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The Reactions of Hydrogen and Deuterium Atoms with Four Ketenes

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The rate constants of the reactions of hydrogen and deuterium atoms with four ketenes have been measured using a pulse radiolysis-resonance absorption technique. For hydrogen atoms, the temperature dependence was also examined in the range of 240—440 K. The rate constants were well expressed by these Arrhenius equations: $k(\mathrm{H+ketene})=3.9\times10^6 \exp(-975/T)$; $k(\mathrm{H+methylketene})=7.4\times10^6 \exp(-881/T)$; $k(\mathrm{H+ethylketene})=4.4\times10^6 \exp(-728/T)$; $k(\mathrm{H+dimethylketene})=6.0\times10^6 \exp(-773/T)$, in units of $\mathrm{m^3\,mol^{-1}\,s^{-1}}$. No isotope effect between H and D atoms could be observed except for the gas-kinetic-collision frequency.

In the reaction of oxygen atoms with simple olefins, it was found that the rate constants increase with the increase in the number of substituted alkyl radicals: ethylene<propene≃1-butene<2-methylpropene≃*cis*- and *trans*-2-butene<2-methyl-2-butene<2,3-dimethyl-2-butene.[1] On the other hand, in the reactions of hydrogen atoms, the order is quite different: ethylene≃*cis*- and *trans*-2-butene≃2,3-dimethyl-2-butene<propene≃1-butene≃2-methyl-2-butene<2-methyl-propene.[2,3] The rate constants for deuterium atoms were found to be always $1/\sqrt{2}$ of those for hydrogen atoms, suggesting that this isotope effect is due to the difference in collision frequency.[3,4]

Recently, we measured the rate constants of the reactions of oxygen atoms with four ketenes: ketene and methyl-, ethyl-, and dimethylketenes, and found that the rate constants increase with the increase in the number of substituted alkyl radicals, the order is similar to that obtained with olefins: ketene<methylketene≃ethylketene<dimethylketene. It was also found that the reactions of the last three ketenes have negative activation energies.[5]

For a comprehensive understanding of this type of reaction, we have measured the Arrhenius parameters for the reactions of hydrogen atoms with these four ketenes, since no previous work has shown these parameters except for the reaction of hydrogen atoms with the simplest ketene.

Experimental

The details of the preparation of ketenes were described in a previous paper.[5] The method of the rate-constant measurement was similar to that described previously,[4,5] except that a wave memory (NF Circuit Design Block Co., WM-852) and an X-Y recorder (Riken Denshi Co., F-35) were used to record the decay of the hydrogen and deuterium atoms. Briefly, about 80 kPa of $H_2(D_2)$ gas containing a small amount of a ketene (1—10 Pa) was irradiated with an electron pulse generated by a Febetron 706 apparatus (Hewlett Packard Co.). After the pulse, the decay in the H(D) atoms was measured by the absorption of Lymann-α. As has been discussed previously,[2] the H(D)-atom concentration is less than 1/100 that of the ketene present in the reaction chamber. Therefore, the pseudo-first-order reaction rate can be determined from this decay curve. The temperature of the reaction vessel was controlled by winding it with a heating tape or by introducing N_2 gas from boiling liquid nitrogen to the surrounding copper tubing. The reactant temperature was measured with a copper-constantan thermocouple at the center in the reaction chamber prior to pulse-irradiation.

Results

The experimental results for hydrogen atoms are summarized in Fig. 1 in the form of Arrhenius plots. All the data are well characterized by Arrhenius equa-

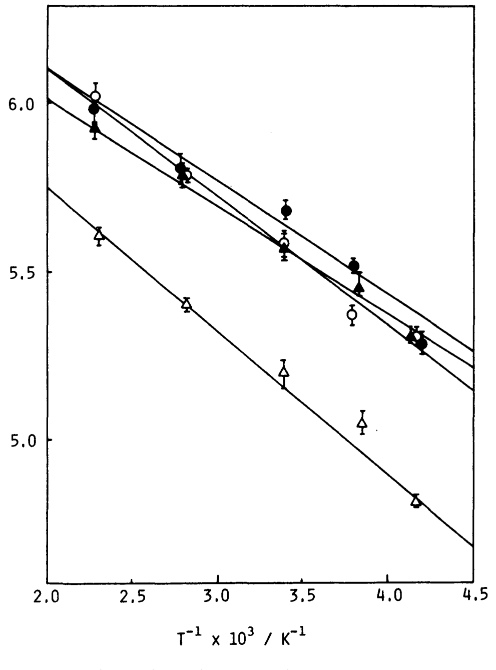


Fig. 1. Arrhenius plots for reactions $H+CH_2CO$ (△), $H+CH_3(CH)CO$ (○), $H+C_2H_5(CH)CO$ (▲), and $H+(CH_3)_2CCO$ (●). The indicated error limits are 1σ diviations of the fit.

