Research Report

Estimation of Rate Parameters in Low Temperature Oxidation of Alkanes

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アルカンの低温酸化反応－速度定数の推定

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Abstract

Rate parameters for nine types of reactions, which are supposed to be important in the low temperature chemistry of alkane oxidation, were estimated based on the knowledge of thermochemistry described in literature available. The estimation includes the low temperature degenerate branching reaction $O_2QOOH \rightarrow R'OOH + OH$, isomerization $RO_2 \rightarrow QOOH$, the reactions following or preceding them, and others. The results of computer simulation using a model of n-butane autoignition chemistry, which was constructed with the reactions estimated in this article, is also presented.

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要　旨

飽和炭化水素（アルカン）の低温酸化過程において重要と考えられる9種の反応の速度定数を各種文献に記述された熱化学的知見に基づいて推定した。推定された反応は，低温での縮退分岐反応 $O_2QOOH \rightarrow R'OOH + OH$ や異性化反応 $RO_2 \rightarrow QOOH$，あるいは，それらの反応の前後に起きる反応などである。これらの推定された反応を含むノルマルブタンの自着火反応モデルを構築したが，そのモデルを用いた計算機シミュレーションの結果についても述べる。

Keywords　Chemical kinetics, Rate constant, Combustion, Hydrocarbon, Autoignition, Simulation

Nomenclature

A	A factor of reaction rate constant k (see below)
$A\ (1,n)$	A factor for the 1, n H-atom transfer of isomerization
E	Activation energy of reaction
$E\ (1,n)$	Activation energy for the 1,n H-atom transfer of isomerization
E_n	Activation energy for reactions with n-membered ring transition state
k	Reaction rate constant $k=A\ \exp\ (-E/RT)$ where R is gas constant and T is temperature
$k\ (1,n)$	Reaction rate constant for the 1, n H-atom transfer of isomerization
K	Equilibrium constant
K_{adj}	Adjusted equilibrium constant
K_{add}	Equilibrium constant deduced from additivity rule
S_n	Strain energy of a n-membered ring transition state
ΔH_T^0	Enthalpy change of reaction or enthalpy of species at temperature T and standard pressure 1 atm
ΔS_T^0	Entropy change of reaction or entropy of species at temperature T and standard pressure 1 atm

1. Introduction

The oxidation of hydrocarbon fuels is an important process in modelling combustion in automobile engines, such as flame propagation, autoignition and exhaust emissions. However, the autoignition chemistry at temperatures lower than 900 K has not completely been clarified, especially for their reaction rate constants although the outline of the mechanism has been inferred.

In this article the author reports his estimates for some of reaction rate parameters supposed to be important in the low temperature chemistry of autoignition, which were estimated from literature data by thermochemical analysis.

Since the estimated rate parameters have been utilized to construct a model of n-butane autoignition chemistry [1], some results of computer simulation with that model are also presented.

2. Methods of Estimation and Results

Reactions whose rate parameters were rationally estimated by the author are listed in Table 1. (In Table 1, nine types of reactions

Table 1 Nine types of reactions estimated by the author.

Reactions in generic form	Parameters estimated by the author	Sections concerned
$R + O_2 \rightarrow RO_2$ (R = alkyl radical, QOOH, QOH)	A, E, K	2.1. O_2 Addition
$RO_2 \rightarrow QOOH$	A, E	2.2. Isomerization of RO_2 (Internal H-Absraction)
$O_2QOOH \rightarrow R'OOH + OH$	A, E	2.3. Decomposition of Dihydrocarbonperoxides (Formation of Degenerate Branching Species)
$RO \rightarrow QOH$	A, E	2.4. Isomerization of Alkoxyl Radicals
$O_2QOH \rightarrow$ 2 Aldehydes + OH	A, E	2.5. Formation of Aldehydes
$QOOH \rightarrow$ O-heterocycle + OH	$(A)^a, E$	2.6. Decomposition of QOOH and O_2QOOH
$O_2QOOH \rightarrow$ Carbonyl compound + 2 Aldehydes + OH	(A, E)	
$QOOH \rightarrow$ Olefin + Aldehyde + OH	A, E	
$R'O \rightarrow$ Carbonyl compound + Carbonyl radical	$(A)^b$	2.7. Decomposition of Alkoxyl Radicals

[a] Parameters in parentheses are estimated rather temporarily.
[b] The activation energies were estimated by Baldwin, et al. [3].

estimated are given in generic forms, in which R, Q, R', Aldehyde, etc. stand for the chemical species appearing in the reactions: For example, R stands for an alkyl radical, etc.)

