Reactions of Hot Hydrogen Atoms with Halocarbons

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The reactions of hot hydrogen atoms with a series of gaseous halocarbons have been studied. Recoil tritium from the nuclear reaction $He^3(n,p)H^3$ was used as the source of hot hydrogen. In monohalomethanes substitution for both halogen and hydrogen as well as hydrogen abstraction reactions appear to occur freely. The ease of displacement of halogens is in the order previously found by Rowland in solid systems, $Br > Cl > F \cong H$. This trend correlates somewhat better with collision cross-section than bond energy. As the number of halogen substituents in halomethanes is increased, substitution for H atoms, per C–H bond, decreases moderately indicating a possible steric obstruction by the halogen atoms. There is a very sharp drop in substitution for halogen atoms in halomethanes having substituents other than that being displaced. Thus the yield of T for F substitution is much lower in CH_2F_2 than in CH_3F. This startling effect becomes reasonable on considering the inertia of both the displaced atom and other substituents of the central C atom in the impact model of hot atom reactions. The inertial factor also accounts for certain hitherto unexplained trends in minor products from hot hydrogen attack on C–C bonds in alkanes.

Hot hydrogen displacement of two atoms, to form a radical, is relatively prominent in monohalomethanes and even more so in dihalomethanes. The data indicate that such double substitution can proceed in a single direct displacement, although a two-step process involving dissociation of the second atom from an excited intermediate may be contributing. These reactions provide further indication of the importance of the inertial factor. The present results as well as earlier data on the absence of Walden inversion processes suggest the following generalization: substitution reactions of hot hydrogen atoms requiring the motion of heavy atoms or groups tend to be forbidden. This rule for hot atom reactions can be considered as being somewhat analogous to the Franck–Condon principle for electronic transitions.

Introduction

Recent studies on the interaction of recoil tritium with hydrocarbons have led to the qualitative formulation of some basic reaction mechanisms of hot hydrogen atoms.[2–4] According to the model as presently developed, very high energy collisions are not likely to lead to processes in which the hot atom enters combination; such reactions appear to take place chiefly at energies in the range 2–10 e.v. This energy range is still sufficiently large to make the collision time comparable to vibrational relaxation times ~10^{-14} sec. In such a brief period energy cannot flow far from the impact site and the collision is therefore localized with only one or two bonds being broken. As a result, the principal reactions of the hot hydrogen atom are either abstraction of, or substitution for, a single atom or group. Thus with alkanes the chief products of recoil tritium reaction are HT, the tritium substituted parent alkanes and smaller tritiated alkanes formed by alkyl group displacement. Lesser yields of tritiated radicals formed by two group displacement are also observed.

Bond strengths do not appear to be of primary importance in determining the course of direct hot substitution reactions. Instead, steric factors appear to be more dominant.[2] Thus displacement occurs much less frequently at the weaker but less exposed C–C than at the stronger C–H bond. Whether a bound H atom is abstracted or displaced by the incoming hot T appears primarily dependent on the angle of approach to the C–H bond: there is evidence that the larger angles seem to lead primarily to displacement.[2] Inertial considerations also appear to be important in the reactions of hot hydrogen atoms: this has been discussed in connection with the observation that displacement in these systems does not proceed by Walden inversion.[5]

The purpose of the present work on simple halocarbons is to discover to what extent these mechanisms, developed using hydrocarbon systems, may be extended to other systems. In particular, the inertial effects of

higher mass substituents seem most interesting. The systems chosen were various halogen substituted methanes and ethanes in the gas phase. Some previous work of White and Rowland[6] dealt with certain more complex halogen-substituted molecules in the solid phase.

One of the more salient results of the present study has appeared in a preliminary Communication to the Editor.[7]

Experimental

General Method.—The basic techniques of studying the reactions of hot hydrogen atoms using recoil tritium have been described previously.[2]

The halocarbon, together with small added quantities of He^3 and a scavenger (either Br_2, I_2 or O_2) and contained in a quartz ampoule, was exposed to neutrons. Recoil tritium was produced by the $He^3(n,p)T$ reaction. The scavenger combined with and removed any tritium atoms reaching thermal energies. If the scavenger was I_2 or Br_2 it also served by combining with tritiated radicals produced by hot reaction (e.g., $CH_2T\cdot$) to give readily identifiable products (e.g., CH_2TI). After irradiation the products were separated by gas chromatography and assayed by an internal flow counter.[8]

No analysis was made for tritium which combined at thermal energies with the scavenger or which underwent hot reaction to form tritium halides. However, the total amount of tritium reacting was assayed by means of a monitor.

Procedure.—Halocarbons, He^3 and scavenger were sealed in quartz ampoules on a vacuum line. The pressure of halocarbon was of the order of 1 atmosphere except where the vapor pressure at ambient temperature was limiting. Then it was kept slightly below such a limit to ensure that all material was in the vapor phase. Individual ampoules were bound in a bundle along with a butane monitor ampoule. Bundles were exposed for periods of the order of 2 days to low thermal neutron fluxes (~2×10^9 n. cm.$^{-2}$ sec.$^{-1}$) at ~$25°$ in the "Instrument Tunnel" of the reactor at Brookhaven National Laboratory. The radioactivity of the majority of samples was 1–6×10^6 disintegrations per minute.

The "monitor" sample included with each bundle provides a measure of the total amount of tritium produced per unit amount of He^3. It consists of a measured quantity of He^3 and enough n-butane so that essentially no tritium recoiled into the walls. The total gaseous activity in such samples was measured without prior separation. It was assumed that this represented the total activity produced, there being no way in which either hot or thermal tritium could combine in unscavenged butane to give a non-volatile product.

