

環境汚染化学物質の放電分解における 原子・分子データ

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1. 背景とアプローチ
2. 環境汚染化学物質の放電分解における原子・分子データ
 - 2.1 大気圧コロナ放電によるアセトン分解と分解過程の解明における原子・分子データの利用
 - 2.2 ベンゼン、トルエン、キシレン分解過程の解明における原子・分子データの必要性
3. まとめ

Background

化学物質の排出量

(平成18年度 PRTR: Pollutant Release and Transfer Register))

- ◆ 固定排出源 … 24.5万トン
 - 大気中: 21.7万トン(88%)
 - 公共用水域: 1.1万トン(4%)

- ◆ 届出外排出源 … 31.5万トン
 - 移動体(36%), 非対象業種(31%),
 - 対象業種(17%), 家庭(16%)

大気汚染防止法の改正

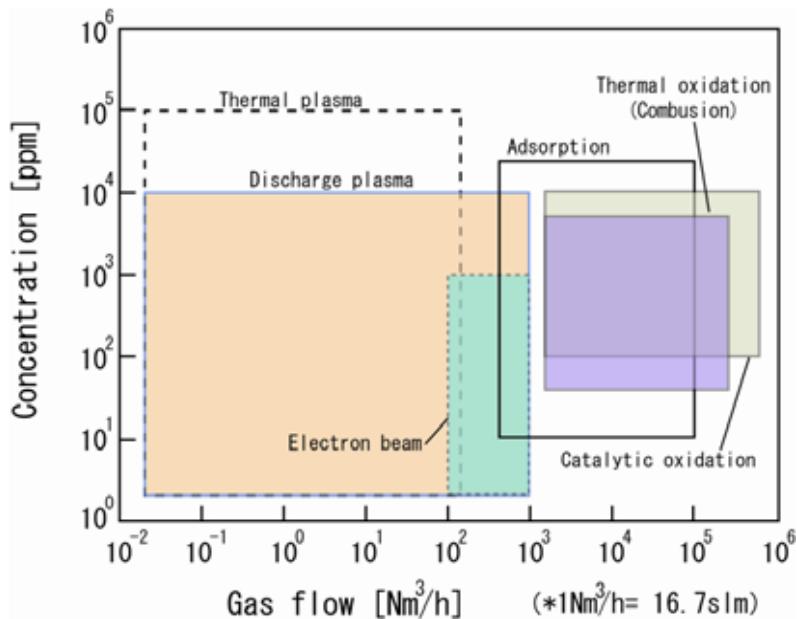
(環境省, 「大気汚染防止法の一部を改正する法律の施行について」(2005))

- ほぼ全てのVOC (メタノール、アセトンを含む) が規制対象
- 2010年度までに2000年度比で30%削減
- 総量規制 (低濃度でも対策が必要)



Background

排ガス中の有害物質(VOC)の処理法(分解・除去)



直接燃焼法、触媒燃焼法、吸着法：

大流量の排ガス処理が可能($1,000Nm^3$ 以上)
100ppm ~ 10,000ppmの濃度範囲

放電プラズマによる処理：

低流量の排ガス処理($\sim 10,000Nm^3$ 以下)
数ppm ~ 数1,000ppmの濃度範囲
ベンゼン環のように安定な化学物質も分解可能

微量でも有害な物質の処理に適用できる

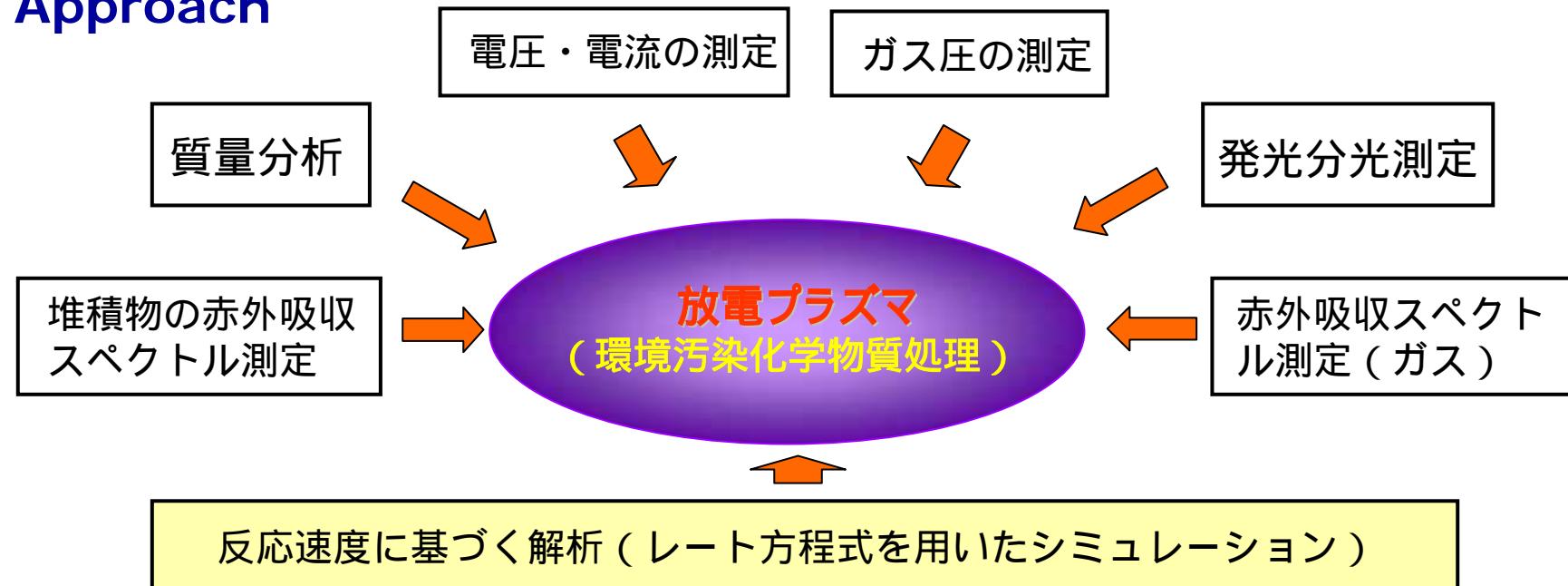


Goal & Approach

Goal…有害化学物質を、効果的に、安全な物質に分解する。

- fragments と by-products の詳細な把握(安全性、回収と再利用)
- 分解に関わる粒子(電子、イオン、ラジカル) と 分解過程の解明

Approach



VOCs decomposed by discharge plasma

物質名	分子式	濃度[ppm]	除去率[%]	物質名	分子式	濃度[ppm]	除去率[%]
メタン	CH ₄	113~1,000	15~90	キシレン(o-,m-,p-)	C ₆ H ₅ (CH ₃) ₂	2~200	100
メチルアルコール	CH ₃ OH	400	95	エチルベンゼン	C ₆ H ₅ C ₂ H ₅	0.2	100
ホルムアルデヒド	HCHO	40~100	97	スチレン	C ₆ H ₅ C ₂ H ₃	1,000~5,370	>90
エタン	C ₂ H ₆	1,000	51	スカトール	C ₉ H ₉ N	2.4	100
エチレン	C ₂ H ₄	1,000	96	四フッ化炭素	CF ₄	1,000	32
アセトアルデヒド	CH ₃ CHO	5~282	100	ジクロロメタン	CH ₂ Cl ₂	1,000	60~99
アセトン	CH ₃ COCH ₃	100~20,000	99	四塩化炭素	CCl ₄	200~3,000	60~100
イソプロピルアルコール	C ₃ H ₇ OH	100~1,000	99	臭化メチル	CH ₃ Br	1,000	100
酢酸メチル	CH ₃ COOCH ₃	1,000	50~95	ジクロロジフルオロメタン	CCl ₂ F ₂	1,000	90
ブタン	C ₄ H ₁₀	1,000	58~90	バーフロロエタン	C ₂ F ₆	1,750~3,000	66
メチルエチルケトン	CH ₃ OCC ₂ H ₅	113	85	1,2-ジクロロエタン	C ₂ H ₄ Cl ₂	1,000	99
酢酸エチル	CH ₃ COOC ₂ H ₅	1,000	50~80	トリクロロエタン	C ₂ H ₃ Cl ₃	450~1,000	90
酢酸ブチル	CH ₃ COOC ₄ H ₉	1,000	70	トリクロロエチレン	C ₂ HCl ₃	50~23,000	90~100
ヘキサン	C ₆ H ₁₄	113	55	テトラクロロエチレン	C ₂ Cl ₄	100~1,000	99
シクロヘキサン	C ₆ H ₁₂	113	65	トリクロロトリフルオロエタン	C ₂ Cl ₃ F ₃	1,000~10,000	90~100
ヘキセン	C ₆ H ₁₂	113	95	エチレングリコールモノエチルエーテル	C ₂ H ₅ OOC ₂ H ₄ OH	50~2,300	100
ベンゼン	C ₆ H ₆	10~650	98~100	三フッ化窒素	NF ₃	294~2,191	10~92
トルエン	C ₆ H ₅ CH ₃	60~2,000	36~100	アンモニア	NH ₃	21~55	95

