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Ab Initio CI Treatment of the Termolecular Reaction of $3H_2$: Hexagonal H_6

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Abstract: The results of a near-exact theoretical treatment of the termolecular reaction of three H_2 molecules, reacting via a six-centered transition state, are reported. The transition state considered is that of a hexagon with D_{6h} symmetry. The energetics of the reaction were calculated with a large contracted [4s3p2d1f] Gaussian basis set, combined with a multireference configuration interaction calculation where all six electrons were correlated. The reference wave function was determined in a CASSCF calculation for six electrons in six active orbitals. We find the energy barrier to lie at 67.4 kcal/mol at this level and at 66.5 kcal/mol if a mutireference Davidson's correction is employed. Our calculations were calibrated against a full CI, which employed a double-ζ plus polarization basis. On the basis of these calculations, we estimate that our results are within ±1 kcal/mol of the exact, fixed nuclei result for this transition state. This large barrier height is consistent with the absence of HD formation in shock-heated mixtures of H_2 and D_2 when atomic mechanisms are excluded by the experimental conditions.

I. Introduction

The general exchange reaction

$$AB + XY \rightarrow AX + BY \qquad (1)$$

is well-known in chemistry, although in the gas phase such reactions are rare and only occur for highly restricted families of reactants. An example of one of the simplest such reactions is the isotope-exchange reaction between molecular hydrogen and deuterium to produce HD. This reaction has received much attention, since up until a few years ago there appeared to be a sharp divergence between the best experimental results and the most detailed quantum chemical calculations because virtually all of the theoretical studies have been at odds with the first experimental results on this reaction.[1] In the initial shock tube work, Bauer and Ossa[2] found a low activation energy of 39–44 kcal/mol for a "bimolecular reaction". Subsequent shock tube studies implied a confirmation of this result.[3,4] Later studies[5-7] suggested that an atomic chain mechanism would be dominant. Most of this earlier work has been summarized by Bauer.[1] The experimental resolution of this reaction has come from the work of Lifshitz and co-workers[8] who, using an ultraclean shock tube coupled to an atomic resonance absorption spectrometer (for measuring H atom concentrations by Lyman α absorption), found no, or $\leq 1\%$ HD, production if no H atoms were present. They suggested that the high rate for H/D exchange seen previously was caused by hydrogen atoms generated by impurities, probably from traces of pump oil or hydrocarbons in the reagent gases. More recently, Rabinowitz and Gardiner[9] have confirmed a lower limit of 70 kcal/mol for the barrier to a four-center molecular exchange using optical spectroscopy in a shock tube. This technique was developed to avoid the possibility of impurity contaminants at the sampling orifice or at the walls.

A critical assumption in the early theoretical analysis of this reaction centered on the assertion that it proceeded via a bimolecular mechanism. However, the four-center reaction shown in (2) is a classic example of a Woodward–Hoffmann symmetry-

$$H_2 + D_2 \rightarrow 2HD \qquad (2)$$

forbidden reaction, at least if a square-planar transition state[10] is assumed. The past 20 years have seen extensive theoretical calculations on a variety of possible transition-state structures,[11] some of which could be ruled out immediately on the basis of symmetry arguments alone,[12] while all of the others considered produced calculated barriers that were substantially above the dissociation energy of an H_2 molecule. These theoretical calculations had thus provided a quantitative basis for the symmetry-forbidden aspect of this reaction. Furthermore, the early theoretical calculations strongly supported the suggestion that a bimolecular mechanism involving H/D exchange was not possible since all suggested low-energy pathways involved the rupture of the H_2 bond.

