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Large Statistical Secondary Isotope Effects in Non-Equilibrium Reaction Systems. Unimolecular Decomposition of Chemically Activated Ethyl-d_1 and Ethyl-d_3 Radicals.*

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Abstract

Hydrogen atom rupture from chemically activated ethyl-d_1 radicals has been studied and is compared with a similar reaction of ethyl-d_3 radicals. The activation reactions were D atom addition to ethylene or to trans-ethylene-d_2. A very large normal statistical intermolecular secondary kinetic isotope effect of $\gtrsim 1.5$ per D atom substituent was found. The experimental results are in concordance with the theory and conform to the formulation of these effects previously given (reference 2). The calculated effect is ~ 1.6. These magnitudes per D atom are considerably enhanced over those obtained for butyl radicals. This is expected since the average excess energy of ethyl is less.

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INTRODUCTION

The existence of relatively large statistical secondary intermolecular kinetic isotope effects in non-equilibrium unimolecular has been pointed out and their nature described.[1,2] These effects, being statistical rather than mechanistic in nature, have magnitudes which depend on the degree of isotopic substitution of one molecule with respect to the other. Depending upon the nature of the activation process both <u>inverse</u> and <u>normal</u> isotope effects may arise. The two effects are related.

The former effect, which arises by thermal activation, need not be considered in detail at this time. A quantitative quantum statistical formulation of its magnitude was given by Rabinovitch, Schneider and Setser[1] in terms of the RRKM[3] description of unimolecular processes, and further discussion has since been given.[2,4] Experimental verification of the occurrence of inverse effects has been obtained with the isocyanide isomerization system and the observed and predicted magnitudes agree quite well.[5]

The normal effect may arise more generally by several activation techniques which so far have included chemical activation,[2,6] photosensitization[7,8] and electron impact.[9,10] Of these, the former seems the most exemplary at present and permits facile exploration of the energy dependence of the magnitude of the secondary isotope effect. An outline of the theory of the effect was described by Rabinovitch and Current,[2] and may be considered in more detail in its relevance to the present study as follows.

DESCRIPTION OF NORMAL STATISTICAL ISOTOPE EFFECT

General Expression

Consider a species A which is energized to levels above the threshold ε_o for reaction i.e. is activated. Then depending upon the pressure of the system, either reaction (say decomposition) or collisional stabilization will occur

$$A(\varepsilon)^* \xrightarrow{k_\varepsilon} \text{products} \qquad (D_\varepsilon)$$

$$A(\varepsilon)^\dagger + M \xrightarrow{\omega} A \qquad (S)$$

The nature and efficiency of the collisional stabilization process is not of importance here and will simply be characterized as an assumed known effective collision rate, which is independent of ε. Then if both processes D_ε and S are taken[11] to be intrinsically random[12] in nature, as seems to be a good assumption for some modes of activation,[4,13] $k_\varepsilon = \omega D_\varepsilon/S$, where ε refers to a particular level of activation. For more than one energy state, an average rate constant is expressed as $k_a = \omega D/S$, where D and S are total amounts; k_a is measured, in this case, relative to the stabilization process as time clock. (For other techniques, such as mass spectral measurements, other measures of k_ε or k_a may be obtained.) For a particular activation technique which gives rise to energy distribution functions $f(\varepsilon)$ of the activated isotopic species, k_a is[11]

$$k_a = \omega \int_{\varepsilon \geq \varepsilon_o} \frac{k_\varepsilon}{k_\varepsilon + \omega} \cdot f(\varepsilon)\, d\varepsilon \Big/ \int_{\varepsilon \geq \varepsilon_o} \frac{\omega}{k_\varepsilon + \omega} \cdot f(\varepsilon)\, d\varepsilon \qquad (1)$$

