Table IV. Transmission Coefficient D of DHSiO and HDSiO

	$-\ln D$ $((m_e/\mathrm{amu})^{1/2})$	
E (kcal/mol)	DH	HD
105	3.05	3.65
100	7.95	9.54
95	12.97	15.61
90	18.21	21.90
85	23.64	28.48
80	29.27	35.34
75	35.15	42.60
70	41.41	50.96

one is greater and it controls the whole mechanism.

The isotope effect of tunneling is estimated by the transmission coefficient (eq III.5) and is shown in Table IV. Because the transmission coefficients of "DH" are always greater than those of "HD", it is easier for "DH" than "HD" to dissociate through tunneling. This verifies the mechanism of division in the isotope effect of the potential profile along the IRC (Figure 12).

IV. Concluding Remarks

In the present paper, we have studied the new aspect of the "stability" of reaction coordinate. We have emphasized the importance of quantum mechanical dynamics and the accompanying dynamical electronic processes. The mechanism of tunneling crossover is the first characteristic finding. This may be utilized as the global design of potential energy surface of chemical reaction. Secondly, the multistep isotope effect is considered the most typical feature of chemical reaction dynamics where successive rearrangement of atoms takes place. It is remarkable that if we fix SiO in the space, then the essential asymmetry is observed in the direction of dissociation between HDSiO and DHSiO as the result of the multipe isotope effect. Using this property, we may design the "dynamic" stereoselective reaction or the orientation selective transfer of isotopes in amorphous materials. Since the symmetry of molecular vibrational modes plays an important role in the reaction dynamics, the mode-selective chemistry should be the most direct application. Irradiation by laser may be most effective. The interplay between the tunneling crossover and the multistep isotope effect may then yield fruitful applications. This direction of research should be enhanced in the future.

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Molecular Structure of Allyl Radical from Electron Diffraction

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Abstract: The molecular structure of free allyl radical was determined from high-temperature electron diffraction augmented with mass spectrometry. The free radicals, with 75% relative abundance, were produced by vacuum pyrolysis of 1,5-hexadiene at 960 °C in the diffraction experiment. The data are consistent with a planar symmetric geometry, C–C bond length (r_g) 1.428 ± 0.013 Å, and C–C–C bond angle 124.6 ± 3.4°.

For the first time we determined the molecular structure of the free allyl radical from high-temperature electron diffraction augmented with mass spectrometry. Application of our technique[2,3] to a direct study of this unstable reactive species yielded experimental values of bond length, bond angle, and vibrational amplitudes. Our results are consistent with previous structural information on the allyl radical from ESR,[4] IR,[5] and PE[6] spectroscopy and quantum chemical calculations.[7]

The allyl radicals were generated by vacuum pyrolysis of 1,5-hexadiene[5] in a quartz reactor at about 960 °C in our electron diffraction nozzle system.[8] Electron intensity[9] and quadrupole mass spectrometric[10] measurements facilitated the choice of experimental conditions. The nozzle capillary (length of 25 mm) was wider (1 mm),[11] the vapor pressure was lower (<0.2 Torr), the primary electron beam intensities were higher (0.2 and 0.6 μA for 50 and 19 cm camera ranges, respectively), and the exposures were longer (6–10 min) than usually employed. Accordingly, the noise level of the data was also higher than usual.

The inlet system was tested in a separate mass spectrometric unit[12] to determine the temperature dependence of the vapor composition. The following relative amounts of the pyrolysis products were found at the conditions of the diffraction experiment: radical 70 mol %, propene 10 mol %, allene 15 mol %.

The electron diffraction analysis was similar to that described elsewhere.[13] Molecular intensities and radial distributions are shown in Figures 1 and 2.

The radical geometry was defined by C–C and C–H bond lenghts and C–C–C and C–C–H bond angles. Local C_{2v} symmetry was assumed for the CCH_2 moieties. A mean C–H bond length was refined assuming the methylene C–H to be shorter by 0.002 Å than the methine C–H.[7] No information could be gained on the possible deviation of the CH_2 groups from the CCC plane.

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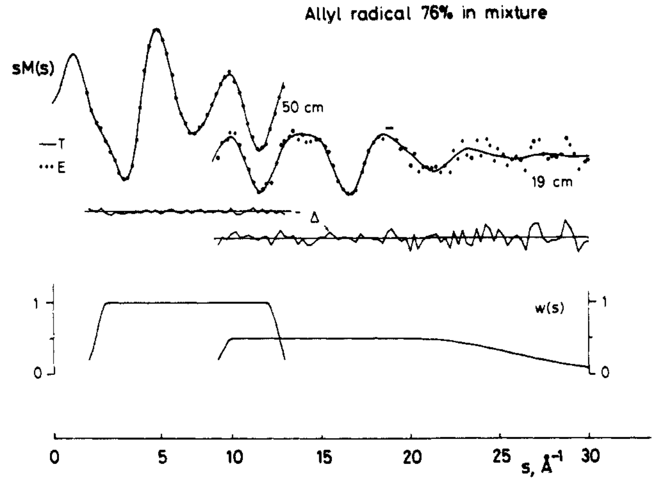

Figure 1. Experimental (E) and theoretical (T, see Table I) molecular intensities ($sM(s)$), differences ($\Delta = E - T$), and weights ($w(s)$) used in the refinements. For the 50 cm camera range only every second point is shown. R values: 50 cm 0.048, 19 cm 0.326, total 0.101.

