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RECOIL TRITIUM REACTIONS WITH METHYLCYCLOHEXENE: A TEST OF THE ASSUMPTION OF ENERGY RANDOMIZATION PRIOR TO UNIMOLECULAR DECOMPOSITION[1]

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June 1973

Abstract

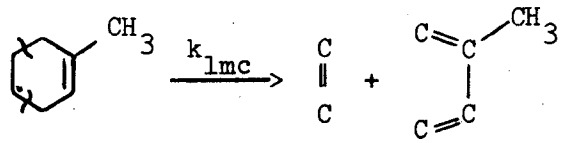
The reactions of recoil tritium atoms with the three methylcyclohexene isomers have been studied in the gas phase at 135°C. T was produced by $^3He(n,p)T$. Ninety percent of the gas phase products resulted from recoil tritium atom abstraction, addition, or T-for-H substitution reactions. Following activation by T-for-H substitution, the unimolecular decomposition of 4-methylcyclohexene-t (to give propylene-t or butadiene-t) and the unimolecular decomposition of 3-methylcyclohexene-t (to give ethylene-t or 1,3-pentadiene-t) was established from the pressure dependence of the product yield in the 300-1200 Torr pressure range. The apparent rate constants for these unimolecular decomposition processes was determined as 1×10^7 sec^{-1} and 3×10^6 sec^{-1}, respectively. The rate constants for the unimolecular decomposition of cyclohexene-1-t and cyclohexene-3-t (formed by T-for-methyl substitution on 1-methylcyclohexene and 3-methylcyclohexene, respectively) were nearly equivalent. In addition, the average energy of excitation following T-for-methyl substitution is the same in cyclohexene-1-t and cyclohexene-3-t, namely 6.0 to 6.5 eV. It was concluded that the RRKM (Rice, Ramsperger, Kassel, and Marcus[2]) assumption of energy randomization prior to unimolecular decomposition is valid for the recoil tritium initiated unimolecular decomposition of cyclohexene.

Introduction

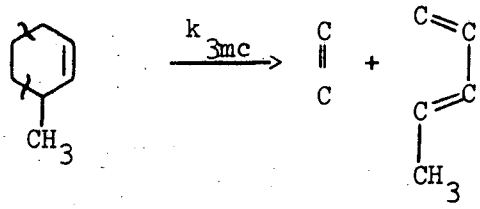
For many years, the role of translational energy in promoting virtually all chemical reactions has been emphasized. One method of producing translationally excited ("hot") atoms for chemical studies is by nuclear reaction and resulting recoil. Recoil tritium atom reactions have now been observed with over one hundred parent molecules.[3-5] The main reaction channels are: (1) Addition. Recoil tritium atom addition to a double bond forms an alkyl-t radical. The alkyl-t radical is capable of further reaction by abstraction of a hydrogen atom from the hydrocarbon system to form a tritiated alkane; by addition to the double bond of the parent compount to initiate a (tritiated) radical chain; or by unimolecular decomposition/isomerization processes. (2) Abstraction. Recoil tritium atom abstraction forms HT. (3) Substitution. Recoil T-for-H atom substitution forms a tritiated parent molecule. The tritiated parent molecule possesses an average excitation energy of 5 eV (1 eV = 23 kcal $mole^{-1}$) following recoil T-for-H substitution.[6,7] This large energy of excitation often produces characteristic unimolecular decomposition of the tritiated parent molecule as a secondary process following recoil T-for-H substitution. In this respect recoil T-for-H substitution may be viewed as a chemical activation process.

We are interested in the reaction of recoil tritium atoms with the positional isomers of methylcyclohexene. The characteristic unimolecular decomposition reactions of the methylcyclohexene isomers as determined by pyrolysis[8,9,10] shock tube[11] and mercury sensitized photolysis[12,13] studies are shown in eqs. 1 to 3.

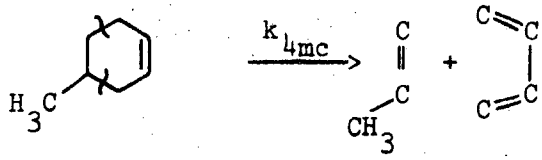
(mc = methylcyclohexene)



[8,9] (1)



[11,12,13] (2)



[12]

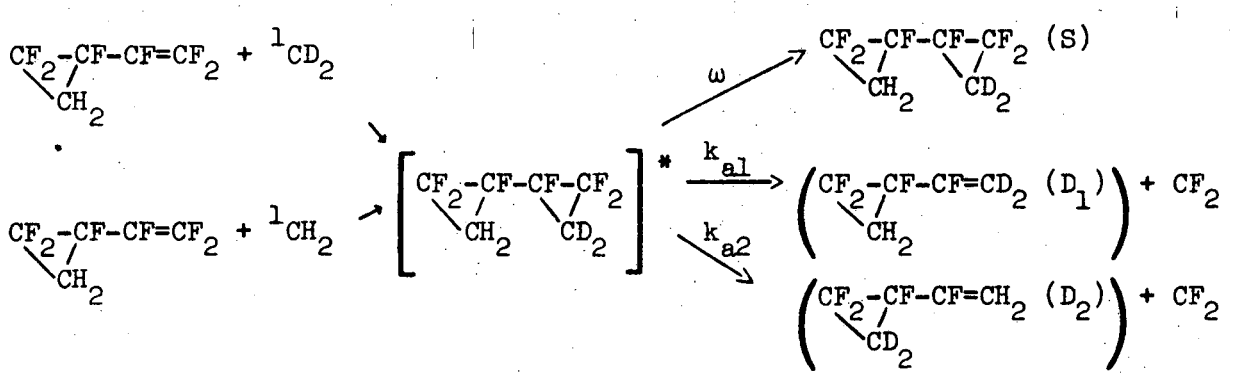
$$k_{4mc} = 10^{14.94} \exp(-64{,}900/kT) \quad [10]$$

$$k_{4mc} = 10^{15.13} \exp(-66{,}600/kT) \quad [11]$$

(3)

