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The Abstraction of Hydrogen from Hydrocarbons by Energetic Tritium Atoms[1]

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Abstract: The correlation of increasing HT yield with decreasing RH bond dissociation energy has been confirmed for recoil tritium reactions with hydrocarbons in a series of moderators: $c\text{-}C_4F_6$, 1,3-C_4F_6, Ar, and N_2. The correlation is the same in both gas- and liquid-phase experiments with $c\text{-}C_4F_6$, indicating that the abstraction mechanism is quite similar in both phases. The precision of the relative HT yield measurements is much greater than that of the bond dissociation energies available for comparison. The *per bond* yields of HT vary by a factor of 8 between cyclopentane and acetylene. Variations of this magnitude can be explained by an energy cut-off model, in which the weaker C–H bonds both permit abstraction at lower energies and also increase the probability of reaction per collision in the energy range available for reaction. The HT yield from a given molecule, RH, varies in the ratio 4.7 ± 0.2:2.2 ± 0.1:1.0 when RH is present at the same low mole fraction in the moderators $Ar/N_2/c\text{-}C_4F_6$. The average logarithmic energy loss is about twice as large in N_2- as in Ar-moderated systems.

The abstraction of hydrogen atoms by energetic tritium atoms, as in eq 1, has been observed for all kinds of C–H bonds so far tested.[3–5] Intramolecular

$$T^* + RH \longrightarrow HT + R \qquad (1)$$

$$T^* + RH \longrightarrow RT + H \qquad (2)$$

comparison of the yields from this reaction *vs.* that from the substitution reaction 2 disclosed wide variations in the magnitude of the yield ratio, HT/RT.[6] Intermolecular comparison of reaction 2 in molecules with different C–H bond types indicated that the prime source of this variation lay in the HT yields and suggested a correlation with the bond dissociation energies of the C–H bonds involved.[7] Experiments then confirmed that a close correlation with bond dissociation energies existed for the hot HT yields from many hydrocarbon molecules when compared in excess C_2D_4.[8,9]

The tritium atoms formed in these reactions are created with several factors of 10 too much energy for successful bond formation in molecular interactions and must lose almost all of this excess energy prior to the occurrence of the energetic abstraction reaction. Accordingly, the absolute yield of this reaction in a given system is very dependent upon the energy-loss processes in these higher energy ranges, and these processes could *a priori* vary widely from system to system. Indeed, the measurements thus far do indicate sufficient variation to exclude direct comparisons of absolute yields of HT in different systems as a satisfactory general procedure.

The most direct influence of these energy-loss processes occurs in the energies just above, or actually in, the range of bond-forming chemical reactions, for the energy losses in these collisions determine the total number of collisions that may be possible in passing

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[3] F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Intern. Ed. Engl.*, 3, 769 (1964).

[4] R. Wolfgang, *Progr. Reaction Kinetics*, 3, 97 (1965).

[5] "Chemical Effects of Nuclear Transformations, "International Atomic Energy Agency, Vienna, 1965, two volumes.

[6] D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, 83, 2982 (1961).

[7] J. W. Root and F. S. Rowland, *ibid.*, **84**, 3027 (1962).

[8] W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*' **39**, 2374 (1963).

[9] J. W. Root, W. Breckenridge, and F. S. Rowland, *ibid.*, **43**, 3694 (1965).

through this reaction range; *e.g.*, large energy loss in one collision may lower the residual energy below the threshold for hot reaction and thus prevent subsequent reaction in any but thermal reaction modes. Moreover, the probability of collision, and of chemical reaction, in the lower part of this reaction range is dependent upon the survival of the atom in an unbonded state from higher energy collisions.

The absolute yield of the abstraction reaction in a particular system is thus critically dependent upon the energy-loss processes and reaction probabilities characteristic of that system. However, if the general concept of these reactions elaborated above is correct, the relative yields from different C–H bonds should maintain a consistent relationship to one another when compared under equivalent conditions; as a minimum, the same rank order of increasing HT yields from different molecules should be observed in different bulk moderators. The quantitative evaluation of the relationships from one system to another can then lead to information about the relative number of tritium atom collisions in different energy ranges for various molecular systems.

The current experiments have involved the measurement of HT yields from a particular set of hydrocarbon molecules in small concentrations in different scavenger–moderator combinations: c-C_4F_6/O_2; CF_2-$CF{=}CFCF_2/O_2$; N_2/O_2; Ar/O_2. These (and all such previous comparisons)[8,9] have been carried out in gas-phase experiments. The measurements have also been extended to the liquid phase with experiments based upon c-C_4F_6/I_2 as the moderator–scavenger pair.

