Kinetics of the reaction $C_2H_5 + H_2 \rightarrow C_2H_6 + H$ from 1111–1200 K

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A system for the measurement of the rate constant for the elementary reaction

 $C_2H_5 + H_2 \rightarrow C_2H_6 + H$

in the temperature range 1111-1200 K is described and is based on the thermal production of an equilibrium concentration of hydrogen atoms. In a mixture of hydrogen with about 10 ppm ethylene this reaction is the rate-controlling step in the hydrogenation of ethylene. The product ethane undergoes rapid secondary dissociation and the final product is methane. The values obtained in the present work, which are represented by the following expression,

 $\log k (L \mod^{-1} s^{-1}) = 10.6 - 23000/2.3RT$

 $(R = 1.987 \text{ cal mol}^{-1} \text{ deg}^{-1})$ are compared to those obtained at lower temperature (820–350 K) and to those calculated from measurements of the reverse reaction.

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On décrit un système de mesure de la constante de vitesse de la réaction élémentaire

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dans l'intervalle de température allant de 1111 à 1200 K. Ce système se base sur la formation thermique d'une concentration à l'équilibre des atomes d'hydrogène. Dans un mélange d'hydrogène avec environ 10 ppm d'éthylène, cette réaction constitue l'étape déterminante de la réaction d'hydrogénation de l'éthylène. L'éthane obtenu subit une dissociation secondaire rapide et conduit au méthane comme produit final. On a comparé les valeurs obtenues que l'on représente par l'expression suivante

 $\log k (L \mod^{-1} s^{-1}) = 10.6 - 23000/2.3RT$

 $(R = 1,987 \text{ cal mol}^{-1} \text{ deg}^{-1})$, avec celles obtenues à plus basse température (820–350 K) et avec celles calculées à partir des mesures de la réaction inverse.

[Traduit par le journal]

Introduction

There has been much interest in recent years in extending measurements of rate constants for elementary reactions of hydrocarbon radicals into a high-temperature region. Few rate constants for these radicals have been measured at temperatures above 1000 K, yet many thermal reaction systems involving these radicals have been studied at these temperatures and higher. In order to understand the mechanisms of these reactions it is essential to have reliable measurements of the rate constants for the elementary reactions involved, many of which are obtained by extrapolation from measurements made at much lower temperatures. Serious errors may be introduced in this procedure by the non-Arrhenius behavior observed for the reactions of hydrogen atoms and small radicals (1). This behavior, which is not unexpected over a wide temperature range, is of theoretical as well as practical importance in the understanding of reaction mechanisms and the details of reaction pathways (2).

A new system for the measurement of rate constants for radical reactions at temperatures above 1000 K has been explored in this laboratory. The method is based on the premise that at these temperatures and moderate pressures of hydrogen an equilibrium concentration of hydrogen atoms can be maintained in the system. A small quantity of reactant, in our studies, ethylene, in concentrations of a few ppm, is added to the hydrogen and the rate of consumption of ethylene and appearance of the products is measured. The assumption is made, and tested by the kinetics, that the equilibrium between hydrogen molecules and atoms is not significantly perturbed by the addition of the reagent. In the present study, it is shown that as well as the equilibrium concentration of hydrogen atoms, an equilibrium concentration of ethyl radicals is attained by addition of hydrogen atoms to ethylene and the rate-controlling step is the abstraction reaction of ethyl radicals with hydrogen.

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

Measurements of the rate of disappearance of ethylene thus lead to values for the rate constant for this reaction over the temperature range 1111-1200 K. Only four measurements of this rate constant have been reported (3-6), all of which are below

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820 K. New measurements should therefore be valuable in establishing this rate constant in the high temperature region. Many measurements of the rate constant for the reverse reaction have been reported (7) and it is of interest to compare these values with those of the forward reaction through the equilibrium constant. It will be shown that agreement between the forward and reverse rate constants can be achieved only if the heat of formation of the ethyl radical is somewhat larger than has previously been accepted (8).

