Investigation of a New Pathway Forming Naphthalene by the Recombination Reaction of Cyclopentadienyl Radicals

Yoshinori Murakami,* Taweesak Saejung, Chikako Ohashi, and Nobuyuki Fujii[†]
Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-2188
[†]*Life Engineering Center, Niigata Sangyo University, 4730 Karuigawa, Niigata 945-1395*

(Received July 14, 2003; CL-030631)

Mechanism of naphthalene (c-$C_{10}H_8$) formation by the recombination of cyclopentadienyl radicals (c-C_5H_5) was investigated by monitoring the time profiles of H atom behind the reflected shock of trifluoromethoxybenzene ($C_6H_5OCF_3$) highly diluted with Ar. The rate constant for $c\text{-}C_5H_5 + c\text{-}C_5H_5 \rightarrow c\text{-}C_{10}H_8 + 2H$ was determined to be $3.3 \times 10^{17} \exp(-135\,\text{kJ}/RT)\,\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$.

In spite of the significant advances in the understanding of soot formation, it is still difficult to simulate the soot formation in combustion processes using a numerical code including chemical reactions.[1] Since most of the numerical model of soot formation are based on the growth of the polycyclic aromatic hydrocarbons (PAHs) followed by the coagulation of the particles and surface growth through PAH condensation, it is very important to understand how these PAHs are formed from aliphatic hydrocarbons in combustion processes. Therefore a lot of researchers have tried to establish the mechanism for the reactions forming the first aromatic ring such as benzene and phenyl radicals,[2–4] but little works were performed on the formation kinetics of larger PAH from smaller PAH. Recently Melius et al.[5] theoretically predicted that naphthalene would be formed by reaction of $c\text{-}C_5H_5 + c\text{-}C_5H_5 \rightarrow c\text{-}C_{10}H_8 + 2H$. However there are no experimental evidences of naphthalene formation from c-C_5H_5 radicals.

In this letter, we report on the kinetic investigation for the reaction of $c\text{-}C_5H_5 + c\text{-}C_5H_5 \rightarrow c\text{-}C_{10}H_8 + 2H$ using a diaphragmless shock tube combined with atomic resonance absorption technique, which enables to detect H atoms produced by the reaction of $c\text{-}C_5H_5 + c\text{-}C_5H_5$ with high sensitivity. Figure 1 shows the schematic of the experimental set-up. The diaphragmless shock tube consisted of high-pressure and low-pressure sections and a piston divides these two sections. By moving backward the main piston, helium gas filled in the high-pressure section flows to the low-pressure section and finally the generated shock wave heats up the sample gas filled in the low-pressure section. The sample gas used in this work is trifluoromethoxybenzene ($C_6H_5OCF_3$) highly diluted with Ar (4–50 ppm). Here, $C_6H_5OCF_3$ molecules are applied as the precursor of c-C_5H_5 radical, because $C_6H_5OCF_3$ dissociates to C_6H_5O and CF_3 followed by subsequent dissociation of C_6H_5O to c-C_5H_5 and CO; $C_6H_5OCF_3 \rightarrow C_6H_5O + CF_3$; $C_6H_5O \rightarrow c\text{-}C_5H_5 + CO$. Although $C_6H_5OCH_3$ molecule is most commonly used precursor for C_6H_5O radical,[10] we used $C_6H_5OCF_3$ molecule to avoid the H-atom formation from the subsequent reactions of CH_3 radical formed by the thermal decomposition of $C_6H_5OCH_3$ molecule. The temperature and pressure behind the reflected shock were calculated from the incident shock velocities measured by four piezoelectric transducers attached to the shock-tube. The relationship between the absorption and the concentration of H atom was obtained by measuring absorption of H atom behind the reflected shock of C_2H_5I/Ar mixtures, since the yield of H atom formed by the decomposition of C_2H_5I is already established by Michael et al.[5,6]

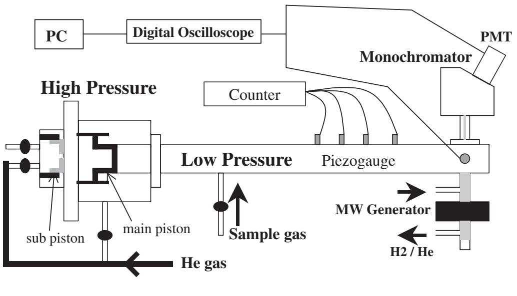

Figure 1. Experimental setup.

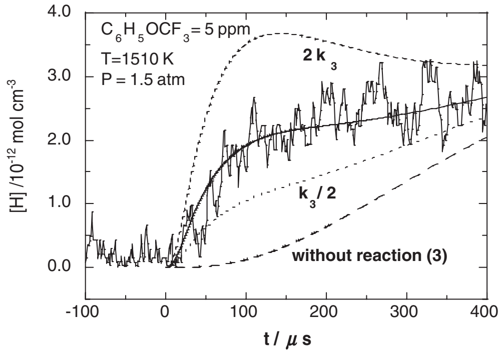

Figure 2. Typical example of the time profile of H atom behind the reflected shock of $C_6H_5OCF_3/\text{Ar} = 5\,\text{ppm}$ mixtures ($T = 1510\,\text{K}$, $P = 1.5\,\text{atm}$) with computer simulations.

