PHYSICAL AND INORGANIC CHEMISTRY

Mechanisms of Hot Hydrogen Atom Displacement Reactions with Alkanes[1]

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The reaction mechanisms of hot hydrogen atoms with alkanes have been studied. Recoil tritium from nuclear reaction was used as the source of hot hydrogen and iodine or oxygen served as scavengers to suppress interference from the minority of tritium atoms that reach thermal energies. 99.5% of the products may be accounted for by replacement of one or possibly two hydrogen atoms or alkyl groups by the incoming hydrogen. The detailed product spectrum provides strong support for a model of the mechanism in which the incoming hydrogen displaces another group directly, without forming any metastable intermediate. The point and direction of impact as well as the energy of the hot species is thus paramount in determining the course of the reaction. The greater tendency to break C–H rather than C–C bonds is then simply due to the greater exposure of the former. Other details in product distribution may be explained similarly by variations in steric obstruction to certain modes of impact. Hydrogen atom abstraction appears to follow axial approach of the hot atom along the C–H bond axis; while displacement occurs (without Walden inversion) as a result of attack at larger angles to the bond axis.

Introduction

The chemical reactions of "hot" or high kinetic energy hydrogen atoms have been the subject of several recent investigations. As source of the hot hydrogen, recoil tritium from the nuclear reactions $He^3(n,p)T$ and $Li^6(n,\alpha)T$ has been used. This tritium is produced in the system being investigated at energies in the kilovolt range. It is slowed down by successive collisions with molecules of the medium and may eventually reach thermal energies. However, it has been shown that it usually will react to become combined in a molecular entity while it is still hot[3] (i.e., has greater than thermal energy). The products of such reaction are detected by virtue of the radioactivity of the incorporated tritium.

Previous work with gas phase methane and ethane[3,4] has indicated the existence of hot displacement reactions in which H, 2H or an alkyl group is displaced by the entering tritium atom. The kinetics of these processes have been examined in some detail. Similar reactions also have been observed in simple liquid alkanes,[5] alcohol,[6] acetone[6] and carboxylic acids.[7] Available evidence indicates that this displacement mechanism occurs in one step, without the formation of an internally equilibrated metastable intermediate.

The present study examines the modes of the hot hydrogen displacement reaction in a series of higher gaseous alkanes and formulates a more detailed model of the reaction mechanism involved.

General Method.—As in previous work[3,4] a small pressure of He^3 was mixed with the alkane being investigated and the tritium then produced

(1) Some of the results of this work have been presented in preliminary form as part of a review paper at the symposium on Fundamental Aspects of Atomic Reactions, Montreal, 1960: M. Henchman, D. Urch and R. Wolfgang, *Can. J. Chem.* **38**, 1722 (1960).

(2) Queen Mary College, Mile End Road, London, U. K.

(3) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661, 2665 (1960).

(4) M. El-Sayed, P. J. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(5) R. Wolfgang, J. Eigner and F. S. Rowland, *ibid.*, **60**, 1137 (1956).

(6) F. S. Rowland and W. J. Hoff, *J. Am. Chem. Soc.*, **79**, 4867 (1957).

(7) A. M. Elatrash, R. H. Johnsen and R. Wolfgang, *J. Phys. Chem.*, **64**, 785 (1960).

under reactor neutron irradiation by the He^3-$(n,p)H^3$ reaction. The tritiated products were separated by chromatography and assayed by a flow-proportional counter.[8a,b] The products observed in such a simple experiment represent both those formed by hot reaction of the tritium and those formed by thermal reaction of tritium which had lost its excess energy. To eliminate the thermal reactions, experiments also were performed in which O_2 and I_2 were added in small amounts.[3] These "scavengers" do not affect the highly efficient hot reactions but do remove the thermal species. Furthermore, to confirm the thermal origin of certain products excess helium was added in some experiments.[3] Helium acts as a moderator for tritium atoms, increasing the number reaching thermal energies and thus emphasizing the relative importance of thermal processes. (For a more complete discussion of the use of scavengers and moderators in distinguishing hot and thermal reactions see ref. 3.)

Experimental

Materials.—All reactions were performed in the gas-phase in quartz vessels (5–30 cm.[3]), fitted with capillary break-off tips.[4] The hydrocarbons were supplied by the Phillips 66 Co. and the Matheson Co.; they were C.P. grade (>99% pure) and were used directly, without further purification. Helium-3 was obtained from the Oak Ridge National Laboratory and was purified from contaminant air and tritium, etc.,[9] by allowing aliquots to stand over activated charcoal at liquid nitrogen temperature for fifteen minutes.

Irradiations.—Each reaction vessel was filled on a vacuum line with the hydrocarbon under investigation, helium-3 and other gases as required. Sealing-off was performed while the volatile components were frozen down in liquid nitrogen. Details of the composition of typical samples are given in Table II. Irradiations were performed in the reactor at the Brookhaven National Laboratory. The low thermal neutron fluxes ($\sim 2 \times 10^9$ n.cm.$^{-2}$sec.$^{-1}$) in the "Instrument Tunnel" were used for most irradiations because the low background of high-energy radiation kept radiation damage to a minimum. Irradiations at high flux were performed in the "Pneumatic Tube" facility. Total neutron doses of about 1–3 $\times 10^{15}$ neutrons cm.$^{-2}$ were used; this formed about 2–6 $\times 10^{13}$ tritons in a typical sample containing about 1 cm./Hg pressure of helium-3. The corresponding

(8) (a) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958); (b) R. Wolfgang and C. MacKay, *Nucleonics*, **16**, No. 10, 69 (1958).

(9) J. K. Lee and F. S. Rowland, *J. Inorg. and Nuclear Chem.*, **10**, 336 (1959).

TABLE I

CHROMATOGRAPHIC COLUMNS USED FOR ANALYSIS

Column	Temp., °C.	Length, feet	Separation
Silica gel	25	10	H_2, CH_4, C_2H_6
Alumina[a]	25	3	H_2 + CH_4, C_2H_6, C_2H_4, C_3H_8
1,3-Propanediol, saturated with silver nitrate, mounted on firebrick	25[b]	6	Olefins C_2–C_6 (all saturated hydrocarbons through C_6 not retained)
Dimethylformamide mounted on firebrick	0[c]	10	General analysis C_2–C_5, olefins preferentially retained
Silicone oil, mounted on firebrick	25	10	General analysis C_2–C_6. Log(relative retention time) proportional to boiling point for hydrocarbons
Silicone oil, mounted on firebrick	25	1.5	General analysis of C_5–C_8 hydrocarbons
Special scan			The sample was divided into saturated and unsaturated parts by a preliminary analysis on the silver nitrate column. Each part was then analyzed on the 10 ft. silicone column

[a] Needs frequent re-activation by heat to 200°.   [b] Greatly enhanced separations at 0°.   [c] Slow elution of substrate even at 0°.

radioactivity was about 4–12 × 10⁴ disintegrations per second.