These reactions are supposed to be important in the low temperature oxidation of alkane: Indeed the autoignition delays of n-butane/air mixtures at temperatures lower than 900 K are sensitive to a series of reactions; $R + O_2 \rightarrow RO_2$; $RO_2 \rightarrow QOOH$; $QOOH + O_2 \rightarrow O_2QOOH$; $O_2QOOH \rightarrow R'OOH + OH$; and $R'OOH \rightarrow R'O + OH$ [1], while the others in Table 1 may be responsible to the formation of species characteristic to the low temperature oxidation.

Rate parameters for these reactions were estimated by thermochemical analysis exemplified by Refs. [2] and [3], and the method and the result of the estimation for each type of reaction are described separately as follows.

2.1 O_2 Addition

The reactions of this type $R + O_2 \rightarrow RO_2$ are further categorized into three groups; a group whose R stands for an alkyl radical; a group for QOOH; and a group for QOH, where QOOH and QOH stand for $(CH_2OOH)CH_2$ and $(CH_2OH)CH_2$, for example, respectively.

As for the group for an alkyl radical, the forward rate parameters for small alkyl radicals are well known, and these values can be assigned to the other groups, presuming that forward rate parameters for QOOH and QOH are the same as for an alkyl radical which has an unpaired electron in the same site and the same number of carbon atoms as each QOOH and QOH has. For example, the rate parameters for $(CH_2OOH)CH_2$ should be roughly the same as those for C_2H_5.

Because at low temperatures the reactions of this type are equilibrated in the induction period of autoignition and the delay of autoignition is very sensitive to these equilibrium constants [1], the equilibrium constants must correctly be estimated: The equilibrium constants can be estimated by the group-additivity rule of Benson [4] with the following adjustment which is crucial in modelling autoignition at low temperatures.

In Table 2 the equilibrium parameters for the reactions $R + O_2 \rightarrow RO_2$ with various R radicals, which were determined or compiled by Gutman's group [5, 6], are listed; and this table shows that the difference between the values determined experimentally and those determined by the group additivity are large except for CH_3: The averages of the differences in ΔH_{298}^0 and ΔS_{298}^0 for the three larger alkyl radicals are –23 kJ/mol and –20 J/mol/K, respectively. Therefore, it seems reasonable to adjust the group-additivity equilibrium parameters and the group-additivity heats of formation of RO_2, O_2QOOH and O_2QOH (except CH_3O_2) as follows.

$$K_{\mathrm{adj}} = K_{\mathrm{add}} \bullet \Delta K$$
$$\Delta H_{T\ \mathrm{adj}}^{0} = \Delta H_{T\ \mathrm{add}}^{0} + \Delta\Delta H_{T}^{0}$$

Table 2 Equilibrium parameters for $R + O_2 \rightarrow RO_2$ cited from Refs. [5] and [6].

R	$-\Delta H_{298}^0$ (kJ/mol)			ΔS_{298}^0 (J/mol/K)		
	Measured	Group additivity	Difference	Calculated	Group additivity	Difference
CH_3	136.7	129.7	7.0	–130.1	–130.1	0.
C_2H_5	148.0	124.7	23.3	–150.2	–138.1	–12.1
$i\text{-}C_3H_7$	152.4	128.4	24.0	–166.9	–138.1	–28.8
$t\text{-}C_4H_9$	150.7	128.9	21.8	–171.9	–152.3	–19.6

where

$\Delta K = \exp(-\Delta\Delta S_T^0/R) \exp(-\Delta\Delta H_T^0/RT)$,

$\Delta\Delta S_T^0 = -20$ J/mol/K and

$\Delta\Delta H_T^0 = -23$ kJ/mol.

2.2 Isomerization of RO_2 (Internal H abstraction)

Since the method of the present estimation closely follows Baldwin et al. [2, 7, 8, 9, 10], their estimation procedure is concisely reviewed here before describing the present method.

Baldwin et al. have determined the rate parameters for the isomerization $RO_2 \rightarrow$ QOOH for various R and Q at 753 K, in one of the following three ways through the experiments using the reactive systems shown in Fig. 1.

