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UV Absorption Studies of the Pyrolysis of Isobutane in Shock Waves

Tohru Koike* and Kihei Morinaga

Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239

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The UV absorption measurements at 216 nm were carried out for two shock-heated mixtures, 1.5 and 2.0% i-C_4H_{10} diluted in Ar, in the temperature range of 1300—1800 K, and at an atmospheric pressure of about half. From the initial absorption rise attributed to the CH_3 growth, the rate constant of the initiation reaction, $i\text{-}C_4H_{10} = CH_3 + i\text{-}C_3H_7$, was evaluated as $k = 10^{12.8\pm0.5}\exp[-(60.8\pm4.6)\ \mathrm{kcal}/RT]/\mathrm{s}^{-1}$. A comparison between the k value so derived and the formerly reported values was made. A computer modeling using a 39-reaction mechanism could reproduce the absorption at the early stage of the reaction at temperatures lower than 1550 K, whereas the modeled absorption was smaller than the measured at much high temperatures. The absorption by C_3H_5 (allyl radical) must be taken into account in order to lessen this difference.

Computer modeling has been used often in studying complex reaction mechanisms. We ourselves demonstrated the capability of the method in studies of C_3H_8[1] and n-C_4H_{10}[2] pyrolysis and have proposed reaction mechanisms for them.

In comparison with the n-C_4H_{10} pyrolysis, the i-C_4H_{10} pyrolysis can be interpreted rather simply, as in the case of the C_3H_8 pyrolysis, since it gives only one initiation reaction:

$$i\text{-}C_4H_{10} = CH_3 + i\text{-}C_3H_7. \qquad (1)$$

Therefore, if the k_1 value can be determined precisely by means of a time-resolved measurement of the growth or the decay of any species appearing in Reaction (1), only secondary reactions, the k values of most of which are available in the existing literature, need to be examined. Computer modeling shows its usefulness in such a case.

Bradley[3] proposed the basic reaction mechanism of the i-C_4H_{10} pyrolysis from his discernment of alkane pyrolysis at high temperatures. He measured the product distribution of the pyrolysis in the temperature range of 1200—1500 K by means of a single-pulse shock-tube technique and confirmed the validity of the mechanism by computer modeling. At lower temperatures than Bradley's, many studies of the pyrolysis by other experimental techniques have been reported.[4–8] Pratt and Rogers[4] investigated the pyrolysis around 1000 K using a wall-less reactor and proposed a reaction mechanism after surveying almost all of the i-C_4H_{10} pyrolysis studies ever reported. They also compared their own k_1 value with those reported by several other workers.[3,5–8] The k_1 value obtained by Bradley[3] exhibited a distinct fall-off with a smaller activation energy than those reported around 1000 K.

Since Bradley's study is the only one carried out in the high-temperature range, as far as we are aware, and since it gave a k_1 value different from others, another shock-tube study of the pyrolysis, especially devised to check the k_1 value, is required. In this study, we measured the 216 nm absorption in the i-C_4H_{10} pyrolysis behind incident shock waves. From the initial increase in the absorption attributed to the CH_3 growth alone, the k_1 value was evaluated. The k_1 value thus obtained is incorporated into a reaction mechanism of the pyrolysis, and the absorption at 10 μs in lab. time, when C_2H_4 and C_3H_6 are expected to appear much and when these species as well as CH_3 absorb the 216 nm light, is elucidated by computer modeling.

Experimental

The shock tube and the optical system used in this study have been described in detail in a preceding paper.[9] Briefly, the test gases, i-C_4H_{10}/Ar = 1.5/98.5 and 2.0/98.0, prepared from 99.8% pure i-C_4H_{10} (Takachiho Co.) and 99.999% pure Ar (Nippon Sanso Co.) at starting pressure of 20.0 ± 0.5 Torr (1 Torr ≈ 133.322 Pa) were heated up to high temperatures (1300—1800 K) by means of incident shock waves. The reaction profile was observed by means of UV absorption spectroscopy with a D_2-lamp (Hanau, D200F). The light from the lamp was passed through the shock-tube windows and was detected by means of a photomultiplier (Hamamatsu-TV, R208) with a monochromator (Jarrell-Ash, JE25; dispersion = 3.3 nm/mm, entrance and exit slit width = 1 mm).