These studies have been largely limited to determining that the reaction indicated in eqs. 1 to 3 is the principle unimolecular reaction for each isomer. Only for the unimolecular decomposition of 4-methylcyclohexene has a full kinetic study (leading to determination of the rate constant) been made. Nevertheless, a comparison of the decomposition products indicates that the principle unimolecular process is retro-Diels-Alder cleavage as shown.

Our interest in recoil T + methylcyclohexene reactions was chiefly in studying unimolecular decomposition following T-for-H substitution <u>and</u> in testing the RRK-RRKM[2] assumption of energy randomization prior to unimolecular decomposition. Recently Rynbrandt and Rabinovitch[14] reported the first positive example of energy non-randomized unimolecular decomposition. Their reaction sequence is shown in eq. 4.



(4)

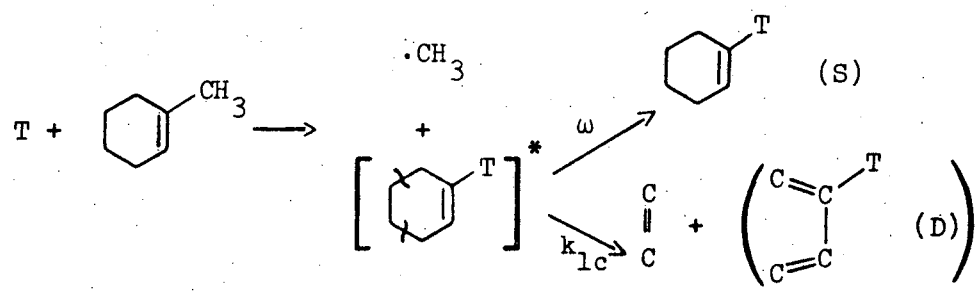
In chemical activation studies such as this, k_a, the apparent rate constant of unimolecular decomposition, is determined from[14]

$$k_a = \omega\left(\frac{D}{S}\right) = Z\left(\frac{D}{S}\right) P \qquad (5)$$

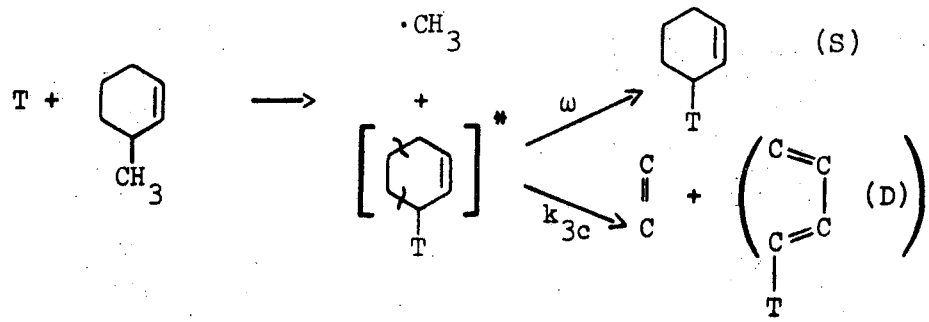
where $\omega = ZP$ = collision frequency; Z is the collision number;[15] P is the sample pressure in Torr; D is the yield of decomposition product; and S is the yield of collisionally stabilized product; that is, S is the yield of activated molecules which were collisionally stabilized prior to unimolecular decomposition. Hence the stabilization (S)/decomposition (D) ratio should vary linearly with pressure for a unimolecular process. A plot of S/D versus pressure is usually extrapolated to S/D = 1. At the pressure where S/D = 1, k_a equals ω.

In the reaction scheme shown in eq. 4, if energy was randomized prior to decomposition, $k_{a1} = k_{a2}$. That is, decomposition in each ring was equally probable. However, analysis showed that regardless of the isotopic labeling of the added methylene, the newly formed ring was more probable to decompose. The conclusion was that energy non-randomized unimolecular decomposition was occuring.

We propose to test the RRK-RRKM[2] assumption of energy randomization prior to unimolecular decomposition with the following reaction scheme for recoil T + methylcyclohexene reactions.



(6)



(7)

If $k_{1c} = k_{3c}$, excited cyclohexene-t molecules decompose with the same probability regardless of the site of energy input. That is, energy randomization occurrs prior to unimolecular decomposition. If $k_{1c} \neq k_{3c}$, energy non-randomized unimolecular decomposition occurrs.