Experimental Section

Neutron Flux. The measurement of the yields of the hot abstraction reaction for purposes of intermolecular comparison requires that the tritium flux at each energy be reproducible from sample to sample. Thus flux consistency has been obtained in earlier experiments through the use of C_2D_4 as the bulk ingredient, with the RH compound to be measured included as a minor component.[9] The chief function of the C_2D_4 is its role as the major molecule in the system, both as moderator and as hot reactant, such that the processes of moderation and hot reaction will only be perturbed, but not substantially changed, by changes in the molecule RH from sample to sample. The C_2D_4 simultaneously fills the additional purpose of providing a good scavenger molecule for the removal of thermalized tritium atoms from the system, while meeting the necessary criterion that hot tritium reactions with it will not lead to the formation of HT. The formation of DT from the hot abstraction reaction with C_2D_4 necessitates an analytical separation of HT from DT, while providing at the same time an internal monitor for possible perturbations in the tritium atom flux.

The current experiments have been carried out with nonhydrogenous materials as the major moderator molecules. The isotopic molecular separation is therefore not required, and measurement of the tritiated molecular hydrogen is directly a measurement of the HT yield. The absence of a useful internal monitor requires careful duplication of the thermal neutron flux from sample to sample, since intersample comparisons are made on the assumption that the thermal neutron flux is identical for each sample. The thermal neutron flux is equalized in these experiments, as in previous irradiations, through the use of the rotating specimen rack facility of a General Atomic TRIGA reactor. The estimated reproducibility of the neutron flux during simultaneous irradiations is approximately ±1%; the over-all measurement of the HT yield, including the errors in radio gas chromatography, is estimated as approximately ±2%.

Formation of Recoil Tritium. The general experimental techniques are quite similar to those used in many earlier recoil tritium experiments and have been described previously.[3–5] The gas-phase experiments have utilized the nuclear reaction $He^3(n,p)T$ as the tritium atom source and have been carried out at about 1 atm total pressure. The liquid-phase experiments were conducted in capillaries containing LiF, permitting tritium formation from the reaction $Li^6(n,\alpha)T$. All analyses have been performed by radio gas chromatography,[10] described elsewhere.[11] Extensive descriptions of the general experimental procedures are available in the literature[3–5] and in published theses.[11,12] The most important deviations from the usual experimental procedures are discussed briefly below.

Analysis of HT and He^3. The most critical measurements in the gas-phase experiments are those of radioactivity as HT and of the amount of He^3 present during irradiation. Although the He^3 is accurately measured manometrically during filling of the gas samples, some loss by back-diffusion is possible during the subsequent introduction into the sample bulbs of the other gaseous components.[13] Accordingly, the actual calculations have been based upon the He^3 content measured by thermal conductivity monitoring of one aliquot from each sample. The radioactivity measurements of HT content have also been performed on the same aliquot, so that the actual measurement is the number of observed tritium decays from HT *vs.* the thermal conductivity response from He^3 in the same aliquot of the sample.

The other measurement of great importance in the gas samples is the ratio of RH to moderator molecule. This ratio has also been determined from thermal conductivity recordings of both molecules on a single sample aliquot. The macroscopic quantities were calculated from thermal response constants measured for each of the molecules used in the experiments. In all cases tested (all except the deuterated molecules), the thermal conductivity response was demonstrated to be linear with sample size over the entire range of interest for these measurements.

Liquid-Phase Samples. The irradiation procedure followed with liquid-phase samples, involving a heterogeneous mixture of liquid sample and solid LiF, does not readily permit accurate control over the total production of tritium (proportional to weight of LiF), and especially over the fraction of the tritium atoms stopped in each phase (dependent upon particle size and distribution). Each of the liquid samples contained a ternary mixture of perfluorocyclobutene as the major component (>80%), C_3D_8, and the protium-containing molecule of interest; molecular I_2 was present in each sample as a scavenger molecule. The tritium flux in each sample was monitored internally through the production of DT from C_3D_8, and the experimental yields of HT were normalized through this DT measurement. (The C_3D_8, RH, and c-C_4F_6 composition was determined through thermal conductivity measurements.) This procedure assumes no appreciable effect of changes in RH upon the yield of DT from C_3D_8 and is consistent with the observed independence of the yield ratio of DT/C_2D_3T from C_2D_4 with variations in the nature of the RH molecule being measured.[9] A correction was made for the HT observed from reactions with C_3D_7H impurity in the C_3D_8, amounting to 0.046(DT yield).[14]

Perfluorocyclobutene is miscible with most hydrocarbons, and the solutions showed only a single liquid phase to visual inspection. Following our customary procedure, the gas space above the liquid in the capillary was kept to a minimum, and the great bulk of C_3D_8 and RH was actually in solution in the perfluorocyclobutene.

Materials. Perfluorocyclobutene was obtained from the Du Pont Co., by courtesy of Dr. H. L. Jackson, and from the Chemical Procurement Laboratories, New York, N. Y. The compound was purified by freeze-pumping several times before introduction into the sample bulb. Its purity was shown to be greater than 99.5% by gas chromatographic analysis. Perfluorobutadiene, also from Chemical Procurement Laboratories, was similarly purified to the same level. Argon and nitrogen gases from Matheson Co. (prepurified grades) were used without additional purification; the listed purities were 99.97 and 99.997%, respectively. Oxygen gas (Linde Co.) containing less than 1% impurities was used as obtained. The iodine used as scavenger in the liquid experiments was Baker Analyzed grade. Most of the hydrocarbons used in this work were from Matheson Co. in the highest grade available in

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(10) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

(11) E. Tachikawa, Ph.D. Thesis, University of California, Irvine, Calif., 1967.

