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Mercury-Photosensitized Decomposition of Ethylbenzene

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The decomposition of ethylbenzene sensitized by Hg($^3P_1$) was studied in gas phase. Hydrogen, methane and ethane were obtained as the main gaseous products. Their rates of formation were determined as a function of the pressure of ethylbenzene or xenon. To decide whether methyl or ethyl radical is the primary product in the photolysis, ethylbenzene-β-d_1 was photolyzed. It was concluded that methyl radical is the primary product, since methane-d_1 and ethane-d_2 were obtained as products. A probable reaction mechanism is proposed to interpret the effect of pressure and light intensity on the rate of formation of ethane and methane. It is suggested that a biphotonic process is involved, which can explain the fact that the rate of formation of ethane is proportional to the square of light intensity.

Studies on the decomposition of organic compounds by excited mercury atoms have been reported by many authors.[1] The mechanism of the reaction is generally classified into two types; (a) the abstraction of hydrogen atom by excited mercury atom as found in the decomposition of alkanes, and (b) the excitation transfer from excited atoms to organic compounds as in the decomposition of unsaturated compounds such as ethylene and butenes. In (b), the acceptor compound should have its triplet state below the level of Hg($^3P_1$).

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[1] R. J. Cvetanović, "Progress in Reaction Kinetics," Vol. 2, Pergamon Press, London (1964), p. 39.

Unsaturated compounds generally have larger cross sections than saturated ones. Until recently, the formation of triplet state of unsaturated compounds by mercury-sensitization was only presumed from the spin conservation rule and relatively long lifetime of the intermediate. Recently Burton and Hunzicker[2] gave direct evidence of the formation of triplet benzene and toluene by excitation transfer from Hg($^3P_0$), by means of modulation type kinetic spectroscopy. However, not many studies have been made on the mercury-sensitized decomposition of aromatic compounds, probably due to their low vapor pressure, and details of the mechanism have not been clarified yet. Scott and Steacie[3] reported the mercury-photosensitized reaction of benzene, and Sehon and Darwent[4] proposed a mechanism involving two types of excited toluene in the reaction of toluene with Hg($^3P_1$). Hentz and Burton[5] studied the photochemistry of toluene, mesitylene and ethylbenzene in comparison with radiation chemistry. The present authors[6] reported preliminary results of mercury photosensitized decomposition of ethylbenzene. Yamamoto *et al.* also photolyzed ethylbenzene with mercury and investigated the reaction products.[7] We report herewith on the study of mercury-photosensitized decomposition of ethylbenzene, taking into consideration the effects of pressure of ethylbenzene and xenon and light intensity on the rate of formation of gaseous products. Since the compound has both alkyl and phenyl groups in one molecule, it may be interesting to decide whether abstraction of hydrogen or excitation transfers reaction plays the more important role in a single molecule in mercury-photosensitized decomposition.

Experimental

Materials. Commercial ethylbenzene was purified by gas chromatographic separation through a DOP column, dried with sodium and distilled in a reaction cell. Ethylbenzene-β-d_1 was prepared from 2-phenylethyl bromide by the Grignard reaction with deuterium oxide of 99.9% isotopic purity, and fractionated by gas chromatography. No impurity was found either in ethylbenzene or ethylbenzene-β-d_1 by FID through the DOP column. Isotopic purity of ethylbenzene-β-d_1 was determined to be about 90% by reduced ionization voltage technique of mass spectrometer. Xenon (Takachiho Co.) was used without further purification.