In the postulation and discussion of the reaction scheme shown in eqs. 6 and 7, there are several necessary assumptions:

(a) <u>T-for-methyl substitution occurs as indicated</u>, without a shift of the double bond. Chemical degradation to determine the intramolecular tritium content has shown recoil T-for-X substitution (X = alkyl, $-NH_2$, -COOH) to occur

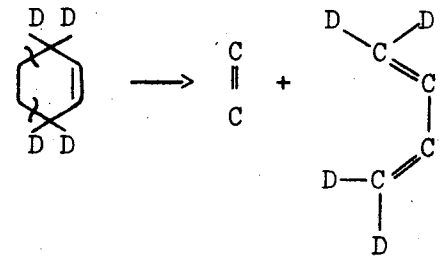
with 85 to 95 percent of the T being bonded at the position within the molecule recently occupied by the X species.[16]

(b) The only reaction of excited cyclohexene-t molecules is either stabilization or retro-Diels-Alder cleavage as indicated to give butadiene-t. The unimolecular decomposition of cyclohexene to give primarily ethylene and butadiene has been well established in pyrolysis,[10,17-21] shock tube,[11,22,23] photolysis,[24,25] and mercury sensitized photolysis[12] studies. Of the total unimolecular decompositions, 96% occur giving ethylene and butadiene, 3% occur by H_2 elimination to give cyclohexadienes and benzene, and the remaining 1% give C_5 and smaller hydrocarbons presumably through a free radical mechanism.[20,21,25] A possible radical contribution to the ethylene and butadiene yield has been proposed from cyclohexyl radicals via H-atom addition to cyclohexene.[11,22] However, addition of scavenger does not affect the ethylene and butadiene yield.[12,20,25] The unimolecular rate constant for cyclohexene decomposition

$$k_a = 10^{15.3} \exp(-66{,}900 \text{ cal/kT}) = A \exp(-E_o/kT) \qquad (8)$$

has been so well determined that cyclohexene is used as an internal standard in shock tube studies.[22,23]

Strong evidence for the retro-Diels-Alder cleavage of cyclohexene comes from the photolysis of cyclohexene-3,3,6,6-d_4. The photolysis of cyclohexene-3,3,6,6-d_4 occured as shown in eq. 9 to give C_2H_4 and $C_4H_2D_4$ in 98% of the decompositions at 4.9 eV photolysis energy and 86% of the decompositions at 8.4 eV photolysis energy. At 8.4 eV the remaining 14% of the decompositions gave $C_2H_2D_2$ and $C_4H_4D_2$.[25]



(9)

Further evidence for the retro-Diels-Alder cleavage of cyclohexene comes from the pyrolysis of cyclohexene-1-t and cyclohexene-3-t to give primarily butadiene-t and the pyrolysis of cyclohexene-4-t to give primarily ethylene-t.[17]

(c) The reaction sequence shown in eqs. 6 and 7 is the only reaction channel leading to the formation of butadiene-t from recoil T + 1-methylcyclohexene reactions and recoil T + 3-methylcyclohexene reactions. This assumption is supported by the retro-Diels-Alder cleavage of the methylcyclohexenes shown in eqs. 1 to 3.

(d) Corrections can be made for possible differences in the average energy of excitation of cyclohexene-1-t versus cyclohexene-3-t formed by T-for-methyl substitution in eqs. 6 and 7, respectively. Differences in the average energy of excitation of cyclohexene-1-t versus cyclohexene-3-t may arise from: (i) differences in the average energy of the recoil T atom initiating the T-for-methyl substitution. This effect should be very small. Changes in structure from 1-methylcyclohexene to 3-methylcyclohexene should not drastically affect the recoil tritium atom energy distribution.[3-5] (ii) differences in the average energy carried away by the unlabeled methyl radical in eq. 6 versus 7. (iii) differences in the C-CH_3 and C-T bond strengths. A crudely estimated differential of as much as 1 eV more energy may be required to break the C-CH_3 bond in 1-methylcyclohexene (in comparison to

3-methylcyclohexene). The difference in the ΔH of cyclohexene-t formation in eqs. 6 and 7 is probably small, however. An estimated energy differential of as much as 1 eV more energy may be released by the formation of the C-T bond in cyclohexene-1-t (in comparison to cyclohexene-3-t). The possible difference in the ΔH of cyclohexene-t formation in eqs. 6 and 7 is certainly small compared to the estimated 6 to 7 eV energy excitation deposited in the tritiated molecule following recoil T-for-methyl substitution.[27] The chief concern is that the low energy cut-off point for the recoil T-for-methyl substitution reaction may be as much as 1 eV higher for 1-methylcyclohexene than 3-methylcyclohexene.

We assumed that this ambiguity concerning possible differences in the average energy of excitation of cyclohexene-1-t versus cyclohexene-3-t could be resolved using the RRK formulation of the energy dependence of the unimolecular rate constant.[28-31] Namely,

$$k_a = A\left[\frac{E - E_o}{E}\right]^{s-1} \tag{10}$$

where k_a is alternately k_{1c} or k_{3c} which are determined from the stabilization (S)/decomposition (D) ratios from eqs. 6 and 7, respectively; E_o and A for the unimolecular decomposition of cyclohexene are given in eq. 8; the s parameter is taken as s = 24 from the unimolecular decomposition of cyclohexene-t following recoil T-for-H substitution;[32] and E is the average energy deposited in the cyclohexene-t molecule following recoil T-for-methyl substitution on methylcyclohexene. If E_{1c} and E_{3c} (from reactions 6 and 7, respectively) are nearly equal, the small difference may be attributed to the

energy factors discussed previously (i to iii). If E_{1c} and E_{3c} are different by more than 1 eV (reflecting large differences in k_{1c} and k_{3c}) this difference can be attributed solely to energy non-randomized unimolecular decomposition of cyclohexene-t following recoil T-for-methyl substitution on methylcyclohexene.