ジェチルエーテル, テトラヒドロフラン, ヘプタン, クロロホルム, アセトニトリル

環境汚染化学物質の放電分解における 原子・分子データの利用

~大気圧コロナ放電によるアセトン分解と分解過程の解明を例として~

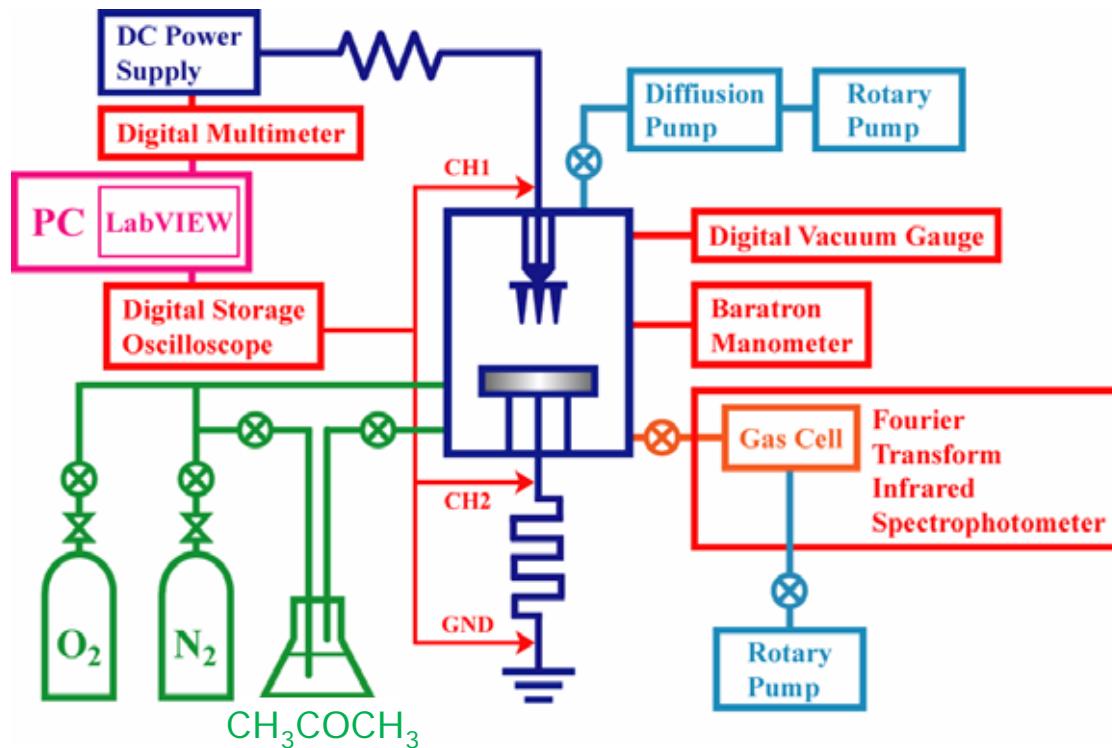
装置の概要

赤外吸収分光分析による分解生成物等の測定

化学反応速度論に基づいた分解過程の検討



Experimental apparatus, conditions & procedure



Discharge chamber
197mm in inner diameter
300mm in height
stainless steel

Multi-needle electrode
Thirteen needles of $\phi 4 \times 45\text{mm}$
stainless steel
Needle holder: $\phi 50\text{mm}$ (brass)
Needle density : $0.66/\text{cm}^2$

Plane electrode
 $\phi 80\text{mm}$
stainless steel

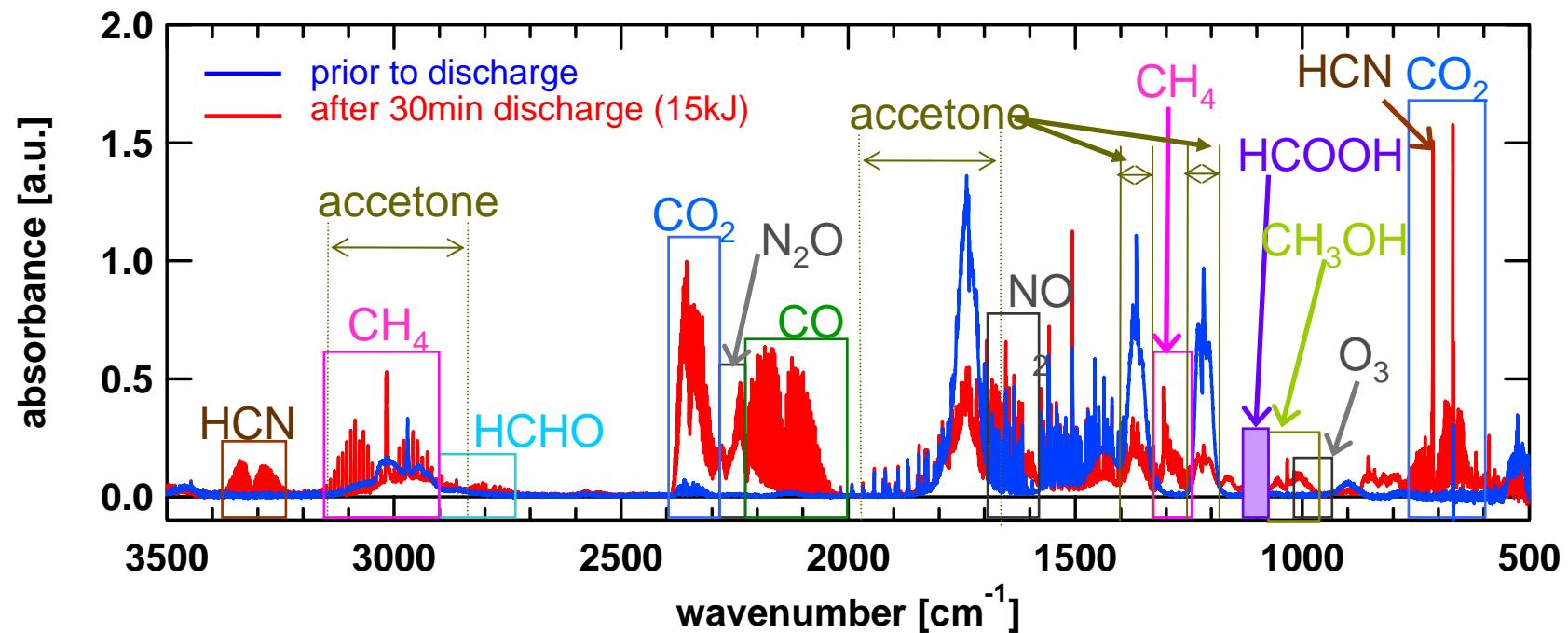
Gas Cell
(Infrared Analysis, 10-PA)
Optical path length: 10m

