Crystallite Size Effect in the Selective Oxidation of Butene to Butadiene on Iron Oxide. 2. Reaction Studies

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The selective oxidation of 1-butene to butadiene was studied over a series of silica-supported and unsupported iron oxide catalysts of average crystallize sizes ranging from 2.5 to 61 nm. The reaction was studied at 300, 350, and 375 °C under conditions that resulted in low conversions. The selectivity for butadiene ranged from about 80% to below 50%. In general, it was higher for catalysts of smaller crystallite sizes and lower for larger crystallize sizes. The areal rate appeared to have a small dependence on the crystallite size. However, this trend could be due to the fact that the iron oxide surface areas were calculated by using the average crystallite sizes, which did not properly account for the different crystallite size distributions. Possible explanations for the variation of selectivity with crystallize sizes were discussed.

Introduction

Among binary transition-metal oxides, iron oxide is one of the most selective and active catalysts for the production of butadiene in the oxidation of butene.[1] It has been reported that the selectivity under identical reaction conditions depends on the exact state of the iron oxide. In particular, the selectivity appears to depend on the specific surface area of the catalyst[1] and on its crystallographic form.[2,3] γ-Fe$_2$O$_3$, of a spinel structure, has been found to be much more selective than α-Fe$_2$O$_3$, of a corundum structure. Therefore, it is interesting to investigate whether the different catalytic behavior of iron oxides of different preparations is due to different specific surface areas as an intrinsic crystallite size effect or to the presence of different amounts of α- and γ-phases. Results of such an investigation are reported here.

Two series of catalysts were studied. One was iron oxide supported on silica gel, and the other was unsupported. The preceding paper[4] reported on the physical characterization which aimed at the identification of the iron oxide phases present and the determination of the average crystallite sizes. Briefly, results from X-ray diffraction, Mössbauer spectroscopy, and magnetization measurements could be adequately explained by the presence of α-Fe$_2$O$_3$ for all the catalysts, including the smallest crystallite size silica-supported sample 2.5-FeO/SiO$_2$-400. (The first number denotes the average crystallite size in nanometers. The second number denotes the calcination temperature. FeO/SiO$_2$ denotes silica-supported catalysts; FeO denotes unsupported catalysts.) There was no evidence of γ-Fe$_2$O$_3$ or reaction between SiO$_2$ and iron oxide. Relatively speaking, the crystallite size distribution was narrow for the supported samples and was very broad for the unsupported samples. These samples covered a broad range of average crystallite sizes. For the supported samples, the average crystallite size ranged from 2.5 to 9.5 nm; for the unsupported samples, the range was from 14 to 61 nm.

Experimental Section

The preparation and the characterization of the catalysts have been reported in the preceding paper.[4]

1-Butene oxidation was carried out in a conventional flow system. The reactor was a quartz U-tube of about 8-mm diameter. The feed was a mixture of O$_2$ (UHP hydrocarbon-free grade, Linde), 1-butene (CP grade, Linde), and He (UHP grade, Linde) which were used without further purification, and its composition was 1:1:13 (by volume) of O$_2$/1-butene/He. No significant changes in activity or selectivity were detected even if this ratio

was changed by 20%. The small flow rates of O$_2$ and 1-butene were measured by Brooks thermal mass flowmeters. Since the selectivity of the catalysts depended on the conversion, the total flow rate of the reactants and the weight of the catalyst were adjusted to keep the conversion below 10% whenever possible. At such low conversions, the dependence of the selectivity on conversion was small. Normally, a total flow rate of 15–150 mL/min and an amount of catalyst of 0.01–0.4 g were used. The reaction products were analyzed by gas chromatography using a column packed with 80–100-mesh Chromosorb W(AW) coated with 20% dimethylsulfolane at 0 °C. Butene isomers, butadiene, and CO$_2$ were the only products detected. From the GC peak areas and the relative GC sensitivities for these compounds, the activity, defined as the percent of butene reacted, and the selectivity, defined as the amount of butadiene divided by the sum of the amounts of butadiene and CO$_2$/4, were calculated. The silica gel used was found to show negligible activity in this reaction.

