Direct Observation of Equilibration in the System $H + C_2H_4 \rightleftharpoons C_2H_5$: Standard Enthalpy of Formation of the Ethyl Radical

Mark A. Hanning-Lee,^{‡,§} Nicholas J. B. Green,^{‡,∥} Michael J. Pilling,^{*,†} and Struan H. Robertson^{‡,⊥}

School of Chemistry, Leeds University, Leeds LS2 9JT, U.K., and Physical Chemistry Laboratory, South Parks Road, Oxford 0X1 3QZ, U.K.

Received: June 11, 1992; In Final Form: September 8, 1992

The approach to equilibrium in the reaction $H + C_2H_4 \rightleftharpoons C_2H_5$ has been studied at 800 K in He. Exciplex laser flash photolysis at 193.3 nm of ethene-helium mixtures was used to generate H atoms, which were detected by time-resolved resonance fluorescence. Rate coefficients k_a and k_d for the forward and reverse reactions were deduced from measurements of the equilibrium constant and relaxation rate coefficient at nine pressures in the range $97 \le P/\text{Torr} \le 600$. Values of the equilibrium constant, K_p , were combined with the entropy of reaction (calculated from literature data), $\Delta H^{\circ}_{1,298}(H)$, and $\Delta H^{\circ}_{1,298}(C_2H_4)$ to give a value of $\Delta H^{\circ}_{1,298}(C_2H_5) = 120.2$ \pm 0.9 kJ mol⁻¹. The Troe factorization technique was applied to values of k_a from this work and the literature to find Troe parameters for the forward reaction over the range $285 \le T/K \le 800$. Master equation methods were developed to describe the association reaction under both reversible and irreversible conditions. Consideration of a model three-level (Lindemann) system demonstrated that association rate coefficients obtained from an analysis of an irreversible association reaction and from decomposition of the relaxation rate coefficient for a reversible reaction into forward and reverse rate coefficients are equivalent provided the steady-state approximation can be applied to the energized adduct. A similar conclusion was reached analytically from consideration of an extended distribution of energized molecules with a strong collision assumption and numerically for weak collisions using a master equation analysis. The fall-off data were analyzed using both master equation models, and the values of k_a returned agreed to better than 1%.

I. Introduction

In a recent publication we monitored the approach to equilibrium in the reaction

$$H + C_2 H_4 \stackrel{k_a}{\underset{k_4}{\rightleftharpoons}} C_2 H_5$$

following the generation of H by exciplex laser flash photolysis of C₂H_{4.}¹ The experiments were limited to a single pressure of 200 Torr in a helium diluent. Analysis of the data yielded equilibrium constants which were employed to determine the enthalpy of formation of the ethyl radical. The value obtained, $\Delta H^{\circ}_{1,298} = 118.7 \pm 1.7$ kJ mol⁻¹, supported the high value for $\Delta H^{\circ}_{1,298}(C_2H_5)$ proposed by Tsang² rather than the low value of 108 ± 5 kJ mol⁻¹ favored by Golden and Benson.³ Since then, several experimental determinations⁴⁻⁶ have provided additional support for a value in the range 118-120 kJ mol⁻¹.

In a parallel investigation, rate coefficients for the forward reaction were determined at lower temperatures (285–600 K) over a range of helium pressures.⁷ The data were analyzed using the Lindemann-Hinshelwood procedure, as modified by Troe and co-workers,⁸⁻¹¹ to obtain estimates of k_a^{∞} and k_a^{0} , the limiting high- and low-pressure rate coefficients. Excellent agreement was obtained with earlier low-temperature measurements of k_a^{∞} by Lee et al.¹² and by Sugawara et al.¹³

In the present paper we examine the equilibration at 800 K over a range of pressures. The aims are 3-fold. The experimental data provide a further means of determining the enthalpy of formation of the ethyl radical. The fall-off data for k_a also enable the Troe parameters determined at low temperatures to be refined and their range of validity to be extended. Finally, a master equation technique is developed which permits the rate coefficients for relaxation to equilibrium to be analyzed directly. The impetus for this analysis was provided by a recent paper by Quack¹⁴ in which he questioned the equivalence of rate coefficients, such as $k_{\rm a}$, determined or calculated under irreversible conditions and those returned from an analysis of an equilibrating system. The analysis presented here demonstrates that such rate coefficients are equivalent, at least to experimental precision, for the H + $C_2H_4 \rightleftharpoons C_2H_5$ system. This conclusion supports our recent analysis of an equilibrating isomerization reaction, where we demonstrated the equivalence of forward and reverse rate coefficients for reversible and irreversible reaction systems provided that the steady-state approximation could be applied to the energized molecules¹⁵ and provided that allowance was made for the back reaction from energized product molecules in the irreversible case. The steady-state approximation is fulfilled for all such isomerization reactions provided $(E/RT) \gg 1$, where E is the activation energy. In the present context, the equivalence of the rate coefficients enables the high-temperature measurements reported in this paper to be employed, together with the low-temperature irreversible rate coefficients reported previously, in an extended Troe analysis.

II. Experimental Section

The apparatus and procedures used to measure the equilibration of $H + C_2H_4 \rightleftharpoons C_2H_5$ have previously been described in detail¹ and are summarized here. The unfocused 193.3-nm output (≈ 3 Hz) of a Lumonics TE861S exciplex laser was directed through the center of a bakeable spherical stainless steel reactor. Gas in the photolysis region was replenished between laser pulses. The gas mixture comprised ethene (typically ≈ 100 ppm) and the bath gas He. Ethene photolysis at 193.3 nm yields enough H to obviate the use of other H atom sources.¹

The reaction mixture was studied in the photolysis region on a timescale much faster than that required for diffusion to the

[†] Leeds University.

 ¹ Physical Chemistry Laboratory.
 ⁴ Present address: Jet Propulsion Lab, Mail Stop 67-201, 4800 Oak Grove Drive, Pasadena, California 91109.

Present address: Department of Chemistry, King's College, Strand, London WC2R 2LS, U.K.

[⊥] Present address: Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6.



Figure 1. Typical hydrogen atom fluorescence decay trace: $[C_2H_4] = 3.1 \times 10^{14}$ molecule cm⁻³, total pressure (helium) = 158 Torr, laser energy = 67 mJ.

walls. H atom resonance radiation at 121.6 nm, from a microwave discharge in H_2 -He, was directed into the cell. A solar-blind photomultiplier tube viewed the fluorescence through a MgF_2 window and a 3-cm flowing dry N_2 filter in a direction at right-angles to the exciting light. The signal was amplified and digitized; up to 1000 shots were summed before analysis. Figure 1 shows a typical averaged decay trace.

Gases were supplied with the following purities (from the manufacturer's analysis): He (BOC CP grade, 99.999%, 2 ppm each Ne, N₂); H₂ (BOC CP grade, 99.9992%, 5 ppm N₂, 2 ppm H₂O, 1 ppm O₂); N₂O (BDH, 99.6%, impurities not stated); C₂H₄ (BDH, 99.9%, 700 ppm CH₄ and C₂H₆). N₂O and C₂H₄ were distilled at least three times from and to liquid N₂, discarding the most volatile fractions (CH₄, C₂H₆, and entrained air) and least volatile (entrained H₂O) each time. H₂ and He were passed through Oxisorb filters (Messer-Griesheim) to reduce O₂ and H₂O to 0.2 ppm.

III. Experimental Results

A simple kinetic scheme was chosen to model the time dependence of [H]:

$$C_{2}H_{4} \xrightarrow{h\nu} H + C_{2}H_{3} \quad (t = 0)$$

$$H + C_{2}H_{4} \rightarrow C_{2}H_{5} \quad k_{a}$$

$$C_{2}H_{5} \rightarrow H + C_{2}H_{4} \quad k_{d}$$

$$H \rightarrow \quad k_{2} \text{ (escape)}$$

$$C_{2}H_{5} \rightarrow \quad k_{3} \text{ (escape)}$$

At 800 K, dissociation of C_2H_3 to yield H proceeds more slowly than all other reactions involving H;¹⁶ in addition, the radical and atom concentrations are small (see below), so C_2H_3 is assumed to be inert. Solving the differential equations describing this simple scheme, and setting fluorescence intensity, *I*, proportional to [H]:

$$I_t = I_+ \exp(\lambda_+ t) + I_- \exp(\lambda_- t)$$
(1)

$$2\lambda_{\pm} = -k'_{\text{loss}} \pm [(k'_{\text{loss}})^2 + 4(k'_ak_d - k'_Hk'_{\text{El}})]^{1/2}$$
$$= -k'_{\text{loss}} \pm [(k'_H - k'_{\text{El}})^2 + 4k'_ak_d]^{1/2}$$

$$k'_{loss} = k'_{H} + k'_{Et}$$
$$k'_{H} = k'_{a} + k_{2}$$
$$k'_{a} = k_{a}[C_{2}H_{4}]$$
$$k'_{Et} = k_{d} + k_{3}$$

and

$$I_{\pm} = \frac{\mp I_0(k'_{\rm H} + \lambda_{\pm})}{\lambda_{\pm} - \lambda_{\pm}}$$

where I_0 is the value of I at zero time. Each H fluorescence decay was fitted to eq 1, using the Marquardt algorithm for nonlinear least squares fitting.¹⁷ I_0 , k'_a , and k_d were floated. The procedure was checked by demonstrating that input parameters could be recovered from fits to simulated data.

 k_2 was determined from separate experiments on N₂O-H₂-He mixtures; the decays were sensibly exponential over the experimental timescale so that a first-order description of diffusive loss is adequate, with a time-independent value for k_2 . Each H decay was fitted by the Marquardt algorithm to a single exponential decay of rate constant k_2 . These values of k_2 were plotted against P^{-1} (where P = pressure), giving

$$k_2(800 \text{ K,He})/\text{s}^{-1} =$$

(30 ± 17) + [(17 000 ± 1500) Torr]/P

For C_2H_5 diffusion, k_3 was estimated as $k_2/7$ on the basis of cross sections and masses for H, He, and C_2H_5 . Values of k'_a and k_d were only feebly sensitive to the value of k_3 used in the fits.