(12) J. W. Root, Ph.D. Thesis, University of Kansas, Lawrence, Kan., 1964.

(13) E. K. C. Lee, G. Miller, and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 190 (1965).

(14) The HT yield from ostensibly fully deuterated molecules is higher with I_2 as the scavenger than with a few per cent of O_2 as scavenger; see ref 12.

lecture bottles; cyclobutane was supplied by Merck Sharp and Dohme of Canada. All gaseous compounds were purified by several freezing and pumping cycles. The tritium sources were He^3 and LiF, as described previously.[9]

Results

Effects of Finite RH Concentrations. The basic purpose for carrying out comparisons of a series of molecules in the presence of an excess of some other moderator molecule is to ensure that the reactions are being studied under conditions of equal exposure to tritium atoms over the range of energies in which chemical reaction is possible. This ideal is, however, compromised by the inclusion of the RH molecules themselves, which contribute to the moderating ability of the mixture crudely in proportion to their mole fraction, and which also remove some of the energetic tritium atoms by bond-forming chemical reactions. The validity of the approximation that the exposure to energetic tritium atoms is constant from sample to sample can be checked by varying the amount of a particular RH molecule present in a given moderator; in the limit of infinite dilution, the fate of energetic tritium atoms must then be determined by reactive and nonreactive collisions with the moderator molecule alone. If the HT yield per bond is independent of the mole fraction of RH over a range of dilute mole fractions, then the exposure to energetic tritium atoms can be assumed to be essentially that characteristic of the moderator molecule alone.

Such tests have been carried out for some typical mixtures, CH_3Cl in $c\text{-}C_4F_6$, and C_2H_6 in N_2, with the results summarized in Table I. The yield of HT from C_2H_6 in N_2 varies at higher C_2H_6 mole fractions but is constant within the accuracy of measurement to concentrations of about 10%. No deviations were observed to 18% CH_3Cl in $c\text{-}C_4F_6$. The general conclusion can be drawn that valid comparisons can be made up to rather high concentrations of C–H bonds in $c\text{-}C_4F_6$ and at low concentrations in unreactive moderators such as N_2 and Ar.

Table I. Dependence of HT Yield on Mole Fraction of RH from Recoil Tritium Reactions in RH-$c\text{-}C_4F_6$ Mixtures

Filling pressure, cm				Mole fraction of	Rel HT
He^3	O_2	CH_3Cl	$c\text{-}C_4F_6$	CH_3Cl	yield/bond
1.48	1.75	1.84	74.63	0.023	3110 ± 70
1.48	1.66	4.90	70.08	0.063	3070 ± 70
1.48	1.48	8.43	66.43	0.108	3030 ± 70
1.48	1.48	14.40	60.38	0.185	3110 ± 70

Filling pressure, cm				Mole fraction of	Rel HT
He^3	O_2	C_2H_6	N_2	C_2H_6	yield/bond
1.40	1.57	2.39	72.28	0.031	6040 ± 150
1.40	1.52	5.92	69.94	0.075	6130 ± 150
1.40	1.70	8.40	66.27	0.108	5950 ± 150
1.40	1.63	14.53	60.42	0.186	4040 ± 100

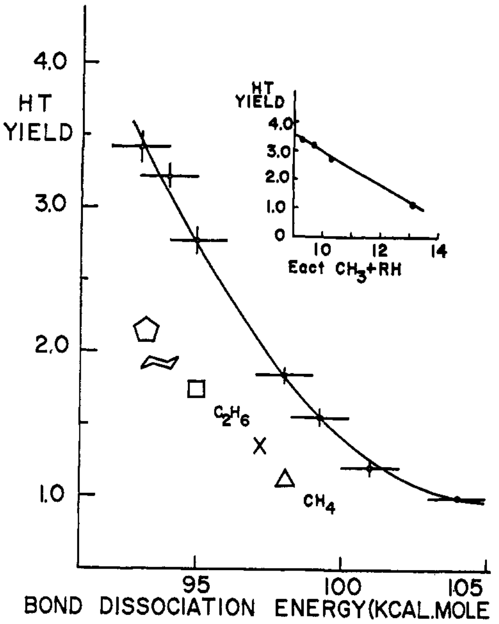

Figure 1. Correlation with RH bond dissociation energies of HT yield per bond from recoil tritium reactions with RH in perfluorocyclobutene moderator; decreasing HT yields in the order $c\text{-}C_5H_{10}$, $c\text{-}C_6H_{12}$, $c\text{-}C_4H_8$, C_2H_6, *neo*-C_5H_{12}, $c\text{-}C_3H_6$, CH_4. Inset: Correlation of HT yield with activation energy for abstraction of H by methyl radicals; decreasing HT yields in the order $c\text{-}C_5H_{10}$, $c\text{-}C_6H_{12}$, $c\text{-}C_4H_8$, $c\text{-}C_3H_6$.