The catalysts were pretreated by heating in O$_2$ (30 mL/min) at 400 °C for 0.5 h. Sometimes a O$_2$/He (1:3 by volume) mixture was used without detectable differences. Afterwards, the reactor temperature was adjusted to the reaction temperature and the reactor was purged with He for 20 min. Then, the stream of reactants of a preadjusted composition was directed to flow through the reactor by a switching valve. The first sample was taken for analysis after 10 min. Subsequent samples were taken every 30 min afterwards. As described later, the catalysts underwent loss of initial activities. This pretreatment restored the initial activities.

Reactions were run at 300 and 350 °C. In a few experiments, 375 °C was used. Because of the higher activity at higher temperature, more heat was released by the reaction at 350 °C than at 300 °C. In a few experiments at 350 °C, the reactor temperature, as measured by a thermocouple touching the reactor wall at the position of the catalyst bed, rapidly increased 10–20 °C higher than the set temperature and then gradually dropped back to the set temperature as the catalyst deactivated. A similar phenomenon was not observed at 300 °C. The data reported here were from experiments in which the temperature remained constant.

Results and Discussion

The activity and selection of a catalyst were found to depend on the time on stream, the reaction temperature, and the nature of the catalyst. Figure 1 shows typical activity data for the catalyst 7.5-FeO/SiO$_2$-400 at 300 and 350 °C. At 300 °C, the activity declined rapidly in the first 40–60 min after which a rather stable activity was obtained which was about half to one-third of the initial value. However, the activity never truly reached a steady state. Deactivation was found to continue, although very slowly, beyond 6 h of operation. At 350 °C, the decline in activity was much slower. Even after 24 h of operation, no significant loss of activity was observed. Figure 2 shows the corresponding data

(1) Th. Simons, E. Verheijen, Ph. Batist, and G. Schuit, *Adv. Chem. Ser.*, No. 76, 261 (1968).

(2) M. Misono, K. Sakata, F. Ueda, Y. Nozawa, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, **53**, 648 (1980).

(3) M. Misono, Y. Nozawa, and Y. Yoneda, *Proc. Int. Congr. Catal. 6th, 1976*, **1**, 386 (1977).

(4) F. Hong, B. L. Yang, L. H. Schwartz, and H. H. Kung, *J. Phys. Chem.*, preceding paper in this issue.

TABLE I: Summary of Activity and Selectivity Data

reacn temp, °C	catal[a]	specific area of Fe_2O_3[b]	catal wt, mg	butene conversion,[c] %	10^{16}(areal activity),[d] $m^{-1} s^{-1}$	select for butadiene,[c] %
300	2.5-FeO/SiO$_2$-400	458	37.9	2.30–1.25	1.8	84.0–77.0
	7.5-FeO/SiO$_2$-400	153	41.0	1.94–1.00	2.3	81.3–71.1
	9.5-FeO/SiO$_2$-450	120	39.9	1.62–0.85	0.75	84.3–68.3
	14.5-FeO-400	79	19.5	5.8–3.2	1.7	58.1–53.5
	14.5-FeO-500	79	14.4	2.4–1.5	1.1	56.0–51.0
	18.5-FeO-500	62	30.0	3.2–1.8	0.80	52.0–49.0
	25.0-FeO-525	46	32.0	2.4–1.5	0.84	60.0–51.0
	51.5-FeO-750	22	64.7	1.1–0.5	0.30	60.0–54.0
	61.0-FeO-675	19	106.5	2.0–1.1	0.43	52.0–47.0
350	2.5-FeO/SiO$_2$-400		19.0	9.9–9.5	27.8	85.4–84.7
	7.5-FeO/SiO$_2$-400		20.5	8.9–8.6	39.1	81.8–80.6
	9.5-FeO/SiO$_2$-450		20.0	8.4–8.3	14.5	79.0–76.0
	14.5-FeO-500		18.2	e-35.0	19.9	e-69.0
	25.0-FeO-525		12.5	11.0–10.0	14.3	69.0–70.0
	61.0-FeO-675		30.4	4.0–5.0	7.2	55.0–60.0
375	2.5-FeO/SiO$_2$-400		12.6	20.1–20.3	89.5	86.8–86.3
	7.5-FeO/SiO$_2$-400		13.7	15.7–18.9	127	84.0–82.6
	9.5-FeO/SiO$_2$-450		13.3	38.7–22.3	57.9	77.2–80.4