After irradiation, sufficient time was allowed to permit any halogen activity induced by radiative neutron capture to decay. The gas chromatography columns used to separate the products are listed in the table in the Appendix. The method of counting

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(2) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961). This is the article on which the present work is largely based. It contains references to prior work. For earlier general background information see ref. 3 and 4.

(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) M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961).

(6) R. M. White and F. S. Rowland, *ibid.*, **82**, 4713 (1960).

(7) R. Odum and R. Wolfgang, *ibid.*, **83**, 4668 (1961).

(8) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

TABLE I

RESULTS OF REACTIONS OF TRITIUM WITH HALOMETHANES[g]

Reacting halomethane	Run no. (scavenger)	H abstraction		H displacement		Halogen displacement		2H displacement		H + halogen displacement		2 halogen displacement	
		Product	Yield, %	Product	Yield, %	Product	Yield, %	Product[d]	Yield, %	Product[d]	Yield, %	Product[d]	Yield, %
CH_4	28(I_2)[a]	HT	28.8 ± 2	CH_3T	30.8 ± 2	—	—	CH_2TI	3.0 ± 1.0	—	—	—	—
CH_3F	19(I_2)[b]	HT	24.1 ± 1.2	CH_2TF	12.1 ± 0.5	CH_3T	4.4 ± 0.4	$CHTFX$	1.2 ± 0.2	CH_2TX	2.7 ± 0.3	—	—
CH_3Cl	23(I_2) 60(Br_2)	HT	22.3 ± 1.0	CH_2TCl	8.3 ± 0.1	CH_3T	7.1 ± 0.2	$CHTClX$	0.5 ± .3	CH_2TX	8.1 ± 0.7	—	—
CH_3Br	26, 46(I_2) 77(I_2)	HT	18.1 ± 1.2	CH_2TBr	9.7 ± 1.3	CH_3T	12.0 ± 1.6	$CHTBrX$	<0.6 ± .4[c]	CH_2TX	4.7 ± 1.6	—	—
CH_2F_2	90, 96 (I_2) 91 (Br_2) 97(O_2)	HT	19.6 ± 2.6	$CHTF_2$	5.5 ± 0.7	CH_2TF	1.5 ± 0.2	CHF_2X	0.5 ± .1	$CHTFX$	1.4 ± 0.1	CH_2TX	0.5 ± 0.1
CH_2Cl_2	48, 102 (Br₂) 103(I_2)	HT	19.1 ± 1.8	$CHTCl_2$	2.9 ± .4	CH_2TCl	1.7 ± .2	$CTCl_2X$	<0.6	$CHTClX$	1.8 ± 0.2	CH_2TX	2.9 ± 0.4
CHF_3	56(I_2) 57(Br_2)	HT	7.9 ± 1.2	CTF_3	2.9 ± .3	$CHTF_2$	0.7 ± .1	—	—	CTF_2X	0.5 ± 0.1	$CHTFX$	0.1[e]
CF_4	58(I_2) 59(Br_2)	—	—	—	—	CTF_3	0.2 ± .1	—	—	—	—	CTF_2X	0.2
CF_3Br	54(I_2)	—	—	—	—	CTF_3	<0.2	—	—	—	—	—[f]	—[f]
CCl_4	17 (I_2)	—	—	—	—	$CTCl_3$	<0.2	—	—	—	—	—[f]	—[f]

[a] Includes data from three runs taken from P. J. Estrup and R. Wolfgang, J. Am. Chem. Soc., 82, 2661 (1960). [b] Includes data from three runs of ref. 10. [c] Product only identified positively in run 85 with bromine scavenger; includes information on upper limits that could be present in I_2 runs. [d] X stands for I if I_2 scavenger and for Br if Br_2 scavenger. [e] Only detected in run 57 with Br_2 scavenger. [f] Possible products not sought. [g] Yields expressed as % of total tritium; errors indicated are average deviation from the mean.

the separated fractions as they flowed from the chromatograph has been discussed previously.[6]

Errors.—Radiation damage was kept to a minimum by utilizing a thermal neutron flux facility where the relative level of high energy radiation is low. In addition, care was taken to check each analysis to see that no detectable macro quantities of material other than reactant were present in the sample after irradiation. The size sample employed and sensitivity of the detectors in the gas chromatography apparatus makes the limit of such impurities about 0.1%.

The poor reproducibility of certain irradiations with respect to trace quantities of scavenged products was probably due to sensitized radiation decomposition of those polyhalides containing I and Br. Often products scavenged by bromine would have higher yields than corresponding iodine-scavenged products. In view of this, the significance of the absence of any yield of polyhaloiodomethanes is perhaps subject to some question. The logical experiment of adding carrier to protect these traces was not performed because any macro quantity of these materials quenches the counter. Exposure to radiation was reduced to as low a level as practical in these cases in order to minimize any radiation decomposition of possible products.

During the course of early experiments it was noticed that replicate analysis of the same sample showed decreasing quantities of methyl iodide. It appeared that trace quantities of methyl iodide were decomposed while in the vacuum line under room lighting. The simple precaution of keeping the sample in the dark eliminated this source of error. It was also assumed that trace quantities of other alkyl iodides and possibly bromides could also be appreciably photolyzed under these conditions, and the approriate precautions were taken.

Statistical errors in the counting were of the order of 1–3% for most of the major products and ranged up to 10% for some of the minor yields. Reproducibility of the relative yields for a single run from replicate scans on the same column or other columns was of the order of ±2% for major peaks. In general, the average of at least two and often more replicate analyses per column was found and the average yields from all columns finally used.

