ferred to the carbonyl group of these peptides. Instead, the pmr results suggest to these authors that the acid proton remains hydrogen bonded to the peptide carbonyl oxygen. As the concentration of acid increases, acid–polypeptide interaction and hydrogen binding without proton transfer increases. Intramolecular hydrogen bonding is, therefore, suppressed in favor of intermolecular hydrogen bonding between the acid and the polypeptide. This then is the driving force converting the polypeptide from the helical to the random coil form.

The slight low-field shift and the small degree of line broadening of the I phenolic proton peak in the presence of poly-γ-benzyl-L-glutamate and poly-L-methionine, respectively, encountered in the present studies also suggest that I hydrogen bonds to these polypeptides and that proton transfer does not occur. The pmr spectrum of poly-γ-benzyl-L-glutamate was not altered in the presence of I. This indicates that either the low solubility or the moderate acid strength of I could not elicit peptide confirmational changes of the type previously reported for trifluoroacetic acid–polypeptide systems.[21,23]

Hexachlorophene has now been shown to strongly hydrogen bond to polypeptides. The conclusions from the present investigations are useful in understanding the more complex interactions that occur between I and proteins.

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Reactions of Sulfur Atoms. XIII. Experimental and Calculated Secondary Hydrogen–Deuterium Kinetic Isotope Effect for the S(^{3}P) + Ethylene Reaction

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Abstract: An experimental and theoretical study has been made of the secondary H/D kinetic isotope effect in the addition of S(^{3}P) atoms to ethylene. The values of the experimental k_D/k_H ratios were 1.14, 1.07, and 1.04 for the C_2D_4–C_2H_4, CD_2CH_2–C_2H_4, and *cis*-CHDCHD–C_2H_4 reactant pairs, respectively. Calculation of the isotope effect was carried out within the framework of transition-state theory for two basic models of the transition state, a symmetrical ring and an asymmetrical ring-distorted structure. Either model can be made compatible with the experimental results by an appropriate and reasonable choice for the structural parameters of the transition state. Calculation of the isotope effect arising from each normal vibrational mode clearly shows that, contrary to current notions, the most important single factor inducing a secondary H/D isotope effect in addition reactions involving olefinic double bonds is not the out-of-plane bending motions of the CH bonds, but the gain in the isotopically sensitive vibrational degrees of freedom on going from reactant to activated complex.

The addition of both $^1D_2$ excited and ^3P ground-state sulfur atoms to olefins has been extensively investigated.[1–6] The unique feature of the reaction is that not only singlet, but triplet atom addition as well, follows a stereospecific course. This has been attributed[7,8] to a correlation with an (n,σ^*) excited state of the product thiirane, which retains CC bonding but is unstable with respect to CS ring opening. Thus the product thiirane would form essentially in its final nuclear configuration *via* a symmetric transition state in a suprafacial, spin- and symmetry-allowed concerted step. A conceptual alternative which is also supported by molecular orbital calculations[9] and kinetic considerations is an asymmetrical, ring-distorted ($\angle$(CCS) $\sim$ 100°) (n,σ^*) triplet thiirane with a relatively large (23.6 kcal/mol) energy barrier for rotation around the CC bond. Formation of this intermediate does not conserve orbital symmetry; symmetry conservation, however, is not an *a priori* condition for reaction since, as discussed by Hoffmann and coworkers,[8] symmetry-allowed motions which are facile are initiated in the excited reactants and there is no need to reach the symmetry-allowed state of the product.

There is a small but clearly defined activation energy associated with the reaction.[5] The value of this is 1.5 kcal for the ethylene reaction and gradually decreases with increasing number of alkyl substituents on the doubly bonded carbons to a negative value of -1.5 kcal/mol in the tetramethylethylene reaction.[5] The negative activation energy is interpreted as being due to intersection of potential energy surfaces manifesting the nonadiabatic nature of the reaction. The frequency factor of the reaction is large, of the order

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(3) E. M. Lown, E. L. Dedio, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1056 (1967).

(4) E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *ibid.*, **90**, 7164 (1968).

(5) O. P. Strausz, W. B. O'Callaghan, E. M. Lown, and H. E. Gunning, *ibid.*, **93**, 559 (1971).

(6) J. Connor, A. van Roodselaar, R. W. Fair, and O. P. Strausz, *ibid.*, **93**, 560 (1971).

(7) E. Leppin and K. Gollnick, *Tetrahedron Lett.*, 3819 (1969).

(8) R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, **19**, 113 (1970).