1. The rate constant k_d is deduced by measuring $K_a \bullet k_d / k_c$ where the values of K_a and k_c are known or estimated by thermochemical analysis [2, 9].
2. The rate constant k_d is deduced by measuring $K_a \bullet k_d / k_b$ where the values of K_a and k_b are known or estimated by thermochemical analysis [7].
3. Same as 2 but the value of k_b is deduced by measuring k_c / k_b where the value of k_c is known or estimated by thermochemical analysis [8, 10].

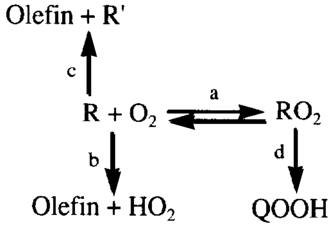


Fig. 1 Reactive system employed by Baldwin, et al. [2, 7-10].

In order to determine the rate parameters, i.e., the A factor and the activation energy E for the isomerization, Baldwin et al. [2] have made the following six assumptions:

1. The rate parameters for the same type of internal H abstraction (H-atom transfer) are independent of the nature of R and Q.
2. The A factor for 1,5 H-atom transfer is equal to $1.0 \times 10^{12} s^{-1}$ per C-H bond, which was deduced from a 1,5p H-atom transfer of neopentyl peroxide isomerization [2]. (This is a basis to estimate; A factors for other transfers (see points 3 and 4); and activation energies (see point 5)).
3. The A factor per C-H bond is decreased by a factor of 8 each time the size of the ring transition-state is increased by one atom, based on transition-state theory.
4. The A factor per C-H bond is independent of the transferred H-atom position, i.e., whether it is primary (p), secondary (s), or tertiary (t).
5. The activation energy for a particular type of H-atom transfer can be obtained from the value of the rate constant determined only at 753 K using the A factor obtained by points 2-4.
6. The change in the activation energy with the ring size of the transition state is equal to the difference in the ring strain-energies (Eq.(2) in Section 2.6) and independent of the transferred H-atom position.

The validity of their estimation is supported by the following [2]:

1. Where two determinations of the rate constant are available for a particular type of H-atom transfer in their estimation, there is good agreement, particularly on a per C-H bond basis.

2. A directly determined rate constant ratio of the 1,4t to 1,5p H-atom transfers in $(CH_3)_2CHCH_2OO$ radical, i.e., a value of $k(1,4t)/k(1,5p)=24.7$ [9] agrees with values of 29 and 18 for the ratio using two values of $k(1,5p)$ from Ref. [2] together with a value of $k(1,4t)$ from Ref. [9].
3. The values of the difference $E(1,4) - E(1,5)$ are consistent with the difference in ring strain-energies between five-membered and six-membered rings estimated by Fish [11], i.e., 27 – 2.5 = 24.5 kJ/mol.
4. Strain energies involved in the 1,7 transfers are likely to be so small that the estimated activation energies should approximate to activation energies for intermolecular H-abstraction from alkanes by RO_2 radicals. No experimental values are available for these reactions, but on thermochemical grounds their activation energies should be virtually identical to those of the equivalent reactions of HO_2 radicals. A value of 81.7 ± 8 kJ/mol obtained for the H-abstraction from tetramethylbutane (all primary C-H) by HO_2 radicals is in excellent agreement with $E(1,7p) = 82$ kJ/mol. The lower values for the abstraction (1, 7 transfer) at secondary and tertiary C-H positions are consistent with the decrease in the endothermicity of these reactions.

The present estimation is a modification of the one by Baldwin et al. [2] and proceeds as follows:

1. The author reestimated A factor for the 1,4 H-atom transfer $C_2H_5O_2 \rightarrow C_2H_4OOH$ (1,4p), using the recent values of A_b and E_b for $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ [12] together with the K_a estimated by the author (Section 2.1). Although the values of K_a are not significantly changed from those originally employed by Baldwin et al. [2] except for the adjustment described in the previous section, the change in k_b, and its effect on k_d, are so large that the reestimated A_d (1,4 H-atom transfer) is inconsistent with the ratio $A(1,4)/A(1,5)=8$ assumed by Baldwin et al. [2] if the value of $A(1,5)$ is the one estimated by Baldwin et al. [2].
2. Since the values of A_c and E_c, with which Baldwin, et al. [2] determined $A(1,5)$, were estimated [2] in seemingly a more unreliable way than the author's reestimation of $A(1,4)$ (point 1), the author selected his reestimated $A(1,4)$ as a basis of the present estimation instead of $A(1,5) = 1.0 \times 10^{12} s^{-1}$ employed as a basis by Baldwin, et al. [2].
3. Except for the basis $A(1,4)$ determined from the 1,4p H-atom transfer, $C_2H_5O_2 \rightarrow C_2H_4OOH$, method or assumption for the present estimation is the same as the original one by Baldwin et al. [2].