Although the Woodward–Hoffmann rules do provide information as to the "symmetry-allowed" nature of a transition state, they do not provide any information as to the energy of such a structure. In 1970 Wright[13] proposed an alternative termolecular process

$$2H_2 + D_2 \rightarrow 2HD + H_2 \qquad (3)$$

and tried to substantiate it with SCF calculations. His SCF calculations with a double-ζ basis placed the energy of H_6 above the $2H_2 + 2H$ asymptote. Subsequent calculations were offered by Dixon, Stevens, and Herschbach[14] who performed a series of ab initio SCF-CI calculations on H_6 using an STO basis of the form {2s1p1d}. At the SDCI level, including a correction for quadruple excitations,[15] they obtained a ΔE of 68.7 kcal/mol for the energy of H_6 above three ground-state hydrogen molecules. The $D_e(H_2)$ at this level was 107.7 kcal/mol. These calculations

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Table I. Total Energies, Bond Distances, and Symmetric Stretching Frequencies for H_6 and the $3H_2$ Asymptote[a]

basis set	wave function	$-E(3H_2)$	$R_e(H_2)$	$\omega_e(H_2)$	$-E(H_6)$	$R_e(H_6)$	$\omega_e(H_6)$	$D_e(H_2)$	$\Delta E(H_6)$
DZP	CAS	3.448 929	0.755	4232	3.319 314	1.007	1845	93.9	81.3
DZP	SOCI	3.499 216	0.743	4465	3.386 284	0.983	1971	104.4	70.9
DZP	SOCI+Q	3.500 096	0.742	4473	3.387 854	0.983	1976	104.6	70.4
DZP	FCI	3.499 818	0.742	4470	3.387 198	0.983	1973	104.5	70.7
[4s3p2d1f]	SOCI	3.520 856	0.742	4381	3.413 473	0.988	1926	108.9	67.4
[4s3p2d1f]	SOCI+Q	3.522 315	0.742	4387	3.416 354	0.987	1928	109.3	66.5

[a] Total energies in E_h, bond lengths in angstroms, frequencies in reciprocal centimeters. The energy differences are reported in kilocalories per mole.

clearly showed the energy of H_6 in D_{6h} symmetry to be below the dissociation energy of H_2, and therefore a molecular, but not bimolecular, mechanism could indeed be considered for the exchange process. This D_{6h} symmetry structure was confirmed as a transition state, with one negative curvature direction of b_{2u} symmetry, at the CI level using a double-ζ STO basis.

In the early 1970's there was further experimental evidence that suggested the possibility of a termolecular reaction when Dixon, King, and Herschbach investigated[16] the halogen exchange between bromine and chlorine using crossed molecular beams, as shown in (4). No halogen exchange was found at collision

$$Br_2 + Cl_2 \rightarrow 2BrCl \qquad (4)$$

energies up to 25 kcal/mol. However, they did observe[17] the termolecular halogen-exchange reaction, with Cl_2 dimer at thermal energies less than 3 kcal/mol. This sequence of experiments was consistent with the suggestion that a termolecular process for H/D exchange would be symmetry-allowed and would proceed through a D_{6h} symmetry transition state.

Although the initial calculations cited above were considered to be state of the art at the time they were performed, it was not possible to account for higher order excitations beyond the use of Davidson's correction.[15] The calculations at the asymptote were quite accurate, giving a D_e for H_2 within 2 kcal/mol of the exact value.[18] Since the Davidson correction for the H_6 transition state was not small—5.7 kcal/mol—a more refined treatment could prove it to be much larger: the missing higher order excitations could significantly lower the calculated barrier. With the advent of large-memory computers, it is not possible to perform full configuration interaction (FCI) calculations on systems with up to eight electrons with modest but realistic basis sets, double-ζ plus polarization.[19-21] These studies have shown that excellent agreement with the full CI results can be obtained by using a complete active space self-consistent field (CASSCF) calculation[22] followed by a multireference singles and doubles CI (MRCI).

There have also been advances in the determination of good one-particle basis sets to be used with the above techniques to account for correlation. Almlöf and Taylor[23] have recently designed new and very efficient general contractions of large primitive Gaussian basis sets, based on atomic natural orbitals (ANO's), with very little contraction loss in either the SCF or in the correlation energy. These basis sets span both the valence and polarization spaces and provide contraction errors of "chemical accuracy", within 1 kcal/mol. We have chosen to employ these large one-particle basis sets in this investigation of the structure and energetics of H_6.