(9) O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, to be published.

of 10^{10} l. mol^{-1} sec^{-1}, and consequently the activated complex must have a loose structure,

Experimental and theoretical investigation of kinetic isotope effects is a potential diagnostic tool for the elucidation of reaction mechanisms. Secondary H/D effects are small but can be informative. Relatively little effort has been expended to date on secondary H/D effects in cycloadditions, although data are available on simple addition reactions involving olefinic double bonds. For these reasons, and also because of the desirability of learning more about the nature of the activated complex of the $S(^3P) + C_2H_4$ reaction, we carried out an experimental and theoretical study of the effect of deuteration on the reaction.

Experimental Section

The high-vacuum apparatus, general vacuum technique, and handling of materials were similar as in previous studies on sulfur atom reactions from this laboratory.[1-5]

The 100 × 50 mm cylindrical reaction vessel was surrounded with an aluminum block furnace, the temperature of which could be maintained to ±0.1°. Irradiation was effected by a Hanovia medium-pressure mercury lamp through the Vycor glass window of the furnace, which provided a cutoff for the effective radiation reaching the cell at λ 2290Å.

Carbonyl sufide (Matheson) was purified by bubbling it through saturated NaOH solution, followed by drying and distillation at −130°. It was subsequently degassed at −160°. The carbon dioxide (Airco assayed reagent grade) was used without further purification. The ethylene (Phillips research grade) and the deuterated ethylenes (Merck) were purified by distillation at −160°.

Product episulfides were separated from the reaction mixture by distilling off the excess reactants at −139° (ethyl chloride slush), and from minor contaminants such as CS_2 and vinyl mercaptan by gas chromatography, using an 8-ft 10% tricresyl phosphate on Diatoport WAW column. The isotopic composition of the purified episulfide was then determined by mass spectrometric analysis on an AE-MS10 instrument.

Results

Rate constants for the addition of $S(^3P)$ atoms to C_2D_4, CH_2CD_2, and *cis*-CHDCHD were measured relative to C_2H_4 by the competitive chemical method. The source of $S(^3P)$ atoms was the *in situ* photolysis of COS in the presence of an excess of carbon dioxide and an equimolar mixture of C_2H_4 and the deuterated ethylene. The overall reaction is comprised, as has been shown before,[1-5] of the following elementary steps.

$$COS + h\nu \longrightarrow CO + S(^1D_2) \tag{1}$$

$$S(^1D_2) + CO_2 \longrightarrow S(^3P_{0,1,2}) + CO_2 \tag{2}$$

$$S(^3P_{0,1,2}) + C_2H_4 \longrightarrow C_2H_4S \tag{3}$$

$$S(^3P_{0,1,2}) + C_2H_XD_{4-X} \longrightarrow C_2H_XD_{4-X}S \tag{4}$$

Relative rate constants were then obtained from isotopic analyses of the binary mixtures of episulfides by mass spectrometry. The mass spectrometer was accurately calibrated by using standard samples prepared by the addition of S atoms to the appropriate pure deuterated ethylene. The mass peaks involved in the measurements and their relative intensities are listed in Table I.

The rate constant measurements extended over a 120° temperature range at very low conversion (≪1%) of the ethylenes. The results for the three deuterated ethylene species are tabulated in Table II. Random imprecision in the data is estimated to be about 1%, and the systematic error is probably in the same order.

Table I. Calibration of the Mass Spectrometer for Ethylene and Deuterated Ethylene Sulfides

C_2D_4S[b]	C_2H_4S[b]	$C_2D_4S/$ C_2H_4S	64[a]/59	64[a]/60
	~2		0	0
~2			78	5.1
1.63	1.94	0.840	1.100	0.913
1.63	1.96	0.831	1.100	0.897
1.60	1.94	0.8251	1.110	0.926
1.93	1.61	1.199	1.092	0.907
		Av	1.100	0.911
$C_2H_2D_2S$[b]		$C_2H_2D_2S/$ C_2H_4S	2 62[a]/60	
~2			2.4	
1.78	1.80	1.011	1.042	
1.55	2.02	1.303	1.044	
2.08	1.58	0.760	1.017	
		Av	1.034	
cis- CHDCHDS[b]		*cis*- CHDCHDS/ C_2H_4S	62[a]/60	
~2			2.2	
1.89	1.81	0.958	1.118	
1.66	2.08	1.253	1.097	
2.17	1.66	0.765	1.098	
		Av	1.104	

[a] Corrected to equimolar concentrations of the two episulfides. Electron-accelerating voltage is 70 eV. [b] μmoles.

