

The Thermal Dissociation of Ethane

A Study of the Reaction over an Extended Pressure Range

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The rates of dissociation of ethane into two methyl radicals have been determined by measuring the rate of formation of methane at 862 K at pressures in the range 0.01–30 Torr.† The results coupled with earlier measurements provide rate coefficients for the dissociation reaction over a pressure region where the reaction order varies from *ca.* 1.9 to 1.1. The data have been fitted to an RRKM model over this range. There are indications of the occurrence at the lower end of the pressure range of a heterogeneous process leading to methane formation, which prevented the extension of the investigation to even lower pressures. Application of the results obtained from this study to a recently proposed expression for rate coefficients of unimolecular reactions in the fall-off region shows that there is good agreement in this case between theory and experiment.

The dissociation of ethane has been the subject of more investigations than has any other bond-fission reaction,¹ and the available data have been used to assess various theories of unimolecular reactions. It is therefore of value to have as much information as possible on this particular reaction, and the work described herein has been carried out with a view to filling a gap in our present knowledge of the rate coefficients for the dissociation process. Previous investigations^{2–6} have for any given temperature covered pressure ranges of between two and three orders of magnitude, over which the order of the unimolecular reaction changes by a factor of *ca.* 0.5. Such a variation is hardly sufficient to allow a fair test of theoretical expressions relating first-order rate coefficients to the pressure of the reactant. At the top end of the various pressure ranges which have been studied the dissociation is generally close to first order, so there is nothing to be gained by extending to even higher pressures. By contrast, no data are available for rate coefficient at pressures < 1 Torr, and it is in this area that the present investigation has been centred.

EXPERIMENTAL

MATERIALS

Matheson Gas Products Research Grade ethane was used after purification by the procedure described previously.⁶ 99.99% purity methane (Air Products) was used for gas-chromatographic calibration.

APPARATUS AND PROCEDURE

A spherical silica reaction vessel of 5.25 dm³ capacity was used; this had a surface/volume ratio of 0.28 cm⁻¹. In experiments carried out to ascertain the effect of a three-fold increase in surface/volume ratio, the vessel was packed with thin silica tubing. The vessel, which had

† 1 Torr \approx 133.3 N m⁻².

a thermocouple well along its diameter, was heated in a well lagged $30 \times 30 \times 30 \text{ cm}^3$ box fitted with heating elements and a circulating fan. Temperatures in the box were controlled by an AEI temperature controller and measured using a calibrated Pt/Pt-Rh thermocouple. During the course of the longest runs (120 min) the temperature in the reaction vessel remained within $\pm 1 \text{ K}$ of the reported value. At 862 K there was a difference in temperature of 3 K between the top and the bottom of the vessel, the temperature reported being that at the centre of the vessel. The 'dead space' of connecting tubing outside the heated zone amounted to only 0.4% of the total, so that corrections for this error were unnecessary.⁷

Before the investigation was started, the surface of the reaction vessel was cleaned and deactivated⁸ using $10 \text{ mol dm}^{-3} \text{ NaOH}$ followed by $10 \text{ mol dm}^{-3} \text{ HNO}_3$ and then thoroughly washed with distilled water. The vessel was connected to a vacuum system and storage bulbs through greaseless taps (J. Young Ltd) and these were used in all parts of the apparatus which came into contact with reactant or products. Ethane was introduced into the reaction vessel from any one of four sharing vessels of different sizes ranging from 5 to 500 cm^3 ; this allowed the admission of reproducible amounts at any of the pressures studied. Pressures in the reaction vessel were measured using a precision pressure gauge (Texas Instruments) and also, for the lowest pressures, a calibrated tilting McLeod gauge. After the required heating time the reaction vessel was connected to a 5 dm^3 vessel at room temperature for a time sufficient to allow the pressure to equilibrate. Samples of products were then withdrawn from the 5 dm^3 vessel through a mercury diffusion pump to a sample vessel attached to the top of a Topley-McLeod gauge. The methane content of the samples was determined by gas chromatography using a 1 m silica-gel column at 50°C in conjunction with a flame ionisation detector.