Apparatus. We constructed a low pressure spiral type mercury lamp, its light intensity being determined occasionally by mercury-photosensitized decomposition of propane, and found to be 9.7—12$\times 10^{15}$ photon/sec. Variation in lamp intensity in a series of experiments was small. A slight gradual decrease of absorbed light was due to the decrease of transparency of the quartz window of the reaction cell caused by the deposition of reaction products. The reaction cell, a cylindrical one of 1 cm length and 5 cm diameter and connected to a glass bulb of 500 ml was placed in an electric furnace with temperature regulated to ± 1°C. A filter (Toshiba UVD 25) placed in front of the reaction cell removed 184.9 nm light. The pressure of ethylbenzene was measured with a glass Bourdon gauge outside the furnace. Ethylbenzene with mercury vapor was circulated with a glass fan and a mercury booster pump. The pressure of mercury was not determined, but was presumed to be fairly high from the temperature of the furnace. Two metal valves are fitted to the inlet and outlet parts of the reaction system. In order to control incident light intensity, single or double blackened gauzes were inserted in front of the reaction cell. Transmission of the gauze was calibrated both by spectrophotometry and actinometry with mercury-photosensitized decomposition of propane. Both methods gave almost the same ratios of transmission.

Analysis of Reaction Products. After irradiation, the reaction mixture was passed through two helical traps kept at -196 °C. Hydrogen and methane were collected in Toepler gauge, and the combined amount of hydrogen and methane was measured first. Hydrogen was oxidized to water in copper oxide combination tube at 300 °C, and unoxidized gas was assumed to be methane. Ethane was pumped out by warming the traps up to -140 °C with a refrigerant mixture. In the quenching experiment with Xe, the quantitative determination of ethane was carried out by gas chromatography with FID, but the amounts of methane and hydrogen were not determined.

Results and Discussion

Long Irradiation Experiment and Direct Photolysis of Ethylbenzene. The rate of decomposition of ethylbenzene with mercury at 253.7 nm at room temperature is too small to be measured. Reactions at 150—300 °C gave hydrogen, methane and ethane as main products of low boiling point with a small amount of propane, but no ethylene was detected. The formation of toluene and styrene was confirmed by gas-chromatography, but not conclusive. Yamamoto *et al.*[7] reported on the formation of benzene, toluene, isopropylbenzene, bibenzyl, and 1,2-diphenylpropane, but not styrene. A detailed comparison of the present results with theirs may be not appropriate, since the experimental conditions differ. However, as far as gaseous products are concerned, qualitative results of both experiments seem to be in good agreement. In Fig. 1, the rates of formation of hydrogen, methane and ethane (R_{H_2}, R_{CH_4}, $R_{C_2H_6}$[8]) are plotted against irradiation time under 1.9 Torr of ethylbenzene at 150 °C. $R_{C_2H_6}$ is constant for 3 hr, and R_{CH_4} is also almost constant irrespective of time. It seems that R_{H_2} decreases gradually with time. This may be explained as being caused by internal scavenging by some unsaturated product as known in mercury-

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[2] C. S. Burton and H. E. Hunzicker, *Chem. Phys. Lett.*, **6**, 352 (1970).

[3] E. J. Scott and E. W. R. Steacie, *Can. J. Chem.*, **29**, 233 (1951).

[4] A. H. Sehon and B. deB Darwent, *J. Chem. Phys.*, **23**, 822 (1959).

[5] R. R. Hentz and M. Burton, *J. Amer. Chem. Soc.*, **73**, 532 (1951).

[6] A. Takase, M. Murano, H. Mikuni, and M. Takahasi, Preprints of International Conference on Photochemistry, Tokyo, (1965), p. 39.

[7] Y. Yamamoto, S. Takamuku, and H. Sakurai, This Bulletin, **44**, 574 (1972).

[8] $R_{C_2H_6}$ is proportional to the square of light intensity. Thus, we use rate instead of quantum yield. The apparent quantum yield of ethane at 2 Torr of ethylbenzene, 1.2×10^{16} photon and 150 °C is 0.04.

photosensitized decomposition of alkanes.[9] However, since our result on styrene formation was not conclusive, it is left for future investigation.