Experimental

The samples were perpared in 1720 Pyrex glass capsules (14 ml internal volume) with a vacuum line technique similar to that employed in other laboratories.[33] Further details of sample preparation are provided elsewhere.[34] The ^{3}He (Mound Laboratories) was certified as 99.7 mole % ^{3}He with a tritium content of 1.0×10^{-11} mole %. A standard radio-gas-chromatographic analysis[35] of an unirradiated aliquot of ^{3}He containing at least twice the moles normally sealed in the 1720 Pyrex capsules showed no measurable tritiated contaminant. The ^{3}He was used directly from the Mound Laboratories' container without further purification. The parent methylcyclohexene isomers were API Standard Reference Materials certified at greater than 99.8% chemically and isomerically pure. All other materials used were research grade.

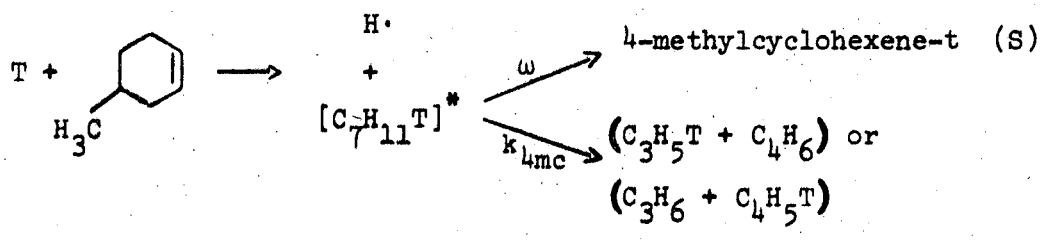
The samples were irradiated in the Hohlraum of The Berkeley Campus Nuclear Reactor in a specially designed irradiation container.[36] Temperature control during irradiation was maintained at 135 ± 0.5°C. The samples were irradiated for 24 hrs at a flux of 3.9×10^8 n cm^{-2} sec^{-1}. Radiolysis damage due to recoils following the ^{3}He(n,p)T reactions was less than 1%.

The samples were analyzed on a specially designed radio-gas-chromatographic system described elsewhere.[35] Good resolution of major peaks was obtained in an analysis time of 15 hours. "Polymer-t" is defined as high molecular weight tritiated hydrocarbons not eluted in the normal radio-gas-chromatographic analysis. The recovery and analysis of "polymer-t" was similar to that previously described.[37] Reported here are the results from the analysis of two identical samples that agreed to within 5% on major products unless otherwise stated.

Results and Discussion

The reactions of recoil tritium atoms with gas phase 1-methylcyclohexene, 3-methylcyclohexene, and 4-methylcyclohexene were studied at 135°C. The major gas phase products observed from each methylcyclohexene isomer were: (a) Methylcyclohexane-t formed by recoil tritium atom addition to the double bond of methylcyclohexene to form a methylcyclohexyl-t radical. The methylcyclohexyl-t radical then abstracts a hydrogen atom from the bulk hydrocarbon system to form methylcyclohexane-t. (b) HT formed by the recoil tritium atom abstracting a hydrogen atom from methylcyclohexene. (c) Tritiated methylcyclohexene formed by a T-for-H substitution reaction. These three products composed 90% of the total observed gas phase tritiated products.

Among the tritiated products observed in small yield were those which may have resulted from the retro-Diels-Alder cleavage of the methylcyclohexene-t isomers following recoil T-for-H substitution. Activation (energization) by T-for-H substitution and the resultant unimolecular decomposition of 4-methylcyclohexene is shown in eq. 11



$$D = C_3H_5T \text{ (propylene-t)} + C_4H_5T \text{ (butadiene-t)} \qquad (11)$$

Analogous equations can easily be written for 1-methylcyclohexene and 3-methylcyclohexene from eqs. 1 and 2. The pressure dependences of the

stabilization (S)/decomposition (D) ratios from the retro-Diels-Alder cleavage of 4-methylcyclohexene-t and 3-methylcyclohexene-t are shown in Figures 1 and 2, respectively. The data in Figures 1 and 2 may be represented by a linear pressure dependence. The analogous plot of S/D versus pressure from the unimolecular decomposition of 1-methylcyclohexene-t to ethylene-t or isoprene-t is not shown. The data points were widely scattered and a pressure effect was not observed. The lack of a linear dependence of S/D on pressure may result from the extreme reactivity of isoprene-t. Isoprene polymerization[38] may prevent an accurate determination of the isoprene-t yield from the unimolecular decomposition of 1-methylcyclohexene-t.

The abscissa in Figures 1 and 2 is the effective collisional deactivation pressure in the sample defined as

$$P_{eff} = 1.0\ P_{C_7H_{12}} + 0.17\ P_{^3He} \qquad (12)$$

Each sample contained 300 Torr of ^3He (at 135°C) and a variable amount of methylcyclohexene isomer (C_7H_{12}). On a pressure for pressure basis, ^3He is estimated to be only 17 percent as effective as methylcyclohexene in collisionally deactivating excited methylcyclohexene-t molecules.[39] The use of the effective pressure for the P in eq. 5 is an attempt to correct for the effect of a weak collider in the system, ^3He. Otherwise, it is assumed that only a single collision between an activated methylcyclohexene-t molecule and an unlabeled methylcyclohexene molecule is necessary for complete deactivation of the excited methylcyclohexene-t species. We point out that this "strong collision"[2] assumption may not be valid at the high energies of excitation encountered in recoil tritium experiments.