Analysis.—The method of analysis used has been described previously.[4,8] Samples were broken under vacuum in a special vessel from which aliquots were taken by expansion into a U-tube (∼ 8 cm.³). The sample in the U-tube had a pressure of about 2–5 cm./Hg and was analyzed by gas-phase chromatography followed by proportional flow counting. Helium was used as the flow gas and methane was bled into the stream prior to the counter. Seven or eight scans were made on each sample using the chromatographic columns described in Table I.

The columns generally were standardized with samples of known hydrocarbons. However, some of the C_7 and C_8 compounds were tentatively identified using the proportionality between the logarithm of the relative retention time and the boiling point that holds for silicone columns. Cross-reference from scan to scan ensured both a qualitative and quantitative check for each compound.

Radiation Damage.—The radiation present during the production of the recoil tritium tends to decompose the system to form reactive intermediates, *i.e.*, radicals and ions. Because of the very high collision efficiency of hot reactions, the small concentrations of impurities which result do not affect the hot reaction directly (unless, of course, radiation damage is so severe that the final decomposition products became a major component of the system). Such reactive impurities may, however, affect the yield distribution by reacting with the products of hot reaction, *e.g.*, H atoms produced by radiation damage may reduce labeled ethylene produced by hot tritium. This effect may be minimized by scavenging the intermediates with I_2 or O_2.

If no scavenger is present the radicals and ions produced by radiation damage may greatly affect the fate of tritium atoms that reach *thermal* energies. This is due to the very low collision efficiency for reaction of thermal atoms, which permits them to have a lifetime sufficiently long so that they may collide with reactive impurities. It is for this reason (discussed more fully elsewhere[4]) that reproducibility is much poorer in unscavenged runs. Such effects of radiation damage on thermal hydrogen reactions are, of course, of no great relevance to this study of hot reactions.

Most of the radiation damage is due to the energy release in the $He^3(n,p)H^3$ reaction, which produces about 0.8 Mev. divided between triton and proton. Assuming a G value of about 10 the total decomposition in a typical run should be of the magnitude of 10¹⁸ molecules or 0.1–1% of the total system. This is about what was observed. It is a level of radiation damage which is readily controlled by scavenger. The results indicate that at this level, even in the absence of scavenger, there is no major effect on the hot reaction products.

Errors and Reproducibility.—Due to the nature of the radioactive decay process errors of a purely statistical kind are inherent in the results. In most scans the activity of the parent peak was of the order of 10,000 counts: a rough estimate for the standard deviation is therefore 0.1 $\sqrt{R}$, where R is the relative yield of any compound, as quoted in Table II. Including other sources of error (such as those from averaging from scan to scan) the total uncertainty may be set at ±0.3 $\sqrt{R}$ or ±3%, whichever is greater.

In Table II results are presented for scavenged, unscavenged and moderated runs. In the scavenged runs, there are no errors from secondary thermal reactions (such as discussed under "radiation damage"), and a comparison of yields from two similar scavenged runs should show only the uncertainty estimated above. A comparison of such runs (*e.g.*, those on propane) bears out this expectation.

In the absence of scavenger, however, products of the thermal reactions are also detected and they are much more poorly reproducible. Such thermal reactions are sensitive to radical and ion concentrations, which in turn are dependent on the radiation flux, and also, very sensitively, on the presence of trace impurities (*e.g.*, air, mercury vapor, water, etc.) which may act as scavengers. Thus, results on unscavenged propane have been obtained by Willard[10] and by Rowland[11] as well as in this work: but a comparison of the yields of methane, ethane and ethylene from this system shows poor agreement. Products such as these which tend to have irreproducible yields are invariably larger than in the scavenged system, the variable excess having a thermal origin.

Products derived from the reactions of thermal tritium atoms will predominate in helium moderated experiments. Wide variations in product yield are thus expected and are found. However, these experiments have some use in identifying products formed in the reactions of thermal tritium atoms.

This discussion has emphasized that the unscavenged and He moderated runs are primarily useful only for drawing qualitative comparisons between hot and thermal reactions. To study the hot reactions themselves the scavenged runs provide much better data and are used almost exclusively in the following discussion.

Results

The results are shown in Table II. All yields are normalized to 100 for the yield of the tritiated form of the irradiated compound. A more satisfactory form of presentation would have been to express the yields as percentages of the total tritium reacting. However, uncertainties involving the neutron flux and recoil loss[3] make the calculated values of the total tritium available for chemical reaction inaccurate for some of the experiments. (During the course of this work the loading of the Brookhaven reactor was gradually changed and the neutron fluxes were only known approximately (∼ ±30%). Even so, after allowance for recoil loss (that tritium which recoils into the quartz wall and is not available for reaction) it was found that the observed total activity was in rough agreement with that calculated.)

(10) M. C. Sauer and J. E. Willard, *J. Phys. Chem.*, **64**, 359 (1960).
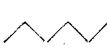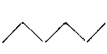
(11) J. K. Lee, B. Musgrave and F. S. Rowland, *J. Am. Chem. Soc.*, **82**, 3545 (1960).

TABLE II

RESULTS OF THE REACTIONS OF TRITIUM ATOMS WITH ALKANES[a]

All irradiations were performed at a flux of 2–6 × 10⁹ neutrons. cm.⁻², sec.⁻¹ for 2 to 7 days. Results are normalized to 100 for the activity in the parent molecule. Molecules are indicated by carbon skeletons, e.g., iso-pentane: [skeleton]. Symbols have the following meaning: tr., trace (i.e., <1.0); 0 ≤ 0.1; ..., not sought. Spread of averaged results containing a large error are indicated thus: 35 ± 10. Products not listed were not observed.

| Alkane Reacting	CH_4[b]	CH_4[c]	C_2H_6	C_2H_6	[propane]	[propane]
(cm. Hg)			104.2	87.6	101.6	79.8
Additives (cm. Hg) He³			2.3	1.8	2.3	1.5
Scav. I₂	0.02	...	0.02	...	0.02	...
Scav. O₂	...	...	...	2.1	...	1.9
Tritiated products						
H_2	106 ± 5	150 ± 5	181	187	193	200
CH_4	100	100	12.5	11.1	9.6	12.7
C_2H_6	Tr.	24 ± 2	100	100	3.8	4.2
C_2H_4	...	...	9.8	11.5	4.4	6.2
C_2H_2	...	...	0	Tr.	0	0
[propane]	...	...	1.7	Tr.	100	100
[propene]	...	...	1.3	1.5	1.7	2.4
[n-butane]	...	...	2.8	0	0	0
Above C_4	0	35 ± 10[d]	0	0	0	0
MeI	12	...	14	...	6.4	...
EtI	0	...	3	...	4.4[e]	...
Oxygen compounds	...	...	...	46	...	59