In the previous study¹ we determined that the effects of radicalradical reactions could be eliminated by measuring k_a and k_d as a function of laser energy and extrapolating to zero energy. The same approach was adopted in the present study. The effects were slight: for an increase in laser energy from 40 to 70 mJ, the measured k_a fell by 8%, and the measured k_d fell by 16%. At higher laser energies, more C₂H₃ is formed and reacts with H and C₂H₅, thus reducing the relaxation rate of the system and the apparent k_a and k_d . All the results obtained in this study used laser energies \leq 80 mJ.

Table I presents the results for k_a , k_d , and K_p . The quoted errors in k_a and k_d are 1σ and are simply taken from the extrapolation analysis without any regard for other possible systematic errors. Errors in K_p neglect any covariance of k_a and k_d ; there is no systematic dependence of K_p on pressure. Figure 2 presents a fall-off curve for k_a .

Experiments were conducted over a range of values of $[C_2H_4]$ ($\{0.47-8.0\} \times 10^{14}$ molecule cm⁻³), laser energy (26–77 mJ total energy per pulse), and pulse frequency (1–3 Hz). The results showed no systematic dependence on $[C_2H_4]$ or laser pulse frequency.

IV. Discussion

1. The Standard Enthalpy of Formation of C_2H_5 . The standard enthalpy of reaction for $H + C_2H_4 \rightleftharpoons C_2H_5$ was calculated from

$$\frac{\Delta H^{\circ}_{298}}{T} = \Delta S^{\circ}_{298} - R \ln K_{\rm p} + \int_{298}^{T} \Delta C^{\circ}_{\rm p} d \ln T' - \frac{1}{T} \int_{298}^{T} \Delta C^{\circ}_{\rm p} dT'$$

Values of K_p were taken from section III; all other quantities were calculated from partition functions. For each species, the total molecular partition function was separated into translational and, where appropriate, rotational, internal rotational, vibrational, and electronic components. To calculate $q_{\rm vib}$, it was assumed that all oscillators are harmonic. All rotations were regarded as

where

P/Torr	$[C_2H_4]/10^{14} \text{ cm}^{-3}$	<i>E</i> / ^b /mJ	k_2^{c}/s^{-1}	<i>k</i> ₃ ^c /s ⁻¹	k _a d	$k_{\rm d}/{\rm s}^{-1}$	$\ln \left(K_{\rm p} / \rm{atm}^{-1} \right)$
97	0.65-1.61	35-71	205	29	1.97 ± 0.32	220 ± 17	11.32 ± 0.18
157	1.05-4.03	38-77	138	20	2.51 ± 0.08	201 ± 12	11.64 ± 0.07
204	1.37-3.38	38-77	113	16	2.83 ± 0.21	174 ± 29	11.90 ± 0.18
258	0.82-3.45	35-72	96	14	3.12 ± 0.24	222 ± 28	11.76 ± 0.15
295	0.94-3.96	27-56	88	13	3.06 ± 0.06	281 ± 19	11.51 ± 0.07
374	1.23-4.93	38-77	75	11	3.64 ± 0.04	378 ± 1	11.38 ± 0.01
455	1.45-6.13	34-69	67	10	3.61 ± 0.14	342 ± 27	11.48 ± 0.08
524	1.78-6.93	3367	62	9	4.01 ± 0.19	348 ± 7	11.56 ± 0.05
600	2.00-8.07	26-53	58	8	4.66 ± 0.21	356 ± 16	11.69 ± 0.06

^a Each value of k_a or k_d was determined from 64 experiments. ^b E_l is the laser pulse energy. ^c k_2 and k_3 were determined separately (see text) and fixed in analysis. ^d Units: 10^{-12} cm³ molecule⁻¹ s⁻¹.

$\Delta H_{f,298}^0(C_2H_5)/kJ \text{ mol}^{-1}$	system	ref		
120.2 ± 0.9	$H + C_2H_4 \rightleftharpoons C_2H_5$	this work		
118.7 ± 1.7	$H + C_2 H_4 \rightleftharpoons C_2 H_5$	1		
119 ± 2	review	2		
108 ± 5	$HI + C_2H_5I \rightleftharpoons C_2H_6 + I_2$	3		
120 ± 3	$Br + C_2H_6 \Rightarrow HBr + C_2H_5$	4		
118.4	$Cl + C_2D_6 = DCl + C_2D_5$	5		
120 ± 2.5	$Br + C_2H_6 \Rightarrow HBr + C_2H_5$	6		
117 ± 4	$R + C_2H_5I \rightleftharpoons RI + C_2H_5$	20		
117	$H + C_2H_6 \Longrightarrow H_2 + C_2H_5$	21		

TABLE II: Literature Values for $\Delta H_{f,298}^0(C_2H_5)$

classical at and above 298 K. The largest rotational constant is $(a_1 + a_2)$, which describes the (nearly free) internal rotation of C_2H_5 . Even at 298 K, $k_BT/\{hc(a_1 + a_2)\} = 14.1$, so high-temperature expressions were valid for all rotations. The spectroscopic data employed are listed in Appendix I and give $\Delta S^{\circ}_{298} = -86.73 \text{ J mol}^{-1} \text{ K}^{-1}$. The molar heat capacities at constant volume, C°_{ν} , were evaluated for each species from the partition functions. In a procedure based on that of Brouard et al., $^{1}\Delta C^{\circ}_{p}$ was evaluated at 300, 310, ..., 800 K and fitted to $\Delta C^{\circ}_{p} = b_1 + b_2 T$, where $b_1 = -17.35 \text{ J mol}^{-1} \text{ K}^{-1}$ and $b_2 = 9.898 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}$, thus reproducing calculated ΔC°_{p} to within 3% in this temperature range.

From the data of Table I ln $(K_p(800 \text{ K})/\text{atm}^{-1}) = 11.58 \pm 0.06$ (1 σ) giving $\Delta H^{\circ}_{298} = -150.16 \text{ kJ mol}^{-1}$. Now

$$\Delta H^{\circ}_{f,298}(C_{2}H_{5}) = \Delta H^{\circ}_{298} + \Delta H^{\circ}_{f,298}(H) + \Delta H^{\circ}_{f,298}(C_{2}H_{4})$$

Since $\Delta H^{\circ}_{f,298}(H) = 217.86 \text{ kJ mol}^{-1} \, {}^{18} \text{ and } \Delta H^{\circ}_{f,298}(C_2H_4) = 52.47 \text{ kJ mol}^{-1}, {}^{19} \Delta H^{\circ}_{f,298}(C_2H_5) = 120.2 \text{ kJ mol}^{-1}$. As in ref 1, errors from 1n K_p and the measurement of T were identified and propagated, together with that in ΔS°_{298} arising from the uncertainty in the lowest frequency, ν , of C_2H_5 . Including these errors gives $\Delta H^{\circ}_{f,298}(C_2H_5) = 120.2 \pm 0.9 \text{ kJ mol}^{-1}$, where the error refers to 2σ . The errors in $\Delta H^{\circ}_{f,298}$ for H and C_2H_4 were assumed to be negligible.

Table II compares the present measurement of $\Delta H^{\circ}_{f,298}$ with literature values. There is excellent agreement between all of the recent measurements based both on halogen and on purely hydrocarbon chemistry. The "higher" value is clearly established and a weighted mean of all the experimental values shown in Table II (i.e., with the exception of the review values of Tsang² and of Golden and Benson³) gives $\Delta H^{\circ}_{f,298}(C_2H_5) = 119 \pm 3 \text{ kJ}$ mol⁻¹ (2 σ).

2. Parameterization of k_a . In the model of Troe and co-workers⁸⁻¹¹ the Lindemann-Hinshelwood model for pressuredependent reactions is extended by including two factors. The first, F^{SC} , allows for the dependence of the microcanonical dissociation rate constant on internal energy. The second, F^{WC} , allows for the weakness of collisions. The important parameters in these models are k^0 , the low-pressure limiting rate coefficient, k^{∞} , the high-pressure limiting rate coefficient, and F_{cent} , the value of the broadening factor $F(=F^{SC}F^{WC})$ at the center of the fall-off curve.

The experimental data for $k_a(800 \text{ K})$ were fitted in three different ways. Fits starting from values for each parameter

TABLE III: Troe Parameters for $H + C_2H_4 \rightleftharpoons C_2H_5$ at 800 K^a

	fit 1	fit 2	fit 3	ref 7
$k_{\rm a}^0/10^{-30}$ cm ⁶ molecule ⁻² s ⁻¹ $k_{\rm a}^\infty/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹	6.60 13.2	6.53 13.3	7.61	6.83 11.3
$\log F_{\rm cent}$	-0.424	-0.422	0.409	-0.422 (He)



Figure 2. Experimental association rate coefficients at 800 K as a function of pressure, O; the error bars represent $\pm 1\sigma$. The curves are the results of the fits obtained using the Troe method:⁸⁻¹¹ solid line, fits 1 and 2; --, fit 3; ---, fall-off curve calculated using the parameters of Lightfoot and Pilling⁷ for M = He. The points (•) are the results of the irreversible master equation model using the high-pressure limiting rate coefficient of Lightfoot and Pilling⁷ and the optimal $(\Delta E)_{down}$ values shown in Table V.