[a] Catalysts are designated as follows. The first number denotes the average crystalline size in nanometers as determined by X-ray diffraction. The second number denotes the calcination temperature in degrees Celcius. FeO/SiO$_2$ denotes silica-supported catalysts; FeO denotes unsupported catalysts. [b] These were calculated from the average crystallite sizes by assuming spherical crystallites. [c] The first number is the initial value after 10 min of reaction. The second number is the steady-state value after 2 h of reaction (reaction conditions: O$_2$ = 2.0 cm^3/min, 1-butene = 2.0 cm^3/min, He = 26 cm^3/min). [d] These were calculated as number of butene molecules reacted per m^2 of Fe$_2$O$_3$ per second at steady state. [e] This was not determined.
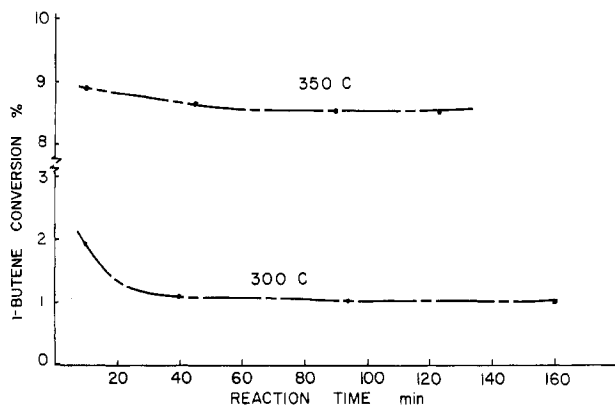

Figure 1. The conversion data as a function of time on stream for catalyst 7.5-FeO/SiO$_2$-400. Conditions of the experiment: reactant flow rate 30 mL/min, 41.0 mg of catalyst.
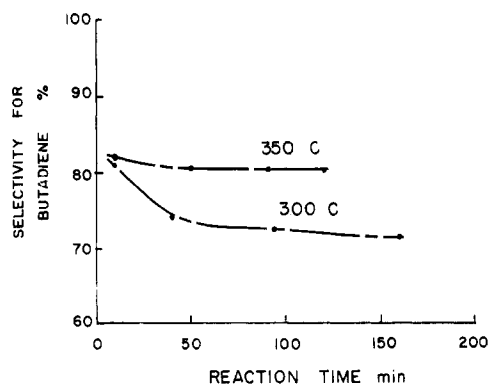

Figure 2. The selectivity for butadiene as a function of time on stream for catalyst 7.5-FeO/SiO$_2$-400. Same reaction conditions as in Figure 1.

for the selectivity for butadiene. Similar to the activity data, the selectivity at 300 °C first declined and then became rather stable. The decline at 350 °C was rather small. These data are rather typical of most of the catalysts studied. The magnitude of the decline in activity and selectivity was seldom larger than these