It was confirmed that no pure thermal reaction of ethylbenzene took place up to 300°C. Since ethylbenzene has an absorption band below 270 nm, the direct photolysis of ethylbenzene may be involved to some extent in the mercury-photosensitizing reaction system. Although quantitative determination of the relative amounts of light by mercury and ethylbenzene is not possible, the amount of light absorbed directly by ethylbenzene is presumed to be much less than that by mercury. For the sake of comparison, ethylbenzene of 10 Torr was photolyzed at 25°C in the reaction system where the contamination of mercury vapor was carefully avoided. It was found that $R_{C_2H_6}$ was 0.93×10^{-10} mol/sec, fairly less than the value 5.7×10^{-10} mol/sec obtained in the mercury photosensitizing reaction system (Fig. 1). Hentz and Burton[5] reported the rough quantum yields of gaseous products in the direct photolysis of ethylbenzene to be the order of 10^{-4}. We may presume that the mercury photosensitizing reaction predominates in the present reaction system, but we can not eliminate completely the possibility of involvement of direct photolysis.

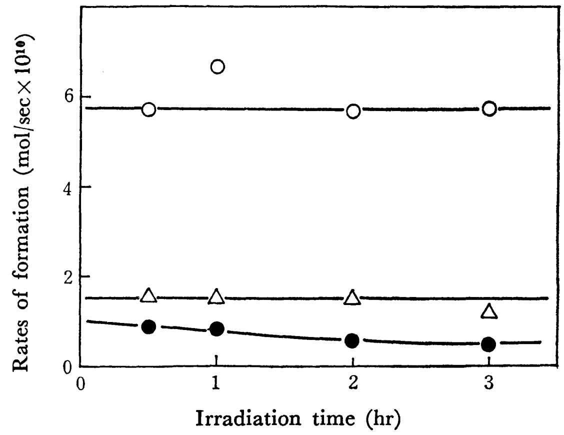

Fig. 1. The variations of $R_{C_2H_6}$, R_{CH_4} and R_{H_2} with irradiation time.
○ ethane, △ methane, ● hydrogen.

Except for long irradiation experiments, we carried out our experiments keeping the conversion below 10% to avoid complication of internal scavenging.

Mercury-Photosensitized Decomposition of Ethylbenzene-β-d_1. In order to decide whether methyl or ethyl radical is the primary reaction entity to give ethane, ethylbenzene-β-d_1 was irradiated for 3 hr at 150°C under pressure of 2 Torr of ethylbenzene-β-d_1. The mole ratios of deuterium substituted methanes and ethanes were determined by mass spectrometry. The results are given in Table 1.

TABLE 1. MOLE RATIOS OF DEUTERIUM SUBSTITUTED METHANES AND ETHANES PRODUCED BY MERCURY-SENSITIZED PHOTOLYSIS OF ETHYLBENZENE-β-d_1

CH_4	CH_3D	C_2H_6	C_2H_5D	$C_2H_4D_2$
15	85	0	20	80

It is seen that the main primary product in the reaction is methyl radical considering the following reaction scheme.

$$C_6H_5CH_2CH_2D(\text{excited}) \rightarrow C_6H_5CH_2\cdot + CH_2D\cdot$$

$$CH_2D\cdot + C_6H_5CH_2CH_2D \rightarrow CH_3D + C_6H_5\underset{\cdot}{C}HCH_2D$$

$$2\ CH_2D\cdot \rightarrow CH_2DCH_2D$$

The presence of about 20% C_2H_5D in the products can be explained by the reaction of undeuterated ethylbenzene contained in the reactant.

Effect of Pressure of Ethylbenzene and Xenon on $R_{C_2H_6}$, R_{CH_4} and R_{H_2}. The effect of pressure of ethylbenzene on $R_{C_2H_6}$, R_{CH_4} and R_{H_2} was investigated at 150°C. The variable range of pressure of ethylbenzene was limited in a narrow range due to its low vapor pressure, but we see that a maximum exists in $R_{C_2H_6}$ at 1 Torr, but no maximum for R_{CH_4} and R_{H_2} (Fig. 2). Sehon and Darwent[4] observed a similar maximum in the quantum yield of hydrogen at 2 Torr, but no maximum for methane and ethane in the mercury-photosensitized decomposition of toluene. An interpretation of the decrease of the rates of formation below 1 Torr may not be so simple, as Cvetanović pointed out.[1] The incomplete quenching of excited mercury atom by ethylbenzene and/or the inefficient absorption of radiation due to the decrease of pressure broadening[10] might cause the fall-off. The decrease of $R_{C_2H_6}$ above 1 Torr is understood in terms of the collisional deactivation of excited ethylbenzene of relatively long lifetime by normal ethylbenzene as proposed in the case of ethylene[11] and toluene.[4] A good linearity was obtained by plotting $1/R_{C_2H_6}{}^{1/2}$ against pressure of ethylbenzene, although the pressure is