Experimental

The reaction was studied in a static system with provision for storage, mixing, introduction, and sampling of the reactants and products. The reaction vessel was a guartz cylinder with diameter 4.4 cm and volume 182 cm3, and was placed in the center of a Lindberg three-zone tubular furnace. A second vessel of similar dimensions and packed with quartz tubes to give a S/V ratio of 7.5 cm⁻¹ was used to test for the importance of surface reactions. Mixtures were prepared in a 2-L spherical flask with minimum dead space by introducing first the small pressure of ethylene and then filling with hydrogen. After a mixing period of 12h the composition of the mixture was homogeneous and invariant. Ethylene was Research Grade (99.98%) obtained from Matheson of Canada, Whitby, Ont. Hydrogen was purified by passage through a Molecular Sieve 5A column at liquid nitrogen temperature with a residence time of 1-2s. Such treatment is usually sufficient to reduce the oxygen impurity to less than 1 ppm (9), although the present analysis system, using gas chromatography with a thermal conductivity detector, could not detect less than 6 ppm.

The products were analyzed by expansion into a Toepler pump from which duplicate samples were taken for analysis. Analyses were made on a Hewlett-Packard model 5750 with FID detector, using a 1.2 m column of Durapak (phenylisocyanate on Porasil) maintained at 30°C. The reactant ethylene and the products methane and ethane were measured for reaction times from 1–40 min.

Results

The rate of hydrogenation of ethylene in the unpacked vessel was measured at 1111 K for five concentrations of ethylene in hydrogen ranging from 9-36 ppm. At each concentration the rate was measured at four or five total pressures ranging from 100-300 Torr. These data allowed the determination of the order with respect to each reactant. The rate was also measured at five temperatures over the range 1111-1192 K. In addition, at 1192 K, the total order of the rate with respect to both reactants was measured.

The primary product of the hydrogenation was ethane, but at the temperature of the reaction, secondary decomposition was rapid and the final product was methane. The yields as a function of time at 1111 K are shown in Figs. 1, 2, and 3. It is clear that ethane is an intermediate product and even at the lowest temperature its yield is small. It gradually became undetectable as the temperature



FIG. 1. Variation in mole fraction of reactant and products at 1111K and total pressure of 182 Torr. \Box , C₂H₄; O, CH₄; \triangle , C₂H₆. Open symbols refer to unpacked vessel (S/V ~ 1 cm⁻¹) and filled symbols refer to packed vessel (S/V ~ 7 cm⁻¹).

was increased. It should be noted that equilibrium in this system corresponds to almost complete conversion of ethylene to methane. The reaction was therefore followed by the disappearance of ethylene and the appearance of methane.

The measurement of the initial rates from the data involved a search for an equation giving the best linear extrapolation. Integrated equations for orders of 0.5, 1, 1.5, and 2 were tested and the best extrapolation was obtained with the function 1/x against time. A summary of the measurements is given in Table 1. In fact, these initial rates were within about 25% of those estimated directly from the yield-time plots or from the function $\log x$ against time. It should be emphasized that the function used to estimate the initial rates is not particularly significant in terms of the mechanism of the reaction during the initial stages.

The dependence of the rate on the initial concentration of the reactant is the characteristic of most importance to the mechanism. The rate of disappearance of ethylene may be written as

$$-R_{C_{2}H_{4}} = k[H_{2}]^{m}[C_{2}H_{4}]^{n}$$

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FIG. 2. Mole fraction of ethane as a function of time at various temperatures. Initial concentration of ethane: 9.33 ppm; total pressure: 182 Torr. \bigcirc , 1111 K; \bigcirc , 1131 K; \square , 1171 K; \bigcirc , 1192 K; \triangle , 1151 K. Open symbols refer to unpacked vessel (S/V ~ 1 cm⁻¹) and filled symbols refer to packed vessel (S/V ~ 7 cm⁻¹).

where k represents an over-all rate constant and m and n represent the order of the rate with respect to hydrogen and ethylene, respectively. Designating the mole fraction of each reactant by X and making the approximation that $X_{\rm H_2} = 1$,

$$-R_{\rm C_{2H_4}} = k P^{m+n} X_{\rm C_2H_4}^n$$

where P is the total pressure.

