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A Theoretical Analysis of the Reaction of H with C₂H₅

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Abstract:

The interaction of H with C₂H₅ is analyzed at the CAS+1+2 level employing a correlation-consistent polarized valence double zeta basis set. These *ab initio* calculations show three barrierless pathways, two leading to association and one for abstraction. The association channels are substantially more attractive than the abstraction one, and thus dominate the kinetics. An analytic representation of the *ab initio* data is implemented in a variable reaction coordinate transition state theory study of the temperature dependence of the association kinetics. These theoretical estimates for the high pressure association rate constant are directly compared with related experimental measurements in an effort to resolve the discrepancy between recent and earlier results.

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Introduction

The reaction of ethyl radicals with H atoms, which is of general importance in hydrocarbon combustion, is one of the simpler examples of a radical-radical reaction. For such reactions there is considerable interest in understanding the extent and direction of any temperature dependence for the high pressure association kinetics. Knowledge of this temperature dependence is of general importance in extrapolating room temperature experimental data to the conditions of importance in the combustion environment.

The reaction scheme for the title reaction is:

Another key question for such reactions regards the branching between abstraction (channel 1) and association [which leads to addition (channel 2) and/or elimination products (channel 3)].

Relatively sophisticated theoretical analyses may be applied to the study of this reaction due to its small molecular size. Here, the interaction of the two radicals is first characterized via high level *ab initio* quantum chemical simulations. The paths for both association and abstraction are examined and analytical potential energy surfaces are derived. These potentials are then implemented in transition state theory (TST) based procedures for estimating the reaction kinetics and the results are compared with related experimental observations [1,2,3,4,5,6,7,8].

Potential Surface Calculations

A. Methodology

The basis set used in most calculations was the correlation-consistent, polarized valence double zeta (cc-pvdz) basis set of Dunning [9,10,11]. All of the electronic structure results reported here come from multi-reference configuration interaction (MR-CI) calculations employing orbitals from complete active space, self-consistent field (CASSCF) calculations. For the calculations on the abstraction path, the CASSCF reference wavefunction consists of four active electrons and four active orbitals (the two radical orbitals of the reactants along with σ and σ^* orbitals for the CH bond being broken). For the calculations on the association paths, the CASSCF reference wavefunction consists of only two active orbitals (the two radical orbitals of the reactants) and two active electrons. This is the minimum necessary to describe the reactant asymptote. In either case the CASSCF orbitals were used in multi-reference configuration interaction (CAS+1+2) calculations to which a multi-reference Davidson correction was added to account for the effects of higher order excitations. All calculations were carried out using the COLUMBUS package of codes [12].

B. Results

Four sets of calculations were done: (i) characterization of the abstraction path as a function of two coordinates (R_{HH} and R_{CH}); (ii) characterization of a three dimensional surface for the interaction of a hydrogen atom with an un-relaxed ethyl radical for use in the TST calculations; (iii) characterization of a minimum energy path for the association reaction; and (iv) characterization of changes in the umbrella and torsional modes of the ethyl radical as the hydrogen atom approaches along the association path.

Although one might expect to find pathways for the direct abstraction of each of the three hydrogens on the methyl side of the ethyl radical, preliminary calculations showed that, only one pathway exists. This is a barrier-less pathway leading to the

abstraction of the methyl hydrogen in the symmetry plane of the radical. Minimum energy paths for abstracting either of the other hydrogens are predicted to first involve an internal rotation about the CC bond to bring the desired hydrogen into the symmetry plane, followed by a barrier-less abstraction in the symmetry plane. An approximate reaction surface for the abstraction path was obtained by optimizing the angular coordinates of the two active hydrogens for a two dimensional grid of CH and HH distances, keeping the other geometric parameters fixed at the equilibrium values of the ethyl radical. A plot of this surface is shown in Fig 1.

Characterization of the potential surface for the association reaction was initially done by mapping out a three dimensional surface corresponding to motion of the atomic hydrogen reactant around the ethyl radical, which was kept fixed at its equilibrium geometry. The coordinates chosen to describe this motion were the CH distance, the H-C-C angle and an H-C-C-H dihedral angle. With this coordinate system, energies were evaluated at a 44x37x5 grid of points and fit using a two dimensional spline for the CH distance and HCC angle and a Fourier series expansion for the dihedral angle dependence. The portion of this potential corresponding to the H atom in the symmetry plane of the ethyl radical is shown in Fig 2. From this plot it can be seen that there are two barrier-less routes for the association reaction, one from each side of the radical center. Since the radical center is slightly non-planar these two pathways are not equivalent.