The presently estimated values of the rate parameters for the internal H abstraction are listed in Table 3 in a form similar to table 3 in Ref. [2], and the present values significantly differ from the original. Without the adjustment of the equilibrium parameters for $R + O_2 \rightarrow RO_2$ described in the previous section, the difference becomes more significant because in Table 3 the A's have been multiplied by 11.1 and the E's have been increased by 23 kJ/mol according to the adjustment.

The validity of the present estimation is supported by the same evidences used by Baldwin et al. [2], because the differences of the A factor and activation energy E between the two estimations are almost the same for all types of H-atom transfers (the ratio of the two *A* factors is ca. 11.5 and the difference between the two activation energies is ca. 7.5 kJ/mol) and the value of $E(1,7p) = 74.8$ kJ/mol is still consistent with the value 81.7 ± 8 kJ/mol for the abstraction of H atoms from tetramethylbutane by HO_2 radicals.

2.3 Decomposition of Dihydrocarbonperoxides (Formation of Degenerate Branching Species)

The reactions of this type $O_2QOOH \rightarrow R'OOH + OH$ have been considered to be an origin of degenerate branching in the low temperature chemistry of autoignition, that is, each reaction produces an OH radical and a species R'OOH, which itself produces an OH radical through a decomposition $R'OOH \rightarrow RO + OH$ (whose rate parameters are relatively well known [13, 14]).

Since this type of reaction forms a transition state similar to the isomerization of RO_2, it is likely that the rate parameters are the same as those estimated in the previous section. Therefore, it seems reasonable to assign the values for the corresponding types of H-atom transfer in Table 3 to the reactions of this type.

2.4 Isomerization of Alkoxyl Radicals

Since this type of reaction $RO \rightarrow QOH$ forms a ring transition-state similar to the isomerization of RO_2, it seems reasonable to assign the *A* factors for the corresponding types of H-atom transfer in Table 3 to the

Table 3 Rate parameters for internal H-abstraction in RO_2 radicals.

Reaction	Ref.	Type of H atom transfer	k s^{-1}	k (per C-H) s^{-1}	A (per C-H)[a] s^{-1}	E $kJmol^{-1}$	E (recommended) $kJmol^{-1}$
$CH_3CH_2(CHOO)CH_3 \rightarrow CH_3CH_2(CHOOH)CH_2$	8	1,4p	2.2 (3)[d]	7.3 (2)	6.93 (11)	137.3	138
$C_2H_5O_2 \rightarrow C_2H_4OOH$ [b]	7	1,4p	1.95(3)	6.5 (2)	6.93 (11)[b]	138.1	
$(CH_3)_3(CH_2OO) \rightarrow (CH_3)_3(CH_2OOH)$	2	1,5p	9.2 (4)	1.02(4)	8.7 (10)	107.8	110
	2	1,5p	5.7 (4)	6.3 (3)	8.7 (10)	110.8	
$(CH_3)_2CH(CH_2OO) \rightarrow CH_3(CH_2CH)(CH_2OOH)$	9	1,5p	4.45(4)	7.4 (3)	8.7 (10)	109.8	
$CH_3CH_2CH_2(CH_2OO) \rightarrow CH_2CH_2CH_2(CH_2OOH)$	8	1,6p	6.0 (4)	2.0 (4)	1.08 (10)	90.6	91
$CH_3CH_2CH_2CH_2(CH_2OO) \rightarrow CH_2CH_2CH_2CH_2(CH_2OOH)$	10	1,7p	9.3 (4)	3.1 (4)	1.35 (9)	74.8	75
		1,3s			5.54 (12)	(161)[c]	161
$CH_3(CHOO)CH_2CH_3 \rightarrow CH_3(CHOOH)CHCH_3$	8	1,4s	2.4 (4)	1.2 (4)	6.93 (11)	119.8	118
$CH_3(CHOO)CH_2CH_2CH_3 \rightarrow CH_3(CHOOH)CHCH_2CH_3$	10	1,4s	4.7 (4)	2.35(4)	6.93 (11)	115.6	
$CH_3CH_2CH_2(CH_2OO) \rightarrow CH_3CHCH_2(CH_2OOH)$	8	1,5s	2.0 (5)	1.0 (5)	8.7 (10)	93.5	92
$CH_3(CHOO)CH_2CH_2CH_3 \rightarrow CH_3(CHOO)CH_2CHCH_3$	10	1,5s	3.0 (5)	1.5 (5)	8.7 (10)	91.0	
$CH_3CH_2CH_2CH_2(CH_2OO) \rightarrow CH_3CHCH_2CH_2(CH_2OOH)$	10	1,6s	6.6 (5)	3.3 (5)	1.08 (10)	73.0	73
		1,7s			1.35 (9)	(57)	57
$CH_3(CHOO)CH_2CH_3 \rightarrow CH_3(COOH)CH_2CH_3$	8	1,3t	1.5 (3)	1.5 (3)	5.54 (12)	145.8	146
$(CH_3)_2CH(CH_2OO) \rightarrow (CH_3)_2C(CH_2OOH)$	9	1,4t	1.83(5)	1.83(5)	6.93 (11)	102.7	103
		1,5t			8.7 (10)	(75)	75
		1,6t			1.08 (10)	(56)	56
		1,7t			1.35 (9)	(40)	40