Table II. H/D Isotope Effect as a Function of Temperature

Temp, °C	64/59	C_2D_4[a] $C_2D_4S/$ C_2H_4S	64/60	$C_2D_4S/$ C_2H_4S	k_D/k_H
29	1.211	1.101	1.037	1.138	1.154
29	1.212	1.102	0.994	1.091	1.130
96	1.178	1.071	1.057	1.160	1.150
157	1.201	1.092	1.024	1.124	1.142
				Av	1.14

CH_2CD_2[b]			*cis*-CHDCHD[c]		
Temp, C°	60/62	k_D/k_H	Temp, °C	60/62	k_D/k_H
28	0.955	1.062	27	1.059	1.028
29	0.945	1.07	28	1.036	1.050
98	0.945	1.073	93	1.059	1.028
158	0.955	1.062	156	1.036	1.051
	Av	1.07		Av	1.04

[a] Pressure (Torr) of COS, 20; CO_2, 940; C_2H_4, 34.7; C_2D_4, 33.6. [b] Pressure (Torr) of COS, 23; CO_2, 920; CH_2CD_2, 31.1; C_2H_4, 30.33. [c] Pressure (Torr) of COS, 24; CO_2, 920; *cis*-CHDCHD, 32.7; C_2H_4, 32.2.

Calculations

The calculations were carried out within the framework of transition state theory using the eq I,[10] in which the dagger signifies the transition state and the numbers 1 and 2 refer to the light and heavy molecules, respectively. *I* is the principal moment of inertia, *M* the molecular mass, $U_i = hc\omega_i/kT$, and ω_i is a normal vibrational frequency.[11]

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(10) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 15 (1958).

(11) In eq I and throughout this paper, the effect of isotopic substitution on the transmission coefficient and tunneling is neglected.

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \left[\frac{\left(\frac{I_{\mathrm{A}_2}I_{\mathrm{B}_2}I_{\mathrm{C}_2}}{I_{\mathrm{A}_1}I_{\mathrm{B}_1}I_{\mathrm{C}_1}}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}}{\left(\frac{I_{\mathrm{A}_2}{}^{\ddagger}I_{\mathrm{B}_2}{}^{\ddagger}I_{\mathrm{C}_2}{}^{\ddagger}}{I_{\mathrm{A}_1}{}^{\ddagger}I_{\mathrm{B}_1}{}^{\ddagger}I_{\mathrm{C}_1}{}^{\ddagger}}\right)^{1/2}\left(\frac{M_2{}^{\ddagger}}{M_1{}^{\ddagger}}\right)^{3/2}}\right] \times \left[\frac{\prod_i^{3N-6}\left[\frac{1-\exp(-U_{1i})}{1-\exp(-U_{2i})}\right]}{\prod_i^{3N^{\ddagger}-7}\left[\frac{1-\exp(-U_{1i}{}^{\ddagger})}{1-\exp(-U_{2i}{}^{\ddagger})}\right]}\right] \times \left[\frac{\exp\left[\sum_i^{3N-6}(U_{1i}-U_{2i})/2\right]}{\exp\left[\sum_i^{3N^{\ddagger}-7}(U_{1i}{}^{\ddagger}-U_{2i}{}^{\ddagger})/2\right]}\right] \qquad \text{(I)}$$

The first factor of this equation arises from the translational and rotational partition functions and is designated as MMI. The second factor is the contribution of vibrational excitation, denoted as EXC, and the last factor contains the vibrational zero-point energies, abbreviated as ZPE. Thus, eq I has been rewritten in the form[12]

$$k_{\mathrm{H}}/k_{\mathrm{D}} = \mathrm{(MMI)(EXC)(ZPE)}$$

It is apparent from the equation that the kinetic isotope effect depends on the properties of the activated complex. Since there is no way to determine these properties experimentally, eq I cannot be solved explicitly. Instead, reasonable models are assumed until agreement of calculated and experimental values is achieved.

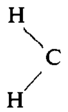
The vibrational frequencies of the activated complex are obtained from the normal-coordinate analysis of the assumed model, for which Schachtschneider[13] has written a computer program. In the present study the Wolfsberg-Stern[12] modification of the Schachtschneider program was used, which gives $k_{\mathrm{D}}/k_{\mathrm{H}}$ directly.

Two basic models, a symmetrical and an asymmetrical, adopted from molecular orbital calculation,[8,9] were used.

The Symmetrical Model. The S atom is allowed to approach the ethylene in a suprafacial, least motion, symmetrical fashion, as postulated by Hoffmann, *et al.*[8] Bond formation proceeds simultaneously and to an equal extent to both carbon atoms.

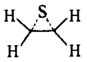
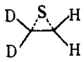
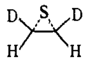
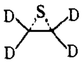
The first factor in eq I is the ratio of the principal moments of inertia, which depends only on the geometry and atomic masses. We find this factor not to be sensitive to slight structural changes as long as the symmetrical nature of the approach is maintained. Thus, varying the S-atom distance from the center of the C–C bond between 1.9 (*cf.* ref 8) and 1.66 Å (as in the stable thiirane), the numerical values for the first factor change from 1.51 to 1.56, or, expressing these values as $k(\mathrm{C_2D_4})/k(\mathrm{C_2H_4})$, from 0.665 to 0.642.