TABLE IV: $k_a(H+C_2H_4,800 \text{ K})/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Experimental Values and Troe Fits^a

P/Torr	k _a ^{expt}	$k_{\rm a}^{(1,2)}$	k _a ⁽³⁾
97	1.97	1.96	2.00
157	2.51	2.45	2.47
204	2.83	2.75	2.76
258	3.12	3.05	3.05
295	3.06	3.23	3.23
374	3.64	3.57	3.57
455	3.61	3.89	3.88
524	4.01	4.13	4.11
60 0	4.66	4.37	4.34

" The fits are described in the text. Fits 1 and 2 gave the same values.

differing by a factor of 10 converged to the same results. In one approach, k_a^{0} , k_a^{∞} , and log F_{cent} were varied in a three-parameter fit (fit 1). In another approach (fit 2), log F_{cent} was calculated using literature data²² and k_a^{0} and k_a^{∞} were floated. In the third approach (fit 3), k_a^{∞} was extrapolated from lower temperatures, and k_a^{0} and log F_{cent} were fitted to data. The results of all fits are shown in Table III and Figure 2.

The parameters extrapolated from lower temperatures from ref 7 are also given in Table III, and the fall-off curve calculated with these parameters is shown in Table IV and Figure 2. The agreement between the different fitted parameters is excellent, and the experimental data do not distinguish between them. The present results demonstrate that the parameters proposed by Lightfoot and Pilling⁷ can be used with confidence at least at temperatures up to 800 K. Lightfoot and Pilling gave expressions for F_{cent} with M = He, N₂, and C₂H₆ and k_a^0 values for these

three gases. Note that, for a given diluent, the limiting parameters, k_a^{-} and k_a^{0} , are insensitive, within the quoted error limits, to the value of $\langle \Delta E \rangle_{down}$ employed in the fits to the experimental data, as is the overall representation of $k_a(T,P)$ via the three Troe parameters. This observation is important given the results of the master equation calculations presented below.

V. Master Equation Analysis of Reversible and Irreversible Association Reactions

1. Introduction. The Troe model provides an ideal vehicle for parameterizing experimental data to obtain a compact representation for modeling purposes. One of its many advantages is the comparative insensitivity of the fitted values of k^0 and k^{∞} to $\langle \Delta E \rangle_{down}$, so that no a priori knowledge of energy transfer is needed for satisfactory analysis, even with a limited data set. The converse of this insensitivity, however, is that a Troe analysis is not an ideal means of determining energy-transfer parameters, unless a priori assumptions are made, e.g., of the strong collision zero pressure rate coefficient, or in the case of the determination of relative efficiencies for a range of diluent gases.

We recently reported an alternative approach using a master equation analysis, coupled with the determination of the microcanonical rate constants for dissociation of the adduct by inverse Laplace transformation of the high-pressure limiting rate coefficient for association.²³ The method was used for $CH_3 + NO_3$, an iterative approach being adopted using three variable parameters, $(\Delta E)_{down}$ and the Arrhenius parameters, A and E, for k_a^{∞} . The analysis returned unusually large values for $\langle \Delta E \rangle_{down}$, and it was proposed that association might also occur via the excited, bound triplet surface correlating with ground-state fragments. The advantages of the approach are firstly that it requires no a priori assumptions since the microanonical rate constants, k(E), are linked to experimental parameters and secondly that these rate constants provide a self-consistent internal clock against which $\langle \Delta E \rangle_{down}$ is determined. The disadvantage is that a valid expression for $k_a^{\infty}(T)$ is needed over a very wide (strictly infinite) range of temperatures if an accurate representation of k(E) is to be obtained. The problems are likely to be most severe near threshold; model calculations on $CH_3 + CH_3$, however, have demonstrated a remarkably satisfactory performance for the approach.²⁴ One aim of the present section is to use this method to reanalyze the lower temperature data of Lightfoot and Pilling⁷ and the data presented in section III to determine $\langle \Delta E \rangle_{\text{down}}$ and to examine its temperature dependence.

The fall-off data shown in Figures 2 and 3 were obtained by the analysis of the approach to equilibrium of $(H + C_2H_4)$ and C_2H_5 , coupled with first-order diffusive loss of H and C_2H_5 . As far as the reacting system is concerned, the latter processes represent a trivial modification and the system can be viewed, for the present purposes, as an unperturbed equilibration. The classical analysis of such a system:

$$\mathbf{A} \underset{k_{\mathbf{a}^{(e)}}}{\overset{k_{\mathbf{d}^{(e)}}}{\Longrightarrow}} \mathbf{B} + \mathbf{C}$$

is based on the pseudo-first-order relaxation rate coefficient, k_{rel} , which is related to $k_d^{(e)}$ and $k_a^{(e)}$ via the equilibrium constant:

$$k_{\rm d}^{\rm (e)} = k_{\rm rel} / (1 + [\rm C] / K_{\rm c})$$
 (2a)

$$k_{a}^{(e)} = k_{rel} / ([C] + K_c)$$
 (2b)

where it has been assumed that $[C] \gg [B]$, so that both forward and reverse reactions show pseudo-first-order kinetics.²⁵ Although the analysis presented in section III makes no explicit recognition of k_{rel} and K_c , it is effectively based on the same procedure, i.e., it is the rate coefficients $k_d^{(c)}$ and $k_a^{(c)}$ that are extracted from the experimental data. Quack¹⁴ has questioned the analysis of



Figure 3. Comparison of experimental association rate coefficients, k_a , with the results of the irreversible master equation model (as in Figure 2). The error bars show the $\pm 1\sigma$ limits for the experimental k_a . The model results for k_a are as follows: 0, 285 K; \oplus , 400 K; \blacksquare , 511 K; \square , 604 K.

reversible unimolecular reactions, in particular the relationship between rate coefficients derived using eqs 2a and b and those derived under irreversible conditions. He suggested that " $k_d^{(c)}$ and $k_{a}^{(e)}$ have no direct relationship to the true rate of reaction events and are best conceived to be a replacement of the measurable pair of quantities $(k_{rel} \text{ and } K)$ by a new pair of quantities $(k_d^{(e)} \text{ and } k_a^{(e)})^{n_14}$ where his notation has been altered to that used in the present paper. In a previous paper we have discussed at length the problems of extracting forward and reverse rate coefficients from analysis of a relaxation experiment for an isomerization reaction.¹⁵ It can easily be shown that the fall-off of the forward rate coefficient (for example) extracted in the usual way contains a contribution both from depletion of the reactant states above threshold and also from an overpopulation of the product states, which can then react back to reform reactant before collisional stabilization. It is evident that the usual type of irreversible calculation, which takes no account of the back reaction, cannot be expected to give the correct fall-off (except when the densities of states are such that the back reaction is negligible). Quack has also demonstrated clearly that the "true" rate coefficients describing the fluxes between reactants and products are time-dependent, relaxing exponentially toward their equilibrium (high-pressure limiting) values with the relaxation rate coefficient. This is the origin of this suggestion that $k_a^{(e)}$ and $k_{d}^{(e)}$, as usually obtained from an experiment, have no physical meaning. In our previous paper we showed that, although all these observations are true, forward and reverse schemes for an isomerization reaction can be constructed by judicious placement of "cemetery states" from which no reexcitation above threshold is likely until the whole Boltzmann distribution below threshold has been sampled at length. Such irreversible schemes are described by forward and reverse rate coefficients which are identical to those found from a relaxation analysis. Furthermore the entire relaxing population distribution can be decomposed into a sum of the distributions arising from the irreversible schemes

The behavior of reversible dissociation-association reactions is somewhat different. There is no back reaction following dissociation, because there are no states corresponding to the energized product states in an isomerization reaction. There is, however, a back reaction following association, which is routinely included in master equation models of association reactions. An equilibrating association-dissociation reaction thus differs from an equilibrating isomerization reaction, but retains some of its features. In particular, the distributions of energized adduct molecules, e.g., $C_2H_3^*$, differ qualitatively under reversible and irreversible conditions. Under the latter, a steady-state distribution is rapidly established in which the normalized population density is perturbed compared with the Boltzmann density. The distribution depends on pressure, tending to the Boltzmann distribution in the limit of infinite pressure. Under reversible conditions, by contrast, the energized population density distribution is perturbed at short times, but tends to the Boltzmann distribution as the system relaxes to equilibrium, i.e., the form of the distribution is now time-dependent. The canonical rate constants for the system depend intimately on these distributions and the equivalence of these rate constants under reversible and irreversible conditions is by no means self-evident.

We need, therefore, to investigate what physical interpretation can be given to $k_a^{(c)}$ and $k_d^{(c)}$, the "experimental" association and dissociation rate coefficients. Following the approach adopted for isomerization, we do this in three ways: firstly we consider a simple Lindemann type scheme for the association reaction assuming it to be pseudo-first-order; next we extend this analysis in the usual way for an extended distribution of energized molecules, assuming strong collisions; finally we discuss how the full master equation can be modified to produce irreversible schemes for dissociation and association which correspond to the experimental rate coefficients. The aim of these analyses is to demonstrate the relationship between reversible and irreversible association-dissociation reactions, drawing on the experience gained from our examination of isomerization reactions. The experimental data for $H + C_2H_4 \rightleftharpoons C_2H_5$ provide an ideal vehicle for applying these ideas to a real system.

