

Thermal oxidation of acetone behind reflected shock wave

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Abstract

The thermal oxidation and the thermal decomposition of acetone, diluted with argon, has been observed using the UV absorption and IR emission behind the reflected shock wave. The time histories of absorption intensity at 270 nm and of emission intensity at 3.4 μm due to CH_3COCH_3 , of absorption intensity at 216 nm due to CH_3 , of absorption intensity at 310 nm due to OH, and of emission intensity at 4.2 μm due to CO_2 were followed. The oxidation schema $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{COCH}_2(\text{CH}_3\text{CHO}, \text{CH}_3) \rightarrow \text{H}_2\text{C}_2\text{O} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CO} \rightarrow \text{CO}_2$ was obtained by comparing the experimental profiles with the profiles of computer simulation.

Introduction

Acetone will be one of the fuels for automobile engine in the future. Miyashiro et al.[1] reported that (1) The spark ignition engine could run smoothly using acetone fuel. (2) Acetone has practically high octane number. So they could make the compression ratio high. (3) The CO concentration was about 1/10 of gasoline engine. However, NO_x, HC, aldehyde, acetic acid were more than those of gasoline engine. Therefore the knowledge of elementary oxidation mechanism is demanded from the engineering side. Beside this, acetone is one of ketone and the oxidation must be studied from various sides. In this work we tried to observe the time histories of IR-emission and UV-absorption intensities according to the previous shock tube methods.[2, 3]

Experimentals

Acetone is chemically active, so the mixture of acetone and oxygen could not be kept for a long time in a steel container, while it needs a long mixing time in order to reach the homogeneous gas phase. In this work the experiments were performed by using a stainless container and a stainless mixing system. We tried to check the stability of mixtures in a container by two methods: (1) The first was the measurement of the rates of pressure change in the container. There were no pressure change within error of 1 % in 17 hours for the mixtures of 20% acetone + 80% oxygen at initial pressures of 53kPa(400torr) 66kPa(500torr). The pressure of pure acetone (100%) at 13kPa(100torr) changed 4 % in 17 hours. Since the pressure was nearly in saturated condition, the condensation could occur during the checking time. At lower initial acetone pressure (8 kPa(60torr)) there was less pressure change, i.e. 3 % in 60 hours. (2) In the second check we observed the time histories of absorption at 270 nm and of emission at 4.2 μm in the mixture of 1 % acetone in argon for both cases of 1 hour and 13 hours after mixing. We observed also the time histories of absorption at 220 nm and of emission at 4.2 μm in the mixture of 1 % acetone + 4 % oxygen in argon for both cases of 2 and 36 hours after mixing. In both cases we have not observed the visible differences. Therefore we considered that there was little chemical reaction in the containers, because we used much more diluted mixtures. We took the signals in 10 hours after mixing. The experiments were performed in a usual shock tube, whose diameter is 100 mm. The low pressure section is 4250 mm long, while the high pressure section is 2020 mm. Four platinum resistance gauges were used for the attenuation measurement of incident shock velocity. The photomultiplier and the infrared detectors served for the measurements in the ultraviolet region and the infrared region, respectively. The purities of gases, which were used without further purification, were: 99.5 % CH_3COCH_3 ($\text{H}_2\text{O} \leq 0.3\%$, $\text{CH}_3\text{COOH} \leq 0.0015\%$, $\text{HCHO} \leq 0.002\%$, $\text{CH}_3\text{OH} \leq 0.05\%$), 99.9 % O_2 , and 99.9995 % Ar. The mixtures 0.02-0.5% CH_3COCH_3 %, 0.04-10% O_2 diluted with Ar were used for the measurement.

Results and discussion

Mainly the ultraviolet absorption due to CH_3COCH_3 and the infrared emission due to CO_2 were measured to obtain the concentration profiles. Fig. 1 shows one example of the signal. In the figure the line CO_2 $4.2 \mu\text{m}$ shows an IR emission at $4.2 \mu\text{m}$. The line CH_3COCH_3 270nm is a UV absorption profile at 270 nm . The line CO_2calc and $\text{CH}_3\text{COCH}_3\text{calc}$ are the calculated concentration profiles of CO_2 and CH_3COCH_3 .