The plot of S/D versus effective pressure [actually log (S/D) versus log (effective pressure)] was extrapolated to S/D = 1. From Figure 1, S/D = 1 at 1.3 Torr; $k_{4mc} = 1.5 \times 10^7$ sec^{-1}. From Figure 2, S/D = 1 at 0.29 Torr; $k_{3mc} = 3.4 \times 10^6$ sec^{-1}. The value of the methylcyclohexene collision diameter used to calculate Z in eq. 5 was estimated[39] at 6.12×10^{-8} cm. Using this value of k_{4mc} for k_a in eq. 10 and the average of the rate parameters from eq. 3, the s parameter in the RRK formulation of the rate constant for the unimolecular decomposition of 4-methylcyclohexene was determined as s = 22. E, in this case, was set at 5 eV, the average energy of excitation following a recoil T-for-H substitution.[6,7] For a fixed $s = 25 \approx \frac{1}{2}(3N - 6)$, E was determined as 5.4 eV. For a fixed $s = 34 \approx \frac{3}{4}(3N - 6)$, E was determined as 6.8 eV. N is the number of atoms in the methylcyclohexene molecule.

The data in Figures 1 and 2 are for unscavenged samples. Scavenging with butadiene-d_6 revealed that the butadiene-t yield was not depleted by reactions with radiolysis produced H-atoms. This result is similar to recoil T + cyclohexene reaction results under similar irradiation conditions[32] but contrasts with recoil T + cyclohexene reaction results at 25°C.[40,41] Nitric oxide scavenging at the lowest methylcyclohexene pressure displayed in Figures 1 and 2 showed: (a) a 15% radical contribution to the propylene-t yield in Figure 1. (b) No radical contribution to the 1,3-pentadiene-t yield but a 14% radical contribution to the ethylene-t yield in Figure 2. The data in Figures 1 and 2 were crudely "corrected" by subtracting a constant 15% radical contribution from the propylene-t yield and a 14% radical contribution from the ethylene-t yield at all pressures. The resultant plots of "corrected" S/D ratio versus pressure were extrapolated to S/D = 1 at 42 Torr and 0.48 Torr for "corrected" data from Figures 1 and 2, respectively.

Other interesting scavenger effects were noted:

(a) Methylcyclohexane-t. The proposed methylcyclohexyl-t radical precursors to the methylcyclohexane-t yield were intercepted by 9 mole % nitric oxide (NO) scavenger. With nitric oxide scavenging, the methylcyclohexane-t yield decreased to 1 to 4% of the unscavenged yield value. Similar concentrations of H_2S, O_2, and SO_2 scavenger did not affect the methylcyclohexane-t yield. This may indicate bulk chemical reactions between the parent hydrocarbon and the scavenger similar to those previously postulated in the T + cyclohexene system.[40] The methylcyclohexane-t yields from T + 3-methylcyclohexene reactions and T + 4-methylcyclohexene reactions were nearly equal. The yield of methylcyclohexane-t from T + 1-methylcyclohexene reactions was only about one-half that from T + 3- and 4-methylcyclohexene reactions. This is consistent with the methylcyclohexyl-t radical formed by tritium atom addition to 1-methylcyclohexene being less reactive via H-atom abstraction than the methylcyclohexyl-t radicals formed by tritium atom addition to 3- and 4-methylcyclohexene. In tritium atom addition to 1-methylcyclohexene, formation of the tertiary radical may be favored over the formation of the secondary radical by as much as twenty to one.[42] The adjacent methyl group by the tertiary methylcyclohexyl-t radical from T + 1-methylcyclohexene reactions probably hinders H-atom abstraction compared to H-atom abstraction by the secondary methylcyclohexyl-t radicals from T + 3- and 4-methylcyclohexene reactions.

(b) Methylcyclohexene-t isomers other than the parent. The parent isomers were API Standard Reference Materials certified at greater than 99.8% chemically and isomerically pure. The radio-gas-chromatographic system employed for analysis[35] would not resolve small amounts of 3-methylcyclohexene from a larger

4-methylcyclohexene peak and vice-versa. The 1-methylcyclohexene peak was well resolved from the 3-/4-methylcyclohexene peak. The mass tracing during the radio-gas-chromatographic analysis did not reveal the presence of any methylcyclohexene isomers other than the parent compound. However, tritiated methylcyclohexene isomers other than the parent compound were observed in greater than 0.2% abundance compared to the tritiated parent compared to the tritiated parent compound.

For example, T + 4-methylcyclohexene reactions gave 1-methylcyclohexene-t in both unscavenged and nitrix oxide scavenged samples. The 1-methylcyclohexene-t yield from T + 4-methylcyclohexene reactions was: (a) 4.8% as large as the 4-methylcyclohexene-t yield in unscavenged samples. (b) decreased by 60% with nitric oxide scavenging. This is consistent with a high energy and a thermal route to 1-methylcyclohexene-t formation from T + 4-methylcyclohexene reactions. The high energy (unscavengeable) route is probably hydrogen atom "scrambling" following a high energy recoil T-for-H substitution reaction. The low energy (scavengeable) route is probably via loss of a hydrogen atom from a methylcyclohexyl-t radical formed by tritium atom addition to 4-methylcyclohexene. Similar H-atom loss mechanisms have been postulated in other recoil tritium reaction studies.[43]

In unscavenged T + 1-methylcyclohexene reactions, the combined 3- and 4-methylcyclohexene-t yield was 9% as large as the 1-methylcyclohexene-t yield. In unscavenged T + 3-methylcyclohexene reactions, the 1-methylcyclohexene-t yield was only 3% as large as the 3-methylcyclohexene yield. In both T + 3-methylcyclohexene and T + 1-methylcyclohexene reactions the yield of the non-parent methylcyclohexene-t isomer(s) doubled with nitric oxide scavenging.

