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LBL-1906

RECOIL TRITIUM REACTIONS WITH CYCLOHEXENE AND ALKENES: DETERMINATION OF RATE PARAMETERS*

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June 1973

ABSTRACT

Kinetic rate parameters can be determined from recoil tritium reaction studies although the energy distribution of the reacting tritium atoms is not known. T is produced by $^3He(n,p)T$. Recoil T-for-H substitution on cyclohexene gives excited cyclohexene-t molecules. The dependence of product yield on pressure (in the 300 to 1500 Torr pressure range) showed that the excited cyclohexene-t molecules decomposed unimolecularly to give ethylene-t and butadiene-t with an apparent rate constant (at 135° C) of 5×10^6 sec^{-1}. The s parameter in the RRK (for Rice, Ramsperger and Kassel) treatment of the unimolecular decomposition of cyclohexene was determined as s = 24. Similarly, the pressure dependence of product yield showed that cyclohexyl-t radicals which are formed by recoil T atom addition to cyclohexene decomposed unimolecularly to give n-hexene-t, 1-butene-t and methane-t with rate constant 8×10^3 sec^{-1}, 3×10^4 sec^{-1}, and 5×10^2 sec^{-1},

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respectively. The relative rate of abstraction versus addition of radicals in alkenes was determined from the scavenger dependence of the yields of products with a radical precursor.

A Maxwell-Boltzmann distribution of the thermal energies of reactive species is a barrier to the study of high energy bimolecular reactions. Of two competing reactions, the reaction with the lower energy threshold tends to predominate simply because of the larger number of molecules with sufficient energy for reaction. For many years, the role of translational energy in promoting virtually all reactions has been emphasized. This suggests that the energy barrier to the study of high energy bimolecular reactions may be circumvented. One (or both) of the reactants could be a translationally excited species whose energy is not given by a Maxwell-Boltzman distribution. Translationally excited ("hot") atoms have been introduced into a system via nuclear reaction and resulting recoil.[1,2]

We are interested in the study of recoil tritium atoms. Recoil tritium studies are often limited by the lack of knowledge of the energy of the tritium atom when it reacts. The tritium atom is produced via nuclear recoil with an energy (192 keV, 1 eV = 23 k cal/mole) which is virtually infinite on the chemical scale. The tritium ion (atom) undergoes a series of energy-losing collisions with its environment until it enters the energy region below 20 eV where reactions which produce stable tritium-labeled products are thought to occur. The tritiated product distribution which is experimentally measured is the summation of tritrium atom reactions at all energies from 20 to 0.02 eV (thermal energies). Experimental determinations of the tritium atom energy distribution in the 20 to 0.02 eV range have not been made.[1,2] Attempts to calculate a theoretical tritium atom energy distribution that would explain the existing recoil tritium reaction data have not been too successful.[3-7]

At most, the Wolfgang-Estrup kinetic theory of hot atom reactions would determine the "reactivity integral," the area under a plot of reaction cross section versus the logarithm of the energy of the reacting tritium atom. To date, application of Wolfgang-Estrup has been unable to determine convincingly even the relative average energy of the hydrogen atom abstraction versus T-for-H substitution process.[8-11]

In recoil tritium reactions, the only well known energy "bench mark" is that T-for-H substitution deposits an average excitation energy of 5 eV in the resultant tritiated molecule.[12, 13] This relatively high energy of excitation, unless removed by collision, may cause the tritiated molecule to undergo unimolecular decomposition. In fact, analysis of the pressure dependence of the unimolecular decomposition of cyclobutane-t (following T-for-H substitution) with the RRKM theory (Rice, Ramsperger, Kassel and Marcus) of unimolecular reactions[14, 15] led to the 5 eV figure. The average energy of the reacting tritium atom is still not known. As Rowland[1] points out, measurements have not been made of the kinetic energies of the replaced hydrogen atoms. Therefore there is no direct indication as to whether an excitation energy of 5 eV corresponds to a 10 eV T atom knocking out a 5 eV H atom or a 5.5 eV T atom giving rise to a 0.5 eV H atom.

Because of the lack of knowledge of the energy of the tritium atom when it reacts and because the average energy of excitation is not too useful in analyzing competing unimolecular reaction channels, kinetic parameters often cannot be extracted from recoil tritium reaction studies. Even the simplest concepts of rate processes include an explicit energy dependence (see Refs. 14 and 15 and references therein).

In this paper we attempt to show that kinetic parameters can be determined from selected, carefully designed recoil tritium experiments, namely: (1) studying the pressure dependence of the unimolecular decomposition of excited tritiated molecules following T-for-H substitution, (2) studying the pressure dependence of the unimolecular decomposition of an excited tritiated alkyl radical following T atom addition to an alkene, (3) studying the scavenger dependence of alkyl-t radicals formed in a T + alkene system.

EXPERIMENTAL

The samples were prepared in 1720 Pyrex capsules (14 ml internal volume) using vacuum line techniques similar to those previously described.[16] More details of sample preparation are given elsewhere.[17] 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[18] 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. All other materials used were research grade. All irradiations were made in the Berkeley Campus Nuclear Reactor. Irradiations at 25°C were made in the Lazy Susan facility for 10 min. at a flux of 3.8×10^{11} n cm^{-2} sec^{-1}. Irradiations at 135 ± 0.5°C were made in the Hohlraum in a specially designed irradiation container described elsewhere.[19] The irradiations at 135°C were for 8.0 hours at a flux of 3.9×10^8 n cm^{-2} sec^{-1}. Radiation damage due to the recoils following the ^{3}He(n, p)T reaction was less than 1%.