Computer modeling was done using the program mentioned previously.[9] The flow model assumed in the modeling was a laminar-boundary-layer growth with a limiting separation. The thermochemical data of each species were taken from several available sources; these sources are shown in the footnote of Table 1.

Results and Discussion

Figure 1 shows a typical oscillogram of the absorption profile at 216 nm obtained in this study. The absorption increases right after the arrival of the shock at the observation window and thereafter maintains a plateau. Since no absorption was observed at the shock front, i-C_4H_{10} does not absorb the 216 nm light. This is in accordance with the former experimental

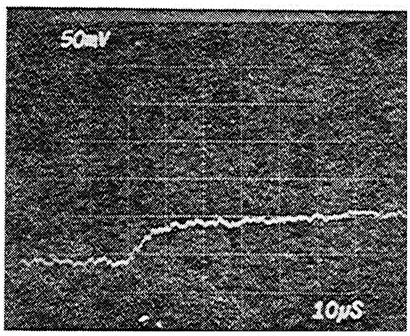

Fig. 1. A representative oscillogram for 1.5% i-C_4H_{10} in Ar mixture, P_1 = 20 Torr, and T_2 = 1478 K.

results reported for small alkanes,[10] such as CH_4,[11] C_2H_6,[11,12] C_3H_8,[13] and n-C_4H_{10},[2] having no absorption band in this wavelength region.

The unimolecular decomposition of i-C_3H_7 produced by Reaction (1) also gives CH_3.

$$i\text{-}C_3H_7 = CH_3 + C_2H_4 \tag{19}$$

The methyl radical so produced reacts mainly with i-C_4H_{10} at early in the reaction as:

$$CH_3 + i\text{-}C_4H_{10} = CH_4 + i\text{-}C_4H_9, \tag{4}$$

$$CH_3 + i\text{-}C_4H_{10} = CH_4 + t\text{-}C_4H_9. \tag{5}$$

Methyl recombination is another important step in the CH_3 disappearance:

$$2CH_3 + M = C_2H_6 + M. \qquad (-27)$$

The computer modeling adopted later indicates that the rates of Reactions (4), (5), (19), and (−27) are much smaller than that of Reaction (1) early in the reaction. Thus, the influence of these secondary reactions on the CH_3 profile can be neglected, and the CH_3 growth rate is given by:

$$d[CH_3]/dt = k_1[i\text{-}C_4H_{10}].$$

It has been reported that the absorptivity of i-C_3H_7 at 216 nm is at least 10 times smaller than that of CH_3.[14] Moreover, i-C_3H_7 is very unstable under the present experimental conditions, and the modeled [i-C_3H_7] is about three orders of magnitude smaller than that of CH_3. Thus, the increase in the absorption early in the reaction can be attributed solely to the CH_3 growth. The above equation implies that the evaluation of the initial slope of the absorption provides the k_1 value with an explicit relation of $[CH_3]_t=\log(I_0/I_t)/(a\cdot d)$, where I_0=incident light intensity, I_t=transmitted light intensity at reaction time t (in particle time), a=absorptivity ($cm^2\ mol^{-1}$), and d=optical path length (7.2 cm). The absorptivity of CH_3 was taken from that reported elsewhere.[11,12] Since the absorptivity reported was measured in an effective bandwidth of 1.6 nm, which is almost equal to the present one, it was assumed to be applicable to the present study without any correction.

The k_1 values so evaluated are shown in Fig. 2. The least-squares calculation provides the following Arrhenius expression for k_1 with one standard error (the data points above 1600 K, which deviate from the linear extrapolation of the low-temperature values, were not taken into account in the calculation):