In the above three dimensional surface, all internal modes of the ethyl radical are kept frozen. In order to assess the importance of allowing these internal modes to relax as the hydrogen atom approaches, a minimum energy path (MEP) for this reaction was calculated. This was accomplished by evaluating the energy for a grid of points, in which the active CH bond distance is kept fixed while other geometrical parameters are allowed to vary. In these calculations the inactive CH distances are also kept fixed as these coordinates correspond to high frequency modes that will not change a great deal along this path. The grid of energies is then fit to a twelve dimensional polynomial expansion which is then used both to locate the minimum in this twelve dimensional subspace and

to define a twelve dimensional force field at the predicted minimum. Frequencies are then calculated using the standard mass-weighted atomic Cartesian formalism. It is important to note that in this procedure the energy dependence along the assumed reaction coordinate (the active CH distance) is neglected.

The MEP frequencies from these calculations are shown in Fig 3. From Fig 3 it can be seen that the frequencies of four modes are changing rapidly as a function of the CH distance. Two of these are the transitional modes corresponding to motions of the active hydrogen atom perpendicular to the reaction path. The other two rapidly changing modes are the internal rotation about the CC bond and inversion about the radical center. For the ethyl radical both of these modes are low frequency, large amplitude modes. Both become significantly stiffer in the product ethane. To assess the importance of changes in these modes as the reaction progresses, a series of two dimensional potential surfaces were calculated. These surfaces sample large amplitude displacements in the inversion and internal rotation coordinates relative to the MEP. The two dimensional surfaces were determined at 13 fixed values of the CH distance, fit with two dimensional splines and used as described in the next section to estimate a correction for both anharmonicity and geometry relaxation in these two coordinates. Some representative plots of these surfaces are provided in Fig 4.

Finally, calculations comparable to those described above were done for the $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$ potential curve using both the cc-pvdz basis and the larger aug-pvtz basis set [9,10,11]. The aug-pvtz basis set is significantly more accurate than the cc-pvdz basis set, having both diffuse function and higher angular momentum functions. The difference between these two calculations, as a function of the CH distance, is taken as a basis set correction to the $\text{H} + \text{C}_2\text{H}_5$ potential surface (with the assumption that the magnitude of the correction depends only on the CH distance).

Kinetics

A. TST Methodology

For radical-radical reactions the transition state (TS) dividing surface is typically located at inter-fragment separations ranging from about 2 to 5 Å. In general, this separation gradually decreases with increasing temperature. This variation in the TS location correlates with a transition from free rotational motions of the fragments to first hindered rotational and then bending motions.

In this work we employ the variable reaction coordinate transition state theory (VRC-TST) approach in the analysis of the reaction kinetics [13]. A key aspect of this approach involves a phase space integral based description of the contribution from the rotational and orbital modes of the two reacting fragments. This description provides a classically accurate treatment of the variation from free rotors to bending motions. The quantum chemically derived analytic potential for the interaction of the H atom with the ethyl radical is employed in the evaluation of these phase space integrals. This contribution from the transitional modes is then convoluted with that arising from the vibrational modes of the fragments. The latter "conserved" mode contribution is evaluated via direct sums over the quantized energy levels.

A variation in the shape of the optimum TS dividing surface often occurs concomitantly with the variation in the inter-fragment separation at the TS. In particular, at large separations the optimum dividing surface generally corresponds to a fixed separation between the centers-of-mass of the two fragments, as assumed in the original flexible TST of Wardlaw and Marcus [14]. In contrast, at shorter separations a bond length provides a better first approximation to the optimum reaction coordinate. Within the VRC-TST approach a whole class of different dividing surfaces is considered, with the optimum dividing surface being that which gives the lowest value for the transition state partition function.

For the present reaction, these dividing surfaces are defined in terms of a given distance R between the H atom and a point A fixed relative to the C_2H_5 molecular framework. The point A is defined here by its distance d from the radical C atom, the ACC bending angle θ , and the ACCH torsional angle ϕ for the ethyl H which is in the Cs symmetry plane. The fixed point A is assumed to lie in the plane with $\phi = 180^\circ$. The determination of the TS then involves a minimization with respect to R , d , and θ of the partition function for motion on the dividing surface.