Agreement of yields between different samples was not as good as agreement of yields within a sample. This is shown in Table I where the uncertainties shown are the average deviations of individual determinations from the mean. (The standard deviation of the mean will of course be smaller in general.) These are errors in the absolute yield caused largely by an imprecise method of measuring the He[3] added to a sample. The uncertainty of relative yields of several products from a single reacting halocarbon is much smaller.

Results

Results on halogen substituted methanes and ethanes are shown in Tables I and II, respectively. Yields are given as percentages of the total tritium reacting, as calculated from the butane monitors. Classification is by the type of reaction, e.g., H abstraction, substitution of T for F, etc. The product actually observed is given with the yield. If I_2 or Br_2 scavenger was present,

tritiated radicals, produced by substitution of tritium for two atoms or groups, appeared as the corresponding iodide or bromide; e.g., for reaction of hot T with CH_3F to substitute for an H and an F atom

$$CH_3F + T^* \longrightarrow CH_2T\cdot$$
$$CH_2T\cdot + X_2 \text{ (scavenger)} \longrightarrow CH_2TX$$
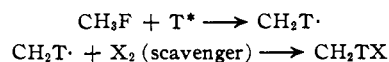
If oxygen was present as scavenger these radicals did not appear in the analysis as observed products.

Only runs in which the thermalized tritium was scavenged by I_2, Br_2 or O_2 are listed. A few runs without scavenger were performed and gave consistent results.

No products other than those indicated were observed in yields greater than 0.5%. As in previous work[2] with alkanes this indicates the absence of reactions in which more than two bonds were broken, or of isomerizations or reactions of the T atom involving more than one molecule.

The chief products in all systems are HT and the labeled form of the parent molecule. In the monohalomethanes, but not in other systems, there are also substantial yields of CH_3T, corresponding to a T for X substitution. Less than 50% of the tritium formed hot products detected in the analysis, with the percentage being even lower for polysubstituted methanes. This compares with a detectable yield of 60–80% for reaction with alkanes. Part of the deficit represents tritium atoms reaching thermal energies where they are scavenged. However, there will also have been an unknown yield of tritium halides, formed by hot halogen abstraction. Because of the lability of the hydrogen atom, trace quantities of tritium halides are difficult to assay, particularly if it is desired to distinguish between that formed in hot reactions and that produced by thermal reaction with scavenger. For this reason no such analysis was attempted in this work.

Some of the more salient features of the results are now summarized. For this purpose summary Tables III and IV are useful. In these tables the yields of abstraction and single substitution reactions are normalized by dividing them by the number of bonds per molecule at which such reactions can occur. The yields of all double displacement (to form radicals) reactions are summed. Certain trends in the various abstraction and substitution reactions are clear: (1) H atom abstractions: Tables III and IV show

TABLE II

RESULTS OF REACTION OF TRITIUM ATOMS WITH HALOETHANES

Haloethane	Run (scavenger)	—H abstraction—		—H displacement—		—X displacement—		Alkyl displacement		Double displacement	
		Product	Yield, %	Product	Yield, %	Product	Yield, %	Product	Yield, %	Product	Yield, %
C_2H_5Cl	43(Br$_2$)							CH_3T	1.1 ± 0.2	CH_3TX^a	2.5 ± 0.9
	44(Br$_2$)	HT	27.1 ± 2.6	C_2H_4TCl	8.9 ± 1.0	C_2H_5T	1.6 ± 0.2	CH_2TCl	~ 0.2	C_2H_4TX	1.1 ± 0.3
	88(O$_2$)									C_2H_3TClX	$<0.5^b$
	89(I$_2$)									C_2H_4	2.3 ± 0.8^c
CH_3CHF_2	100(I$_2$)							CH_3T	1.3 ± 0.2		
	101(Br$_2$)	HT	24.0 ± 4.0	$C_2H_3TF_2$	11.7 ± 0.8	C_2H_4TF	0.4 ± 0.1	$CHTF_2$	<0.2	^{d}	
CH_3CF_3	93(Br$_2$)							CH_3T	0.5 ± 0.03	CH_2TX	1.0
	94(O$_2$)	HT	13.8 ± 1.7	CH_2TCF_3	12.0 ± 0.7	CH_3CTF_2	<0.1	CTF_3	~ 0.03	ZBr^e	1.0^e

^{a} X is symbol for halogen scavenger. ^{b} These products were checked for in runs 43 and 44. ^{c} Product only found in runs 88 and 89. ^{d} Not determined for this reactant. ^{e} Unidentified bromide from run 93.

TABLE III

TRENDS OF ABSTRACTION AND SUBSTITUTION REACTIONS WITH NUMBER OF HALOGEN SUBSTITUENTS

Reacting compound	H Abstraction yield, %/ CH bond	Substitution for H yield, %/ C—H bond	Substitution for X yield, %/ C—X bond	Total yield of double substn., %
Fluoromethanes				
CH$_4$	7.2	7.7	. . .	2.7
CH$_3$F	8.0	4.0	4.4	3.9
CH$_2$F$_2$	9.8	2.8	0.8	2.4
CHF$_3$	7.9	2.9	.2	0.6
CF$_4$	. . .	. . .	.05	<0.2
CF$_3$Br	. . .	. . .	$<0.2^a$	^{a}
Chloromethanes				
CH$_4$	7.2	7.7	. . .	2.7
CH$_3$Cl	7.4	2.8	7.1	8.6
CH$_2$Cl$_2$	9.6	1.5	0.8	5.0
CCl$_4$	. . .	. . .	<0.05	^{a}

^{a} The yields of two group displacement products were not determined for these reactants.

in the sequence CH_4, CH_3F, CH_3Cl. (No further decrease is observed in going to CH_3Br.) If not entirely lacking, such a trend is much less marked for H abstraction to form HT. These observations are entirely in accord with the "impact model" previously described.[2,4] H abstraction was postulated to proceed primarily by attack approximately axial with the C–H bond. It is thus relatively insensitive to the nature of neighboring substituents on the carbon atom. On the other hand, displacement results from attack more nearly normal to the axis of the C–H bond. It is thus sensitive to steric hindrance by neighboring atoms or groups, the extent of the inhibition depending on the number (see Table III) and size (see Table IV) of such atoms. These effects seem clearly evident in both the mono- and dihalomethanes.