Purity
Acetone: 99.5%
Nitrogen: 99.99%
Oxygen: 99.5%



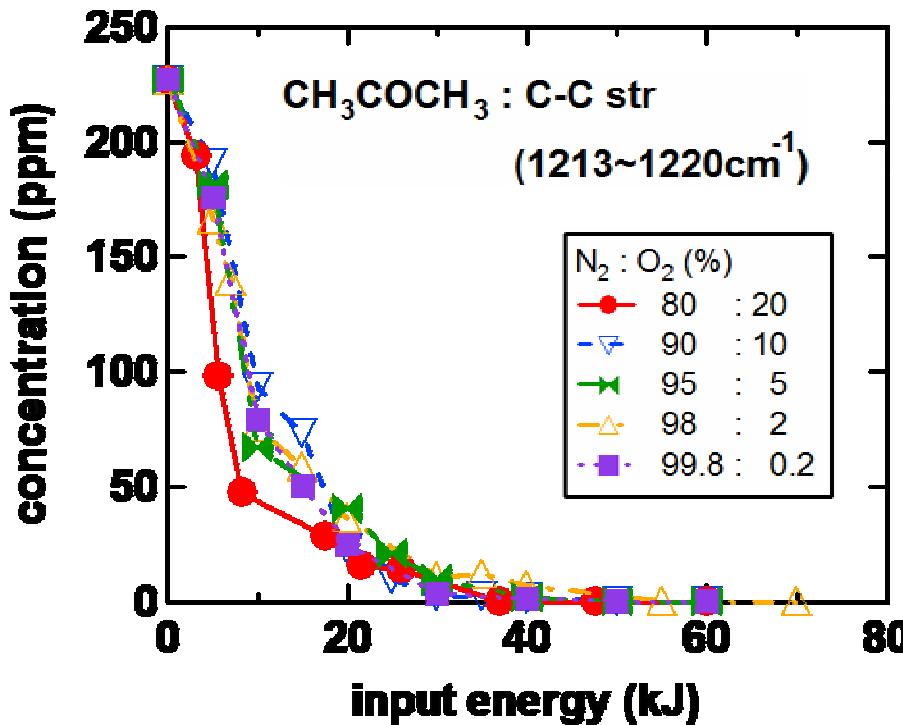
- The initial concentration of acetone is approximately 230 ppm.
- A background gas is nitrogen-oxygen mixture and the mixture ratios (%) are $\text{N}_2 / \text{O}_2 = 80/20, 90/10, 95/5, 98/2$ and $99.8/0.2$.
- Initial gas pressure in the discharge chamber is atmospheric pressure.
- Applied voltage : +25 to 27 kV
- A gas sample is taken from the discharge chamber prior to and following the discharge, and the concentrations of acetone and products in the corona discharge are measured by a FT-IR.

Infrared absorbance spectra after 30min discharge ($N_2 / O_2 = 99.8 / 0.2$)



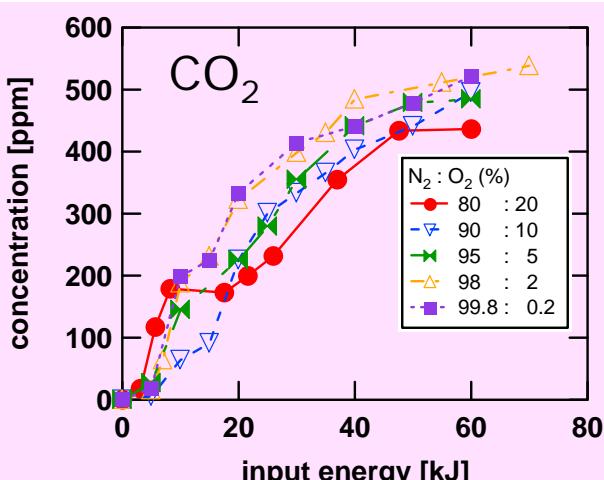
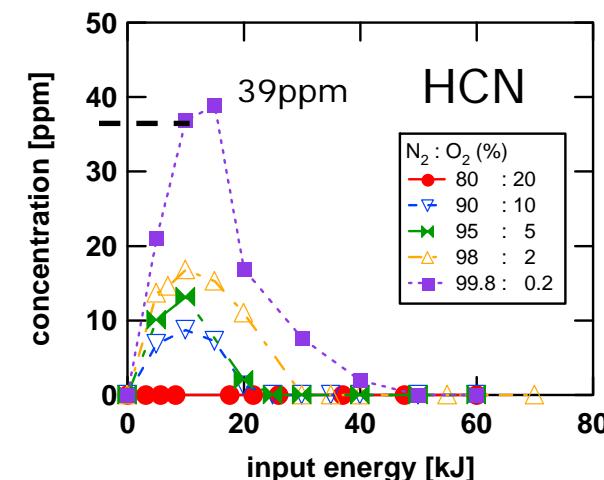
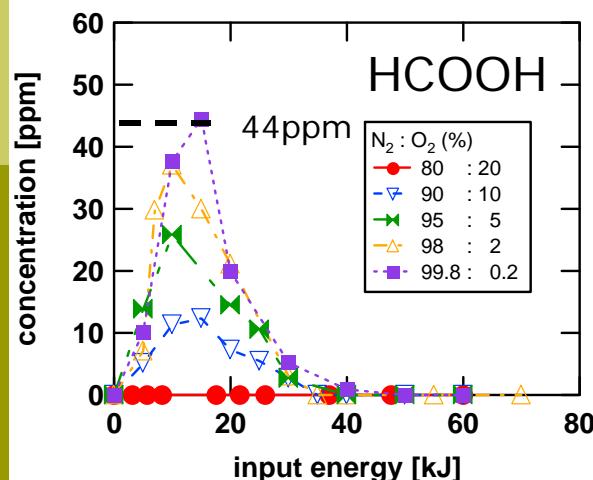
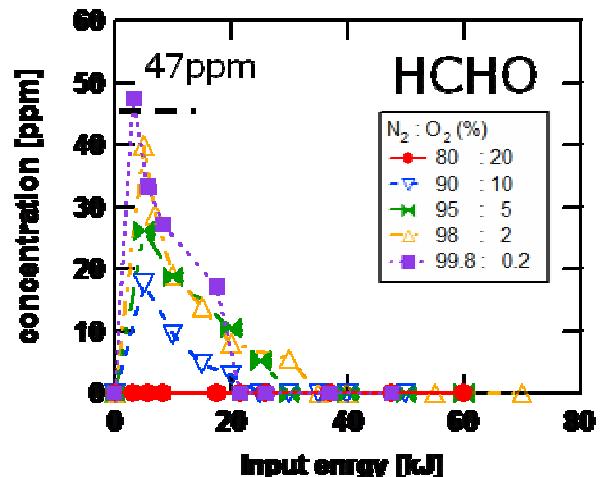
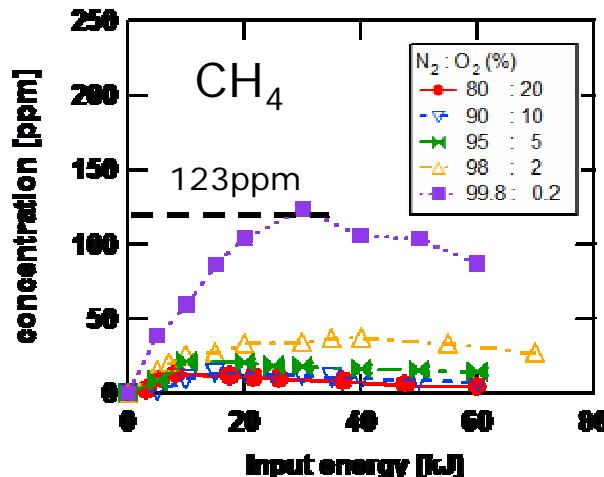
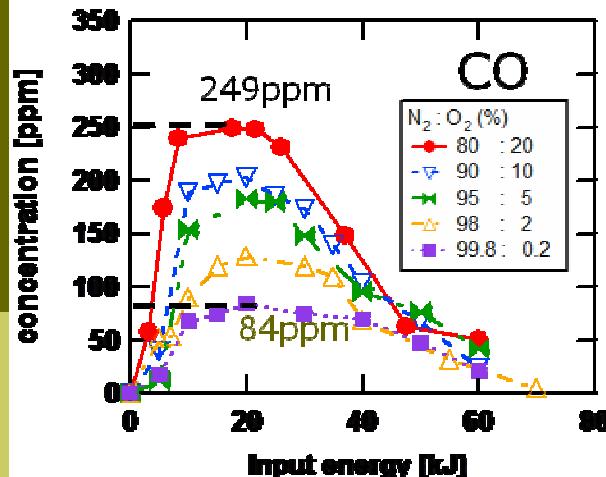
- Absorbance spectra of acetone decrease after 30min discharge, and those of CO_2 , CO , CH_4 , HCHO , HCOOH and HCN , regarded as products from acetone, are newly observed.
- Spectra of N_2O , NO_2 and O_3 are also observed, and these are probably produced mainly from the background gas.