$$k_{aH}/k_{aD} = \frac{\displaystyle\int_{\varepsilon \geq \varepsilon_{oH}} \frac{k_{\varepsilon H} \cdot f(\varepsilon)_H \, d\varepsilon}{k_{\varepsilon H} + \omega}}{\displaystyle\int_{\varepsilon \geq \varepsilon_{oH}} \frac{f(\varepsilon)_H \, d\varepsilon}{k_{\varepsilon H} + \omega}} \Bigg/ \frac{\displaystyle\int_{\varepsilon \geq \varepsilon_{oD}} \frac{k_{\varepsilon D} \cdot f(\varepsilon)_D \, d\varepsilon}{k_{\varepsilon D} + \omega}}{\displaystyle\int_{\varepsilon \geq \varepsilon_{oD}} \frac{f(\varepsilon)_D \, d\varepsilon}{k_{\varepsilon D} + \omega}} \tag{2}$$

where subscripts H and D are used to designate the isotopic species. This expression is too general to be useful for expository purposes. Accordingly, for a pure secondary isotope effect take $\varepsilon_{oH} = \varepsilon_{oD} = \varepsilon_o$, and let $f(\varepsilon)_H = f(\varepsilon)_D = f(\varepsilon)$. Then eq. (2) becomes

$$k_{aH}/k_{aD} = \frac{\displaystyle\int_{\varepsilon \geq \varepsilon_o} \frac{k_{\varepsilon H} \cdot f(\varepsilon) \, d\varepsilon}{k_{\varepsilon H} + \omega}}{\displaystyle\int_{\varepsilon \geq \varepsilon_o} \frac{f(\varepsilon) \, d\varepsilon}{k_{\varepsilon H} + \omega}} \Bigg/ \frac{\displaystyle\int_{\varepsilon \geq \varepsilon_o} \frac{k_{\varepsilon D} \cdot f(\varepsilon) \, d\varepsilon}{k_{\varepsilon D} + \omega}}{\displaystyle\int_{\varepsilon \geq \varepsilon_o} \frac{f(\varepsilon) \, d\varepsilon}{k_{\varepsilon D} + \omega}} \tag{3}$$

For high pressures, $\omega \to \infty$

$$(k_{aH}/k_{aD})_\infty = \int_{\varepsilon \geq \varepsilon_o} k_{\varepsilon H} \cdot f(\varepsilon) \, d\varepsilon \Big/ \int_{\varepsilon \geq \varepsilon_o} k_{\varepsilon D} \cdot f(\varepsilon) \, d\varepsilon = \langle k_{\varepsilon H} \rangle / \langle k_{\varepsilon D} \rangle \tag{4}$$

which is eq. (2) of reference (2).

At low pressures, $\omega \to 0$

$$(k_{aH}/k_{aD})_0 = \left[\int_{\varepsilon \geq \varepsilon_o} \frac{f(\varepsilon) \, d\varepsilon}{k_{\varepsilon H}} \right]^{-1} \Bigg/ \left[\int_{\varepsilon \geq \varepsilon_o} \frac{f(\varepsilon) \, d\varepsilon}{k_{\varepsilon D}} \right]^{-1} = \langle k_{\varepsilon H}^{-1} \rangle^{-1} / \langle k_{\varepsilon D}^{-1} \rangle^{-1} \tag{5}$$

Expressions similar to the numerator and denominator of (3) - (5) have been evaluated in previous papers[13-15] with use of a Marcus-Rice[3] expression for k_ε, together with accurate computation[16] of the quantum statistical energy density expressions involved in k_ε and $f(\varepsilon)$, in the form that the latter takes for chemical activation[11,15]

due to thermal spread of the reactants.