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A log-log plot of the initial rate as a function of $X_{C_{2H_4}}$ is shown in Fig. 4 for four total pressures. Since the concentration of hydrogen is essentially constant for each total pressure, the slope of these plots gives a value for *n* of 1.0 ± 0.1 . The initial rate as a function of the total pressure for each of the concentrations of ethylene is given in Fig. 5. The slope of these plots, all equal to 2.4 ± 0.1 , gives the total order, m + n. A similar plot using the data obtained at 1192 K (Table 1) gives a value for m + n = 2.5. The value of *m* is therefore 1.5 ± 0.1 . An Arrhenius plot of the initial rate gives an activation energy of 33 kcal/mol.

In the packed vessel, rates were measured at total pressures of 116, 182, 274, and 325 Torr for each of three mixtures, 12, 18.5, and 28 ppm ethylene at 1111 K. The results are given as the corresponding filled symbols in Figs. 1, 2, and 4. The results show that heterogeneous processes are not important in the rate-determining steps of the reaction except to a slight extent at the highest pressures.

These results suggest that the hydrogenation of ethylene may occur through a simple set of reactions where the H-atom concentration in the



FIG. 3. Mole fraction of ethylene as a function of time at 1111 K with initial concentration of ethylene of 19.2 ppm. Total pressure: \triangle , 85.5 Torr; \diamondsuit , 117 Torr; \Box , 149 Torr; \bigcirc , 182 Torr.

system is determined by the equilibrium between molecules and atoms.

- [1] $H_2 \rightleftharpoons 2H$
- $[2] \qquad H + C_2H_4 + M \rightleftharpoons C_2H_5 + M$
- $[3] \qquad C_2H_5 + H_2 \rightarrow C_2H_6 + H$
- $[4] \quad C_2H_6 \rightarrow 2CH_3$
- $[5] \qquad CH_3 + H_2 \rightarrow CH_4 + H$
- $[6] \qquad C_2H_5 + H \rightarrow C_2H_6$

Considering only the reactions occurring in the initial stages,

[7]
$$-R_{C_{2}H_{4}} = R_{C_{2}H_{6}} = \frac{k_{3}k_{2}[M]^{x}K_{1}^{1/2}[H_{2}]^{3/2}[C_{2}H_{4}]}{k_{-2}[M]^{x} + k_{3}[H_{2}]}$$

where x, having values between 1 and 0, represents the dependence of the rates [2] and [-2] on the concentration of third body.

The characteristics of the rate depend critically on the ratio of rates $k_{-2}[C_2H_5][M]^x$ and $k_3[C_2H_5]-[H_2]$.

Case 1: If $k_{-2}[M]^x \gg k_3[H_2]$ and the concentration

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T/K	Pressure/ Torr	Х _{с₂н₄} / ppm	$-\frac{d}{dt}$ [CH ₄]/ mol L ⁻¹ s ⁻¹ × 10 ⁻¹⁰	$K_1^{1/2}/$ (mol L ⁻¹) ^{1/2} × 10 ⁻⁹	$\frac{K_2}{(\text{mol } L^{-1})^{-1} \times 10^4}$	$k_3/$ L mol ⁻¹ s ⁻¹ × 10 ⁶
1071	182	10.84	2.64	1.51	3.19	1.31
1111	117	10.84 19.2 27.3 36.6	1.42 1.75 2.65 4.26	3.48	1.72	1.91 1.32 1.42 1.70
	182	9.33 10.84 19.2 27.3 36.6	2.82 3.49 5.23 8.37 11.0			1.39 1.56 1.32 1.49 1.46
	308	10.84 19.7 27.3 36.6	14.8 19.3 28.9 39.3			1.73 1.24 1.34 1.36
1131	182	9.33	3.44	4.89	1.39	1.64
1151	182	9.33 10.84	4.59 5.89	7.00	0.966	2.05 2.18
1171	182	9.33	6.26	10.02	0.729	2.62
1181	182	10.84	8.28	12.8	0.640	2.84
1192	119 182 248	9.33 9.33 9.33	3.18 8.97 19.5	18.1	0.556	3.31 2.98 3.22
			Packed reaction	vessel S/V = 7.0 cm^{-1}		
1111	116	11.85 18.46 27.9	1.91 2.03 2.33	3.48	1.72	1.61 1.22
	182	11.85 18.46 27.9	3.63 4.10 7.17			1.49 1.26
	274	11.85 18.46 27.9	7.60 8.63 15.8			1.09 0.97
	325	11.85	11.4			1.07