The samples were analyzed with a radio-gas-chromatographic technique detailed elsewhere.[18] Good resolution was obtained for all major product peaks in an analysis time of ten hours (for cyclohexene samples) or less (C_2 to C_4 parent hydrocarbons). "Polymer-t" is defined as tritiated material not eluted in the normal radio-gas-chromatographic analysis. "Polymer-t" was recovered and monitored by procedures similar to those previously described.[20] All data reported represents the average of the yields from two identical samples. Unless otherwise stated, the yields of major products from identical samples agreed to within 3%.

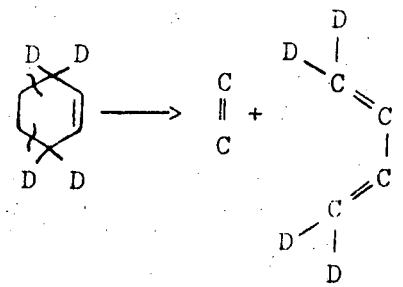
RESULTS AND DISCUSSION

Determination of the s Parameter in the RRK Treatmemt of Cyclohexene Unimolecular Decomposition. The unimolecular decomposition of cyclohexene to give primarily ethylene and butadiene has been well established in pyrolysis,[21-25] shock tube,[26-28] photolysis,[29-30] and mercury sensitized photolysis[31] 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.[23, 24, 30] A possible radical contribution to the ethylene and butadiene yield has been proposed from cyclohexyl radicals via H-atom addition to cyclohexene.[26, 27] However, addition of scavenger does not affect the ethylene and butadiene yield.[23, 30, 31] The unimolecular rate constant for cyclohexene decomposition

$$k_a = 10^{15.3} \exp(-66{,}900 \text{ cal}/kT) = A \exp(-E_o/kT) \qquad (1)$$

has been so well determined that cyclohexene is used as an internal standard in shock tube studies.[27, 28]

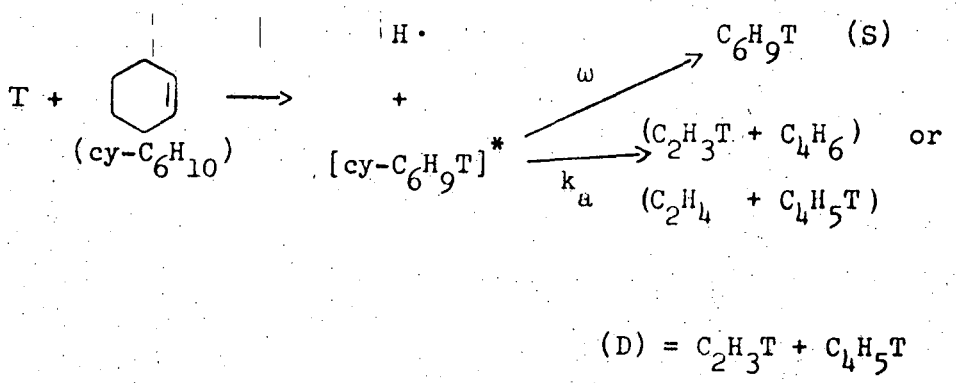
Strong evidence for the retro-Diels-Alder cleavage of cyclohexene comes from the photolysis of cyclohexene-3, 3, 6, 6-d_4. The photolysis



(2)

of cyclohexene-3, 3, 6, 6-d_4 occurred as shown to give C_2H_4 and $C_4H_2D_4$ in 98% of the decomposition 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 $C_4H_4D_2$.

Scavenger studies of recoil tritium reactions with cyclohexene at 25°C[32, 33] show that ethylene-t (C_2H_3T) and butadiene-t (C_4H_5T) are chiefly "hot" reaction products: (a) The ethylene-t yield is reduced by less than 10% with oxygen scavenging. (b) The "hot" butadiene-t yield could <u>only</u> be determined with oxygen or butadiene-d_6 scavenging. Survival in the presence of oxygen scavenging is consistent with ethylene-t and butadiene-t resulting from unimolecular decomposition of cyclohexene-t formed via a T-for-H substitution reaction:



(3)

$$(D) = C_2H_3T + C_4H_5T$$

where $\omega = Z\,P$ = collision frequency,

P = cyclohexene pressure in Torr, Z = collision number,[34]

S = collisional stabilization product, and

D = unimolecular decomposition product.

The apparent rate constant of unimolecular decomposition, k_a, is given by[35]

$$k_a = \omega(D/S) = Z\,(D/S)\,P. \qquad (4)$$

The S/D ratio should vary linearly with pressure for a unimolecular process. The collision frequency at the pressure where S/D = 1 is k_a.

The unimolecular formation of ethylene-t and butadiene-t as shown in Eq. 3 was confirmed by the linear pressure dependence of the stabilization (S)/decomposition (D) ratio shown in Fig. 1. Experiments at elevated temperature were required to obtain a larger pressure range than the (zero to) 7 cm Hg cyclohexene vapor pressure available at 25°C. In Fig. 1, the pressure represents the total effective collisional deactivation pressure in the sample capsule. Each sample contained 98 Torr of ^{3}He at 135°C and a variable pressure of cyclohexene. Relative collisional deactivation efficiencies estimated from published sources[36] show that on

a pressure-for-pressure basis ^3He is only 20% as effective as cyclohexene (C_6H_{10}) in deactivating excited cyclohexene molecules. Hence the "effective" collisional deactivation pressure of cyclohexene in the capsule is defined as

$$P_{effective} = P_{C_6H_{10}} + 0.2 \; P_{^3He} \; . \tag{5}$$

The use of the effective pressure for the P in Eq. 4 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 cyclohexene-t molecule and an unlabeled cyclohexene molecule is necessary for complete deactivation of the excited cyclohexene-t species. We point out that this "strong collision"[14, 15] assumption may not be valid at the high energies of excitation encountered in recoil tritium experiments.