In order to construct a force field for the calculation of the normal frequencies of the activated complex, we started out from the force constants of the stable thiirane molecule, available from the literature.[14] By gradual removal of the S atom with simultaneous alterations of the C–C bond and the out-of-plane angles of the



groups, normal-coordinate analyses were performed with force constants for CS stretch and HCS bend reduced proportionally with the geometrical changes. When the rate constant ratio, calculated by substituting the calculated vibrational frequencies into eq I, showed the closest agreement with that obtained experimentally, that particular modified force field with the corresponding geometrical arrangement was accepted for the activated complex. The normal vibrational frequencies of the activated complexes were then calculated for the different deuterated ethylenes with the same force field, the results of which are compiled in Table III.

Table III. Vibrational Normal Frequencies (cm^{-1}) of the Activated Complexes[a]

				
ν_1	1314	1276	1263	1216
ν_2	1441	1108	1298	1067
ν_3	1424	1369	1318	1052
ν_4	771	714	648	571
ν_5	785	654	633	576
ν_6	974	773	862	749
ν_7	980	960	784	754
ν_8	1080	931	1029	831
ν_9	897	780	854	680

[a] Only frequencies used in the calculation of the isotope effect are listed. The force constants (mdyn/Å) are: $f_{\mathrm{CC}} = 8.2$, $f_{\mathrm{HCH}} = 0.41$, $f_{\mathrm{HCC.HCC}} = -0.3$, $f_{\mathrm{CH}} = 5.1$, $f_{\mathrm{HCC}} = 0.67$, $f_{\mathrm{HCC,HCS}} = 0.16$, $f_{\mathrm{CS}} = 1.4$, $f_{\mathrm{HCS}} = 0.23$.

These frequencies, when substituted into eq I, reproduce the experimental values of the kinetic isotope effect.

Comparison of the symmetry properties of the ethylene molecule with the activated complex provides the basis for correlating normal modes. The ethylene molecule has high symmetry and belongs to the D_{2h} point group. In the formation of the activated complex, some of the symmetry elements (i, $\sigma_{(x,y)}$, $C_{2(x)}$, $C_{2(y)}$) are lost and the complex goes over to the lower, C_{2v} symmetry group. The symmetry species $\mathrm{A_{1g}}$, $\mathrm{B_{1u}}$ in the ethylene transform into $\mathrm{A_1}$ species in the activated complex, the $\mathrm{A_{1u}}$, $\mathrm{B_{1g}}$ species transform into $\mathrm{A_2}$, the $\mathrm{B_{2g}}$, $\mathrm{B_{3u}}$ species transform into $\mathrm{B_1}$, and the $\mathrm{B_{2u}}$ species transforms into $\mathrm{B_2}$.

Table IV gives the potential energy distribution among the internal coordinates in the thiirane molecule. It can be seen that the proportion of the CS stretch and HCS bending coordinates in the normal modes is considerably different, and it is reasonable to assume that a variation in the extent of the linkage between the S atom and the ethylene molecule in the activated complex will not affect every vibrational mode in the same way.

For this reason and also because we wanted to know the increment to the isotope effect caused by each vibrational motion, we calculated the isotope effect as-

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[12] M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964).

[13] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

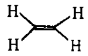
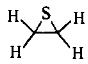
[14] G. B. Guthrie, Jr., D. W. Scott, and G. Waddington, *J. Amer. Chem. Soc.*, 74, 2795 (1952); K. Venkateswarlu and P. D. Joseph, *J. Mol. Struct.*, 6, 145 (1970).

Table IV. Potential Energy Distribution of the Diagonal Elements of the F Matrix in the Thiirane Molecule[a]

		Vibration	C–C stretch	C–S stretch	C–H stretch	H–C–C bend	H–C–S bend
A_1	ν_1	Ring breath	70.7	2.4	1.5	24.4	0.7
	ν_2	Ring deform	4.2	70.6		2.7	22.5
	ν_3	CH stretch	1.3	0.1	98.4	0.1	
	ν_4	CH_2 wag		26.4		10.0	63.6
	ν_5	CH_2 deform	23.7	0.5	0.1	62.6	13.2
A_2	ν_6	CH stretch			98.7	1.1	0.2
	ν_7	CH_2 twist			1.3	88.0	10.7
	ν_8	CH_2 rock				10.9	89.1
B_1	ν_9	Ring deform		86.8	0.1	0.6	12.5
	ν_{10}	CH stretch		0.1	99.8	0.1	
	ν_{11}	CH_2 wag		13.1	0.0	3.4	83.5
	ν_{12}	CH_2 deform			0.0	95.9	4.0
B_2	ν_{13}	CH stretch			99.8	0.6	0.1
	ν_{14}	CH_2 twist			0.0	15.5	84.5
	ν_{15}	CH_2 rock			0.1	84.4	15.4

[a] Values are given in per cent.