Perfluorocyclobutene Experiments. Our most extensive series of experiments has involved measurement of the HT yields from a series of saturated hydrocarbons in excess perfluorocyclobutene. The specific yields per C–H bond in the mixture [(HT yield)/(cm of RH)·(no. of C–H bonds)] for these compounds are summarized in Table II, expressed relative to the specific yield of the C–H bond in methane as 1.00. For comparison purposes, we have included a consistent set of bond dissociation energies for these molecules and the activation energies for abstraction by methyl radical for the cyclanes.[15] (The estimates of the bond dissociation energies of the cyclanes are based on the activation energies for methyl radical attack and upon the Polanyi relationship between activation energy and bond dissociation energy.[15]) The agreement between the series of measurements is excellent and suggests that the quoted error of ±3 kcal/mole for the bond dissociation energies of the cyclanes may be too conservative. The correlation is shown in Figure 1, with ±1 kcal/mole estimated errors for the bond dissociation energies.

Table II. Comparison of Relative HT Yields from Recoil Tritium Reactions with Bond Dissociation Energies of C–H Bonds[a]

Molecule RH	Specific yield[b]	Bond dissociation energy,[15] kcal/mole	Activation energy,[15] Me + RH, kcal/mol
CH_4	(1.00)	104.0 ± 1	
$c\text{-}C_3H_6$	1.21 ± 0.03	101 ± 3	13.1
neo-C_5H_{12}	1.54 ± 0.03	99.3 ± 1	
C_2H_6	1.84 ± 0.05	98.0 ± 1	
$c\text{-}C_4H_8$	2.77 ± 0.10	95 ± 3	10.3
$c\text{-}C_6H_{12}$	3.21 ± 0.08	94 ± 3	9.7
$c\text{-}C_5H_{10}$	3.41 ± 0.11	93 ± 3	9.3

[a] Perfluorocyclobutene moderator, O_2 scavenger. [b] Specific yield per C–H bond relative to that of C–H in methane, all compared in a system containing approximately (cm): He^3, 1.5; O_2, 1.5; RH, 5; $c\text{-}C_4F_6$, 71.

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(15) J. A. Kerr, *Chem. Rev.*, 66, 465 (1966).

Table III. Comparison of Relative HT Yields from Recoil Tritium Reactions with Hydrocarbons in Different Moderators

	Specific HT yields[a]							
	C_2D_4	c-C_4F_6		1,3-C_4F_6	N_2		Ar	
	A	B	C	B	B	C	B	C
C_2H_2	0.52 ± 0.05	0.45 ± 0.05	...	0.43 ± 0.09	0.63 ± 0.02	0.58 ± 0.02	0.56 ± 0.07	(0.56)[c]
C_2H_4	1.00 ± 0.03	0.91 ± 0.03	0.98 ± 0.04	0.78 ± 0.05	0.92 ± 0.03	...	0.94 ± 0.03	...
CH_4	(1.00)	(1.00)	...	(1.00)	(1.00)	...	(1.00)	...
c-C_3H_6	1.27 ± 0.03	1.21 ± 0.03	(1.21)[c]	1.24 ± 0.04	1.13 ± 0.03	(1.13)[c]	0.93 ± 0.03	1.20 ± 0.03
neo-C_5H_{12}	1.59 ± 0.03	1.54 ± 0.03	...	1.30 ± 0.04	1.21 ± 0.05	1.40 ± 0.04 (10%)[b]	0.99 ± 0.03	...
C_2H_6	1.71 ± 0.03	1.84 ± 0.05	...	1.63 ± 0.05	...	1.85 ± 0.06	...	1.86 ± 0.06 (13%)[b]
c-C_4H_8	2.12 ± 0.07	2.77 ± 0.10	...	...	...	...	...	...
c-C_6H_{12}	...	3.21 ± 0.08	...	3.29 ± 0.10	...	...	1.86 ± 0.07	...
c-C_5H_{10}	...	3.41 ± 0.11	...	3.31 ± 0.10	2.54 ± 0.07	...	2.04 ± 0.06	...
Relative yield of c-C_3H_5T			1.00			2.20 ± 0.07		4.74 ± 0.13

[a] Specific yield per C–H bond relative to that of C–H in methane; compared in a system containing approximately (cm): (A) He^3, 1.2; RH, 6; C_2D_4, 65; and He^3, 1.2; RH, 12; C_2D_4, 59; both in agreement; (B) He^3, 1.5; O_2, 1.5; RH, 5; moderator, 71; (C) He^3, 1.5; O_2, 3.5; RH, 5; moderator, 74. [b] Absolute percentage yield by comparison with monitor samples. [c] Used as basis for comparison.