Alkane Reacting	[propane]	[cyclopropane]	[isobutane]		[isobutane]	[n-butane]		[n-butane]
(cm. Hg)	57.8	57.9	121	78	95.8	80	79	101.2
Additives (cm. Hg) He³	1.2	0.48	2.5	1.5	1.8	1.5	1.4	2.0
Scav. I₂	...	...	0.02	...	...	0.02	..	...
Scav. O₂	...	...	...	1.97	...	...	1.8	...
Tritiated products			Average			Average		
H_2	281	123	192		234	199		235
CH_4	24	34	14.1		22.7	6.7		15
C_2H_6	24.5	26.6	0		1.4	4.8		14.7
C_2H_4	3.5	10.8	1.0		2.8	6.6		4.5
[propane]	100	47.1	3.0		11	3.7		6
[propene]	2.5	15.7	7.0		6	1.4		1.2
[cyclopropane]	0	100	0		0	0		0
[n-butane]	Tr.	29.6	0		3.7	100		100
[isobutane]	Tr.	12.5	100		100	0		Tr.
[isobutene]	0	0	1.8		2.3	0		0
[n-pentane]	0	11	0		0	0		0
[isopentane]	2	27	0		0	0		Tr.
Above C_5	12.5	25	0		11[f]	0		6
MeI	...	...	4.6[g]		...	7.2[h]		...
Oxygen compounds	...	...	33		...	64		...

Alkane Reacting	[isopentane]	[n-pentane]	[n-pentane]	[n-pentane]	[isopentane]	[isopentane]
(cm. Hg)	3	52.5	53.0	11.9	60.9	60.2
Additives (cm. Hg) He³	.6	0.43	0.47	0.33	0.40	0.48
Scav. O₂	...	0.75	...	...	0.68	...
He⁴	140	...	...	141	...	...
Tritiated products						
H_2	539	237	364	905	220	300
CH_4	13.5	7.2	18.7	13.1	14.2	19.5
C_2H_6	89	4.4	18	50	2.8	5.6
C_2H_4	6[i]	7.2	4.5[i]	21	3.0	3.0
[propane]	20	4.6	8.1	25	1.4	2.8
[propene]	1.5	1.8	Tr.	12	4.8	5.8
[n-butane]	100	2.7	3.7	22	1.7	2.0
[isobutane]	3.5	0	0	6	1.0	1.6

(continuation of table from previous page)

Alkane (product)						
[CH₂=CH–CH=CH₂ type]	0	Tr.	Tr.	0	1.2	Tr.
[⋁·⋀ + /=\ + >=]	0	0	0	0	Tr.	Tr.
[/\/\]	0	100	100	100	0	Tr.
[⊥/\/]	2	0	1.2	23.5	100	100
C_4H_{10}	0	Tr.	0	0	0	0
Above C_5	34[j]	0	...	9	0	1

Alkane Reacting	neopentane (X)	neopentane (X)	2,2-dimethylbutane (X)	cyclopentane (⬠)	cyclopentene (⬠)	2-methylpentane (/\/\/)	3-methylpentane (/\/\/)
(cm. Hg)	26.5	73.9	56.6	32.1	30.7	12.5	13.7
Additives (cm. Hg) { He³	0.68	1.4	1.3	0.37	0.43	0.70	0.48
Scav. I₂	0.02	..	...	...	...	0.02	...
Scav. O₂	...	1.8	...	0.68	...	...	...
Tritiated products (Average)							
H_2	139	137		361	426.5	328 ± 20	510 ± 30
CH_4	20.9	27.5		3	14.5	9.2	20
C_2H_6	0	4.0		0	6.5	5.2	14.8
C_3H_4	0	4.0[k]		12.5	12.0	10.3	11.0
[△]	0	1.5		Tr.	4.3	5.8	7.5
[△ methyl]	Tr.	2.5		3.5	3.9	Tr.	1.5
CH_2CCH_2	Tr.	...		1.0	Tr.	0	0
[/\/]	0	2.0		0	1.4	7.2	6.0
[>—]	2.5	10.5		0	Tr.	Tr.	Tr.
[/\//]	0	Tr.		0	1.3	Tr.	Tr.
[/\/ + /=\]	0	4.0		0	0	Tr.	0
[>=]	4.2 ± 2	6.0		0	0	0	0
[/\/\]	0	0		Tr.	4.8	4.2	10
[⊥/\/]	0	2.7		Tr.	1.3	1.0	0
[X neopentane]	100	100		0	0	0	0
[⬠ cyclopentane]	0	0		100	100	0	0
[/\/\]	0	0		5	5	0	Tr.
[⬠ cyclopentene]	0	0		Tr.	2.5	0	0
[/\/\/]	...	...		0	0	100	100
Above C_6	0	9[l]		0	0	0	0
MeI	8.8	...		...	...	7[m]	...

ᵃ The results presented in this table may be compared with the references: ethane,[4,10] propane (unscavenged only),[10,11] cyclopropane.[12] ᵇ Averaged results for methane and iodine scavenger taken from refs. 3 and 4. ᶜAveraged results for methane (no scavenger) taken from refs. 3, 4, 10. ᵈ Includes compounds above C₂. ᵉ Includes n-propyl iodide—trace. ᶠ Probably contains: [structure], tr.; [structure], 3; [structure], 5; [structure], 3. ᵍ Also, ethyl iodide, 1.4. ʰ No analysis made for the ethyl iodide expected in this system. ⁱ Also acetylene, tr. ʲ Possibly contains: [structure], 4; [structure], 14. ᵏ Also acetylene, tr. ˡ Also above C₅. ᵐ Also ethyl iodide, tr.

Four types of experiments are represented in Table II. (1) Runs in which tritium reaching thermal energies is removed by iodine scavenger and only the products of hot tritium reactions are observed. (2) Similar runs scavenged with oxygen. (3) Unscavenged runs. In these, any tritium reaching thermal energies is not removed from the system but reacts by hydrogen abstraction or combination with radiation produced species. Thus both hot and thermal products are observed. (4) Unscavenged and helium moderated runs in which the hot products are deemphasized in favor of those of thermal origin.

The excellent reproducibility between runs con-

taining oxygen and those containing iodine is noteworthy. Such agreement despite a difference of vapor pressure of 100 and an entirely different mode of operation is further evidence for the efficient action of both species in scavenging thermal reactions.

Iodine scavenger removes thermal tritium as TI which is not detected in the analysis. Methyl iodide and ethyl iodide which are formed have been shown[3] previously to result from combination of iodine and labeled radicals produced by hot reaction. The situation with oxygenated products found in oxygen scavenged runs is more complex. These products could result either from oxygen combination with simple labeled radicals made by a hot process; or from the decomposition of complex

(12) J. K. Lee, B. Musgrave and F. S. Rowland, J. Am. Chem. Soc., 81, 3803 (1959).