Table V. Calculated Increments of Individual Vibrational Motion to Kinetic Isotope Effect for the Symmetrical Model of the C_2D_4–C_2H_4 Reactant Pair[a]

Vibration, cm^{-1}			$(EXC)^{-1}$	$(ZPE)^{-1}$	$[(EXC)\text{-}(ZPE)]^{-1}$
C–C stretch	1623	1120	0.987	0.992	0.979
CH_2 rock	1236	875	1.044	0.989	1.013
	810	824	0.993	0.988	
CH_2 deform	1342	1470	0.993	1.035	1.049
	1443	1450	1.001	1.019	
CH_2 wag	949	1040	0.996	1.081	1.278
	943	1050	1.011	1.220	
	1027	1100	0.985	0.977	
CH_2 twist		920	1.054	1.536	1.619

$\Pi[(EXC)(ZPE)]^{-1} = 2.153$; $k(C_2D_4)/k(C_2H_4) = [(MMI)(EXC)\cdot(ZPE)]^{-1} = (0.642)(2.153) = 1.38$.

sociated with each normal mode separately. The results for the C_2D_4–C_2H_4 reactant pair are presented in Table V. Perusal of Table IV already indicates that the four normal modes assigned to the CH stretching consist entirely of displacement of the C and H atoms along the C–H bonds, and therefore these motions do not generate isotope effects since they do not undergo any change in the activated complex.

The four in-plane bending modes of the C–H bonds in ethylene (B_{1g}, B_{3u}, A_{1g}, B_{2u}) have the frequencies 1236, 810, 1342, and 1443 cm^{-1}, respectively.[15] The related frequencies of thiirane are 875, 824, 1470, and 1450 cm^{-1}. Of these, the two CH_2 rocking motions cause an inverse isotope effect of 1.013 and the two CH_2 deformations, 1.049.

The three out-of-plane bending modes (B_{1u}, B_{2g}, and A_{1u}) of the ethylene molecule have frequencies of 949, 943, and 1027 cm^{-1}. The related normal frequencies of thiirane are 1040, 1050, and 1100 cm^{-1}, respectively. Rehybridization of the C atoms from sp^2 to sp^3 results in an increase in the frequencies of the out-of-plane normal modes, which leads to a more substantial inverse isotope effect of 1.278. The largest contribution to the isotope effect, however, comes from a single vibration, the asymmetric twist mode of the thiirane which is absent in ethylene. This amounts to a factor of 1.619.

Finally, a small direct contribution to the isotope effect comes from the decrease of the CC stretching frequency which can be related to the π-electron withdrawal from the bond, and the associated increase in C–C bond length in the activated complex.

Thus, the total isotope effect for the case when the activated complex is taken to coincide with the stable thiirane molecule is $k(C_2D_4)/k(C_2H_4) = [(MMI)(EXC)\text{-}(ZPE)]^{-1} = (0.642)(1.062)(2.028) = 1.38$. On comparing this to the experimental value of 1.14, one can estimate from the computation that the transition state in terms of geometrical changes lies about 60% on the product side along the reaction coordinate.

The Asymmetrical Model. Calculations were also performed for a ring-distorted thiirane intermediate with a CCS bond angle of 100°. In this model the S atom is attached only to one of the C atoms. The bonds were assumed to be tetrahedral around this C atom and the vibrational normal frequencies of the CH_2 group were taken to be identical with the corresponding frequencies of the stable ethyl mercaptan molecule.[16] The other C atom was left with its planar structure unaltered in the model and with normal frequencies for the CH_2 group equal to those of the stable ethylene molecule. The distance and stretching frequency of the C–C bond were also taken from the ethyl mercaptan molecule.

Calculations for this model of the activated complex resulted in an isotope effect $k(C_2D_4)/k(C_2H_4) = 1.48$. The increments to the isotope effect of each normal mode of vibration are listed in Table VI. As in the case of the symmetrical model, the most important single contribution to the isotope effect arises from the increase in the number of oscillators during the reaction.

To this point, changes in the rotational barrier of the terminal methylene group were not considered in the calculations. Since a lowering of the rotational barrier decreases the torsional force constant, this change in the transition state model will decrease the value of the inverse isotope effect correspondingly.

Recent quantum mechanical calculations yielded a rotational barrier of 23.6 kcal/mol for the terminal CH_2 group in the ring-distorted triplet-state thiirane intermediate.[9] This barrier is still high enough to justify the corresponding motion of the CH_2 group to be treated

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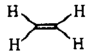
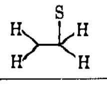
(15) B. L. Crawford, Jr., J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.*, 21, 678 (1953).

(16) D. W. Scott and J. P. McCullough, *J. Amer. Chem. Soc.*, 80, 3554 (1958).

