tunately, the excimer data are less reliable. The steeper slope of −1.8 for exciplex formation is consistent with the idea that a larger capture radius enhances cyclization preferrentially for shorter chains, which would affect the magnitude of the exponent. Unfortunately the differences in slope over this limited range of molecular weights are too small to be taken seriously. Further experiments are needed, particularly with a focus on longer chain lengths.

Figure 1. Geometry of the saddle point of the PES for reaction 1 (C_s symmetry).

Temperature Dependence of the Transition-State Structure for the Disproportionation of Hydrogen Atom with Ethyl Radical

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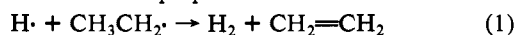
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We present preliminary computational results for one of the simplest radical–radical disproportionation reactions:

$$H\cdot + CH_3CH_2\cdot \rightarrow H_2 + CH_2{=}CH_2 \qquad (1)$$

Three important conclusions emerge from our studies. (1) The reaction appears to have a small potential energy (PE) barrier. (2) The structure of the transition state (TS) is strongly temperature dependent. (3) Above room temperature, conventional transition-state theory (TST) becomes increasingly inadequate for predicting activation parameters for the low-barrier radical–radical reactions. This is in accord with previous results for biradical reactions.[1]

Ab inito calculations were performed with the 4-electron–4-orbital complete active space MCSCF (CASSCF) wave function.[2] This corresponds to a complete CI (20 singlet configurations) within the space of the electrons and orbitals involved most prominently in changes in bonding, and it provides an even-handed description of the entire interaction region. Geometry optimization and force constants were calculated by using the 3-21G basis set.[3a] Energies and gradients of selected geometries were recalculated with 6-31G**.[3b]

The saddle point for the reaction was located (see Figure 1) and was found to lie 3.9 kcal/mol above the reactants (both energies calculated with the 6-31G** basis set). This energy difference becomes 4.4 kcal/mol with the zero point energy correction included. The force constant matrix has one negative
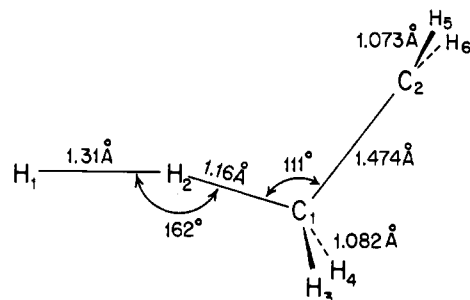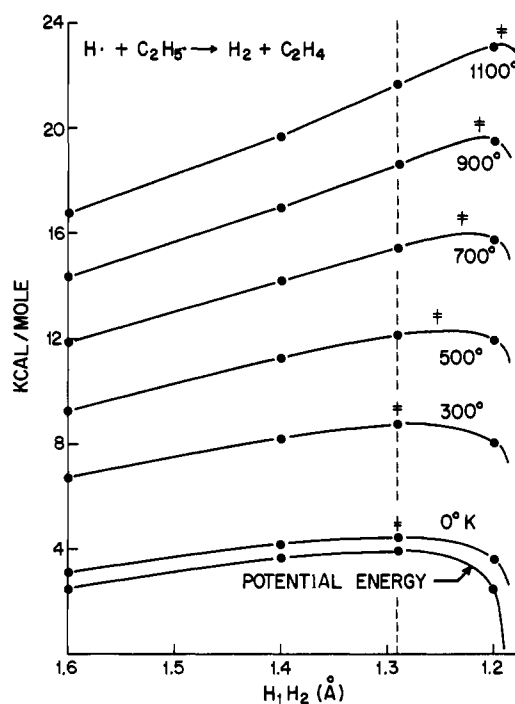

Figure 2. Free energy curves (1 M standard state) for reaction 1 as a function of temperature (K). Each curve is separately referenced to the free energy of reactants at the given temperature. The PE curve was recalculated with the 6-31G** basis set. The saddle point is indicated by the vertical dotted line.

eigenvalue ($1142i$ cm^{-1}) corresponding to the asymmetric $H_1H_2C_1$ stretch. We are not aware of any kinetic studies of reaction 1, but such a high barrier is unprecedented for small radicals. Although this barrier height may be an artifact of the basis set and limited CI, our present purpose concerns the *temperature dependence* of the TS geometry.

A conventional TST calculation of the rate constant[4] would use the vibrational frequencies of the saddle point to calculate the free energy of activation. Our experience with tetramethylene[1] has shown that this can give misleading results. A more appropriate choice of TS structure is at the top of the "free energy" barrier.[5,6] Truhlar[6] has given a convenient computational for-

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malism, based on variational transition-state theory, for finding this barrier. Implementation of Truhlar's canonical variational theory[6] (CVT) requires a somewhat arbitrarily defined reaction path from reactants to products which passes through the saddle point. The barrier is determined as a point on this path. Our path is parametrized by the H_1H_2 distance.[7] Next, the force constant matrix is evaluated at regular intervals along the path to create a free energy curve whose maximum corresponds to the TS. We have done this[8] at five geometries: H_1H_2 = 20.0 (reactants), 1.60, 1.40, 1.31, 1.20 Å. Free energies were calculated from the partition functions as a function of H_1H_2 distance and temperature, and the curves are shown in Figure 2. The internal rotation was treated by assuming a potential of $^1/_2V_0(1 - \cos n\sigma)$ where n = 3 for ethyl radical and n = 2 in the saddle point region. V_0 is the calculated barrier height. The classical hindered rotation partition function was then calculated and the quantum mechanical partition function estimated by the method of Pitzer and Gwinn.[9]