The absorption due to acetone at 270 nm decreased exponentially in the case of stoichiometric mixture behind the reflected shock wave. It had no evident induction period, but it was apparently similar to the signal of thermal decomposition, though the decomposition rate was large. After the absorption vanished, CO_2 emission at $4.2 \mu\text{m}$ appeared. On the contrary the oxygen-rich mixture showed a clear induction period like the case of methane oxidation. Two sorts of induction period were defined using these signals. The one was the time ($\tau_{a,1/2}$) until half value of CH_3COCH_3 absorption and the other was the time of appearance of CO_2 emission (τ_{CO_2}). There was complex influence of the concentration and the temperature on the induction periods. In previous studies the induction periods were expressed with one equation. However, if the experiments will be performed under a wide range of conditions, they cannot be expressed with a single equation. However, in order to compare the general characteristics of acetone oxidation with other hydrocarbon molecules we tried to express the induction periods with one equation for the 0.1 to 1.0 % mixtures. The induction periods of τ_{CO_2} :

$$\tau_{\text{CO}_2} = 1.3 \times 10^{-12} [\text{CH}_3\text{COCH}_3]^{0.29 \pm 0.02} [\text{O}_2]^{-0.53 \pm 0.03} [\text{Ar}]^{-0.25 \pm 0.03} \exp(166 \pm 40 [\text{kJ/mol}]/RT) \quad (1)$$

In Fig. 2 one can see the induction periods τ_{CO_2} . The circles in the figure show the results for the equivalence ratio $\phi = 0.2$, the squares show those of $\phi = 1.0$ and the rhombi show those of $\phi = 2.0$. This figure shows that the induction periods τ_{CO_2} in the mixture, highly diluted with argon could be expressed with one empirical formula.

The induction periods of $\tau_{a,1/2}$ could be expressed with the same form of equation, though the concentration and the temperature dependencies were not the same as τ_{CO_2} . The power dependencies of the acetone and oxygen concentration were small or almost zero. This suggested that the induction periods defined by the concentration profile of fuel itself did not depend on the oxygen. They did not depend on the fuel concentration, if the induction period was defined by the relative concentration profile, such as half value of fuel concentration. This indicated that the reaction at the initial step of the oxidation is mainly due to the thermal decomposition of fuel. This result can be obtained for the oxidation of fuel, which is thermally unstable. We observed such results for the propane and methanol oxidation. When the induction periods were defined by the end products, there must be much larger influence of the oxygen, since the reactions, radical + O_2 must play an important role.

$$\tau_{a,1/2} = 5.0 \times 10^{-12} [\text{CH}_3\text{COCH}_3]^{0.02 \pm 0.06} [\text{O}_2]^{-0.09 \pm 0.04} [\text{Ar}]^{-0.33 \pm 0.04} \exp(157 \pm 40 [\text{kJ/mol}]/RT) \quad (2)$$

Beside these two wavelengths we could observe other absorption and emission signals. The absorption due to acetone itself could be observed between 210 and 370 nm and it had the maximum value between

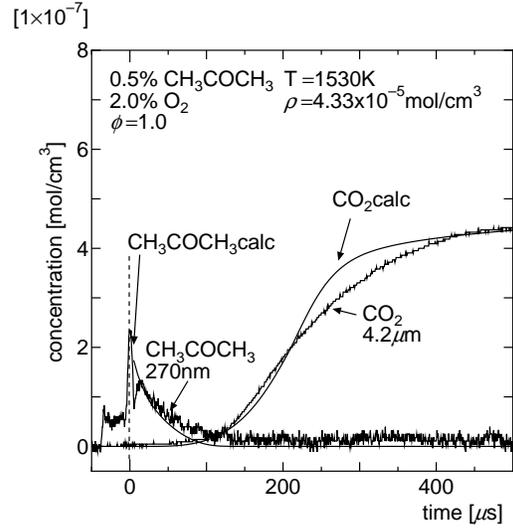


Figure 1: Profiles of absorption due to acetone and emission due to CO_2 .

