5O2_1), and 2-pentenedialdehyde radicals. Important products are vinyl ketene (C=CC=C=O) plus formyl radical.

The need to account for the presence of relatively large concentrations of cyclopentadienyl radicals became apparent during our attempt to construct a mechanism comprising elementary reactions to model benzene formation and loss and for reconstruction of experimental observations in cyclopentadiene, benzene, and toluene oxidation. Cyclopentadienyl radical is highly stabilized (ca. 20 kcal/mol);[18] abstraction of H from stable species such as H_2, CH_4, C_2H_4, C_3H_6, CH_2O, phenol, and toluene by cyclopentadienyl radical is endothermic by 10−23 kcal/mol, respectively. The endothermicity results from ca. 20 kcal/mol of resonant stabilization energy in the cyclopentadienyl radical, and it drives the equilibrium toward the cyclopentadienyl moiety in these reversible reactions. The endothermicity and resonance stabilization also explain the relatively low reactivity (with O_2 and other hydrocarbons) of this radical and, perhaps, part of the octane blending values of aromatics. Cyclopentadienyl radical concentration builds up in aromatic oxidation systems, because of its low reactivity, and it then reacts with

TABLE 2: Chemical Activition Analysis Input Parameters; Cyclopentadienyl Oxidation Reaction System (Channel I); High Pressure Limit Constants

Reactants	Products	A(s^{-1} or cm^3/(mol*s)	n	Ea. (Kcal/mol)
1 CY13PD5. + O2	CPDOO.	3.60E12	0.0	0.0
-1 CPDOO.	CY13PD5.+O2	4.03E13	0.0	12.26
2 CPDOO.	BICYC5.O2	1.93E13	0.0	17.64
-2 BICYC5.O2	CPDOO.	6.71E14	0.0	10.0
3 CPDOO.	CYPDONE + OH	3.61E12	0.0	37.3
4 BICYC5.O2	CYC5O2H5.	1.56E13	0.0	10.0
-4 CYC5O2H5.	BICYC5.O2	3.55E13	0.0	18.41
5 CYC5O2H5.	COC=CC.CO	6.95E15	0.0	4.0
-5 COC=CC.CO	CYC5O2H5.	4.79E11	0.0	62.99
6 COC=CC.CO	C.OC=CCCO	4.79E11	0.0	18.
-6 C.OC=CCCO	COC=CC.CO	4.09E11	0.0	20.87
7 C.OC=CCCO	C=CC=C=O+HCO	7.50E12	0.0	36.82
-7 C=CC=C=O+HCO	C.OC=CCCO	1.00E11	0.0	5.47
8 CPDOO.	CYC5H5O. + O	2.36E14	0.0	58.72
-8 CYC5H5O. + O	CPDOO.	3.00E13	0.0	0.0
9 COC=CC.CO	COC=CKET+H	1.26E13	0.0	41.47
-9 COC=CKET+H	COC=CC.CO	4.82E13	0.0	2.7

Adduct	. Frequency/Degeneracy (CPFIT) Geometry Mean/ Degeneracy	Lennard-Jones parameters	
		σ (A)	ε / κ (K)
CPDOO.	250.8/4.757 923.4/17.544 2621.9/7.199 965.4/29.5	5.8	620
BICYC5.O2	650.9/10.289 654.9/6.146 1588.2/13.565 975.5/30		
CYC5O2H5.	600.4/11.246 636.9/6.088 1825.2/12.666 971.7/30		
COC=CC.CO	377.8/9.866 977.7/10.936 2232.0/7.698 879.2/28.5		
C.OC=CCCO	410.7/10.772 1116.5/11.220 2535.3/6.508 922.6/28.5		

Collision partner and (Lennard-Jones) collision parameters

Partner \ Parameters	σ (A)	ε / κ (K)	$E_{avg.}$ (cal/mol)
N2	3.62	97.5	830
H2	2.82	59.7	621

Species and note

CY13PD5. is cyclopentadienyl radical
CPDOO. is cyclopentadienylperoxy radical
BICYC5.O2 is cyclopente-3,4-cycloperoxy-5yl radical
CYC5O2H5. is 1,3 cycloperoxy-heptadiene-5yl radical
COC=CC.CO is 2-pentenedialdehyde 4yl radical
C.OC=CCCO is form 2-pentenedialdehyde 1yl radical
CYC5H5O. is cyclopentadiene oxy radical
C=CC=C=O is vinyl ketene
COC=CKET is 3 ketene 2 propylene aldyhyde
CYPDONE is cyclopentadienone

References for high pressure limit rate constants and comments

k 1	A 1=3.60E12	Ea. = 0 from C=CC. + O2 ;[1] R = 8.93E-2; dU = -12.26
k-1	A-1=4.03E13	MR; E-a = 12.26
k 2	A 2=1.93E13	LogA2 = 13.55 - (4.3 - 1.7)/4.6 + log2 (loss of one rotor and gain one optical isomer and degeneracy 2) R = 2.875E-2; dU = 7.64 Ea. = dU + 3(ring strain) + 7(addition) = 17.64, [1]
k-2	A-2=6.71E14	MR; E-a = 10 [1]
k 3	A 3=3.61E12	TST; Δ S# = -4.3, loss 1 rotor, degeneracy = 1 Ea = 28 (ring strain) + 9.3 (Evans Polanyi Analysis) = 37.3 Intermediate cyclpentadienyl - hydroperoxy radical dissociates immediately to cyclopentadienone + OH, no reverse reaction considered.
k 4	A 4=1.56E13	MR; Ea. = 10; R = 0.44; dU = -8.41
k-4	A-4=3.55E13	TST; E-a = -dU + 3(ring strain) + 7(addition) = 18.41, see test.
k 5	A 5=6.95E15	MR; Ea. = 4;[1] R = 1.45E4; dU = -58.99
k-5	A-5=4.79E11	LogA-5 = 13.55-4.3 x2/4.6; (loss of two rotors); E-a = -dU + 4 = 62.99
k 6	A 6=4.79E11	LogA-6 = 13.55-4.3 x2/4.6; (loss of two rotors) Ea. = 12(abs) + 6(ring) = 18; R = 1.17; dU = -2.87
k-6	A-6=4.09E11	MR; E-a = -dU + 18 = 20.87
k 7	A 7=7.50E12	MR; Ea. = dU + 5.47 = 36.82; R = 74.9; dU = 31.35
k-7	A-7=1.00E11	from HCO + C2H4; Ea. = 5.47 [2]
k 8	A 8=2.36E14	MR; Ea. = dU = 58.72
k-8	A-8=3.00E13	Radical recombination; E-a = 0
k 9	A 9=1.26E13	estimated, Ea = dU + 2.7 = 41.47; R = 0.2613; dU = 38.77
k-9	A-9=4.82E13	MR; E-a = 2.7 [3]

$R = A_f/A_r$
MR; Microscopic Reversibility
TST; Transition State Theory

TABLE 2 (Continued)

Units: Ea. and U in kcal/mol, for bimolecular reaction ; A and AT^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction A and AT^n in sec^{-1}.

Reference
1 Bozzelli, J.W. and Dean, A.M.; J. Phys. Chem. **1993**, 97, 4427
2 Lesclaux, R.; Roussel, P.; Veyret, B.; Pouchan, C.; J. Am. Chem. Soc. **1986**, 108, 3872
3 Dean, A.M. J. Phys. Chem. **1985**, 21, 4600

TABLE 3: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with O2 (Channel I)

Rate constants k = A T^n exp(-Ea/RT)

Reaction	A	n	Ea
CY13PD5. + O2 = CPDOO.	7.31E07	0.08	-9.57
CY13PD5. + O2 = COC=CC.CO	2.94E10	-0.53	2.60
CY13PD5. + O2 = C.OC=CCCO	1.27E06	0.60	-2.14
CY13PD5 + O2 = CYC5H5O. + O	7.73E15	-0.73	48.74
CY13PD5. + O2 = CYPDONE + OH	3.44E11	-0.01	25.32
CY13PD5. + O2 = COC=CKET + H	6.85E08	0.51	7.98
CY13PD5. + O2 = C=CC=C=O + HCO	1.16E19	-2.48	10.97
CPDOO. = C=CC=C=O + HCO	6.90E16	-2.73	17.62

Rate constants (log k) vs temperature

Reaction \ Temperature K	900	1000	1100	1200	1300
CY13PD5. + O2 = CPDOO.	10.422	10.191	10.006	9.851	9.718
CY13PD5. + O2 = COC=CC.CO	8.282	8.318	8.350	8.375	8.390
CY13PD5. + O2 = C.OC=CCCO	8.405	8.379	8.362	8.351	8.340
CY13PD5 + O2 = CYC5H5O. + O	1.897	3.050	3.985	4.766	5.424
CY13PD5. + O2 = COC=CKET + H	8.393	8.611	8.789	8.940	9.071
CY13PD5. + O2 = CYPDONE + OH	5.363	5.977	6.480	6.899	7.253
CY13PD5. + O2 = C=CC=C=O + HCO	9.070	9.224	9.338	9.425	9.494

Units: Ea and U in kcal/mol, for bimolecular reaction ; A and AT^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction A and AT^n in sec^{-1}.

Collision partner; N2.

radicals such as H, OH, and HO_2 to remove them from the radical pool or undergoes reaction to linear, resonance-stabilized, species.

Bimolecular (chemical activation) and unimolecular reaction of the adducts formed by O_2, H, OH, O, and HO_2 with cyclopentadienyl radical may be important to combustion models on aromatics and cyclopentadiene. We are not aware of any mechanism that predicts the various resonance-stabilized vinylic and carbonyl species that result from decomposition/destruction of cyclopentadienyl radical which we report in this study. Elementary reaction rate constants and reaction path analysis of cyclopentadienyl radical oxidation are not available. We are not aware of data on cyclopentadienyl radical oxidation reactions, other than that of Wang and Brezinsky,[18] where the elementary thermochemical paths or kinetic steps have been evaluated relevant to high-temperature oxidation.

This study focuses on the reaction pathways, thermodynamic properties, and kinetic analysis of cyclopentadienyl radical association with H, OH, O, HO_2, and O_2. The association reactions are in the falloff under combustion conditions, and the rates are further controlled by the radical concentrations. Cyclopentadienyl addition with oxygen molecules is shown to be a relatively slow reaction, but still an important consumption pathway in the combustion environment. The cyclopentadienyl reaction with O_2 to form vinyl ketene plus formyl radical is an important pathway in the C5 → C4 stage.

Thermodynamic Properties

Thermodynamic parameters $H_f{}^\circ{}_{(298)}$, S_{298} and $C_{p(300)}$ to $C_{p(1500)}$ for species in the reaction schemes are listed in Table 1 along with appropriate references. Molecular thermodynamic parameters are calculated primarily from group additivity[26] with peroxy and cyclic group parameters and from recent calculation studies.[27−29] Enthalpies of radicals are from evaluated literature on C−H or O−H bond energies and $\Delta H_f{}^\circ{}_{298}$ of the parent molecule, which has a hydrogen atom at the radical site. Entropies and $C_p(T)$ values are from use of hydrogen bond increments (HBI).[30] The HBI group technique is based on known thermodynamic properties of the parent molecule, enthalpy of reaction (bond energy), and calculated changes in S and $C_p(T)$ from loss or change in vibration frequencies, internal rotations, and symmetry and optical isomers that occur upon formation of a radical via loss of the H atom.

Kinetic Calculations. Unimolecular dissociation and isomerization reactions of the chemically activated and stabilized adducts resulting from addition or combination reactions are analyzed by first constructing potential energy diagrams. Thermodynamic parameters, $\Delta H_f{}^\circ{}_{(298)}$, $S^\circ{}_{298}$, $C_p(T)$, reduced vibration frequency sets, and Lennard-Jones parameters for species in each reaction path are presented.

High-pressure rate constants for each channel are obtained from literature or referenced estimation techniques. Kinetics parameters for unimolecular and bimolecular (chemical activation) reactions are then calculated using multifrequency QRRK analysis for $k(E)$.[31−33] The modified strong collision formalism of Gilbert et al.[34] is used for falloff (β collision) with the steady-state assumption on the energized adduct(s).