Energy Dependence of Isotope Effect

A Simplified Form

In these non-equilibrium systems the detailed nature of $f(\varepsilon)$ is an "accidental" characteristic of the experimental technique and particular reaction being studied. For a particularly simple form of $f(\varepsilon)$, the characteristics of the ratio k_{aH}/k_{aD} are more readily exhibited. For $f(\varepsilon) \approx \delta(\varepsilon)$, a condition that may be readily approximated in practice in some systems, eq. (3) becomes

$$k_{aH}/k_{aD} \simeq k_{\varepsilon H}/k_{\varepsilon D} = \frac{I_{rH} \sum_{\varepsilon^{\dagger}_{vr}=0}^{\varepsilon-\varepsilon_0} P(\varepsilon^{\dagger}_{vr})_H / hN^*_{\varepsilon H}}{I_{rD} \sum_{\varepsilon^{\dagger}_{vr}=0}^{\varepsilon-\varepsilon_0} P(\varepsilon^{\dagger}_{vr})_D / hN^*_{\varepsilon D}} \tag{6}$$

where[3] each I_r is a residue of moments of inertia of rotational partition functions of the molecule and activated complex; the summation term is over the degeneracies of all possible values of active energy states for vibration and rotation of the activated complex; and N^*_ε is the density of active energy states of the activated molecule.

The energy dependent portion of eq. (6) may be rearranged,

$$k_{\varepsilon H}/k_{\varepsilon D} = \frac{I_{rH} \sum P(\varepsilon^{\dagger}_{v})_H \; N^*_{\varepsilon D}}{I_{rD} \sum P(\varepsilon^{\dagger}_{v})_D \; N^*_{\varepsilon H}} \tag{7}$$

Both the activated complex sum and the molecule density for the deuterated species are larger than those for the light species because of the closer energy level spacings of the former. Hence the sum ratio of eq. (7) is less than unity, while the density ratio is much greater than unity; the latter dominates the expression since activated complex energy is at the low level, $\varepsilon - \varepsilon_o$, while molecule energy is ε.

Since the sum ratio varies more strongly with energy than the density ratio, an increase of ε, and therefore of $\varepsilon - \varepsilon_o$, causes a decrease of k_H/k_D. Conversely, the maximum value of eq. (7) for a given chemical system i.e. for a particular characteristic value of ε_o, is obtained when $\varepsilon \to \varepsilon_o$: then $\sum P(\varepsilon_v^\dagger)_H \simeq \sum P(\varepsilon_v^\dagger)_D \simeq 1$, and

$$k_H/k_D \simeq I_{rH}N^*_{\varepsilon D}/I_{rD}N^*_{\varepsilon D} \tag{8}$$

which is eq. (4) of ref. (2). As pointed out in ref. (2), apart from the negligible I_r ratio[17] the maximum value that eq. (8) can attain for active vibrational degrees of freedom is

$$(k_H/k_D)_{max} \quad \prod^{i} \nu_{iH} \Big/ \prod^{i} \nu_{iD} \tag{9}$$

This occurs when $\varepsilon_o \to \infty$, i.e. critical energies such that classidal behavior is followed,[16] so that[18]

$$N^*_\varepsilon = \varepsilon^{s-1} \Big/ \Gamma(s) \prod_{i=1}^{s} h\nu_i \tag{10}$$

where each molecule is described by s active vibrational modes. Active rotations, if any, will at low critical energies ε_o contribute a ratio in moments of inertia, $\prod^{j} I_{Dj}/\prod^{j} I_{Hj}$, which complements the ratio of eq. (9).

C-H, C-D Isotope Effects

As a rough rule of thumb for many C-H, C-D systems, the value of the ratio of eq. (9) is $(\sim 1.3)^3 \simeq 2.2$ for a single substituent; for deuteration of a hydrocarbon molecule with n D atoms, the corresponding order of magnitude ratio is $\sim (1.3)^{3n}$, where the approximate factor 1.3 ± 0.05 and the exact magnitude of the ratio are governed in detail by the Teller-Redlich product rule. The ratios commonly observed for equilibrium (mechanistic) secondary isotope effects are[19] ~ 1.12 total per D substituent, varying a little with temperature, and with statistical effects largely cancelling for the reasons described previously.[2]