Concentration variations of acetone with input energy



- Concentrations decrease to 0ppm at about 40kJ in almost the same manner.
- The oxygen concentration has little influence on the decomposition of acetone.
- Namely, oxygen species make few contributions to the acetone decomposition.

Concentration variations of gaseous products with input energy

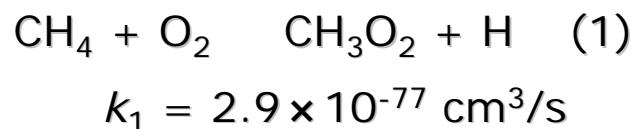


Chemical reaction

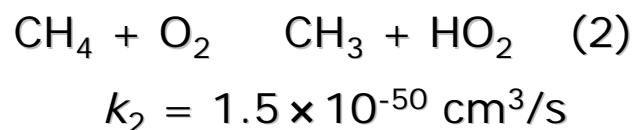
$$lA + mB + nC \xrightarrow{k} l'A' + m'B' + n'C'$$
$$r = k[A]^l[B]^m[C]^n$$

Reaction rate : r (cm⁻³/s)

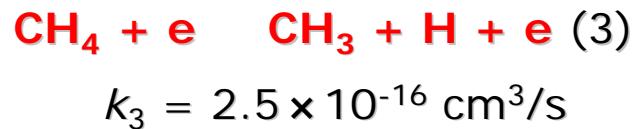
rate constant : k (cm³/s or cm⁶/s)
concentration: [A], [B], [C] (cm⁻³)
order of reaction : l, m, n



$$r_1 = k_1[\text{CH}_4][\text{O}_2] \quad 10^{-46} \sim 10^{-44} \text{ cm}^{-3}/\text{s}$$



$$r_2 = k_2[\text{CH}_4][\text{O}_2] \quad 10^{-19} \sim 10^{-17} \text{ cm}^{-3}/\text{s}$$

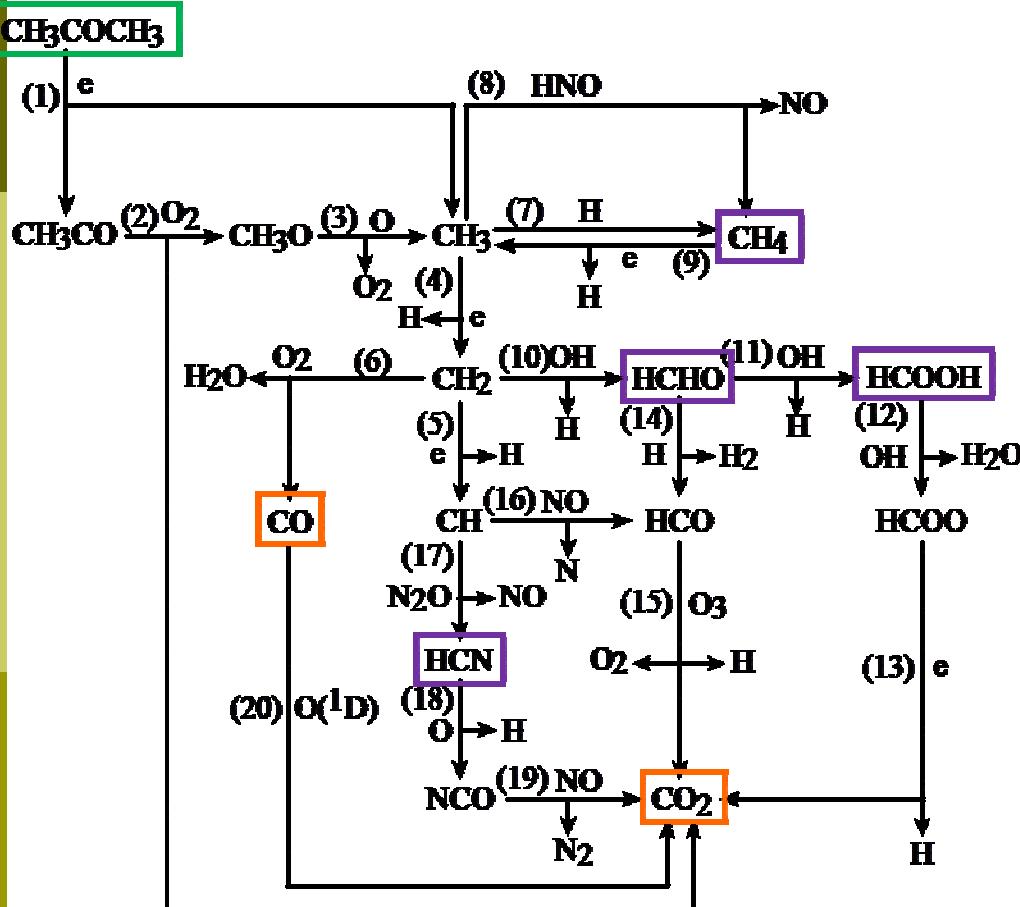


$$r_3 = k_3[\text{CH}_4][e] \quad 10^{13} \sim 10^{14} \text{ cm}^{-3}/\text{s}$$

→ The values of reaction rate indicate principal reactions.



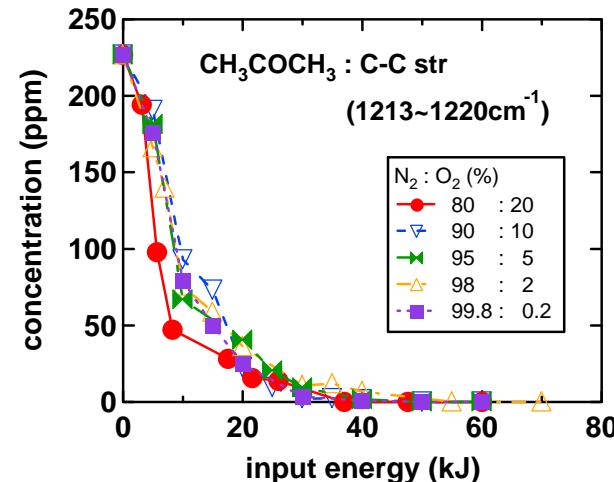
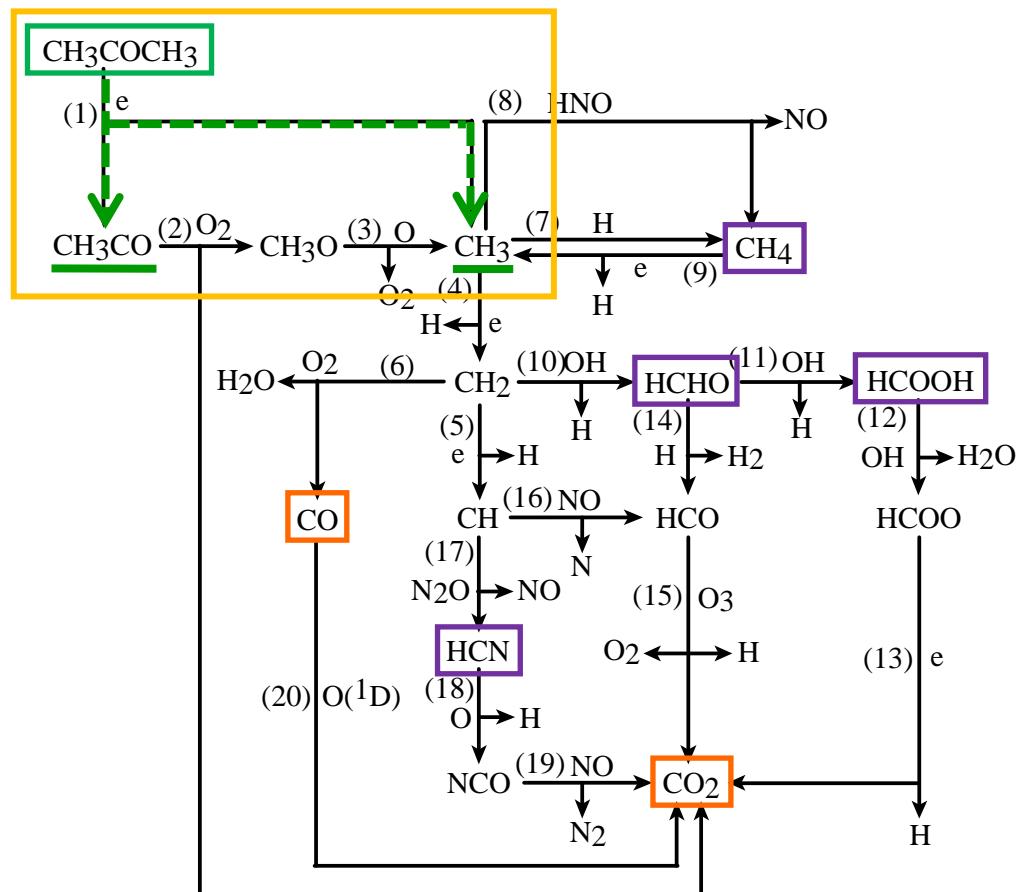
Decomposition process of acetone