Reactions that incur a change in number of moles, such as unimolecular dissociation, have energy of activation calculated as ΔU_{rxn} plus an E_a for the reverse addition, where U is internal energy (E_a reverse is usually 0.0 for simple association reac-

TABLE 4: Activition Analysis Input Parameters; Cyclopentadienyl Oxidation Reaction System (Channel II); High Pressure Limited Constants

Reactants	Products	A(s^{-1}or cm^3/(mol*s)n	Ea.(Kcal/mol)
1 CY13PD5.+O2	CPDOO.	3.60E12 0.0	0.0
-1 CPDOO.	CY13PD5.+O2	4.03E13 0.0	12.26
2 CPDOO.	C5O2H5221	1.93E13 0.0	30.0
-2 C5O2H5221	CPDOO.	4.25E11 0.0	43.75
3 C5O2H5221	BOC5O.	4.65E09 0.0	28.72
-3 BOC5O.	C5O2H5221	3.55E13 0.0	37.38
4 BOC5O.	C5H5O2_1	1.11E15 0.0	10.0
-4 C5H5O2_1	BOC5O.	1.12E12 0.0	15.72
5 C5H5O2_1	COC=CC.CO	3.55E13 0.0	28.72
-5 COC=CC.CO	C5H5O2_1	1.13E12 0.0	60.54
6 COC=CC.CO	C.OC=CCCO	4.79E11 0.0	18.1
-6 C.OC=CCCO	COC=CC.CO	4.09E11 0.0	20.97
7 C.OC=CCCO	C=OCC.KET	3.55E13 0.0	6.64
-7 C=OCC.KET	C.OC=CCCO	1.69E13 0.0	1.0
8 C=OCC.KET	C=CC=C=O+HCO	3.66E12 0.0	31.19
-8 C=CC=C=O+HCO	C=OCC.KET	1.00E11 0.0	5.47
9 COC=CC.CO	COC=CKET+H	1.26E13 0.0	41.47
-9 COC=CKET+H	COC=CC.CO	4.82E13 0.0	2.7

Adduct	Frequency/Degeneracy (CPFIT) Geometry Mean/Degeneracy	Lennard-Jones parameters	
		σ (A)	ε / κ (K)
CPDOO.	250.8/4.757 923.4/17.544 2621.9/7.199 965.4/29.5	5.8	620
C5O2H5221	315.0/10.443 401.0/2.425 1250.5/17.132 705.9/30.0		
BOC5O.	789.6/9.973 801.6/10.560 2366.2/9.467 1122.4/30.0		
C5H5O2_1	483.4/9.223 800.2/10.002 2165.1/9.775 953.4/29.0		
C=OCC. KET	250.1/9.678 953.1/11.820 2479.0/7.002 765.3/28.5		
COC=CC.CO	377.8/9.866 977.7/10.936 2232.0/7.698 879.2/28.5		
C.OC=CCCO	410.7/10.772 1116.5/11.220 2535.3/6.508 922.6/28.5		

Species and note

CY13PD5. is cyclopentadienyl radical
CPDOO. is cyclopentadienylperoxy radical
C5O2H5221 is bicyclo[221] hexene peroxy radical
BOC5O. is cyclopentene-3,4-epoxy-5-oxy radical
C5H5O2_1 is 4,5-epoxy-2-pentenal-5yl radical,
C=OCC. KET is 3 ketene propane aldehyde 3yl radical
COC=CC.CO is 2-pentenedialdehyde 4yl radical
C.OC=CCCO is 2-pentenedialdehyde 1yl radical
CYC5H5O. is cyclopentadiene oxy radical
C=CC=C=O is vinyl ketene

References for high pressure limit rate constants and comments

k 1	A 1=3.60E12	Ea = 0 from C=CC. + O2 [1]; R = 8.92E-2; dU = -12.26
k-1	A-1=4.03E13	MR; E-a = -dU = 12.26
k 2	A 2=1.93E13	logA2 = 13.55-(4.3-1.7)/4.6 + log2 (loss one rotor and gain one optical isomer and degenecy 2); R = 45.4; dU = -13.75 Ea = 30 (MOPAC)
k-2	A-2=4.25E11	MR; E-a = 13.75 + 30 = 43.75
k 3	A 3=4.05E09	MR; R = 1.31E-4; dU = -8.56 Ea = 27(ring strain)- dU/2 + 6(addition) = 28.72,
k-3	A -3=3.55E13	logA-3 = 13.55 (TST); E-a = 28.72 + 8.56 = 37.38
k 4	A 4=1.11E15	MR; R = 985.3; dU = -5.72 Ea = 3(ring strain) + 7(addition) = 10, [1]
k-4	A-4=1.12E12	log A-4 = 13.55-(4.3x2-1.7)/4.6; E-a = 5.72 + 10 = 15.72
k 5	A5 = 3.55E13	logA5 = 13.55 TST; R=31.4; dU-5 = -31.72 Ea = 27(ring strain)- dU/2 + 6(addition) = 28.72,
k-5	A-5=1.13E12	MR; E-a = 60.54
k 6	A 6=4.79E11	MR; R = 1.17; dU = -2.87 Ea = 6(ring strain) + 12.1(E_{abs}) = 18.1 [1] E_{abs} = 13 - Δ H/3.3 Evens-Polanyi rule (Δ H = -2.87)
k-6	A-6=4.09E11	logA-6 = 13.55-(4.3-1.7)/4.6 (loss of one rotor and gain one optical isomer); E-a = 20.97
k 7	A 7=3.55E13	TST; R = 2.1; dU = 5.64; Ea = dU + 1 = 6.64
k-7	A-7=1.69E13	MR; E-a = 1.
k 8	A 8=3.66E12	MR; Ea = dU + 5.47 = 31.19; dU = 25.72; R = 36.6
k-8	A-8=1.00E11	E-a = 5.47 [4]

TABLE 4: (Continued)

k 9	A 9=1.26E13	from C3H5 to Allene + H [1]; Ea = dU + 2.7 = 41.47; dU= 38.77; R = 0.2613
k-9	A-9=4.82E13	MR; E-a = 2.7 [1]

$R=A_f/A_r$
MR; Microscopic Reversibility
TST; Transition State Theory

Units: Ea and U in kcal/mol, for bimolecular reaction ; A and AT^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction A and AT^n in sec^{-1}.

1 Bozzelli, J.W. and Dean, A.M.; J. Phys. Chem. **1993**, 97, 4427
2 Santiago O, and Albert S, J. Am. Chem. Soc. **1991**, 113, 8628
3 This work see test
4 Lesclaurc, C.; Roussel, P.; Veyret, B.; Pouchan, C.; J. Am. Chem. Soc. **1986**, 108, 3874

TABLE 5: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with O2 (channel II)

Rate constants k = A T^n exp(-Ea/RT)

Reaction	A	n	Ea
CY13PD5. + O2 = CPDOO.	1.54E13	-1.44	-5.80
CY13PD5. + O2 = COC=CC.CO	3.592EE	-3.68	35.06
CY13PD5. + O2 = C.OC=CCCO	5.69E46	-10.58	48.86
CY13PD5. + O2 = O=CCC.KET	4.81E46	-10.51	46.64
CY13PD5. + O2 = C=CC=C=O + HCO	1.94E33	-6.19	44.00
CY13PD5. + O2 = COC=CKET + H	3.3E25	-3.88	40.83

Rate constants (log k) vs Temperature

Reaction \ Temperature	900	1000	1100	1200	1300
CY13PD5. + O2 = CPDOO.	10.357	10.152	9.975	9.824	9.695
CY13PD5. + O2 = COC=CC.CO	3.167	3.853	4.395	4.835	5.201
CY13PD5. + O2 = C.OC=CCCO	3.618	4.327	4.854	5.259	5.583
CY13PD5. + O2 = O=CCC.KET	4.310	4.970	5.455	5.825	6.123
CY13PD5. + O2 = C=CC=C=O + HCO	4.324	5.118	5.728	6.219	6.630
CY13PD5. + O2 = COC=CKET + H	4.133	4.955	5.598	6.124	6.569

Units: Ea and U in kcal/mol; for bimolecular reaction, A and AT^n in cm^3 $mole^{-1}$ sec^{-1} , for unimolecular reaction, A and AT^n in sec^{-1}.

Collision partner; N2

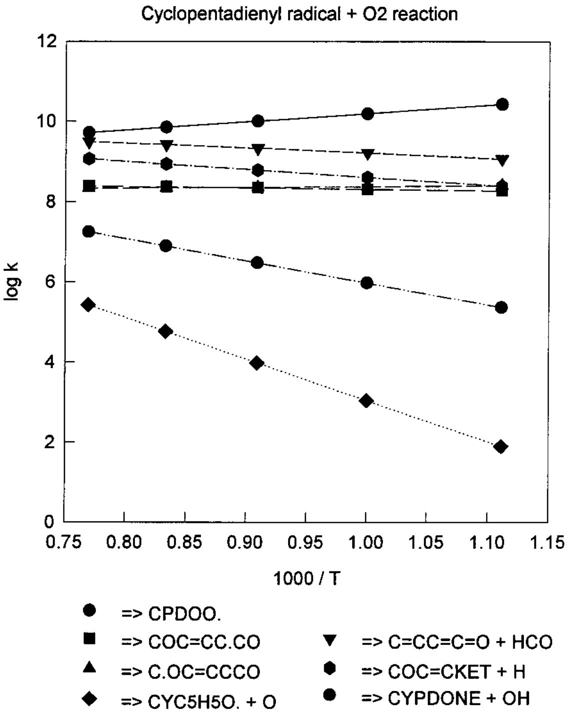

Figure 5. Cyclopentadienyl radical reaction with oxygen molecule rate constants calculated by QRRK β collision analysis; log(*k*) vs 1000/*T* at 1.0 atm pressure.

tions). Enthalpies and E_a's in the text and in PE diagrams are at 298 K, while those in the tables listing data input to the chemical activation reactions are for 1000 K, which we select as representative of modeled combustion experiments.

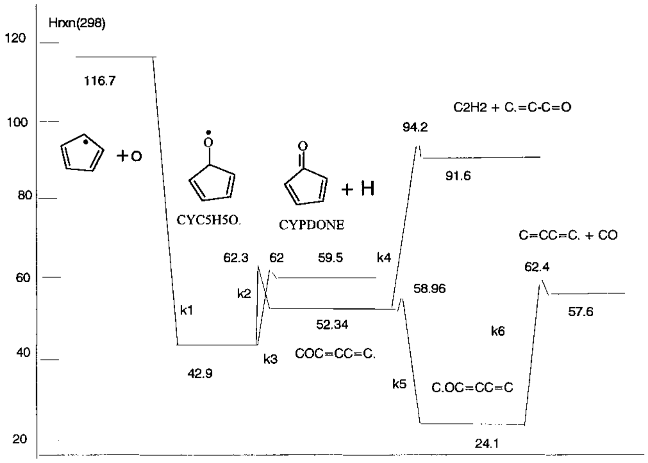

Figure 6. Potential energy diagram for cyclopentadienyl radical association with oxygen atom (channel 1). Ring-opening reaction is a β scssion reaction of the adduct with 19.4 kcal/mol activation energy at room temperature. Final products are 2,4-cyclopentadienone, 2,4-pentadienal-1-yl radical, 1,3-butadienyl radical, CO, and hydrogen atom.