Similar anomolous increases with nitric oxide scavenging have been observed in the recoil T + trans-2-butene system.[44]

(c) Methane-t. The yield of methane-t in nitric oxide scavenged systems is roughly the same from recoil tritium atom reactions with 3- and 4-methylcyclohexene and roughly twice the yield of methane-t from nitric oxide scavenged T + 1-methylcyclohexene reactions. The methane-t yield in nitric oxide scavenged methylcyclohexene systems probably results from a direct T-for-cyclohexene substitution process.[3-5] This trend of the methane-t yields is consistent with decreased probability for T-for-cyclohexene substitution to give methane-t when the cyclohexene-CH_3 bond strength is increased.

A test of the RRK-RRKM assumption of energy randomization prior to unimolecular decomposition.— The formation of cyclohexene-t (S) and butadiene-t (D) by the reaction pathways shown in eqs. 6 and 7 was a small reaction channel (less than 3% of the gas phase tritiated products) in the recoil tritium reactions with 1- and 3-methylcyclohexene. The pressure dependence of the S/D ratio in eqs. 6 and 7 could not be determined in high pressure unscavenged T + 1-methylcyclohexene and T + 3-methylcyclohexene systems, respectively. The adjacent methylcyclohexane-t peak[35] was broadened by column overloading in the high pressure samples. Consequently, the cyclohexene-t peak could not be resolved from the methylcyclohexane-t peak. Good resolution of the cyclohexene-t peak and the methylcyclohexane-t peak was obtained at the lowest pressure samples. A comparison of unscavenged and nitric oxide scavenged samples at the lowest methylcyclohexene pressure showed that the yield of cyclohexene-t and butadiene-t was unaffected by scavenger. The results of the determination of the S/D ratios from eqs. 6 and 7 in nitric oxide scavenged samples are shown in Table I.

Considering the range of unimolecular rate constants[15] and the uncertainties of this method, k_{1c} and k_{3c} are nearly equivalent.

The near equivalence of the unimolecular rate constants and the average energies of excitation for cyclohexene-1-t and cyclohexene-3-t (from T-for-methyl substitutions on 1-methylcyclohexene and 3-methylcyclohexene, respectively) shows: (a) The RRK-RRKM assumption of energy randomization prior to unimolecular decomposition is valid for the recoil-tritium-initiated unimolecular decomposition of cyclohexene.

(b) A T-for-methyl substitution reaction leaves an average energy of excitation of 6.0 to 6.5 eV in the resultant tritiated molecule. The energy of the $C-CH_3$ bond broken in the T-for-methyl substitution process apparently has little effect on the average energy deposited in the resultant tritiated molecule.

The proven RRK-RRKM assumption of energy randomization prior to unimolecular decomposition can now be put to use. There are ten possible T-for-H substitution sites in cyclohexene. Assuming retro-Diels-Alder cleavage of cyclohexene, T-for-H substitution at four of the sites results in ethylene-t; at six of the sites in butadiene-t. By analogy to T-for-methyl substitution in methylcyclohexenes, the average energy of excitation in cyclohexene-t following T-for-H substitution is probably independent of the strength of the C-H bond that was broken. This

means that the cyclohexene-t molecule formed by T-for-H substitution has the same average energy of excitation, regardless of the site of the T label. Because all cyclohexene-t molecules have the same average excitation energy and energy is randomized in cyclohexene prior to unimolecular decomposition, cyclohexene-t molecules should decompose with equal probability regardless of the site of the T label. Consequently, the 1,3-butadiene-t/ethylene-t ratio should be 1.5 to 1.0 from the retro-Diels-Alder cleavage of cyclohexene-t formed in T + cyclohexene reactions.

The butadiene-t/ethylene-t ratio from scavenged T + cyclohexene systems was 1.00 at 25°C and 1.05 at 135°C. Similarly the 1,3-pentadiene-t/ethylene-t ratio at 135°C is scavenged T + 3-methylcyclohexene reactions (see eq. 2) was 0.68. However, the butadiene-t/propylene-t ratio at 135°C in scavenged T + 4-methylcyclohexene reactions (see eq. 11) was 1.20. Only when ethylene-t is not the smaller of the assumed retro-Diels-Alder cleavage products does the ratio of the tritiated products approach the statistical prediction based of equal unimolecular decomposition per T-for-H substitution site. An explanation consistent with this observation is the production of ethylene-t from a non-retro-Diels-Alder reaction. Ethylene-t from a non-retro-Diels-Alder-cleavage pathway has been observed in cyclohexene-3,3,6,6-d_4 decompositions[25] (see eq. 9). The postulated non-retro-Diels-Alder cleavage of methylcyclohexene-t is supported by the observation of a 1,3-pentadiene-t peak 14% as large as the butadiene-t peak in nitric oxide scavenged T + 4-methylcyclohexene reactions.

Summary and Conclusions

In the reactions of recoil tritium atoms with the three methylcyclohexene isomers ninety percent of the reactions which gave gas phase products can be attributed to: (a) abstraction to form HT. (b) Addition to form a methylcyclohexyl-t radical which may abstract a hydrogen atom to form methylcyclohexane-t.