[a] All *A* factors, except for the reaction marked (b), have been calculated from the *A* factor for the reaction marked (b) based on transition state theory.

[b] The determination of the rate parameters are described in the text.

[c] Activation energies given in brackets are calculated on the assumption described in the text, i.e., the difference in activation energies is equal to the difference in the strain energies in the ring transition-states, for example, $E(1,3s)=E(1,4s)+E(1,3t)-E(1,4t)$.

[d] The numbers in parentheses are exponents of 10.

reactions of this type. But the activation energies were estimated as follows.

Baldwin et al. [3] pointed out that activation energy for each reaction of this type is equal to the sum of the strain energy of the transition state and activation energy for the reaction RH + RO → R + ROH, and gave the values listed in Table 4. Although Table 4 gives the strain energies of the 5-membered ring and the 6-membered, the model of autoignition [1] requires the strain energy of a 4-membered ring because the product QOH for 4-membered ring is also a product of OH addition to olefins and the backward reactions of this type for 4-membered ring may be active (though the computer simulation with the model of Ref. [1] shows that both forward and backward reactions of this type with the presently estimated rate parameters are not active in the autoignition process of n-butane/air mixtures). Therefore, the author estimated the strain energy of the 4-membered ring, using the value of activation energy for the reaction $C_2H_5O \rightarrow C_2H_4OH$, 142 kJ/mol [15] together with the activation energy for the primary H-abstraction given in Table 4, that is, as $142 - 30 = 112$ kJ/mol.

Thus the activation energies were estimated as $112 + 17 = 129$ kJ/mol for the 1,3s H-atom transfer and 142 kJ/mol for the 1,3p H-atom transfer.

The rate parameters estimated in this manner are listed in Table 5.

Table 4 Data from Ref. [3] for estimation of the reaction RO → QOH.

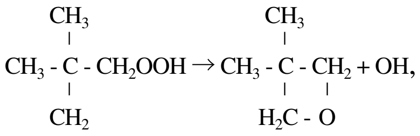
Strain energy for the transition state of the reaction RO → QOH (kJ/mol)		Activation energy for the reaction RH + RO → R + ROH (kJ/mol)	
5-membered ring	6-membered ring	Primary H abstraction	Secondary H abstraction
25	2.1	30	17

2.5 Formation of Aldehydes

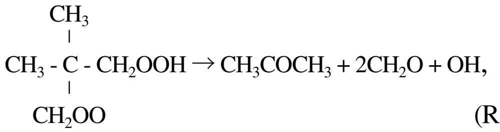
The formation of aldehydes, which is a characteristic of the cool flame of alkane oxidation, is partly attributed to the reactions of the type, $O_2QOH \rightarrow$ 2 Aldehydes + OH, for whose rate parameters the same consideration as for the decomposition of dihydrocarbonperoxides (Section 2.3) holds.