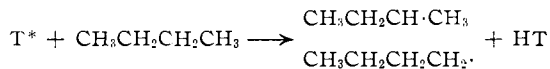molecules (probably peroxides) produced by the scavenging of thermal tritium atoms. It is not possible to distinguish between these processes, and for this reason the oxygenated products are not nearly as useful as the iodides observed in iodine scavenged runs.

As with other systems the major products are HT and the labeled parent. Other yields are much smaller though still significant. The effect of I_2 and O_2 scavengers is clearly evident in the virtual elimination of certain minor products in their presence. The thermal origin of such products is further demonstrated by the increase in their yield when excess helium is added in the absence of scavenger. Using these criteria it appears that 90 ± 10% of the yield of the labeled "parent" is due to hot reaction (by comparing the absolute yield in scavenged and unscavenged runs with the calculated amount of tritium produced). Although the relative yield of HT is generally somewhat reduced in the presence of scavenger, this product also derives mostly from hot rather than thermal abstraction. With minor products the situation varies, some being relatively unaffected and others being virtually eliminated by scavenger. The indicated thermal origin of the latter accords well with the fact that in nearly every case these products would be difficult or impossible to produce by other postulated hot displacement mechanisms, (e.g., iso-butane from butane or iso-pentane from n-pentane). The general pattern of the effect of scavengers is thus consistent with previous observations on gaseous methane[3] and ethane[4] and certain liquid systems[13] and requires no further discussion here. This study is primarily concerned with the hot reactions which are unaffected by scavengers. (The thermal products which are thus affected have been discussed elsewhere, particularly by Willard.[10]) For the discussion that follows, the scavenged runs (in which the thermal products are not detected) are therefore the most useful and should be referred to exclusively, unless otherwise indicated.
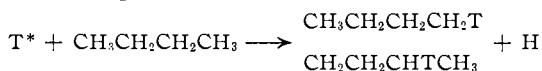
Discussion

All but a fraction of 1% of the products can be accounted for by several specific displacement processes. The types of reactions found are as follows, in decreasing order of relative importance (butane is used as example).

(I) Hydrogen atom abstraction. This reaction is the only one observed at thermal energies. With hot hydrogen it occurs with a much higher collision yield.[4]

$$T^* + CH_3CH_2CH_2CH_3 \longrightarrow \begin{array}{l} CH_3CH_2CH \cdot CH_3 \\ \\ CH_3CH_2CH_2CH_2 \cdot \end{array} + HT$$

(II) Hydrogen atom displacement to form the labeled parent alkane

$$T^* + CH_3CH_2CH_2CH_3 \longrightarrow \begin{array}{l} CH_3CH_2CH_2CH_2T \\ \\ CH_2CH_2CHTCH_3 \end{array} + H$$

(III) Replacement of alkyl group to form a degraded alkane

(13) J. B. Evans, J. E. Quinlan, M. C. Sauer and J. E. Willard, J. Phys. Chem., 62, 1351 (1958), and references therein.

$$T^* + CH_3CH_2CH_2CH_3 \longrightarrow \begin{array}{l} CH_3T + CH_3CH_2CH_2 \cdot \\ CH_3CH_2T + CH_3CH_2 \cdot \\ CH_3CH_2CH_2T + CH_3 \cdot \end{array}$$
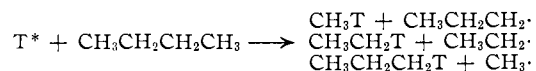
(IV) Radical formation. This may proceed by two mechanisms

(a) By displacement of two hydrogen atoms or an alkyl group and a hydrogen atom, e.g.

$$T^* + CH_3CH_2CH_2CH_3 \longrightarrow \begin{array}{l} CH_3CH_2CHT \cdot + CH_3 \cdot + H \\ \\ CH_3CH_2CHT \cdot + CH_4 \end{array}$$
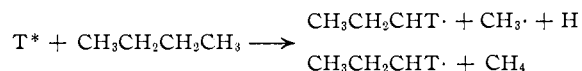
(b) By displacement of a single atom or group, leaving the primary product with sufficient excitation energy so that it subsequently decomposes

$$T^* + CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2T^* + H$$

$$CH_3CH_2CH_2CH_2T^* \longrightarrow CH_2TCH_2CH_2 \cdot + CH_3 \cdot$$
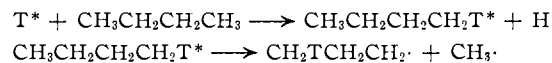
A radical, resulting from either of these two mechanisms, may then react in two ways. It may decompose into a smaller radical and an alkene by C-C bond rupture without rearrangement

$$CH_3CH_2CH_2CHT \cdot \longrightarrow CH_3CH_2 \cdot + CH_2=CHT$$

This type of decomposition has been independently observed for similar radicals made by hot atom addition to alkenes.[14] If the radical cannot rapidly decompose in this manner it may react with scavenger. This accounts for the methyl and ethyl iodides observed.

Table III summarizes and classifies the product distributions according to these possible modes of formation.[15] Thus row 3, "Degraded alkane," includes all products which could be produced by removing an alkyl group. In the case of neo-pentane this would be the yield of methane (produced by displacing isobutyl) and iso-butane (by displacing methyl).

"Rearranged and built-up products" include all products which cannot be produced by the postulated displacement mechanisms and includes degraded alkanes which cannot be formed by alkyl replacement. Thus in the case of neo-pentane this would include labeled ethane, propane, n-butane, iso-pentane, n-pentane—all straight chain alkanes, as well as other degradation and the "synthesis" products having more than five carbon atoms. The fact that these "unaccounted for" products are entirely negligible, amounting to less than 0.5% of the observed yield, is a strong argument in itself for the validity of the hot atom displacement mechanism concept.

It is evident that although the relative importance of these reaction types generally declines in the same order, there are sharp and specific variations from system to system. These variations are important in the later discussion of the detailed mechanism of the displacement processes.

Hydrogen Abstraction and Replacement Reactions.—By far the major products of the reaction of hot hydrogen atoms with alkanes are HT and the tritium substituted parent hydrocarbon (Table III). In all cases studied the sum of these was remarkably constant at 90 ± 3% with all other

(14) D. S. Urch and R. Wolfgang, J. Am. Chem. Soc., 81, 2025 (1959).

(15) Cyclopentane is omitted from this table since its cyclic structure will change the nature of the products expected from alkyl and two-group replacment.