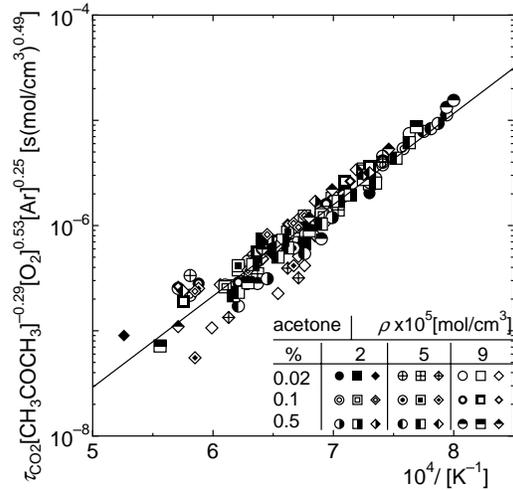


Figure 2: Reduced induction periods for mixtures: 0.02, 0.1, 0.5 % CH_3COCH_3 , $\rho = 2, 5, 9 \times 10^{-5} [\text{mol/cm}^3]$ in argon.

270 and 300 nm. At the wavelength between 200 and 210 nm there were also absorption due to acetone. It increased with decreasing wavelength. The absorption under 200 nm could not be measured with our optical system. At the wavelengths between 210 and 250 nm there were several molecules which had absorption. At first the absorption had a stepwise signal due to acetone and oxygen behind reflected shock wave, and adding to this stepwise signal, the signal increased more or less due to the absorption of intermediates, whose extinction coefficients are larger than that of acetone. The CH_3 radical absorption was observed at 216 nm in both cases of thermal decomposition and oxidation. It appeared behind the reflected shock wave rapidly and disappeared soon due to the followed reactions[4].

We measured the rate constant k_1 of the thermal decomposition of acetone using the acetone absorption signals at 270 nm and the methyl radical absorption at 216 nm for the mixture 0.02 % acetone. The rate constant was defined as follows: (1) $d[I_{270nm}]/dt = -k_1[I_{270nm}]$ by considering that the absorption of 0.02% mixture at 270 nm is due to acetone. (2) $d[\text{CH}_3]/dt = 2 \times k_1[\text{CH}_3\text{COCH}_3]$ by considering that the absorption at 216 nm is due to methyl radical at the beginning of the reaction, i.e. near $t=0$. From these results we estimated the rate constant of thermal decomposition. We did not measure the rate constant in a wide range of pressure, because we found that we could use the values of Ernst[5]. Around 216 nm there was also the absorption of other intermediates after the absorption reached the maximum. The decadic molar extinction coefficients ϵ are at 220 nm $\epsilon=8 \times 10^5 \text{ cm}^2/\text{mol}$ by $\text{H}_2\text{C}_2\text{O}$ at 1300 K, 4×10^4 by C_2H_2 at 1400 K, 2×10^4 by C_2H_4 at 1400 K, 8×10^5 by HO_2 at 1200 K, 7×10^4 by H_2O_2 at 1400 K, 1.4×10^3 by O_2 at 1400 K, 2×10^3 by CO_2 , while they were 2×10^6 by CH_3 and 1.2×10^3 by CH_3COCH_3 . The wavelength dependences of the $-\log(I_{max}/I_0) = \epsilon c_{max}$ obtained at thermal decomposition of acetone showed similar profile of ketene + methyl radical. The absorptions around 210-250 nm went to quasi equilibrium state, after the absorption reached the maximum. The wavelength dependences of the $-\log(I_{equil}/I_0) = \epsilon c_{equil}$ was similar to those of ethylene or acetylene.