Although there are considerable variations in the strengths of the C–H bonds involved (listed in Table IV), there seems to be no obvious correlation with any trend in abstraction or displacement. These results tend to confirm further the hypothesis that bond energy effects do not determine the course of the primary reactions of hot hydrogen atoms, and that instead steric effects are dominant.

TABLE IV

TRENDS OF ABSTRACTION AND SUBSTITUTION REACTIONS WITH HALOGEN TYPE

Reacting compound	C–H bond^a strength, kcal.	C–X bond^a strength, kcal.	H abstraction yield, %/C–H bond	Substitution for H yield, %/C–H bond	Subst. for X yield, %/C–X bond
CH$_4$	101	—	7.2	7.7	—
CH$_3$F	102 $\pm$ 2	118	8.0	4.0	4.4
CH$_3$Cl	97.4	83.5	7.4	2.8	7.1
CH$_3$Br	95.2	67.5	6.0	3.2	12.0
CH$_2$F$_2$	101	118	9.8	2.8	0.8
CH$_2$Cl$_2$	93.2	78.5	9.6	1.5	.9
CHF$_3$	103 $\pm$ 4	118	7.9	2.9	.2
CF$_4$	—	121 $\pm$ 4	—	—	.05

^{a} Bond strengths taken from N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., 1958, pp. 10–28.

there are no obvious strong trends with the number and kind of substituents, in the probability of abstraction per C–H bond. (2) H atom displacement: The probability of displacement of H atoms/C–H bond decreases with the number and size of substituents. (3) Halogen atom displacement: (a) Halogen atoms are readily substituted by T in monosubstituted methanes (Table IV); ease of replacement is in the order F < Cl < Br. (b) Table III shows a very strong and most significant trend. The probability of T for halogen substitution shows a very sharp inverse dependence on the number of heavy substituents on the methane. Thus Cl displacement with substitution is much less probable in CH_2Cl_2 than in CH_3Cl.

Discussion

Reaction at the C–H Bond.—Hot tritium atom substitution for H per C–H bond drops by a factor of 2–3

Reaction at Carbon–Halogen Bonds.—Two trends are observed in substitution reactions of hot hydrogen at carbon–halogen bonds. There is a moderate increase in the probability of substitution with the atomic number of the halogen; and there is a very sharp decrease as the number of substituents on the central atom is increased. These effects appear to have different origins and will be discussed separately.

Relative Ease of Halogen Substitution.—In Table IV there is clearly a moderate trend favoring substitution of heavier halogen atoms, F < Cl < Br. Such a trend has already been observed in substituted benzoic acids by White and Rowland.[6]

There are two obvious explanations for this effect: (1) The weakening of the C–X bond (see Table IV) with increasing atomic number of the halogen; (2) the larger collision cross-section of the higher halogens which may well be reflected in a larger reaction cross-

section. White and Rowland[6] favor the first explanation; we tend toward the second. It would be consistent with other observations that steric, rather than energy, factors are dominant when C–H and C–C bonds are involved (see ref. 2 and following paper). Under the circumstances it would be surprising if C–X bonds behaved differently. More particularly, in the present system, the probability of T substitution for F in CH_3F is very similar to that of substitution for H, per C–H bond, despite the much greater strength of the C–F bond. (Note that it is not meaningful to make such a comparison for CH_2F_2, or for that matter CH_2Cl_2. As discussed below a more dominant inertial effect supervenes in the disubstituted methanes.)

It is worth noting that the dependence on the atomic number of the halogen appears to be greater in the halobenzoic acids studied by White and Rowland[6] than it is in these systems. This may be due to a contribution by a *thermal* addition reaction resulting in substitution

$$T(\text{thermal}) + X\langle\bigcirc\rangle\text{--COOH} \rightarrow {}_{T}^{X}\!\!\rangle\!\!\langle\bigcirc\rangle\text{--COOH} \longrightarrow$$

$$X + T\langle\bigcirc\rangle\text{--COOH}$$
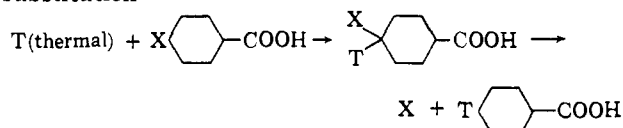
Since these compounds are solid, no scavenger could be present to suppress such processes. As thermal reactions they might be strongly dependent on bond strength.

Inertial Factors in Halogen Substitution.—The most important finding[7] of this investigation is the rather startling dependence of the probability of halogen substitution on the presence of substituents other than that being displaced. As is seen in Table III, the probability of displacement with substitution, of F by T, is much smaller in CH_2F_2 than in CH_3F, and in CHF_3 and CF_4 it is virtually zero. An exactly similar trend is noted for other halides. Furthermore, the probability of chlorine substitution in ethyl chloride is down sharply from methyl chloride: The indications are thus that any second substituent on the central carbon atom will serve to inhibit T substitution for the first. As will be seen below, this appears to be true in substitution for alkyl groups as well as halogen atoms.