In an effort to resolve the previous theoretical uncertainties and ambiguities we report here several calculations on the H_6 system. The first calculations, intended as a calibration, were based on a full CI treatment employing a modest DZP basis set while the remaining calculations employed the best approximate treatment of electron correlation utilizing a large one-particle basis to find the energy of the H_6 transition state relative to three separated H_2 molecules. These results yield an essentially exact ab initio solution for this six-electron problem.

II. Methods

The first set of calculations consisted of both full CI as well as multireference CI treatments of electron correlation. These were done with a DZP basis with the s orbitals from Dunning[24] and a p orbital with an exponent of 1.0. This basis set had the form (4s1p)/[2s1p]. The full CI calculations were done with a modified version of the Knowles and Handy[25] code interfaced to the MOLECULES-SWEDEN program system. The full CI calculations were performed on the NAS Cray-2 and were composed of 2.1 million determinants or about 750 000 configurations. When this same basis set was used, CI calculations were performed where all configurations from a CASSCF were used as references in the multireference CI. The CASSCF calculations featured six electrons in six active orbitals, giving 58 configuration state functions (CSF's). All configurations from the CASSCF were used as references in the calculations that are denoted MRCI, for multireference CI. The multireference analogue of the Davidson correction was included and is denoted +Q. This correction can be written as $\Delta E_{SD}(1 - \sum_r C_r^2)$, where ΔE_{SD} is the difference between the energy of the reference CSF's and the multireference CI. The C_r are the coefficients of the reference configurations in the MRCI wave function. All of these calculations were performed with the MOLECULE-SWEDEN program system[26,27] on the NASA Ames Cray XMP/48. A second set of calculations was done with the much larger one-particle basis of Almlöf and Taylor.[23] This basis set was derived from an (8s6p4d3f) primitive set and was contracted to [4s3p2d1f]. The 3s and 4p components of the cartesian functions were delected, yielding 180 contracted functions on H_6. Calculations up through the level of MRCI+Q were performed as described above with the NAS Facility Cray2. The CI calculations for the dissociated product limit were performed on three H_2 molecules each separated by $20a_0$ in a linear structure, to minimize size-consistency errors. The calculations on hexagonal H_6 employed D_{6h} symmetry geometries. For both structures, the wave functions were actually calculated in D_{2h} symmetry. The H–H distance in the three hydrogen molecules and in H_6 was optimized at the various CI levels, using a finite difference grid of $0.05a_0$.

In order to account for vibrational corrections, a set of calculations was also performed at the SCF level on H_6, within D_{6h} symmetry, using a TZP basis[28] of the form (5s1p)/[3s1p] at the SCF-optimized geometry. The geometry was gradient optimized[29] and a complete molecular force field was determined with analytic second derivatives.[30] These calcu-

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lations were done with the program[31] GRADSCF on the Cray XMP/48.

III. Results

The total energies, bond distances, and frequencies for the symmetric stretch are given in Table I. The bond distances and frequencies were fitted by functions in $1/r$. This method has been shown to provide a more rapidly convergent expansion of the potential energy about a given point than that of a simple r expansion and has been the subject of extensive discussions in the literature,[32] since it does allow for the incorporation of some of the anharmonicity in the surface. The fit in $1/r$ yields essentially the same bond distances and energies, as one in r, but shows some deviations in the computed frequencies. The experimental[18] bond distance for H_2 is 0.741 44 Å. All of the calculations give slightly too long a value for r_e, 0.002 Å longer than experiment, except for the CASSCF calculations at the DZP level, which yield a value that is 0.014 Å too long. The experimental value for ω_e is 4401 cm^{-1} with an $\omega_e x_e$ term of 121 cm^{-1}. At the DZP level, (excluding the CASSCF values) the frequencies are all to high by about 70 cm^{-1} while the calculations with the [4s3p2d1f] basis produce a frequency that is too low by about 10–20 cm^{-1} when compared to experiment.