TABLE III

SUMMARY OF PRODUCT DISTRIBUTION FROM NON-CYCLIC ALKANES

(Relative to yield of labeled parent molecule)

Reaction type	T-labeled product	Corresponding replacement	Molecule reacting with hot hydrogen								
			CH₄	C₂H₆	∧	∧/	≻—	∧∧	≻—∖	+	∧∧/
I	HT	Abstraction	1.0	1.82	1.97	1.99	1.92	2.37	2.20	1.40	3.28
II	Parent molecule	H atom	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
III	Degraded alkane	Alkyl group	..	0.12	0.15	0.15	0.17	0.19	0.21	0.23	0.33
IV	Methyl iodide[a] (initially (CH₂T·)	Alkyl group[b] + H atom	0.12[b]	.14	.06	.07	.05	.08[d]	.09[d]	.09	.07
IV	Alkene (initially radical)	Alkyl group + H atom or 2 H atoms	..	.11	.08	.08	.09	.10	.09	~ .05	.12
V	Rearranged and built-up products	Unaccounted for[c]	..	~ .03	.00	.01	.01	.00	.00	.01	.02

[a] In presence of I₂ scavenger only.   [b] 2 H displacement in case of CH₄.   [c] Not compatible with formation as direct consequence of a hot displacement reaction.   [d] From runs not listed in Table II.

products accounting for only $10 \pm 3\%$ of the hot tritium.

Energy Considerations.—The ratio of HT to T substituted parent shows significant variations, increasing with the relative number of primary H atoms in the reactant and decreasing if a relatively larger number of secondary and tertiary hydrogen atoms are present. A similar trend already has been noted for the reactions of hot hydrogen with liquid carboxylic acids.[7] It is tempting to associate such a trend with differences in bond strengths of the various C–H bonds. However, there is no immediately apparent reason why such bond strength differences should affect the ratio of abstraction to displacement. The lower bond strength of the C–C bond (82 kcal.) relative to the C–H bond (100 kcal.) does not result in a greater proportion of products formed by breaking the C–C bonds. On the contrary, products formed by rupture of C–C bonds are a significantly smaller fraction of the total yield than the ratio of C–C bonds. (See Table III and later discussion of alkyl group displacement.)

A relatively sensitive dependence on the energy of the bond to be broken would be expected if the reaction passed through an intermediate, metastable, quasi-equilibrated intermediate. (Such a dependence was actually found for addition reaction of hot hydrogen atoms to double bonds in alkenes[14]; in that system the intermediate is an alkyl radical which has a strong preference for decomposing by breaking a C–C bond rather than a C–H bond.) For the displacement reactions under present consideration bond strength is apparently not the primary determining factor. This supports the earlier hypothesis[3,4] that displacement occurs in a single step in a time span comparable to the period of one bond vibration, *i.e.*, 10^{-14} sec. All other data on the systematics of the hot displacement reaction are also consistent with this view of a fast direct displacement as the primary reaction of hot hydrogen in saturated system. There appears to be no evidence for the contrary view[16] that an internally equilibrated or longer lived intermediate is formed.

Stereochemistry.—If hot reactions are thus not controlled by energetics or the statistically deter-

mined decay of a common collision complex, we must turn to stereochemical factors affecting displacement and abstraction processes, as the major determinant of hot atom reactions. For example, it appears to be a reasonable hypothesis that the C–H bond is attacked more readily than the C–C bond because of its greater exposure. Two related questions then arise: (1) Does hydrogen displacement proceed by a Walden inversion mechanism and (2) what determines whether the hydrogen atom is displaced or abstracted. The answers to these questions have been sought in experiments on the retention of spatial configuration during hydrogen displacement. The accompanying paper[17] discusses this problem and reaches the conclusion that in the gaseous as well as the solid state, hydrogen displacement by hot hydrogen occurs with substantially complete retention of configuration.

Mechanism.—The data on retention of configuration suggests that to react with a bound hydrogen the incoming hot hydrogen must approach within a wide cone about the C–H bond axis (see Fig. 1). If, however, the approach is directly along this axis, displacement could not occur as it would be difficult to juxtapose the position of the H and T atoms. The calculations of Gorin, *et al.*,[18] show that such axial attack is instead the most favorable route for hydrogen abstraction. This is also consistent with the finding of Rowland that there is no appreciable isotope effect in the hot abstraction reaction with CH_2D_2.[19] The tentative conclusion is then that hot hydrogen attack at small angles in a narrow cone about the C–H bond axis normally leads to abstraction, whereas approach at larger angles is required for displacement (see Fig. 1).

Test of Model.—Though crude and obviously oversimplified this model can be tested. Consider the steric obstruction to various angles of attack at a given C–H bond. Groups attached to the carbon will hinder the large angle approaches and will diminish the probability of displacement of the hydrogen atom. Abstraction is not affected since there is no hindrance to small angle attack.

(16) This view has been applied to the reactions of lower energy hot atoms produced by photochemical means: J. L. Magee and W. H. Hamill, *J. Chem. Phys.*, **31**, 1380 (1959).
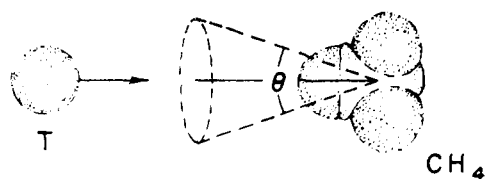
(17) M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961).

(18) E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1933).

(19) J. K. Lee, B. Musgrave and F. S. Rowland, *J. Phys. Chem.*, **64**, 1950 (1956).

a) H Atom Abstraction

b) Displacement of H Atom

Ejected H
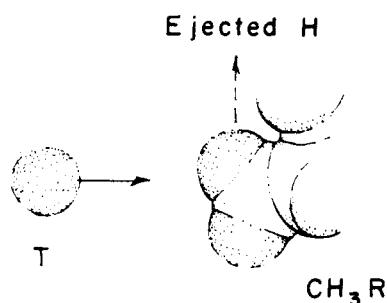
Fig. 1.—Stereochemistry of the abstraction and displacement of hydrogen from an alkane.

Consider that displacement reaction in methane is unobstructed but that substitution of one of the hydrogens by a methyl or larger group reduces the probability of displacement relative to abstraction by a factor of $(1 - \Omega)$, at each of the remaining hydrogens. Since the ratio abstraction/displacement is found to be unity in methane, we can consider the intrinsic probabilities for these processes to be equal if there is no steric hindrance. On this simple picture, for an alkane containing n hydrogens of which n_1 are primary, n_2 secondary and n_3 tertiary

$$\frac{\text{abstraction}}{\text{displacement}} = \frac{n}{n_1(1 - \Omega) + n_2(1 - \Omega)^2 + n_3(1 - \Omega)^3}$$

The experimental and calculated values of this ratio are listed in Table IV. The obstruction parameter Ω was given a value of 0.45 to provide the best fit. Such a simple-minded calculation has evident shortcomings, the most obvious being to attribute the same amount of obstruction to any attached group regardless of whether it is methyl, isopropyl or even cyclic. Nevertheless, despite this use of only a single fitted parameter, a remarkably good correlation between calculation and experiment is found. This is evidence for the validity of the general assumption that the course of the reaction of hot hydrogen is controlled primarily by the point and direction of impact. It also supports the more detailed postulate that axial approach toward the C–H bond leads to abstraction, while approach at larger angles causes displacement.