Some trend in this direction would be expected for purely steric reasons, since the second group partially blocks approach to the first. But the magnitude of the effect seems much too large to attribute primarily to a steric factor. If the physical size of the second substituent will not account for the effect, one must therefore turn to its mass, i.e., to inertial considerations.[9] The only previous treatment of the effect of the moment of inertia of the atom being displaced is the so-called "billiard-ball hypothesis." However this has recently been shown to be inappropriate for describing the gas phase reactions of recoil tritium. In any case, in these systems it would not predict any marked effect of a second substituent, and it would predict a. trend in F, Cl, Br substitution opposite to that observed.

This inertial effect of heavy substituents can be readily understood and predicted by a detailed consideration of the simple classical model proposed previously for displacement reactions.[2,4,5] Such a classical treatment is limited in what it can achieve quantitatively, but its qualitative use is well justified, the DeBroglie wave length of a one electron volt tritium atom being quite small (0.2 Å.) compared to the dimensions involved.

Hot hydrogen atom displacement of a hydrogen atom has been discussed previously.[2] The impinging hot atom approaches in a direction approximately

(9) R. J. Cross and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961).

EFFECT OF SUBSTITUENT MASS ON ORBITAL AVAILABILITY FOR HOT ATOM CAPTURE.

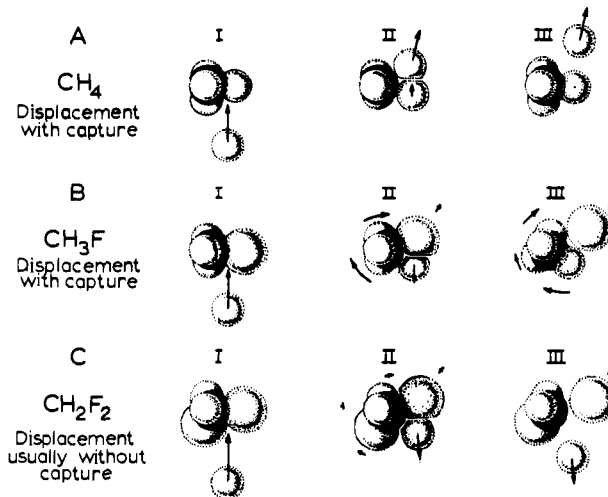Length of arrows represents relative velocity.

Fig. 1.—Schematic depiction of hot hydrogen attack on substituted methanes. Length of arrows is a measure of velocity. Possible capture of the hot hydrogen atom by the atom displaced is not shown.

normal to the C–H bond and, on collision, ejects the bound hydrogen with a velocity comparable to that of its own approach. It can thus occupy the position previously held by the ejected atom (see Fig. 1 AI, AII). However, if its initial energy was very high it will not combine, and the net reaction is displacement without substitution

$$T^* + CH_4 \longrightarrow CH_3\cdot + T\cdot + H\cdot$$
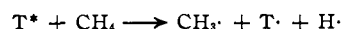
If the initial energy is lower, perhaps between 2 and 10 e.v., then the tritium atom can combine. Depending on its spin alignment and also on the kinematics of the particular collision, such combination will be with either the central carbon atom or the displaced hydrogen (see Fig. 1, AIII). The net results are substitution or abstraction

$$CH_4 + T \longrightarrow CH_3T + H\cdot, \text{ or } CH_3\cdot + HT$$
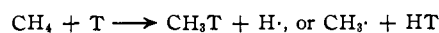
As has previously been observed, the kinematic factor in a collision approximately normal to the C–H axis should favor displacement.

A model of hot hydrogen displacement of a halogen atom cannot be as simple. The hot atom approaching the C–X bond at an approximately normal angle can on collision break it, primarily by displacing the binding electrons thus weakening the bond. It also imparts a major fraction of its momentum—but with it rather little energy—to the halogen. However, the comparatively large inertial mass of the halogen causes it to move out only slowly. (A fluorine atom having a kinetic energy of 1 e.v. covers only 0.2 Å. in 10^{-14} sec.—the characteristic time of a hot tritium reaction.) As a result the tritium atom comes momentarily to rest, having expended its kinetic energy against the repulsive cores of the carbon and halogen atoms (see Fig. 1, BI, BII), but without having as yet spatially displaced the halogen atom. If its electron spin opposes that of the carbon atom, a formal C–T bond can be said to exist. However this bond is very weak because the system is far from the equilibrium position for tetrahedral sp^3 bonding. Since the tritium is also in a position of high repulsive potential with respect to the fluorine it will therefore tend to recoil and escape. However, the system can be considered

as a proto–CH$_3$T molecule which is vibrationally distorted in one bending mode (see Fig. 1, BII). As such it will tend to its equilibrium tetrahedral position by motion of the H atoms with respect to the T. The C–T bond can be thus strengthened and the tritium retained, but such a restoring motion must be completed before the T atom recoils and escapes. The time available is of the order of the collision time of 10^{-14} sec. (the time required for a T atom with a kinetic energy of a few electron volts to move 1 Å.). Knowing the magnitude of the potential energy of distortion that becomes available for the restoring rotation (approximately the energy of forming a strong C–T bond), and the moment of the inertia of the substituents for rotation around the carbon atom, the relaxation period for establishing tetrahedral bonding with the T atom can be calculated. If the substituents are hydrogen this relaxation will indeed occur within the collision time thus making capture of the hot atom possible (see Fig. 1, BIII).

By contrast, if the residual group has heavy substituents in addition to that being displaced, its much greater moment of inertia will preclude rapid rotation to strengthen the C–T bond (see Fig. 1, CI–CIII). Such rotation would require of the order of tens of e.v. and there is no efficient coupling mechanism to provide this much energy. As a result, attack on a C–X bond in a polysubstituted methane is unlikely to result in capture of the hot tritium by the carbon atom. On the other hand, an abstraction-type reaction, to form XT, should not be significantly affected by the presence of other heavy substituents.