Recent modifications to the quantum RRK calculation include (a) use of a manifold of three frequencies plus incorporation of one external rotation for the density of states, $\rho(E)/Q$ and in calculation of $k(E)$ and of $F(E)$; (b) calculation of the collision efficiency β_c with the calculated FE(T) factor instead of the previously assigned 1.15 value; β_c is now calculated from Gilbert et al.,[34] eq 4.7; (c) calculation of the

TABLE 6: Chemical Activition Analysis Input Parameters; Cyclopentadienyl + O Reaction System (Channel I); High Pressure Limit Rate Constant

Reactants	Products	A(s^{-1} or $cm^3/(mol*s)$	n	Ea. (Kcal/mol)
1 CY13PD5. + O	CYC5H5O.	6.03E13	0.0	0.0
-1 CYC5H5O.	CY13PD5. + O	1.25E15	0.0	72.5
2 CYC5H5O.	CYPDONE + H	2.00E14	0.0	18.68
-2 CYPDONE + H	CYC5H5O.	4.00E14	0.0	2.5
3 CYC5H5O.	COC=CC=C.	6.82E13	0.0	20.32
-3 COC=CC=C.	CYC5H5O.	4.79E11	0.0	10.0
4 COC=CC=C.	C.=CC=O + C2H2	2.51E13	0.0	42.47
-4 C.=CC=O + C2H2	COC=CC=C.	5.57E10	0.0	3.6
5 COC=CC=C.	C.OC=CC=C	4.79E11	0.0	6.62
-5 C.OC=CC=C	COC=CC=C.	1.45E12	0.0	35.0
6 C.OC=CC=C	C=CC=C. + CO	7.74E13	0.0	36.56
-6 C=CC=C. + CO	C.OC=CC=C	1.50E11	0.0	4.81

Adducts	Frequency(cm^{-1})/Degeneracy (CPFIT) Geometry Mean (cm^{-1})/Degeneracy	Lennard-Jones parameter σ (A) ε/k (K)
CYC5H5O.	686.2/14.037 1618.6/10.258 3562.9/2.705 1121.2/27.0	5.82 617
COC=CC=C.	403.4/9.612 984.5/10.689 2778.9/5.69 888.3/26.0	
C.OC=CC=C	413.3/8.787 921.6/10.625 2643.9/6.588 917.9/26.0	

Species and note

CY13PD5. is cyclopentadienyl radical
CYC5H5O. is cyclopentadiene oxy radical
CYPDONE is cyclopentadienone
COC=CC=C. is 2,4-pentadienal-5yl a vinyllic radical
C.=CC=O is 2-propenal-4yl radical
C.OC=CC=C is 2,4-pentadienal-1yl radical
C=CC=C. is 1,3 butadienyl radical

References for high pressure limit rate constants and comments

k 1	A 1 = 6.03E13	Ea = 0 as C=CC. + O; [1] R = 4.84E-2; dU = -72.5
k-1	A-1 = 1.25E15	MR; E-a = -dU = 72.5
k 2	A 2 = 2.00E14	Ea = 2.5 + dU = 18.68 as CH3O.-> CH2O+ H; [2]
		R = 0.5; dU = 16.18
k-2	A-2 = 4.00E14	MR; E-a = 2.5
k 3	A 3 = 6.82E13	MR; R = 142.4; dU = 10.32;
		Ea = dU + 10 = 20.32;
k-3	A-3 = 4.79E11	logA-3 = 13.55-4.3 x 2/4.6; (lose two rotors)
		E-a = 3(ring strain) + 7 (addition) = 10; [3]
k 4	A 4 = 2.51E13	Ea = dU+3.6=42.47; as C=CC=C. -> C2H2 + C2H3; [4]
		R = 450.3; dU = 38.87
k-4	A-4 = 5.57E10	MR; E-a = 3.6
k 5	A 5 = 4.79E11	logA 5 = 13.55-4.3 x 2/4.6 (lose two rotors);
		Ea = 1(ring strain) + 5.62(Habs) = 6.62
		R = 0.331; dU = -28.38
k-5	A-5 = 1.45E12	MR; E-a = -dU + 6.62 = 35.
k 6	A 6 = 7.74E13	MR; Ea = 4.81 + dU = 36.56; R=516.1; dU=31.75
k-6	A-6 = 1.50E11	E-a = 4.81 as C2H3 + CO; [5]

$R = A_f / A_r$
Habs; Abstraction Ea's are estimated as $13-|\Delta H|/3$ in exothermic reaction
MR; Microscopic Reversibility

Units; Ea and U in kcal/mol, for bimolecular reaction; A and A T^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction; A and A T^n in sec^{-1}

1 Tsang, W. J. Phys. Chem. Ref. Data, **1991**, 20, 221
2 Heicklen, J. Advances in Photochem. **1988**, 14, 177
3 Bozzelli, J.W. and Dean, A.M.; J. Phys. Chem. **1993**, 97, 4427
4 Dean, A.M.; J. Phys. Chem. **1985**, 89, 4603
5 Tsang, W.; Hampson, R.F. J. Phys. Chem. Ref. Data, **1986**, 15, 1087

Leonard-Jones collision frequency Z_{LJ} by the $Z_{LJ} = Z\ \Omega$ integral[35-37] obtained from the fit of Reid et al.[37]

The QRRK analysis with the "modified strong collision approach" and constant FE for falloff has been used to analyze a variety of chemical activation reaction systems, Westmoreland et al.,[31,38] Dean et al.,[39] Bozzelli et al.[40-42] There are a number of recent publications by other researchers that utilize the QRRK formalism with a more exact calculation of FE (as in this study) in the modified strong collision analysis[43-48] or utilize just a QRRK formalism.[49,50] Bauman notes its suitability for explanation of product ratios in ion–molecule reaction systems.[49] It is shown to yield reasonable results in these applications and provides a framework by which the effects of temperature and pressure can be evaluated.

Input Data Requirements for QRRK Calculation. High pressure limit preexponential factors (Arrhenius *A* factors, *A*(*T*)) for bimolecular addition and combination reactions are obtained from the literature and from trends in homologous series of

TABLE 7: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with O Atom

Rate constants k=A T^n exp(-EA/RT)

Reactions	A	n	Ea
CY13PD5. + O = CYC5H5O.	1.12E-12	5.87	-17.31
CY13PD5. + O = C.OC=CC=C	7.18E02	1.54	-14.06
CY13PD5. + O = H + CYPDONE	5.81E13	-0.02	0.02
CY13PD5. + O = CO + C=CC=C.	3.20E13	-0.17	0.44
CY13PD5. + O = C2H2 + C.=CC=O	8.22E-6	5.19	0.46
CYC5H5O. = H + CYPDONE	5.43E09	-0.17	5.86
CYC5H5O. = CO + C=CC=C.	2.27E42	-9.28	39.46
CYC5H5O. = C2H2 + C.=CC=O	3.46E-12	6.17	36.65

Rate constants (log k) vs Temperature

Reactions \ Temperature K	900	1000	1100	1200	1300
CY13PD5. + O = CYC5H5O.	9.592	9.411	9.339	9.275	9.236
CY13PD5. + O = C.OC=CC=C	10.817	10.552	10.330	10.153	10.016
CY13PD5. + O = H + CYPDONE	13.716	13.716	13.715	13.715	13.715
CY13PD5. + O = CO + C=CC=C.	12.911	12.914	12.916	12.917	12.917
CY13PD5. + O = C2H2 + C.=CC=O	10.143	10.390	10.616	10.821	11.006

Units; Ea and U in kcal/mol, for bimolecular reaction; A and A T^n in cm^3 $mole^{-1}sec^{-1}$ and for unimolecular reaction; A and A T^n in sec^{-1}

Collision partner, N2

reactions. *A* factors for isomerizations are obtained from transition-state theory, usually from the estimated entropy of the transition-state structure. Activation energies come from endothermicity of reaction and include ΔH_{rxn}, plus barriers by analogy with similar reactions with known energetics. Activation energies include analysis of Evans−Polanyi relationships for abstractions plus evaluation of ring strain energy when cyclic TSTs are present. Data on derivation of each rate coefficient are included in the table describing the reaction system.

The three vibration frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter[26] and Bozzelli et al.[51] Vibration frequency sets for the adducts are listed with the input parameters.

Lennard-Jones parameters, σ (Å) and e/k (K), are obtained from tabulations[37] and from a calculation method based on molar volumes and compressibility.[52]

Results and Discussion

Reaction with Oxygen Molecules. Cyclopentadienyl combines with oxygen molecules to form the chemically activated cyclopentadienyl−peroxy adduct (CPDOO$^\bullet$), which can either react back to reactants or to vinyl ketene plus formyl radical via 2-pentene dialdehyde intermediates as shown in Figures 2, 3, and 4. Stabilization of the cyclopentadienyl−peroxy adduct (CPDOO$^\bullet$) is negligible because of the rapid reverse reaction, due to entropy and the shallow well. This 13 kcal/mol well does not provide enough energy in formation of the activated complex (formation of a weak cyclopentadienyl C−OO$^\bullet$ bond) to drive the unimolecular dissociation to new products. The low E_a required for reverse reaction, combined with the relatively high *A* factor, makes reverse reaction the dominant pathway for dissociation of the cyclopentadienyl−peroxy adduct. A small, but important, fraction of the collisions react to form new products, as described below, mainly via the chemically activated peroxy adduct. Forward reaction occurs when the peroxy radical adds (intramolecular) to the adjacent unsaturated carbons (addition at the adjacent position is most important) to form the cyclopentene-3,4-cycloperoxy-5-yl radical (dioxitane, BICYC5$^\bullet$O2 − pathway I) or adds to the 2 position to form the bicyclo[2.2.1.]hexene peroxy radical (C5O2H5221) (pathway II).

Cyclopentanone plus OH is not an important channel, due to the estimated high barrier (37.3 kcal/mol) for ipso hydrogen abstraction by the peroxy radical through a four-member ring transition state. Alternatively, the weak peroxy O−O bond can cleave to form cyclopentadiene oxy radical plus an oxygen atom. This O−O bond cleavage reaction needs ca. 45 kcal/mol above the entrance channel and is only important above 1400 K.

Pathway I. Intramolecular Peroxy Radical Addition at the 2 Position. Intramolecular peroxy addition to an adjacent unsaturated carbon forms the cyclopentyl-3,4-cycloperoxy-5-yl radical (a dioxitane, BICYC5$^\bullet$O2), with an activation energy $E_a = dU + 10 = 17.6$ kcal/mol. This energy barrier between cyclopentadiene peroxy radical and cyclopentene-3,4-cycloperoxy-5-yl radical is the highest along the reaction pathway, Figure 3. The potential energy surface shows that most of the peroxy radical will decompose back to the initial reactants.

The energized cyclopentene-3,4-cycloperoxy-5-yl radical (BICYC5$^\bullet$O2) can react back to the peroxy radical with an estimated activation energy $E_a = 3$ (ring strain) + 7 (E_a addition) = 10 kcal/mol[28] or break an internal dioxitane C−C bond to form 1,3-cycloperoxyheptadien-5-yl radical (CYC5O2H5$^\bullet$) with an estimated activation energy $E_a = 10$ kcal/mol. This E_a is estimated from reverse reaction, which includes 3 kcal/mol for ring strain and 7 kcal/mol for addition of a carbonyl radical to a C═C double bond. High pressure limit rate constant parameters for the elementary reactions are listed in Table 2.

The 1,3-cycloperoxyheptadien-5-yl radical (CYC5O2H5$^\bullet$) once formed will rapidly cleave the weak O−O bond, opening the ring and forming strong carbonyl bonds. The initial product is a linear, resonance-stabilized, dicarbonyl radical O═C−C═C−C$^\bullet$−C═O. An important product is the result of H elimination from the carbonyl of this radical to O═C−C═C−C═C═O. The dialdehyde radical can also undergo an intramolecular H shift reaction, then dissociate to formyl radical (HCO) plus a stable vinyl ketene, as shown in Figure 3. The dicarbonyl radical formed (after isomerization) is the 2-pentenedialdehyd-4-yl radical (O═CC═CC$^\bullet$C═O), a carbon-centered radical that is lower in energy than its electronic isomer, an oxygen-centered (alkoxy) radical, 2,4-pentadienal-5-oxy radical (O═C−C═C−C═C−O$^\bullet$), Figure 3. The overall reaction is ca. 40 kcal/mol exothermic. The linear radicals are initially formed with ca. 73 kcal/mol excess energy above their ground state. The energized 2-pentenedialdehyd-4-yl (O═CC═CC$^\bullet$C═O) can abstract H from the carbonyl group (intramolecular reaction) to form the second dialdehyde radical. The internal 1,4 H shift reaction

TABLE 8: Chemical Activition Analysis Input Parameters; Cyclopentadienyl + O Reaction System (Channel II); High Pressure Limit Rate Constant

Reactants	Products	A(s^{-1} or cm^3/(mol*s))	n	Ea.(Kcal/mol)
1 CY13PD5. + O	CYC5H5O.	6.03E13	0.0	0.0
-1 CYC5H5O.	CY13PD5. + O	1.25E15	0.0	72.5
2 CYC5H5O.	CYPDONE + H	2.00E14	0.0	18.68
-2 CYPDONE + H	CYC5H5O.	4.00E14	0.0	2.5
3 CYC5H5O.	BICYC5H5O.	6.83E11	0.0	6.0
-3 BICYC5H5O.	CYC5H5O.	5.38E13	0.0	7.65
4 BICYC5H5O.	CYC5ODE	3.55E13	0.0	12.
-4 CYC5ODE	BICYC5H5O.	5.85E12	0.0	43.78
5 CYC5ODE	COC=CC=C.	8.86E14	0.0	50.75
-5 COC=CC=C.	CYC5ODE	4.79E11	0.0	7.0
6 COC=CC=C.	C.=CC=O+C2H2	2.51E13	0.0	42.47
-6 C.=CC=O+C2H2	COC=CC=C.	5.57E10	0.0	3.6
7 COC=CC=C.	C.OC=CC=C	4.79E11	0.0	6.62
-7 C.OC=CC=C	COC=CC=C.	1.45E12	0.0	35.0
8 C.OC=CC=C	C=CC=C.+CO	7.74E13	0.0	36.56
-8 C=CC=C.+CO	C.OC=CC=C	1.50E11	0.0	4.81