The least-squares fitted line of the S/D ratio versus pressure [actually log (S/D) versus log (pressure)] was extrapolated to S/D = 1.0. The pressure at which S/D was 1.0 was 0.50 Torr. A previous determination by Weeks and Garland of the pressure at which the S/D ratio from the recoil tritium initiated unimolecular decomposition of cyclohexene equalled 1.0 gave a pressure of 0.2 Torr. However, in these previous experiments, the temperature ranged from 25°C for the lowest pressure unscavenged sample to 135°C for the highest pressure unscavenged sample.[37]

The data shown in Fig. 1 are for unscavenged samples at 135°C. For both O_2 and SO_2 scavenger, a (scavenger)/(scavenger + cyclo-

hexene) ratio of 0.08 was insufficient to intercept the cyclohexyl-t radical intermediate to the cyclohexane-t yield. At 25° C, this concentration of scavenger was sufficient to intercept cyclohexyl-t radicals.[32,33] The failure of both SO_2 and O_2 scavenger at 135° C may be due to macroscopic reactions between cyclohexene and the scavenger. The reaction of cyclohexene with oxygen scavenger has been discussed.[32] For oxygen scavenging, a (scavenger)/(scavenger + cyclohexene) ratio of 0.14 was sufficient to intercept the cyclohexyl-t radicals. At this scavenger concentration and with 300 Torr cyclohexene pressure the ethylene-t yield relative to the sum of yields from excited cyclohexene-t molecules (C_2H_3T + C_4H_5T + cy-C_6H_9T) was decreased by 9% with O_2 scavenging. This indicates that at 135° C (as at 25° C) ethylene-t results largely from "hot" tritium atom reactions. The unscavenged data were "corrected" by subtracting a 9% radical contribution to the ethylene-t yield at all pressures. The resultant "scavenged" plot of S/D versus effective pressure extrapolated to S/D = 1 at 0.33 Torr.

Another interesting scavenger effect was noted. At 135° C, unlike 25° C,[32, 33] the butadiene-t yield is the same in O_2 scavenged, butadiene-d_6 scavenged, and unscavenged samples. Apparently the butadiene-t yield was not selectively depleted by radiolysis-produced H atoms in unscavenged samples at 135° C (unlike 25° C). The butadiene-t is selectively depleted because butadiene is extremely reactive with H atoms (see Table I). The total radiolysis damage in the samples at 135° C was similar to samples at 25° C. The temperature effect on the individual rate constants for H-atom addition to cyclohexene and for H-atom addition to butadiene is not known. The temperature effect on the competitive

rates of H-atom addition to cyclohexene versus butadiene is probably slight. In unscavenged T + cyclohexene reactions at 25°C, the butadiene-t yield was increased to within 10% of the oxygen scavenged value when the irradiation period was increased from 10 min to 8 hours (with total dose similar to that previously reported.[32, 33]) Apparently the butadiene-t yield is not selectively depleted by reactions with radiolysis produced H atoms when the irradiation period is 8 hours. This trend is consistent with a decreased steady-state concentration of H-atoms with the lower tritium atom production rate that existed in 8 hour (versus 10 min) irradiations.

The apparent rate constant, k_a, for the unscavenged unimolecular decomposition of cyclohexene-t to ethylene-t or butadiene-t was calculated from Eq. 4 as 5.1×10^6 sec^{-1}. The calculation of Z was made with an estimated[36] collision diameter for cyclohexene of 5.47×10^{-8} cm. Using this value of k_a and an average excitation energy (following T-for-H substitution) of 5 eV for the E in Eq. 6, the s parameter in the RRK treatment[38-41] of the unimolecular decomposition of cyclohexene was determined as s = 24. The A and E_o used were from Eq. 1.

$$k_a = A \left[\frac{E - E_o}{E}\right]^{s-1} . \qquad (6)$$

For a fixed s = (1/2) (3N-6) = 24, E was 4.6 eV. For s = (2/3) (3N-6) = 28, E was 5.6 eV. For a fixed s = 32 ≈ (3/4) (3N-6), E was 6.2 eV.

Determination of the Apparent Rate Constants of the Unimolecular Decomposition/Isomerization of Cyclohexyl Radicals. The cyclohexane-t yield in T + cyclohexene reactions at 25° C appears to have a radical precursor.[32, 33] The cyclohexane-t yield: (a) decreases to nearly zero with O_2 or SO_2 scavenging. (b) decreases with butadiene-d_6 scavenging. (c) increases with H_2S scavenging. All of these trends indicate a radical precursor. The proposed mechanism of cyclohexane-t formation was tritium atom addition to the double bond of cyclohexene to form a cyclohexyl-t radical. The cyclohexyl-t radical could then abstract a hydrogen atom from the bulk system to form cyclohexane-t. Hydrogen atom abstraction by cyclohexyl radicals to form cyclohexane has been observed in other systems.[42] Addition of a moderator should increase the number of tritium atoms which survive collisions in the 20 to 0.02 eV energy range and ultimately react as thermal tritium atoms. The lowest activation energy process for thermal tritium atoms is addition to the double bond. The monotonic increase in the cyclohexane-t yield (from T + cyclohexene reactions at 25° C) with increasing amounts of added moderator that was observed with helium,[43] krypton,[43] and nitrogen[44] as moderators was reproduced in this laboratory with neon as a moderator.