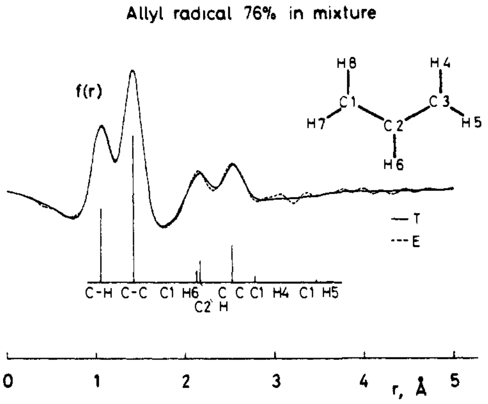

Figure 2. Experimental (E) and theoretical (T) radial distributions with damping constant $a = 0.002$ Å^2. Relative contributions from the allyl radical are indicated.

Mean amplitudes of vibration, l(SP), and perpendicular correction terms, K(SP),[14] were computed for the electron diffraction nozzle temperature of 960 °C, employing force fields adjusted[15] to experimental frequencies of allyl radical,[5] propene,[16,17] and allene.[18] Some computed l values and, for similar distances, their differences were kept constant in the refinements.

Table I. Molecular Parameters of Allyl Radical from Electron Diffraction (ED)[a,b] and Spectroscopic Calculations (SP)

parameter[c]	r_g(Å); $\angle_a$ (deg)	l(ED), Å	l(SP), Å	K(SP), Å
C–C[d]	1.428 (13)	0.069 (20)	0.061	0.008
(C–H)$_{\text{mean}}$[e]	1.069 (16)	0.088 (18)	0.080	h
∠C–C–C	124.6 (34)			
∠C2–C–H	120.9 (34)			
C···C	2.528 (20)	0.088 (12)[f]	0.098	0.002
C2···H	2.178 (38)	0.116 (20)[g]	0.115	i
C1···H6	2.145 (70)	0.117 (20)[g]	0.116	0.025
C1···H4	2.808 (20)	0.188 (13)[f]	0.198	0.070
C1···H5	3.480 (17)	0.353 (126)	0.118	0.077

[a] Estimated total errors (see text) are parenthesized in units of the last digit. [b] Sample composition from ED data: allyl radical 75 (11) mol %, propene 10 (assumed) mol %, allene 8 (9) mol %, 1,5-hexadiene 7 (4) mol %. [c] See Figure 2 for the numbering of atoms. [d] Asymmetry parameter $\kappa = 4.8 \times 10^{-6}$ Å^3 assumed. [e] $\kappa = 13.8 \times 10^{-6}$ Å^3 assumed. [f,g] l's with fixed differences. [h] K for C3–H4 = 0.159 Å, C3–H5 = 0.290 Å, C2–H6 = 0.035 Å. [i] C2···H4 = 0.073 Å, C2···H5 = 0.162 Å.

The allyl radical alone and mixtures of the allyl radical with other species were used to fit the experimental data. Known geometries from room temperature experiments were used for propene[16] and allene.[19] The parent 1,5-hexadiene was also considered with an estimated geometry. Possible temperature effects in the assumed geometries were introduced as enlargement scale factors between 1 and 3%. However, their introduction resulted in changes of the parameters for the radical within one standard deviation only, while the least-squares fit has somewhat worsened. A more elaborate approach was not feasible, which would include different scale factors for all distances, as some may even "shrink" at higher temperatures. The assumed geometries were thus kept at their room temperature experimental data. The uncertainties related to the presence of mixture were considered also in the error estimation (vide infra).

The known propene geometry alone did not fit the experimental data well, and when refined some parameters became unreasonable. For example, one of the two C–C bonds of propene appeared to be shorter than in the room temperature experiment (1.483 Å vs. 1.503 Å[16]). The allyl radical alone and in mixture gave reasonable geometries. A notable difference occurred, however, between the two refinements in l(C–C), viz., 0.085 Å vs. 0.069 Å, respectively, the latter being closer to the spectroscopically calculated value 0.061 Å. The mass spectra also indicated strongly the presence of other species.

The parameters of the radical selected as the best representation of this study originated from a refinement on the mixture and are given in Table I. The symmetric model fits the diffraction data well; attempts to introduce unequal C–C bonds did not improve the agreement, and the resulting differences were comparable with their standard deviations.

Three components were considered in estimating total errors (see Table I): experimental scale error (0.2%), standard deviation from the least-squares calculations (multiplied by $\sqrt{2}$ to take consequences of data correlation into account),[13] and parameter differences in the refinements with the allyl radical alone vs. the mixture to take into account the uncertainty of the vapor composition. The estimated total error for l(C–H)$_{\text{mean}}$ was doubled in Table I to make it more realistic.

The agreement between the electron diffraction and the ab initio multiconfiguration Hartree–Fock calculated[7] structures is excellent for the C–C–C bond angle of the allyl radical. The experimental C–C bond appears to be longer than the calculated one, 1.388 Å. Part of this can be attributed to the r_g/r_e difference, especially since the experimental r_g refers to a rather high temperature. Also, the experimental estimated total error is relatively large. Note, however, that a longer C–C bond in the free allyl radical as compared with 1.39 Å in free π-allylcobalt tricarbonyl[20] is in accordance with the lowering of the asymmetric stretching vibrational frequency ν_{as}(CCC) in the radical[5] relative to that in the π-complex.[21]

Registry No. Allyl, 1981-80-2; 1,5-hexadiene, 592-42-7.

Supplementary Material Available: Table of total experimental electron diffraction intensities (2 pages). Ordering information is given on any current masthead page.

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