(c) Substitution of T-for-H to form the tritiated parent isomer. Small yield reaction channels have also been observed: (i) Unimolecular Decomposition. The unimolecular decomposition of 4-methylcyclohexene-t to give propylene-t or butadiene-t; and the unimolecular decomposition of 3-methylcyclohexene-t to give ethylene-t or 1,3-pentadiene-t has been established from the pressure dependence of the tritiated products. The apparent rate constants for these unimolecular decomposition processes are 1×10^7 sec^{-1} and 3×10^6 sec^{-1}, respectively. (ii) T-for-Methyl Substitutions. The average energy of excitation following recoil T-for-methyl substitution is the same for cyclohexene-1-t and cyclohexene-3-t, namely 6.0 to 6.5 eV. From this we concluded that the energy of the $C-CH_3$ bond broken in T-for-methyl substitution has little effect on the average energy deposited in the resultant molecule. In addition, the rate constants for the unimolecular decomposition of cyclohexene-t were nearly the same for cyclohexene-1-t and cyclohexene-3-t (formed by recoil T-for-methyl substitution on 1-methylcyclohexene and 3-methylcyclohexene, respectively).

We therefore conclude that the RRK-RRKM assumption of energy randomization prior to unimolecular decomposition is valid for the recoil tritium initiated unimolecular decomposition of cyclohexene.

Footnotes and References

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Table I. The Unimolecular Decomposition of Cyclohexene-t at 135°C[a]

Effective Pressure[b], Torr	S/D Eq. 6	S/D Eq. 7	k_{1c} 10^9 sec^{-1}	k_{3c} 10^9 sec^{-1}	E_{1c} eV	E_{3c} eV
360	2.8	1.7	1.6[c]	2.7	6.4	6.5
970	3.2	1.6	3.4	6.7	5.9	6.1

[a]Activated cyclohexene-t molecules formed by recoil T-for-methyl substitution with methylcyclohexene.

[b]Effective pressure = $1.0\ P_{C_7H_{12}} + 0.17\ P_{^3He} + 0.24\ P_{NO}$.

[c]Determined with an estimated[39] collision diameter for cyclohexene of 5.47×10^{-8} cm and 6.12×10^{-8} cm for methylcyclohexene.

Figure Captions

Fig. 1. The unimolecular decomposition of 4-methylcyclohexene-t to give propylene-t or butadiene-t; unscavenged data at 135°C. Activated 4-methylcyclohexene-t molecules are formed by recoil T-for-H substitution. The abscissa is the effective collisional deactivation pressure (in the sample capsule) defined as: effective pressure = 4-methylcyclohexene pressure + 0.17 (helium-3 pressure).

Fig. 2. The unimolecular decomposition of 3-methylcyclohexene-t to give ethylene-t or pentadiene-t; unscavenged data at 135°C. Activated 3-methylcyclohexene-t molecules are formed by recoil T-for-H substitution. The abscissa is the effective collisional deactivation pressure (in the sample capsule) defined as: effective pressure = 3-methylcyclohexene pressure + 0.17 (helium-3 pressure).

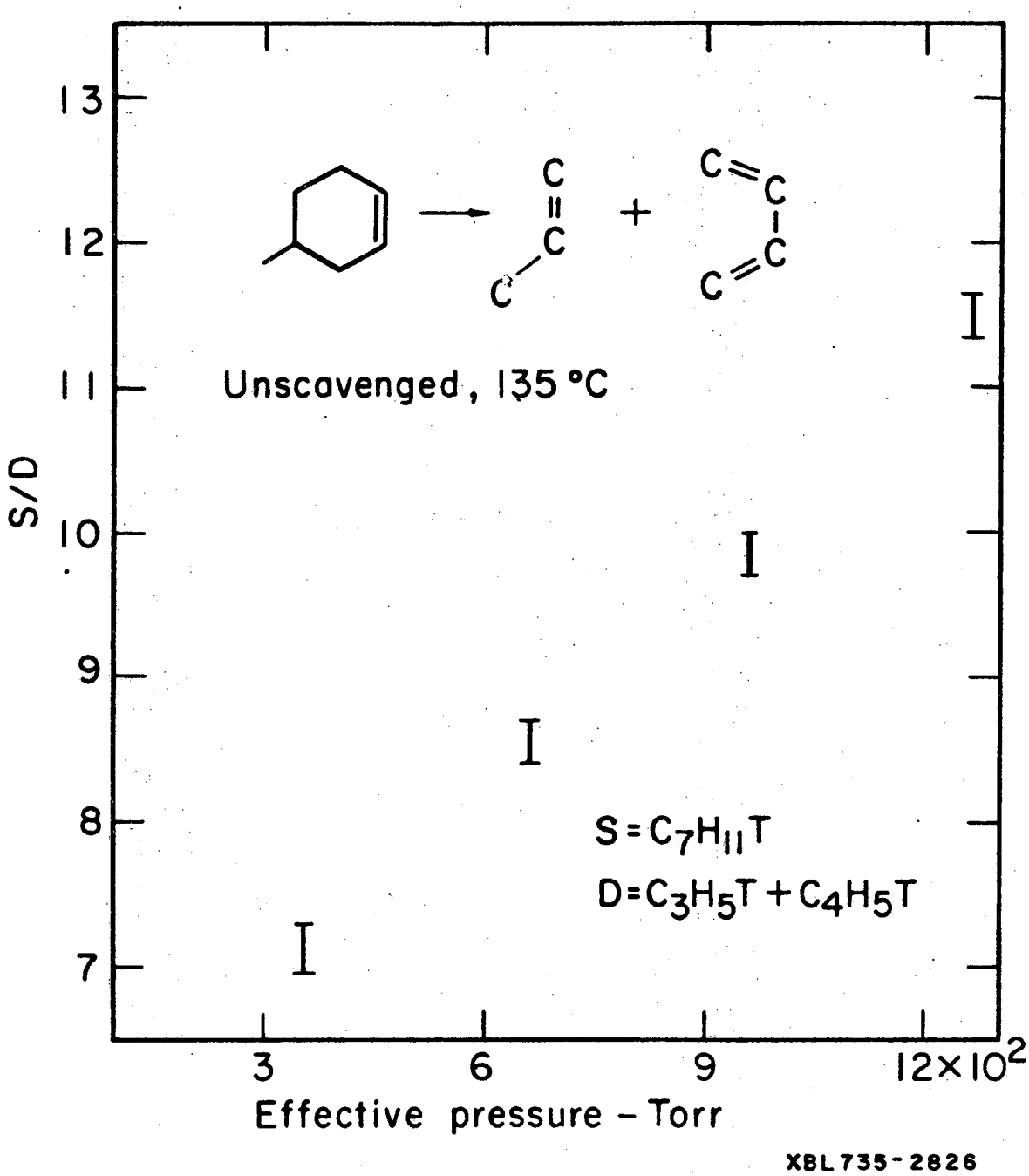
13
12
11
10
9
8
7
S/D
Unscavenged, 135 °C
S = C7H11T
D = C3H5T + C4H5T
3
6
9
12×10²
Effective pressure – Torr
XBL 735-2826