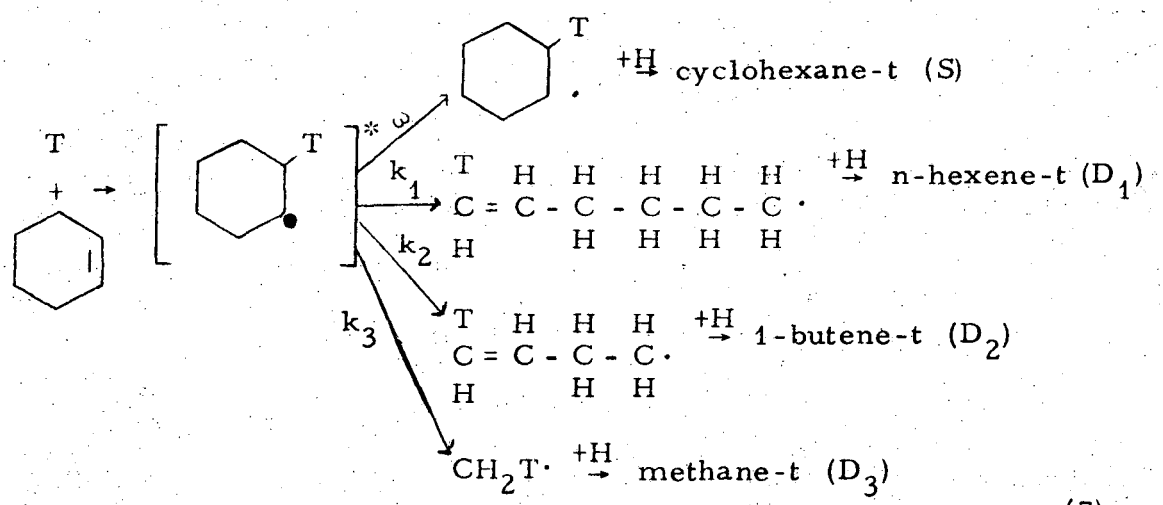
Cyclohexyl radicals have also been observed to add to the double bond of cyclohexene to initiate a radical chain.[45, 46] The radical chain initiated by a cyclohexyl-t radical would eventually undergo termination and be monitored as "polymer-t". The yield of "polymer-t" also increased with increasing amounts of added moderator. All this

indicates the presence of relatively large amount of cyclohexyl-t radicals in the T + cyclohexene system. Cyclohexane-t alone is a major product.

Cyclohexyl radicals have also been observed to undergo decomposition or isomerization.[47-49] The isomerization of cyclohexyl radicals to straight-chain alkenyl radicals has been postulated as the first step of a unimolecular decomposition process which leads to a complex series of products including methane, ethane, ethylene, propane, propylene, butenes, and methylcyclopentane.[47-49] The formation of n-hexenyl radicals without a cyclohexyl radical precursor results in: (a) n-hexene via H-atom abstraction, (b) methylcyclopentane via an isomerization reaction.[50] The decomposition (isomerization) of cyclohexyl-t radicals from T + cyclohexene reactions may result in any or all of the aforementioned products from cyclohexyl radicals being tritium labeled.

Many of the species which may result from the decomposition/isomerization of cyclohexyl-t radical are observed as tritiated products in T + cyclohexene reactions. This list includes methane-t, ethane-t, ethylene-t, propane-t, propylene-t, 1-butene-t, trans-2-butene-t, cis-2-butene-t, and n-hexene-t/methylcyclopentane-t.[51] These products are observed in small yields. Both at 135° C and 25°C roughly 85% of unscavenged T + cyclohexene reactions which gave gas phase products resulted from abstraction to form HT, addition to form cyclohexyl-t radicals (a portion of which were monitored as cyclohexane-t) and T-for-H substitution to form cyclohexene-t. Some of

these small-yield tritiated products show the same scavenger dependence as the cyclohexane-t yield. At 25° C the yields of methane-t, ethane-t, 1-butene-t and n-hexene-t decrease to nearly zero with O_2 or SO_2 scavenging and increase with H_2S scavenging, indicating a radical precursor. Therefore we propose the following reaction scheme for excited cyclohexyl-t radicals formed by the addition of a tritium atom to cyclohexene.



(7)

The site of the tritium label in the n-hexenyl-t radical and the 1=butenyl-t radical shown in Eq. 7 is purely arbitrary and is shown only for the sake of material balance along the reaction path. In unscavenged T + cyclohexene systems, tritiated radical products, once collisionally stabilized, may: (a) abstract a hydrogen atom to form a tritiated alkane or alkene. This is indicated by the + H over the arrow in Eq. 7. (b) add to the double bond of cyclohexene.

With H_2S scavenging,[33] all the radicals react rapidly with H_2S to abstract a hydrogen atom before they add to cyclohexene to eventually form "polymer-t". (See Table II for a comparison of the rate constants of reaction of alkyl radicals with H_2S versus alkenes of 25°C. Similarly, at 135°C, the rate constant of the reaction of alkyl radicals with H_2S is larger than with alkenes by several orders of magnitude.) For example, all n-hexenyl-radicals formed by channel 1 (with rate constant k_1) are monitored as n-hexene-t when H_2S is employed as a scavenger. The pressure dependence of the S/D ratio for reaction channel 1, 2, and 3 (with rate constants k_1, k_2, and k_3) are shown in Fig. 2.

The pressure dependence of the S/D_1 and S/D_2 ratio may be well-represented by a line for the unimolecular decomposition/isomerization of cyclohexyl-t radicals to give n-hexenyl-t and 1-butenyl-t radicals, respectively. The increase scatter in the pressure dependence of the S/D_3 ratio for the unimolecular decomposition of cyclohexyl-t to give methyl-t radicals results from the small yield of methane-t. A small uncertainty in the methane-t yield is reflected in a large uncertainty in the S/D_4 ratio. In this respect the yield of ethane-t is so small that the resultant uncertainty in the S/D ratio for D = ethane-t makes observation of a pressure dependence impossible.

The rate constants k_1 and k_2 were determined from extrapolation of S/D versus effective pressure to S/D = 1. The calculation of Z was made with an estimated collision diameter of 5.67×10^{-8} cm for

cyclohexyl-t radicals.[36] The values of the calculated rate constants at 135°C and the pressure at which S/D = 1 were: $k_1 = 8.4 \times 10^3$ sec^{-1} (7.9×10^{-4} Torr), $k_2 = 3.4 \times 10^4$ sec^{-1} (3.2×10^{-3} Torr). Using Eq. 4 to determine k_3 at each effective pressure and comparing k_3 with k_1 and k_2 values similarly derived allowed k_3 to be estimated as 5×10^2 sec^{-1}. The large uncertainty in the cyclohexane-t/methane-t ratio, as indicated by the large error bars in Fig. 2, prevented meaningful extrapolation over a large pressure range to the pressure of which S/D = 1.