2.6 Decomposition of QOOH and O_2QOOH

Baldwin et al. [2] estimated rate parameters for the following three reactions:



$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_2}{|}}{C}}-CH_2OOH \rightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle H_2C-O}{|\quad\;\,|}}{C-CH_2}} + OH, \quad \cdots\cdot(R1)$$



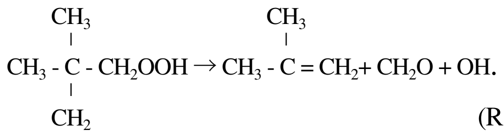
$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_2OO}{|}}{C}}-CH_2OOH \rightarrow CH_3COCH_3 + 2CH_2O + OH, \qquad (R2)$$

and

Table 5 Rate parameters for isomerization of alkoxyl radicals.

Type of H-atom transfer	A (per C-H)[a] s^{-1}	E $kJmol^{-1}$	Ring Size of Transition-State
1,3p	5.54(12)[b]	142[c]	4-membered
1,3s	5.54(12)	129[d]	4-membered
1,4p	6.93(11)	55[e]	5-membered
1,4s	6.93(11)	42[e]	5-membered
1,5p	8.7 (10)	32[e]	6-membered
1,5s	8.7 (10)	19[e]	6-membered

[a] A factors in Table 3 are assigned.
[b] The numbers in parentheses are exponents of 10.
[c] Ref. [15].
[d] This work.
[e] Ref. [3].



$$\mathrm{CH_3-\underset{CH_2}{\overset{CH_3}{C}}-CH_2OOH \rightarrow CH_3-\overset{CH_3}{C}=CH_2+CH_2O+OH.} \qquad \text{(R3)}$$

Since their estimation was based on the unreliable rate parameters A_c and E_c mentioned in Section 2.2, their estimated parameters for R1-3 are also unreliable. Therefore, the author corrected the values of the A_c and the E_c, calculated rate parameters for R1-3 in the same way as Baldwin et al. did, and assigned the values for R1 and R2 to the reactions of the types, QOOH → O-heterocycle + OH and O_2QOOH → Carbonyl compound + 2 Aldehydes + OH, respectively; although the activation energy for QOOH → O-heterocycle + OH must be corrected according to the size of its ring transition-state as described below.

Baldwin et al. [2] estimated rate parameters for R1-3 using the following three relations:

1. For R3, they assumed $A_{R3} = A_c$ and $E_c - E_{R3} = 12$ kJmol^{-1}.
2. For R1, their experiment showed that $A_{R3}/A_{R1}=225$ and $E_{R3} - E_{R1} = 43$ kJmol^{-1}.
3. For R2, their experiment and other considerations showed that $A_{R2}/A_{R1}=6.19$ and $E_{R2} - E_{R1} = 24.1$ kJmol^{-1}.

The present author deduced the A_c and the E_c as follows:

1. A_c and E_c were deduced by substituting the proper values of K_a and k_d (see point 2) into the relation $K_a \bullet k_d / k_c = 7.2 \times 10^{-3}\exp(-113/\mathrm{kJmol^{-1}})$ cm^{3}mol^{-1} obtained experimentally by Baldwin et al. [2].
2. The author assigned the values for 1,5p H-atom transfer in Table 3 to k_d, and employed the group-additivity value of $K_a = 2.7 \times 10^{-2}\exp(105.1/\mathrm{kJmol^{-1}})$ cm^{3}mol^{-1} given by Baldwin et al. [2] together with the adjustment $K_a \bullet \Delta K$ described in Section 2.1.

The present values for R1-3 are listed in Table 6.

Each reaction of the type QOOH → O-heterocycle + OH has a ring transition-state, and each activation energy may be expressed as

$$E_n = E_4 + (S_n - S_4)/4 \cdots\cdots\cdots\cdots\cdots (1)$$

where E_n is activation energy for the reactions with n-membered ring transition-state, and S_n is the strain energy of the transition state [11, 16].

The strain energies of such ring transition-states were estimated by the activation energies for the type RO_2 → QOOH, using the relation [2]

$$E(1,n-1) - E(1,m-1) = S_n - S_m \cdots\cdots (2)$$

which holds if the following relation given by Baldwin et al. [2] holds.

$$E(1,n-1) = E(\mathrm{RO_2 + RH \rightarrow RO_2H + R}) + S_n \qquad (3)$$

Table 6 Newly estimated rate parameters for R1-3.