Adducts	Frequency(cm^{-1})/Degeneracy (CPFIT) Geometry Mean (cm^{-1})/Degeneracy	Lennard-Jones parameter σ (A) ε/k (K)
CYC5H5O.	686.2/14.037 1618.6/10.258 3562.9/2.705 1121.2/27.0	5.82 617
BICYC5H5O	769.4/8.685 801.1/8.685 2240.9/9.630 1141.1/27.0	
CYC5ODE.	743.2/10.448 737.9/6.867 1787.5/9.676 1016.1/27.0	
COC=CC=C.	403.4/9.612 984.5/10.689 2778.9/5.69 888.3/26.0	
C.OC=CC=C	413.3/8.787 921.6/10.625 2643.9/6.588 917.9/26.0	

Species and note

CY13PD5. is cyclopentadienyl radical
CYC5H5O. is cyclopentadiene oxy radical
CYPDONE is cyclopentadienone
BICYC5H5O. is cyclopenten-3,4-epoxy-5yl radical
CYC5ODE is pyran-1yl radical
C.=CC=O is 2-propenal-4yl radical
C.OC=CC=C is 2,4-pentadienal-1yl radical
COC=CC=C. is 2,4-pentadienal-5yl radical
C=CC=C. is 1,3 butadienyl radical

References for high pressure limit rate constants and comments

k 1	A 1 = 6.03E13	Ea = 0 as C=CC. + O; [1] R = 4.84E-2; dU = -72.5
k-1	A-1 = 1.25E15	MR; E-a = -dU = 72.5
k 2	A 2 = 2.00E14	Ea = 2.5 + dU = 18.68 as CH3O.-> CH2O+ H; [2] R=0.5; dU=16.18
k-2	A-2 = 4.00E14	MR; E-a=2.5
k 3	A 3 = 6.83E11	MR; Ea= 6 [3]; R=1.27E-2; dU=-1.65
k-3	A-3 = 5.38E13	[4] E-a= 6 - dU = 7.65
k 4	A 4 = 3.55E13	Ea = 12; [4] dU = -31.78; R = 6.073
k-4	A-4 = 5.85E12	MR; Ea = 12 - dU = 37.78
k 5	A 5 = 8.86E14	MR; Ea = dU + 7 = 50.75; dU=43.75; R=1853
k-5	A-5 = 4.79E11	log A-5 = 13.55-4.3 x2/4.6 (lose two rotors) E-a = 7 (addition); [5]
k 6	A 6 =2.51E13	Ea = dU + 3.6 = 42.47; from C*CC*C. -> C2H2 + C2H3 [6] R = 450.3; dU = 38.87
k-6	A-6 = 5.57E10	MR; E-a = 3.6
k 7	A 7 = 4.79E11	logA 7= 13.55-4.3 x 2/4.6 (lose two rotors); Ea = 1(ring strain) + 5.62(Habs) = 6.62; R = 0.331; dU = -28.38
k-7	A-7 = 1.45E12	MR; E-a = -dU + 6.62 = 35.
k 8	A 8 = 7.74E13	MR; Ea = 4.81 + dU = 36.56; R = 516.1; dU = 31.75
k-8	A-8 = 1.50E11	E-a = 4.81 as C2H3 + CO; [7]

$R = A_f / A_r$
Habs; Abstraction Ea's are setimated as 13-| ΔH | /3 in exothemric reaction
MR; Microscopic Reversibility

Units; Ea and U in kcal/mol, for bimolecular reaction; A and A T^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction; A and A T^n in sec^{-1}

Reference

1 Tsang, W. J. Phys. Chem. Ref. Data, **1991**, 20, 221
2 Heicklen, J. Advances in Photochem. **1988**, 14, 177
3 Santiago, O., Albert, S.; J. Am. Chem. Soc. **1991**, 113, 8628
4 This work see test
5 Bozzelli, J. W.; Dean, A, M.; J. Phys. Chem. **1993**, 97, 4427
6 Dean, A, M.; J. Phys. Chem. **1985**, 89, 4603
7 Tsang.W,; Hampson, R.F. J. Phys. Chem. Ref. Data, **1986**, 15, 1087

TABLE 9: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with O Atom

Rate constants k = A T^n exp(-Ea/RT)

Reactions	A	n	Ea
CY13PD5. + O = CYC5H5O.	8.05E11	-0.69	-1.00
CY13PD5. + O = CYC5ODE.	1.44E30	-6.83	-0.92
CY13PD5. + O = C.OC=CC=C	5.42E06	0.03	-12.18
CY13PD5. + O = H + CYPDONE	5.71E13	0.01	0.00
CY13PD5. + O = CO + C=CC=C.	2.54E17	-1.71	2.19
CY13PD5. + O = C2H2 + C.=CC=O	6.27E-4	4.19	0.81

Rate constants (log k) vs Temperature

Reactions \ Temperature K	900	1000	1100	1200	1300
CY13PD5. + O = CYC5H5O.	10.119	10.061	10.015	9.974	9.933
CY13PD5. + O = CYC5ODE.	10.190	9.865	9.555	9.277	9.037
CY13PD5. + O = C.OC=CC=C	9.780	9.493	9.246	9.043	8.879
CY13PD5. + O = H + CYPDONE	13.775	13.775	13.776	13.776	13.776
CY13PD5. + O = CO + C=CC=C.	11.834	11.809	11.782	11.754	11.725
CY13PD5. + O = C2H2 + C.=CC=O	8.992	9.202	9.393	9.565	9.721

Units; Ea and U in kcal/mol, for bimolecular reaction; A and A T^n in cm^n mole^{-1} sec^{-1} and for unimolecular reaction; A and A T^n in sec^{-1}

Collision partner, N2

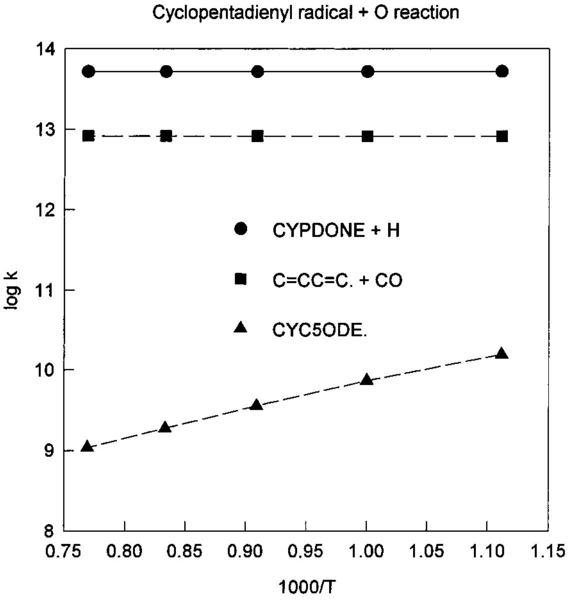

Figure 7. Cyclopentadienyl radical reaction with oxygen atom rate constants calculated by QRRK β collision analysis; log(k) vs 1000/T at atmospheric pressure.

(five-member-ring transition state) has an estimated activation energy E_a = 6 (ring strain) + 12 (abstraction) = 18 kcal/mol to form 2-pentenedialdehyd-1-yl radical (O=C$^•$C=CCC=O). An alternate H shift reaction (4,5 H shift) has a three-member-ring transition state and an estimated activation energy E_a = 26 (ring strain) + 12 (abstraction) = 38 kcal/mol to form 2-pentenedialdehyd-5-yl radical (O=CC=CCC$^•$=O). This 4,5 H shift reaction is not included in the calculation due to its higher barrier.

The 2-pentenedialdehyd-1-yl radical (O=C$^•$C=CCC=O) can dissociate to vinyl-1,3 ketene (C=CC=C=O) plus formyl radical (HCO) with an activation energy 5.5 kcal/mol above the H_{rxn}. The A factor is estimated from the reverse reaction.

Pathway II. Intramolecular Peroxy Radical Addition to the 3 Position. The cyclopentadienyl peroxy radical (CPDOO$^•$) can undergo intramolecular addition to the double bond at the 3 position, which is exothermic, and forms a bicyclo[2.2.1.]-hexene peroxy radical (C5O2H5221), Figure 4, path II. The activation energy is estimated as 30 kcal/mol. The high E_a is due to the significant rotation (twist) in the double bond for peroxy radical attack on the π bond to occur. The bicyclo-[2.2.1.]hexene peroxy radical (C5O2H5221) has the radical site at the secondary carbon (C/C2/H2). Forward reaction results in O−O cleavage with C=O carbonyl bond formation to form cyclopenten-3,4-epoxy-5-oxy radical (BOC5O$^•$) with an esti-

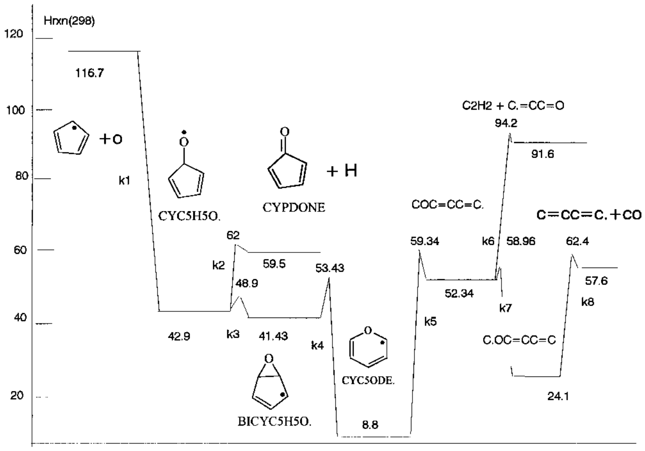

Figure 8. Potential energy diagram for cyclopentadienyl radical association with oxygen atom (channel 2): isomerization, ring-opening, and β scssion reactions. Final products are 2,4-cyclopentadienone plus H, 2,4-pentadienal-1-yl radical, and 1,3-butadienyl radical plus CO.

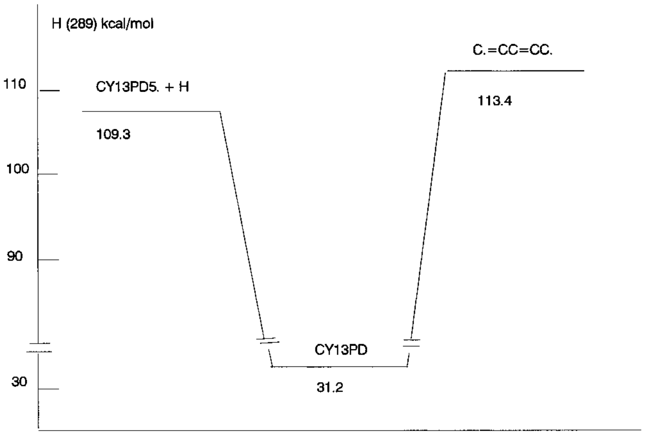

Figure 9. Potential energy diagram for cyclopentadienyl radical association with hydrogen. Stabilized cyclopentadiene is the primary product.

TABLE 10: Chemical Activition Analysis Parameters; CY13PD5$^•$ + H Reaction System; High Pressure Limited Constants

Reactants	Products	A(s^{-1} or cm^3/(mol*s)	n	Ea.(Kcal/mol)
1 CY13PD5. + H	CY13PD5	3.20E14	0.0	0.0
-1 CY13PD5	CY13PD5. + H	2.15E15	0.0	77.91
2 CY13PD5	C.=C-C=C-C.	5.52E14	0.0	83.09
-2 C.=C-C=C-C.	CY13PD5	4.79E11	0.0	0.0

Adduct	Frequency(cm^{-1})/Degeneracy (CPFIT) Geometry Mean (cm^{-1})/ Degeneracy	Lennard-Jones Parameters σ (A) ε/k (K)
CY13PD	707.6/11.136 1405.8/10.711 3186.9/5.15 1238.2/27.0	5.25 483

Species and note

CY13PD5. is cyclopentadienyl radical
CY13PD is cyclopentadiene
C.=C-C=C-C. is 1,3 pentadiene diradical -singlet

References for high pressure limit rate constant and comments

k 1 A 1=3.20E14 as C=C-C=C. + H ;[1] Ea = 0; R = 0.148; dU = -77.91
k-1 A-1=2.16E15 MR; E-a = 77.91
k 2 A 2=5.52E14 MR; Ea = dU = 83.09; R= 1152
k-2 A-2=4.79E11 log A-2 = 13.55- 4.3 x 2 / 4.6 (loss of two rotors); E-a=0

1. Dean, A.M. J. Phys. Chem. **1985**, 89, 4600.

R = A_f/A_r
MR; Microscopic Reversibility

Units: Ea and dU in kcal/mol; for bimolecular reaction, A and AT^n in cm^3 $mole^{-1}$ sec^{-1} , for unimolecular reaction, A and AT^n in sec^{-1}.