2. Lindemann Model—The Three Level System. In the simplest analysis, the association–dissociation equilibrium can be described by a reversible Lindemann scheme.

$$\mathbf{A} \stackrel{\alpha[\mathbf{M}]}{\underset{\beta[\mathbf{M}]}{\rightleftharpoons}} \mathbf{A}^* \stackrel{k}{\underset{k_a}{\rightleftharpoons}} \mathbf{B} + \mathbf{C}$$

We assume, as will usually be the case, that one of the fragments, C, is in large excess so that the association step occurs with a pseudo-first-order rate constant $f = k_a^{\infty}[C]$. In the experiments reported in this paper C_2H_4 is in large excess over both H and C_2H_5 . A full analysis of the time-dependence of this system shows that it is governed by three eigenvalues of which one is zero. The two nonzero eigenvalues are the negatives of the two rate constants, k_{fast} and k_{rei} , describing the biexponential approach to equilibrium:

$$k_{\text{fast}} = (\eta/2) + (1/2)\sqrt{\eta^2 - 4(\alpha f[M] + \beta f[M] + \alpha k[M])}$$
$$k_{\text{rel}} = (\eta/2) - (1/2)\sqrt{\eta^2 - 4(\alpha f[M] + \beta f[M] + \alpha k[M])}$$
$$\text{where } \eta = \alpha[M] + \beta[M] + k + f$$

and the equilibrium constant is

$$K_{\rm c} = \frac{\alpha k}{\beta k_{\rm a}^{\infty}} = \frac{\alpha k}{\beta f} [\rm C]$$

For a typical system, $k_{\text{fast}} \gg k_{\text{rel}}$, with k_{fast} comparable with the collision frequency, so that the timescales of the two exponential processes are well separated. k_{fast} describes the initial "transient" term while k_{rel} describes the rate of relaxation to equilibrium. In experiments on all but the shortest of timescales, it is the slower process that is investigated. Furthermore, very little net reaction occurs on the faster timescale, provided $k_{\text{fast}} \gg k_{\text{rel}}$.

In an alternative and more familiar terminology, k_{fast} determines the rate at which the quasi-steady-state in A^{*} is established. k_{rel} then describes the relaxation of the system to equilibrium with A^{*} in this quasi-steady-state. Thus, provided we limit our attention to this latter regime, we can apply the simplifications inherent in the application of the quasi-steady-state approximation, which applies in the limit $\alpha[M], f \ll k, \beta[M]$. The relaxation rate expression then reduces to that obtained from the quasisteady-state approximation

$$k_{\rm rel} = \frac{k\alpha[M] + \beta f[M]}{k + \beta[M]}$$

Applying the usual relaxation method to these values we find the "experimental" rate coefficients

$$k_{d}^{(e)} = \frac{k'_{c}k_{rel}}{1+K'_{c}} = \frac{k\alpha[M]}{k+\beta[M]}$$
$$k_{a}^{(e)} = \frac{k_{rel}}{[C](1+K'_{c})} = \frac{k_{a}^{*}\beta[M]}{k+\beta[M]}$$

where $K'_c = K_c/[C]$. Now we consider the reactive fluxes which correspond to the actual flux of species crossing the dividing surface between reactants and products in the associative or dissociative direction. The associative flux is f[B] so that the "true" pseudofirst-order association rate constant corresponding to this flux is f, which corresponds to the high-pressure limiting rate coefficient, k_a^{∞} ($f = k_a^{\infty}[C]$). Thus the true associative flux is equal to $k_a^{(e)}[B][C]$ only in the high-pressure limit, where $\beta[M] \gg k$. The dissociative flux is

$$k[A]^* = k(\alpha[A][M] + f[B])/(k + \beta[M])$$

and is identified with the true dissociation rate coefficient

$$k(\alpha[M] + f[B]/[A])/(k + \beta[M])$$

which is clearly time-dependent since the ratio [B]/[A] relaxes toward equilibrium. This finding mirrors that reported previously for isomerization reactions,¹⁵ and we conclude that the true reactive fluxes cannot be described by the experimental rate coefficients, nor indeed by *any* time-independent rate coefficients.

The interpretation of the rate coefficients, $k_a^{(e)}$ and $k_d^{(e)}$, is guided by our analysis of the isomerization system. $k_d^{(e)} = k\alpha[M]/(k + \beta[M])$ is easily recognized to be the Lindemann rate coefficient for the irreversible scheme

$$\mathbf{A} \stackrel{\alpha[\mathbf{M}]}{\rightleftharpoons} \mathbf{A}^* \stackrel{k}{\to} \mathbf{B}$$

and $k_a^{(e)} = \beta f[M]/(k + \beta[M])$ is the equivalent for the scheme

$$\mathbf{B} \underset{k}{\overset{f}{\rightleftharpoons}} \mathbf{A}^{*} \overset{\beta[\mathsf{M}]}{\twoheadrightarrow} \mathbf{A}$$

Thus $k_{a}^{(c)}$ and $k_{d}^{(c)}$ may be interpreted in terms of the coupling of these two irreversible schemes.



The upper (dissociation) scheme, and therefore $k_d^{(c)}$, describes the dissociative flux from A^{*} to B, but is limited to only those A^{*} which derive from activation of A and excludes those A^{*} which are formed by association. Thus it effectively describes

the reactive flux $A \rightarrow B$, rather than $A^* \rightarrow B$. Similarly the lower scheme $(k_a^{(c)})$ describes the flux from $A^* \rightarrow A$ but limits the A^* to those formed by association, so that it effectively describes the steady-state flux from $B \rightarrow A$ rather than from $A^* \rightarrow A$. We therefore conclude that the experimental rate coefficients *do* have a physical meaning, describing the overall fluxes from reactants to products. Because there is no backward flux across the dividing surface for the dissociation reaction, $k_d^{(e)}$ corresponds to the rate coefficient for the normal irreversible Lindemann scheme. By contrast, the fall-off in $k_a^{(e)}$ arises exclusively from the redissociation, $A^* \rightarrow B$, which must therefore be taken into account in the irreversible association scheme.

3. Strong Collision Model. This very simple analysis can be generalized to a detailed energy level distribution in the strong collision approximation. $\beta[M]$ is now replaced by ω , the collision frequency, and $\alpha[M]$ by $\{\omega\rho(E)e^{-E/k_BT}\}/q$ where $\rho(E)$ is the density of states of A at energy E and q is the partition function for the corresponding internal modes of A. The microcanonical pseudo-first-order association rates are obtained from detailed balance

$$f(E)[\mathbf{B}]_{eq} = k(E) \{\rho(E)e^{-E/k_{\rm B}T}/q\}[\mathbf{A}]_{eq}$$

We now find

$$k_{\rm rel} = \int_{E_0}^{\infty} \frac{k(E)\omega\rho(E)e^{-E/k_{\rm B}T}/q + \omega f(E)}{k(E) + \omega} dE$$
$$= \left(1 + \frac{1}{K'_c}\right) \frac{\omega}{q} \int_{E_0}^{\infty} \frac{k(E)\rho(E)e^{-E/k_{\rm B}T}}{k(E) + \omega} dE$$

from which

$$k_{d}^{(e)} = \frac{\omega}{q} \int_{E_0}^{\infty} \frac{k(E)\rho(E)e^{-E/k_{\rm B}T}}{k(E) + \omega} dE$$
$$k_{a}^{(e)} = k_{d}^{(e)}/K_{\rm c}$$

As before the dissociative flux is controlled by the time-dependent rate coefficient

$$\int_{E_0}^{\infty} k(E) \frac{\omega \rho(E) e^{-E/k_{\rm B}T}/q + f(E)[{\rm B}]/[{\rm A}]}{k(E) + \omega} \, \mathrm{d}E$$

and the associative flux by

$$\int_{E_0}^{\infty} f(E_0) \, \mathrm{d}E_0$$

neither of which corresponds to $k_a^{(e)}$ or $k_d^{(e)}$.

Similarly, $k_d^{(e)}$ is the strong collision rate coefficient for the irreversible dissociative scheme $A \rightleftharpoons A^* \rightarrow B + C$, and $k_a^{(e)}$ is a similar rate coefficient for the scheme $B + C \rightleftharpoons A^* \rightarrow A$. The interpretation is exactly the same as for the three-level scheme: $k_d^{(e)}$ describes the steady-state flux from A to B + C with competition from collisional stabilization of A^* , and $k_a^{(e)}$ describes the steady-state flux from B + C to A with competition from the back redissociation reaction.

4. Master Equation Analysis. The above sections have demonstrated that the association and dissociation rate coefficients for a reversible, equilibrating system are equal to those for the corresponding irreversible reactions, for a three-level Lindemann scheme and for a multilevel strong collision system, provided the steady-state approximation is valid for the energized molecules. In this section we seek to extend the analysis to a more realistic multilevel system with weak collisions. A master equation is generally employed to describe the relaxation of the energy distribution in such a system and in this section we develop a master equation for both irreversible and reversible associationdissociation reactions. Irreversibility in the association reaction is introduced by switching off the rates of excitation from states at and below a certain level in A which we call the cemetery state.