TABLE IV

RATIO OF HYDROGEN ABSTRACTION TO HYDROGEN DISPLACEMENT IN ALKANES

Alkane	Abstraction displacement in terms of obstruction parameter Ω	Calcd. ratio for $\Omega = 0.45$	Exp. ratio
CH_4	1	1.00	1.0
/	$\dfrac{1}{1 - \Omega}$	1.82	1.82
+	$\dfrac{1}{1 - \Omega}$	1.82	1.40
⟩—	$\dfrac{10}{9(1 - \Omega) + (1 - \Omega)^3}$	1.95	1.92
⌃	$\dfrac{4}{3(1 - \Omega) + (1 - \Omega)^2}$	2.05	1.97
⟩—⟨	$\dfrac{12}{9(1 - \Omega) + 2(1 - \Omega)^2 + (1 - \Omega)^3}$	2.09	2.20
⋀/	$\dfrac{5}{3(1 - \Omega) + 2(1 - \Omega)^2}$	2.22	1.94
⋀⋀	$\dfrac{2}{(1 - \Omega) + (1 - \Omega)^2}$	2.36	2.37
⋀⋁/	$\dfrac{7}{3(1 - \Omega) + 4(1 - \Omega)^2}$	2.44	3.28
⬠	$\dfrac{1}{(1 - \Omega)^2}$	3.33	3.61

Displacement of Alkyl Groups.—Reactions of hot hydrogen to form degraded alkanes is quantitatively of rather minor importance accounting for only about 5% of the yield. Nevertheless, there are some obvious facets of the data which suggest that this reaction also proceeds by a displacement mechanism. As previously mentioned, degraded alkanes which could not be formed by this mechanism are almost completely absent. Furthermore, the yield of a given alkane depends on the number of alkyl groups in the parent which on being displaced could give that product. Thus the yield of CH_3T depends on the number of methyl groups. For the series of isomeric pentanes this yield increases in the order: cyclopentane < n-pentane < iso-pentane < neo-pentane. Similar generalizations hold for other systems and other products. In particular a similar effect has been noted in liquid carboxylic acids.[7]

The almost total absence of degraded alkanes from cyclopentane is particularly striking evidence for the alkyl displacement mechanism. Such a mechanism in cyclic systems would of course lead to radical rather than degraded alkane formation.

In trying to postulate a detailed mechanism for alkyl displacement we are hampered by the present lack of direct evidence on retention of configuration during such reaction. Nevertheless, the data are well in accord with a model for alkyl displacement similar to that which appears to be successful for displacement of hydrogen atoms. The tritium attacks in a direction approximately normal to the C–C bond axis. It becomes attached to one of the carbon atoms simultaneously ejecting the conjugate alkyl group (see Fig. 1).[20] By recourse to molec-

(20) Two alternative mechanisms for the production of degraded alkanes may be considered in place of the alkyl displacement process. (1) Alkyl groups are "abstracted" by hot hydrogen atoms, i.e., they are displaced with Walden inversion. (2) Displacement (or abstraction) of alkyl groups is unimportant. Instead the degraded alkanes are formed by a sequence of reactions following hydrogen atom displace-

TABLE V

COMPARISON OF PRODUCTS YIELDS FROM ATTACK ON C–C AND C–H BONDS

System	Degraded alkanes [a] $\overline{\text{HT + T labeled parent}}$	C–C bonds $\overline{\text{C–H bonds}}$	Prob. attack on C–C bond [b] $\overline{\text{Prob. attack on C–H bond}}$	$\dfrac{\text{Prob. attack on C–C bond}}{\text{Prob. attack on C–H bond}}$ to give displacement only
C_2H_6	$\dfrac{0.12}{2.82} = 0.042$	0.16	0.26	0.75
C_3H_8	$\dfrac{0.15}{2.97} = .050$	.25	.20	.60
$n\text{-}C_4H_{10}$	$\dfrac{0.15}{2.99} = .050$	.30	.17	.50
$iso\text{-}C_4H_{10}$	$\dfrac{0.17}{2.92} = .058$	.30	.19	.57
$n\text{-}C_5H_{12}$	$\dfrac{0.19}{3.37} = .056$	.33	.17	.57
$iso\text{-}C_5H_{12}$	$\dfrac{0.21}{3.20} = .065$	.33	.20	.63
$neo\text{-}C_5H_{12}$	$\dfrac{0.23}{2.39} = .096$	.33	.29	.70
$n\text{-}C_6H_{14}$	$\dfrac{0.31}{4.28} = .072$	.36	.20	.86

[a] Total yield of products from alkyl displacement (TableIII, row 3) divided by product yield from C–H rupture (Table III, rows 1 and 2). [b] Second column divided by third column.
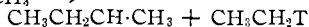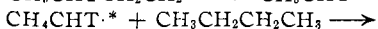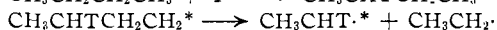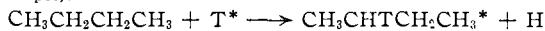
ular models several consequences of this mechanism are apparent.

(1) Obstruction by the alkyl groups limits approach to a C–C bond to a smaller solid angle than is the case for similar attack on a C–H bond. The experimental evidence for this is analyzed in Table V. For all systems studied the probability of reaction involving rupture of a C–C bond is only about 0.2 compared to reactions rupturing a C–H bond. (If only displacement reactions are considered, the probability of reaction at C–C is about 0.6 times that at C–H.)

(2) Table VI shows the products to be expected by alkyl displacement at each C–C bond and their yields. The total yield of products obtained by breaking each type of C–C bond then is obtained (relative to the yield of parent hydrocarbon, representing the yield of H displacement in the whole molecule, which is taken as 100). This shows that the position of the C–C bond does not greatly affect the probability of displacement there. Such a finding is quite plausible, for molecular models show that most types of C–C bonds are about equally exposed to attack.

(3) Table VI shows a striking trend favoring formation of the smaller of the two possible labeled hydrocarbons which can be formed by alkyl displacement. The disparity in yields is proportional

ment to give an excited primary product (n-butane is used as an example).