TABLE II: Dependence of Selectivity on Conversion

catal	reacn temp, °C	catalyst weight, mg	butene conversion,[a] %	butadiene selectivity,[a] %
7.5-FeO/ SiO$_2$-400	350	30.2	11.2–10.2	82.9–80.3
	350	20.1	6.0–6.2	85.4–81.9
9.5-FeO/ SiO$_2$-450	350	16.0	6.6[c]	75.9[c]
	350	16.0	3.9[c,d]	75.3[c,d]
	350	16.0	2.9[c,e]	74.9[c,e]
2.5-FeO/ SiO$_2$-400	300	106.4	4.5–2.0	83.6–73.0
	300	37.9	2.3–1.3	84.0–77.0
61.0-FeO-675	300	294.9	4.8–2.4	54.0–44.0
	300	106.5	2.0–1.1	52.0–47.0
	300	102.0	0.20–0.18[b]	47.0–45.0[b]
25.0-FeO-525	300	32.0	2.4–1.5	60.0–50.0
	300	24.0	1.7–1.2	56.0–50.0
	300	22.4	0.31–0.29[b]	56.0–52.0[b]

[a] The first number is the initial value after 10 min of reaction. The second number is the steady-state value after 2 h of reaction (reaction conditions: O$_2$/1-butene/He = 1:1:13, total flow rate 30 mL/min). [b] The total flow rate was 300 mL/min (same composition). [c] These are steady-state data. [d] The total flow rate was 60 mL/min (same composition). [e] The total flow rate was 90 mL/min (same composition).

(see Table I). For catalysts 25.0–FeO–525 and 61.0-FeO-675, the activity and selectivity actually increased slightly at 350 °C with time on stream.

The dependence of the selectivity on the conversion was investigated for some catalysts by changing the weight of the catalyst used or the flow rate while keeping the temperature and the composition of the reactant mixture fixed. The results are shown in Table II. It can be seen that, for the low conversions obtained in these experiments, the dependence of selectivity on conversion is weak. Nonetheless, there is a tendency that the selectivity is slightly higher at lower conversion. This weak dependence suggested that a meaningful comparison among catalysts can be made althought the reaction data were obtained under somewhat dif-

ferent conversions. These data also showed the dependence of reaction rate on the residence time. The areal rate was found to increase slightly with shorter residence time. Such a dependence cannot be explained by a local heat spot in the catalyst bed, which would be more severe at longer residence time and result in a dependence opposite to that observed. However, it can be explained by the existence of a stagnant layer around a catalyst particle, the thickness of which decreases with faster flow rate. Since this effect was small and it did not affect the selectivity, it was not investigated further.

The absence of pore diffusion influence was tested on the supported catalyst 2.5-FeO/SiO$_2$-400. A sample of the catalyst was carefully crushed without any grinding motion. Optical microscopy showed that the catalyst particles were crushed to about one-tenth the original size. The activity and selectivity of the crushed catalyst were tested at 350 °C and were found to be within experimental error the same as the original catalyst. Thus, the data reported here were not affected by the pore diffusional effect.

Table I summarizes the activity and selectivity data for 300, 350, and 375 °C. Both the initial (10 min after commencement of the reaction) and steady-state (2 h after commencement) activities and selectivities are presented. The areal rates were calculated by assuming that the crystallites were spherical and that the surfaces of all the crystallites were available for reaction. Inspection of the data suggested that the crystallite size dependence of activity and selectivity is more pronounced at lower temperatures. At 300, 350, and 375 °C, the areal rates varied by a factor of 8, 5, and 2, respectively. They appeared to be higher for smaller crystallite sizes. Such a trend may be more apparent than real. These areal rates were based on the average crystallite sizes that were determined by X-ray line broadening using the Scherrer formula. This formula weighs the larger crystallites more heavily than the smaller crystallites. This in turn results in an underestimation of the specific areas of small crystallite samples. In view of this systematic error, it was concluded that there is no significant variation of the areal activity with crystallite size.

The variation of the selectivity for butadiene with crystallite size, however, was much larger. In general, the selectivity was higher for smaller crystallite sizes. This appeared to be true over the range of temperatures studied and for both the initial and the steady-state selectivities although the initial selectivity data were less reliable because of experimental uncertainties.