Experimental evidence bearing on the above discussion has been obtained for chemical activation of sec-butyl radicals which decompose to methyl + propylene. The average value $\langle\varepsilon\rangle$ of the reacting radicals derived from H atoms and cis-butene-2 is a function of pressure:[13] at 300° K, $(\langle\varepsilon\rangle_{p=\infty} - \varepsilon_0) = 11.4$ kcal mole^{-1}; $(\langle\varepsilon\rangle_{p=0} - \varepsilon_0) = 9.9$ kcal mole^{-1}; at 195° K, the same quantities are 9.0 and 8.5 kcal mole^{-1}, respectively; also $\varepsilon_0 = 33$ kcal. For the system cis-butene: cis-butene-d_8, some experimental ratios are[6] $(k_{aH}/k_{aD})_\infty = 4.4$ and 5.7 at 300° and 195°, respectively; $(k_{aH}/k_{aD})_0 = 6.5$ at 300° K. The detailed forms of eqs. (4) and (5) that apply have been given previously.[3,5] Good agreement with theoretical values, calculated by accurate evaluation of the equations with use of the appropriate frequency models, was obtained;[6] both the observed and calculated magnitudes correspond to rate ratio total factors of ~ 1.20 (p = 0) and ~ 1.26 (p = ∞), respectively, per D atom substituent.

Enhancement of the observed ratio should accompany further decrease of $(\langle\varepsilon\rangle - \varepsilon_0)$, as by use of trans-butene reactants. However, for atom addition as the activation reaction, $(\langle\varepsilon\rangle - \varepsilon_0)$ remains quite

large for sec-butyl decomposition since the formation of one bond type (C-H) is followed by rupture of a weaker bond type (C-C). Decrease of $(\langle\varepsilon\rangle - \varepsilon_o)$ may be readily effected in principle by use of a system in which the same bond type is made and broken; e.g. an ethyl radical is formed on D atom addition to ethylene or ethylene-d_2, and addition is followed by rupture (most frequently) of a C-H bond.

The energy quantities involved are a little different for ethyl-d_1 and ethyl-d_3 due to a small difference in heat capacities and thermal energies for these species. Also, since the excited species are fractionated a little with respect to energy by simultaneous H and D rupture, the average excess energy of the formed radicals $\langle\varepsilon^+\rangle_f$ does not quite coincide with the average energy of the radicals reacting (by H rupture) at $p = 0$, i.e. $\langle\varepsilon^+\rangle_{Ho}$; and is thus still a little further different for ethyl-d_1 and ethyl-d_3. (This slight complication is absent for species such as sec-butyl which decompose by a single path.) As compared with the butyl system, $(\langle\varepsilon\rangle_{p=o} - \varepsilon_o)$ is reduced to 2.8 and 3.6 kcal mole^{-1} at 195° and 300° K, respectively, as an average for the two ethyl radicals, according to the values of CR.

The Ethyl-d_1 : Ethyl-d_3 System

The present paper reports the comparative study of ethyl-d_1 and ethyl-d_3 decomposition at 195° and 300° K. The reaction scheme for the ethyl-d_1 system is

$$D + C_2H_4 \longrightarrow C_2H_4D\cdot^* \qquad (1)$$

$$C_2H_4D\cdot^* \xrightarrow{k_{\varepsilon_1}} C_2H_3D + H \qquad (2)$$

$$C_2H_4D\cdot^* \xrightarrow{k^o_{\varepsilon_1}} C_2H_4 + D \qquad (3)$$

$$C_2H_4D\cdot^{*} + M \xrightarrow{\Omega} C_2H_4D\cdot + M \qquad (4)$$

The corresponding scheme for the ethyl-d_3 system is

$$D + \underline{trans}\text{-}C_2H_2D_2 \longrightarrow CHDCHD_2\cdot^{*} \qquad (1a)$$

$$CHDCHD_2\cdot^{*} \xrightarrow{k_{\varepsilon a}} C_2HD_3 + H \qquad (2a)$$

$$CHDCHD_2\cdot^{*} \xrightarrow{k'_{\varepsilon a}} \underline{cis}\text{-}C_2H_2D_2 \text{ (or } \underline{trans}\text{-}C_2H_2D_2) + D \qquad (3a)$$