Inspection of the data shows that the relative measurements of HT yields are about a factor of 10 more precise than the best existing bond dissociation energy measurements. Further conclusions about the detailed validity of this observed correlation must therefore await more accurate measurements of relative bond dissociation energies.

Perfluorobutadiene, Nitrogen, and Argon Systems. To confirm that the observed correlation between HT yield and C–H bond dissociation energy is a general trend in recoil tritium reactions, and not an artifact of the particular moderator gas used, similar measurements of relative specific HT yields have been performed using different moderators, including perfluorobutadiene, nitrogen, and argon, each with oxygen present as a scavenger. The experimental values of the relative specific HT yields with these moderator–scavenger systems are listed in Table III, together with the earlier data for C_2D_4–O_2.[9]

The trends in HT yields are quite similar in all of the moderators, although differences certainly exist. The results obtained in c-C_4F_6 and 1,3-C_4F_6 indicate that the effects of these two isomeric molecules are essentially the same. In both of these fluorocarbon systems, lower energy tritium atoms can react readily with the double bonds of the moderator molecules, and the inclusion of a small concentration of O_2 probably has a rather small effect on the energetic tritium atom reactions while scavenging thermal radicals efficiently.

The measurements with Ar (and with N_2 over most of the energy range) fall into the category of inert moderator experiments. Under the experimental conditions labeled C, the concentration ratio of O_2 to RH is 0.7, and hot reactions with O_2 may have yields comparable with RH over much of the hot-energy range. The absolute percentage yields of HT (as high as 10–13% for some products listed in Table III) indicate that substantial hot yields are still found for the inert moderator systems. Our experiments with Ar and N_2 show (a) the same general trends of HT yield with molecular identity, and (b) relative yield variations with O_2/RH ratio. Consequently, we assume semiquantitative agreement in all moderator systems and will not consider the specific quantitative deviations in Ar and N_2, as shown in Table III, without further experiments with varying O_2/RH ratios.

The irradiation involving experimental condition C permitted direct comparison of absolute yields of HT in various moderators, as indicated in the bottom line of Table III; the absolute yields of HT from c-C_3H_6, a measure of the relative probability for reactive collision between T* and RH, decreased in the order Ar > N_2 > c-C_4F_6.

Liquid-Phase Experiments. While other experiments have demonstrated that the differences between gas and liquid phases are very small for the primary reactions of recoil tritium and result largely from the changes in collisional efficiency for deexcitation of excited product molecules,[3-5,16] we have carried out a brief test to confirm that the bond dissociation energy correlation can also be observed in liquid-phase experiments.

Each sample has contained about 80–85 mole % of perfluorocyclobutene as moderator, and 15–20 mole % of C_3D_8 internal standard plus reactant RH, with I_2 as a scavenger. All of these have been heterogeneously mixed with solid LiF in the capillary for irradiation. The yield of DT from C_3D_8 is used as an internal standard, and the HT specific yield is measured and expressed as an HT/DT ratio, as shown in Table IV. These data are in complete agreement with the correlation found for perfluorocyclobutene moderator in the gas phase, with essentially the same relative yield values in each phase. This close agreement suggests that possible contributions to the HT yield from the decomposition of excited molecules must be quite small, since these contributions would depend upon the activation energies for molecular hydrogen elimination and not upon the strengths of various C–H bonds. Furthermore the mechanisms of abstraction must be quite similar in both phases, in agreement with previous deductions from comparison of HT/RT ratios in gas and liquid phases.[17]

Discussion

The data of Tables III and IV shows an excellent correlation in a variety of systems between higher HT yields and lower C–H bond dissociation energies, with variations in yield as high as a factor of 8 among the

(16) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 3085 (1962).

(17) E. K. C. Lee and F. S. Rowland, *ibid.*, **84**, 3085 (1962).

Table IV. Intermolecular Competition in the Liquid Phase. Yields of HT from RH *vs.* DT from C_3D_8

RH	Rel amounts present RH	C_3D_8	Radioactivity[a] HT	DT	Yield ratio[b]	Yield ratio/ no. of C–H bonds	Rel yield
...	...	4	560 ± 100	11790 ± 180	$\left(\frac{HT}{DT} = 0.046\right)$	...	
...	...	4	460 ± 90	10480 ± 170		...	
c-C_3H_6	3.53	4.10	2870 ± 190	4950 ± 150	0.674	0.112	1.5
c-C_3H_6	2.96	3.63	1830 ± 190	3410 ± 150	0.659	0.110	
CH_4	10.05	4.51	3820 ± 210	5740 ± 150	0.298	0.074	(1.0)
c-C_5H_{10}	3.28	3.26	17760 ± 200	6130 ± 200	2.88	0.288	3.9
neo-C_5H_{12}	5.45	5.17	12700 ± 240	8190 ± 180	1.47	0.123	1.7

[a] The HT yield listed for samples containing both RH and C_3D_8 has been corrected for HT from C_3D_7H by subtracting 0.046(DT) from the measured HT yield. [b] HT × (C_3D_8)/DT × (RH).