These data also revealed that the silica-supported catalysts all showed higher selectivity than the unsupported samples. While this can be attributed to the crystallite size effect, it could also be due to some special type of interaction between SiO$_2$ and α-Fe$_2$O$_3$. The characterization of the catalysts before use did not give any indication of the formation of compounds between silica and iron oxide.[4] However, substitution of Si into an iron oxide lattice as reported by Lund and Dumesic[5] is still possible during reaction. They reported that such substitution is promoted by water vapor, which is a product of the oxidation reaction. If such substitution takes place, its extent should increase with the time on stream. Two experiments were performed to test this possibility. First, the silica-supported catalyst of the lowest selectivity, 9.5-FeO/SiO$_2$-450, was used in a reaction run for an extended time period of 65 h at 350 °C. The selectivity and activity were found to stay constant over the entire period, except for the normal initial deactivation in the first 30 min. In the second experiment, a physical mixture of silica gel and an unsupported iron oxide catalyst, 25.0-FeO-525, of a weight ratio of 30:1 was used as catalyst at 350 °C. Again, no gradual increase in selectivity was observed over 7 h of reaction. In fact, the catalytic behavior of this physical mixture was the same as the behavior of iron oxide alone, even if it was first heated in water vapor (about 10 torr) at 350 °C for 13 h, or 400 °C for 3 h, or 450 °C for 1 h. The results of these experiments strongly indicated that our data were not influenced by Si substitution into the catalysts.
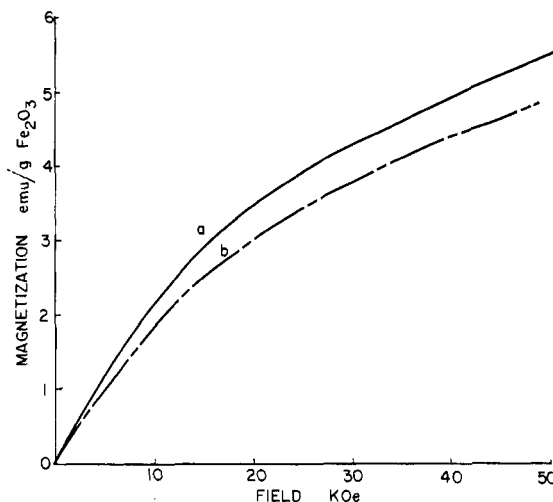
(5) C. R. F. Lund and J. A. Dumesic, *J. Phys. Chem.*, **86**, 130 (1982); **85**, 3175 (1981).

Figure 3. Magnetization at 1.7 K of catalysts before and after reaction: (a) 7.5-FeO/SiO$_2$-400 before reaction, (b) after reaction.

Finally, the effect of severe heat treatment on the catalytic behavior was tested. A batch of the 2.5-FeO/SiO$_2$-400 catalyst was calcined in air at progressively higher temperatures of 450 °C (12 h), 500 °C (0.5 h), 600 °C (0.25 h), 780 °C (1 h), and 920 °C (1 h). After each heat treatment, the catalytic activity was tested at 350 °C by using a total flow rate of 30 mL/min. Within experimental error, the selectivity remained unchanged up to a calcination temperature of 780 °C. After the 920 °C calcination, the selectivity increased from 85.6% to 87.4%. The activity gradually declined with heating temperature to about one-third of the original value after 780 °C heating. Again, the invariance of the selectivity indicated that the reaction data were not affected by possible reaction between iron oxide and silica. It also excluded the possible presence of γ-Fe$_2$O$_3$. These conclusions were also supported by the Mössbauer characterization of the catalysts before and after the severe heat treatment.[4] Furthermore, we attribute the decrease in activity to a loss in accessible iron oxide surface area due to collapse of some of the silica pores instead of sintering of the iron oxide crystallites. The very low loading resulted in well-separated crystallites that hindered crystallite size growth. A similar decrease in activity but not in selectivity was observed for the 9.5-FeO/SiO$_2$-450 catalyst after an additional heating in air at 460 °C for 48 h. The resistance to sintering also indicated strong iron oxide–silica interaction.