TABLE 11: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with O2

Rate constant, k = A T^n exp($-E_a/RT$)

Reaction	A	n	E_a
CY13PD5. + H => CY13PD5	9.908E31	-5.12	9.79
CY13PD5. + H => C.=C-C=C-C.	9.096E20	-5.26	36.01

Collision partner, N2

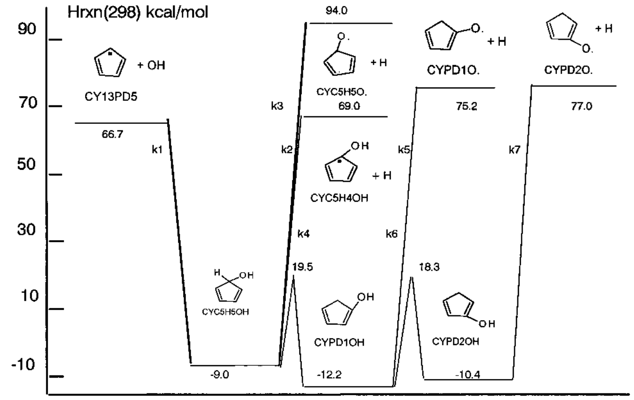

Figure 10. Potential energy diagram for cyclopentadienyl radical association with hydroxyl radical. Cyclopentadienol, cyclopentadien-1-ol, and cyclopentadien-2-ol are major products.

mated activation energy E_a = 27 (ring strain) − 4.3 ($\Delta U_{rxn}/2$) + 6 (E_a addition) = 28.7 kcal/mol.

The cyclopenten-3,4-epoxy-5-oxy radical is 36 kcal/mol lower than the entrance channel, and the chemically activated intermediate can open the cyclopentene ring to form 4,5-epoxy-2-pentenal-5-yl radical (C5H5O2_1) with the activation energy E_a = 3 (ring strain) + 7 (E_a addition) = 10 kcal/mol, as estimated from the reverse addition reaction.

The 4,5-epoxy-2-pentenal-5-yl radical with about 42 kcal/mol excess energy can cleave a strained bond in the epoxy ring to form the energized 2-pentenedialdehyd-4-yl radical (O=CC=CC$^•$C=O). The subsequent reactions are discussed under pathway I (above).

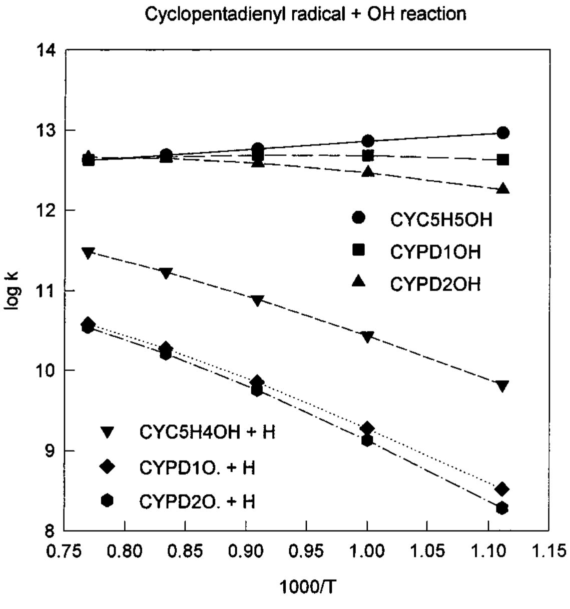

Figure 11. Rate constants of cyclopentadienyl radical combination with hydroxyl radical calculated by QRRK β collision analysis; log(k) vs 1000/T at atmospheric pressure.

Intramolecular peroxy addition to both the 1 position and 2 position results in formation of similar intermediates (linear, conjugated, unsaturated dicarbonyls) and final products. Reactions in pathway II have low reaction rates to the linear intermediates, about 3 orders of magnitude lower than reactions in pathway I, due to the high E_a for transition states in steps k2 and k3, Figure 4. The energy level diagrams for cyclopenta-

TABLE 12: Chemical Activition Analysis Input Parameters; Cyclopentadienyl Plus OH Reaction; High Pressure Limit Rate Constants

Reactants	Products	A(s^{-1} or cm^3/(mol*s)	n	Ea.(Kcal/mol)
1 CY13PD5+OH	CYC5H5OH	1.51E13	0.0	0.0
-1 CYC5H5OH	CY13PD5+OH	1.09E15	0.0	74.12
2 CYC5H5OH	CYC5H4OH+H	6.00E14	0.0	77.94
-2 CYC5H4OH+H	CYC5H5OH	4.62E13	0.0	0.0
3 CYC5H5OH	CYC5H5O.+H	1.09E16	0.0	103.66
-3 CYC5H5O.+H	CYC5H5OH	4.08E15	0.0	0.0
4 CYC5H5OH	CYPD1OH	1.34E11	0.0	28.5
-4 CYPD1OH	CYC5H5OH	1.19E11	0.0	31.75
5 CYPD1OH	CYPD1O.+H	6.00E14	0.0	87.43
-5 CYPD1O.+H	CYPD1OH	1.21E14	0.0	0.0
6 CYPD1OH	CYPD2OH	1.34E11	0.0	30.5
-6 CYPD2OH	CYPD1OH	7.40E10	0.0	28.91
7 CYPD2OH	CYPD2O.+H	6.00E14	0.0	87.44
-7 CYPD2O.+H	CYPD2OH	1.19E14	0.0	0.0

Adducts	Frequency/Degeneracy (CPFIT) Geometry Mean/ Degeneracy	Lennard-Jones parameter σ (A) ε/k (K)
CYC5H5OH	654.0/14.476 1561.9/11.26 3613.3/3.765 1134.0/29.5	5.5 450
CYPD1OH	670.1/14.800 1587.7/10.994 3999.3/3.705 1156.6/29.5	
CYPD2OH	612.9/12.603 1581.0/13.793 3999.8/3.104 1162.9/29.5	

Species and note

CY13PD5. is cyclopentadienyl radical
CYC5H5OH is cyclopentadienol
CYC5H4OH is cyclopentadienol-1yl radical
CYC5H5O. is cyclopentadiene oxy radical
CYPD1OH is cyclopentadiene-1ol
CYPD1O. is cyclopentadiene-1oxyl
CYPD2OH is cyclopentadiene-2ol
CYPD2O. is cyclopentadiene-2oxyl

References for high pressure limit rate constants and comments

k 1	A 1 =1.51E13	Ea = 0.0 as allyl plus OH; [1] R = 1.388E-2; dU = -74.12
k-1	A-1 =1.08E15	MR; E-a = -dU = 74.12
k 2	A 2 =6.00E14	as cyclopentadiene to cyclopentadienyl plus H; [2] R = 13; Ea = dU = 77.94
k-2	A-2 =4.62E13	MR; E-a = 0.0
k 3	A 3 =1.09E16	as phenol to phenoxy plus H; [3] R = 2.671; Ea = dU = 103.66
k-3	A-3= 4.08E15	MR; E-a = 0.0
k 4	A 4 =1.34E11	TST; Ea = 28.5; [4] R = 1.125; dU = -3.25
k-4	A-4= 1.19E11	MR; E-a = 28.5 -dU = 31.75
k 5	A 5= 6.00E14	as cyclopentadiene to cyclopentadienyl plus H; [2] R = 4.97; Ea = dU = 87.43
k-5	A-5=1.21E14	MR; E-a = 0.0
k 6	A 6=1.34E11	TST; dU = 1.59; R = 1.81; Ea = 30.5; [4]
k-6	A-6=7.40E10	MR; E-a = 28.91
k 7	A 7=6.00E14	as cyclopentadiene to cyclopentadienyl plus H; [2] R = 5.028; Ea = dU = 87.44
k-7	A-7=1.19E14	MR; E-a = 0

$R = A_f/A_r$
MR; Microscopic Reversibility
TST; Transition State Theory

Units: Ea and dU in kcal/mol; for bimolecular reaction, A and AT^n in cm^3 $mole^{-1}$ sec^{-1} , for unimolecular reaction, A and AT^n in sec^{-1}.

1. Tsang.W; J. Phys. Chem. Ref. Data, **1991**, 20, 221-274
2. Ritter E.R., Bozzelli, J.W.; J. Phys. Chem. **1990**, 94, 2493
3. Manion, J.A.; Louw, B. J.. Phys. Chem. **1989**,93,3563
4. Melius.C, Coluin, M.C., Marinov.N., Pitz,W., Senkan,S., Twenty-Sixth Symp (Int'l) on Combustion **1996**, pp 234

dienyl reaction with oxygen molecules are shown in Figures 3 and 4, where formation of the stabilized peroxy adduct is only ca. 13 kcal/mol exothermic due to loss of resonance.

Input parameters for the cyclopentadienyl oxidation reactions and respective references are listed in Tables 2 and 4. Tables 3−5 show the estimated rate constant of cyclopentadienyl−oxygen reaction from 900 to 1300 K. Figure 5 shows the calculated rate constants for major products vs 1000/*T* at atmosphere pressure. Important rate constants calculated by the QRRK/falloff code (chemdis) are listed in the submodel, and Table 17. This ring-opening reaction is an important path in the overall oxidation of benzene and substituted benzene, where cyclopentadienyl radical is the direct product of phenoxy degradation and is present in high concentrations relative to other active species. The chemical activation analysis shows that reaction of cyclopentadienyl with O_2 serves as an important path to linear C5 and C4 species. The stabilized 2-pentenedialdehyde radicals can further react with O_2 to form smaller oxides.

The 2-pentenedialdehyd-1-yl radical (O=C$^•$C=CCC=O) can undergo an internal 1,5 H shift via a six-member-ring transition

TABLE 13: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with OH Radical

Rate constants k = A T^n exp(-Ea/RT)

Reactions	A	n	Ea
CY13PD5. + OH = CYC5H5OH	6.49E14	-0.85	-2.73
CY13PD5. + OH = CYC5H4OH + H	3.51E57	-12.18	48.35
CY13PD5. + OH = CYPD1OH	1.15E43	-8.76	18.73
CY13PD5. + OH = CYPD1O. + H	2.22E69	-15.58	60.99
CY13PD5. + OH = CYPD2OH	1.06E59	-13.08	33.45
CY13PD5. + OH = CYPD2O. + H	5.94E82	-19.33	71.55

CY13PD5. + OH = CYC5H5O. + H	1.36E51	-10.46	57.10
CYC5H5OH = CYC5H5O. + H	7.89E35	-6.33	110.65

Rate constants (log k) vs Temperature

Reactions \ Temperature K	900	1000	1100	1200	1300
CY13PD5. + OH = CYC5H5OH	12.958	12.859	12.764	12.685	12.622
CY13PD5. + OH = CYC5H4OH + H	9.819	10.430	10.893	11.233	11.483
CY13PD5. + OH = CYPD1OH	12.622	12.677	12.686	12.664	12.623
CY13PD5. + OH = CYPD1O. + H	8.516	9.278	9.852	10.273	10.582
CY13PD5. + OH = CYPD2OH	12.248	12.463	12.586	12.644	12.659
CY13PD5. + OH = CYPD2O. + H	8.281	9.130	9.756	10.209	10.538
CY13PD5. + OH = CYC5H5O. + H	6.363	7.270	7.973	8.521	8.959

Units: Ea and U in kcal/mol; for bimolecular reaction, A and AT^n in cm^3 mole^{-1} sec^{-1} , for unimolecular reaction, A and AT^n in sec^{-1}.

Collision partner, N2

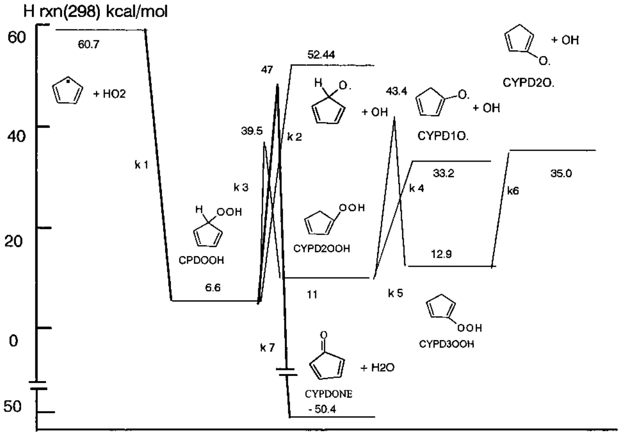

Figure 12. Potential energy level diagram for cyclopentadienyl radical association with HO_2. The energized cyclopentadienyl hydroperoxide will dissociate to cyclopentadienoxy radical plus hydroxyl radical or dissociate to H_2O plus cyclopentadienone through low-energy channels before being collision stabilized.