In the master equation model, the energy of the adduct A is divided into a contiguous set of grains. Each grain has the same width, δ , and contains a bundle of states to which is ascribed a common, averaged energy, E_{i} , and a microcanonical rate coefficient for dissociation, k_i . The master equation describes the evolution of the grain populations, n_i . For the case of irreversible association of $\mathbf{B} + \mathbf{C}$, the master equation takes the form

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \phi_i + \omega \sum_j P_{ij} n_j - (\omega + k_i) n_i$$

where ϕ_i represents the input rate from B + C, ω the collision frequency, and P_{ij} the probability of energy transfer from grain *j* to grain *i* on collision. The master equation for the reversible case is discussed below. The grains have an upper cutoff at E_{max} = $m\delta$. An exponential-down model was employed for P_{ij} :

$$P_{ij} = A_j \exp[-\alpha(E_j - E_i)]; \quad j \ge i$$

where α is a parameter governing the efficiency of energy transfer; at high energies, $\alpha^{-1} = \langle \Delta E \rangle_{\text{down}}$, the average energy transferred in a single collision in a downward direction. The upward transition probabilities are determined by detailed balance:

$$P_{ij} = A_i(N_iN_j) \exp[-(\alpha + \beta)(E_i - E_j)]; \quad j < i$$

where $\beta = 1/k_{\rm B}T$ and N_i and N_j are the numbers of states in grains *i* and *j*, respectively. A_i and A_j are normalization constants obtained from the normalization conditions

$$\sum_{i} P_{ij} = 1$$

The input rate is determined by detailed balance:²⁶

$$\phi_i = \frac{k_a^{\infty} k_i N_i \exp(-E_i/k_B T)[B][C]}{\sum_i k_i N_i \exp(-E_i/k_B T)}$$

Finally, the master equation is cast in matrix form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n} = \mathbf{\Phi} - \mathbf{Q}\mathbf{n} \tag{3}$$

where $\mathbf{Q} = \mathbf{K} + \omega(\mathbf{I} - \mathbf{P})$, **n** is a vector of grain populations, $\mathbf{\Phi}$ is a vector of input rates, **P** is a matrix of transition probabilities, **I** is the identity matrix, and **K** is a diagonal matrix containing the microcanonical rate constants, $K_{ij} = k_i \delta_{ij}$.

4.1 Irreversible System. As discussed above, irreversibility was simulated by designating one of the energy grains, c, lying below the dissociation threshold, as a cemetery state.²⁷ c represents a grain located sufficiently far below the threshold that reactivation from that grain before complete deactivation into the Boltzmann reservoir may be considered negligible. In effect, c acts as an absorbing barrier and the collisional energy transfer matrix, **P**, is formulated such that transfer into c from higher grains is allowed, while the reverse transfer from c into those grains is not. The general procedure for constructing **P** is discussed elsewhere.²⁷

Under experimental conditions, a steady-state population distribution is established (see Appendix II) and, for constant [B][C], dn/dt = 0, from which

$$\mathbf{n} = \mathbf{Q}^{-1} \mathbf{\Phi} \tag{4}$$

The net rate of formation of A can be calculated from the flux

into the cemetery state:

$$k_{a} = \omega \sum_{i>c} P_{ci} n_{i} / ([B][C])$$
(5)

or from the difference between the net input rate and the net rate of dissociation:

$$k_{a} = \{\sum_{i>c} \phi_{i} - \sum_{i>c} k_{i} n_{i}\} / ([B][C])$$
(6)

4.2 Reversible System. In order to simulate a reversible system, it was first recognized that the $H + C_2H_4 \implies C_2H_5$ reaction was studied under pseudo-first-order conditions for the forward reaction ($[C_2H_4] \gg [H]_0$, $[C] \gg [B]$). The master equation was then extended to allow [B] to vary with time by adding an additional element to the population vector, **n**, so that the element i = m + 1 corresponds to [B] (\equiv [H]). This technique can be applied to a pseudo-first-order system involving a radical rather than an atom, provided the radical is maintained in a Boltzmann distribution by the bath gas. The master equation is then expressed in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n} = \omega \mathbf{M}\mathbf{n} \tag{7}$$

where M is a net transfer matrix describing energy transfer in A, dissociation of A to form B (and C), and formation of A from the element i = m + 1. The master equation can now describe the time evolution of both A and B.

The form of the matrix M is

$$\mathbf{M} = \begin{bmatrix} C_{11} & C_{12} & \dots & C_{1m} & \phi'_1/\omega \\ C_{21} & C_{22} & \dots & C_{2m} & \phi'_2/\omega \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ C_{m1} & C_{m2} & \dots & C_{mm} & \phi'_m/\omega \\ k_1/\omega & k_2/\omega & \dots & k_m/\omega & -k_a^{\infty}[\mathbf{C}]/\omega \end{bmatrix}$$

where

$$C_{ji} = P_{ji} - (1 + k_i/\omega)\delta_{ij}$$

and $\phi'_i = \phi_i/[B]$

The use of detailed balance to formulate Φ ensures that the system evolves toward equilibrium across all m + 1 grains; i.e., the longtime solution is equilibrium for the A, (B + C) system.

Equation 7 may be solved by diagonalizing M to give³³

$$\mathbf{n} = \sum_{k=1}^{m} c_k e^{\omega \lambda_k t} \mathbf{u}_k$$

where \mathbf{u}_k are the right eigenvectors of \mathbf{M} and λ_k the corresponding eigenvalues. The c_k are determined by the superposition of the \mathbf{u}_k to form the initial state, \mathbf{n}_0 . If the eigenvalues are ranked in order of increasing magnitude, $\lambda_1 = 0$, and \mathbf{u}_1 describes the timeindependent equilibrium (Boltzmann) distribution. It can be shown that $c_1 = 1$ by considering the $t \rightarrow \infty$ limit of \mathbf{n} . Since the system has a unique long-time limit, all other eigenvalues must be negative and describe transients of varying durations. Most eigenvalues have large magnitudes and represent very short-lived transients. λ_2 describes the longer time behavior of the grain concentrations. On long (experimental) timescales, the system relaxes exponentially with time constant $-\lambda_2$ to the equilibrium distribution \mathbf{u}_1 :

$$\mathbf{n} = \mathbf{u}_1 + c_2 e^{\omega \lambda_2 t} \mathbf{u}_2 \tag{8}$$

If n_B is the element of **n** describing [B], then

$$[\mathbf{B}]_{t} = n_{\mathbf{B}}$$
$$= (\mathbf{u}_{1})_{\mathbf{B}} + c_{2}(\mathbf{u}_{2})_{\mathbf{B}}e^{\omega\lambda_{2}t}$$
and
$$[\mathbf{B}]_{\infty} = (\mathbf{u}_{1})_{\mathbf{B}}$$
thus
$$[\mathbf{B}]_{t} - [\mathbf{B}]_{\infty} = c_{2}(\mathbf{u}_{2})_{\mathbf{B}}e^{\omega\lambda_{2}t}$$
and
$$\frac{\mathbf{d}}{\mathbf{d}t}\ln([\mathbf{B}]_{t} - [\mathbf{B}]_{\infty}) = \omega\lambda_{2}$$

Thus [B] relaxes exponentially to the equilibrium value (eq 8) with rate constant $-\omega\lambda_2$, i.e.,

$$k_{\rm rel} = -\omega \lambda_2$$

The behavior of the reversible system is qualitatively different from that of the irreversible system, where **n** maintains a constant shape (eq 4) during the exponential decay phase, i.e., when the short-time transients have decayed away. For the reversible system, **n** is time-dependent but

$$\mathbf{n} - \mathbf{u}_1 = c_2 e^{\omega \lambda_2 t} \mathbf{u}_2$$

Thus the difference from the equilibrium distribution relaxes exponentially, and if we examine specific elements,

$$\frac{n_j(t) - (\mathbf{u}_1)_j}{n_j(t) - (\mathbf{u}_1)_j} = \frac{(\mathbf{u}_2)_j}{(\mathbf{u}_2)_j}$$

we can see that it maintains a constant shape. Exactly the same differences in behavior have previously been reported for isomerization reactions.¹⁵

4.3 Relationship of Rate Coefficients for Reversible and Irreversible Reactions. The numerical analysis presented below demonstrates the equivalence, within numerical accuracy, of the comparable rate coefficients for reversible and irreversible association-dissociation reaction schemes. It is of value to comment at this point on the analysis made of isomerization reactions ($A \Rightarrow B$) for weak collision systems, in relationship to the analysis presented above in sections 1 and 2.

A master equation analysis of isomerization reactions was presented in ref 15, calculating the forward and reverse rate coefficients, $k_{f}^{(e)}$ and $k_{r}^{(e)}$, for an equilibrating system, via the equivalent of eqs 2a and b and the corresponding irreversible rate coefficients, $k_{f}^{(c)}$ and $k_{r}^{(c)}$, which were determined by the incorporation of a cemetery state. It was demonstrated that the corresponding rate coefficients agreed well provided the threshold energy for reaction, E_0 , was not too small. As E_0 became smaller, the first nonzero eigenvalue, λ_1 , became comparable in magnitude to λ_2 , so that a well-resolved exponential relaxation regime was not established. Such behavior corresponds to conditions where the steady-state approximation cannot be applied and the population of the energized states, A* and B*, is significant. This observation agrees with the conclusions reached from the analysis presented above in sections 1 and 2. Furthermore, guided by the analysis of the Lindemann type and strong collision models for isomerization reactions, it was demonstrated for the reversible system that, under conditions where the steady-state approximation holds and exponential relaxation pertains, the vector describing the population density of the two isomers, A and B, can be constructed from the population vectors of the irreversible forward and reverse reactions. In other words, exactly the same type of decomposition of the reversible reaction into forward and reverse fluxes for overall irreversible reactions can be applied to isomerization reactions.

The analysis presented above for the three-state, Lindemann, and strong collision models suggests that similar behavior applies to association-dissociation reactions and we should indeed expect

rate coefficients from eqs 2a and b to be close to the corresponding rate coefficients for the irreversible reactions. The following numerical analysis demonstrates that this is so.