TABLE 1. Initial rates of reaction of ethylene and values for k_3

of ethyl radicals is controlled by the equilibrium reaction [2],

[8]
$$-R_{C_2H_4} = k_3K_2K_1^{1/2}[H_2]^{3/2}[C_2H_4]$$

Case 2: If $k_{-2}[M]^x \ll k_3[H_2]$
[9] $-R_{C_2H_4} = k_2[M]^xK_1^{1/2}[H_2]^{1/2}[C_2H_4]$

The order of the rate is consistent with either case if x is close to 1. The activation energy of the rate, 33 kcal/mol, is, however, consistent only with the first case where an equilibrium concentration of ethyl radicals is maintained. Taking $\Delta H_2 = -41.0$ kcal/mol (see Appendix) and $\Delta H_1 = 104.2$ kcal/mol, case 1 gives $E_3 = 22$ kcal/mol. It will be shown later that this is a reasonable value at temperatures in the region of 1100 K. On the other hand, from eq. [9]

describing case 2, and using a value of E_2 of about 4 kcal/mol (7), the activation energy of the rate will be about 56 kcal/mol, far outside the measured value. A calculation of the relative magnitude of k_{-2} and $k_3[H_2]$ is not conclusive (although ar estimate gives k_{-2} about five times greater thar $k_3[H_2]$) because rather long extrapolations are required in both cases and for k_{-2} both the value of the rate constant and its pressure-dependence mus be obtained. It may be concluded that the mechanism is best described by the conditions imposed by case 1 and that eq. [8] adequately expresses the rate of disappearance of ethylene in the system.

The order with respect to hydrogen and the activation energy of the rate strongly suggest tha hydrogen atoms are maintained at an equilibrium

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FIG. 4. Logarithm of the initial rate of reaction of ethylene as a function of the logarithm of the initial mole fraction of ethylene for various total pressures at 1111 K. \diamond , 307 Torr, slope = 0.95; \blacktriangle , 274 Torr, slope = 0.97; \bigcirc , 183 Torr; slope = 0.98; \square , 117 Torr, slope = 1.03. Open symbols refer to unpacked vessel (S/V \sim 1 cm⁻¹) and filled symbols refer to packed vessel (S/V \sim 7 cm⁻¹).



FIG. 5. Logarithm of the initial rate of reaction of ethylene as a function of the logarithm of the total pressure at 1111 K for various initial concentrations of ethylene.

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concentration. It may be questioned, however, that the homogeneous rate of dissociation of hydrogen is sufficiently fast to produce the equilibrium concentration in the short times of these reactions. Calculations based on the value of the rate constant for combination of hydrogen atoms measured at room temperature (10) (an upper limit) and the equilibrium constant at the temperature of the reaction, show that homogeneous dissociation is indeed too slow by at least a factor of 10². It must be concluded that dissociation is catalyzed by the quartz surface. The fact that the rate was not affected by an increase in S/V ratio of the reaction vessel further suggests that an equilibrium concentration of hydrogen atoms is rapidly attained in both vessels.