$$CHDCHD_2\cdot^{*} + M \xrightarrow{\Omega} CHDCHD_2\cdot + M \qquad (4a)$$

The chemically activated radicals are formed in a non-equilibrium distribution (relative to the ambient temperature) at an estimated[14] minimum energy above the vibrational ground state of 41.3 kcal mole^{-1}. The tri-deuterated radical is assumed to be formed with the same minimum energy as for the mono-deuterated radical, and ε_0 for reaction (2a) is assumed to be the same as for reaction (2), given as 39.6 kcal mole^{-1} by CR. ε_0 is here raised a little above the value for the butyl system, but the principal variation between the two systems is the excess energy and not the critical energy.

Data and detail for ethyl-d_3 have been given by CR; the thermochemical quantities and expressions for k_a are also valid for the ethyl-d_1 case. Details of the experimental results for ethyl-d_1 are presented here.

EXPERIMENTAL

The experimental method was the H atom diffusion apparatus described earlier. All aspects of the technique and analysis are similar to those employed previously. Phillips research grade of light

ethylene was used without further purification.

RESULTS

Interpretation of the Analytical Data

The number of ethyl-d_1 radicals which decomposed by reaction (2), D_h, was measured by the amount of ethylene-d_1 formed in the reaction. The rate of this reaction is determined by the competition with reac- (4). The number of stabilized ethyl-d_1 radicals S_d was determined from the stabilization reaction products. Assuming unit collisional deactivation and a molecular diameter of 4.95 Å for both ethylene and ethyl radicals, the apparent average experimental rate of hydrogen rupture was determined as $k_{ah} = \omega D_h/S_d$.

Reaction (3) does not result in new products so it could not be experimentally observed, but it does not offer a serious complication. From the work of CR it may be estimated to represent 15 - 20% of the total decomposition processes by reactions (2) plus (3). Allowance for reaction (3) is made in the theoretical calculations; it tends to fractionate the ethyl radicals, particularly those formed at the higher energies.

Stabilization

Reaction (2) resulted in the formation of H atoms in the reactor. These produced light ethyl radicals and it was necessary to consider this in the interpretation of the products. Methyl radicals, which arose following the addition of an atom to an ethyl radical to form a "hot" ethane molecule, combined with ethyl radicals to give propane. Methyl radicals arose more frequently from the addition of an atom to light ethyl radicals which were present in larger steady state

concentration than ethyl-d_1 radicals as a consequence of the occurrence of reaction (2). The total number of light ethyl radicals which were collisionally stabilized is given by the expression

$$S_\ell = (1 + \text{ethane/butane})(2\ \text{butane-}d_0 + \text{butane-}d_1) + 1.5\ \text{propane-}d_0 + 7/8\ \text{propane-}d_1 + 1/4\ \text{propane-}d_2.$$

The collisionally stabilized ethyl-d_1 radicals may be expressed as

$$S_d = (1 + \text{ethane/butane})(\text{butane-}d_3 + 2\ \text{butane-}d_1) + 5/8\ \text{propane-}d_1 + 1.25\ \text{propane-}d_2.$$

The first terms in these equations account for the stabilized radicals which were measured as butane and ethane, and the last terms for those which resulted in propane formation. The formulation of such equations to describe the products was considered in more detail by CR.

Decomposition

Decomposition by H rupture of an energized ethyl-d_1 radical produced ethylene-d_1. Some of this product was removed by further reaction with a hydrogen or deuterium atom; ignoring any slight isotopic difference in rates of atom addition to ethylene-d_1 and light ethylene, the amount removed is given by the ethylene-d_1 fraction of the total ethylene which reacted with an atom and was converted into stabilized products, plus also the ethylene-d_2 which was formed by D addition followed by H rupture. Some extra ethylene-d_1 is also formed by the disproportionation of ethyl radicals. Thus the amount of decomposition of $C_2H_4D\cdot^*$ by hydrogen atom rupture is

$$D_h = \underline{\text{mono}} + \frac{\text{mono}}{\text{ethylene}}(S_\ell + S_g) + \text{ethylene-}d_2$$
$$- \frac{\text{ethane}}{\text{butane}}\left(\frac{1}{3}\ \text{butane-}d_1 + \frac{2}{3}\ \text{butane-}d_2\right)$$

More detailed corrections, including removal of ethylene-d_1 by H addition followed by D rupture, were actually applied to the experimentally determined quantities[14] but these were insignificantly different in magnitude from the corrections described.