4.4 Input Parameters. Appendix I summarizes the data used in applying the reversible and irreversible master equations to the H + C₂H₄ reaction. Rovibrational numbers of states were calculated using the modified Beyer–Swinehart algorithm²⁸ by dividing the energy space into a contiguous set of cells of width 1 cm⁻¹. The master equations were solved using grain widths, δ , equal to 100 cm⁻¹, and the number of states, N_i, and the mean energy, E_i, of a particular grain were calculated from the sums

$$N_{i} = \sum_{j(i)} C_{j(i)}$$
$$E_{i} = \{\sum_{j(i)} C_{j(i)} E_{j(i)}\} / N_{i}$$

where $C_{j(i)}$ is the number of states in the *j*th cell of energy $E_{j(i)}$ and the summation is carried out over all the cells in grain *i*. At high energies, E_i is well approximated by the midgrain energy, but this is not the case at low energies which must be accommodated in the master equation treatment of reversible systems. The quality of the averaging procedure was checked by comparing rigid rotor, harmonic oscillator rovibrational partition functions for C₂H₄ and C₂H₅ with the Boltzmann weighted state sums over the grains:

$$q_{\rm rv} = \sum_{i=0}^{m} N_i \exp(-\beta E_i)$$

The agreement was better than 0.8% at 285 K and was $\approx 0.3\%$ for $T \ge 400$ K.

The collisional transition probabilities, P_{ij} , were calculated using the exponential down model, with α as a variable parameter. The collision frequency was calculated for a Lennard-Jones model (Appendix I). The normalization constants, A_j , were calculated by back-substitution.

The microcanonical rate constants for dissociation, k_i , were calculated using inverse Laplace transformation of the highpressure limiting rate coefficient for association, $k_a^{\infty,29}$ This technique has been shown to give satisfactory results in model calculations. It has the advantage that k_i is linked directly to experimental parameters without the intermediate step of constructing a model. In the present context, for

$$k_a^{\circ} = A_a^{\circ} \exp(-E_a^{\circ}/k_BT)$$

$$k(E)\rho_{A}(E) = \frac{2C'A_{a}^{\infty}}{\sqrt{\pi}} \int_{0}^{E-E_{a}^{\infty}-\Delta E^{\circ}_{0}} \rho_{BC}(E_{BC}) \{E-E_{a}^{\infty}-\Delta E^{\circ}_{0}\}^{1/2} dE_{BC}$$

where $\rho_A(E)$ is the rovibrational density of states of the adduct, C₂H₅, at energy *E*, referred to the zero point energy of C₂H₅ as energy zero, $\rho_{BC}(E_{BC})$ is the rovibrational density of states of the fragments (in this case just of C₂H₄ = C), at energy E_{BC} , referred to the zero point energy of the fragments as energy zero, ΔE°_{0} is the difference in zero point energy between fragments and adduct and

$$C' = [2\pi m_{\rm B} m_{\rm C} / (h^2 m_{\rm A})]^{3/2}$$

This procedure was used to calculate the rate constants $k_{j(i)}$ for reaction from the *j*th cell of the *i*th grain. The mean grain rate constants for dissociation were calculated from

$$k_i = \{\sum_{j(i)} C_{j(i)} k_{j(i)}\} / N_i$$

Consistency was checked by calculating k_d^{∞} from

$$k_{d}^{\infty} = \frac{\sum_{i=0}^{\infty} k_{i} N_{i} \exp(-\beta E_{i})}{\sum_{i=0}^{\infty} N_{i} \exp(-\beta E_{i})}$$

and comparing it with $k_a \,{}^{\infty} K_c$, where $k_a \,{}^{\infty}$ is the input value for the association rate coefficient and K_c is the equilibrium constant. The agreement was within 1.3% at room temperature improving to <0.1% at 800 K for typical input parameters. Over this temperature range, $k_d \,{}^{\infty}$ changes by 19 orders of magnitude.

4.5 Methods of Solution. The irreversible model (eq 4) was solved by Gaussian elimination and backward substitution.²⁹ At each temperature, the sum of squares

$$\sum_{l=1}^{L} (k_{a,l}^{expt} - k_{a,l}^{theory})^2$$

over the set of L experimental rate coefficients was minimized by varying only $\alpha (= \langle \Delta E \rangle_{down}^{-1})$.

The reversible model was solved by eigenvalue analysis and by sorting the eigenvalues, λ_k , in order of increasing magnitude. The smallest eigenvalue was always zero, within numerical precision. $k_{\rm rel}$ was equated to $-\omega\lambda_2$, and $k_a^{(e)}$ and $k_d^{(e)}$ were calculated from eqs 2a and b.

Finally, a cemetery state was introduced into the reversible model to allow direct comparison with the irreversible model. The size of the matrix **M** was retained, so that there were, in effect, c cemetery states and c zero eigenvalues. k_a was equated to $-\lambda_{c+1}\omega$.

A range of tests was performed on the models. The maximum energy, $E_{max} = m\delta$, was varied at 800 K, where the population distribution will be most extended, and the convergence checked. λ_2 was independent of E_{max} for $E_{max} > 27\ 000\ \text{cm}^{-1}$ in the reversible model, and k_a changed by <0.05% for $E_{max} > 24\ 000\ \text{cm}^{-1}$ in the irreversible model. A value $E_{max} = 30\ 000\ \text{cm}^{-1}$ was adopted throughout the calculations.

The grain size was reduced in steps of 10 cm^{-1} from 100 to 40 cm⁻¹. The rate coefficient was little affected although a slight decrease in the best fit value of $\langle \Delta E \rangle_{\text{down}}$ was observed at the lowest temperatures. In consequence, the values for $\langle \Delta E \rangle_{\text{down}}$ tabulated below may be slight (10%) overestimates at low temperatures.

The height of the cemetery state, $E_{\rm cem} = c\delta$, was varied, and it was established that k_a was changed by <0.01% provided that $E_{\rm cem}$ lay $\gtrsim 15k_{\rm B}T$ below the threshold.

With the irreversible model, the pressure was increased to 10^8 Torr to simulate the high-pressure limit, which agreed with the input values of k_a^{∞} to within 0.1%; at all pressures, the two methods for calculating k_a (eqs 5 and 6) agreed to within 10^{-4} %. The agreement between the calculated high-pressure limit and the input k_a^{∞} was also satisfactory for the reversible model, agreement being within 1.3%. There was always good separation of the eigenvalues, with the larger eigenvalues being at least 10^3 times larger than λ_2 (or λ_{c+1}).

4.6 Results. The initial calculations were carried out using the parameters for $k_a^{\infty}(T)$ determined by Lightfoot and Pilling.⁷ Such an approach is internally consistent, since k_a^{∞} is insensitive to the choice of $\langle \Delta E \rangle_{down}$ in the Troe analysis.⁷ Figures 2 and 3 show the best fits to k_a for $285 \le T/K \le 800$ using the irreversible model. The reversible + cemetery state model returned essentially identical results. $\langle \Delta E \rangle_{down}$ was the only variable parameter, and Table V shows the best fit values, which increase substantially as T increases. The calculations were repeated using the

TABLE V: Fitted Values for $\langle \Delta E \rangle_{\rm down}$ for the Irreversible Master Equation Model

$\langle \Delta E \rangle_{\rm down}/{\rm cm}^{-1}$		
A, ref 7 ^a	B, ref 30 ^b	
46.7	32.8	•
56.6	52.5	
85.3	83.1	
118.2	115.7	
200.6	191.7	
	$\frac{(\Delta E)_{dc}}{A, ref 7^{a}}$ 46.7 56.6 85.3 118.2 200.6	$\begin{tabular}{ c c c c }\hline & (\Delta E)_{\rm down}/\rm cm^{-1} \\ \hline A, ref 7^a & B, ref 30^b \\ \hline 46.7 & 32.8 \\ 56.6 & 52.5 \\ 85.3 & 83.1 \\ 118.2 & 115.7 \\ 200.6 & 191.7 \\ \hline \end{tabular}$

^a A: for $k_a^{\infty} = 43.9 \times 10^{-12} \exp(-1093 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^b B: for $k_a^{\infty} = 6.97 \times 10^{-12} (T/300 \text{ K})^{1.49} \exp(-500 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

TABLE VI: Comparison of Association Rate Coefficients at 800 K Calculated Using Reversible and Irreversible Models

log (P/Torr)	$\frac{10^{12}k_{\rm a}/\rm{cm}^3}{\rm{molecule}^{-1}~\rm{s}^{-1}}$	$10^{12}k_a^{(e)}/cm^3$ molecule ⁻¹ s ⁻¹	$k_{\rm a}/k_{\rm a}^{(e)}$
-3	1.034 × 10 ⁻⁴	1.035×10^{-4}	0.999
-2	9.645 × 10 ⁻⁴	9.653 × 10 ⁻⁴	0.999
-1	8.657 × 10 ^{−3}	8.664 × 10 ⁻³	0.999
0	0.06887	0.06892	0.999
1	0.4345	0.4348	0.999
2	1.894	1.895	0.999
3	5.265	5.268	0.999
4	9.082	9.086	1.000
5	10.88	10.89	0.999
6	11.24	11.25	0.999
7	11.29	11.29	1.000
8	11.29	11.30	0.999

recommendation of Tsang and Hampson³⁰ for k_a°

$$k_{a}^{\infty} = 6.97 \times 10^{-12} (T/300 \text{ K})^{1.49} \times$$

 $\exp(-500 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

which requires a reformulation of the ILT relationship:

$$k(E)\rho_{\rm A}(E) = Q \int_0^{E-E_{\rm a}^{\,\circ}-\Delta E^{\,\circ}_{\,0}} \rho_{\rm BC}(E_{\rm BC}) X \, \mathrm{d}E_{\rm BC}$$
$$Q = \frac{C'A_{\rm a}^{\,\infty}}{(300k_{\rm B})^{n^{\circ}} \Gamma(1.5+n^{\circ})}$$
$$X = [E - E_{\rm BC} - E_{\rm a}^{\,\circ} - \Delta E^{\,\circ}_{\,0}]^{(n^{\circ}+0.5)}$$

where

$$k_a^{\infty} = A_a^{\infty} (T/300 \text{ K})^{n^{\infty}} \exp(-E_a^{\infty}/k_B T)$$
 and $n^{\infty} > -1.5$

Similarly good fits are obtained, and Table V lists the best fit values of $\langle \Delta E \rangle_{down}$.