Reaction	Rate parameters	
	A (s^{-1})	E (kJ/mol)
R1	1.30(10)[a]	62.9
R2	8.02(10)	87.0
R3	3.29(12)	105.9

[a] The numbers in parentheses are exponents of 10.

where $E(1, n-1)$ is the activation energy for 1,n–1 H-atom transfer of RO_2 → QOOH and $E(RO_2 + RH \rightarrow RO_2H + R)$ is the one for the intermolecular H-abstraction from RH by RO_2.

Assuming $S_8 = 0$, the strain energy of any transition state was successively calculated using Eq.(2) together with the values of $E(1, n-1)$ and $E(1, m-1)$ in Table 3. The results are listed in Table 7, although the value for 3-membered ring is cited from Ref. [4] because the value of $E(1,2)$ is unknown.

Using Eq.(1) with the values in Table 7 and assuming $E_4=E_{R1}$ the activation energies for the type QOOH → O-heterocycle + OH can be estimated, while A_{R1} may be assigned to the A factors irrespective of the ring size n. Table 8 lists the rate parameters estimated in this way.

It is noted that the activation energy for oxetane formation 62.9 kJ/mol is consistent with the value 63 kJ/mol estimated by Benson [17] but the A factor is smaller than Benson [17] by a factor of 7.7.

The characteristic of the type of reaction O_2QOOH → Carbonyl compound + 2 Aldehydes + OH is that the reactant O_2QOOH must have a C atom placed between COOH and COO groups, and other types of O_2QOOH do not decompose in this manner. To all the reactions of this type the rate parameters for R2 may be assigned.

The characteristic of the type of reaction QOOH → Olefin + Aldehyde + OH is that the reactant QOOH must have a C atom with one unpaired electron placed beyond one C atom from COOH group, and other types of QOOH do not decompose in this way.

Baldwin et al. [2] suggested that activation energy for this type of reaction is smaller than that for the corresponding alkyl-radical decomposition by 12 kJ/mol and that the A factor is the same as for the latter, where the corresponding alkyl radical has the same structure as that of QOOH if the OOH group is replaced by a H atom. (The same consideration was used in the deduction of the rate parameters for R3.)

2.7 Decomposition of Alkoxyl Radicals

The reactions of this type R'O → Carbonyl compound + Carbonyl radical may occur subsequent to low temperature degenerate branching, i.e., the sequence of the reactions O_2QOOH → R'OOH + OH and R'OOH → R'O + OH (See Section 2.3).

A. C. Baldwin et al. [3] showed that the activation energies for the decomposition of alkoxyl radicals can be calculated with the following equations:

Table 7 Strain energy of ring transition-state.

Ring size n	Strain energy (kJ/mol)
8	0
7	16
6	35
5	62
4	105
3	115.5[a]

[a] The value of cyclopropane and ethylene oxide [4].

Table 8 Rate parameters for QOOH→O-heterocycle + OH.

O-heterocycle	Ring size n	Rate parameters	
		A (s^{-1})	E (kJ/mol)
Oxirane	3	1.3 (10)[a]	65.5
Oxetane	4	1.3 (10)	62.9
Tetrahydrofuran	5	1.3 (10)	52.2
Tetrahydropyran	6	1.3 (10)	45.4

[a] The numbers in parentheses are exponents of 10.

$$E = 53.6 + 3.0\Delta H \text{ kJ/mol} \quad \text{for } \Delta H > 0$$
$$E = 53.6 \quad \text{kJ/mol} \quad \text{for } \Delta H \leqq 0$$

where ΔH is the heat of reaction. To construct the model of n-butane autoignition chemistry [1] the author applied this equation, and assumed that all the A factors are equal to $1.0 \times 10^{14} s^{-1}$ because Ref. [3] gave $A = 8 \times 10^{12}$ to $2 \times 10^{15} s^{-1}$ for various alkoxyl radicals.

3. Application

Using the above methods and the results of estimation, the author estimated the low temperature reactions of n-butane oxidation to construct a model of n-butane autoignition chemistry. The model consists of 461 elementary reactions (81 of them were estimated as above) and 141 species including inert Ar and N_2 [1], and autoignition delays predicted with it agree with those obtained by a shock-tube experiment [18] and a rapid compression experiment [19], that is, the model has been validated at temperatures over 1200-1400 K for a stoichiometric mixture of n-butane/O_2/Ar and over 720-830 K for the mixtures of n-butane/air with equivalence ratios of 0.5-1.3 [1].