TABLE 1. RATE CONSTANTS OF H- OR D-ATOM ADDITION TO KETENES AT 295 K IN UNITS OF $10^6\ \mathrm{m^3\,mol^{-1}\,s^{-1}}$

	CH_2CO	$CH_3(CH)$-CO	$C_2H_5(CH)$-CO	$(CH_3)_2$-CCO
H	1.6±0.2	3.8±0.3	3.7±0.4	4.8±0.3
D	1.2±0.1	2.8±0.2	2.5±0.3	4.1±0.2
k_D/k_H	0.76	0.75	0.68	0.85

Uncertainties are standard deviations.

Table 2. Arrhenius parameters for $H+$ketene reactions

Ketene	E_a/kJ mol^{-1}	A/10^6 m^3 mol^{-1} s^{-1}
CH_2CO	8.1 ± 0.6	3.9 ± 1.1
$CH_3(CH)CO$	7.3 ± 0.8	7.4 ± 2.4
$C_2H_5(CH)CO$	6.1 ± 0.5	4.4 ± 0.8
$(CH_3)_2CCO$	6.4 ± 1.5	6.0 ± 3.8

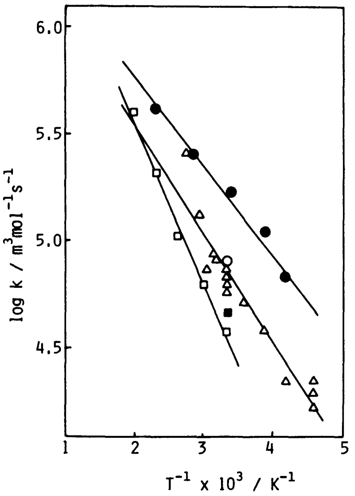


Fig. 2. Arrhenius plots for the reaction $H+CH_2CO$; △: Šlemr and Warneck; □,■: Michael *et al.*; ○: Carr *et al.*; ●: this work.

tions. The results at room temperature are also shown in Table 1. The Arrhenius parameters, as determined by the least-squares method, are listed in Table 2.

Discussion

There have been previous measurements of the temperature dependence of the reaction between hydrogen atoms and the simplest ketene.[6,7] Figure 2 compares their data with ours. Unfortunately, no two of the three measurements are in good agreement with each other. In this figure, two other measurements carried out at room temperature are also included.[7,8]

Šlemr and Warneck used a discharge-flow method combined with a mass-spectrometer.[6] Hydrogen atoms were generated by microwave discharge in a low-pressure helium-gas flow containing hydrogen. Ketene was introduced into the flow behind the discharge. The sampling of the gas mixture for mass-spectroscopic analysis was carried out *via* a pin hole located at the bottom of the cylindrical reactor. The rate constant was estimated by measuring the decrease as the concentration of ketene as a function of the distance of the reaction zone, in which atomic hydrogen was present in excess. The concentration of hydrogen atoms was measured in different runs by titration with nitrogen dioxide. The authors stated that a large error could be expected to occur in the estimation of the concentration of hydrogen atoms. If their measured concentration is twice as large, the rate constants they obtained will be in good agreement with ours. In the present experiments, however, the absolute concentration of hydrogen atoms is not necessary to estimate the rate constants.

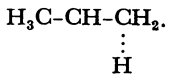
Michael *et al.* used two techniques, flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.[7] The temperature dependence was measured only by the former method. In this measurement, hydrogen atoms were produced by the flash photolysis of a mixture of methane, ketene, and diluent argon at $\lambda>105$ nm or by the flash photolysis of a two-component mixture of ketene and argon at $\lambda>165$ nm. The time-resolved detection of hydrogen atoms was accomplished by observing scattered resonance fluorescence at 121.6 nm. According to their paper, they had difficulty in creating appropriate conditions under which the rate measurment could be carried out, because ketene strongly absorbs the resonance fluorescence from excited hydrogen atoms.