$$k_1 = 10^{12.8\pm0.5}\exp[-(60.8\pm4.6)\ \text{kcal}/RT]/\text{s}^{-1}.$$

Tsang[5] estimated the rate constants of alkane decompositions within the high-pressure limit, k^∞, around 1100 K by means of a single-pulse-shock-tube experiment. Recently, he studied the temperature dependence of the k^∞ value and reached the conclusion that these A factors decrease with an increase in the temperature in the temperature range of 300—1100 K. If such an effect is negligibly small in a narrower temperature range, and if the $k_1{}^\infty$ value, the k_1 value within the high-pressure limit, is extrapolated to above 1100 K, as is shown in Fig. 2, we can see a distinct deviation of the present k_1 value from the $k_1{}^\infty$ value with an increase in the temperature, though the present k_1 is almost equal to the $k_1{}^\infty$ value at temperatures around 1300 K. Besides the $k_1{}^\infty$ value by Tsang,[5] several $k_1{}^\infty$ values measured around 1000 K have been reported. One of them is by Golden *et al.*[8] This $k_1{}^\infty$ value, however, can not be comparable with others, since it is doubtful if the VLPP technique used to obtain it is free from the surface effects, which may lead to a high $k_1{}^\infty$ value. Another one is by Pratt and Rogers.[4] At 1300 K, their $k_1{}^\infty$ value extrapolated is about 10 times smaller than the present k_1 value. Even if the decrease of the $A_1{}^\infty$ factor of the $k_1{}^\infty$ value is expected as above, we can not explain such a large difference between the two values. Therefore, the $k_1{}^\infty$ value by Pratt and Rogers[4] seems also to have some error.

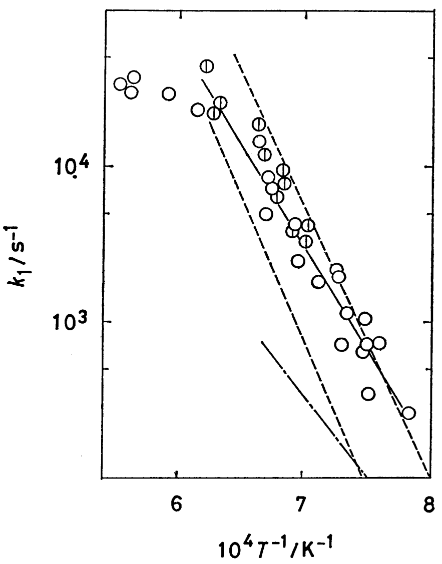

Fig. 2. Arrhenius plots for k_1.
The symbols used are as follows: ○; for 2% i-C_4H_{10} in Ar mixture and ⦶; for 1.5% i-C_4H_{10} in Ar mixture. The solid line shows a least squares fit for the data points below 1600 K. The upper and lower broken lines show the k_1 values in Ref. 5 (Tsang) and in Ref. 4 (Pratt and Rogers), respectively. The chain line shows the k_1 value in Ref. 3 (Bradley).

Although it has been confirmed qualitatively that the present k_1 value above 1300 K is in the fall-off range, it is difficult to find precisely where the present k_1 value is on the fall-off curve, for the present k_1 value was measured at almost equal pressures (P_2=0.45—0.60 atm, 1 atm=101325 Pa) and there is an ambiguity in the $k_1{}^\infty$ value at high temperatures. Further experiments at different pressures might be necessary to ascertain the exact fall-off behavior of the k_1 value. The k_1 value reported by Bradley,[3] which is considered to be in the fall-off range, will be referred to later.

As the pyrolysis proceeds, many kinds of products appear, and the absorption is an aggregated one by these products. We interpreted the absorption profile with the aid of computer modeling and tried to propose a reaction mechanism of the i-C_4H_{10} pyrolysis. To facilitate the computer modeling, we adopted the absorption at lab. time 10 μs, $A_{10}=\ln(I_0/I_{10})$ for the

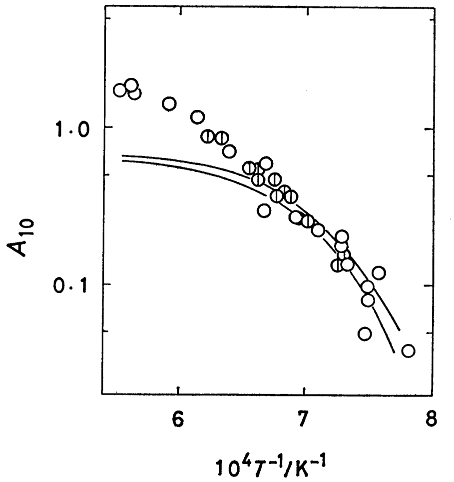

Fig. 3. A comparison between measured and modeled A_{10}.
The symbols are as in Fig. 2. The upper and lower lines show the modeled A_{10} for the 2% and 1.5% mixtures, respectively.