A sample plot of the optimized TS dividing surface for the association channel at a temperature of 650 K is provided in Fig 2. For this TS surface $R = 2.5 \text{ \AA}$, $d = 1.2 \text{ \AA}$, and $\theta = 105^\circ$. This dividing surface is seen to have a shape which follows the potential contours near the MEP and then moves toward the most repulsive regions of the potential far from the MEP.

The TS partition functions may be evaluated at the energy E and total angular momentum J resolved, E resolved, or T resolved levels. At the E/J resolved level, which is the fundamentally correct level, the TS, as specified by (R, d, θ) , is a function of both E and J . In contrast, at the E and T resolved levels the TS is a function of only E and T , respectively. The latter approaches, while incorrectly providing somewhat larger estimated rate constants, require substantially less computational effort. They also provide a means to more simply consider the variations in the TS.

The contour plot of the potential energy surface provided in Fig 2 suggests that the H atom may add to the ethyl radical from either of two different sides and that the contribution from these two sides would be quite different. In reality, however, attack from the less attractive side will generally lead to inversion of the CH_2 umbrella bending mode (α) coupled with a torsional rotation (τ) by 60° to produce a structure which is equivalent in energy to that of the more attractive side. In the ethyl radical by itself the motion from $(\alpha, \tau) = (-4^\circ, 0^\circ)$ to $(\alpha, \tau) = (4^\circ, 60^\circ)$ connects two equivalent minima on the potential energy surface (cf Fig 4). In the presence of the H atom, this symmetry is broken and the torsion-inversion potential reduces from six-fold to three-fold symmetry.

For CH separations corresponding to the TS region (i.e., r_{CH} values of about 6 to 8) the barriers along the torsion-inversion MEP are sufficiently small that one expects the ethyl radical to be continually sampling all the minima. Thus, regardless of any momentary side of attack, one expects the potential to be sampling both minima in the potential shown in Fig 2.

The plots presented in Fig 4 also illustrate the strong coupling of the umbrella and torsional motions to the reaction coordinate. Indeed, their harmonic frequencies vary from 540 and 122 cm^{-1} at infinite separation [15] to on the order of 900 cm^{-1} in ethane. This variation is accounted for here by estimating the ratio of the canonical partition function for the 2-dimensional (α, τ) motion in the TS region to the corresponding value at infinite separation. The value of this correction factor at the CH separation corresponding to the canonical TS location is appended as a correction factor to the final VRC-TST rate constants.

For simplicity, we evaluate the umbrella and torsional mode contributions to this ratio separately. The umbrella mode contribution is evaluated on the basis of the r_{CH} dependence of the diagonal force constant, employing a harmonic oscillator partition function. The neglect of anharmonicity effects for this mode should roughly cancel in taking the ratios of the partition function in the transition state region to that at infinite separation. For the torsional mode, the frequency and barrier heights are so low that a classical hindered rotor description seems more appropriate. The optimized (with respect to α) potential along the torsional coordinate is employed in the determination of classical configurational integrals. The ratio of the r_{CH} dependent values to the value at infinite separation then provides a 1-dimensional torsional mode correction.

In reality, the umbrella and torsional modes are probably best considered as transitional rather than conserved modes. However, their inclusion in the transitional mode set would increase the dimensionality of the required potential energy surface from three to five. The development of a five-dimensional surface is sufficiently complicated that we have instead taken the simpler alternative of evaluating the effect of their

variation along a minimum energy path and then assumed that this effect is independent of the orientation. One might also consider employing a two-dimensional quantization of the α and τ motions. However, the corrections obtained would largely cancel in taking the ratios of the transition state and reactant partition functions and so the simpler 1-dimensional treatments were deemed sufficient.

As can be seen from Fig 3, the remaining conserved vibrational modes vary negligibly from the separated fragments to the transition state region (i.e., 3-4 Å). In this case, the ratio of their contributions to the transition state and reactant partition functions cancel. The optimization of the TS partition functions then involves the minimization of the product of the transitional mode phase space integrals with the two 1-dimensional conserved mode correction factors. An electronic degeneracy factor of $\frac{1}{4}$ is employed under the assumption that the reaction cannot occur on the triplet state which is asymptotically degenerate with the singlet state at large separations.

A direct product of evenly spaced grids in R , d , and θ was employed in the full E/J resolved minimization. The R values ranged from 3.375 to 1.75 Å with a 0.125 Å spacing, the d values ranged from 0.6 to 1.4 Å with a 0.2 Å spacing, and the θ values ranged from 90 to 120° with a spacing of 10°. Preliminary calculations employing a more widely varying grid indicated that this grid adequately spans the range of transition state locations. 10,000 Monte Carlo points were generally employed in evaluating the transitional mode phase space integrals providing convergence to about 5% or better in the integration.