Table VI compares the values for k_a calculated from the irreversible model and from k_{rel} via the reversible model over a wide range of pressures at 800 K. The agreement between the two sets of calculated values is excellent (agreement to 0.1% or better) and the discrepancy is primarily associated with numerical inaccuracies in the k_i (as derived from the inverse Laplace transform technique), rather than with any intrinsic difference between k_a and $k_a^{(c)}$.

4.7 Discussion. The master equation analysis of the experimental data has permitted estimates of $\langle \Delta E \rangle_{down}$ to be made. The analysis was conducted for two parameterized forms of $k_a^{\infty}(T)$ (Table V), and it is interesting to note the form of the agreement between the two sets of results. The disagreement is most marked at low temperatures and derives from two sources. Firstly, the reaction is closest to the high-pressure limit and, for a given set of parameters ($k_a^{\infty}(T)$ and the molecular parameters for reactants and product), the simulated rate coefficients are least sensitive to $\langle \Delta E \rangle_{down}$. Secondly, the distribution of energized molecules is least extended at low temperatures, so that the reaction is most sensitive to the behavior of the states close to



Figure 4. Temperature-dependence of experimental association rate coefficients at the high-pressure limit, k_a^{∞} . Data points: O, this work and Lightfoot and Pilling, ⁷ •, Lee et al.;¹² \triangle , Sugawara et al.¹³ The error bars represent $\pm 2\sigma$. The solid straight line represents the Arrhenius fit of Lightfoot and Pilling;⁷ the broken curve denotes the non-Arrhenius fit of Tsang and Hampson.³⁰

threshold. The inverse Laplace transform technique is at its most unreliable in this region and depends on the exact form of the Arrhenius expression employed: the two expressions used differ substantially in form, being of Arrhenius⁷ and non-Arrhenius form.³⁰ Although they agree well at temperatures of ≈ 400 K, the k_a value of Tsang and Hampson³⁰ exceeds that of Lightfoot and Pilling by 40–50% at 200 K and 800 K, the limits of available experimental data for H + C₂H₄. Although the model of Hase and Schlegel predicts significant positive curvature, the experimental data conform well to a simple Arrhenius treatment (Figure 4), and the expression of Lightfoot and Pilling⁷ provides a more satisfactory representation than the earlier, non-Arrhenius form of Tsang and Hampson. It is likely, therefore, that the estimates of $\langle \Delta E \rangle_{down}$ based on the Arrhenius form of $k_a^{\infty}(T)$ are the more reliable.

Despite these uncertainties, the experimental data clearly show a strong increase in $\langle \Delta E \rangle_{\text{down}}$ with temperature. The results are also in excellent agreement with the parallel analysis by Feng et al.,³¹ who used an equivalent basis for ω , based on low-pressure measurements of C_2H_5 dissociation and on the present data on $H + C_2H_4$. It should be noted that, as discussed by Feng et al.,³¹ the former measurements provide more precise estimates of $\langle \Delta E
angle_{
m down}$, because they are closer to the low-pressure limit. Walter et al.³² have noted a similar increase for $CH_3 + CH_3$, which was studied over the temperature range 200-900 K, although there was little energy transfer information available from the experiments at T < 300 K. They reported that $\langle \Delta E \rangle_{tot}$ became increasingly negative as the temperature increased. $\langle \Delta E \rangle_{tot}$ is the mean total energy transferred per collision and contains contributions from both upward and downward transitions. Since upward transitions become more favored as the temperature increases, a change in the magnitude of $\langle \Delta E \rangle_{tot}$ indicates an even larger increase in $\langle \Delta E \rangle_{\text{down}}$ with temperature.

The dependence of $\langle \Delta E \rangle_{down}$ on temperature may be directly linked to the increasing impulsiveness of the collisions with increase in temperature or to a dependence of $\langle \Delta E \rangle_{down}$ on energy. The latter is the more likely although the available experimental data, which have been discussed by Gilbert and Smith,³³ are ambiguous. Some calculations were performed using a modified master equation treatment with α expressed in the energy-dependent form $\alpha = \alpha_0/E$. Satisfactory fits were obtained, although it was necessary to vary α_0 with T. Gilbert and Smith propose the form $\alpha = A + BE$. The present experimental approach is not, however, well suited to the facile testing of models of the energy dependence of α .

It should also be noted that rotational relaxation has not been explicitly treated in the analysis. The inverse Laplace transform technique only permits calculation of microcanonical rate constants, $k_a(E)$, averaged over rotational states; the J-specific rate

constant, k(E,J), cannot be calculated. Gilbert and Smith³³ and Barker³⁴ have pointed out that neglect of differential rates of rotational and vibrational energy transfer may significantly affect the overall relaxation and hence the canonical rate constants. The shortcomings of the inverse Laplace transform technique are, however, mirrored by the inadequancies of current master equation procedures which cannot realistically accommodate these differential rates, although some progress has recently been made.³³

The good agreement between k_a calculated using the irreversible model and that derived from a decomposition of k_{rel} from the reversible model is in accord with the results of Green et al.¹⁵ for isomerization equilibria. Although the distributions of energized molecules differ substantially for reversible and irreversible models, the association rate coefficients agree within numerical precision. Similar agreement was found for isomerization provided the steady-state approximation was valid for the energized molecules;15 its validity may be linked directly to the difference in magnitude of the lowest nonzero eigenvalue and the higher eigenvalues. Provided this difference is substantial, an exponential reaction or relaxation period pertains on the experimental timescale, during which the shape of the population distribution (for irreversible reactions) or of the difference from the Boltzmann distribution (for reversible reactions) is constant. This separability is related to the activation energy for dissociation. If E_d^{∞} is comparable to k_BT ($E_d^{\infty} \leq 10k_BT$), then the difference in the eigenvalues is too small and the simple relaxation analysis becomes invalid. Such a situation clearly does not pertain under the present conditions. The observation of the equivalence of rate coefficients under reversible and irreversible conditions is also of significance for the modeling of complex chemical reactions and demonstrates that canonical rate coefficients can be used with confidence under conditions where sets of reactants are close to or well removed from equilibrium.

Despite the uncertainty in $\langle \Delta E \rangle_{down}$ at low temperatures, the present paper demonstrates, once again, the value of the ILT/ master equation approach. The technique relies directly on experimental data, and so compatibility with experiment is automatically incorporated and the need to construct a transition state model is avoided. The master equation analysis is more computationally intensive than the simpler Troe approach,⁸⁻¹¹ but it allows a greater insight into the reaction mechanism and a more direct testing of reaction parameters, particularly $\langle \Delta E \rangle_{down}$. The present results confirm the advantages discussed elsewhere in studies of CH₃ + NO²³ and *i*-C₃H₇ decomposition.³⁵

VI. Conclusions

This paper has reported experimental measurements of the approach to equilibrium following generation of H from the laser flash photolysis of C_2H_4 at 800 K over a range of pressures. The data were analyzed using the Troe technique and a master equation approach coupled with inverse Laplace transformation of the limiting high-pressure rate coefficient for association. In particular, the latter approach was used to model both reversible and irreversible conditions for the H + C_2H_4 , C_2H_5 system. The main conclusions are summarized below.

1. The heat of formation of C_2H_5 was determined from K_p for the H + $C_2H_4 \Longrightarrow C_2H_5$ reaction, coupled with calculated values for ΔS° . A value for $\Delta H^\circ_{f,298}$ (C_2H_5) of 120.2 \pm 0.9 kJ mol⁻¹ was obtained. A weighted mean of values of recent experimental determinations of this quantity gives $\Delta H^\circ_{f,298}(C_2H_5) = 119 \pm 3$ kJ mol⁻¹.

2. Analysis of the fall-off curve for k_a at 800 K confirms at least up to this temperature the parameters determined by Lightfoot and Pilling⁷ which are given in Table III for a He diluent and in ref 7 for N₂ and C₂H₆.

3. An inverse Laplace transformation/master equation analysis of the experimental data permits $\langle \Delta E \rangle_{down}$ to be determined for

TABLE VII: Molecular Data for $H + C_2H_4 \rightleftharpoons C_2H_5^*$

quantity	value
C ₂ H ₄ rotational constants	$A = 4.844, B = 0.908 \text{ cm}^{-1}$
$C_2H_4 \sigma$	4
C_2H_4 frequencies	3105, 3103, 3026, 3021, 1630, 1440, 1342, 1220, 1073, 949, 943, 826 cm ⁻¹
C ₂ H ₅ rotational constants	$A = 3.440, B = 0.7133, a_1 = 9.268,$ $a_2 = 5.471 \text{ cm}^{-1b}$
C ₂ H ₅ σ	6
C_2H_5 frequencies	3112, 3033, 2987, 2920, 2842, 1440, 1440, 1439, 1366, 1186, 1175, 1138, 802, 540 cm ⁻¹
C ₂ H ₅ Lennard-Jones parameters	$s = 0.3497 \text{ nm}, \epsilon/k_{\text{B}} = 46.95 \text{ K}^{\circ}$
$\nu_i, \tilde{C}_2 H_5^*$	3036, 3009, 2955, 2944, 1504, 1446, 1218, 1185, 944, 938, 869, 821, 399, 369 cm ⁻¹
ΔE_0^0	$145.57 \text{ kJ mol}^{-1} = 12168 \text{ cm}^{-1}$
0 K barrier for H + C ₂ H ₄ \rightarrow C ₂ H ₅	$9 \text{ kJ mol}^{-1} = 752 \text{ cm}^{-1}$

^a Reference 22 except where stated. ^b a from geometry of ref 36. ^c See appendix I.