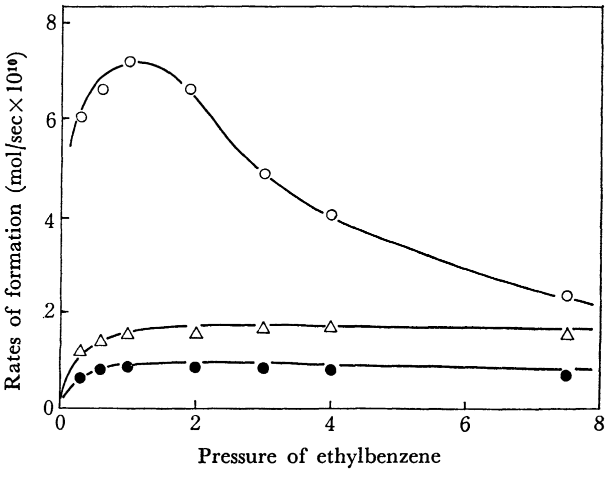

Fig. 2. The variations of $R_{C_2H_6}$, R_{CH_4} and R_{H_2} in terms of pressure of ethylbenzene.
○ ethane, △ methane, ● hydrogen.

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[9] See, for example, a) R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959), b) K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961).

[10] K. Yang, *J. Amer. Chem. Soc.*, **86**, 3941 (1964).

[11] A. B. Callear and R. F. Cvetanović, *J. Chem. Phys.*, **24**, 873 (1956).

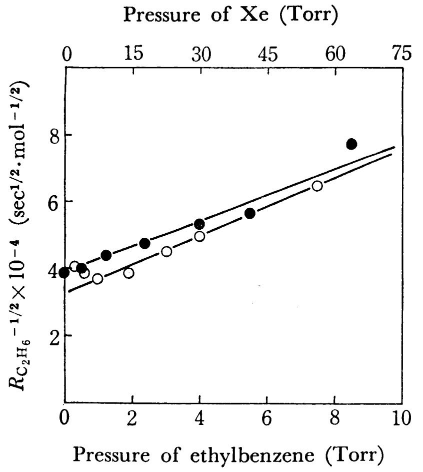

Fig. 3. Plots of $R_{C_2H_6}^{-1/2}$ against pressure of ethylbenzene and Xe.
○ for change of pressure of ethylbenzene. ● for change of pressure of Xe.

limited to a narrow range. We investigated the effect of pressure of Xe on $R_{C_2H_6}$ up to 66 Torr, keeping the pressure of ethylbenzene at 2.0 Torr at 150 °C. A good linearity was also obtained between $1/R_{C_2H_6}$ and the pressure of Xe, as shown in Fig. 3. The fact that $R_{C_2H_6}$ decreased with the increase of the pressure of ethylbenzene or of Xe indicates that the concentration of methyl radical decreased with the increase of pressure of these quenching substances. R_{CH_4} is almost constant above 1 Torr of ethylbenzene. This might be qualitatively interpreted by considering the compensation of the decrease of methyl radical concentration by the increase of ethylbenzene (see equation (3)). The behavior of R_{H_2} against the pressure of ethylbenzene is apparently similar to that of R_{CH_4}, but the mechanism of hydrogen formation may be more complicated.

Dependence of $R_{C_2H_6}$, R_{CH_4} and R_{H_2} on Light Intensity. $R_{C_2H_6}$, R_{CH_4} and R_{H_2} were measured at 150 °C at 2 Torr of ethylbenzene, varying the light intensity with blackened copper gauzes. When log R^0/R is plotted against log I^0/I, where R^0 and I^0 are the reaction rate and light intensity, respectively, without gauze, a good linearity for $R_{C_2H_6}$, R_{CH_4} and R_{H_2} each is obtained. Each slope gives 2 for ethane, 1 for methane and 0.5 for hydrogen. The findings that $R_{C_2H_6}$ is proportional to square of light intensity and that R_{CH_4} is proportional to light intensity suggest that some biphotonic process may be involved.