No.	reaction formulae	rate constants:k
(2)	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CO}_2$	$4.7 \times 10^{-13} \text{ cm}^3/\text{s}$
(3)	$\text{CH}_3\text{O} + \text{O} \rightarrow \text{CH}_3 + \text{O}_2$	$1.6 \times 10^{-11} \text{ cm}^3/\text{s}$
(4)	$\text{CH}_3 + \text{e}^- \rightarrow \text{CH}_2 + \text{H} + \text{e}^-$	$7.7 \times 10^{-9} \text{ cm}^3/\text{s}$
(5)	$\text{CH}_2 + \text{e}^- \rightarrow \text{CH} + \text{H} + \text{e}^-$	$3.2 \times 10^{-9} \text{ cm}^3/\text{s}$
(6)	$\text{CH}_2 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	$4.0 \times 10^{-13} \text{ cm}^3/\text{s}$
(7)	$\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$	$2.4 \times 10^{-10} \text{ cm}^3/\text{s}$
(8)	$\text{CH}_3 + \text{HNO} \rightarrow \text{CH}_4 + \text{NO}$	$9.0 \times 10^{-12} \text{ cm}^3/\text{s}$
(9)	$\text{CH}_4 + \text{e}^- \rightarrow \text{CH}_3 + \text{H} + \text{e}^-$	$2.5 \times 10^{-16} \text{ cm}^3/\text{s}$
(10)	$\text{CH}_2 + \text{OH} \rightarrow \text{HCHO} + \text{H}$	$3.0 \times 10^{-11} \text{ cm}^3/\text{s}$
(11)	$\text{HCHO} + \text{OH} \rightarrow \text{HCOOH} + \text{H}$	$2.0 \times 10^{-13} \text{ cm}^3/\text{s}$
(12)	$\text{HCOOH} + \text{OH} \rightarrow \text{HCOO} + \text{H}_2\text{O}$	$3.2 \times 10^{-13} \text{ cm}^3/\text{s}$
(13)	$\text{HCOO} + \text{e}^- \rightarrow \text{CO}_2 + \text{H} + \text{e}^-$	$1.1 \times 10^{-12} \text{ cm}^3/\text{s}$
(14)	$\text{HCHO} + \text{H} \rightarrow \text{HCO} + \text{H}_2$	$5.7 \times 10^{-14} \text{ cm}^3/\text{s}$
(15)	$\text{HCO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 + \text{H}$	$8.3 \times 10^{-13} \text{ cm}^3/\text{s}$
(16)	$\text{CH} + \text{NO} \rightarrow \text{HCO} + \text{N}$	$1.3 \times 10^{-11} \text{ cm}^3/\text{s}$
(17)	$\text{CH} + \text{N}_2\text{O} \rightarrow \text{HCN} + \text{NO}$	$1.3 \times 10^{-16} \text{ cm}^3/\text{s}$
(18)	$\text{HCN} + \text{O} \rightarrow \text{H} + \text{NCO}$	$5.0 \times 10^{-18} \text{ cm}^3/\text{s}$
(19)	$\text{NCO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$	$2.0 \times 10^{-11} \text{ cm}^3/\text{s}$
(20)	$\text{CO} + \text{O}^{(1D)} \rightarrow \text{CO}_2$	$8.0 \times 10^{-11} \text{ cm}^3/\text{s}$

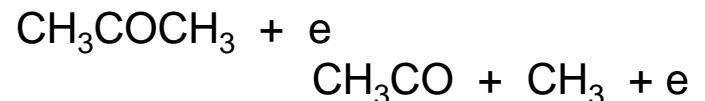


Acetone decomposition

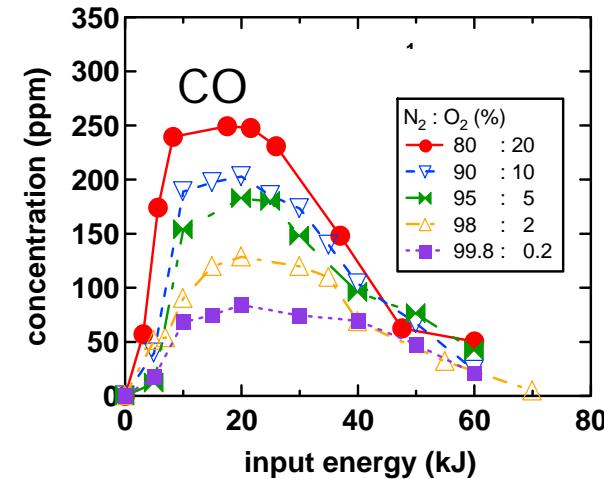
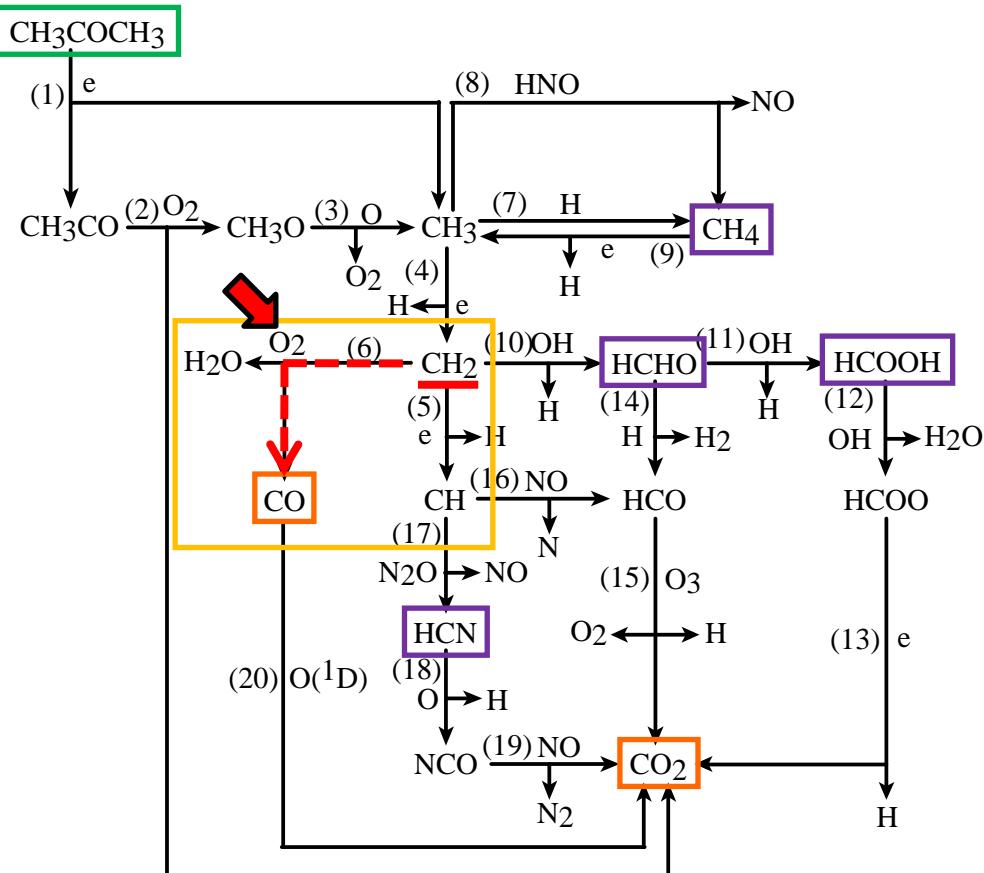


➤ The decomposition process of acetone has little dependence on the oxygen concentration.

➤ Acetone is assumed mainly by to be electron collision.



