LETTERS

Resolution of a Paradox Concerning the Forward and Reverse Rate Constants for C_2H_5 ⇌ H + C_2H_4

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Results of recent ab initio calculations and a revised value for the ethyl radical heat of formation are used in an analysis of the rate constants for the C_2H_5 ⇌ H + C_2H_4 system. It is found that RRKM and activated complex theory rate constants agree with the experimental ones for both the recombination and dissociation reactions.

The C_2H_5 ⇌ H + C_2H_4 system provides a severe test of the RRKM and activated complex theories of chemical reaction rates. For hydrogen atom addition to ethylene the high-pressure bimolecular rate constant has been measured vs. temperature,[1-3] and the pressure dependence of the recombination rate constant has been studied extensively at 300 K.[4,5] The C_2H_5 dissociation reaction has also been investigated, and values of the unimolecular rate constant have been reported vs. both temperature and pressure.[6,7]

For some time a significant paradox has existed between the recombination and dissociation rate constants.[1] The same activated complex model will fit the measured unimolecular rate constant and the pressure dependence of the recombination rate constant.[4,5] However, when this activated complex is applied to the H + C_2H_4 high-pressure bimolecular rate constant it overestimates the experimental value by an order of magnitude.[1] Several dynamical interpretations of this finding have been postulated[1] and studied with classical trajectory calculations.[8-11] The major finding from the classical trajectories is that recrossing of the dividing surface between reactants and

products, defined by the activated complex, is unimportant for H + C_2H_4 ⇌ C_2H_5.[12] Thus, activated complex theory is expected to be valid for the recombination reaction.

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(12) In the first trajectory study, ref 8a, a microcanonical ensemble was approximated at the dividing surface and from the results it was concluded that recrossing of the dividing surface is important for trajectories initiated at the dividing surface. It was discovered that a sampling error existed in these calculations and when removed recrossing was found to be unimportant, ref 8b and 9. For thermal relative translational energies quasi-classical trajectory calculations show that recrossing of the dividing surface is insignificant for H + C_2H_4 collisions (ref 10 and 11). The H + C_2H_4 → C_2H_5 quasi-classical trajectory rate constant agrees to within 20% of the activated complex theory one with a Wigner tunnelling correction (ref 11).

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From recent ab initio calculations, several ambiguities about the $C_2H_5 \rightleftharpoons H + C_2H_4$ potential energy surface have been eliminated.[13] This has allowed a more-definite analysis of the recombination and dissociation rate constants in terms of the RRKM and activated complex theories. The result of this analysis is given in this work.

To calculate the $H + C_2H_4$ recombination and C_2H_5 decomposition rate constants with the RRKM and activated complex theories requires equilibrium geometries and vibrational frequencies for ethylene, the activated complex, and the ethyl radical, and the 0 K thresholds. Of these parameters, only the equilibrium geometry[14] and vibrational frequencies[15] for ethylene are known in total from experiment. However, in very recent work, Pacansky and Dupuis[16] measured all the vibrational frequencies for the ethyl radical except the CH_2 bend (A'), CH_3 rocking (A''), CH_2 asymmetric bend (A''), and the torsion (A''). As found from ab initio calculations[13a,16,17] and experiment[18] the torsion can be treated as a free rotor. Frequencies for the remaining three modes can be estimated from HF/4-31G frequencies for C_2H_5 by comparison with experimental and HF/4-31G frequencies for the same modes in deuterated ethylenes.[16] The resulting estimated frequencies for C_2H_5 in cm^{-1} are CH_2 bend (A') of 1439, CH_3 rocking (A'') of 1186, and CH_2 asymmetric bend (A'') of 802.

Vibrational frequencies for the activated complex can be estimated by scaling those calculated at the HF/3-21G level[13a] by the factor 0.89. This factor is found to give the best agreement between harmonic and HF/3-21G frequencies and anharmonic experimental frequencies for a large number of molecules.[19] The scale factor for ethylene varies between 0.82 and 0.93, and that for the ethyl radical varies between 0.86 and 1.21.[13a] The best evaluation of the equilibrium geometries for the ethyl radical and activated complex are the calculations at the MP2/3-21G level[13a] and they are used in calculating the moments of inertia for these two species.