 $C_2H_5^*$ /He collisions. (ΔE)_{down} was found to increase from ≈ 50 cm⁻¹ at 285 K to ≈ 200 cm⁻¹ at 800 K.

4. A master equation model for reversible associationdissociation reactions was also developed. It was employed to demonstrate that the use of relaxation measurements to determine forward and reverse rate coefficients is valid for reactions such as $H + C_2H_4$ and generates rate coefficients that agree, within numerical accuracy, with those determined under strictly irreversible conditions.

Acknowledgment. SERC are thanked for their support through an equipment grant at Oxford and research studentships to M.A.H.-L. and S.H.R. (in a C.A.S.E. collaboration with I.C.I.). M.A.H.-L. thanks Jesus College, Oxford for financial support.

Supplementary Material Available: Tables of experimental rate coefficients k_a and k_d presented at 800 K in 97–600 Torr of He, and calculated rate coefficients k_a at 285, 400, 511, 604, and 800 K in 10⁻³, 10⁻², ..., 10⁸ Torr of He, using different models as described in the text (5 pages). Ordering information is given on any current masthead page.

Appendix I

The molecular parameters employed in the Troe and master equation calculations are shown in Table VII. Following Lightfoot and Pilling,⁷ and in order to conform as closely as possible to their approach, we employed a value of $\langle \Delta E \rangle_{\text{down}} = 285 \text{ cm}^{-1}$ in the calculation of F_{cent}^{WC} . The best fit values of k_a^0 and k_a^∞ are comparatively insensitive to this parameter, however.⁷

The geometry reported in ref 36 corresponds to $\sigma(C_2H_5) = 1$; however, the barriers to motion are small and the more symmetric geometry (corresponding, in effect, to sp², sp³ hybridization of the carbon atoms) is appropriate.

The collision frequency, ω , employed in the master equation calculations was calculated using the expression given by Neufeld et al.³⁷ for the collision integral, $\Omega^{(2,2)}$; the Lennard-Jones parameters for He and C₂H₅ were taken from ref 38, with the C₂H₆ data being used for C₂H₅. The values of mean (arithmetic) cross section and mean (geometric) well depths employed were 0.3497 nm and 46.95 K (ϵ/k_B) respectively.

Appendix II

The formal solution of eq 3:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n} + \mathbf{Q}\mathbf{n} = \mathbf{\Phi} \tag{3}$$

is obtained by diagonalizing Q:

$$\mathbf{\Lambda} = \mathbf{U}^{-1}\mathbf{O}\mathbf{U}$$

where Λ has diagonal elements equal to the eigenvalues of \mathbf{Q}, λ_k , and U is a matrix of the right eigenvectors, \mathbf{u}_k . Q, U, and A are all time-independent. Defining the vectors $\mathbf{q} = \mathbf{U}^{-1}\mathbf{n}$ and $\mathbf{f} =$ $U^{-1}\Phi$, eq 3 may be transformed to give

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{q} + \mathbf{\Lambda}\mathbf{q} = \mathbf{f}$$

which has equations for each component of the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}q_i + \lambda_i q_i = f_i$$

which may be integrated to give

$$q_i = e^{-\lambda_i t} q_{i,0} + \frac{1}{\lambda_i} (1 - e^{-\lambda_i t}) f_i$$

where $\mathbf{q}_0 = \mathbf{U}^{-1}\mathbf{n}_0$ and \mathbf{n}_0 is the zero time population vector. Substituting for q and f in the corresponding vector equation gives

$$\mathbf{U}^{-1}\mathbf{n} = e^{-\Lambda t}\mathbf{U}^{-1}\mathbf{n}_0 + \Lambda^{-1}(1 - e^{-\Lambda t})\mathbf{U}^{-1}\mathbf{\Phi}$$

from which

$$\mathbf{n} = \mathbf{U}e^{-\Lambda t}\mathbf{U}^{-1}\mathbf{n}_0 + \mathbf{U}\Lambda^{-1}(1-e^{-\Lambda t})\mathbf{U}^{-1}\boldsymbol{\Phi}$$

OF

$$\mathbf{n} = e^{-\mathbf{Q}t}\mathbf{n}_0 + \mathbf{O}^{-1}(1 - e^{-\mathbf{Q}t})\mathbf{\Phi}$$

All the eigenvalues of Q are positive since every state communicates and there is a net loss factor due to stabilization of the energized adduct. Thus $e^{-Qt} \rightarrow 0$ as $t \rightarrow \infty$ and the steady-state solution, which results for $\lambda_1 t \gg 1$ (where λ_1 is the numerically smallest eigenvalue) has the form:

$$\mathbf{n} = \mathbf{O}^{-1}\mathbf{\Phi}$$

c.f. eq 4. Note that, in this case, λ_1 is not the unimolecular rate coefficient.

References and Notes

(1) Brouard, M.; Lightfoot, P. D.; Pilling, M. J. J. Phys. Chem. 1986, 90, 445.

- (2) Tsang, W. Int. J. Chem. Kinet. 1978, 10, 821.
- (3) Golden, D. M.; Benson, S. W. Chem. Rev. 1969, 69, 125.
 (4) Russell, J. J.; Scetula, J. A.; Gutman, D. J. Am. Chem. Soc. 1988, 110, 3092.
 - (5) Parmar, S. S.; Benson, S. W. J. Am. Chem. Soc. 1989, 111, 57.
 - (6) Seakins, P. W.; Gutman, D.; Pilling, M. J. To be published
 - (7) Lightfoot, P. D.; Pilling, M. J. J. Phys. Chem. 1987, 91, 3373.
 - (8) Troe, J. J. Chem. Phys. 1977, 66, 4745. (9) Troe, J. J. Chem. Phys. 1977, 66, 4758.
 - (10) Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 161.
 - (11) Gilbert, R. G.; Luther, K.; Troe, J. Ber. Bunsen-Ges. Phys. Chem.
- 1983, 87, 169. (12) Lee, J. H.; Michael, J. V.; Payne, W. A.; Stief, L. J. J. Chem. Phys.
- 1978, 68, 1817. (13) Sugawara, K.; Okazaki, K.; Sato, S. Bull. Chem. Soc. Jpn. 1981, 54, 2872.
 - (14) Quack, M. Ber. Bunsen-Ges. Phys. Chem. 1984, 88, 94.
- (15) Green, N. J. B.; Marchant, P. J.; Perona, M. J.; Pilling, M. J.; Robertson, S. H. J. Chem. Phys. 1992, 96, 5896.
- (16) Baulch, D.; Cox, R. A.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Warnatz, J.; Walker, R. W.; Frank, P. J. Phys. Chem. Ref. Data 1992, 21, 411.
- (17) Marquardt, D. M. J. Soc. Ind. Appl. Math. 1963, 11, 431.
 (18) Wolniewicz, L. J. Chem. Phys. 1983, 78, 6173.

- (19) JANAF Thermochemical Tables, 2nd ed.; National Bureau of Standards: Washington DC, 1971; Vol. 37.
 - (20) Cao, J.-R.; Back, M. H. Int. J. Chem. Kinet. 1984, 16, 961.
- (21) Castelhano, A. L.; Marriott, P. R.; Griller, D. J. Am. Chem. Soc. 1981, 103, 4262
- (22) Hase, W. L.; Schlegel, H. B. J. Phys. Chem. 1982, 86, 3901. (23) Davies, J. W.; Green, N. J. B.; Pilling, M. J. J. Chem. Soc. Faraday
- Trans. 1991, 87, 2317. (24) Davies, J. W.; Green, N. J. B.; Pilling, M. J. To be published.
- (25) Eigen, M.; Kurtze, G.; Tamm, K. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 103. (26) Robinson, P. J.; Holbrook, K. A. Unimolecular Reactions;
- Wiley-Interscience: London, 1972. (27) Davies, J. W.; Green, N. J. B.; Pilling, M. J. To be published.

 - (28) Stein, S. E.; Rabinovitch, B. S. J. Chem. Phys. 1973, 58, 2438.
 (29) Davies, J. W.; Green, N. J. B.; Pilling, M. J. Chem. Phys. Lett. 1986,
- 126. 373.
- (30) Tsang, W.; Hampson, R. F. J. Phys. Chem. Ref. Data 1986, 15, 1087.
- (31) Feng, Y.; Niiranen, J. T.; Bencsura, A.; Knyazev, V. D.; Gutman, D.; Tsang, W. J. Phys. Chem., following paper in this issue.
 (32) Walter, D.; Grotheer, H.-H.; Davies, J. W.; Pilling, M. J.; Wagner,
- A. F. 23rd Symp. (Int.) Comb. 1990, 107.
- (33) Gilbert, R. G.; Smith, S. C. Theory of Unimolecular and Recombination Reactions; Blackwell Scientific Publications: Oxford, 1990.
- (34) Barker, J. R. Private communication. (35) Seakins, P. W.; Robertson, S. H.; Pilling, M. J.; Slagle, I. R.;
- Gmurczyk, G. W.; Bencsura, A.; Gutman, D.; Tsang, W. To be published. (36) Pacansky, J.; Schrader, B. J. Chem. Phys. 1983, 78, 1033.
 (37) Neufeld, P. D.; Janzen, A. R.; Aziz, R. A. J. Chem. Phys. 1972, 57,
- 1100.
- (38) Reid, R. S.; Prausnitz, J. M.; Sherwood, T. K. The Properties of Gases and Liquids, 3rd ed.; McGraw-Hill: London, 1987.