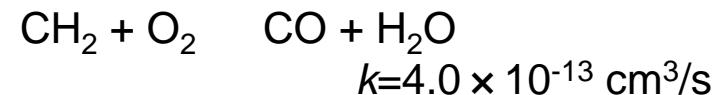
CO production



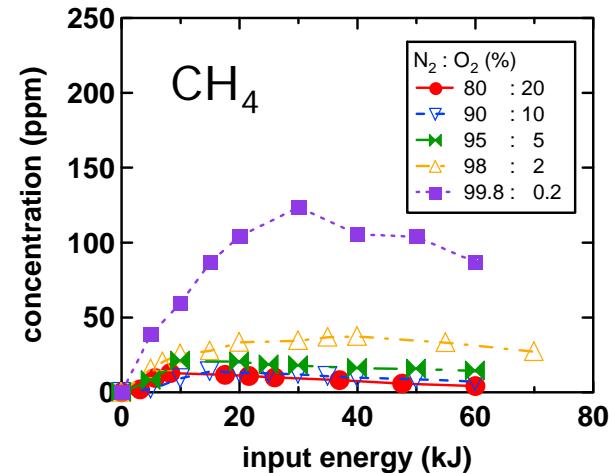
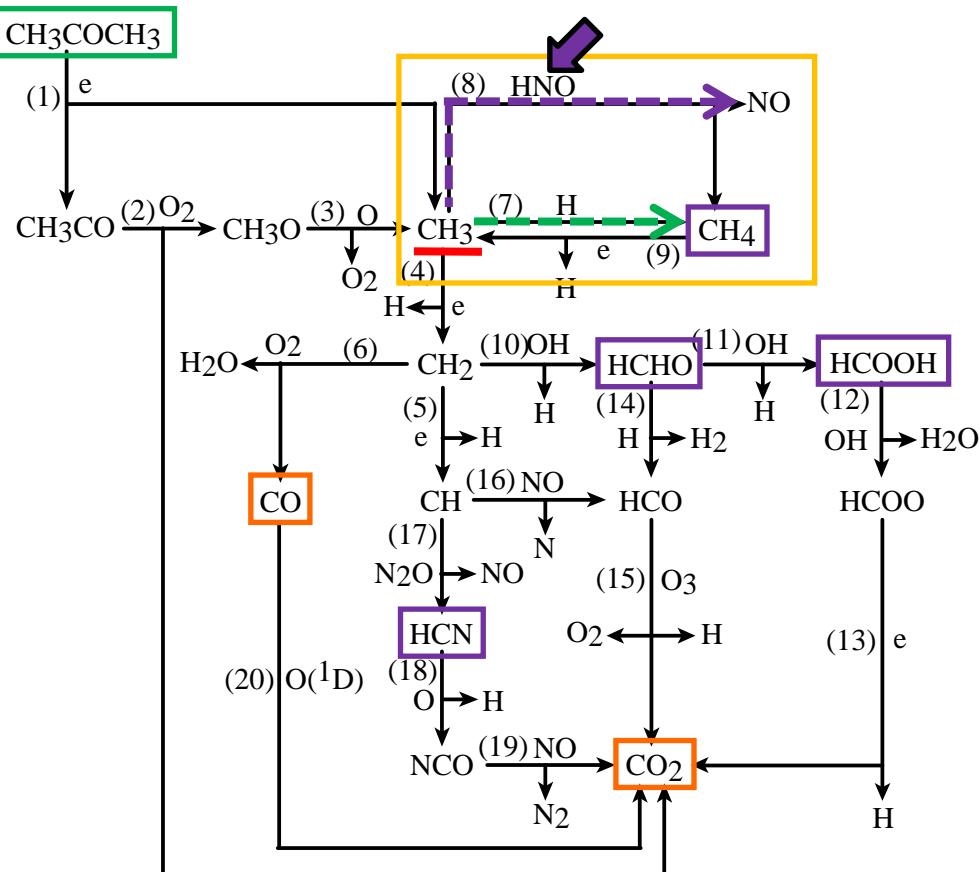
➤ The concentration of CO increases with the increase of oxygen concentration.



➤ Following reaction is suggested as CO production.



CH₄ production



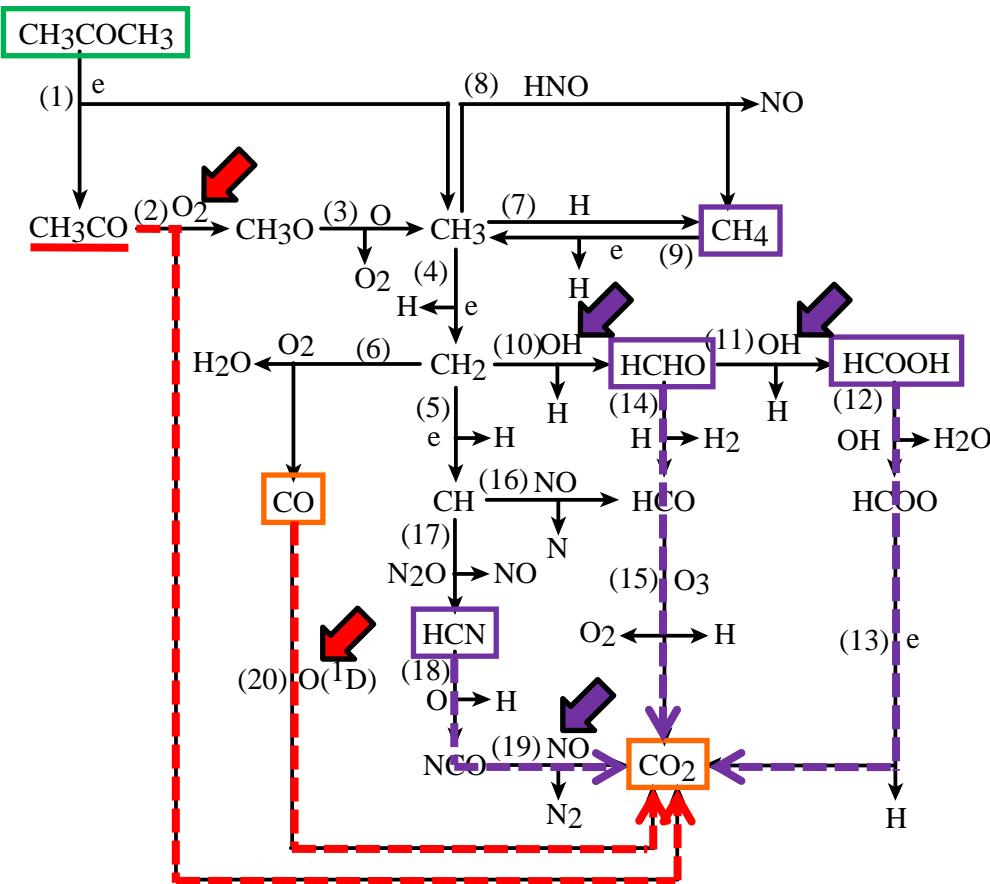
- CH₄ is probably produced by $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$, $k = 2.4 \times 10^{-10} \text{ cm}^3/\text{s}$
- CH₃ + HNO → CH₄ + NO, $k = 9.0 \times 10^{-12} \text{ cm}^3/\text{s.}$
- HNO radical is produced by $\text{NO} + \text{H} + \text{M} \rightarrow \text{HNO} + \text{M}$ (M:a third body)

The concentration of NO increases at low oxygen concentration.

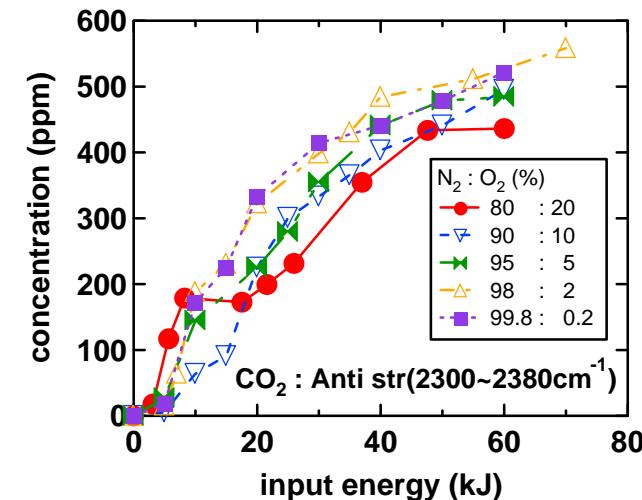
CH₄ produced this process increases at low oxygen concentration.