Determining the threshold energies for $H + C_2H_4$ recombination and C_2H_5 decomposition is a particularly difficult task, since the ab initio calculations do not provide quantitative numbers.[13b] In this work the recombination threshold is deduced by fitting the temperature dependence of the high-pressure bimolecular rate constant with activated complex theory. The vibrational frequencies and moments of inertia detailed above for ethylene and the activated complex are used in the calculation. Tunnelling is accounted for by the Wigner correction[20]

$$1 + |h\nu/k_bT|^2/24$$

where ν is the imaginary frequency associated with the reaction coordinate (the HF/3-21G value scaled by 0.89 is 546i cm^{-1}). Agreement with the experimental rate constants is found with a recombination threshold of 2.5 kcal/mol and the fit is shown in Figure 1.[21] The Wigner
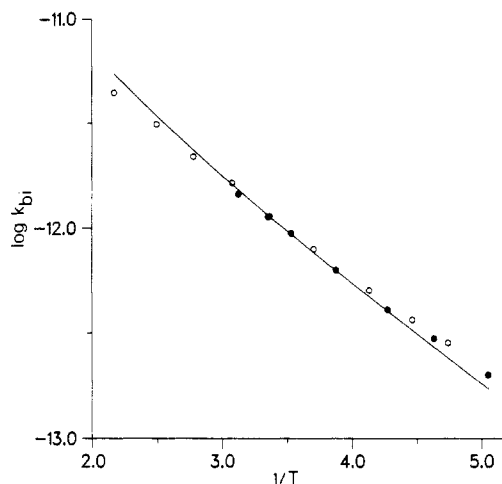

Figure 1. Plot of log k_{bi} (cm^3/(molecule s)) vs. inverse temperature (10^{-3} K^{-1}). The O and ● data points are from ref 3b and 1, respectively.

TABLE I: Parameters for the RRKM and Activated Complex Theory Calculations

	ethyl radical	activated complex	ethylene
frequencies, cm^{-1}	3112	3036	3105
	3033	3009	3103
	2987	2955	3026
	2920	2944	3021
	2842	1504	1630
	1440	1446	1440
	1440	1218	1342
	1439	1185	1220
	1366	944	1073
	1186	938	943
	1175	869	949
	1138	821	826
	802	399	
	540	369	
		546i	
internal rotation moment of inertia, amu A^2	1.12		
external rotation moments of inertia,^{a} amu A^2	24.5, 22.8, 4.90	22.2, 21.6, 6.30	20.4, 16.9, 3.48
symmetry number	6	1	4
0 K thresholds, kcal/mol			
$H + C_2H_4 \rightarrow C_2H_5$	2.5		
$C_2H_5 \rightarrow H + C_2H_4$	38.0		

^{a} The external rotation degrees of freedom are treated adiabatically in the RRKM calculations.

correction to the activated complex theory rate constant varies from 1.64 at 200 K to 1.13 at 450 K.

From the experimental $C_2H_5 \rightleftharpoons H + C_2H_4$ heat of reaction at 0 K[22] and the $H + C_2H_4$ threshold, the C_2H_5 dissociation threshold can be determined. The value is 38.0 ± 1.0 kcal/mol.

With the above energies, all the necessary ingredients for an activated complex theory calculation have been assembled.[23] Vibrational frequencies, moments of inertia,

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(21) A least-squares fit of the activated complex theory rate constant times the Wigner correction at temperatures of 200, 250, 300, 350, 400 and 450 K gives $A = 6.59 \times 10^{-11}$ cm^3/(molecule s) and $E_a = 2.37$ kcal/mol.

(22) The most recent estimate of $\Delta H_f(C_2H_5)$ at 300 K is 28.0 ± 1.0 kcal/mol; A. T. Castelhano, P. R. Marriott, and D. Griller, *J. Am. Chem. Soc.*, **103**, 4262 (1981). This heat of formation is supported by an analysis of thermal kinetic data for butane dissociation: W. Tsang, *Int. J. Chem. Kinet.*, **10**, 821 (1978). The heats of formation for H· and C_2H_4 are 52.103 and 12.496 kcal/mol at 298.15 K, respectively: D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). Correcting for the thermal enthalpy yields a heat of reaction of 35.5 ± 1.0 at 0 K.
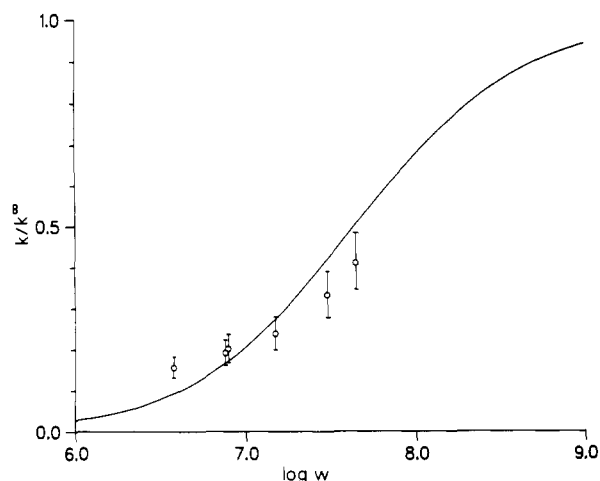
Figure 2. Plot of k_r/k_r^∞ vs. log ω (s^{-1}) for H + C$_2$H$_4$ recombination with SF$_6$ as the bath gas. Experimental points are from ref 4 and 5.