The calculations for the present data are not directly applicable to some recently reported experiments,[20] since the ethylene-d_1 was not given.

Low Pressure Rate Constants

The products for runs at 195° and 300° K are listed in Table I.

Only lower pressure measurements were made on this system i.e. only the lower range of S/D values was accessible with the present experimental technique. The highest value of S/D observed was 0.5 at 195°. The data are limited.

Of the four determinations of k_a at 300° K, the measurement at highest pressure, 2.6 mm (S/D = 0.22), is also in a region where experimental error increases rapidly with the present technique. Hence the three lowest values were averaged to give k_{ao}; since they correspond to very low S/D ratios from 0.023 - 0.098, this is permissible because the calculated values in Table I indicate only 5% rise in k_a above k_{ao} at S/D = 0.098. At 195°, the highest pressure (2.5 mm) value corresponds to S/D = 0.5, which is much too high a value to be included in the average, and only the two lowest values at S/D = 0.062 and 0.17 were used to obtain k_{ao}. These values are presented in Table II along

with earlier determinations of k_{ao} for ethyl-d_3. When allowance is made for reaction path degeneracy (two for ethyl-d_1 and one for ethyl-d_3), values of 2.4 and 3.1 for the secondary isotope effect at 195° and 300° K, respectively, are obtained. These quantities are inverted with regard to the expected temperature effect; lowering of the average energy as given by $f(\varepsilon)$, upon lowering of temperature, should cause the magnitude at 195° to be the larger. This theoretically expected effect is actually quite small (Table II), but obviously the experimental accuracy is not high either. The data for both temperatures may be expressed by the average ratio 2.7.

Further recognition may be given to experimental error by calculation of the minimum ratio offered by the data. The least value of k_{ao} at 300° is found from the two lowest (also lowest pressure) values: these are 10.6 and 10.3 x 10^7 sec^{-1}, or an average of 10.5 x 10^7 sec^{-1}; the least (also lowest pressure) value of k_{ao} at 195° is 3.54 x 10^7 sec^{-1}. Comparison with the k_{ao} values for ethyl-d_3 of Table II yields the k_H/k_D ratios, 2.6 at 300°, and 1.8 at 195°, or an average for the two temperatures of 2.2. This lower estimate for the magnitude of the measured average corresponds to the value quoted in a preliminary communication.[2]

DISCUSSION

Molecular Models and Calculated Rates

The formulation of the calculated rate constants for ethyl-d_1 was made as for ethyl-d_3 and ethyl-d_2. The molecular model and activated complex for which calculations were made were chosen on the basis of the criteria provided by the various ethyl-d_3 and ethyl-d_2 models previously examined by CR. On this basis only the model with

one active internal rotation and one active overall rotation for the radical, and with an active overall rotation for the complex, was used in the calculations (Appendix I). The activation energy for D addition to C_2H_4 was taken as 1.6 kcal, identical with the value previously used for $C_2H_2D_2$. All other thermochemical quanties are also as described previously. The reaction path for H rupture from the ethyl-d_1 radicals is doubly degenerate. The secondary isotope effect is obtained by dividing the rate of H rupture as calculated for ethyl-d_1 radicals by twice the rate of H rupture from ethyl-d_3 radicals.

Table II summarizes the calculated rates and secondary isotope effects for the system. The isotope effect has a maximum value of 1.66 per substituted atom, at p = 0 and 195°. The corresponding value at 300° is only slightly smaller, 1.63. The observed average total isotope effect per substituent is 1.5 or greater.