Many studies have been reported[12] on photophysical and photochemical processes by flash technique involving biphotonic processes. However, even in steady irradiation experiments with usual lamps several studies[13a-d] indicate the participation of some biphotonic process. Strausz and Gunning[13d] reported that in the mercury-photosensitized decomposition of carbon dioxide at 253.7 nm the rate of decomposition of carbon dioxide is proportional to the square of light intensity. Considering that the mechanism of formation of ethane is most simple in the present system, we will discuss mainly the mechanism of formation of methyl radical. In order to interpret result where $R_{C_2H_6}$ is proportional to the square of light intensity, the following three mechanisms are considered for a possible biphotonic process to produce methyl radicals.

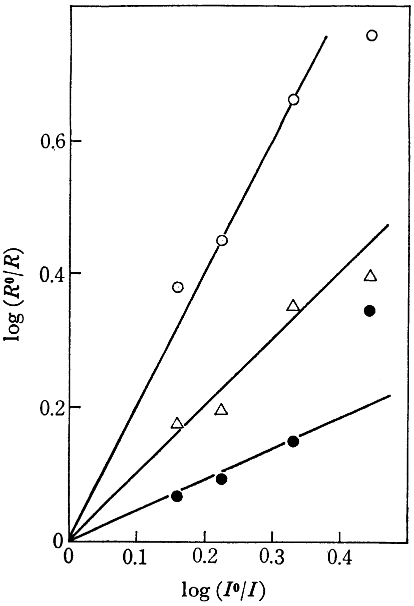

Fig. 4. The dependence of $R_{C_2H_6}$, R_{CH_4} and R_{H_2} against light intensity in log–log plot.
○ ethane, △ methane, ● hydrogen.

$Hg + h\nu \rightarrow Hg^*$	I_a	common to all three processes below
$Hg^* \rightarrow Hg + h\nu$	k_2	
$Hg^* + E \rightarrow Hg + E^*$	k_3	
$E^* + E \rightarrow 2E$	k_4	
$E^* + Xe \rightarrow E + Xe$	k_5	
(a) $E^* + h\nu' \rightarrow E^{**}$ (triplet)		possible three processes
or		
(b) $E^* + Hg^* \rightarrow E^{**}$ (singlet or triplet) $+ Hg$		
or		
(c) $E^* + E^* \rightarrow E^{**}$ (singlet or triplet) $+ E$	k_6	
$E^{**} \rightarrow C_6H_5CH_2\cdot + CH_3\cdot$	k_7	common to all three processes
E^{**}(singlet) $\rightarrow E + h\nu''$	k_8	
$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$	k_9	
$CH_3\cdot + E \rightarrow CH_4 + C_6H_5\dot{C}HCH_3$	k_{10}	

(E is ethylbenzene)

At present, we have no conclusive evidence to select one mechanism from these three, but process (c) seems to be most suitable to interpret our experimental results. In process (2), T-T absorption of 253.7 nm

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[12] *Cf. e. g.*, "Photophysics of Aromatic Molecules," by J. B. Birks, John Wiley & Sons, (1970).

[13] a) A. Terenin, "Recent Progress in Photobiology", ed. by E. J. Bowen, Oxford, 1965, p. 3, b) A. Proch, M. Djibelian and S. Sullivan, *J. Phys. Chem.*, **71**, 3378 (1967), c) B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1793 (1966), d) O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, **39**, 2244 (1961).

by triplet ethylbenzene is assumed. Burton and Hunzicker[2] reported the absorption spectra of triplet benzene and toluene formed by Hg($^3P_0$). T–T absorption spectrum of toluene covers the region 210—370 nm. A similar absorption spectrum can be expected for ethylbenzene. However, the amount of light absorbed by triplet ethylbenzene under our experimental conditions should be very small, considering the fact that our light source consists of atomic lines of a low pressure mercury lamp and that the molar extinction coefficient of triplet ethylbenzene may be much less than that of mercury. Assuming process (a) or (b), the rate equations in terms of pressure of ethylbenzene or Xe and light intensity were derived, but they were not in line with our experimental results. If process (c) is assumed, the following expression is derived.