Some comments concerning the importance of other reactions which might affect the concentration of radicals in the system may clarify the mechanism. The occurrence of reaction [6] could reduce the concentration of hydrogen atoms below equilibrium. At 1111 K and a pressure of hydrogen of 182 Torr, the equilibrium concentration of hydrogen atoms is 1.7×10^{-10} mol L⁻¹. Under the same conditions, with 10 ppm C₂H₄, the equilibrium ratio of C_2H_5/H equals 1×10^{-3} . Taking again the value of k_{-1} measured at room temperature (10) and a value of 1×10^{10} L mol⁻¹ s⁻¹ for k_6 , the homogeneous rates of reaction [-1] and [6] are comparable. We have, nevertheless, argued that the dissociation of hydrogen and the combination of hydrogen atoms must occur on the surface much more rapidly than in the gas phase. The measurements by Sepehrad, Marshall, and Purnell (19) of the rate of combination of hydrogen atoms on the surface show that this is the case. In their system hydrogen atoms disappeared at the wall in a first-order process,

 $[W] \qquad H \rightarrow \frac{1}{2}H_2$

and a value of k_w of $20 \pm 15 \text{ s}^{-1}$ was obtained at temperatures in the region of 800 K. In the present system wall recombination is probably slower since the steady-state concentration of hydrogen atoms is less than in the flow system of Sepehrad *et al*. Nevertheless use of their value for k_w provides an upper limit to the rate of removal of hydrogen atoms. The ratio of the rates of reactions [W] and [6] may be expressed as follows:

$$R_{\rm w}/R_6 = k_{\rm w}/k_6K_2[{\rm H}][{\rm C}_2{\rm H}_4]$$

and with the conditions described above (K_2 at 1111 K = 1.7×10^4 L mol⁻¹),

 $R_{\rm w}/R_6 = 2.6 \times 10^4$

Therefore termination by reaction [6] is probably not sufficiently important to reduce the concentration of hydrogen atoms significantly below equilibrium. Furthermore, this reaction probably requires collisional stabilization, without which the ethane molecule will dissociate into two methyl radicals which will rapidly convert to methane, returning hydrogen atoms to the system.

A possible initiation process is the reaction of ethylene with hydrogen to give an ethyl radical and a hydrogen atom,

$$10] \quad C_2H_4 + H_2 \rightarrow C_2H_5 + H$$

If termination occurs by reaction [6], then, under steady-state conditions,

$$[C_2H_5] = k_{10}[C_2H_4][H_2]/k_6[H]$$

The rate constant for reaction [10] may be estimated from values of ΔH and ΔS and may be expressed as

$$\log k_{10}$$
 (L mol⁻¹ s⁻¹) = 9.8 - 65300/2.3RT

At 1111 K, $k_{10} = 9.6 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$. Taking again the conditions of 182 Torr hydrogen and 10 ppm C₂H₄ and assuming $k_6 \sim 1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (an upper limit),

$$[C_2H_5] \sim 3 \times 10^{-14} \text{ mol } L^{-1}$$

This value, although only approximate, is lower than the equilibrium concentration of ethyl radicals of $\sim 2 \times 10^{-13}$ estimated under the same conditions. Reaction [10] may therefore be neglected as a significant source of ethyl radicals. Furthermore, a contribution by ethylene to the initiation process would increase the order of the rate with respect to the concentration of ethylene.

It can also be shown that reaction [10] cannot itself account for the disappearance of ethylene. According to reaction [10] the rate of disappearance of ethylene may be written as

$$-R_{C_2H_4} = k_{10}[C_2H_4][H_2]$$

Taking the same conditions as an example, the rate of disappearance of ethylene may be estimated as 6×10^{-14} mol L⁻¹ s⁻¹, while the observed rate is 3×10^{-10} mol L⁻¹ s⁻¹ (Table 1). One further possibility for consumption of ethylene is the unimolecular dissociation,

$$[11] \quad C_2H_4 \to C_2H_3 + H$$

This reaction has been observed and measured in the shock-tube pyrolysis of ethylene (11, 12) as a second-order process. A reasonable value for the unimolecular dissociation is

$$\log k_{11}$$
 (s⁻¹) = 16 - 104000/2.3RT

and at 1111 K, $k_{11} = 3.5 \times 10^{-5} \text{ s}^{-1}$. Taking the same conditions as above,

$$-R_{C_{2H_4}} = k_{11}[C_2H_4] = 8.8 \times 10^{-13} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

This must be an upper limit since the dissociation will undoubtedly be partly pressure-dependent at the temperature of these experiments. Therefore neither reaction [11] nor reaction [10] are sufficiently fast to account for the rate of disappearance of ethylene.