A previous determination by Weeks and Garland of k_1 in a recoil tritium-cyclohexene system showed that $S/D_1 = 1.0$ at 26 Torr. As discussed before, the temperature control employed by Weeks and Garland was inadequate.[37] It is interesting to note that the effect of inadequate temperature control in determining the pressure at which S/D = 1.0 was larger for cyclohexyl-t radical unimolecular decomposition/isomerization than for the unimolecular decomposition of cyclohexene-t. This is consistent with cyclohexene-t decomposition being a higher energy process.

<u>Determination of the Relative Rate of Abstraction Versus Addition of Radicals in Alkenes.</u> Collisionally stabilized alkyl-t radicals which are formed from T + alkene reactions can react only by abstraction of a hydrogen atom to form an alkane-t species or by addition to the double bond — provided, of course, that the concentration of radicals from radioylsis damage is kept low enough to make radical-radical reactions negligible. The addition of a tritiated alkyl radical to the alkene may sufficiently energize the newly formed alkyl-t radical to cause it to

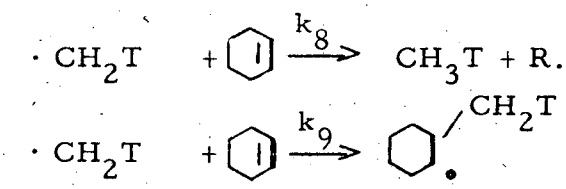
undergo unimolecular decomposition/isomerization. The newly formed alkyl-t radical, once collisionally stabilized, may also abstract a hydrogen atom to form a tritiated alkene or add to the alkene to lengthen the tritiated radical chain. Tritiated dimers from recoil tritium reactions with alkenes have been monitored by radio-gas-chromatography.[52, 53]

Methylcyclohexane-t has been observed in unscavenged T + cyclohexene systems. Methylcyclohexane-t presumably arises from the addition of CH_2T radicals to cyclohexene. In O_2 and SO_2 scavenged systems, the yield of methylcyclohexane-t was zero. Either the CH_2T radical or the methylcyclohexyl-t radical precursor to the methyl cyclohexane-t yield could be scavenged by O_2 or SO_2. In neon moderated systems, the yield of methylcyclohexane-t increased with increasing amounts of added moderator. This is consistent with increased stabilization of the methylcyclohexyl-t radical formed from CH_2T addition to cyclohexene.

In H_2S scavenged T + cyclohexene systems, the yield of methylcyclohexane-t was also zero. A precursor to the methylcyclohexyl-t radical was being intercepted by H_2S. If methylcyclohexyl-t radicals were formed directly from T + cyclohexene reactions, H_2S would readily donate a hydrogen atom to the methylcyclohexyl-t radical and the yield of methylcyclohexane-t would increase with H_2S scavenging. As shown by the data in Table II, H_2S would intercept the CH_2T radical (to form methane-t) before the CH_2T radical could add to the parent alkene, cyclohexene. The yield of methane-t increased with H_2S scavenging.

We propose that: (a) The increase in the methane-t yield with

H_2S scavenging represents that portion of the total CH_2T radicals formed by T + alkene reactions that add to the parent alkene in unscavenged systems. (b) The decrease in the methane-t yield with O_2 or SO_2 scavenging represents that portion of the total CH_2T radicals formed from T + alkene reactions that abstract a hydrogen atom from the parent alkene in unscavenged systems. This allows the determination of the relative rate constants of addition versus abstraction by alkyl radicals in alkenes. The method is shown in Eqs. 8-13 for the specific methyl-t radical + cyclohexene case, but is readily generalized. The argument is analogous to previous determinations of the rates of methyl radical addition to alkenes by "methane deficiency" type experiments.[54]



(8)

(9)

$$\frac{d[CH_3T]}{dt} = k_8[\cdot CH_2T][C_6H_{10}] \tag{10}$$

$$\frac{d[C_7H_{12}T]}{dt} = k_9[\cdot CH_2T][C_6H_{10}] \tag{11}$$

$$CH_3T(H_2S) - CH_3T\ (\text{unscavenged}) \approx \Delta[C_7H_{12}T] \tag{12}$$

$$CH_3T\ (\text{unscavenged}) - CH_3T(O_2) \approx \Delta[CH_3T] \tag{13}$$

Both reactions (8) and (9) occurred in the same sample capsule. The concentrations of methyl-t radicals and cyclohexene are identical in Eq. 10 and 11, hence

$$\frac{CH_3T\,(\text{unscavenged}) - CH_3T(O_2)}{CH_3T(H_2S) - CH_3T\,(\text{unscavenged})} = \frac{k_8}{k_9} \tag{14}$$

The subtraction of the O_2 scavenged methane-t yield value removes that portion of the methane-t yield which is formed by an unscavengeable, non-radical reaction path. This non-scavengeable methane-t yield may result from a direct T-for-alkyl substitution process on the terminal carbon in the carbon chain.[1,2]

The implicit assumption in this determination of the abstraction/addition ratio of CH_2T radicals (or other tritiated radicals) in T + alkene systems is that the added scavenger does not affect the production of CH_2T radicals. The added scavenger has two effects:

(a) Increased pressure. Increasing the pressure of the system may increase the stabilization of the alkyl-t radical (cyclohexyl-t radical) formed from tritium atom addition to the alkene (cyclohexene). With increased stabilization there is less unimolecular decomposition of the alkyl-t radical to form CH_2T radicals. The increase in the effective collisional deactivation pressure is small, however. The scavenger pressure is usually only 5 to 10% of the hydrocarbon pressure. In addition, the scavenger is usually less efficient as a collisional de-activator than the parent alkene. The effect of increased effective pressure on CH_2T radical production is very probably less than the experimental error.