The total energies for the dissociated product at the DZP level show that the MRCI+Q calculations overestimate the true full CI energy by 0.3 mE_h (0.2 kcal/mol). For hexagonal H_6 the MRCI total energies underestimate the full CI results by 0.9 mh (0.6 kcal/mol) whereas the MRCI+Q results overestimate the full CI result by 0.7 mh (0.4 kcal/mol). Thus, the differences in total energy are slightly larger for the transition state than for the $3H_2$ asymptote. At the full CI level with the DZP basis the barrier is 70.7 kcal/mol. The barrier at the MRCI level is 0.2 kcal/mol higher and the barrier at the MRCI+Q is 0.3 kcal/mol lower. The computed dissociation energies (D_e) of H_2 are also given in Table I. The CI results with the DZP basis are about 104.5 kcal/mol, which is 5 kcal/mol less than the experimental value of 109.5 kcal/mol.[18] The MRCI+Q results overestimate the full CI dissociation energy by less than 0.1 kcal/mol.

The comparison of the second-order CI results with those of the full CI offers us a direct calibration of the n-particle space and allows us to gauge the accuracy of the second-order calculations as the one-particle space is saturated. In previous calculations the multireference Davidson's correction was found to overestimate the full CI results for a variety of molecules.[19,20] In our case the overestimation of the full CI result by the MRCI+Q calculation is not surprising due to the rather small number of electrons involved. The correction for quadruples tends to the incorrect limit for two-electron systems since the +Q correction for two electrons is nonzero even though there are no higher order excitations. Even with six electrons, this treatment can produce some residual errors.

The D_e of H_2 is dramatically improved by increasing the size of the one-particle basis set. When the large ANO basis is used, the D_e of H_2 is within 0.6 kcal/mol of the experimental value at the MRCI level and within 0.3 kcal/mol at the MRCI+Q level. Thus, the D_e of H_2 is calculated to well within the accepted chemical accuracy of ±1 kcal/mol at both levels. With the large ANO basis set, the barrier heights are 67.4 kcal/mol at the MRCI level and 66.5 kcal/mol at the MRCI+Q level. On the basis of the full CI results with the DZP basis, we estimate that a full CI calculation with this ANO basis would yield a barrier of 66.9 kcal/mol. Considering the errors in the dissociation energy of H_2, this barrier height should be within 1 kcal/mol of the true barrier for this process.

The symmetric stretch frequency for H_6 is about 1970 cm^{-1} at the DZP level for all of the correlated wave functions, while improving the basis set lowers the frequency to 1927 cm^{-1}. On the basis of the results for H_2, this fit can be expected to be 20–25 cm^{-1} too low and the "harmonic" stretching frequency is estimated to be 1950 cm^{-1}. This value is similar to the value of 1936 cm^{-1} obtained in the previous CI calculations.[14]

Table II. Vibrational Frequencies (cm^{-1}) for H_6 (D_{6h})

sym	ν(SCF)	ν(SDCI)^a	descriptn
a_{1g}	2005	1936	symm str
a_{2u}	1308	1484	out of plane puckering
b_{1u}	704	1122	trigonal deformn
b_{2u}	3226i	3038i	asym str (TS)
e_{2g}	2318	1908	asymm deformn
e_{2g}	1612	1574	asymm deformn
e_{1u}	2169	1978	asymm str/deformn
e_{2u}	1263	1326	out of plane torsion

^{a}Values taken from ref 16.