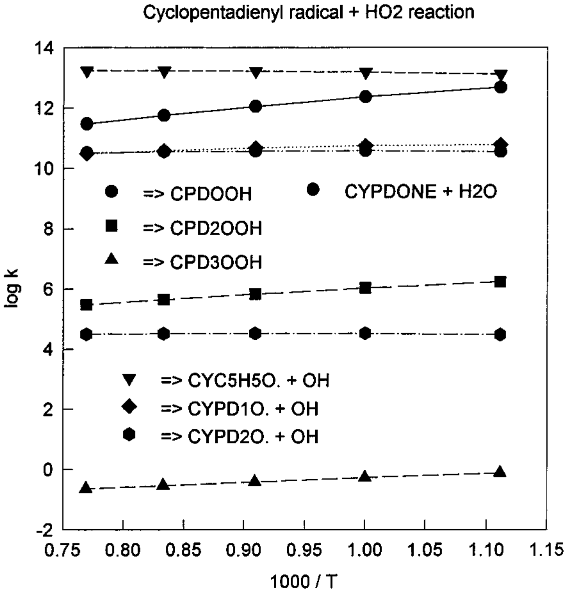

Figure 13. Rate constants of cyclopentadienyl radical combination with HO_2 calculated by QRRK β collision analysis; log(*k*) vs 1000/*T* at atmospheric pressure.

state with an estimated activation energy E_a = 1 (ring strain) + 12 (abstraction) = 13 kcal/mol to form 2-pentenedialdehyd-5-yl radical (O=CC=CCC•=O), Figure 4. Transition-state analysis shows that this reaction path has a low *A* factor due to loss of three rotors.

Reaction of O_2 with cyclopentadienyl radical is important. The reaction forms an energized adduct which is either stabilized or dissociates back to reactants; only a small fraction of the collisions lead to further reaction. The two reactants are, however, present in relatively high concentrations in a typical aromatic oxidation process, and a pseudoequilibrium exists. The continued combination/dissociation process leads to conversion via the fraction of reactions that undergo intramolecular addition of the energized peroxy radical to the unsaturated carbons and further reaction.

Reaction with Oxygen Atoms. $O^{(3P)}$ addition to cyclopentadienyl radical forms the energized cyclopentadienoxy radical adduct (CYC5H5O•) with ca. 73.8 kcal/mol excess energy above the ground state; this adduct can undergo β scission (elimination reaction) to the H atom plus cyclopentadienone as one important reaction channel, Figure 6. A second reaction pathway is ring-opening to 2,4-pentadienal-5-yl, a vinylic radical (C•=CC=CC=O). This energized intermediate has ca. 64 kcal/mol excess energy above its ground state and can isomerize to the lower energy, resonance-stabilized, 2,4-pentadienal-1-yl radical (C=CC=CC•=O). This 2,4-pentadienal-1-yl radical (C=CC=CC•=O) will dissociate to CO plus butadienyl radical. The 2,4-pentadienal-5-yl radical (C•=CC=CC=O) can also undergo β scission reaction to form acetylene plus 2-propenal-4-yl radical (C•=CC=O). These reactions are exothermic with energy barriers below the entrance channel. The branching ratio is determined by the entropy (tightness) of transition states.

These reactions are limited by oxygen atom concentration and will have important contribution to the combustion system under fuel-lean and stoichiometric conditions at high temperatures. The input high pressure limit rate constant parameters

TABLE 14: Chemical Activition Analysis Input Parameters; CY13PD5$^\bullet$ + HO_2 Reaction; High Pressure Limit Rate Constants

High Pressure Limit Rate Constants

Reactants	Products	A(s^{-1} or cm^3/(mol*s)	n	Ea.(Kcal/mol)
1 CY13PD5.+HO2	CPDOOH	1.80E13	0.0	0.0
-1 CPDOOH	CY13PD5.+HO2	7.07E14	0.0	50.79
2 CPDOOH	CYC5H5O.+OH	4.00E15	0.0	44.27
-2 CYC5H5O.+OH	CPDOOH	1.34E14	0.0	0.0
3 CPDOOH	CYPD2OOH	1.34E11	0.0	32.62
-3 CYPD2OOH	CPDOOH	2.19E11	0.0	28.5
4 CYPD2OOH	CYPD1O. + OH	4.00E15	0.0	20.68
-4 CYPD1O. + OH	CYPD2OOH	3.90E13	0.0	0.0
5 CYPD2OOH	CYPD3OOH	1.34E11	0.0	32.08
-5 CYPD3OOH	CYPD2OOH	7.38E10	0.0	30.5
6 CYPD3OOH	CYPD2O. + OH	4.00E15	0.0	20.70
-6 CYPD2O. + OH	CYPD3OOH	3.86E13	0.0	0.0
7 CPDOOH	CYPDONE + H2O	2.00E12	0.0	40.4
-7CYPDONE+H2O	CPDOOH	1.14E12	0.0	98.7

Adducts	Frequency/Degeneracy (CPFIT) Geometry Mean/ Degeneracy	Lennard-Jones parameters σ (A)	ε / κ (K)
CPDOOH	250.1/5.58 937/19.454 2518.6/6.966 923/32.	5.2	425
CYPD2OOH	610.8/ 17.516 1629.0/11.121 3533.7/3.362 1033.3/32.0		
CYPD3OOH	578.9/16.096 1640.8/13.020 3995.4/2.883 1052.7/32.0		

Species and note

CY13PD5. is cyclopentadienyl radical
CPDOOH is cyclopentadienylicperoxide
CYC5H5O. is cyclopentadiene oxy radical
CYPD2OOH is 2-cyclopentadienylicperoxide
CYPD1O. is cyclopentadiene-1oxyl
CYPD3OOH is 3-cyclopentadienylicperoxide
CYPD2O. is cyclopentadiene-2oxyl
CYPDONE is cyclopentadienone

References for high pressure limit rate constants and comments

k 1	A 1=1.80E13	Ea = 0.0; from CH3 + HO2; [1] R = 2.544E-2; dU = -50.79
k-1	A-1=7.08E14	MR; E-a = 50.79
k 2	A 2=4.00E15	CH3OOH -> CH3O. + OH; [1] R = 29.85; Ea = dU = 44.27
k-2	A-2=1.34E14	MR; E-a = 0
k 3	A 3=1.34E11	TST; R = 0.6107; dU = 4.12; Ea = 4.12 + 28.5 = 32.62
k-3	A-3=2.19E11	MR; E-a = 28.5
k 4	A 4=4.00E15	CH3OOH -> CH3O. + OH; [1] R = 102.6; Ea = dU = 20.68
k-4	A-4=3.90E13	MR; E-a=0
k 5	A 5=1.34E11	TST; R = 1.816; dU = 1.58; Ea = 1.58 + 30.5 = 32.08
k-5	A-5=7.38E10	MR; E-a = 30.5
k 6	A 6=4.00E15	CH3OOH -> CH3O. + OH ;[1] R = 103.6; Ea = dU = 20.70
k-6	A-6=3.86E13	MR; E-a=0
k 7	A 7=2.00E12	TST; R = 1.75; dU = -58.3; Ea = 40.4
k-7	A-7=1.14E12	MR; Ea = 98.4

$R = A_f / A_r$
MR; Microscopic Reversibility
TST; Transition state theory

Units; Ea and dU in kcal/mol, for bimolecular reaction; A and A T^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction; A and A T^n in sec^{-1}

1 Baulch,D.L.; Cobos,C.J.; Cox,R.A.; Esser,C.; Frank,P.; Just,Th.; Kerr,J.A.; Pilling, M.J.; Troe,J.; Walker,R.W.; Warnatz, J.; J. Phys. Chem. Ref. Data **1992**, 21, 411-429

are listed in Table 6. The calculated rate constants at atmospheric pressure are listed in the Table 7a.

The pyran-1-yl radical (CYC5ODE$^\bullet$) may be formed as an additional product, Figure 6b. The cyclopentadienoxy radical can form the cyclopenten-3,4-epoxy-5-yl radical (BICYC5H5O$^\bullet$) with an estimated 6 kcal/mol activation energy. The cyclopenten-3,4-epoxy-5-yl internal C−C bond cleavage leads to the pyran-1-yl radical with an estimated activation energy of 12 kcal/mol. The pyran-1-yl radical is resonance stabilized and can continue to react with O_2 to form smaller oxides. The pyran-1-yl can also undergo ring-opening reaction leading to 2,4-pentadienal-5-yl radical (C$^\bullet$=CC=CC=O) with an activation energy $E_a = 43.75$ (dU) + 7 (addition) = 50.75 kcal/mol. The subsequent reaction of this aldehyde radical is discussed above. The QRRK calculation shows that this reaction channel is not important compared with the β scission reaction (H atom elimination). The input high pressure limit parameters are listed in Table 8. The calculated rate constants at atmospheric pressure are listed in the Table 9. Figure 7 shows the calculated rate constants of major products vs 1000/T at atmosphere pressure.

Cyclopentadienyl Radical and H atom Association Reaction. The association of the hydrogen atom with cyclopentadienyl radical initially forms an energized cyclopentadiene. The

TABLE 15: QRRK Calculated Rate Constants for Cyclopentadienyl Radical Association with HO_2 Radical

Rate constant k = A T^{n} exp(-Ea/RT)

Reactions	A	n	Ea
CY13PD5. + HO2 = CPDOOH	1.08E50	-11.88	9.21
CY13PD5. + HO2 = CPD2OOH	1.54E27	-6.73	4.34
CY13PD5. + HO2 = CPD3OOH	1.13E06	-2.26	-2.12
CY13PD5. + HO2 = CYC5H5O. + OH	6.27E29	-4.69	11.65
CY13PD5. + HO2 = CYPD1O. + OH	5.53E45	-10.35	18.05
CY13PD5. + HO2 = CYPD2O. + OH	1.16E24	-5.62	12.19
CY13PD5. + HO2 = CYPDONE + H2O	1.19E33	-6.52	13.40
CPDOOH = CYC5H5O. + OH	7.20E65	-15.51	63.69

Rate constant (log k) vs Temperature

Reactions \ Temperature K	900	1000	1100	1200	1300
CY13PD5.+HO2=CPDOOH	12.684	12.374	12.056	11.754	11.481
CY13PD5.+HO2=CPD2OOH	6.235	6.038	5.840	5.655	5.487
CY13PD5.+HO2=CPD3OOH	-0.122	-0.269	-0.412	-0.535	-0.637
CY13PD5.+HO2=CYC5H5O. + OH	13.114	13.188	13.220	13.234	13.240
CY13PD5.+HO2=CYPD1O. + OH	10.789	10.761	10.685	10.590	10.491
CY13PD5.+HO2=CYPDONE+H2O	10.557	10.590	10.581	10.554	10.521
CY13PD5.+HO2=CYPD2O. + OH	4.485	4.530	4.534	4.521	4.503

Units; Ea and U in kcal/mol, for bimolecular reaction; A and A T^{n} in cm^{3} mole^{-1} sec^{-1} and for unimolecular reaction; A and A T^{n} in sec^{-1}

Collision partner, N2

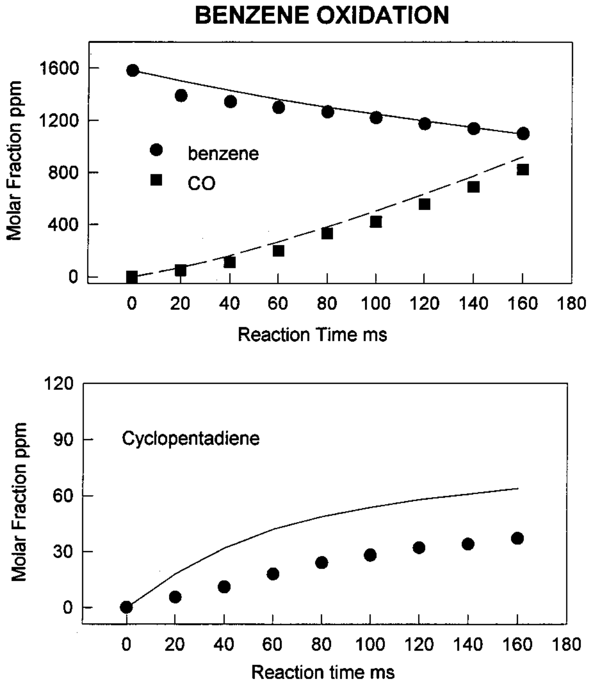

Figure 14. Comparison of model prediction with experimental data on benzene oxidation at constant temperature. Product levels reported by Lovell et al.[1] (symbols), at 1 atm pressure, 1097 K (average) temperature, $\phi = 1.36$, (fuel rich). Lines are model prediction.