(b) Removal of thermal tritium atoms. Scavenging of the thermal tritium atoms (which constitutes the majority of tritium atoms which undergo addition[52]) before they add to the alkene reduces the number

of excited alkyl-t radical precursors to the CH_2T yield. From the data in Table I, oxygen is obviously capable of removing all thermalized tritium atoms. This does not affect the proposed determination of the abstraction/addition ratio. Oxygen scavenging of thermalized tritium atoms means that oxygen has two chances (thermal T atom and CH_2T radical) to eliminate a radical contribution to the methane-t yield. The methane-t yield which remains with oxygen scavenging is truly the result of a high energy, non-scavengeable process.

The data in Table I also show that H_2S is not too efficient in removing H atoms. In fact, the rate constant of tritium atom addition to the alkene may be slightly larger than the rate constant for the tritium atom to abstract a hydrogen atom from H_2S to form HT.

$$T + \text{alkene} \xrightarrow{k_{15}} \text{alkyl-t radical} \tag{15}$$

$$T + H_2S \xrightarrow{k_{16}} HT + HS\cdot \tag{16}$$

$$\frac{-d[T]}{dt} = k_{15}[T]\,[\text{alkene}] + k_{16}[T]\,[H_2S] \tag{17}$$

$$\begin{array}{l}\text{fraction of thermalized}\\ \text{tritium atoms scavenged}\\ \text{by } H_2S\end{array} = \frac{k_{16}[H_2S]}{k_{15}[\text{alkene}] + k_{16}\,H_2S]} \tag{18}$$

The fraction of thermalized tritium atoms scavenged by H_2S may be: (a) lessened by using the minimum mole % scavenger required for complete scavenging of alkyl-t radicals, (b) corrected for if k_{15} and k_{16} are known. When corrections are made for the reaction of thermal tritium atoms with H_2S, the denominator of Eq. 14 becomes (to first order)

$$CH_3T(H_2S) - CH_3T\,(\text{unscavenged}) + \frac{k_{16}[H_2S]}{k_{15}[\text{alkene}] + k_{16}[H_2S]}\,[CH_3T(H_2S) - CH_3T(O_2)]\,. \qquad (19)$$

The quantity $[CH_3T(H_2S) - CH_3T(O_2)$ represents the total CH_3T yield from a radical precursor formed by the addition of a tritium atom to the alkene parent. Without the correction factor the abstraction/addition ratio [k_8/k_9 from Eq. 14] would be overestimated.

The results in Table II are for uncorrected k_8/k_9 values. The comparison to literature values of abstraction/addition ratios is made on the assumption of a negligibly small secondary isotope effect in the reactions of the alkyl-t (versus fully protonated) radicals. The differences between the k_8/k_9 values for methyl-t radicals from recoil tritium reactions (this work) and for methyl radicals from photolytic methods (Ref. 65) may indicate differences in the energy spectra of the methyl-t versus methyl radicals. "Hot" methyl-t radicals may comprise a significant portion of the methyl-t radicals produced by recoil tritium reactions.

The determination of relative rate constants may be extended to a system with two alkenes in the same sample. The relative rate constants for the addition of CH_2T radicals to the two alkenes may be determined with two sets of yield and pressure (of each parent alkene) values substituted into two equations with two unknowns. If for one of the alkenes $k_8/k_9 \approx 0$ (as is the case for butadiene) the simpler set of equations does not require simultaneous solution. For the butadiene-

d_6/cyclohexene system, k_9(butadiene-d_6)/k_9(cyclohexene) was determined as 7.5 and 5.0 for two sets of yield and pressure values. Although there is a large spread in the data, the determination that k_9 for butadiene is larger than k_9 for cyclohexene is consistent with the trend of rate constants in Table II. Similarly for the butadiene/1-butene system, k_9(butadiene)/k_9(1-butene) was determined as 76 and 309 for two sets of yield and pressure values. The literature value of k_8/k_9 for 1-butene of 0.37 (Table II) was used. The reported value of k_9(butadiene)/k_9(1-butene) from Table II is 160. Once again the determination that k_9 for butadiene is larger than k_9 for 1-butene is qualitatively correct. The large spread in the values is inherent in the extention of the determination of relative rate constants to a system with two alkenes in the same sample. Determination of relative k_9 values depends on taking the difference of two yield values which are nearly equal. This small difference between two large numbers is often only a factor of 2 or 3 larger than the uncertainty of each of the large yield values. The resultant spread in the data is obvious. This effect is also inherent in determining k_8/k_9 but is not as serious.

SUMMARY AND CONCLUSIONS

Recoil tritium studies often are limited by the lack of knowledge of the energy of the tritium atom when it reacts. This often precludes determining kinetic parameters from hot atom studies. More frequently kinetic parameters from other chemical methods are used with recoil tritium reaction yields to further the study of recoil tritium

reactions. In this paper we have tried to use recoil tritium reactions to determine kinetic parameters. First, the pressure dependence (in the 300-1500 Torr range) of the unimolecular decomposition of cyclohexene-t to ethylene-t and butadiene or ethylene and butadiene-t was determined. The apparent rate constant of cyclohexene unimolecular decomposition at 135°C (5.1×10^{6} sec^{-1}) and the s parameter in RRK treatment of the unimolecular decomposition of cyclohexene (s = 24) were calculated from these data. Second, the unimolecular decomposition/isomerization of cyclohexyl-t radicals to give n-hexene-t, 1-butene-t, and methane-t was established and the individual rate constants for these processes were determined as 8.4×10^{3} sec^{-1}, 3.4×10^{4} sec^{-1}, and 5×10^{2} sec^{-1} respectively. Finally, the scavenger dependence of yields with an obvious radical precursor was used to determine the relative rate constants of abstraction versus addition of that radical in the alkene parent compound. This area looks promising. Further comparisons of abstraction/addition ratios from recoil tritium experiments with conventional kinetic determinations are necessary.