Most of the catalysts studied deactivated in the first hour of reaction at 300 °C before a quasi-steady state was reached. The deactivation became less pronounced and eventually disappeared as the reaction temperature increased. An attempt to elucidate the cause of this deactivation was made on the catalyst 7.5-FeO/SiO$_2$-400, by making X-ray and magnetization measurements on the catalyst after reaction. A batch of the catalyst that was used in 1 h of reaction was quenched to room temperature in a flowing reactant feed by removing the furnace. The temperature fell to near room temperature in 5 min. The catalyst was then removed from the reactor. Results of the magnetization measurements on this and the fresh catalyst are shown in Figure 3 curves b and a, respectively. Except for a reduction in magnitude of about 18%, the magnetization after reaction was essentially identical with that before reaction. This reduction in magnitude can be explained by a combination of two effects. First, hydrocarbon molecules are adsorbed onto the SiO$_2$ support and the catalyst. In calculating the specific magnetization, we neglected the weight of the adsorbed hydrocarbons. Thus, the weight of iron oxide in the sample was overestimated, and the specific magnetization was underestimated. Second, owing to the small amount of catalyst used in this measurement (about 20 mg), there could be an error in the weight of the catalyst. In view of the similarity in the shape of the magnetization curves, it is concluded that there were no changes in the bulk structure of the catalyst

after reaction. This conclusion was substantiated by the X-ray diffraction results which did not indicate any differences between a fresh and a used catalyst.

Summarizing the results, it appears that the different selectivities observed for different samples can be correlated with the different crystallite sizes. The dependence becomes important for sizes smaller than about 10 nm. Evidence does suggest that the effect is not due to the formation of other detectable iron oxide phases or compounds due to reaction, nor to the pore diffusional effect. In addition, the silica support stabilizes the iron oxide crystallites against sintering.

What are the likely causes of the crystallite size dependence of selectivity? A definite answer is not provided by this study. There are a number of possibilities. First, the reaction may be crystal face specific. Thus, when the ratios of different crystal faces change with crystallite size, the selectivity changes accordingly. Detailed knowledge of the distribution of exposed crystal faces is not available. X-ray diffraction data showed that the relative intensities of the various diffraction peaks were similar for the different catalysts. This implied that the shape of the α-Fe_2O_3 crystallites remained the same for the different sizes and that epitaxial growth of α-Fe_2O_3, which might lead to the exposure of one particular crystal plane, was not present. Second, the production of butadiene may require a specific site such as anion or cation vacancies. The density of such specific sites may be higher on smaller crystallites. Indeed, the requirement of a site involving an anion vacancy has been proposed for butadiene production.[6] Third, the reaction mechanism has been proposed to involve an oxidation–reduction cycle of the catalyst.[6-11] Therefore, if the oxidation–reduction property of the oxide crystallite depends on its size, its catalytic propety would also change. This has been used to explain the effect of a second

component in ferrites.[11] The dependence of the oxidation–reduction property on crystallite size for unsupported oxides is not well-known. In silica-supported samples, it has been reported that small iron oxide crystallites are much more difficult to be reduced than large crystallites.[12-16] This may be a result of the silica–oxide interaction coupled with the crystallite size effect. Fourth, it was reported that the difference between the selectivities for butadiene on α- and γ-Fe_2O_3 is partly due to the different rates of desorption of the butadiene product and partly due to the different susceptibility of the butadiene or its precursor to degradation by weakly adsorbed oxygen.[17,18] Therefore, it is conceivable that the activation of this weakly adsorbed oxygen on α-Fe_2O_3 is crystallite size dependent. This would be possible if activation of such oxygen requires charge transfer from the solid. Such activation could be more difficult on smaller crystallites for which electron transfer results in a large shift in the potential of the entire crystallite, thereby making such electron transfer more difficult. This results in a slower rate of degradation of adsorbed butadiene and a higher selectivity.