$CH_3CH_2CH_2CH_3 + T^* \longrightarrow CH_3CHTCH_2CH_3^* + H$
$CH_3CHTCH_2CH_2^* \longrightarrow CH_3CHT\cdot^* + CH_3CH_2\cdot$
$CH_4CHT\cdot^* + CH_3CH_2CH_2CH_3 \longrightarrow$
$\qquad\qquad\qquad CH_3CH_2CH\cdot CH_3 + CH_3CH_2T$

Since internally excited radicals are known to decompose rather than abstract hydrogen, the second step of this mechanism will have to yield radicals of high kinetic energy. This makes such a reaction path appear rather improbable. It seems very difficult to account for the observed yield distributions on the basis of either of mechanisms 1 or 2, and we believe that neither contributes significantly. These mechanisms can be finally excluded by experiments on retention of configuration during alkane formation. Mechanism 1 above would predict inversion, mechanism 2 racemization whereas alkyl displacement should result in retention of configuration.

to the relative complexity of the groups joined by the C–C bond. Thus with neo-pentane there is produced about eight times as much methane as iso-butane. Three factors may be responsible for this trend. Steric considerations could favor those approaches to the C–C bond which tend to culminate in combination with the simpler group. However, recourse to molecular models does not make obvious either the magnitude or direction of any such effect.

Although it is primarily steric considerations that determine the probability of attack on a given bond, if such attack is approximately normal to the bond axis, other factors may then be dominant in deciding which of the resulting fragments can capture the hot atom. Thus another possible explanation for the effect considered here is that the hydrogen combines with the group with which it makes the stronger bond: and with alkanes the R–H bond is stronger if R is small. Such an effect of bond strength is qualitatively plausible; when the hot atom breaks a bond it is obviously more likely to be captured by the group which presents to it the deeper and more extensive well. Quantitatively, however, it seems doubtful that the 10–15% range in the strengths of R–H bonds could have a large effect on the manner of combination of atoms with excess kinetic energy. A third and related factor is perhaps more important: whether the capturing group (e.g., methyl or isobutyl in C–C attack on neopentane) can make available during the time of collisions an orbital that is properly directed to strongly interact with the hot tritium. Current studies of R. Odum on other systems are intended to determine the relative importance of these three factors.

Reactions Yielding Labeled Radicals.—The production of small amounts of labeled methyl and also ethyl iodide in scavenged runs shows that hot hydrogen is capable of reacting to become incorporated in labeled radicals (Table II, reaction type 4). Although no higher alkyl iodides were

TABLE VI

ANALYSIS OF YIELDS OF DEGRADED HYDROCARBONS AS PRODUCED BY DISPLACEMENT ATTACK AT C–C BONDS

Reacting alkane	Bond attacked C₁–C₂ Anticipated product	Yield[a]	Total yield per bond[a,b]	Bond attacked C₂–C₃ Anticipated product	Yield[a]	Total yield per bond[a,b]	Bond attacked C₃–C₄ Anticipated product	Yield[a]	Total yield per bond[b]
C_2H_6	CH_4	11.8	11.8						
C_3H_8	CH_4	11.0	7.5	CH_4	11.0	7.5			
	C_2H_6	4.0		C_2H_6	4.0				
n-C_4H_{10}	CH_4	6.7	5.2	C_2H_6	4.8	4.8	CH_4	6.7	5.2
	C_3H_8	3.7					C_3H_8	3.7	
i-C_4H_{10}	CH_4	14.1	5.7						
	C_3H_8	3.0							
n-C_5H_{12}	CH_4	7.2	5.0	C_2H_6	4.4	4.5	C_2H_6	4.4	4.5
	C_4H_{10}	2.7		C_3H_8	4.6		C_3H_8	4.6	
i-C_5H_{12}	CH_4	4.7[c]	5.7	C_2H_6	2.8	4.2	CH_4	9.5[c]	5.6
	i-C_4H_{10}	1.0		C_3H_8	1.4		n-C_4H_{10}	1.7	
neo-C_5H_{12}	CH_4	20.9	5.9						
	i-C_4H_{10}	2.5							
n-C_6H_{14}	CH_4	9.2	6.7	C_2H_6	5.2	6.2	C_3H_8	5.8	5.8
	C_5H_{12}	4.2		C_4H_{10}	7.2				

[a] Relative to yield 100 for total hydrogen displacement. [b] Total yield of alkanes which may be produced by breaking given bond divided by number of such bonds. [c] Assuming that yield of methane from either type of terminal C–C bond is the same.

observed, it is probable that higher tritiated alkyl radicals were produced but decomposed before they could be scavenged by I_2.

$$e.g., CH_3CH_2CHT\cdot \longrightarrow CH_3\cdot + CH_2{=}CHT$$
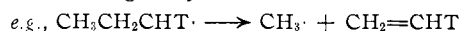
This mode of decomposition involves rupture of the weakest bond without rearrangement to form a smaller radical and an alkene. It has been previously characterized for other systems.[21,22] In particular it has been observed for excited radicals produced by hot tritium atom addition to alkenes.[14] Such a decomposition must occur before the radical encounters a scavenger molecule, i.e., in about 10^{-7} sec. The process will, of course, be accelerated by excitation energy in the radical: and it is likely that the processes forming the radical endow it with excess energy.

That methyl and ethyl radicals may survive long enough to react with scavenger follows because they would have to decompose by breaking a C–H bond rather than a weaker C–C bond.

This mechanism thus accounts for the absence of higher alkyl iodides and the presence of alkenes. Since the preferred mode of decomposition is by rupture of a C–C bond, only alkenes containing less carbon atoms than the reacting alkane should in general be expected. This is found to be the case. Significantly, the only exceptions in the non-cyclic alkanes[23] to this are small yields of ethylene from ethane, propylene from propane and iso-butene from iso-butane. Only in these systems can radicals be formed that cannot decompose to an alkene by simple C–C bond rupture without rearrangement: a C–H bond must be broken.[22]

(21) J. McNesby, D. Drew and A. Gordon, J. Chem. Phys., 24, 1260 (1956).

(22) F. P. Lossing and J. B. de Sousa, J. Am. Chem. Soc., 81, 281 (1959).

(23) Pentene-1 from cyclopentane is a special case because of the cyclic nature of the system. This product probably results from an isomerization of pentamethylene

$$\cdot CH_2CH_2CH_2CH_2CHT\cdot \longrightarrow CH_3CH_2CH_2CH{=}CHT$$
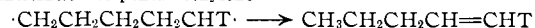
Such internal hydrogen abstraction reactions involving a 1–4 shift have been observed by Gordon and McNesby (J. Chem. Phys., 31, 853 (1959)).

$$e.g., CH_3\overset{\cdot}{C}TCH_3 \longrightarrow CH_3CT{=}CH_2 + H$$
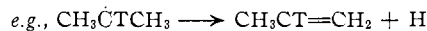
Although the yields involved are quite small, this specificity in the product spectrum is quite striking evidence for the radical origin of the alkenes.

The origin of the labeled radicals themselves is more obscure. There are two possible mechanisms for their production.