RESULTS AND DISCUSSION

All experiments were performed with the reaction vessel at 862 K. At all but the two highest pressures studied, where rate coefficients were based on single measurements, a series of runs was performed in which methane yields were obtained for different heating times. Graphs of methane against time were invariably linear and initial rates of formation of this product were obtained from least-squares estimates of the slopes. Rate coefficients for the dissociation of ethane were derived using the expression $k = (1/2[\text{C}_2\text{H}_6]_0)(d[\text{CH}_4]/dt)_0$.

The rate coefficients obtained in this investigation are listed in table 1 and a logarithmic plot of the rate coefficients against pressure is shown in fig. 1. The RRKM curve, also shown in fig. 1, is based on the data reported previously⁶ with the exception that a collision diameter of 2.6 \AA was used rather than the quoted value of 2.8 \AA . The position of an RRKM curve is quite sensitive to the value chosen for the collision diameter and the value used here, although significantly less than the value of 4.45 \AA derived from viscosity data,⁹ gives the best agreement between theory and experiment. The difference between the calculated collision diameter and that used to obtain a fit may be linked with the low collisional deactivating efficiency of ethane. This leads to a value of 0.35 for the parameter λ , which appears in the RRKM expression¹⁰ for k_{uni} and is a measure of the deactivating efficiency.

It will be seen from fig. 1 that the data obtained at the two lowest pressures show that an increasing positive deviation of $\log k_{\text{uni}}$ from the theoretical estimates arises as the pressure of ethane is lowered. This deviation may reasonably be ascribed to the formation of methane by a heterogeneous process in amounts which, for ethane pressures $< 0.04 \text{ Torr}$, are significant in comparison with the methane formed homogeneously. This view is supported by the observation that with the packed reaction vessel rate coefficients at pressures $> 0.1 \text{ Torr}$ are in line with those obtained using the empty vessel, but at $< 0.1 \text{ Torr}$ deviations from the theoretical curve are progressively more marked than those with the unpacked vessel.

Values obtained for rate coefficients in the pressure region which overlaps that

Table 1. Rate coefficients for the pyrolysis of ethane at 862 K

$[\text{C}_2\text{H}_6]/\text{Torr}$	$k/10^{-8} \text{ s}^{-1}$
0.010	0.90 ± 0.5 (6)
0.020	1.18 ± 0.25 (14)
0.042	1.75 ± 0.29 (10)
0.057	2.56 ± 0.25 (6)
0.082	3.10 ± 0.14 (5)
0.102	3.62 ± 0.07 (5)
0.146	4.43 ± 0.20 (5)
0.208	5.90 ± 0.14 (5)
0.300	8.26 ± 0.30 (5)
0.415	9.11 ± 0.19 (5)
0.620	12.4 ± 0.5 (5)
0.82	13.4 ± 0.3 (6)
1.02	15.9 ± 0.9 (6)
1.81	22.5 ± 1.2 (5)
2.57	29.5 ± 0.5 (5)
6.86	43.3 ± 2.0 (5)
12.6	56.2 (1)
31.25	78.0 (1)
4.04 ^a	31.3
10.11 ^a	47.7
21.49 ^a	62.9
43.73 ^a	79.7
87.89 ^a	95.3
175.5 ^a	109
347.2 ^a	121
686 ^a	128
0.0095 ^b	5.0 ± 0.4 (4)
0.020 ^b	3.06 ± 0.21 (5)
0.057 ^b	3.27 ± 0.17 (5)
0.125 ^b	4.62 ± 0.10 (6)
0.422 ^b	9.76 ± 0.18 (5)

^a Results obtained previously.⁵ ^b Data obtained using the packed reaction vessel.

studied previously⁶ show close agreement, so that the combined data may be taken to cover the pressure range 0.04–680 Torr. Whilst at the higher end of the pressure range studied the reaction order is close to 1.1, at the lower end it is *ca.* 1.9 as determined from estimated slopes of the RRKM fall-off curve. Thus the rate of formation of methane from 0.04 Torr of ethane should provide a rough estimate for the low-pressure second-order rate constant. The value found for 862 K is $2.83 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is in reasonable agreement with the value of $3.48 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ calculated from RRKM theory [p. 78 of ref. (9)]. This latter value varies markedly with the value taken for E_0 , the difference between the above two values corresponding to a change of 1 kJ mol⁻¹ in E_0 .