The rates of reactions [10] and [11] may also be compared to the rate of dissociation of hydrogen, in order to compare the rate of production of hydrogen atoms in the system. A value for the rate of dissociation of hydrogen on the surface may be obtained from the equilibrium represented by reaction [W], and again represents an upper limit.

$$K_{\rm w} = k_{-\rm w}/k_{\rm w} = (K_{\rm H_2})^{1/2}$$

Using the value for k_w as already discussed,

$$k_{-w} = 7.0 \times 10^{-8} \, (\text{mol/L})^{1/2} \, \text{s}^{-1}$$

The ratio of rates may be expressed as follows:

$$\frac{R_{-w}}{R_{10}} = \frac{k_{-w}[H_2]^{1/2}}{k_{10}[C_2H_4][H_2]} = 5.8 \times 10^4$$
$$\frac{R_{-w}}{R_{11}} = \frac{k_{-w}[H_2]^{1/2}}{k_{11}[C_2H_4]} = 4.2 \times 10^3$$

Even though this represents an upper limit to the rate of formation of hydrogen atoms from hydrogen, it is unlikely that reactions [10] or [11] are important in the present system.

Rate of formation of methane

The rate of formation of methane may be equated to the rate of disappearance of ethane if all methyl radicals react by reaction [5].

$$R_{\rm CH_{4}} = 2k_4 [\rm C_2 H_6]$$

The maximum concentration of ethane is given as follows,

$$[C_2H_6]_m = \frac{k_3[C_2H_5][H_2]}{k_{-3}[H] + k_4}$$

If the concentration of both the ethyl radical and the hydrogen atom are given by the relevant equilibrium constant the maximum rate of formation of methane is

[12]
$$R_{\text{CH}_4} = \frac{2k_4k_3K_2K_1^{1/2}[\text{H}_2]^{3/2}[\text{C}_2\text{H}_4]}{k_{-3}K_1^{1/2}[\text{H}_2]^{1/2} + k_4}$$

since $k_{-3} = k_3/K_3$ the rate constant k_3 may be expressed as

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	$\frac{d}{dt}$ [CH ₄]/			
T/K	mol L^{-1} s ⁻¹ × 10 ⁻¹⁰	$K_3/10^{-3}$	k_4/s^{-1}	$k_3/L \text{ mol}^{-1} \text{ s}^{-1} \times 10^6$
1111	2.50	3.87	0.0676	1.10
1131	3.96	4.06	0.151	1.46
1151	4.92	4.21	0.282	1.76
1171	6.42	4.37	0.525	2,27
1192	8.62	4.54	1.00	2.29

TABLE 2. Initial rate of formation of methane and values for k_3 , total pressure: 182 Torr; $X_{C_2H_4}$: 9.33 ppm

[13]
$$k_3 = \frac{R_{CH_4}k_4}{K_1^{1/2}[H_2]^{1/2} \left[2k_4K_2[H_2][C_2H_4] - \frac{R_{CH_4}}{K_3} \right]}$$

Since the product ethane achieves its maximum concentration at a very short time of reaction, the maximum rate of formation of methane may be obtained by an extrapolation procedure similar to that used to obtain the initial rate of disappearance of ethylene. In other words, a maximum rate will be indistinguishable from an initial rate on the time scale of the present experiments. These rates of formation of methane are shown in Table 2.

The relative importance of the terms in the denominator of eq. [12] may be deduced from the measured activation energy of the rate of formation of methane, which was 38 kcal/mol. If $k_4 \gg k_{-3}K_1^{1/2}[H_2]^{1/2}$ and ethane is removed primarily by dissociation, the rate of formation of methane becomes

[14] $R_{CH_4} = 2k_3K_2K_1^{1/2}[H_2]^{3/2}[C_2H_4]$

which is exactly twice the rate of disappearance of ethylene. Since the activation energies for the rate of disappearance of ethylene and the rate of formation of methane were similar, it may be concluded that the simplified expression, eq. [14], closely describes the mechanism for formation of methane. The other situation, in which k_4 may be neglected in the denominator, would predict a much higher activation energy, about 63 kcal/mol. Nevertheless, the initial rate of formation of methane was not exactly twice the initial rate of disappearance of ethylene, indicating that some ethane may be lost by the reverse of reaction [3]. The complete eq. [13] was therefore used to calculate k_3 .