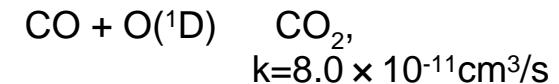
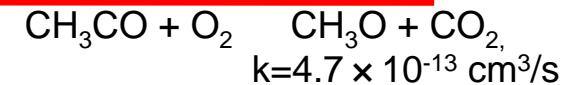
CO₂ production



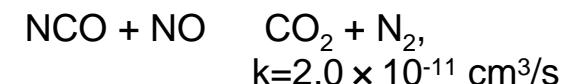
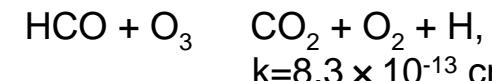
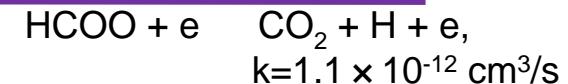
- Further study is needed for a quantitative understanding of the independence of the oxygen concentration for CO₂ concentration.



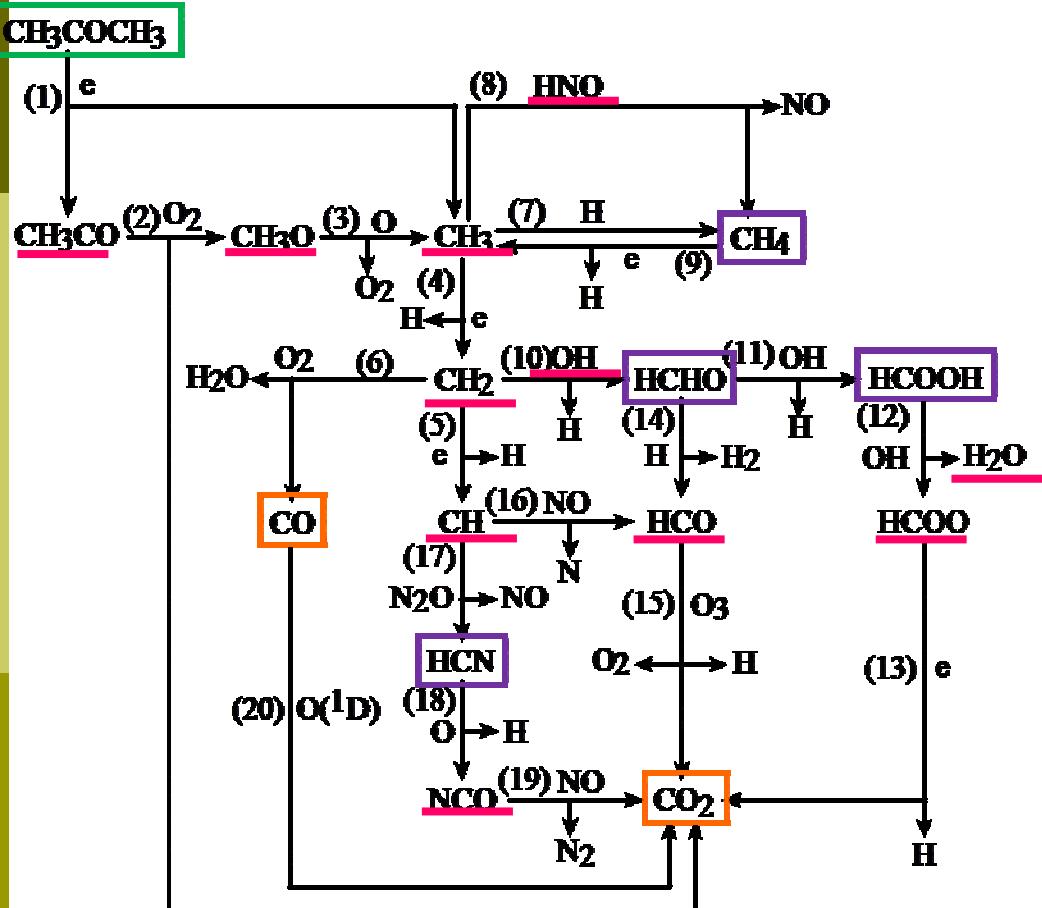
- CO₂ may be produced at high oxygen concentration



- at low oxygen concentration



Predicted products



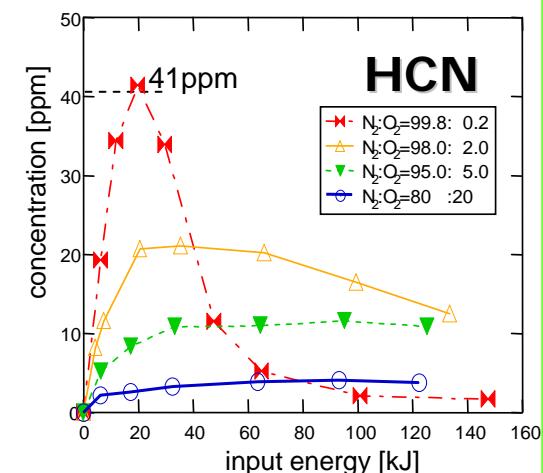
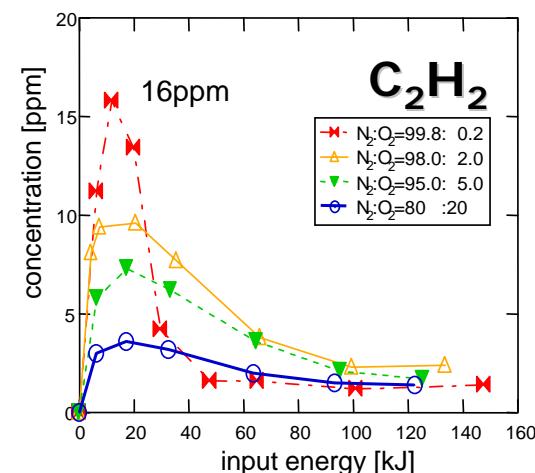
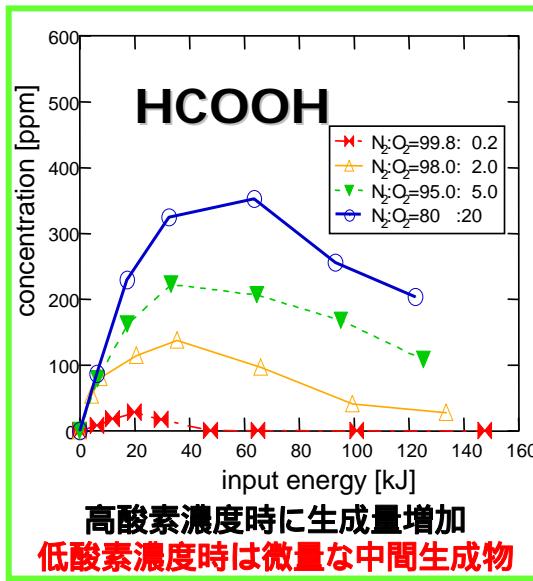
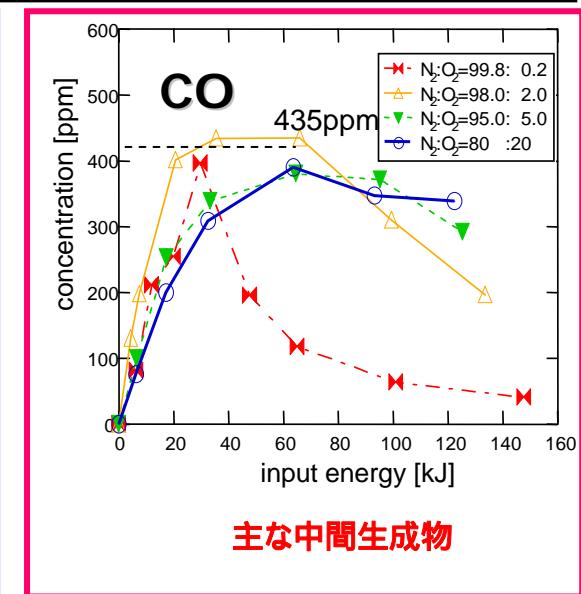
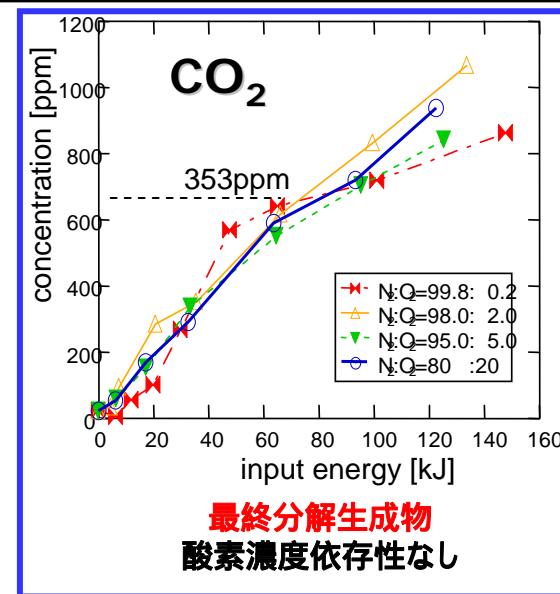
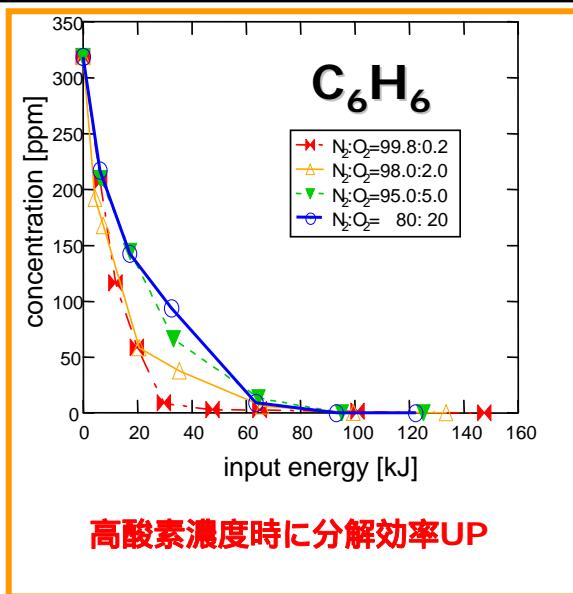
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(4)	$\text{CH}_3 + e \rightarrow \text{CH}_2 + \text{H} + e$	$7.7 \times 10^{-9} \text{ cm}^3/\text{s}$
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(9)	$\text{CH}_4 + e \rightarrow \text{CH}_3 + \text{H} + e$	$2.5 \times 10^{-16} \text{ cm}^3/\text{s}$
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(14)	$\text{HCHO} + \text{H} \rightarrow \text{HCO} + \text{H}_2$	$5.7 \times 10^{-14} \text{ cm}^3/\text{s}$
(15)	$\text{HCO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 + \text{H}$	$8.3 \times 10^{-13} \text{ cm}^3/\text{s}$
(16)	$\text{CH} + \text{NO} \rightarrow \text{HCO} + \text{N}$	$1.3 \times 10^{-11} \text{ cm}^3/\text{s}$
(17)	$\text{CH} + \text{N}_2\text{O} \rightarrow \text{HCN} + \text{NO}$	$1.3 \times 10^{-16} \text{ cm}^3/\text{s}$
(18)	$\text{HCN} + \text{O} \rightarrow \text{H} + \text{NCO}$	$5.0 \times 10^{-18} \text{ cm}^3/\text{s}$
(19)	$\text{NCO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$	$2.0 \times 10^{-11} \text{ cm}^3/\text{s}$
(20)	$\text{CO} + \text{O}^{(1D)} \rightarrow \text{CO}_2$	$8.0 \times 10^{-11} \text{ cm}^3/\text{s}$