compounds listed. The implication of this correlation, at least for saturated hydrocarbons, is that there exists no factor with an influence upon the energetic hydrogen-atom abstraction other than those factors which directly influence the bond dissociation energy of the molecule concerned.[18] One specific factor which must therefore be negligible in these hydrocarbons is a steric factor: the angles of approach which lead to abstraction from the C–H bond in methane are not more inclusive than those which lead to abstraction from cyclobutane, containing only secondary C–H groups. Suggestions that hydrogen abstraction tends to occur along the C–H axis would imply that no steric factor should be expected; the absence of steric factors in abstraction would present only a minor limitation on the possible angles of approach for the proposed stripping mechanism at right angles to the C–H bond axis of the atom being abstracted.[4] It is quite apparent, however, that successful use of the yields *per C–H bond* implies that possibly reactive collisions with C–H bonds are geometrically independent of intermolecular or intramolecular location. Since, for example, the collision cross section of n-C_4H_{10} is not 2.5 times larger than that of CH_4, the total of reactive plus nonreactive collision cross sections is *not* proportional to the number of C–H bonds. Estimates of energy loss in nonreactive collisions must reflect this difference in the geometric considerations.[12]

Mechanistic considerations of the abstraction reaction have chiefly involved suggestions concerning the geometry of approach[4,6] and the energetic factors involved in reaction.[7–9] The early suggestion of an approach along the C–H axis *assumed* no dependence of HT yield upon the nature of the C–H bond attacked;[6] the discovery of the actual strong dependence on bond dissociation energy merely invalidates this assumption without necessarily invalidating the hypothesis of preferential axial approach for the abstraction reaction. Two models have been proposed which can account for the observed energy dependence: an "energy cut-off" model[9] and the stripping reaction model.[4]

Energy Cut-Off Model for Abstraction. The energy cut-off model qualitatively assumes that potentially reactive collisions with C–H bonds can occur down to lower energies for weaker C–H bonds, thereby increasing the total HT yield through a wider reaction energy range accessible for reaction with such bonds. This model is consistent with the well-known correlation (Polanyi rule)[19] of activation energy (and therefore threshold energy) with the heat of reaction, since the relative heats of reaction for abstraction are directly related to the bond dissociation energies of the R–H bonds.

Some models for reaction probability curves will facilitate discussion of the kinetic considerations involved in this model. One simple cut-off model, illustrated at the top of Figure 2, has a common maximum energy for abstraction for all RH molecules, a flat probability of reaction independent of RH over most of the energy range, and a minimum energy for reaction which is a function of the bond dissociation energy of the C–H bond. As the dissociation energies of the C–H bonds decrease, extension of the threshold for abstraction to slightly lower energies would occur. If the average logarithmic energy loss (α) is constant over the entire chemical reaction range,[4] then the collision density will be constant over the reaction range on a logarithmic scale except for depletion by chemical reaction, as shown with (a) of the upper diagram of Figure 2. A reaction probability curve of this form, coupled with the constant collision density, would lead only to very small increases in the HT yields from weaker bonds; it is completely unable to account for increases by a factor of 8, as actually observed.

Two kinds of modification to this simple model can be considered in an effort to obtain better agreement with experiment. One modifies the assumption that the average logarithmic energy loss is independent of energy. Calculations indicate that variations with energy are certainly reasonable for α, although the assumption of a constant value may be a satisfactory approximation over a substantial energy range.[4,20–22] Pertinent experimental information is almost completely absent in the 2–20-eV range for all of the systems involved here. If the average logarithmic energy loss *does* change rapidly with energy, such that the frequency of collisions becomes much denser in the lower energy range, as shown in (b) on Figure 2, then the yield of HT

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(18) One kind of exception has been identified, as illustrated with the abstraction of H from $CH_3CD{=}CD_2$. In this case, the yield of HT is lower than anticipated from the bond dissociation energy correlation because the relaxation of $CH_2CD{=}CD_2$ to the allylic configuration requires more time than is available during the abstraction process. Consequently, HT formation occurs while the allyl radical is still excited and not all of the resonance energy is available for lowering the bond dissociation energy to its equilibrium value (E. Tachikawa, Y.-N. Tang, and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 3584 (1968)). The differences between CHF_3 and the alkanes also reflect partial nonequilibration of the hydrocarbon radicals.

(19) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

(20) P. Estrup, *J. Chem. Phys.*, **41**, 164 (1964).

(21) R. M. Felder and M. D. Kostin, *ibid.*, **43**, 3082 (1965).

(22) R. M. Felder, *ibid.*, **46**, 3185 (1967).