The profiles of acetone oxidation were also similar between 200 and 230 nm. Here, I_{max} was the maximum absorption behind reflected shock wave. The absorption signal went to zero after it reached the maximum. There was a similar influence at 270 nm, whose wavelength was used in this work to define the induction period. Namely, the coefficients ϵ were 3×10^3 by CH_3CHO , 4×10^4 by $\text{H}_2\text{C}_2\text{O}$, 2×10^4 by C_2H_2 , 2×10^2 by C_2H_4 , 8×10^4 by HO_2 , 4×10^4 by HO_2 at 1250 K, furthermore as some examples, for complex higher hydrocarbons 2×10^4 by CH_2CCH_2 , 2×10^3 by $\text{CH}_3\text{C}_2\text{H}$, 8×10^3 by $\text{n-C}_7\text{H}_{10}$, while ϵ was 2×10^4 by CH_3COCH_3 . Beside these molecules there must have been some absorption due to CH_3CO and CH_3COCH_2 , but we could not obtain the coefficients. If one used the same coefficients for these two molecules, then the sum of absorption intensities for the molecules made the measured absorption signal similar.

At 310 nm the OH absorption could be observed like other oxidation of hydrocarbons. However, this absorption included the absorption of acetone itself, whose decadic molar extinction coefficient was $\epsilon = 1.7 \times 10^4$ at 1100 K. The absorption of acetone was observed behind reflected shock wave, and showed at first constant signal there. At the moment that the absorption decreased after a certain period τ_{OH} , it increased due to OH production again. The acetone had an emission at $3.4 \mu\text{m}$ like other hydrocarbons. At $4.8 \mu\text{m}$ the emission of CO was observed around 4.7 and $4.9 \mu\text{m}$. Fig. 3 shows the induction periods. Interesting is that the decay time of acetone at 270 nm defined by $d[\text{CH}_3\text{COCH}_3]/dt = 1/\tau_{a,m}[\text{CH}_3\text{COCH}_3]_0$ had almost the same apparent activation energy as other induction periods. The induction periods $\tau_{a,i}$ were defined at the moment when the acetone decay began. This induction period could not be measured, because it was almost 0 in most cases. The induction period used in this work is equal to $\tau_{a,i} + \tau_{a,m}/2$. Therefore the apparent activation energy of our induction period $\tau_{a,1/2}$ was similar to that of $\tau_{a,m}$, because it was practically half of $\tau_{a,m}$. The induction period τ_{OH} was $\tau_{a,i} + \tau_{a,m}$.

We tried to obtain the concentration profiles by computer simulation. One result can be seen in Fig. 1, indicated with the suffix (calc). The rate constants were used in Table 1:

One sensitivity check of the rate constants for reactions 1-5 showed the several changes of absorption

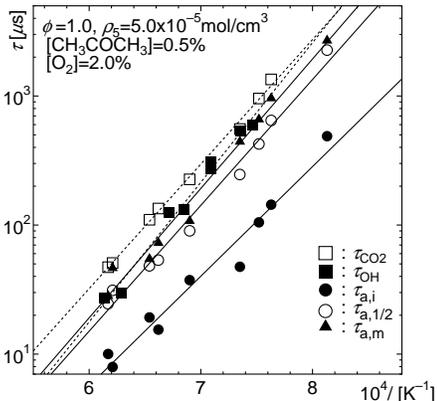


Figure 3: Induction periods for mixtures: 0.5 % CH_3COCH_3 , $\phi = 1.0$ in argon. τ_{CO_2} is the moment of appearance of CO_2 emission, τ_{OH} is the appearance of OH absorption. $\tau_{a,i}$ and $\tau_{a,1/2}$ are the moment of acetone decay and the moment of half value of acetone signal, and $\tau_{a,m}$ is the decay time of acetone in the main reaction zone.