parameter, as in the study of the n-C_4H_{10} pyrolysis reported before. In Fig. 3, the A_{10} values so evaluated are shown *vs.* $10^4/T$. The output of the computer modeling given by the time variation in the concentration of each species is converted to the absorption as: $A=2.303\times a_i[C_i]d$, where $[C_i]$ is the modeled concentration of each species. The A value at the same lab. time is considered to correspond to the above A_{10}. The species which were assumed to absorb the 216 nm light were CH_3,[11,12] C_2H_4,[9] and C_3H_6.[2] The absorptivities of the latter two species, which were measured with the same optical set-up as the present, were mentioned in a previous paper.[9] The absorption by C_2H_2 is expected to be negligible under the present experimental conditions, since a negligible effect of C_2H_2 absorption on the A_{10} value was seen in the modeling of the n-C_4H_{10} pyrolysis previously reported.[2] The absorption by i-C_4H_8 was assumed to be negligible.

Figure 3 shows that a nice agreement between the modeled and measured A_{10} values is established at lower temperatures below 1550 K; at much higher temperatures, however, the modeled A_{10} values are much smaller than the measured ones. The sensitivity test to be discussed later indicates that there might be no way of improving the disagreement only by changing any k values in Table 1. In the modeling of the absorption, there does not seem to be any species which appears in a large amount and which shows a large absorption at higher temperatures.

With an increase in the temperature, the modeled concentration of $C_3H_5(CH_2\text{=}CH\text{–}\dot{C}H_2)$ gets much larger than those of other radicals and is comparable to the concentrations of stable products, such as CH_4 and C_2H_4. The strong absorption of C_3H_5 in this wavelength range was observed in the C_3H_6 pyrolysis measured in shock waves[2] and in the 1-C_4H_8 photolysis at room temperature.[16] If we adopt the absorptivity of about $2\times10^7\ cm^2\ mol^{-1}$ reported in the latter study, the modeled A_{10} values drastically go up to near the measured values. Besides the main route of forming C_3H_5 *via* C_3H_6, the following route *via* i-C_4H_8 may be present in the i-C_4H_{10} pyrolysis:

$$i\text{-}C_4H_8 = CH_3 + (CH_2\text{=}\dot{C}\text{-}CH_3).$$

The radicals thus formed is expected to be stabilized to the allyl radical after a few collisions, since it has been reported that,[17] due to the resonance, the heat of formation of the allyl radical is about 20 kcal/mol smaller than that of $(CH_2\text{=}\dot{C}\text{–}CH_3)$. Thus, in the modeling of the high-temperature absorption of the i-C_4H_{10} pyrolysis, it is necessary to clarify the route of forming C_3H_5 and to take into account the absorption by the allyl radical.

Table 1 shows the reaction mechanism of the i-C_4H_{10} pyrolysis derived in this study. The reaction mechanism can explain the absorption profile early in the reaction at temperatures lower than 1550 K. Pratt and Rogers' mechanism,[4] which includes explicitly the reactions of C_4H_9 isomers, is the original of the present mechanism. The reactions accompanying the species having more than 5 carbons and the reactions which may have an influence on the overall reaction at a later time were not included. Since the reaction temperature of this experiment is much higher than that of Pratt and Rogers,[4] some of the major products may be expected to decompose further. From this point of view, Reactions (15)—(18), (22)—(26), (28), and (30)—(35) were included as in the study of the reaction mechanism of the n-C_4H_{10} pyrolysis previously reported.[2] Most of the k values of these reactions are identical with those used in the previous study.[2] Among the reactions which were considered to be important under the conditions of Pratt and Rogers' experiment,[4] the k values of unimolecular reactions, (14) and (27), adopted were those determined in an experiment similar to the present one.[13,18]

Since the primary reactions of C_4 species giving the major products have been discussed in detail by Pratt and Rogers,[4] we will give our attention here to the fates of the smaller hydrocarbons produced. The major products in the pyrolysis in the temperature range of 1200—1500 K have been reported to be CH_4, C_2H_6, C_2H_4, C_3H_6, and i-C_4H_8; no appreciable amount of C_3H_8 has been detected.[3] It may be seen from the product distribution reported at that time[3] that $[i\text{-}C_4H_8]$ decreases abruptly with an increase in the temperature and it is less than 5% of the concentration sum of the products at the upper end of the reaction temperature; a similar tendency of the modeled $[i\text{-}C_4H_8]$ above 1500 K will also be seen later. Thus, no consideration will be given here to the fates of i-C_4H_8 and C_3H_8. Among the major products left, CH_4 and C_2H_4 are relatively stable in this temperature range, and their direct decompositions, Reaction (33), $C_2H_4=C_2H_2+H_2$, and $C_2H_4=C_2H_3+H$, are considered to be negligible. Only H-atom abstractions, Reactions (34) and (35), are effective in accounting for the disappearance steps of the molecules. Since the reactivities of C_2H_6 and