We conclude that rate parameters can be determined in carefully designed recoil tritium experiments.

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Table I. Hydrogen Atom Reaction Rate Constants at 25°C

Reactant	Addition [10^9 cm^3 $mole^{-1}$ sec^{-1}]	Abstraction [10^9 cm^3 $mole^{-1}$ sec^{-1}]
Butadiene	1500 Ref. [55, 56]	22 [55, 56]
Isobutene	770 [55, 56]	25 [55, 56]
Cyclohexene	600 [57]	n. d.[a]
1-Butene	320 [55, 56]	30 [55, 56]
Propylene	300 [55, 56]	25 [55, 56]
O_2	300 [58, 59]	–[b]
Ethylene	200 [55, 56]	13 [55, 56]
H_2S	–	160 [55, 56]
SO_2	6 [60]	–
n-Butane	–	0.6 [61]

[a]Not determined.
[b]Not applicable.
Addition by H-atoms forms a radical; abstraction by H atoms forms H_2.

Table II. Radical Reaction Rate Constants at 25°C

Reactants		k_9[a]	k_8/k_9[b]	k_8/k_9
Radical	Double bond	10^6 cm^3 $mole^{-1}$ sec^{-1}	Literature	This work
Methyl	O_2	300,000 [62]	n.a.[c]	—[d]
	SO_2	5,000 [63]	n.a.	—
	H_2S	3,000[e] [64]	n.a.	—
	Butadiene	160 [65]	—	0.0019[f]
	Ethylene	1.2 [65]	0.015 [65]	0.0028
	Propylene	1.2 [65]	0.096 [65]	0.060
	1-Butene	1.0 [65]	0.37 [65]	0.075
	Isobutene	4.0 [65]	0.040 [65]	0.086
	Cyclohexene	—	—	0.36
Ethyl	Ethylene	—	—	0.091
	Cyclohexene	—	—	0.37
Propyl	Propylene	—	—	0.15
n-Butyl	1-Butene	—	—	0.16
Ethyl	Cyclohexene	—	—	0.35
Cyclohexyl	Cyclohexene	—	—	0.29
n-Hexenyl	Cyclohexene	—	—	0.32

[a] k_9 = rate constant of radical addition to the double bond.
[b] k_8/k_9 = ratio of abstraction/addition rate constants of radicals with alkenes.
[c] Not applicable.
[d] Not determined.
[e] For H-atom abstraction.
[f] The typical sample contained 110 Torr parent hydrocarbon (55 Torr in the case of cyclohexene), 16 Torr ^3He and ~10 mole % scavenger when used.

FIGURE CAPTIONS

Fig. 1. The unimolecular decomposition of cyclohexene-t to give ethylene-t or butadiene-t; unscavenged data at 135°C. Activated cyclohexene-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 = cyclohexene pressure + 0.2 (helium-3 pressure).

Fig. 2. The unimolecular decomposition of cyclohexyl-t radicals to n-hexene-t, 1-butene-t or methane-t; H_2S scavenged data at 135°C. Activated cyclohexyl-t radicals are formed by recoil T atom addition to cyclohexene. The abscissa is the effective collisional deactivation pressure (in the sample capsule) defined as: effective pressure = cyclohexene pressure + 0.2 (helium-3 pressure) + 0.5 (hydrogen sulfide pressure).