profiles at 270 nm. The values in Table 1 were the best fit of the profiles at thermal decomposition and thermal oxidation. Ernst et al. [5] performed precise experiments for the thermal decomposition of acetone in a wide range of pressure, and gave $k_{1,ernst} = 1.5 \times 10^{13} \exp(-64000/RT)$ [1/s] for the rate constant at $\rho = 1.2 \times 10^{-4}$ [mol/cm³]. The activation energies were taken from their values and the absolute rate constant k_1 at the same density in this work were obtained from the decay rate of absorption at 270 nm and the increasing rate of the methyl radical, as mentioned above, and the k_1 was 4 times larger than their values. On the contrary we needed to make the rate constant smaller than our values k_1 , in order to make the decay rate fit in with the values measured in the acetone+oxygen+argon mixtures. Therefore one can consider that the rate constant is in two values. The reactions O and H atoms with CH₃COCH₃ must play a large role in the oxidation mechanism. However, since there were no main reaction sequences, we did not check the sensitivity analysis. In this work we could obtain a rough estimation for the acetone oxidation mechanism. Further study will provide us with more precise information.

Table 1: Reaction mechanism of acetone oxidation, adding to the reaction mechanism ([2, 3, 4] and others). k_1 and k_2 are values at $\rho = 1.2 \times 10^{-4}$. Units: kJ,mol,cm,s

no.	reactions	k (rate constants)	units
1	CH ₃ COCH ₃ + (Ar) → CH ₃ CO + CH ₃ + (Ar) ;	$6.0 \times 10^{13} \exp(-266000/RT)$	[1/s]
2	CH ₃ COCH ₂ + (Ar) → H ₂ C ₂ O + CH ₃ + (Ar) ;	$5.0 \times 10^{11} \exp(-209000/RT)$	[1/s]
3	CH ₃ COCH ₃ + CH ₃ → CH ₃ COCH ₂ + CH ₄ ;	$1.0 \times 10^{13} \exp(-46000/RT)$	[cm ³ /mol s]
4	CH ₃ COCH ₃ + OH → CH ₃ COCH ₂ + H ₂ O ;	$2.0 \times 10^{12} \exp(-42000/RT)$	[cm ³ /mol s]
5	CH ₃ COCH ₂ + O ₂ → H ₂ C ₂ O + CH ₂ O + OH ;	$1.0 \times 10^{12} \exp(-147000/RT)$	[cm ³ /mol s]
6	CH ₃ COCH ₃ + O → CH ₃ COCH ₂ + OH ;	$1.0 \times 10^{12} \exp(-21000/RT)$	[cm ³ /mol s]
7	CH ₃ COCH ₃ + H → CH ₃ COCH ₂ + H ₂ ;	$1.0 \times 10^{12} \exp(-21000/RT)$	[cm ³ /mol s]
8	CH ₃ COCH ₃ + HO ₂ → CH ₃ COCH ₂ + H ₂ O ₂ ;	$1.0 \times 10^{12} \exp(-24000/RT)$	[cm ³ /mol s]
9	CH ₃ COCH ₃ + OH → CH ₃ CHO + CH ₃ O ;	$2.0 \times 10^{12} \exp(-63000/RT)$	[cm ³ /mol s]
10	CH ₃ COCH ₃ + O → CH ₃ CO + CH ₃ O ;	$1.0 \times 10^{12} \exp(-42000/RT)$	[cm ³ /mol s]
11	CH ₃ COCH ₃ + H → CH ₃ CHO + CH ₃ ;	$1.0 \times 10^{12} \exp(-42000/RT)$	[cm ³ /mol s]
12	CH ₃ CO → CH ₃ + CO ;	$2.0 \times 10^{11} \exp(-15000/RT)$	[1/s]
13	CH ₃ CHO oxidation		
14	H ₂ C ₂ O oxidation		

Conclusion

The time histories of chemical species, CH₃COCH₃, CO₂, OH, CH₃, H₂C₂O were observed in the thermal decomposition and the thermal oxidation of acetone behind reflected shock waves. The oxidation sequences could be followed by comparing the concentration profiles with those of the computer simulation.

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