Conclusions

A large secondary isotope effect has been predicted for the present system and an approximate correct magnitude has been found. Inasmuch as the D substituents are adjacent to the reaction site the effect under study is partly mechanistic. This part is associated with the hybridization change $sp^3 \rightarrow sp^2$, for a net of one C–H bond as contrasted with one C–D bond, and there seems little point in making special discussion of its magnitude. The observed magnitudes indicate the essentially statistical character of the secondary isotope effect in this system.

Appendix I

Vibration Frequency Models

Ethyl-d_1 radicals

The frequencies were assigned in manner similar to before as follows: 3000 (4), 2180, 1445 (2), 1310 (2), 1045 (3), 770 (2).
[3000 (2), 2200 (3), 1260 (3), 1020 (4), 680 (2)].

The internal rotation was taken as free and the figure axis rotation as active.

Moments of inertia for the radical were calculated, assuming a tetrahedral CH_3 groups and an angle of 118° on the CH_2 group. The moments are 24.3, 21.5, and 5.97 g $Å^2$ $mole^{-1}$; [27.4, 25.9, 7.88]. The reduced moment for internal rotation is 1.23 g $Å^2$ $mole^{-1}$ [1.74].

Quantities in square brackets refer to ethyl-d_3.[14]

Ethyl-d_1 activated complexes

The ethyl-d_1 complexes were also chosen in the same manner as the ethyl-d_2 complexes. The resulting models are

H rupture complex: 3050 (3), 2275, 1560, 1350 (2), 1065 (2), 815 (3), 150 (2).

D rupture complex: 3050 (4), 1580, 1340 (3), 930 (4), 110 (2).

The difference in zero point energies is 1.7 kcal $mole^{-1}$. The moments of inertia in gm $Å^2$ $mole^{-1}$ are for H rupture: $I_A^\dagger = 22.9$, $I_B^\dagger = 20.6$, $I_C^\dagger = 6.77$; and for D rupture: $I_A^\dagger = 21.1$, $I_B^\dagger = 22.4$, $I_C^\dagger = 8.22$.

The product rule agreement between the various ethyl-d_1 and the ethyl-d_3 species was 2.4%, 1.1% and 9.6% for the radicals, H atom decomposition complex, and D atom decomposition complex, respectively.

Some mention of symmetry number and reaction path degeneracy is

desirable. One may use the appropriate total symmetry numbers of the particular radical and complex, with the total number of distinguishable activated complexes, to obtain the total reaction path degeneracy. Alternatively,[21] to assist in deciphering the situation, one may consider a radical of hypothetically lowered rotational symmetry (by "marking" the rupturing H atom) and then use the number of distinguishable complexes multiplied by the number of equivalent rupturable C–H bonds to obtain the total path degeneracy. The existence of internal complicates the situation, but the result is, in both cases, the same; the rate of rupture is, of course, not affected by the symmetry of the radicals as such, after allowance is made for the number of rupturable atoms.

TABLE I

Summary of Products for Decomposition of Ethyl-d_3 [a]