Table 1. Reaction mechanism and rate constants
$k=A\exp(-E/RT)$ (cm, mol, s, and kcal units)

Reaction	log A	E	Footnote
1) $i\text{-}C_4H_{10}=CH_3+i\text{-}C_3H_7$	12.8	60.8	This work
2) $H+i\text{-}C_4H_{10}=H_2+i\text{-}C_4H_9$	13.7	68.0	a)
3) $H+i\text{-}C_4H_{10}=H_2+t\text{-}C_4H_9$	13.7	68.0	a)
4) $CH_3+i\text{-}C_4H_{10}=CH_4+i\text{-}C_4H_9$	13.2	16.3	b)
5) $CH_3+i\text{-}C_4H_{10}=CH_4+t\text{-}C_4H_9$	12.5	12.9	b)
6) $i\text{-}C_4H_9=CH_3+C_3H_6$	14.2	32.7	c)
7) $i\text{-}C_4H_9=C_2H_4+C_2H_5$	20.2	74.2	a)
8) $t\text{-}C_4H_9=H+i\text{-}C_4H_8$	14.6	43.1	c)
9) $t\text{-}C_4H_9=C_2H_4+C_2H_5$	22.4	92.1	a)
10) $CH_3+t\text{-}C_4H_9=CH_4+i\text{-}C_4H_8$	$15.0-0.75\log T$	0	d)
11) $H+i\text{-}C_4H_8=H_2+C_4H_7$	13.7	5.0	a)
12) $CH_3+i\text{-}C_4H_8=CH_4+C_4H_7$	14.0	17.6	b)
13) $C_4H_7=C_2H_4+C_2H_3$	14.0	37.0	e)
14) $C_3H_8=CH_3+C_2H_5$	13.6	67.9	f)
15) $CH_3+C_3H_8=CH_4+i\text{-}C_3H_7$	12.6	10.3	g)
16) $CH_3+C_8H_8=CH_4+n\text{-}C_3H_7$	12.6	10.3	g)
17) $H+C_3H_8=H_2+i\text{-}C_3H_7$	13.8	8.0	h)
18) $H+C_3H_8=H_2+n\text{-}C_3H_7$	13.8	8.0	h)
19) $i\text{-}C_3H_7=C_2H_4+CH_3$	12.0	34.5	c)
20) $n\text{-}C_3H_7=C_2H_4+CH_3$	13.8	33.2	c)
21) $i\text{-}C_3H_7=H+C_3H_6$	14.3	41.3	c)
22) $n\text{-}C_3H_7=H+C_3H_6$	13.8	38.0	c)
23) $C_3H_6+M=CH_3+C_2H_3+M$	18.0	74.0	i)
24) $C_3H_6=C_3H_5+H$	13.0	78.0	j)
25) $H+C_3H_6=H_2+C_3H_5$	10.1	1.5	k)
26) $C_3H_5=C_3H_4+H$	13.6	70.0	k)
27) $C_2H_6+M=2CH_3+M$	$111.3-25.26\log T$	160.0	l)
28) $C_2H_6+H=C_2H_5+H_2$	14.1	9.4	m)
29) $C_2H_5+M=C_2H_4+H+M$	15.3	30.1	l)
30) $CH_3+CH_3=C_2H_5+H$	14.9	26.6	n)
31) $CH_3+CH_3=C_2H_4+H_2$	16.0	32.0	n)
32) $C_2H_5+H=C_2H_4+H_2$	12.3	0	m)
33) $CH_4+M=CH_3+H+M$	17.5	90.6	o)
34) $CH_4+H=CH_3+H_2$	14.9	15.1	p)
35) $C_2H_4+H=C_2H_3+H_2$	15.7	22.9	q)
36) $CH_3+C_2H_5=CH_4+C_2H_4$	11.7	0	r)
37) $i\text{-}C_3H_7+i\text{-}C_4H_{10}=n\text{-}C_3H_7+i\text{-}C_4H_{10}$	9.8	9.5	b)
38) $t\text{-}C_4H_9+i\text{-}C_4H_{10}=i\text{-}C_4H_9+i\text{-}C_4H_{10}$	9.5	9.5	b)
39) $i\text{-}C_4H_9=H+i\text{-}C_4H_8$	13.7	36.6	c)