環境汚染化学物質の放電分解における 原子・分子データの必要性

VOCに関するデータの現状 ~ Benzene, Toluene & Xylene ~



Concentration variations in N₂-O₂-C₆H₆



Reactions for benzene

Benzene			
Reaction	T [K]	k(T) [cm³/molecule s]	Number
Benzene + O ₂ Products	300	3.16x10 ⁻¹⁴	[1]
Benzene + O ₂ Adduct	300	1.85x10 ⁻¹⁴	[1]
Benzene + O ₃ Products	298	2.03x10 ⁻²²	[2]
Benzene + N ₂ (A ^{3Σ_u⁺) Products}	-----	1.6x10 ⁻¹⁰	[3]
Benzene + NO ₂ Phenyl + HNO ₂	600 – 1100	4.15x10 ⁻¹⁰ exp(-177/RT)	[4]
Benzene + NO ₃ Products	298	3.01x10 ⁻¹⁷	[5]
Benzene + OH Products	300	1.28x10 ⁻¹²	[6]
Benzene + OH Adduct	296	1.3x10 ⁻¹²	[7]
Benzene + OH Phenyl + H ₂ O	300	4.73x10 ⁻¹⁴	[8]
Benzene + Phenyl Biphenyl + H	300	8.14x10 ⁻¹⁶	[9]
Benzene + Phenyl Products	298	3.01x10 ⁻¹⁵	[10]
Reaction	T [K]	k(T) [s⁻¹]	Number
Benzene Products	1200 – 1500	8.99x10 ¹⁵ exp(-450/RT)	[6]
Benzene Phenyl + H	1520 – 2500	4.57x10 ¹³ exp(-372/RT)	[11]

- Reaction coefficients between electrons & benzene ?

Reactions for toluene

Toluene			
Reaction	T [K]	k(T) [cm³/molecule s]	Number
Toluene + O ₂ Products	300	7.91x10 ⁻¹⁴	[1]
Toluene + O ₃ Products	298	4.53x10 ⁻²²	[2]
Toluene + NO ₂ Products	295	2.09x10 ⁻²⁰	[12]
Toluene + NO ₃ Products	298	6.79x10 ⁻¹⁷	[5]
Toluene + OH Products	300	6.12x10 ⁻¹²	[13]
Toluene + OH Adduct	300	6.93x10 ⁻¹²	[6]
Toluene + OH Benzyl + H ₂ O	298	6.96x10 ⁻¹²	[14]
Reaction	T [K]	k(T) [s⁻¹]	Number
Toluene Products	1090 - 1190	1.23x10 ¹³ exp(-315/RT)	[15]
Toluene Benzyl + H	1000 - 2500	7.75x10 ¹⁴ (T/296) ^{0.68} exp(-373/RT)	[16]
Toluene Phenyl + CH ₃	1000 - 2500	2.24x10 ¹⁸ (T/296) ^{-1.73} exp(-436/RT)	[16]

- Reaction coefficients between electrons & toluene ?



Reactions for xylene

p-Xylene

Reaction		T [K]	k(T) [cm ³ /molecule s]	Number
<i>p</i> -Xylene + O ₂	Products	300	2.37x10 ⁻¹³	[17]
<i>p</i> -Xylene + O ₃	Products	300	1.54x10 ⁻²¹	[2]
<i>p</i> -Xylene + NO ₃	Products	298	4.53x10 ⁻¹⁶	[5]
<i>p</i> -Xylene + OH	Adduct	300	1.4x10 ⁻¹¹	[6]
<i>p</i> -Xylene + OH	Products	300	1.52x10 ⁻¹¹	[13]

Reaction		T [K]	k(T) [s ⁻¹]	Number
<i>p</i> -Xylene	Products	949 - 1030	3.79x10 ⁷ exp(-284/RT)	[20]
<i>p</i> -Xylene	Methylbenzyl + H	1100 - 1900	1.78x10 ¹⁶ exp(-369/RT)	[19]
<i>p</i> -Xylene	Benzyl + CH ₃	1210 - 1380	9.29x10 ¹² exp(301/RT)	[21]



Conclusions

大気圧コロナ放電によるVOC分解のfragments、by-productsを詳細に測定し、分解プロセスを検討した。

◆ 化学反応速度を指標として、アセトンの分解過程を示すことができた。

測定にかかるないby-productsの生成を予測できる。

電子による分解率は未定。

(予定) レート方程式解析により、副生成物等の生成量を得る。

◆ アセトンの他に、10種類以上のVOCの分解を試み、分解特性を得た。しかし、ほとんどのVOCの分解に関する基礎的データが少なく(反応係数、特に電子とVOCの反応、電子衝突断面積など)、分解過程の予測が困難である。

(予定) 分解実験の結果から、電子-VOC反応係数を求める。