Table VI. Calculated Increments of Individual Vibrational Motion to Kinetic Isotope Effect for the Asymmetrical Model of the C_2D_4–C_2H_4 Reactant Pair

	Vibration, cm^{-1}						
			(EXC)$^{-1\,a}$	(EXC)$^{-1\,b}$	(ZPE)$^{-1\,a}$	(ZPE)$^{-1\,b}$	[(EXC)(ZPE)]$^{-1}$
C–C stretch	1623	975	1.006	1.006	0.980	0.980	0.986
CH_2 rock	1236	1236	1.000	1.000	1.000	1.000	1.000
	810	750	1.012	1.012	0.986	0.986	0.998
CH_2 deform	1342	1450	0.991	0.991	1.032	1.032	1.023
	1443	1443	1.000	1.000	1.000	1.000	1.000
CH_2 wag	943	1260	0.990	0.990	1.260	1.260	1.250
	949	949	1.000	1.000	1.000	1.000	1.000
CH_2 twist	1027	1027[a]	1.000		1.000		1.000[a]
		1310	1.022	1.022	1.780	1.780	1.810
Lower barrier	1027	772[b]		1.012		0.853	0.864[b]

[a] $\Pi[(EXC)(ZPE)]^{-1} = 2.28$, $k(C_2D_4)/k(C_2H_4) = [(MMI)(EXC)(ZPE)]^{-1} = 1.48$. [b] $\Pi[(EXC)(ZPE)]^{-1} = 1.97$, $k(C_2D_4)/k(C_2H_4) = [(MMI)\cdot(EXC)(ZPE)]^{-1} = 1.28$.

as a vibration. For the stable ethylene molecule, a barrier height of 40 kcal/mol has been estimated[17] from the assigned torsional vibrational frequency of 1027 cm^{-1}. The lower torsional barrier in the ring-opened intermediate corresponds to a lower vibrational frequency of 772 cm^{-1}. Applying this lower value instead of the 1027 cm^{-1} value for the torsional frequency in the calculations yields a lower isotope effect, $k(C_2D_4)/k(C_2H_4) = 1.28$.

Discussion

The effect of isotopic substitution on reaction rates is termed a secondary kinetic isotope effect if the isotopic atom does not undergo chemical transformation. Halevi[18] distinguishes between secondary isotope effects of the first and secondary kinds, the criterion being whether bonds to the isotopic atoms undergo spatial reorientation or not.

Solvolysis reactions account for the majority of secondary kinetic isotope effects which have been measured, and in fact the first observation of the effect was made in solvolyses.[19] Other types of reaction in which secondary effects have been measured include homolytic thermal decomposition,[20] hydrogen transfer,[21] radical and atom addition to olefins,[22] and cycloaddition.[23]

The first observation of a secondary effect of the first kind (α effect) was reported by Streitwieser and Fahey[19] in 1957 for an SN1 solvolysis reaction where k_H/k_D was 1.16. The secondary α effects measured since then for numerous SN1 solvolyses show a remarkable constancy, averaging 10–12% per α-deuterium atom.

The precise cause of secondary isotope effects is not well understood and is a matter of some conjecture. Wolfsberg and Stern,[12] from their extensive theoretical studies on model systems, concluded that a significant isotope effect can result only when a change occurs in a force constant for a coordinate involving an isotopic atom, but it may be possible to fit an experimental isotope effect with a variety of different force constant changes. Such changes in the force constants may be induced by the effect of electronic, steric, and hybridizational changes on the anharmonicity of the vibrations[18] involving the isotopic atoms.

Using eq I, one can predict a normal kinetic isotope effect ($k_H > k_D$) if the normal vibrational frequencies undergo, in general, a decrease during passage from reactant to transition state, and an inverse effect ($k_H < k_D$) if in the normal frequencies a general increase results during the transition.

Streitwieser, *et al.*,[24] have proposed a simplified form of eq I in which the translational, rotational, and vibrational excitation contributions are neglected and the isotope effect originates from the zero-point energy difference of the protiated and deuterated molecules in the reactant and transition state. Applying this to a solvolysis reaction in which the transition state is considered to be a carbonium ion with the positively charged carbon atom having sp^2 hybridization, the isotope effect appears to arise from the change of the frequencies of the out-of-plane CH bending modes in the sp^2 and sp^3 hybrid states of the carbon atom. This interpretation of secondary α effects has since been widely accepted and applied to other types of reactions. It has also gained support from more detailed calculations on unimolecular thermal decompositions[20] and has been used to estimate the position of the transition state lying between the sp^2 and sp^3 hybrid states.