a) Ref. 3. b) Ref. 7. c) S. W. Benson and H. E. O'Neal, "Nat. Stand. Ref. Data Ser.," NBS, No. 21, (1970). d) Ref. 14. e) K. M. Sundaram and G. F. Froment, *Ind. Eng. Chem., Fundam.*, **17**, 174 (1978). f) Ref. 13. g) A. Lifshitz and M. Franklach, *J. Phys. Chem.*, **79**, 686 (1975). h) A. F. Trotman-Dickenson and G. S. Milne, "Nat. Stand. Ref. Data Ser.," NBS, No. 9, (1967). i) A. Burcat, *Fuel*, **54**, 87 (1975). j) K. J. Laidler and B. W. Wojciechowski, *Proc. R. Soc. London, Ser. A*, **259**, 257 (1960). k) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **67**, 1242 (1963). l) Ref. 18. m) P. Camilleri, R. M. Marshall, and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1434 (1974). n) Ref. 11 and K. A. Bhaskaran, P. Frank, and Th. Just, "Proc. 12th Shock Tube Symp.," Hebrew Univ. Press, Jerusalem (1980), in press. o) W. C. Gardiner, Jr., T. Koike, and T. Tanzawa, manuscript in preparation. p) Th. Just and P. Roth, *Ber. Bunsenges. Phys. Chem.*, **79**, 682 (1975). q) Th. Just, P. Roth, and R. Damm, "16th Int. Symp. Combust.," The Combustion Institute, Pittsburgh (1977), p. 961. r) Assumed. The sources of the thermochemical data of species are: $i\text{-}C_4H_{10}$: S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **4**, 859 (1975); C_3H_8 and C_2H_6: S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, *ibid.*, **2**, 427 (1973); C_3H_6: J. Chao and B. J. Zwolinski, *ibid.*, **4**, 251 (1975); CH_4, C_2H_4, C_2H_2, CH_3, H_2, and H: D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, NSRDS-NBS, 37 (1971); C_2H_5: Ref. 18; $i\text{-}C_3H_7$, $n\text{-}C_3H_7$, $i\text{-}C_4H_9$, and $t\text{-}C_4H_9$: c) and J. A. Karr, *Chem. Rev.*, **66**, 465 (1966); C_4H_7, C_3H_5, and C_2H_3: R. E. Duff and S. H. Bauer, *J. Chem. Phys.*, **36**, 1754 (1962); $i\text{-}C_4H_8$ and C_3H_4: F. D. Rossini *et al.*, "Selected Values of Properties of Hydrocarbons and Related Compounds," NBS-API Research Project 44, NBS (1947).

C_3H_6 are larger than those of the above two species, the disappearance steps, Reactions (23)—(26) and (27)—(32), are taken into account. At much higher temperatures than the present, the reaction mechanisms of the C_2H_6 and C_3H_6 pyrolysis are not so simple, as has been considered above.[19)]

The radicals larger than C_2, such as C_4H_9, C_3H_7, and C_2H_5, are decomposed to produce H or CH_3 with molecules in this temperature range. Therefore, the chain terminations are accomplished by the radical reactions of H and CH_3. The chain termination for the H-atom are $H+H=H_2$ and Reaction (−33); the rate of former reaction is very small compared with those of the other reactions in Table 1, and so it is not included in the reaction mechanism. The disproportionations, Reactions (31) and (36), as well as the recombinations, Reactions (−14), (−27), and (−33), are chain terminations for the CH_3 radical. Reaction (30) can go in either direction and can not be explained simply. Thus, co-radical reactions with CH_3 are not so simple as in the case of the H-atom.