As discussed below, a complete treatment of the barrier height should include the zero-point corrections to the energy. To this end, a complete force field for H_6, in D_{6h} symmetry, was determined analytically at the SCF level with a TZP basis. There is one negative curvature direction of b_{2u} symmetry, showing that hexagonal H_6 is a true transition state. The motion of this mode leads to dissociation to three H_2 molecules. This is in agreement with the original finite difference calculations.[14] The SCF symmetric stretch frequency of 1908 cm^{-1} is slightly low when compared to our correlated estimate of 1950 cm^{-1} and to the value of 1936 cm^{-1} found previously.[14] An examination of the remaining frequencies found in Table II also shows reasonable agreement. The SCF degenerate stretches are somewhat higher in frequency than the CI–SD values, as is the value of the imaginary frequency. The greatest discrepancy is found in the lowest energy b_{2u}, mode, which we find to be 350 cm^{-1} lower. From this data the unscaled zero-point energy at the SCF level is 26.2 kcal/mol. We calculate a value for $\omega(H_2)$ to be 4598 cm^{-1} as compared to the experimental value of 4401 cm^{-1}. If we scale the zero-point energy of the hexagonal H_6 transition state by the ratio of $\omega(H_2)_{expt}/\omega(H_2)_{calc}$ = 0.957, we produce a scaled value for the zero-point energy of hexagonal H_6 of 25.1 kcal/mol. If we include the isotopic substitution of D_2H_4 and D_4H_2, the values for the zero-point energy become 22.9 and 20.4 kcal/mol, respectively.

IV. Discussion

Our calculations have enabled us to establish unambiguously that the potential energy barrier is below 67 kcal/mol for the termolecular process. This is only possible since we were able to calibrate the results against full CI calculations, which allow us to extrapolate the results of an approximate treatment of electron correlation as the basis set is saturated. Previous CI calculations on this system could only speculate as to the effects of saturation in both the one and the n-particle spaces, while this investigation has allowed us to provide realistic error estimates. In fact most of the effect of higher order excitations is accounted for by the Davidson correction in agreement with recent work on a variety of small molecules.[19–21]

In order to obtain barrier heights as a function of temperature, $\Delta E(T)$ and $\Delta H(T)$, we must include the effects of $\Delta E(T)_{trans}$, $\Delta E(T)_{rot}$, and $\Delta E(T)_{vib}$, which are the translational, rotational, and vibrational contributions to the energy. The $\Delta E(T)_{vib}$ term includes the difference in zero-point energies, ΔZPE, and the vibrational energy as a function of temperature. The term ΔZPE can be calculated from the calculated vibrations of H_6 and the known frequency of H_2. This term is not inconsequential and leads to an increase in the barrier of 10.0 kcal/mol. The $\Delta E(T)_{trans}$ and $\Delta E(T)_{rot}$ terms lower the barrier by $3RT$ and $1.5RT$, respectively. At temperatures up to room temperature, the difference in vibrational energy as a function of temperature can be ignored.[14] At 300 K, the ΔE for the barrier height is found to be 72.2 kcal/mol. Converting from ΔE to ΔH, assuming ideal gas behavior, we find ΔH(300 K) to be 73.0 kcal/mol. This enthalpy barrier should be accurate to ±1 kcal/mol. At temperatures above 1000 K $\Delta E(T)_{vib}$ is no longer negligible, and we thus obtain enthalpy barriers ΔH(1000 K) of 69.4 kcal/mol and ΔH(1500 K) of 70.6 kcal/mol. The most recent shock tube studies of reaction 4 by Rabinowitz and Gardiner[9] gave a lower bound of 45 kcal/mol for the barrier height of this six-center reaction. This

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(31) GRADSCF is an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research Institute.

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was based on the absence of detectable isotope exchange during the induction period over a temperature range of 1200–1800 K. Our barrier of about 70 kcal/mol is significantly above their lower bound. The energy of the hexagonal transition state is clearly below the dissociation limit of an individual hydrogen molecule. This can, in principle, provide a molecular pathway for isotope exchange distinct from an atomic pathway. (As discussed in the Introduction, it is clear that a bimolecular pathway has not been observed in shock tubes.)