The present authors also found that the absorption coefficient of ketene at 121.6 nm is larger than those of the olefins, but no difficulties were found in measuring the decay of hydrogen atoms. The discrepancy between the results of the discharge-flow method and the present one may be explained by the difference in the total pressures. Since the present results were obtained in the presence of 80 kPa of hydrogen, the rate constants may be regarded as the high-pressure limits.[2] On the other hand, under low-pressure conditions, such as in the case of the discharge flow, the measured rate constants may not be the limits. This explanation, however, is not applicable to the results of Michael *et al.*, who could observe no total pressure dependence of the rate constants between 2.7 and 13.3 kPa.

In the reactions of oxygen atoms with ketenes, the rate constants increase with the increase in the number of substituted alkyl radicals; the result is similar to that obtained with olefins.[1,5] On the other hand, in the reactions of hydrogen atoms, ketenes and olefins have different tendencies in their reaction rates; in the case of olefins, both activation energies and preexponential factors decrease with the increase in the number of the substituted alkyl radicals, while no systematic change could be observed in the case of ketenes.[3,9,11] Especially, there are no large differences among the rate constants of methyl-, ethyl-, and dimethylketene. This suggests that the reaction paths may be different in the reactions of hydrogen atoms with olefins and ketenes.

An oxygen atom adds to the C=C double bond, and the intermediate complex is believed to be formed either with olefins or with ketenes, although the detailed structure is not known. Cvetanović suggested a π-complex-type structure for the intermediate complex in the reactions of oxygen atoms with olefins.[11] If a similar structure can be assumed for the complex in the reactions with ketenes, the effect of the substituted alkyl radicals may well be similar to those of both olefins and ketenes.

On the other hand, in the hydrogen-atom reactions with olefins, it is believed that the hydrogen atom adds to the C=C double bond at the C-atom with less substituted alkyl radicals. The *ab initio* calculation showed that the geometry at the saddle point in the reaction between the H-atom and propene is:[10]

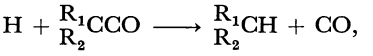


$H_3C\text{-}CH\text{-}\underset{\overset{\vdots}{H}}{CH_2}.$

In the investigation of the reaction mechanism of the reaction between hydrogen atoms and ketene, the following primary step has been proposed:[8)]

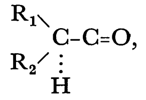
$$\mathrm{H} + \mathrm{CH_2CO} \longrightarrow \mathrm{CH_3} + \mathrm{CO}.$$

If this mechanism is also applicable to other ketenes,



$$\mathrm{H} + {}^{R_1}_{R_2}\mathrm{CCO} \longrightarrow {}^{R_1}_{R_2}\mathrm{CH} + \mathrm{CO},$$

and the intermediate complex can be illustrated as follows:



then the order of the rate constants of ketenes may not necessarily agree with those obtained in the reaction of hydrogen atoms with olefins. Bennett and Mile have found that ketene is unique in the reaction with atomic hydrogen at 77 K.[12)] They employed a rotating cryostat in conjunction with electron-spin-resonance spectroscopy. When water was used as the matrix, acetyl and methyl radicals were detected. This suggests that the initial step of the reaction is the addition of H atoms to the methylene group of ketene to give the $CH_3\text{-}C{=}O$ radical, followed by decomposition into CH_3 and CO. This mechanism was further confirmed by the experiments with D atoms. On the other hand, in a matrix of benzene, the addition of H atoms occurred at the central carbon atom to give the $CH_2\text{-}CH{=}O$ radical, while in a matrix of adamantane, both $CH_3\text{-}C{=}O$ and $CH_2\text{-}CH{=}O$ radicals were observed. They emphasized that no such dependence of the site of addition on the nature of the matrix could be observed in the cases of other unsaturated compounds. Further experiments to identify the initial radical products from H atoms and ketene and alkyl substituted ketenes are highly desirable.

The isotope effect observed in the present experiments between H- and D-atom reactions can be explained by taking into account the difference in collision frequency, as has been discussed in the case of olefin reactions.[4)]

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