In discussing this model several points should be kept in mind:

(1) Contrary to a possible intuitive impression, significant rotation of the CH$_3$ "away" from the tritium is not induced by the collision itself. If in colliding with a C–F bond a 5 e.v. T atom yields half its momentum to the carbon, this would correspond to a kinetic energy of 0.3 e.v. Nearly all this energy is translational, not more than 0.1 e.v. being in rotation about the center of mass of the CH$_3$. This effect is therefore negligible compared to the force inducing rotation in the opposite direction through formation of a C–T bond.

(2) For purposes of simplicity the model has been described exclusively in terms of the rotational relaxation of the molecule. However, there will also be a contribution from the vibrational stretching relaxation of the C–X bond. The effect is not very important, though. Order of magnitude calculations show that the C–X bond cannot stretch nearly far enough in the time of collision to allow a tritium atom with less than 20 e.v. to "squeeze" in between the C and X.

(3) While this classical model appears to be quite successful in the qualitative prediction and rationalization of hot collisions with heavy substituents, it should not be carried too far. Corresponding to the time of collision $\sim 10^{-14}$ sec. there is an energy uncertainty of 0.5 e.v. This means that a detailed energy analysis using the classical model will simply not be meaningful beyond a certain limit. Unfortunately, a rigorous quantum mechanical solution of this system is difficult to formulate and much more difficult still to evaluate. So the classical model must do for now, and, in any case, it is useful in providing an intuitive picture.

The model suggests that if the moment of inertia of the methyl group in a substituted methyl halide is gradually increased one should reach a region where the probability of capture of the tritium drops sharply. Unfortunately it is not practical to use any substituted methyl groups having a moment of inertia between

that of CD$_3$· and that of CH$_2$F· (or ·CH$_2$CH$_3$). In the accompanying paper[10] it is shown that there is no substantial isotope effect for T substitution of F between CH$_3$F and CD$_3$F. If the model postulated here is correct this must mean that the moment of inertia of CD$_3$ for rotation about the C atom ($\sim 1 \times 10^{-39}$ g. cm.^{2}) is not sufficiently large to prevent a rotation rapid enough to capture the tritium. Since substitution of F in CH$_2$F$_2$ is much lower than in CH$_3$F, CH$_2$F· with a much larger moment of inertia for rotation about the carbon atom ($\sim 6 \times 10^{-39}$ g. cm.^{2}) is on the other side of this threshold.

Using this information we may calculate the magnitude of the collision time—a number we have assumed up to now. The time t required for a system with a moment of inertia I starting from rest and acquiring rotational energy E, to rotate through angle θ, is

$$t \cong 2\theta\sqrt{I/2E}$$

If the substituents on the carbon atom rotate through about one radian to restore tetrahedral bonding, and if 5 e.v. become available for such rotation from the strengthening of the C–T bond, then the CD$_3$ would take about 2×10^{-14} sec. and the CH$_2$F· about 5×10^{-14} sec. to turn. The time of collision must therefore be of this order of magnitude, in agreement with earlier postulates.

Inertial Factors in Hot Atom Attack on C—C Bonds.—The model thus developed of the effect of inertial factors in hot hydrogen substitution of heavy atoms accounts for certain hitherto unexplained facets of the reaction of recoil tritium with hydrocarbons.[2] Thus in reaction with neopentane the yield of methane-T is about eight times that of isobutane-T, although both result from attack on the same C–C bond. Similar effects are noted in all other hydrocarbons: in attack on any C–C bond the hot atom is always preferentially captured by the smaller of the resulting radicals. Evidently on rupture of the bond the smaller group can rotate more rapidly and is thus favored in the competition for capture of the hot atom.

Two other explanations may be offered for this effect in the reactions of hydrocarbons, although neither seems particularly satisfactory: (1) Steric considerations could favor those approaches which culminate in combination with the simpler group. (However, not even the direction of such an effect is readily predictable.) (2) The group making the stronger bond, i.e., in general the smaller radical, is favored to capture the hot atom.

A critical test using CH$_3$–CF$_3$ was carried out to provide a final choice between these hypotheses. According to hypothesis 1, the yield ratio CH$_3$T/CF$_3$T should be smaller than the corresponding ratio CH$_3$T/(CH$_3$)$_3$CT from neopentane. This would be expected since F is smaller than CH$_3$ and steric factors are therefore less important in CH$_3$CF$_3$ than in CH$_3$C(CH$_3$)$_3$. Hypothesis 2 would predict a ratio CH$_3$T/CF$_3$T of near unity since the CH$_3$–H and CF$_3$–H bond strengths are virtually equal. (Table IV ref. a). The inertial model, on the other hand, would indicate a ratio CH$_3$T/CF$_3$T at least equal to, and probably greater than, that for CH$_3$T/C(CH$_3$)$_3$T from neopentane.

Tables I and V show that CH$_3$T/CF$_3$T from CH$_3$–CF$_3$ is greater than 15. Hypotheses 1 and 2 are thus clearly inadequate.

In studying the inertial effects of heavy substituents, the hydrocarbons offer an advantage in that both possible products of attack on a C–C bond are readily observable. (In alkyl halides the tritium halide yields are difficult to assay; see Results.) This makes it

(10) H. C. Jurgeleit and R. Wolfgang, J. Am. Chem. Soc., **85**, 1057 (1963).