The most striking feature of the results is that the TS structure shifts away from the saddle point toward the products at higher temperature. (Interpolated maxima are obviously uncertain, but the qualitative conclusion holds.) This can be understood simply by noting that entropy decreases from left to right in Figure 2, and $-T\Delta S^\ddagger$ tends to dominate $\Delta G^\ddagger$ at higher temperature. At 1100 K, for example, the 1.2-Å structure is 1.46 kcal higher than the saddle point in free energy, but 1.45 kcal lower in PE. Tightening the internal rotation accounts for 0.76 kcal, 1.46 kcal comes from vibration, 0.05 kcal from rotation, and 0.64 kcal from zero point energy. In general, *the TS structure shifts in the direction of lower entropy as the temperature is raised.*

One of several important consequences of this principle is that the Arrhenius activation parameters predicted by TST and CVT differ significantly as the temperature increases. At 900–1100 K CVT gives log ($A/M^{-1} s^{-1}$) = 11.2, E_a = 5.5 kcal/mol, whereas TST (obtained from Figure 2 by locating the TS at H_1H_2 = 1.31 Å at all temperatures) gives log A = 11.9, E_a = 6.4 kcal/mol.[10]

A large part of mechanistic chemistry is directed toward discovering the structure and properties of the TS. It is therefore important to keep in mind that properties determined at one temperature (e.g., reactivity–selectivity relations, charge distributions, etc.) may not be transferable to another temperature, especially if the barrier is low. For example, Giese[11] has studied the addition of carbenes to olefins and shown that the carbene selectivities converge on an isoselective temperature and are opposite on either side of that temperature. Houk[12] has shown that this phenomenon can be qualitatively modeled by a simple enthalpy/entropy competition along the reaction path which gives rise to a strong variation of TS structure with temperature. In theoretical investigations, the location of a saddle point on the PES is only the first step toward locating the TS. For low barriers (< ca. 5 kT) or flat barriers, *no claim of a TS structure can be believed without a variational search* (e.g., CVT[6]).

The temperature dependence of the TS structure is actually greater than Figure 2 suggests. At the saddle point the C_2H_4 moiety resembles ethyl radical more than ethylene, but the reverse is true at H_1H_2 = 1.2 Å, where C_1H_2 is now 1.30 Å. At this geometry C_1C_2 = 1.417 Å, C_1H_3 = 1.078 Å, and $H_3C_1C_2$ =

116.7°, closer to their respective values in ethylene (1.335 Å, 1.073 Å, 121.8°) than in ethyl (1.536 Å, 1.084 Å, 110°). We conclude that at high temperature (> ca. 900 K) *the TS for this strongly exothermic reaction resembles the products more than the reactants and does so increasingly as the temperature is raised.*

Novel Dimerization Reaction of Bis(alkylthio)cyclopropenethiones Affording Tetrakis(alkylthio)thieno[3,4-c]thiophenes

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Because of its strain, aromatic character, and high reactivity, cyclopropenethione is of considerable current interest. Although a number of reactions have been reported, they are concerned with only two cyclopropenethiones, 2,3-diphenyl-[1] and 2,3-diamino-[2]substituted ones. Recently, we uncovered a new and unusual dimerization reaction of 2,3-bis(alkylthio)cyclopropenethiones (**1**) to give 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]thiophenes (**2**), derivatives of which are 10π nonclassical thiophenes containing tetravalent sulfur. The thieno[3,4-*c*]thiophene system has received much attention from synthetic and theoretical chemists,[3] but the synthetic work reported so far has been confined to the trapping of unstable 1,3-dimethyl- and 1,3-dicarbomethoxythieno[3,4-*c*]-thiophenes by *N*-phenylmaleimide and the synthesis of the isolable 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene by Cava and co-workers.[4] Herein, we now report the preparation of thieno[3,4-*c*]-thiophene **2** from **1** and the structure determination by x-ray crystallography.

a, $R_1 = R_2 = t\text{-Bu}$
b, $R_1 = t\text{-Bu}, R_2 = Et$
c, $R_1 = t\text{-Bu}, R_2 = Me$
d, $R_1 = R_2 = i\text{-Pr}$
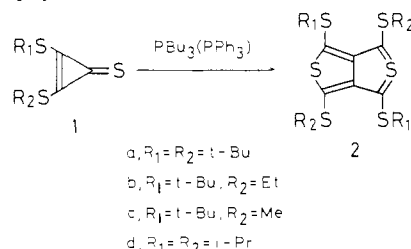
A benzene solution of 2,3-bis(*tert*-butylthio)cyclopropenethione (**1a**)[5] and 1.3 equiv of tributylphosphine was refluxed with stirring

(7) Truhlar[6] recommends a steepest-descent path in mass-weighted cartesian coordinates. Our path is determined by varying the H_1–H_2 distance in small increments from the saddle point and requiring that the potential energy be a minimum at each incremental value of this distance.

(8) Translations and rotations were projected out before diagonalization of the force constant matrix. In the saddle point region the gradient direction then appeared as a large negative eigenvalue.

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