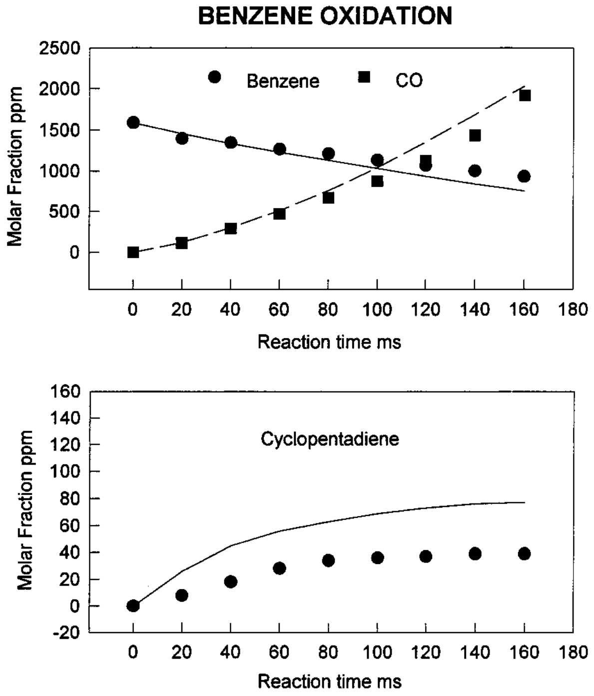

Figure 15. Comparison of model prediction with experimental data on benzene oxidation at constant temperature. Product levels reported by Lovell et al.[1] (symbols), at 1 atm pressure, 1100 K (average) temperature, $\phi = 1.0$, (stoichiometric). Lines are model prediction.

lowest energy dissociation reaction channel accessible to the energized cyclopentadiene is the reverse reaction, back to the H atom plus cyclopentadienyl radical. Other elimination pathways such as molecular elimination to H_2 plus a cyclic 1,3 vinyl acetylene or cyclic allene, and cleavage of a resonance-stabilized vinyl C−H or C−C bond all have endothermicities (relative to the stabilized adduct) of about 100 kcal/mol.

The H atom combination reaction is exothermic (−78 kcal/mol), and the QRRK analysis indicates that this reaction leads to collision stabilization. Ritter et al.[13] estimate the rate constant for the reverse reaction. Cyclopentadiene dissociation to cyclopentadienyl plus H has a rate constant $k = 5.96 \times 10^{14} \exp(-75100/RT)$. Ring-opening to a resonance-stabilized 1,4-pentadiene diradical ($C^{\bullet}{=}CC{=}CC$. $\Delta H_f°_{(298)} = 113.4$ kcal/mol) is endothermic, relative to the reactants.

Melius[25] has shown that the H atoms of the sp^{3} carbon of CyC5H6 can undergo isomerization reaction (move around the ring) with an E_a only on the order of 30 kcal/mol, well below the energy of the cyclopentadiene formed. This isomerization does not lead to new products.

The potential energy level diagram is shown in Figure 9. The input high pressure limit rate constants are listed in Table 10. The QRRK analysis shows that the dissociation reaction (the reverse reaction of the association reaction) rate constant is very close to its high-pressure limit (at atmospheric pressure), and

TABLE 16: Submodel of Cyclopentadiene Oxidation

Reaction		A	n	Ea	Ref
CY13PD + HCO	= CY13PD5. + CH2O	1.08E08	1.9	16000.0	a
CY13PD + HO2	= CYC5H7_1 + O2	1.33E15	-1.07	9530.0	b
CY13PD + HO2	= CY13PD5. + H2O2	1.10E04	2.6	12900.0	a
CY13PD + O2	= CY13PD5. + HO2	4.00E13	0.0	37150.0	a
CY13PD + OH	= DALLYOH	8.18E12	-0.07	850.0	b
CY13PD + OH	= C2H2 + C=CC.OH	1.40E20	-1.81	29040.0	b
CY13PD + OH	= CY13PD5. + H2O	3.08E06	2.0	0.0	a
CY13PD + O	= CY13PD5. + OH	4.77E04	2.71	1106.0	a
CY13PD + O	= C5H5O1_1 + H	8.91E12	-0.15	590.0	b
CY13PD + O	= C5H5O1_2 + H	5.60E12	-0.06	200.0	b
CY13PD + O	= C.C=CC=C=O + H	8.70E51	-11.09	33240.0	b
CY13PD + C6H5	= C6H6 + CY13PD5.	0.10E00	4.0	0.0	a
CY13PD + C=CC=C.	= C=CC=C + CY13PD5.	0.12E00	4.0	0.0	a
CY13PD + C=CC.	= C=CC + CY13PD5.	0.20E00	4.0	0.0	a
CY13PD + C2H3	= C6H6 + CH3	2.12E67	-16.08	42640.0	b
CY13PD + C2H3	= CY13PD5. + C2H4	0.12E00	4.0	0.0	a
CY13PD + CH3	= CY13PD5. + CH4	0.18E00	4.0	0.0	a
CY13PD + H	= CYC5H7_2	2.44E73	-17.85	315000.0	b
CY13PD + H	= CYC5H7_1	1.10E-3	3.57	-14070.0	b
CY13PD + H	= C2H2 + C=CC.	7.74E36	-6.18	32890.0	b
CY13PD + H	= C=CC=CC.	3.03E12	-0.8	2910.0	b
CY13PD + H	= C=CC.C=C	1.14E14	-0.16	3100.0	b
CY13PD + H	= CY13PD5. + H2	1.20E05	2.5	1492.0	a
CY13PD	= CY13PD5. + H	5.96E14	0.0	75100.0	b
CY13PD5.+ C=CC=O	= C=CC.=O + CY13PD	1.00E13	0.0	8843.0	a
CY13PD5.+ HO2	= CYC5H5O. + OH	6.27E29	-4.69	11650.0	b
CY13PD5.+ HO2	= CPDOOH	1.08E50	-11.88	9210.0	b
CY13PD5.+ O2	= CPDOO.	7.31E07	0.08	-9570.0	b
CY13PD5.+ O2	= COC=CC.CO	2.94E10	-0.53	2600.0	b
CY13PD5.+ O2	= C.OC=CCCO	1.27E06	0.60	-2140.0	b
CY13PD5.+ O2	= C=CC=C=O + HCO	1.16E19	-2.48	10970.0	b
CY13PD5.+ O2	= COC=CKET + H	6.85E08	0.51	7980.0	b
CY13PD5.+ OH	= CYC5H4OH + H	3.51E57	-12.18	48350.0	b
CY13PD5.+ OH	= CYC5H5OH	6.49E14	-0.85	-2730.0	b
CY13PD5.+ OH	= CYPD1OH	1.15E43	-8.76	18730.0	b
CY13PD5.+ OH	= CYPD2OH	1.06E59	-13.08	33450.0	b
CY13PD5.+ O	= C2H2 + C.=CC=O	8.22E-6	5.19	460.0	b
CY13PD5.+ O	= C.OC=CC=C	7.18E02	1.54	-14060.0	b
CY13PD5.+ O	= C=CC=C. + CO	3.20E13	-0.17	440.0	b
CY13PD5.+ O	= CYPDONE + H	5.81E13	-0.02	20.0	b
CY13PD5.+ O	= CYC5H5O.	1.12E-12	5.87	-17310.0	b
CY13PD5.+ C=CC	= CPDC=C+CH3	1.49E11	-0.06	29790.0	b
CY13PD5.+ C2H3	= CPDC=C	4.82E13	0.0	0.0	[1]
CY13PD5.+ CH3	= CH3CY24PD	1.85E60	-13.76	25640.0	b
CY13PD5.+ CH3	= H+CYC5H4CH3	4.96E58	-12.80	50650.0	b
CY13PD5.+ HO2	= CYPDONE + H2O	1.19E33	-6.52	13400.0	b

Units: Ea and U in cal/mol, for bimolecular reaction ; A and AT^n in cm^3 $mole^{-1}$ sec^{-1} and for unimolecular reaction A and AT^n in sec^{-1}.

$k = A\ T^n \exp(-Ea/RT)$ in a range of temperature, ~ 900 - 1300 K

a ,Abstraction reaction. The rate constants are estimated in this work. We choose the corresponding abstraction reaction rate constant of propene or propane from literature [1-3]. and adjust Ea down by 1 kcal/mol for increased exothermicity [4]

b, The QRRK calculated rate constant

Reference

1, Tsang W . J. Phys. Chem. Ref. Data. **1991**, 20, 221
2, Tsang W . J. Phys. Chem. Ref. Data. **1988**, 17, 887
3, Baulch.D.L.; Cobos.C.J.;Cox,R.A.; Esser,C.; Frank,P.; Just,Th.; Kerr,J.A.; Pilling, M.J.; Troe,J.; Walker,R.W.; Warnatz,J.; J. Phys. Chem. Ref. Data. **1992**, 21,411
4, Dean, A.M.; Bozzelli, J.W.; Combustion Chemistry, 2nd edition, W.M. Gardiner, editor, **1998**

therefore this combination reaction is an important reaction pathway for cyclopentadiene formation when H atom levels are significant. Ring-opening is not an important reaction (about 10^{-10} that of the combination reaction). Calculated rate constants are in Table 11.

Reaction with Hydroxyl Radical. Association of hydroxyl radical with cyclopentadienyl radical forms cyclopentadienol with 74 kcal/mol excess energy. This energized adduct can isomerize to cyclopentadien-1-ol[25] and cyclopentadien-2-ol before being collision stabilized, Figure 10. Both of these isomers are stable and are formed. The energized cyclopentadienol can also dissociate back to reactants, to cyclopentadienol-1-yl radical (C5H4OH) plus H and cyclopentadienoxy radical ($CYC5H5O^{\bullet}$) plus a H. Each of the H atom elimination channels are endothermic. The stabilization and isomerization reactions are the important reaction paths. The potential energy level diagram for cyclopentadienyl plus OH reaction is illustrated in Figure 10; the input high-pressure limit parameters and respective references are listed in Table 12. The calculated rate constants are shown in the Figure 11 and listed in Table 13.

TABLE 17: Major Reaction Pathways and Rate Constants of Cyclopentadienyl Radical Reactions at Atmospheric Pressure (900−1300 K) in the Form $k = AT^n \exp(-E_a/RT)$ (E_a = kcal/mol)

CY13PD	<-> CY13PD5. + H	$k = 5.96\ 10^{14}\ \exp(-75.1/RT)\ s^{-1}$
CY13PD5. + H	<-> CY13PD	$k = 9.91\ 10^{31}\ T^{-5.12}\ \exp(-9.79/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O_2	<-> 2-pentenedialdehyde-4yl	$k = 2.94\ 10^{10}\ T^{-0.53}\ \exp(-2.60/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O_2	<-> 2-pentenedialdehyde-1yl	$k = 1.27\ 10^{06}\ T^{+0.60}\ \exp(+2.14/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O_2	<-> vinyl ketene + HCO	$k = 1.16\ 10^{19}\ T^{-2.48}\ \exp(-10.97/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O_2	<-> cyclopentadienoxy + O	$k = 7.73\ 10^{15}\ T^{-0.73}\ \exp(-48.74/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O_2	<-> 3 ketene 2 propylene aldehyde + H	$k = 6.85\ 10^{08}\ T^{+0.51}\ \exp(-7.98/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + O	<-> 1 butadienyl + CO	$k = 2.5410^{17}\ T^{-1.71}\ \exp(-2.19/RT)\ cm^{-3}\ mol^{-1}\ s^{-1}$
CY13PD5. + OH	<-> cyclopentadiene-1ol	$k = 1.15\ 10^{43}\ T^{-8.76}\ \exp(-18.73/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + OH	<-> cyclopentadiene-2ol	$k = 1.06\ 10^{59}\ T^{-13.08}\ \exp(-33.45/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5 + HO_2	<-> cyclopentadienoxy + OH	$k = 6.27\ 10^{29}\ T^{-4.69}\ \exp(-11.65/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$
CY13PD5. + HO_2	<-> cyclopentadienone + H_2O	$k = 1.19\ 10^{33}\ T^{-6.52}\ \exp(-13.40/RT)\ cm^{-3}\ mol^{1}\ s^{-1}$

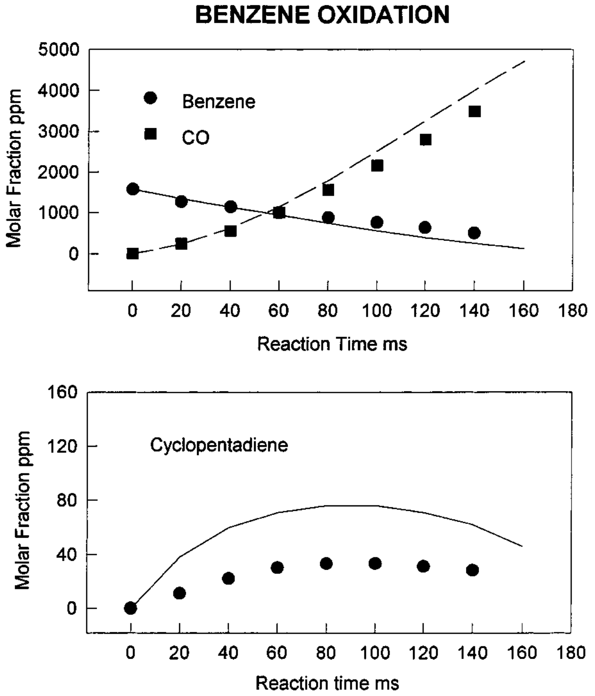

Figure 16. Comparison of model prediction with experimental data on benzene oxidation at constant temperature. Product levels reported by Lovell et al.[1] (symbols), at 1 atm pressure, 1108 K (average) temperature, $\phi = 0.76$, (fuel lean). Lines are model prediction.