The estimated biomolecular rate constant, together with the limiting high-pressure rate constant for the same temperature obtained by extrapolation,⁸ may be used to derive a doubly reduced fall-off curve for the dissociation of ethane using the procedure described by Troe.^{11, 12} Additional items of information necessary for the

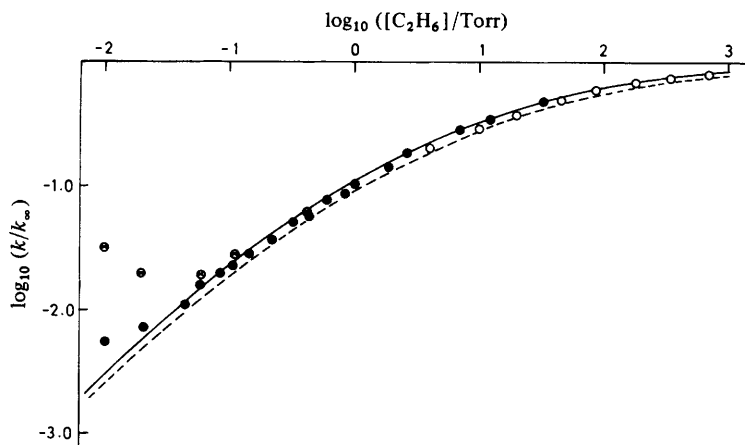


Fig. 1. Experimental and calculated fall-off curves for the dissociation of ethane at 862 K: ●, this work; ⊗, data obtained using packed reaction vessel; ○, data obtained previously.⁵ Broken curve obtained from the equation of Troe;^{11, 12} full curve obtained from RRKM theory (see text for details).

calculation are the vibrational assignments for the reactant molecule and the activated complex, the higher-pressure activation energy and the collision efficiency. The vibrational assignments and activation energy reported previously⁶ have been used, whilst the collision efficiency is given by the expression¹²

$$\beta_c/(1-\beta_c^4) \approx -\langle \Delta E \rangle / F_E kT$$

where

$$F_E \approx \sum_{v=0}^{s-1} \frac{(s-1)!}{(s-1-v)!} \left(\frac{kT}{E_0 + a(E_0) E_z} \right)^v.$$

From the data tabulated in ref. (13) a value of 10 kJ mol⁻¹ was taken for $-\langle \Delta E \rangle$ at 862 K, bearing in mind that this quantity decreases with increasing temperature. This yields a value of 0.4 for β_c , which is close to the estimated collisional deactivating efficiency given above.

Following the procedures described in ref. (11) and (12), the parameter $B' = [E_0 + a(E_0) E_z]/kT$ for ethane was found to be 74 at 862 K, and S_K , given by $(1 + kT^2 d \ln Q^\ddagger/dT)$, has a value of 6.5. With $S = 18$, the tabulated data in ref. (11) yield $B_K = 22$. The two quantities S_K and B_K permit the evaluation of the centre value of the strong-collision broadening factor $F_{\text{cent}}^{\text{sc}} = 0.34$. The weak-collision broadening factor at the centre, $F_{\text{cent}}^{\text{wc}}$, is given by $\log F_{\text{cent}}^{\text{wc}} \approx 0.14 \log \beta_c$, which, with the value derived for β_c , yields $F_{\text{cent}}^{\text{wc}} = 0.88$. Hence $F_{\text{cent}} = F_{\text{cent}}^{\text{sc}} \times F_{\text{cent}}^{\text{wc}} = 0.30$.

Fall-off data are given by the equation

$$\log k/k_\infty = \log \left(\frac{k_{\text{bim}} p/k_\infty}{1 + (k_{\text{bim}} p/k_\infty)} \right) + \frac{\log F_{\text{cent}}}{1 + \left(\frac{\log (k_{\text{bim}} p/k_\infty)}{0.75 - 1.27 \log F_{\text{cent}}} \right)^2}.$$

Using the experimental values for k_{bim} and k_∞ the above equation yields the fall-off curve shown in fig. 1. Agreement between this curve and the experimental data is very satisfactory in view of the estimates involved and reflects the predictive capacity of the

theoretical expressions. Almost exact agreement is obtained with the RRKM curve shown taking the slightly lower but still reasonable values of 5 and 18 for S_K and B_K , respectively.

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