T, °K	300	300	300	300	195	195	195
Press, mm	0.15	0.54	1.00	2.55	0.11	0.50	2.50
Total ethylene	212	282	403	458	228	180	562
ethylene-d_2	0.103	...	...	...	0.24	0.11	...
ethylene-d_1	2.53	2.68	3.07	3.89	7.40	4.22	6.01
ethylene-d_0	209	279	400	454	220	176	556
ethane-d_3	...	...	...	...	...	...	0.001
ethane-d_2	...	...	0.013	0.009	...	0.019	0.059
ethane-d_1	...	0.04	0.062	0.066	...	0.101	0.180
ethane-d_0	...	0.15	0.381	0.184	...	0.836	0.225
propane-d_2	0.004	0.024	0.003	...	0.02	...	0.113
propane-d_1	0.017	0.067	0.044	...	0.13	0.09	0.240
propane-d_0	0.249	0.197	0.410	0.047	0.60	0.91	0.118
butane-d_3	...	...	...	...	...	...	0.01
butane-d_2	...	0.006	0.011	0.084	...	0.04	0.46
butane-d_1	0.044	0.115	0.202	0.527	0.263	0.48	1.32
butane-d_0	0.818	1.10	1.54	0.939	2.15	2.51	1.00
ethane/butane	...	0.165	0.26	0.19	0.20	0.31	0.17
S_ℓ	2.41	3.45	4.58	2.96	6.42	8.00	4.41
S_d	0.061	0.231	0.305	0.836	0.489	0.769	2.98
D_h	2.66	2.71	3.10	3.89	7.88	4.53	6.06
D_h/S_d	43.6	11.7	10.2	4.65	16.1	5.90	2.04
ω, 10^7 sec^{-1}	0.243	0.875	1.62	4.13	0.22	1.00	5.00
k_{ah}(10^7 sec^{-1}	10.6	10.3	16.5	19.2	3.54	5.90	10.2

a. Products are listed in units of 10^{-2} cc. atm. at 298° K.

TABLE II

Secondary Isotope Effect on Specific H Rupture Rate (k_a, 10^7 sec^{-1}) from Ethyl Radicals

	T(°K)	p (mm)	Ethyl-d_3	Ethyl-d_1	Ethyl-d_1 / 2 x Ethyl-d_3
Observed					
k_{ao}	195	(0)	1.0	4.7	2.4
k_{ao}	300	(0)	2.0	12.5	3.1
Calculated					
k_{ao}	195	0	1.60	8.84	2.76
k_{ao}	300	0	2.56	13.56	2.66
k_a	195	0.1	1.68	8.88	
		0.5	1.88	9.04	
		1.0	2.00	9.21	
		3.0	2.22	9.69	
		10.0	2.40	10.5	
		100	--	12.0	
$k_{a\infty}$			2.58	12.46	2.43
k_a	300	0.1	2.72	13.60	
		0.5	3.12	13.9	
		1.0	3.42	14.2	
		3.0	4.10	15.2	
		10	5.02	17.4	
		100	6.46	23.6	
$k_{a\infty}$			7.00	28.6	2.04

Footnotes

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17. These approximate statements are useful because of the large magnitude of the frequency effects involved. Now $(k_H/k_D)_{max}$ depends on

$$\frac{P^{\dagger}_{aH}}{P^{*}_{aH}N^{*}_{aH}} \Big/ \frac{P^{\dagger}_{aD}}{P^{*}_{aD}N^{*}_{aD}} = \frac{\prod^{j}(I^{\dagger}_{j})^{1/2}_{H}}{\prod^{k}(I_{k})^{1/2}_{H}} \cdot \frac{\prod^{k}(I_{k})^{1/2}_{D}}{\prod^{j}(I^{\dagger}_{j})^{1/2}_{D}} \cdot \frac{\prod^{i}\nu_{iH}}{\prod^{i}\nu_{iD}}$$

where the P_a refer to rotational partition functions for adiabatic degrees of freedom, and the first two ratios represent I_{rH} and I^{-1}_{rD}. If overall rotations are not active and if there are no internal rotational degrees of freedom then $j = k = 3$, and $i = 3n - 6$. For ethyl radical one internal and one overall rotation is taken as active, and for the two adiabatic rotations of ethyl-d_1

and ethyl-d_5, $I_{DH}/I_{HD} = 1.01$, and may be neglected. The residual frequency (including for ethyl, the active moments of inertia) ratio is, of course, governed by the Teller-Redlich Product Rule. If preferred, the partial ratio

$$\frac{\prod^{k} (I_k)_D^{1/2} \cdot \prod^{i} \nu_{iH}}{\prod^{k} (I_k)_H^{1/2} \cdot \prod^{i} \nu_{iD}},$$

may be explicitly preserved, and the Product Rule applied to this expression.

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