B. Kinetics Results

The contour plot for the interaction of the ethyl radicals with the H atoms (Fig 2) clearly illustrates the dominance of the association channel over the abstraction channel. However, one should bear in mind that this plot is for an unrelaxed ethyl radical structure. The relaxation energy for the H abstraction channel is large (cf Figs 1 and 2) and clearly much greater than that for the association channel. The effect of this

relaxation on both the MEP energetics and on the orthogonal vibrational frequencies is quantitatively important for HH separations of less than about 3.4 Å. Thus, a simple application of the VRC-TST method is only appropriate for separations greater than this value. Unfortunately, we find that the TS actually lies at separations less than 3.4 Å even for the lowest temperature considered here of 200 K. As a result, we can only estimate an upper bound for the abstraction channel rate constant. At 200 K this upper bound is 15% of the association rate constant. By 1900 K this upper bound rises to about 40%. The actual contribution from the abstraction is likely much smaller than these upper bounds, and so we neglect it altogether in estimating the total rate.

The fact that the elimination channel (3) is substantially lower in energy than the reactants, then suggests that it is appropriate to make direct comparisons of the present estimates for the association rate constant with the experimental observations for the overall rate constant at moderate pressures. The final VRC-TST predictions for the association rate constant are plotted in Fig 5 for temperatures ranging from 200 to 1900 K, together with the various experimental results [1,2,3,4,5,6,7,8]. Interestingly, the results from the only recent experimental study [8] are 4 or more times larger than those of all prior experimental studies [1,2,3,4,5,6,7]. The present theoretical predictions are a factor of 1.7 lower than the experimental data of Ref. 8 for the total rate constant, and a factor of 3 to 5 times greater than recommended in the compilation of Warnatz [16], which is roughly the average of the remaining experimental data. Ref. 8 also provides a breakdown of the total rate into the component rates for the addition ($1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and elimination ($1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) channels. Interestingly, the estimate for the elimination channel is in quantitative agreement with the current theoretical result. Furthermore, the 10 kcal/mol energetic separation between the elimination channel and the entrance channel would seem to suggest that the addition channel should not make as large a contribution as found experimentally.

The theoretical results predict that the association rate constant is nearly independent of temperature, rising from 1.6 to $2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from 200 to 1900 K. The transitional mode contribution shows a somewhat stronger temperature

dependence rising by a factor of 1.6 over the same temperature range. This rise is partly ameliorated by the contribution from the umbrella and torsional modes, which decreases by a factor 0.75.

A consideration of other dependencies provides at least a qualitative indication of the level of accuracy of the quantum chemical results. In particular, employing a potential which neglects the aug-pvtz basis set correction along the reaction path leads to estimated rate constants which are 10-15% lower throughout the temperature range studied here. The neglect of the Davidson correction for the effect of higher excitations in the wavefunction leads to estimated rate constants which are about 5% lower. The smallness of these two variations suggests that the potential is likely quite accurate.

Results obtained at the T resolved level were typically 30% greater than the corresponding E/J resolved results. This reasonably minor difference indicates that a T resolved study of the general form and the variation of the optimum dividing surface should be quite meaningful. At that level the optimum sum of $R + d$ varies from 4.2 Å at 200 K to 3.1 Å at 1900 K, and the optimum θ value is roughly constant at 105° , while the optimum d value decreases from near 1.4 Å at low T to near 0.8 Å at the highest T .

If d and θ had been held fixed at their optimized 650 K values of 1.2 Å and 105° then the predicted rate constant would have been about 15% higher. Alternatively, if we had restricted attention to either the bond length or center-of-mass reaction coordinates alone, then at the T resolved level, the estimated rate constants would have been about 1.4 and 1.8 times greater, respectively. These quite large increases illustrate the importance of optimizing both the location and form of the transition state dividing surface.

Summary

The present coupling of *ab initio* quantum chemical simulations with a variable reaction coordinate transition state theory analysis predicts a rate constant of 1.8×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. The predicted rate constant rises by only a factor of 1.35 over the 200 to 1900 K temperature range. The transitional and conserved modes are found to make opposing contributions to this minor temperature dependence. An increase in the conserved mode bending and torsional frequencies with decreasing radical-radical separation may be quite common in which case the conserved mode contribution would generally decrease with increasing temperature. These theoretical predictions lie between the older [1-7] and the most recent experimental data [8], being somewhat closer to the latter results.