Applying Streitwieser's concept to an addition reaction to double bonds which is accompanied by the sp^2 → sp^3 rehybridization of one or two carbon atoms, one would predict an inverse secondary α isotope effect. The first experimental evidence to this effect was provided by the work of Seltzer[22a] and Denney and Tunkel.[22b] The latter authors compared the relative reactivity of *trans*-stilbene-d_2 and the parent *trans*-stilbene toward a variety of reagents in solvents of varying polarity. The average value of k_D/k_H for seven such reactions was 1.14. In the intervening period, several other measurements of secondary α effects for addition reactions have been reported,[22] which, along

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Table VII. Secondary Isotope Effects for Addition of Atoms and Radicals to Olefins

	Atom or radical				
Olefin	S	H[a]	CH_3[b]	CF_3[b]	CH_2[a]
C_2D_4	1.14		1.05[c]	1.07[c]	
CH_2CD_2	1.07				
cis-CHDCHD	1.04				
$CH_3CH{=}CD_2$			1.12[c]	1.07[c]	
$CD_3CD{=}CD_2$		1.08[d]	1.16[c]	1.09[c]	
$PhCD{=}CD_2$			1.11[c]	1.10[c]	
$CD_2{=}CD\cdot CD{=}CD_2$			1.20[c]	1.09[c]	
$CD_3{-}CD{=}CD{-}CD_3$					0.926[e]

[a] Temperature = 25°. [b] Temperature = 65°. [c] Reference 22c. [d] Reference 22d. [e] Reference 23.

with the present results, are summarized in Table VII. All reactions, with the notable exception of the addition of singlet methylene to perdeuterio-*cis*-2-butene,[23] exhibit an inverse effect.

There is only one attempt described in the literature of a theoretical treatment of an addition reaction. In an early study, Seltzer[25] has attempted to reproduce the experimental secondary isotope effect for the thiocyanate ion catalyzed isomerization of maleic acid to fumeric acid. Since the gas-phase addition of ground-state sulfur atoms to ethylene is a much better defined and understood reaction and lends itself more readily to meaningful calculations, we felt justified to embark upon the detailed theoretical study presented in this paper.

The main conclusion of these calculations may be summarized as follows.

(a) For both models of the transition state which were suggested by molecular orbital calculations, the calculated values of the isotope effect were somewhat greater than the experimental value, if the transition states were assumed to be identical with the final products. By appropriate variation of the molecular geometry and force field it was possible to reproduce the experimental isotope effect with both transition-state models and consequently it is not possible to discriminate against either model on the basis of isotope effects.

(b) In the asymmetric model, a reduction in the torsional frequency of the terminal methylene group causes a reduction in the isotope effect. This transition state model is basically identical with that which prevails in the addition of monovalent atoms or radicals to olefins, and calculations neglecting the change in the torsional frequencies overestimate the magnitude of the isotope effect. For example, the activated complex in the above-mentioned maleic acid isomerization reaction[25] results from the addition of the SCN^- ion to the C=C double bond, and since Seltzer attributed the frequency change only to the rehybridization of the C atom which represents the reaction center, his calculation would overestimate the isotope effect. (Also, because of lack of symmetry, some of the additional vibrations introduced by the SCN^- ion will couple to the CH vibrations and contribute to the isotope effect.) A similar argument applies in the calculation of the isotope effect for the CH_3 and CF_3 + olefin reactions studied by Szwarc and coworkers[22c] who, using Streitwieser's equation, obtained a value of 1.82 for k_D/k_H by considering a completely tetrahedral carbon at the reaction center. Under this condition, however, the bond order of the C=C bond would reduce to one, resulting in the transformation of the terminal methylene torsional vibration into an internal rotation and thereby causing an even larger reduction in the isotope effect.

(c) It is borne out clearly by the present calculations that contrary to current notions the most important single factor contributing to the isotope effect of the S + ethylene reaction is not the change in the out-of-plane CH bending vibrations, but the net gain in the isotope-sensitive vibrational normal mode during passage from reactants to the activated complex. The ethylene molecule has 12 normal modes of vibrations, while thiirane has 15. Thus, besides the reaction coordinate, the net gain in the normal modes is two. One of these, the asymmetric ring deformation in the symmetrical model, is insensitive to isotopic substitution and therefore does not contribute to the isotope effect. The remaining one, however, the asymmetric CH_2 twist in the symmetrical model and the twist of the CH_2 group which constitutes the reaction center toward the CCS plane in the asymmetrical model, is isotope sensitive and is the main source of the isotope effect.

We believe that these computational results are of general validity and apply for all addition reactions involving olefinic double bonds. The symmetrical model is the prototype of a cycloaddition reaction and the asymmetrical model that of a simple addition reaction. In general, for the addition of polyatomic reagents the gain in the normal modes of vibration is six, of which one will coincide with the reaction coordinate. From the remaining five, at least one, the CH_2 twist, will always be isotope sensitive and will generate a substantial inverse isotope effect. It will also be noted that in an olefinic addition reaction the isotopic contributions expressed by the first factor of eq I, arising from changes in the mass and moment of inertia, are by no means negligible.