TABLE V
COMPETITION FOR TRITIUM IN ATTACK ON C–C BONDS

Reacting alkane	Bond attacked	Product	Yield,[a] %	Yield/group,[b] %	Total yield/group,[c] %	Ratio[d]
C_2H_6	C_1–C_2	CH_3T	11.8	5.9	11.8	1
C_3H_8	C_1–C_2	CH_3T	11.0	5.5	7.5	2.7
		C_2H_5T	4.0	2.0		
n-C_4H_{10}	C_1–C_2	CH_3T	6.7	3.3	5.2	1.8
		C_3H_7T	3.7	1.8		
	C_2–C_3	C_2H_5T	4.8	2.4	4.8	1
i-C_4H_{10}	C_1–C_2	CH_3T	14.1	4.7	5.7	4.7
		$(CH_3)_2CHT$	3.0	1.0		
n-C_5H_{12}	C_1–C_2	CH_3T	7.2	3.6	4.9	2.8
		C_4H_9T	2.7	1.3		
	C_2–C_3	C_2H_5T	4.4	2.2	4.5	1.0
		C_3H_7T	4.6	2.3		
neo-C_5H_{12}	C_1–C_2	CH_3T	20.9	5.2	5.8	8.7
		$(CH_3)_3CT$	2.5	0.6		
n-C_6H_{14}	C_1–C_2	CH_3T	9.2	4.6	6.7	2.2
		$C_5H_{11}T$	4.2	2.1		
	C_2–C_3	C_2H_5T	5.2	2.6	6.2	0.7
		C_4H_9T	7.2	3.6		
	C_3–C_4	C_3H_7T	5.8	2.9	5.8	1
CH_3CH_2Cl	C_1–C_2	CH_3T	12.4	12.4	14.7	5.5
		CH_2ClT	2.3	2.3		
CH_3CHF_2	C_1–C_2	CH_3T	11.1	11.1	12.8	>6.6
		CHF_2T	<1.7			
CH_3CF_3	C_1–C_2	CH_3T	4.3	4.3	4.6	>15
		CF_3T	<0.3			

Isopentane data have not been included because of ambiguity arising from presence of two different types of methyl groups.

[a] Yields based on 100 for yield of T for H substitution product (labeled parent). [b] Yield divided by number of relevant alkyl groups per molecule. [c] Total yield of all products from rupture of given bond. [d] Ratio of lighter to heavier product from rupture of given bond.

worthwhile to re-examine this aspect of the hydrocarbon data in some detail. Such an analysis is offered in Table V (based on data from Tables II and VI of the article of Urch and Wolfgang[2]). Relevant data on halosubstituted ethanes are included.

From this table a number of generalizations may be made. In drawing these conclusions it should be kept in mind that, for steric reasons, attack on a C–C bond is a relatively unlikely process. Yields are therefore small and errors quite large. Nevertheless a number of gross features are quite clearly evident: (1) In attack on a hydrocarbon CH_3–R the yield ratio CH_3T to RT is approximately 2 if R is a monoalkylsubstituted methyl, 5 if it is dialkylsubstituted and 9 if it is trialkylsubstituted. This trend is, of course, as expected from inertial considerations. However the effect of an alkyl substituent does not seem to be as large as that of a halogen substituent (compare CH_3–CH_2CH_3 and CH_3–CH_2Cl; CH_3–$C[CH_3]_3$ and CH_3–CF_3). For the higher halogens this could be due to their larger moments of inertia; for fluorine the stiffness with respect to bending of the C–F bond may enhance the inertial effect. (2) The length of the alkyl substituent on a C–C bond being broken seems to have relatively little effect. Thus the "effective" moment of inertia for rotation seems to be less for a monoethylsubstituted than for a dimethylsubstituted methyl. (Compare results of attack on the C_1–C_2 bond in n-C_4H_{10} and i-C_4H_{10}; see Table V.) This is plausible since for a rotation through a relatively small angle the end of a long substituent is only loosely coupled to the central carbon. (3) The *total* yield of product for attack on a given C–C bond in a hydrocarbon is not strongly dependent on the nature of the two alkyl groups. This suggests that, in hydrocarbons at least, the reaction

should be regarded as a competition to capture the hot atom by the two groups which were joined by the bond attacked. If one group has an inertial impediment to combining with the incident hydrogen, this enhances the probability that the other will capture it.

Double Substitution Reactions.—By the term double substitution reactions we refer to those processes in which the hot tritium atom replaces two atoms or groups yielding a radical. If I_2 or Br_2 scavenger is present this radical will then form the corresponding iodide or bromide. Double substitution has previously been observed in alkanes as a minor reaction. Its detailed mechanism, or mechanisms, are quite obscure. The present data seem to shed some light on some factors involved in these processes, but still do not provide any apparent basis for a uniquely correct model.

A few generalizations can be made about the double substitution processes: (1) The relative frequency of double vs. single displacement is greater in monohalomethanes than in methane and greater still in dihalomethanes (see Table III); but in tri- and tetrasubstituted methanes the yield of double displacement drops sharply. (2) Double displacement is more likely in chloro- and bromomethanes than in fluoromethanes. (Further Cl seems more reactive than Br for this process; but as discussed in the Experimental section there is some uncertainty about the yields of bromoiodomethanes.) Note that in CH_2Cl_2 double displacement processes have a frequency on a par with the total of single displacement reactions. (3) The probability that any given heavy atom or group will be ejected in a double substitution is-generally higher than the probability for ejecting any given hydrogen atom. (4) A detailed analysis of net enthalpies of reaction shows no obvious and general correlation between the net energy requirement of a given double substitution process and its yield. Thus in CH_2Cl_2, substitution for 2Cl (either separately or as Cl_2) requires more energy than HCl displacement (either separately or as HCl). Furthermore, a statistical factor should favor HCl substitution; yet 2Cl substitution is more abundant.