In conclusion, it is demonstrated that the selectivity for butadiene production in the oxidation of butene on α-Fe_2O_3 depends on the crystallite size of iron oxide. This phenomenon may be due to changes in a number of properties of the oxide crystallites. In contrast, the specific activity in butene conversion does not depend on crystallite size. The beneficial effect of the silica gel support in stabilizing iron oxide against sintering is also demonstrated.

(6) F. E. Massoth and D. A. Scarpiello. *J. Catal.*, **21**, 294 (1971).
(7) M. C. Kung, W. H. Cheng, and H. H. Kung, *J. Phys. Chem.*, **83**, 1737 (1979).
(8) R. Rennard and W. Kehl, *J. Catal.*, **21**, 282 (1971).
(9) M. Gibson and J. Hightower, *J. Catal.*, **41**, 420 (1976).
(10) W. R. Cares and J. Hightower, *J. Catal.*, **23**, 193 (1971).
(11) H. H. Kung, B. Kundalkar, M. C. Kung, and W. H. Cheng, *J. Phys. Chem.*, **84**, 382 (1980).

(12) G. B. Raupp and W. N. Delgass, *J. Catal.*, **58**, 337 (1979).
(13) M. C. Hobson and H. M. Gager, *J. Catal.*, **16**, 254 (1970).
(14) N. Malathi and S. P. Puri, *J. Phys. Soc. Jpn.*, **31**, 1418 (1971).
(15) J. A. Amelse, J. B. Butt, and L. H. Schwartz, *J. Phys. Chem.*, **82**, 558 (1978).
(16) E. Unmuth, L. H. Schwartz, and J. B. Butt, *J. Catal.*, **61**, 242 (1980).
(17) B. Yang and H. H. Kung, *J. Catal.*, **77**, 410 (1982).
(18) B. Yang, M. C. Kung, and H. H. Kung, submitted for publication in *J. Catal.*

Reaction of Hydrogen Atom with Benzene: Kinetics and Mechanism

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The rate coefficients for the reactions $H + C_6H_6 \rightarrow$ products (k_1) (1), $H + C_6D_6 \rightarrow$ products (k_2) (2), $D + C_6H_6 \rightarrow$ products (k_3) (3), and $D + C_6D_6 \rightarrow$ products (k_4) (4) have been measured in the temperature range of 298–1000 K by using the pulsed photolysis–resonance fluorescence technique. On the basis of the obtained kinetic information, it is shown that the primary path in all these reactions is addition of the atom to the benzene ring to form cyclohexadienyl radical. The rate coefficient for the thermal decomposition of the cyclohexadienyl radical has also been measured. When the rate coefficients for the formation and the decomposition of the cyclohexadienyl radical are used, the standard heat of formation of cyclohexadienyl radical at 298 K is calculated to be 45.7 kcal/mol. The measured values of k_1–k_4 are compared with the results of previous investigations. Most of the observed kinetic behavior in these reactions has been explained on the basis of the addition–decomposition reaction scheme.

Introduction

Reactions of simple free radicals such as OH, $O(^3P)$, and $H(^2S)$ with aromatic hydrocarbons play important roles in the initiation and propagation of aromatic hydrocarbon combustion. The reactions of $H(^2S)$ could play a major role in the hydrogenation of aromatics as well. Direct studies of these free-radical reactions with aromatic hydrocarbons have been limited even though the reactions involving nonaromatic hydrocarbons have been exten-

sively investigated. In recent years we have initiated systematic studies of radical–aromatic hydrocarbon reactions with the aim of measuring kinetic parameters and elucidating the reaction mechanisms as a function of temperature (up to ~1200 K) using the pulsed photolysis–resonance fluorescence technique.[1-4] The

(1) F. P. Tully, A. R. Ravishankara, R. L. Thompson, J. M. Nicovich, R. C. Shah, N. M. Kreutter, and P. H. Wine, *J. Phys. Chem.*, **85**, 2262 (1981).