Fig. 1

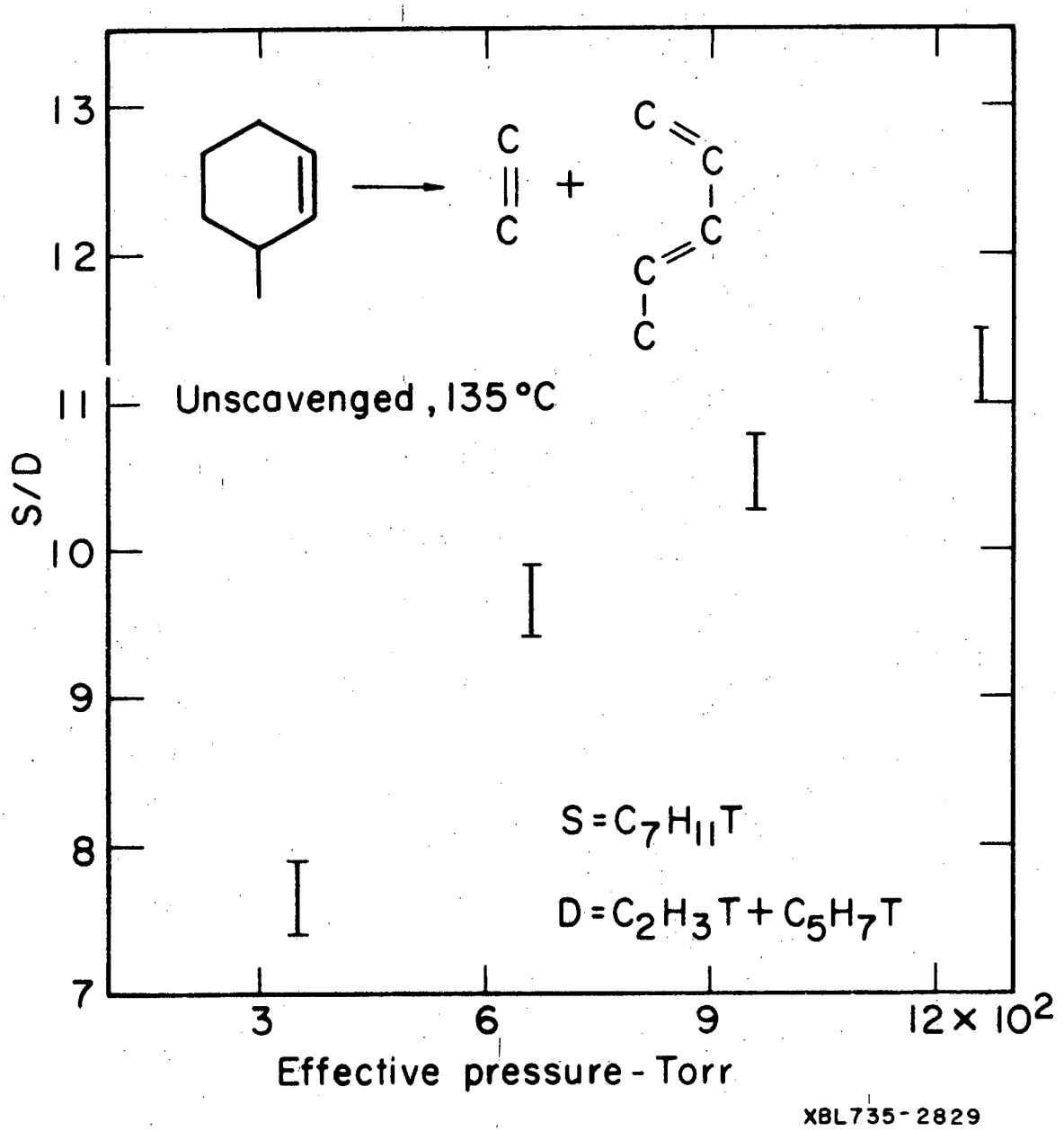
13
12
11
10
9
8
7
S/D
Unscavenged, 135 °C
S = C7H11T
D = C2H3T + C5H7T
3
6
9
12 × 10^2
Effective pressure - Torr
XBL735-2829

Fig. 2

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