Calculation of k₃

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Using eqs. [8] and [13] values of k_3 were calculated from the rate of disappearance of ethylene and from the rate of formation of methane. The results together with the values of k_4 , K_2 , and K_3 used in the calculations, are included in Tables 1 and 2. The fall-off in k_4 was estimated by extrapola-

tion of the results of Lin and Back (13). Other data are given in the Appendix. An Arrhenius plot of k_3 is given in Fig. 6. The activation energy measured for k_3 is 23 ± 2 kcal/mol. These results are shown together with the four other sets of measurements previously reported at lower temperatures as the filled points in Fig. 7. Also on this graph are values of k_3 calculated from the measurements of k_{-3} , and the equilibrium constant K_3 . The points given represent the limits of the temperature range for each set of data and the lines represent the values reported for A and E. The thermodynamic quantities used in the calculation are given in the Appendix.

The measurements of k_3 derived from k_{-3} are somewhat lower than the direct measurements of k_3 , but may be considered in reasonable agreement. Two points concerning the calculations should be noted. The four measurements of k_3 were



FIG. 6. Arrhenius plot for k_3 measured in the present experiments. \Box , 9.3 ppm C₂H₄; \bigcirc , 10.8 ppm C₂H₄; \triangle , calculated from the yield of CH₄; I, range of values at 1111 K for five concentrations of C₂H₄; filled symbols: packed vessel.





FIG. 7. Arrhenius plot for k_3 . Filled symbols represent direct measurements of k_3 . Other symbols represent measurements of k_{-3} converted to k_3 using the calculated values of K_3 . \blacksquare , ref. 3; \blacklozenge , ref. 4; \spadesuit , present work; \blacktriangle , ref. 5; \blacktriangledown , ref. 6; \Box , ref. 27; \bigcirc , ref. 32; \times , ref. 29; \bigcirc , ref. 21; \bigtriangledown , ref. 26; \triangle , ref. 24; \diamondsuit , ref. 30 and 31; \blacksquare , ref. 22; \bigcirc , ref. 23; \heartsuit , ref. 28; \blacksquare , ref. 25; \oslash , ref. 33.

all made relative to the rate constant for the combination of ethyl radicals, k_c , which in each case was taken as 2.2×10^{10} L mol⁻¹ s⁻¹. More recent work indicates that $k_c \sim 1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (14, 15) and these values were therefore lowered by $\sqrt{2.2.}$ The equilibrium constant, K_3 , was calculated using a value of 28 kcal/mol for $\Delta H_{\rm f}(\rm C_2H_5)$. Although this value is given in most references (8, 16) as 26 kcal/mol, k_3 calculated with this value is considerably lower than the direct measurements of k_3 . Recent measurements of the heat of formation of the ethyl radical relative to that of the methyl radical using a radical buffer system in an isooctane solution (17) have given a value of 28 kcal/mol, using $\Delta H_{\rm f}(\rm CH_3) = 34.4$ kcal/mol. The fact that the independent measurements of k_3 and k_{-3} are in reasonable agreement using the value of $\Delta H_f(C_2$ - H_s) = 28 kcal/mol suggests that the higher value

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may be preferable. The difference of 2 kcal/mol increases the calculated values of k_3 by a factor of two. A similar comparison between forward and reverse rate constants for the reaction of methyl radicals with hydrogen led to the acceptance of a higher value (at that time) for the heat of formation of the methyl radical (18). In a recent discussion of this system, the authors concluded that the independent measurements of the forward and reverse rate constants were in agreement within a factor of 2 or 3 (19, 20). A similar agreement is indicated in the present comparison of the system involving ethyl radicals.