In view of the foregoing discussion it is needless to say that the Streitwieser equation, originally proposed for solvolysis reactions, cannot be applied to the addition reactions of olefins to predict the magnitude of secondary α effects. The case also stresses the need for caution and restraint in the interpretation of secondary isotope effects if one is to avoid applying qualitative arguments beyond the range of their validity.

Returning now to the S + ethylene reaction, it is seen from the data in Table VII that the experimental values of isotope effects lie in the range 1.04–1.14, as found for other olefinic addition reactions. The two dideuterated ethylenes exhibit a lower isotope effect than the tetradeuterioethylene, which is again correctly predicted by calculations based on either of the two

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models used. All values of the experimental effects are independent of temperature, Table II, and the variations in the computed values are also negligible in the range covered by experiment.

It should also be pointed out that at the pressure employed in this study, approximately 1000 Torr, a small fraction of the initially formed hot thiirane molecules undergo unimolecular fragmentation to reform the reactants. Since the rate constants for this unimolecular reaction of the deuterated molecules would be somewhat smaller than that of the light ethylene, the transmission coefficient ratios to be applied in eq I would slightly differ from unity. This introduces a small error in the isotope effect determinations, of the order of less than 1% which is well within the overall error limits of the measurements.

Acknowledgments. The authors thank the National Research Council of Canada for continuing financial support, Professor J. E. Bertie and Dr. H. S. Sandhu for helpful discussions, and Professor M. Wolfsberg for providing us with his computer program.

Doubly Charged Ions from Labeled Toluenes. Isotope Effects, Preference Factors, and Hydrogen Randomization

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Abstract: The doubly charged ion mass spectra of toluene, toluene-α-d_3, toluene-*2,3,4,5,6*-d_5, and toluene-d_8 have been obtained. From these spectra it has been calculated that for the fast reactions occurring in the ion chamber of the mass spectrometer there is a preference factor for loss of an individual side-chain atom over the loss of an individual ring atom of 3.3:1; there is an isotope effect for loss of an H· atom over loss of the corresponding D· atom of 1.3:1. For reactions involving loss of H_2, HD, and D_2 fragments, it is shown that randomization of H and D atoms in toluene-α-d_3 and in toluene-*2,3,4,5,6*-d_5 is essentially complete.

The gas-phase chemistry of ionized toluene has long been of interest, largely because of the intriguing problems presented by the structure of the molecular ion and of the $C_7H_7^+$ ion formed by loss of H·. Using isotopic labeling, previous investigators have sought to answer two immediate questions: Is there a "preference factor" for losing an H· (or D·) atom from the side chain rather than from the ring; and, is there an isotope factor which favors the loss of H· over the loss of D· from the same position in the molecule? For "fast" processes, that is, for reactions occurring in the ion chamber, it has been shown[2] that there is a preference factor of 1.32 for loss of methyl hydrogen over the loss of ring hydrogen, and also, that there is an isotope effect of 1.58. Studying the metastable transitions of toluene molecular ions, that is, the "slow" processes occurring in the first field-free region of the double-focusing mass spectrometer, it was found[3] that there is no preference factor in fragmentations involving the loss of a neutral hydrogen atom, but that there is an isotope factor of 3.5 favoring loss of H· over the loss of D·.

In this study we were interested in the behavior of doubly charged toluene molecular ions. One of our objectives was to calculate the preference factor in fast fragmentations involving loss of neutral H· or D· from the doubly charged molecular ions using labeled toluenes. Since these ions readily lose H_2, HD, and D_2, we also wished to examine the extent to which each of these molecules is lost, and thus to determine the amount of randomization in the doubly charged molecular ions prior to these processes. Meyerson[4] has reported that H· loss from doubly charged toluene molecular ions is not preceded by extensive scrambling whereas H_2 loss is.

Experimental Section

All spectra were recorded with an RMH-2 double-focusing mass spectrometer, modified so as to allow the direct introduction of a collision gas into the first field-free region.[5] Ionizing voltage used was 70 eV, emission current 1 mA, source temperature 200°, and accelerating voltage 5 kV. All reagents used were commercial samples of highest available purity. Isotopic purity of the labeled compounds was better than 99%.

Results and Discussion

After a doubly charged ion has undergone a charge-exchange reaction with a collision gas in the first field-free region of a double focusing mass spectrometer, it can be transmitted through the electric sector set at $2E$, where E is the voltage at which the main beam of stable ions is transmitted, and it can subsequently be mass analyzed by the magnetic sector.[6] In this way, a "doubly charged" ion mass spectrum ("$2E$ spectrum") can be obtained without any interference from singly charged ions.

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