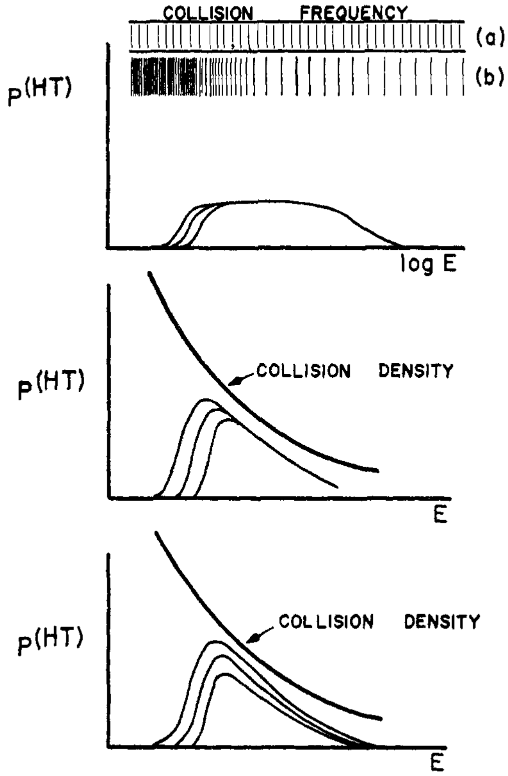

Figure 2. Hypothetical distributions of number of tritium atom collisions with energy. Upper diagram: (a) constant collision density on logarithmic energy scale, *i.e.*, energy-independent α; (b) variable collision density with energy—lower average logarithmic energy losses at lower energy. Middle and lower diagrams: hypothetical reaction probabilities for molecules with different bond dissociation energies.

can rise sharply for reactions with the weaker C–H bonds. However, the required change in α is almost as large as the factor of 8 observed in yields. Moreover, the nearly proportional relationships between HT yields in different moderator systems, as in Table III, imply that such rapid changes in α would have to occur in parallel in each moderator system. Thus, while an energy-dependent α is not unreasonable, consistently large variations in the logarithmic energy loss for such diverse molecules as c-C_4F_6, N_2, and Ar seem quite unlikely, and we conclude that a probability-of-reaction curve such as that shown in the upper part of Figure 2 is not consistent with the actual experimental observations.

Two forms of another modification to the cut-off model are illustrated in the other two diagrams of Figure 2. In each case, the maximum energy for reaction is the same, and the minimum energy for reaction is dependent upon the bond dissociation energy of the C–H bond. However, the weaker C–H bond is also assumed to permit a *higher probability* of energetic abstraction reactions over a substantial portion of the chemical reaction range; *i.e.*, the weaker C–H bond *both* lowers the minimum energy required for reaction *and* increases the probability of reaction in collision above the minimum energy. The cross-product of the rising collision density (note that the energy is no longer plotted on a logarithmic scale) and the larger cross sections at some energies can readily reproduce the necessary dependence of HT yield upon bond dissociation energy. One cannot distinguish yet between distributions such as those shown in the middle and lower diagrams or among similar alternatives, but the data clearly require reaction probability curves of this general kind. The real situation may, of course, be further complicated by some dependence of α on the kinetic energy of the tritium atom.

Stripping Reaction Model. In the stripping model, the abstraction of an H atom is presumed to occur during the close passage of a very high energy tritium atom at approximately right angles to the C–H bond axis.[4] Only a small fraction of the kinetic energy of the tritium atom would then be effective along the line of centers of T–H–C at reaction, and the required sensitivity to small changes in bond dissociation energy could result. Stripping reactions are common phenomena in ion–molecule reactions,[23] in the reactions of alkali atoms with halogens,[24] and in the studies of nuclear reactions.[25] However, strong electrical forces from charge transfer or charge separation are involved in the known chemical stripping reactions and are largely absent in the hydrogen atom abstraction reactions. The current experiments offer no direct information about the angle of orientation of the approaching tritium atom to the C–H bond with which it reacts and can neither confirm nor deny the strong angular correlations implied by the stripping model. However, we believe that the mean energy of the tritium atom involved in the abstraction reaction is no higher than 3 or 4 eV, as described below, and hence that the tritium energies prior to reaction are comparable to or less than the bond strength of the attacked C–H bond in the majority of collisions leading to abstraction. Under these conditions, the abstraction reaction does not correspond to the general concept of a high-energy stripping reaction.

Average Energy of the Abstraction Reaction. An estimate of 5 eV as the mean energy of the reacting recoil tritium atom has been made for the substitution of T for H in cyclobutane through observation of secondary decomposition of excited molecules formed in the primary hot reaction.[26] No comparable inferences can be drawn about the energy of the tritium atom prior to an abstraction reaction because of the absence of secondary reactions of the HT product. However, substantial hot yields (up to 30%) have been found for the reactions with hydrocarbons of photolytically hot H* or D* atoms of 2.8-eV initial energy or less.[27,28] Taken with the complementary knowledge that the ratio of substitution/abstraction is much smaller for 2.8-eV T atoms than in the corresponding recoil tritium systems,[29] the bulk of these reactions must be hot abstraction reactions initiated by tritium atoms in the $\leq$2.8-eV range. Furthermore the absolute yields from such photochemically initiated reactions also show a strong correlation of higher yield with lower C–H bond dissociation energy.[27]

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(23) A. Henglein, K. Lachmann, and B. Knoll, *J. Chem. Phys.*, **43**, 1048 (1965).