$$R_{C_2H_6} = \frac{k_3{}^2k_6[E]^2I_a{}^2}{(k_2+k_3[E])^2(k_4[E]+k_5[Xe])^2} \tag{2}$$

In this derivation we assumed that $k_4[E]+k_5[Xe] \gg k_6[E^{**}]$ and $[CH_3]^2k_9 \gg [CH_3][E]k_{10}$. The first assumption may be justified if we consider that the quantum yields of ethane and methane are fairly small (less than 0.10). The second assumption is generally used in the competitive reactions of abstraction and recombination of methyl radical. We also neglected the radiative process of E**, but this is not essential in the interpretation of pressure and light dependence in the rate expression. The above expression is consistent with the results where $R_{C_2H_6}$ is proportional to the square of light intensity, and the linear relationship between $1/R_{C_2H_6}{}^{1/2}$ and pressure of ethylbenzene or Xe is satisfied. From the slope of the plot in Fig. 4, we can calculate k_4/k_5 to be about 39, indicating that ethylbenzene is much more efficient as a quencher than Xe. In a similar way, we can derive the following expression for R_{CH_4}.

$$R_{CH_4} = \frac{k_{10}}{k_4}\left(\frac{k_3k_6}{k_9}\right)^{1/2}\frac{I_a[E]}{(k_2+k_3[E])} \tag{3}$$

This is consistent with the experimental result where R_{CH_4} is proportional to light intensity and approaches a constant value at high pressure of ethylbenzene.

Comparison of the Rate of Formation of Methyl Radical with That of Hydrogen Atom. A comparison of excitation transfer process with hydrogen atom abstraction process might be of interest, if both processes actually take place in ethylbenzene. There can be no doubt that methyl radical formation proceeds through excited ethylbenzene, but the mechanism of hydrogen formation in the present system is not conclusive. For the formation of atomic hydrogen, the following two processes are possible, (a) abstraction of hydrogen atom from ethylbenzene by excited mercury atom, and (b) decomposition of excited ethylbenzene to produce hydrogen atom. At present, we have no evidence to differentiate the two processes from a consideration of our experimental results, and we therefore can not eliminate the possibility of simultaneous occurrence of excitation transfer process and abstraction process. We tentatively calculated the values $(R_{CH_4}+2R_{C_2H_6})/R_{H_2}$ under various pressures of ethylbenzene, considering the values may correspond to the ratio of rate of production of methyl radical to that of hydrogen atom. Since R_{CH_4} and R_{H_2} do not vary remarkably with pressure of ethylbenzene above 1 Torr (Fig. 2), the value $(R_{CH_4}+2R_{C_2H_6})/R_{H_2}$ mainly depends on the change of $R_{C_2H_6}$, which gradually increases with the decrease of pressure. We obtained the value of about 17 for the ratio in the pressure range 0.6—2 Torr.

The Effect of the Reaction Temperature on $R_{C_2H_6}$, R_{CH_4} and R_{H_2}. We investigated the change of $R_{C_2H_6}$, R_{CH_4} and R_{H_2} with respect to reaction temperatures 100—350 °C at constant light intensity. The pressure of ethylbenzene was kept at 2 Torr at each temperaute. $R_{C_2H_6}$ increases first up to 250 °C and begins to decrease above 250 °C, while R_{CH_4} increases gradually in the whole temperature range. The behavior of $R_{C_2H_6}$ is not completely understood, but its increase up to 250 °C indicates that the rate constant of decomposition of excited ethylbenzene (k_7) is dependent on the reaction temperature, considering that the rate constant of recombination of methyl radicals is almost independent of temperature. Although the amounts of energy contained in E* and E** are not known, it is rather surprising that the decomposition of E** is dependent on temperature, since the bond energy of $C_6H_5CH_2$–CH_3 is reported to be only 63 kcal/mol.[14] The amount of energy of E* must be in the range from the lowest triplet level of ethylbenzene (probably ~85 kcal/mol) up to 112 kcal/mol, which is the maximum amount of energy transferable from Hg($^3P_1$). The decrease of $R_{C_2H_6}$ above 250 °C may be partly interpreted by considering the increase of R_{CH_4} with temperature, but the fact that the sum of $2R_{C_2H_6}+R_{CH_4}$ still decreases above 250 °C is not understood yet.