Figure 3. Plot of log k_{uni} (s^{-1}) vs. log ω (s^{-1}) for C$_2$H$_5$ decomposition. The experimental points are derived from the results of ref 29 by using a temperature-independent ethyl radical recombination rate constant of 2.5 $\times$ 10^{-11} cm^3/(molecule s). The curves are for temperatures of 400, 430, 470, and 500 °C.

symmetry numbers, and threshold energies are summarized in Table I. In addition to this information, RRKM theory requires knowing the frequency of stabilizing collisions to calculate the pressure dependence of the unimolecular rate constants. To find this property we used the same parameters as Michael and Suess,[4] which differ insignificantly from the recommended values of Rabinovitch and co-workers.[24] The collision cross section is determined by multiplying the hard-sphere diameter by the square root of the Lennard-Jones $\Omega^{(2,2)*}$ collision integral.

The two bending frequencies ν_b about the rupturing C–H bond in the activated complex agree with previous activated complex theory calculations for the recombination reaction[1] but are considerably larger than the value of 100 cm^{-1} chosen to fit C$_2$H$_5$ unimolecular decomposition rates.[4,5,25] Our decomposition threshold of 38.0 kcal/mol is smaller than the 40.0 kcal/mol used in the previous calculations. This arises from our use of 28.0 kcal/mol for the 300 K heat of formation for C$_2$H$_5$[22] instead of the long accepted value of 25.9 kcal/mol.[26] One might suspect that with the lower threshold energy the unimolecular rate constant can be fit with a "tighter" activated complex, i.e., larger ν_b values than 100 cm^{-1}. As is shown below this is indeed the case.

The necessary formulae for calculating the temperature and pressure dependence of the C$_2$H$_5$ $\rightarrow$ H + C$_2$H$_4$ unimolecular rate constant are described in detail elsewhere.[27] Of particular significance is the result, from microscopic reversibility, that for a fixed temperature the ratio of the H + C$_2$H$_4$ recombination rate constant to the recombination rate constant at infinite pressure can be equated to the similar ratio for the unimolecular reaction; i.e., $(k_r/k_r^\infty) = (k_{uni}/k_{uni}^\infty)$. Thus, RRKM unimolecular rate theory can be used to calculate the pressure dependence of the recombination rate constant.

A plot of the calculated ratio k_r/k_r^∞ is given in Figure 2 for a temperature of 300 K and with SF$_6$ as the bath gas. The agreement between experiment and theory is nearly
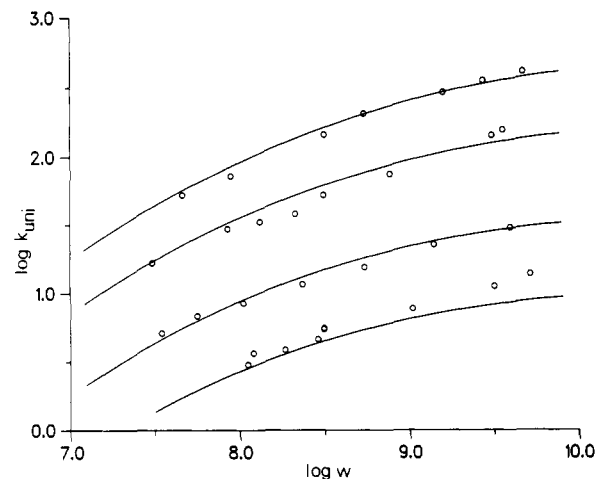
TABLE II: Activated Complex Theory Rate Constants for C$_2$H$_5$ Decomposition^a