Figure 2 is a typical example of time profiles of H-atom formation behind the reflected shock waves of $C_6H_5OCF_3$/Ar mixtures. As shown in Figure 2, H atom-formation was observed without any induction periods behind the reflected shock. There are several possibilities forming H atom behind the shock wave. First, formation of H atom by thermal decomposition of $C_6H_5OCF_3$ such as $C_6H_5OCF_3 \rightarrow C_6H_4OCF_3 + H$ can be the source of H atoms behind the reflected shock of $C_6H_5OCF_3$/Ar mixtures. But the heat of this decomposition reaction is 464 kJ/mol, which is much higher than that of the reaction $C_6H_5O \rightarrow c\text{-}C_5H_5 + CO$ (268 kJ/mol). Other decomposition channles of $C_6H_5OCF_3$ such as $C_6H_5OCF_3 \rightarrow C_6H_5 + OCF_3$ are also excluded from the simple thermochemical considerrations. Thermal decomposition of c-C_5H_5 radical has been recently investigated by Roy et al.[7] According to their results, c-C_5H_5

dissociates to C_3H_3 and C_2H_2. And once C_3H_3 is produced, C_3H_3 dissociates to produce C_3H_2 and H; $C_3H_3 \rightarrow C_3H_2 + H$. Since the rate constant for this decomposition reaction has already been determined as $k = 5.2 \times 10^{12} \exp(-328\,\text{kJ}/RT)\,\text{s}^{-1}$ by measuring H atom behind the reflected shock of C_3H_3I/Ar mixtures,[8] the time profiles of H atom produced by the decomposition of C_3H_2 radical can be simulated using these literature values. The reaction scheme used for these simulations is shown in Table 1. Since the rate constant for the decomposition of $C_6H_5OCF_3$ has not been determined yet, we assumed the rate constant was similar to that for $C_6H_5OCH_3$ decompotion. It was also checked that the calculated time profiles of H atom were not influenced by this rate constant because the decomposition of $C_6H_5OCF_3$ is much faster than the formation of H atom. The rate constants for reactions (4) and (5) were taken from literatures. The result of the calculated time profile of H atom without reaction (3) is shown in Figure 2. As shown in Figure 2, H atom was formed much faster than the simulated profile of H atom calculated from the literature values mentioned above. No other source of H atom than the reaction of c-C_5H_5 + c-C_5H_5 → c-$C_{10}H_8$ + 2H could be found in our experimental conditions. Therefore we concluded that H atom was produced by the reaction of c-C_5H_5 + c-C_5H_5 → c-$C_{10}H_8$ + 2H as was proposed by Melius et al.[5] By varying the rate constant for the reaction of c-C_5H_5 + c-C_5H_5 → c-$C_{10}H_8$ + 2H in Table 1, attempts to fit the experimentally obtained profiles of H atom were performed. The results of the kinetic simulations are also shown in Figure 2. As shown in this figure, good agreements were obtained using the reaction scheme tablated in Table 1. The Arrhenius plots of the rate constant for c-C_5H_5 + c-C_5H_5 → c-$C_{10}H_8$ + 2H are shown in Figure 3. By the least square fits to these plots, the rate constant was determined to be $3.3 \times 10^{17} \exp(-135\,\text{kJ}/RT)\,\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. Miyoshi et al.[9] determined the rate constant to be around $3 \times 10^{12}\,\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for this reaction by measuring H atom behind the reflected shock of $C_6H_5OCH_3$/Ar mixtures[9] and in spite of the difference of the activation energies good agreements for the absolute value were obtained between Miyoshi et al. and us. The difference of the activation energies may be caused by the difference between the reactivity of CH_3 radical and that of CF_3 radical.

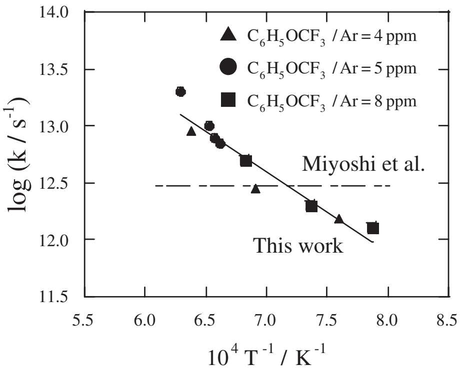

Figure 3. Arrhenius plots for the reaction of c-C_5H_5+c-C_5H_5.

Table 1. Reaction mechanism for thermal decomposition of $C_6H_5OCF_3$

	Reactions	A	n	E	Ref.
1	$C_6H_5OCF_3 \rightarrow C_6H_5O + CF_3$	1.2×10^{16}	0	270	Assumed
2	$C_6H_5O \rightarrow C_5H_5 + CO$	2.5×10^{11}	0	184	[10]
3	$2C_5H_5 \rightarrow C_{10}H_8 + 2H$	3.3×10^{17}	0	135	This work
4	$2CF_3 \rightarrow C_2F_6$	1.4×10^{13}	0	0	[11]
5	$CF_3 + H \rightarrow CF_2 + HF$	2.0×10^{14}	0	0	[12]
6	$C_5H_5 \rightarrow C_5H_5(l)$	3.9×10^{11}	1	323	[7]
7	$C_5H_5(l) \rightarrow C_3H_3 + C_2H_2$	1.4×10^{11}	1	125	[7]
8	$2C_3H_3 \rightarrow C_6H_5 + H$	1.3×10^{13}	0	0	[3]
9	$C_3H_3 \rightarrow C_3H_2 + H$	5.2×10^{12}	0	328	[8]

A: $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ E: kJ mol^{-1}
$k = AT^n \exp(-E/RT)\ \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$

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Published on the web (Advance View) November 10, 2003; DOI 10.1246/cl.2003.1112