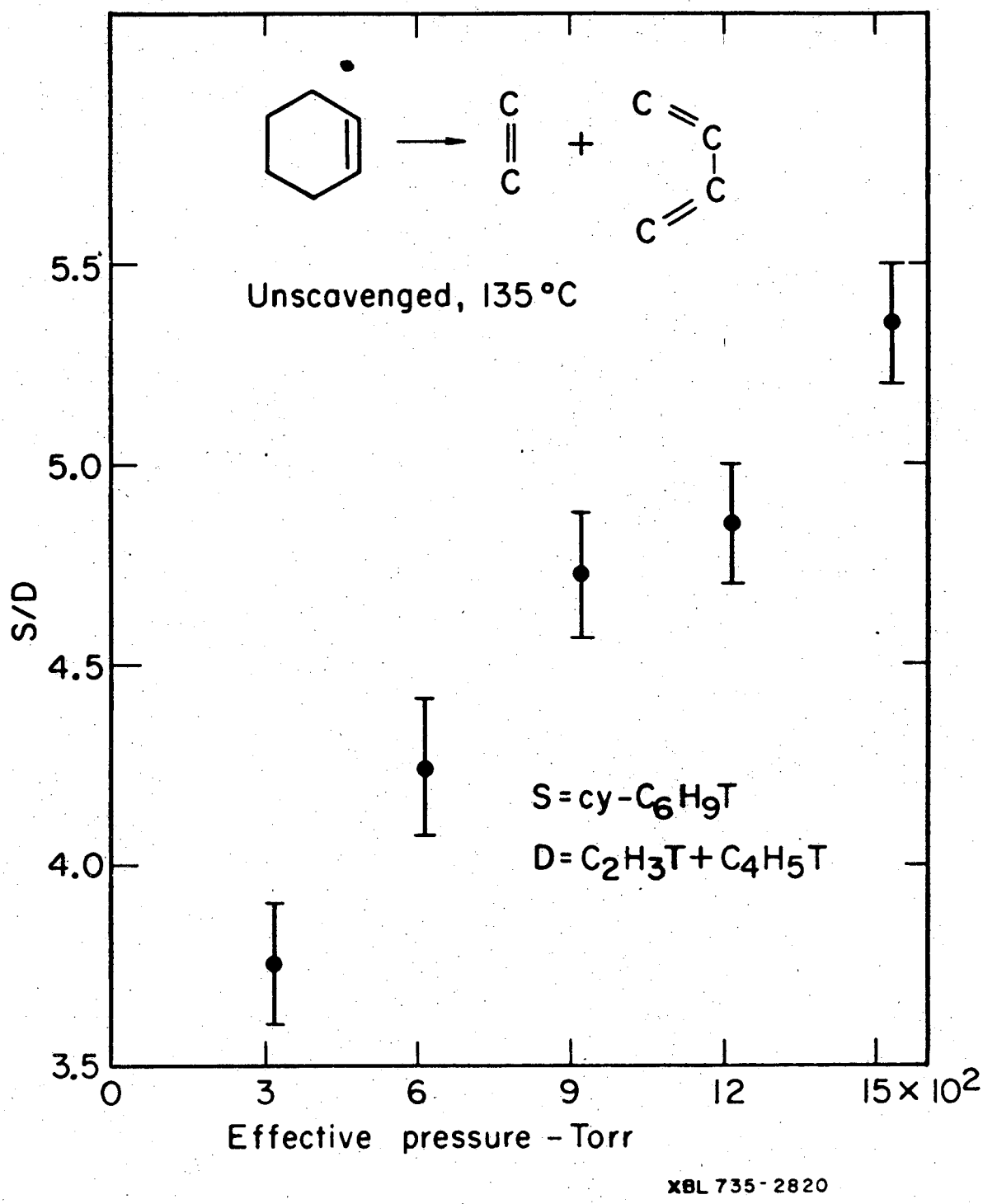
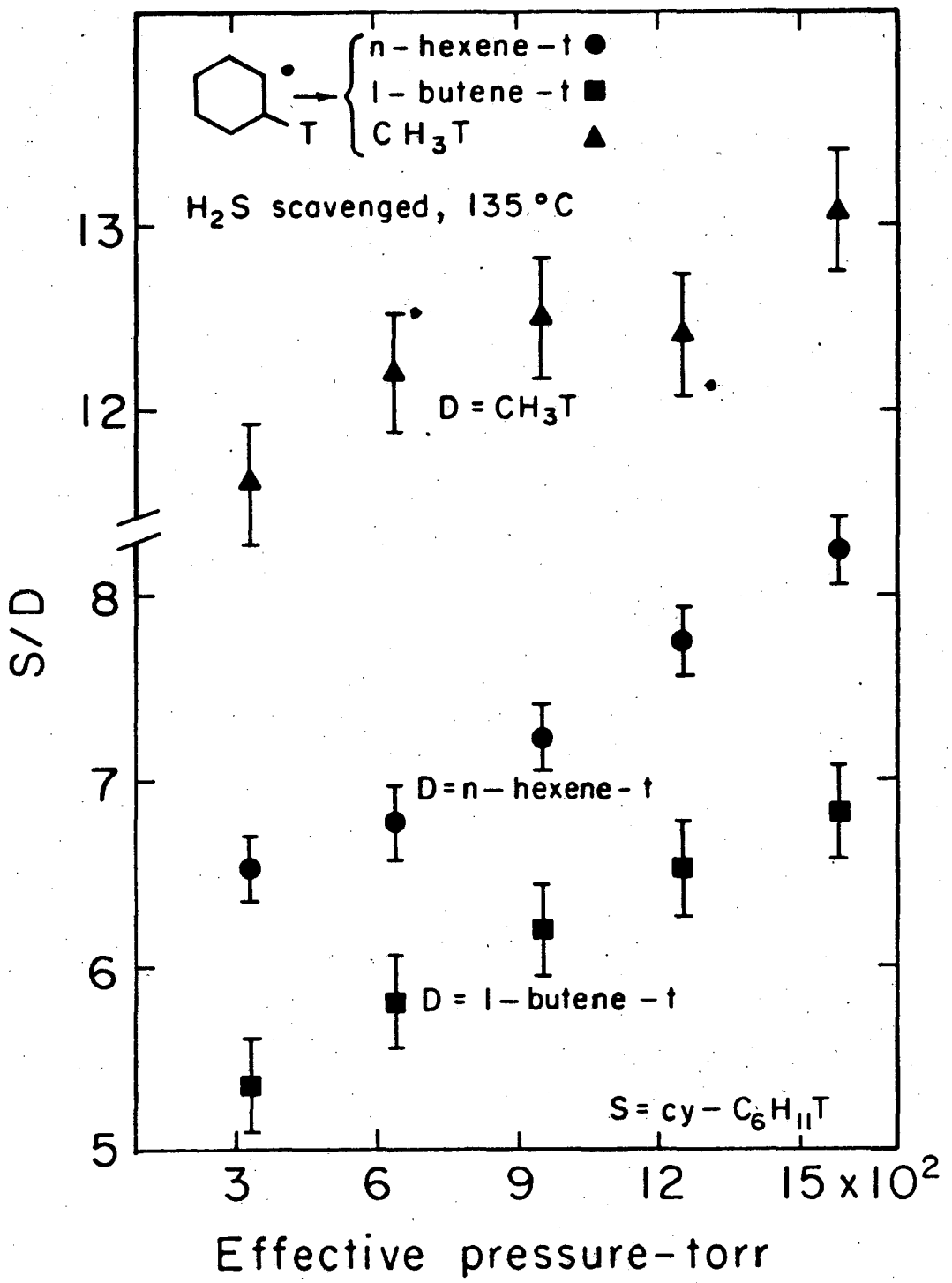

Unscavenged, 135 °C
S/D
5.5
5.0
4.5
4.0
3.5
0
3
6
9
12
15 × 10²
Effective pressure - Torr
S = cy-C6H9T
D = C2H3T + C4H5T
XBL 735-2820

Fig. 1



XBL736-3187

Fig. 2

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