The cyclopentadienol isomers are important intermediates in the cyclopentadiene oxidation process. The cyclopentadienol and the cyclopentadienol-1-yl radical (C5H4OH) will be the important products at high temperature (above 1100 K).

Reaction with Hydroperoxyl Radical. The combination of cyclopentadienyl radical with hydroperoxyl radical is one of the important reactions in our proposed benzene oxidation mechanism at temperatures below 1300 K. One path serves as a pseudo chain branching (acceleration) reaction; it transforms two relatively nonreactive (resonance-stabilized) free radicals into active OH and cyclopentadienoxy radicals. The nonreactive radicals, HO_2, and cyclopentadienyl may build up to relatively high concentrations at temperatures up to 1300 K. Dissociation of the hydroperoxide adduct via the weak RO−OH bond is important.

The potential energy level diagram for cyclopentadienyl plus HO_2 is illustrated in Figure 12; the combination of the two radicals forms an energized cyclopentadienyl peroxide molecule with ca. 54 kcal/mol excess energy above its ground state. It can rapidly dissociate to cyclopentadienoxy radical and hydroxyl radical through a low-energy channel, which has a high *A* factor due to the loose transition state. The hydroxyl radical is more reactive than hydroperoxyl radical and serves to accelerate the overall reaction process via subsequent fast abstraction and addition reactions.

One other channel with some importance is elimination of H_2O with formation of cyclopentadienone, which has a lower *A* factor than RO−OH bond cleavage. The input high pressure limit parameters and respective references are listed in Table 14. The rate constants calculated by the QRRK calculation are listed in Table 15 and shown in Figure 13. The submodel is listed in Table 16, while Table 17 lists the more important cyclopentadienyl reaction paths and rate constants evaluated in this study.

Comparison with Experimental Results. The cyclopentadiene oxidation kinetic data of this study are included in an aromatic compound combustion mechanism and used to describe cyclopentadienyl formation, oxidation, and the C5 → C4 conversion process. Benzene oxidation studies using conditions reported by Lovell et al.[1] are selected because cyclopentadiene is identified as an intermediate, and its concentration vs reaction time is reported at three fuel equivalence ratios. These experiments on benzene oxidation report carbon monoxide levels as the primary product, and CO is also modeled to help validate our kinetic analysis on cyclopentadienyl oxidation.

The model successfully reconstructs the experimental observations of benzene loss and cyclopentadiene plus carbon monoxide formation; data are shown in Figures 14−16 for fuel-rich stoichiometric and fuel-lean conditions, respectively. The model shows excellent agreement for the major species benzene and carbon monoxide loss and formation, but overpredicts the much lower (factor of 100) cyclopentadiene levels at longer times by 20−30 ppm, approximately a factor of 2. Here the cyclopentadiene is a minor product, less than 2% of the initial fuel.

The model analysis shows that both phenoxy degradation and cyclopentadienyl oxidation contribute to carbon monoxide formation. Analysis indicates that the cyclopentadienyl oxidation serves as the primary reaction pathways converting C_5 cyclics to linear species. The linear dialdehyde radical and other oxygenated radical products continue to react with O_2 to form lower molecular weight intermediates and final products including carbon monoxide. Stable products such as cyclopentadiene, cyclopentadienone, and cyclopentadiene alcohols react with the radical pool, through both addition and abstraction reaction paths.

Our model shows good agreement with the experimental observations, with no optimization or adjustment performed to fit this specific experimental data set. This agreement with experimental results on intermediates in benzene oxidation provides some support for our analysis on the major reaction pathways and rate constants of cyclopentadienyl radical reactions in combustion environments. It would be helpful to have data on cyclopentadiene oxidation to further test the model. Additional evaluation of our model for oxidation of aromatics will be included in comparisons on the more extensive experimental data in the literature on benzene, phenol, toluene, and anisole pyrolysis and oxidation.

Summary

Reaction paths and pressure-dependent rate constants for cyclopentadienyl radical association reactions with H and O atoms, OH, HO_2, and O_2 have been evaluated using thermochemical kinetics: quantum RRK theory for $k(E)$ and modified strong collision for falloff. Important pathways lead to linear and cyclic oxygenated products that also contain significant resonance stabilization. A submechanism for cyclopentadienyl reactions with this radical pool is presented. This cyclopentadienyl oxidation submechanism provides pathways for cyclopentadienyl conversion to linear and cyclic C_5 or linear C_4 and lower carbon number species.

Important reaction paths for reaction with O_2 are below 1×10^{10} cm^3 mol^{-1} s^{-1} and involve formation of vinyl ketene + formyl radical and linear pentenedialdehyde radicals. Peroxy radical formation is rapid, but reverse unimolecular dissociation is also fast. Reaction with O atoms leads primarily to cyclopentadienone + H atom, but the channel to linear butadienyl + CO is also important. Association reaction with OH results in hydroxyl cyclopentadiene isomers and some hydroxylcyclopentadienyl radical plus H atom. Reaction with HO_2 results in OH + cyclopentadieneoxy radical and H_2O plus cyclopentadienone. Limited modeling predications show reasonable agreement with product formation and reactant loss data from several experiments for benzene and aromatic oxidation. Cyclopentadiene and carbon monoxide are the important stable products of this submodel.

Results of our reaction pathway analysis indicate that there is a need for kinetic data for oxidation of the alcohol, aldehyde, and ketene species that result from the cyclopentadienyl oxidation steps presented.

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References and Notes

(1) Lovell, A. B.; Brezinsky, K.; Glassman, I. *Twenty-Second Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1988; pp 1063−1074.

(2) Shandross, R. A.; Longwell, J. P.; Howard, J. B. *Twenty-Sixth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1997; pp 711−719.

(3) Lindstedt, R. P.; Skevis, G. *Combust. Flame* **1994**, *99*, 551.

(4) Zhang, H. Y.; Mckinnon, J. T. *Combust. Sci. Technol.* **1995**, *107*, 261−300.

(5) Fujii, N.; Asabi, T. *Fouteenth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1973; p 433.

(6) Bittner, J. D.; Howard, J. B. *Eighteenth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1981; pp 1105−1115.

(7) Brezinsky, K.; Lovell, A. B.; Glassman, I. *Combust. Sci. Technol.* **1990**, *70*, 33−46.

(8) Brezinsky, K.; Litzinger, T. A.; Glassman, I. *Int. J. Chem. Kinet.* **1984**, *16*, 1053.

(9) Manion, J. A.; Louw, R. *J. Phys. Chem.* **1989**, *93*, 3564.

(10) Zhong, X.; Bozzelli, J. W. *Int. J. Chem. Kinet.* **1997**, *29*, 893.

(11) Mackie, J. C.; Doolan, K. R.; Nelon, P. F. *J. Phys. Chem.* **1989**, *93*, 664.

(12) Arends, I.; Louw, R.; Mulder, P. *J. Phys. Chem.* **1993**, *97*, 7914.

(13) Colussi, A. J.; Zabel, F.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 161.

(14) Lin, C.-Y.; Lin, M. C. *Int. J. Chem. Kinet.* **1985**, *17*, 1025.

(15) Olivella, S.; Sole, G.; Raso, A. *J. Phys. Chem.* **1995**, *99*, 10549.

(16) Lin, R.; Morokuma, K.; Mebel, A.; Lin, M. C. *J. Phys. Chem.* **1996**, *100*, 9314.

(17) Venkat, C.; Brezinsky, K.; Glassman, I. *Nineteenth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1982; pp 143−152.

(18) Wang, H.; Brezinsky, K. *J. Phys. Chem.* **1998**, *102*, 1530.

(19) Bittker, D. A. *Combut. Sci. Technol.* **1991**, *79*, 47.

(20) Davis, S. G.; Wang, H.; Brezinsky, K.; Law, C. K. *Twenty-Sixth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1996; pp 1025−1033.

(21) Tan, Y.; Frank P. *Twenty-Sixth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1997; pp 677−684.

(22) Emdee, J. I.; Brezinsky, K.; Glassman, I. *J. Phys. Chem.* **1992**, *96*, 2151.

(23) Brezinsky, K. *Prog. Energy Combust. Sci.* **1986**, *12*, 1−24.

(24) Moskaleva, L. V.; Mebel, A. M.; Lin, M. C. *Twenty-Sixth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1996; p 521.

(25) Melius, C.; Colvin, M. E.; Marinov, N.; Pitz, W. M.; Senkan, S. *Twenty-Sixth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1996; p 685.

(26) Ritter, E. R.; Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1990**, *94*, 2493.

(27) Lay, T. L.; Yamada T.; Bozzelli J. W. *J. Phys. Chem.* **1997**, *101*, 2471.

(28) Lay, T. L.; Bozzelli, J. W. *J. Phys. Chem.* **1997**, *101*, 9505.

(29) Lay, T. L.; Bozzelli, J. W. *Chem. Phys. Lett.* **1997**, *268*, 175.

(30) (a) Lay, T. L.; Bozzelli J. W.; Dean A. M.; Ritter, E. R. *J. Phys. Chem.* **1995**, *99*, 14514. (b) Ritter, E. R.; Bozzelli, J. W. *Int. J. Chem. Kinet.* **1991**, 767.

(31) Westmoreland, P. R.; Howard, J. B.; Longwell, J. P.; Dean, A. M. *AIChE J.* **1986**, *32*, 1971.

(32) Bozzelli, J. W.; Dean, A. M.; Ritter, E. R. *Combust. Sci. Technol.* **1991**, *80*, 69.

(33) Dean, A. M. *J. Phys. Chem.* **1985**, *89*, 4500.

(34) Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 169.

(35) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*, 2nd ed.; Wiley: London, 1963.

(36) Harrington, R. E..; Rabinovitch, B. S.; Hoare, M. R. *J. Chem. Phys.* **1960**, *33*, 744.

(37) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1987.

(38) Westmoreland, P. R. *Combust. Sci. and Technol.* **1992**, *82*, 1515.

(39) Dean. A. M.; Westmoreland, P. R. *Int. J. Chem. Kinet.* **1987**, *19*, 207.

(40) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1990**, *94*, 3313.

(41) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1993**, *97*, 4427.

(42) Bozzelli, J. W.; Chang, A. Y.; Dean, A. M. *Twenty-fifth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1994; p 965.

(43) Sengupta, D.; Chandra, A. K. *J. Chem. Phys.* **1994**, *101*, 3906.

(44) Nguyen, M. T.; Sengupta, D.; Vanquickenborne. *J. Phys. Chem.* **1996**, *100*, 10956.

(45) Nguyen, M. T.; Sengupta, D.; Vanquickenborne. *J. Phys. Chem.* **1996**, *100*, 9730.

(46) Wooldridge, P.; Hanson, R. *Twenty-fifth Symposium (Int'l) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1994; p 983.

(47) Nguyen, M. T.; Sengupta, D. *J. Chem. Phys.* **1997**, *106*, 9703.

(48) Biggs, P.; Canosa Mas, C. E.; Frachebourd, J. M.; Pan, A.; Shallcross, D. E.; Wayne, R. P. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 4163.

(49) Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J. L. *J. Phys. Chem. A* **1997**, *101*, 19−24.

(50) Zhong, M.; Brauman, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 636−41.

(51) Bozzelli J. W.; Chang, A. Y.; Dean, A. M. *Int. J. Chem. Kinet.* **1997**, *29*, 161.

(52) Amotz, B.; Hershbach, D. *J. Phys. Chem.* **1990**, *94*, 3393.