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References

- ¹ Halstead, M. P., Leathard, D. A., Marshall, R. M. and Purnell, J. H., *Proc. Roy. Soc. A*, 316: 575 (1970).
- ² Teng, L. and Jones, W. E., *J. Chem. Soc. Faraday Trans. I*, 68: 1267 (1972).
- ³ Michael, J. V., Osborne, D. T. and Suess, G. N., *J. Chem. Phys.* 58: 2800 (1973).
- ⁴ Camilleri, P., Marshall, R. M. and Purnell, J. H. *J. Chem. Soc. Faraday Trans. I*, 70: 1434 (1974).
- ⁵ Pratt, G. and Veltman, I., *J. Chem. Soc. Faraday Trans. I*, 70: 1840 (1974); Pratt, G. and Veltman, I., *J. Chem. Soc. Faraday Trans. I*, 72: 1733 (1976).
- ⁶ Tabayashi, K. and Bauer, S. H., *Combust. Flame*, 34: 63 (1979).
- ⁷ Pratt, G. and Wood, S. W., *J. Chem. Soc. Faraday Trans. I*, 80: 3419 (1984);
- ⁸ Sillesen, A., Ratajczak, E. and Pagsberg, P., *Chem. Phys. Lett.* 201: 171 (1993).
- ⁹ Dunning, T. H., Jr., *J. Chem. Phys.* 90: 1007 (1989)
- ¹⁰ Kendall, R.A., Dunning, T.H., Jr. and Harrison, R.J., *J. Chem. Phys.* 96, 6796(1992)
- ¹¹ Woon, D.E. and Dunning, T.H. Jr., *J. Chem. Phys.* 98, 1358 (1993)
- ¹² Shepard, R., Shavitt, I., Pitzer, R.M., Comeau, D.C., Pepper, M., Lischka, H., Szalay, P.G., Ahlrichs, R., Brown, F.B. and Zhao, J.-G. *Int. J. Quantum Chem.* S22, 149 (1988)
- ¹³ Klippenstein, S. J., *Chem. Phys. Lett.* 170: 71 (1990); *J. Chem. Phys.* 94: 6469 (1991); 96: 367 (1992); Klippenstein, S. J., *J. Phys. Chem.* 98: 11459 (1994).
- ¹⁴ Wardlaw, D. M. and Marcus, R. A. *Chem. Phys. Lett.* 110: 230 (1984); *J. Chem. Phys.* 83: 3462 (1985); *J. Phys. Chem.* 90: 5383 (1986); *Adv. Chem. Phys.* 170: 231 (1988).
- ¹⁵ Hase, W. L., Schlegel, H. B., Balbyshev, V. and Page, M., *J. Phys. Chem.* 100: 5354 (1996); and references cited therein.
- ¹⁶ Warnatz, J, in *Combustion Chemistry*, edited by Gardiner, W. C., Jr. (Springer, Berlin, 1984), ch. 5.

Figure Captions

Figure 1. Two dimensional potential surface for the $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{H}_2 + \text{C}_2\text{H}_4$ abstraction reaction. Solid contours are positive, dashed contours are negative and the zero energy contour (defined to be the energy of the reactant asymptote) is shown with a heavy solid line. The contour increment is 1.0 kcal/mole and all distances are in atomic units (one atomic unit equals 0.52918 Å).

Figure 2. Two dimensional cut of the three dimensional potential surface for the $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6$ association reaction in the symmetry plane of the ethyl radical. The plotting conventions are as in Fig 1. The point A and the line consisting of series of parallel bars denote a typical fixed point and dividing surface for the TST calculations.

Figure 3. Normal mode harmonic frequencies along the MEP for the $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6$ association reaction. Solid lines are for modes of a' symmetry, dashed lines are for modes of a'' symmetry.

Figure 4. Two dimensional potential surfaces for the C_2H_5 inversion and rotation motions in the presence of the H atom. In these plots the H atom is fixed at its MEP location for the association reaction at the given CH separation. The contour increment is 0.2 kcal/mole and angles are in degrees. Positive inversion angles denote pyramidalization of the radical center towards the H atom, negative angles denote pyramidalization away from the H atom.

Figure 5. Plot of the rate constant versus temperature for the $\text{H} + \text{C}_2\text{H}_5$ reaction.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5