In order to calculate the activation energy of hydrogen abstraction process by methyl radical from ethylbenzene, we derived the following equation by combining equations (2) and (3), assuming $E_9 \cong 0$

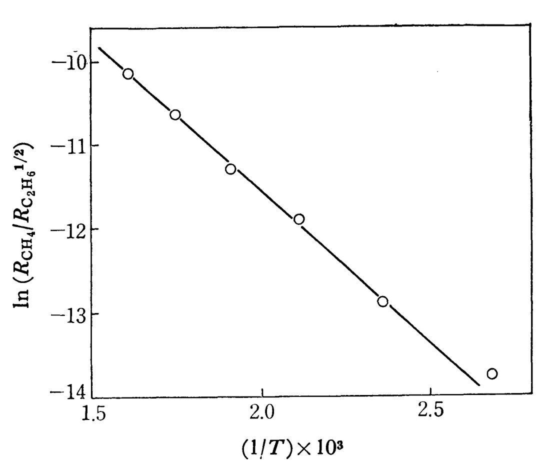

Fig. 5. Arrhenius plot of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ at a constant concentration of ethylbenzene in the temperature range from 100 to 350°C.

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[14] M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

$$R_{\mathrm{CH_4}}/R_{\mathrm{C_2H_6}}{}^{1/2}[\mathrm{E}] = k_{10}/k_9,$$

or

$$\log k_{10}/k_9 = R_{\mathrm{CH_4}}R_{\mathrm{C_2H_6}}{}^{1/2}[\mathrm{E}] = E_{10}/RT + \log A_{10} - \tfrac{1}{2}\log A_9$$

$\log k_{10}/k_9 = \log R_{\mathrm{CH_4}}/R_{\mathrm{C_2H_6}}{}^{1/2}[\mathrm{E}] = E_{10}/RT + \log A_{10} - 1/2 \log A_9$. Thus, $R_{\mathrm{CH_4}}/R_{\mathrm{C_2H_6}}{}^{1/2}$ obtained keeping the pressure of ethylbenzene at 2 Torr at each temperature should be recalculated by dividing it by [E] at each temperature. The Arrhenius plot, recalculated $\log R_{\mathrm{CH_4}}/R_{\mathrm{C_2H_6}}{}^{1/2}$ against $1/T$, gives a good linearity (Fig. 5). From the slope we obtained 7.1 kcal/mol for the activation energy of abstraction of methyl radical, comparable with the reported values of the abstraction of methyl radical from toluene, which are rather scattered as 7[15 a)], 7.3[b)], 9.5[c)] and 11.0[d)] kcal/mol according to the source of radicals and to the authors. It is found that $R_{\mathrm{H_2}}$ also depends on temperature, but since we cannot obtain a unique rate expression for $R_{\mathrm{H_2}}$, we tentatively calculated an apparent activation energy from the Arrhenius plot of $R_{\mathrm{H_2}}$ which gives the value of 4.1 kcal/mol.

We would like to thank Mr. H. Horiguchi for valuable comments and also Mr. S. Hirano and Mr. M. Takakubo for their assistance in the experiments.

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15) a) H. S. Taylor and J. O. Smith, *ibid.*, **8**, 543 (1940), b) R. E. Rebbert and E. W. R. Steacie, *ibid.*, **21**, 1723 (1953), c) M. Cher, *J. Phys. Chem.*, **70**, 877 (1966), d) M. Szwarc and J. S. Roberts, *Trans. Faraday Soc.*, **46**, 625 (1950).