(24) D. Hershbach in "Molecular Beams," J. Ross, Ed., Interscience Publishers, New York, N. Y., 1966, Chapter 9.

(25) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

(26) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

(27) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 3007 (1964).

(28) R. G. Gann and J. Dubrin, *ibid.*, 47, 1867 (1967).

(29) C. C. Chou and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 2612 (1966).

The time scale for these lower energy abstraction reactions may be estimated from the velocity of the tritium atom itself: a 1-eV tritium atom has a velocity of 8×10^{13} Å/sec, and the reaction time scale must thus be $\geq 10^{-14}$ sec.

Specific HT Yields in Different Moderators. The relative values of the specific HT yields for abstraction from c-C_3H_6 in three moderators are given in Table III. The higher such a yield, the proportionally greater must have been the number of tritium atom collisions to which the c-C_3H_6 molecules were exposed. Consequently, the collision density of tritium atoms can be assumed to fall in the ratio 4.7 ± 0.2:2.2 ± 0.1:1.0 for $Ar/N_2/c$-C_4F_6, suitably averaged over the reaction range in which abstraction occurs with c-C_3H_6. The general observation of parallel relative yields in the different moderators further suggests that these relative collision densities may be suitable averages for a wide range of energies.

The three quantities which determine the relative collision densities in each moderator are (a) rate of loss of tritium by chemical reaction; (b) rate of energy loss of tritium in nonreactive collisions; and (c) the relative frequency of collision with each of the components of the mixture, *i.e.*, molecular size or collision cross section. Since all estimates of the molecular radii indicate N_2 and Ar to be very similar in size, and both are essentially inert moderators, the average energy loss in collisions with N_2 must be almost twice as large as in collision with Ar to account for the substantial differences in HT yield. The difference must arise from substantial energy losses in inelastic collisions with nitrogen.

Comparative collision densities can be stated quantitatively through the formalism of the kinetic theory of hot reactions.[4] In the case of a small amount of reacting compound (RH), a large excess of moderator gas (M), and a small quantity of scavenger molecule (O_2), the following limiting expression is obtained[11]

$$\frac{(I_{HT})(\sigma_{RH})}{(\alpha_M)(\sigma_M)} = \frac{P_{HT}(M)}{(RH)} \qquad (3)$$

in which the σ_i's are collision cross sections, I_{HT} is the reactivity integral for HT from RH, P_{HT} is the measured yield of HT, and α_M is the logarithmic energy loss for collisions with M. The cross-product of cross-section and logarithmic energy loss for each moderator ($\sigma_M\alpha_M$) is thus the reciprocal of the HT yield and will have the values, normalized to argon, given in Table V.

Table V. Relative Specific HT Yields and Tritium Collision Densities from Various Moderator Systems

Moderator	$(HT)^0$	$\sigma_M\alpha_M$
Ar	4.7 ± 0.2	(1.0)
N_2	2.2 ± 0.1	2.2 ± 0.1
c-C_4F_6	(1.0)	4.7 ± 0.2

On the Possible Existence of Double Minima in Potential Energy Surfaces of AB_2-Type Molecules[1a]

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Abstract: Recently LCAO-SCF-MO calculations were reported for the low-lying $^1A_1$ states of NO_2^+ and O_3 for several bond angles. Some of these calculated zero-order energy curves were reported to cross. Here it is shown these crossings can be predicted on the basis of Walsh-type diagrams. Further it is suggested that the crossings of the zero-order $^1A_1$ curves lead to double minima in the ground-state potential energy surfaces of AB_2-type molecules with 14–18 valence electrons. On this basis the high-temperature isomer of SO_2 postulated by Norrish and Oldershaw is predicted to be a symmetrical form of SO_2 with a somewhat larger S–O bond distance and a bond angle of about 72°.

The potential energy surfaces of polyatomic molecules arising from changes in bond angle are difficult to investigate experimentally.[2] Recently molecular orbital calculations have been performed that approximate true Hartree–Fock solutions for the molecular energy and predict equilibrium bond angles within 1–2% of the accepted experimental values.[3] In general, however, it is necessary to extend the Hartree–Fock scheme (say by configuration interaction) in order to accurately determine potential energy surfaces.

In an earlier paper,[4] a method was discussed which predicted the additional configurations most likely to alter the energy curves obtained from Hartree–Fock or "best molecular orbital" calculations. It is the purpose

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[2] See, for instance, M. A. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.*, **42**, 2335 (1965); J. Pliva, V. Spirko, and D. Papousek, *J. Mol. Spectrosc.*, **23**, 331 (1967).

[3] L. C. Allen, "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1966, pp 39–80.

[4] E. F. Hayes and G. V. Pfeiffer, *J. Chem. Phys.*, **47**, 5168 (1967).