T, K	A, s^{-1}	E_a, kcal/mol	k, s^{-1}
400	4.29 $\times$ 10^{13}	39.1	1.96 $\times$ 10^{-8}
500	6.87 $\times$ 10^{13}	39.5	3.82 $\times$ 10^{-4}
600	1.00 $\times$ 10^{14}	39.9	2.96 $\times$ 10^{-1}
700	1.36 $\times$ 10^{14}	40.3	3.60 $\times$ 10^{1}
800	1.73 $\times$ 10^{14}	40.6	1.37 $\times$ 10^{3}
900	2.12 $\times$ 10^{14}	41.0	2.37 $\times$ 10^{4}
1000	2.52 $\times$ 10^{14}	41.3	2.36 $\times$ 10^{5}

^{a} The rate constants and Arrhenius parameters are for the high-pressure limit.

the same as that reported previously by Michael and co-workers.[4,5] A better fit could be realized by using a collisional efficiency, β_c, less than unity and by including a tunnelling correction in the unimolecular rate calculations. Since the average energy of the dissociating molecules decreases with pressure, a constant tunnelling correction over the complete pressure range is not strictly valid. The tunnelling correction is expected to be greater at low pressures. This will change the shape of the calculated k_r/k_r^∞ curve and a better fit to the experimental points should be possible. However, given the uncertainties in the activated complex vibrational frequencies, the imaginary frequency and the unimolecular threshold, a detailed calculation including tunnelling does not seem warranted at this time.

In thermal studies of ethane dissociation the ratio of the rate constant for ethyl radical dissociation to the square root of the ethyl radical high-pressure recombination rate constant has been measured at different pressures over the 400–640 °C temperature range.[28,29] Recent experimental measurements indicate no temperature dependence for ethyl radical recombination and give values for k_r^∞ of (1.4 $\pm$ 0.6) $\times$ 10^{-11},[30] (2.3 $\pm$ 0.5) $\times$ 10^{-11},[31] and (1.8 $\pm$ 0.7) $\times$ 10^{-11} cm^3/(molecule s).[32] When k_r^∞ = 2.5 $\times$ 10^{-11} cm^3/(molecule s) is used, agreement is found between the experimental

(23) The variational criterion is unimportant for calculating thermal rate constants for the C$_2$H$_5$ $\rightleftharpoons$ H + C$_2$H$_4$ system and properties of the reaction path are unnecessary; W. L. Hase, *Acc. Chem. Res.*, submitted for publication.

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and RRKM values of k_{uni} vs. pressure. This is illustrated in Figure 3 where the data of Loucks and Laidler[29] is plotted. Infinite pressure rate constants and Arrhenius parameters are listed in Table II. The data of Lin and Back[28] is not included since the experimental k_{uni} values can only be approximated from the published plots. However, other workers have shown that an RRKM model that fits the k_{uni} vs. pressure results of Loucks and Laidler will also fit the results of Lin and Back.[4,33]

A collision efficiency for ethane of unity was used for the calculations in Figure 3. Tunnelling corrections were not made in the RRKM calculations of k_{uni} vs. ω. However, at these temperature they should be unimportant. For example, the Wigner correction at 673 K is 1.06.

As shown in Figures 1–3 agreement is found between the experimental and RRKM and activated complex theory rate constants for the $C_2H_5 \rightarrow H + C_2H_4$ system. Given the uncertainties in the threshold energies, the activated complex frequencies, the tunnelling probabilities, and the collision efficiencies we do not view the small differences between the experimental and theoretical rate constants significant. Thus, the previous dilemma[1] seems to have been eliminated. However, this does not rule out the possibility that as more accurate ab initio results become available, and rate constants and reaction energetics are measured more precisely, theory and experiment may again come into conflict. Also, this study does not bear directly on the inability of activated complex theory com-

bined with ab initio results to fit isotope effects for hydrogen atom addition to ethylene.[3]

Though the ab initio calculations do not provide the threshold energies in the above analysis, they still make needed contributions. They were particularly important in determining the ethyl radical and activated complex geometry and vibrational frequencies. The two bends in the activated complex about the rupturing C–H bond are ~ 400 cm^{-1}, much larger than the previously assumed value of 100 cm^{-1}. This result is crucial in our analysis. The frequency of the CH_2 wag in ethyl radical is like that for CH_3,[34] instead of the higher value found in amines.[35] Also, except at very low temperatures, the torsion in the ethyl radical can be treated as a free rotor. These two findings are particularly important in calculating the entropy and enthalpy of the ethyl radical, which are required in these activated complex theory calculations as well as those for other reactions involving the ethyl radical.[36]

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