Knowledge of potential energy differences alone is often not sufficient to completely characterize the course of a chemical process. Internal energy distribution and content, as well as the dynamical behavior of a system often determines much of the chemistry observed. If a termolecular process were to take place via a six-centered transition state as investigated here, dynamical studies would also require some knowledge of the tunneling probability for the hydrogen atoms. This, however, is beyond the scope of this investigation. In this light we should mention that there has been one quasi-classical trajectory study[33] of the H_6 termolecular reaction, with the reactants being a van der Waals bound dimer and a hydrogen molecule.

$$A_2B_2 + C_2 \rightarrow AB + AC + BC \qquad (5)$$

The potential surface used was constructed to mimic a model reaction with a barrier height of 69 kcal/mol. If only translational energy is provided, this study predicted a dynamic barrier of 90 kcal/mol. However, vibrational energy did significantly enhance the termolecular process. Unfortunately, this study had too few trajectories to provide statistical significance. In a related experiment, Herman[7] studied the reverse reaction to (2), where HD was excited to $v = 5$ ($\Delta E = 47$ kcal/mol) by using a cw intracavity dye laser, but no D_2 production was observed. This laser experiment was not sensitive enough, however, to detect products from a six-center reaction. In another experiment Bauer and co-workers[34] excited room-temperature H_2 or D_2 to $v = 1$ in a bulb using stimulated Raman scattering. They did observe HD product accounting for it by $v - v$ collisionally pumped H_2 ($v \geq 3$) and a bimolecular process. Vibrational enhancement coupled with a termolecular process could also account for this yield although the barrier used in the kinetic model calculations was somewhat low.[14] It is also possible that HD was produced in the stimulated Raman bulb experiments from catalysis on the walls or, as suggested by Herman, from H atoms produced by collisions. All of the results seem to be consistent with the failure to observe a bimolecular mechanism for H/D exchange in H_2/D_2 mixtures under any of the experimental conditions employed thus far.

V. Conclusions

We have reported here an investigation of the transition state for the termolecular reaction involving H_2/D_2 exchange to produce HD. This reaction has been of long-standing interest since historically there has been a sharp divergence between the best experiments and the most detailed theoretical calculations. The calculations presented here suggest that a termolecular process is energetically and possibly even dynamically feasible. The full CI calibration results have shown that with present computational methods we can provide energies within the accepted chemical accuracy of ±1 kcal/mol. The calculations were done with a large one-particle basis, and the level of correlation accounts for most of the molecular correlation in this six-electron system. Detailed studies of other termolecular processes will be forthcoming.

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Single-Crystal EPR Spectrum of the Phosphido-Bridged Radical $Fe_2(CO)_7(\mu\text{-}PPh_2)$

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Abstract: The EPR spectrum of the 33e phosphido-bridged radical $Fe_2(CO)_7(\mu\text{-}PPh_2)$ has been measured in single crystals of the diamagnetic host $FeCo(CO)_7(\mu\text{-}PPh_2)$ at 77 K. **g** and hyperfine interaction tensors for a ^{31}P and two distinct ^{13}C nuclei were determined for the radical in an orthogonal axis system of the triclinic host whose crystal structure was established by X-ray diffractrometry (space group $P\bar{1}$; a = 9.057 (2) Å; b = 13.001 (3) Å; c = 8.713 (3) Å; α = 105.25 (2)°; β = 95.21 (2)°; γ = 84.32 (2)°; Z = 2). The values of the tensor components and their directions in the crystal structure clearly show that the radical is isostructural with the host molecule. Unpaired spin density is essentially confined to the pentacoordinated iron nucleus and two of its carbonyl ligands. These ligands and the two iron nuclei form the equatorial plane (xy) of a distorted trigonal-bipyramidal structure in which the unpaired electron occupies an Fe d_{xy} orbital. Extended Hückel molecular orbital calculations are in excellent agreement with the experimental findings.

In the past 10 years or so considerable progress has been made in the structural determination of precariously stable organometallic molecules. EPR spectroscopy has played no small role in this endeavor, although much still remains to be accomplished. The EPR spectrometer used in conjunction with single-crystal samples offers an unequalled probe for the determination of the atomic orbital composition of the ground electronic wave function of a free radical. As a bonus, the technique supplies information on the disposition of electronically excited states through the measurement of the **g** matrix. While the structures of a number of mononuclear transition-metal radicals have now been established,[1] less progress has been made for polynuclear species.

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