The modeled $[C_3H_6]$ and $[i\text{-}C_4H_8]$ at 1500 K are 1.3×10^{-8} and 1.0×10^{-10} mol cm^{-3} respectively at 10 μs lab. time. At much higher temperatures, for example, at 1700 K, the modeled $[i\text{-}C_4H_8]_{10\mu s}$ is less than 10^{-11}. Thus, because of the smallness of $[i\text{-}C_4H_8]$, it is confirmed that both the influence of the absorption by $i\text{-}C_4H_8$ on the total absorption and the route of forming C_3H_5 *via* $i\text{-}C_4H_8$ are negligible in deriving the present reaction mechanism. On the other hand, it is necessary to examine the C_3H_6 pyrolysis in detail. A recent study of the C_3H_6 pyrolysis in shock waves[19)] has predicted that such expressions as Reactions (23)—(26) are not satisfactory in explaining the reaction profile at high temperatures. Also the absorptivity of C_3H_5 at high temperatures is uncertain and must be measured precisely. Since the situation for the C_3H_5 chemistry is as above, we have left the modeling of the absorption profile at high temperatures unfinished.

The results of sensitivity tests at 1500 K and 1700 K are shown in Fig. 4. It may be seen that the sensitivity spectra given by the values of the percent deviations of each reaction are completely different between the two temperatures. At 1500 K, the reactions accompanying the CH_3 radical, the initiation (1), the chain propagations (5) and (30), and the chain terminations, (−14), (−27), and (31), have large influences on the A_{10} value. Since the sensitivities of Reactions (1) and (27) are much larger than those of the other reactions, the k values of these two reactions should be examined carefully. As for Reaction (1), several factors which may give uncertaities in determining the k_1 value have already been discussed in detail, and the error boundary for the expression has been given. The error boundary of the k_1 value may be given as above, but the error boundary seems to be much smaller than that, since the A_{10} value can not be reproduced by computer modeling when a k_1 value different by a factor of 2 from the value in Table 1 is adopted. As for the k_{27} value, we selected the value determined in the C_2H_6 pyrolysis study[18)] in which conditions similar to those of the present experiment were adopted, because the k_{27} value is expected to show a pressure dependence. Although we can not find the error boundary of the k_{27} value explicitly,[18)] we can elucidate the error boundary to be less by a factor of 2 from the sensitivity spectra shown in the previous report.[18)] Likewise, the present A_{10} value can not be reproduced by computer modeling with a changed k_{27} value as above. As for the C_4H_9 decompositions, the value of the percent deviations of Reactions (7) and (8) are given with different signs when each k value is changed with the same factor; *i.e.*, only small variation of the A_{10} value can be seen by changing the k_7 and k_8 values at the same time. On the other hand, very small deviations were observed for Reactions (6), (9), and (39). These results may indicate that it is possible to reproduce the A_{10} value even after making a fall-off correction for each k value of Reactions (6)—(9) and (39) with a similar factor. From the sensitivity spectra at 1700 K, the percent deviations of most reactions can be expected to get smaller with an increase in the temperature, and it is hard to tell which reaction is more sensitive to the A_{10} value. Thus, the A_{10} value at high temperatures can not be reproduced only by changing any of the k values in Table 1.

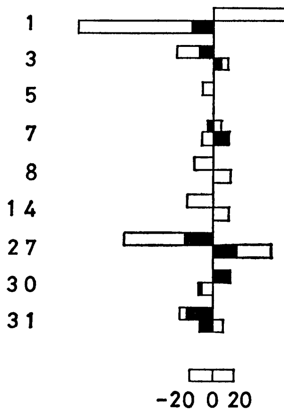

Fig. 4. Sensitivity spectrum for the 2% mixture. The numbers refer to the reaction number in Table 1. The abscissa is percent deviation defined as: $(A_{10}'/A_{10}-1)\times100$. A_{10} is the standard value modeled using Table 1 mechanism and rate constants. A_{10}' is the perturbed value by multiplying each rate constant by 5, upper bar of each reaction; by 0.2, lower bar. The reactions whose percent deviations are less than 5 are not shown.
The bars used are: ▭, T_2=1500 K; ▬, T_2=1700 K.

Since the experimental conditions of the single-pulse shock-tube technique adopted by Bradley[3)] is similar to the present (P_5=0.66—0.91 atm), the computer modeling with reaction mechanism shown in Table 1 can be expected to reproduce his experimental results. However, the modeled decay of $[i\text{-}C_4H_{10}]$ is too fast compared with his results. We are led to assume that the gas-cooling effects due to the boundary-layer growth[20)] existed in his data also.

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