The present measurements are in good agreement with the values of k_3 calculated from measurements of k_{-3} . They appear somewhat below an extrapolation of the values measured below 820 K but are within the limits of error encompassed by both sets of measurements. Most of the measured rate constants are within a factor of two of an average value. On the other hand, values for the Arrhenius parameters are often very different, as can be observed from the variation in slopes of the lines in Fig. 7.

The activation energy of k_3 obtained in the present results appears at first unusually high, although there are no other data for k_3 above about 820 K. It has been observed that the activation energy of similar abstraction reactions rises gradually but substantially above 900 K. For example, in their discussion of non-Arrhenius behaviour in some simple abstraction reactions Clark and Dove (2) showed that the literature data on reaction [-3]can be fitted by a smooth curve giving a continuously increasing activation energy with increasing temperature. From this curve, E_{-3} was about 14 kcal/mol in the temperature range 1100-1200 K. Since ΔH_3 at this temperature is 4.5 kcal/mol (see Appendix), E_3 should be 18.5 kcal/mol, in reasonable agreement with the present results. Closer examination of the combined sets of measurements may, however, throw some doubt on the magnitude of the change in activation energy over the whole temperature range. The results could, in fact, be fitted reasonably well by a linear relation. This was the conclusion reached by Sepehrad, Marshall, and Purnell (19) in a comparison of measurements reported for k_{-5} . Nevertheless, the best fit probably indicates a change in activation energy from 12 kcal/mol in the range 350-550 K to about 17 kcal/ mol from 800-1200 K, which is a smaller increase than previously supposed. The comparison of these two sets of data shows the magnitude of error which can be expected in values for rate constants for radical abstraction reactions. It also illustrates

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the danger in the use of extrapolated values and the need to acquire a consistent set of data.

Evaluation of the method

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A possible source of error in the present measurements which would lead to an underestimate of k_3 is an overestimate of either the hydrogen atom concentration or the ethyl radical concentration. It seems unlikely that the hydrogen atom concentration is much below equilibrium since the large increase in surface area had no effect on the rate. It is known that hydrogen atoms are strongly adsorbed on quartz surfaces, leading to heterogeneous reactions, but the absence of a perturbing effect of the surface is easily explained if atoms and molecules are in equilibrium. The concentration of ethyl radicals, on the other hand, may be reduced below the equilibrium value under conditions where $k_3[H_2]$ may become comparable in rate to the dissociation reaction, [-2]. Estimates of the relative magnitude of these two rates suggests they may be comparable, but the over-all activation energy of the rate was incompatible with the exclusion of reaction [-2] as the rate-controlling removal of ethyl radicals. This factor could cause an underestimate of k_3 by perhaps a factor of two. The estimate of the initial rate also involves some uncertainty, but it seems unlikely that this could be more than 30 or 40%. The system is kinetically simple and offers a well-controlled concentration of atoms. Further studies on other systems should prove useful in providing data on the region above 1000 K.

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Appendix Thermodynamic data

	$\Delta H_{\rm f}(298)/\rm kcal\ mol^{-1}$	S ⁰ (298)/cal deg ⁻¹ mol ⁻¹
Н	52.1	27.4
C₂H₄	12.5	52.4
C_2H_5	28.0	59.0
$\tilde{C_2H_6}$	-20.2	54.9

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Equilibrium constants (a) $H + C_2H_4 \rightleftharpoons C_2H_5$

T/K	$\Delta H_T/\text{kcal mol}^{-1}$	$\Delta S_{\tau}/\text{cal mol}^{-1} \text{ deg}^{-1}$	$K/(\text{mol } L^{-1})^{-1} \times 10^4$
1000	-38.7	-24.5	10.7
1100	-39.0	-24.7	2.03
1200	-39.2	-24.9	0.50
	(b) ($C_2H_5 + H_2 \rightleftharpoons C_2H_6 + H$	

	$\Delta H_r/kcal mol^{-1}$	ΔS_T /cal mol ⁻¹ deg ⁻¹	
1000	4.28	-7.24	3.03
1100	4.39	-7.10	3.80
1200	4.45	-6.98	4.61

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