(1) Simultaneous and direct displacement of two H atoms or alkyl groups by the incoming hot hydrogen

$$e.g., CH_3CH_2CH_3 \longrightarrow CH_3CHT\cdot + CH_3\cdot + H$$
$$or \longrightarrow CH_3CHT\cdot + CH_4$$
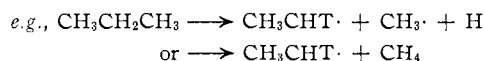
(2) Displacement of a single H atom or group to form a labeled alkane which contains excitation energy and subsequently ruptures

$$e.g., T + CH_3CH_2CH_3 \longrightarrow CH_2TCH_2CH_3^* + H$$
$$CH_2TCH_2CH_3^* \longrightarrow CH_2TCH_2\cdot + CH_3\cdot$$
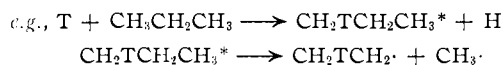
Available evidence indicates that mechanism 1 is probably dominant. Thus radicals containing the same number of carbon atoms as the original alkane appear to be observed. Since mechanism 2 preferentially yields only smaller radicals which can be produced by breaking a weaker C–C rather than a C–H bond, this observation favors mechanism 1. Mechanism 2 may also be expected to become rapidly less important as the size of the reacting molecule increases. A larger molecule means that excitation energy can be distributed in more degrees of freedom and that bond rupture is less likely to occur before collisional deactivation. However, the yield of radicals does not decrease appreciably with larger systems (see Table II). This means that either mechanism 1 is more important or that decomposition by mechanism 2 occurs before the excitation energy resulting from displacement is delocalized.

Summary

(1) Hot hydrogen atoms react with alkanes to give products consistent with the displacement by the incoming hydrogen of a hydrogen atom, an alkyl group or two groups.

(2) HT and the T-labeled form of the parent molecule irradiated account for 90% of the yield. HT is postulated to result from axial attack along the C–H bond, while displacement (without inversion) follows attack toward the central carbon atom. A crude quantitative formulation of the model which takes into account steric factors obstructing attack at certain angles accounts well for the observed ratio of HT to labeled parent.

(3) The detailed pattern of production of labeled alkanes is fully consistent with a mechanism involving displacement of an alkyl group by hot hydrogen attacking in a direction approximately normal to the C–C bond. As expected from steric considerations, alkyl displacement is less likely than H displacement despite the fact that the C–C bond is weaker than the C–H bond.

(4) Production of labeled radicals and alkenes is consistent with displacement of two groups or H atoms by the entering hot hydrogen. A mechanism involving dissociation of an excited labeled molecule formed by single hydrogen or alkyl group displacement is also possible. The radical formed may subsequently decompose to give a smaller radical and labeled alkene.

(5) Products which must be accounted for in terms of mechanisms additional to the simple displacement modes postulated (such as isomerization, break-up of highly excited species) amount to less than 0.5% of the total.

(6) The findings lend further support to a general model of hot hydrogen atom attack postulating a fast, direct displacement. The interval involved is of the order of 10^{-14} sec., the time required for one bond vibration, or for an H atom in the ev. range to traverse 10^{-8} cm. Formation of any metastable intermediate is very unlikely. Furthermore, because of the short duration of the collision and the small size of the hydrogen atom, energy is transferred only to the one or two bonds actually struck. This accounts for our observations that in nearly all of the initial displacements only one, or at most two, bonds are broken, and that the products of such reaction do not contain very large amounts of excitation. The fact that, despite the presence of very energetic hydrogen atoms, the yields of products having a very high energy of formation (e.g., allene from butane) is negligible, also becomes plausible. If the energetic hydrogen can only transfer energy to the immediate area of impact, the amount of energy thus transferred will not be sufficient to cause extensive decomposition.

In this fast displacement, considerations of energy economy are no longer of primary importance in determining the reaction path since ample energy is available for almost any process. Instead the bonds to be broken depend primarily on the point and direction of impact. (Energy factors only enter in determining which of the groups joined by the bond attacked is more likely to capture the hot atom.)

This model contrasts with the various formulations of thermal reactions in which statistical, quasi-equilibrium factors govern the decay of a well-defined intermediate. In hot displacement reactions many different "collision complexes" may be formed as is evident from the very high collision efficiencies observed.[3] But these "collision complexes" have a lifetime of less than one vibration; they are only locally excited and the geometry of their formation determines the products into which they pass. The connotation of the term "collision complex" is thus quite different from that normally assumed for thermal reactions. In hot processes it merely denotes that stage of the collision in which the participants are closest together. To emphasize the importance of the impact parameters of the collision in determining its result, we characterize this formulation of hot displacement reactions by the term "Impact Model."

Stereochemistry of Hot Hydrogen Displacement at sp³ Carbon–Hydrogen Bonds

BY MICHAEL HENCHMAN[1] AND RICHARD WOLFGANG

The stereochemistry of the displacement of hydrogen by hot hydrogen atoms has been studied at an sp³ carbon atom in a gaseous molecule. The system used was the reaction of recoil tritium, from the nuclear reaction $He^3(n,p)H^3$, with optically active 2-butanol. There is $91 \pm 6\%$ retention of configuration for displacement of the hydrogen atom directly bonded to the asymmetric carbon. For the displacement of all the hydrogens throughout the molecule, there is $94 \pm 3\%$ retention of configuration. These results are well in accord with the model of hot hydrogen displacement postulating a fast, localized interaction occurring in about the characteristic period of a C–H bond vibration. According to such a model the short duration of the collision and the small size of the hydrogen atom allow no effective coupling mechanism for the concerted excitation of the several vibrational modes involved in the inversion process.

The reactions of high kinetic energy or "hot" atomic hydrogen, in the form of recoil tritium produced by nuclear reaction, have been the subject of several recent studies.[2-6] At thermal energies the sole reaction of hydrogen atoms with most saturated hydrocarbons is hydrogen atom abstraction.[7] With hot hydrogen, however, products appear of reactions other than abstraction. These reactions have been identified as a series of high energy displacement processes in which the hot hydrogen atom displaces a hydrogen atom, an alkyl group or possibly even two atoms or groups.[4,6]

Previous investigations have shown that these hot displacement reactions occur with high collision efficiency[4] at energies comparable to or higher than the activation energies of the reactions involved. Yield distributions indicate that the mechanism does not appear to involve a common intermediate, with lifetime long enough to permit internal equili-

(1) University Chemical Laboratory, Lensfield Road, Cambridge, England. Studies carried out in partial fulfillment of the requirements for the Ph.D. degree at Yale University.

(2) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661, 2665 (1960).

(3) J. K. Lee, B. Musgrave and F. S. Rowland, *ibid.*, **82**, 3545 (1960).

(4) M. Henchman, D. Urch and R. Wolfgang, *Can. J. Chem.* **38**, 1722 (1960).

(5) J. K. Lee, B. Musgrave and F. S. Rowland, *ibid.*, **38**, 1756 (1960).

(6) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982, 2997 (1961).

(7) R. Klein, J. R. McNesby, M. D. Scheer and L. J. Schoen, *J. Chem. Phys.*, **30**, 58 (1959).