Fig. 2 is an illustration of autoignition delays obtained by our rapid compression experiment [19]. In spite of the importance of autoignition in automobile engines (such as knock in gasoline engines and fuel-spray ignition in diesel engines), such complex behaviors of autoignition delays can neither be interpreted nor predicted without a computer simulation using a model like the one presently stated. For example, the computer simulation explains the existence of the minima of autoignition delays: They appear due to the lower temperature of richer mixtures in compression (due to smaller specific heat ratio) in spite of the intrinsic shorter autoignition delay of richer mixtures. (The shorter delay is obtained when the temperature is the same as that of leaner mixtures.) [1, 19] Also, the behavior that swirl flow only affects autoignition delays on the rich side of the minima is interpreted to be due to a breakdown of the autoignition core whose temperature is maximized by an adiabatic relation, because on the rich side the computer simulation with the adiabatic relation predicts autoignition delays more badly when the swirl speed is higher and higher (Fig. 3) [1, 19]; and the simulation suggests that such a effect of the swirl is suppressed at the temperature region of cool flame (which is a low temperature flame characteristic to hydrocarbons such as alkanes) [1, 19].

Although three-dimensional simulation coupled with fluid dynamics requires a simpler model of chemistry (because the CPU time must be saved), a model like the above gives a fundamental basis for deducing a simple and rational model of chemistry.

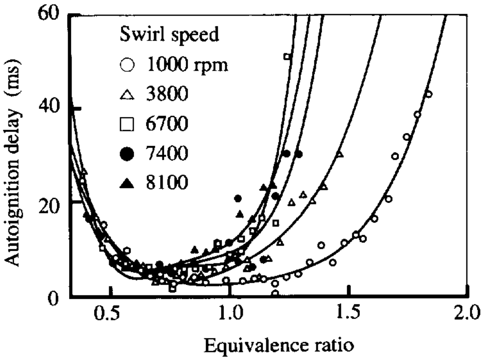
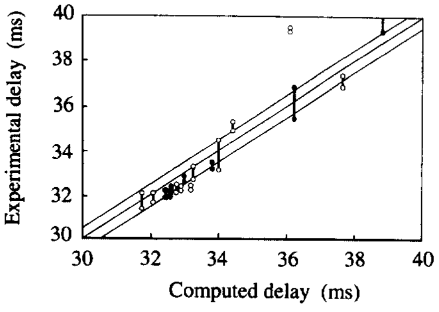
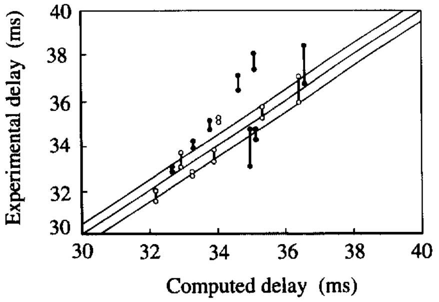


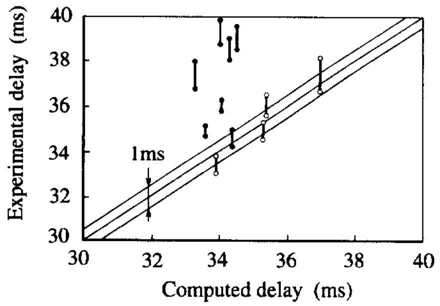
Fig. 2 Autoignition delays obtained by a rapid compression experiment [19] under swirl conditions.



(a) Swirl speed of 1000 rpm



(b) Swirl speed of 3800 rpm



(c) Swirl speed of 8100 rpm

Fig. 3 Comparison of autoignition delay.
○ on the lean side of the minima of autoignition delays shown in Fig. 2, and
● on the rich side.

Three straight lines in each plot are the assistance to show the difference between experiment and computatuion.

4. Summary

Rate parameters for nine types of reactions, which are supposed to be important in the low temperature chemistry of alkane oxidation, were estimated based on the knowledge of thermochemistry described in literature available, and the results of computer simulation using a model based on the present estimation were briefly described.

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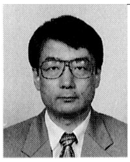

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