A possible mechanism for double substitution involves two steps: Substitution for one atom or group occurs in the usual manner for direct single displacement, but the product molecule is left sufficiently excited subsequently to rupture a second bond. There would then be a preference for the second atom lost to be the one most weakly bound. This work provides no convincing evidence for such a mechanism and some which is clearly against it. Thus in CH_2F_2, substitution of either H or F should be followed by preferential rupture of a weaker C–H bond. Yet despite the fact that initial substitution of F is less likely than that of H (because of inertial factors) the total yield of the substitutions for 2F and 2H are similar.

If we assume that both atoms are displaced in the initial collision the inertial factor discussed previously in connection with single displacement enters. Consider attack on the C–X bond in CH_3X. After breaking this bond a strong C–T bond can be established by rotation of the CH_3. However there is an alternative to such rotation: If an H atom can be lost the remaining $CH_2T\cdot$ radical can quickly reach the optimum orientation for sp^2 bonding. Much of the energy required for dissociating this H atom can come from forming the strong C–T bond. On the basis of these considerations, the fact that in monohalomethanes substitution for HX is comparable in yield to substitution for X becomes reasonable.

The situation becomes more interesting still in considering attack on CH_2X_2. On rupture of a C–X

bond we have seen that the $CH_2X\cdot$ group cannot rotate in time to capture the hot hydrogen atom. However, dissociation of either an H, or more particularly of an X atom, may allow the system to reach easily the proper orientation to form a strong sp^2 bond with the tritium. Thus while inertial factors forbid single displacement of a halogen atom, double substitution would be permitted. It is therefore of more than casual interest to observe (Table I) that in both CH_2F_2 and CH_2Cl_2 double substitution involving a halogen atom is more probable than single halogen substitution. The drop in double substitution in tri- and tetrahalomethanes can then be rationalized on the basis that even if two groups are detached, the remaining radical still has too much inertia to reach sp^2 configuration in the time of collision.

Most of the other aspects of double substitution can be similarly rationalized using a combination of inertial and steric factors. We do not present these considerations in this paper since we feel that the available data are inadequate to provide critical tests of the detailed mechanisms which may thus be proposed.

Summary

The present studies indicate that in addition to steric considerations inertial factors play an important part in determining the course of hot reactions in which tritium substitutes for heavy atoms or groups. In prior work[5] it has been postulated that the absence of hot hydrogen substitution for hydrogen atoms by a Walden inversion mechanism is due to similar causes. The inductive generalization can be made that: *Substitution reactions of hot hydrogen atoms requiring the motion of heavy atoms or groups tend to be forbidden.* The even more general postulate can also be made: *Hot atom substitution reactions requiring relaxation motions that are slow compared to the time of collision tend to be forbidden.* This postulate can be considered as analogous to the Franck–Condon principle. In the electronic transitions governed by the Franck–Condon principle the difference in relaxation times between electrons and nuclei is governing; and in hot hydrogen reactions the difference in relaxation times between hydrogen and heavier atoms plays a somewhat similar part.

Appendix

CHROMATOGRAPHIC COLUMNS USED FOR ANALYSIS

Column	Separation[a]
Sil. gel., 10 ft., 25°	H_2, CH_4
Alumina, 3 ft., 25°	(H_2-CH_4), C_2H_6, C_2H_4
Silicone SF-96 on firebrick, 10 ft., 25°	$(H_2-CH_4-C_2H_6-C_2H_4)$, CH_3Cl, C_2H_5Cl, CH_3I
	$(H_2-CH_4-C_2H_6)$, CH_3Cl, CH_3Br, C_2H_5Cl, C_2H_5Br
	(H_2-CH_4), CH_3Br, CH_3I
	$(H_2-CH_4-CH_3F)$, CH_3I, CH_2FI
	(H_2-CH_4), CH_3Cl, CH_2Cl_2, CH_3I
	(H_2-CH_4), CH_3Cl, CH_3Br, CH_2Cl_2
	$(H_2-CHF_3-CH_2F_2)$, CHF_2I, CH_2FI, CH_3I
	$(H_2-CHF_3-CH_2F_2)$, CHF_2Br, $(CH_2FBr-CH_3Br)$
	$(H_2-CH_4-C_2H_5F)$, CH_3CHF_2, CH_2F_2
Polypropylene glycol on firebrick, 10 ft., 25°	$(H_2-CH_4-C_2H_6-C_2H_4)$, CH_3Cl, C_2H_5Cl, CH_3I
	(H_2-CH_4), CH_3Br, CH_3I
	$(H_2-CH_4-CH_3F)$, CH_3I, CH_2FI
Polypropylene glycol 10 ft., 70°	$(H_2-CH_4-CH_3Cl)$, CH_3I, CH_2ClI
Polypropylene glycol 10 ft., 0°	(H_2-CH_4), CH_3Cl, CH_3I
Diisooctyl phthalate on firebrick, 10 ft., 25°	(H_2-CH_4), CH_3Br
	$(H_2-CH_4-CH_3Cl)$, CH_3I, CH_2Cl_2
Silicone SF-96 on firebrick, 3 ft., 78°	$(H_2-CH_4-CH_3Br-CH_3I)$, CH_2BrI
	$(H_2-CH_4-CH_3Cl-CH_2Cl_2-CH_3I)$, CH_2ClI, $CHCl_2I$
	$(H_2-CH_3Cl-CH_3Br)$, CH_2Cl_2, CH_2ClBr
Hexamethylphosphoramide on firebrick, 10 ft., 0°	(H_2-CH_4), CH_3F
	(H_2-CH_4), C_2H_5F, CH_3CHF_2, CH_2F_2
Hexamethylphosphoramide on firebrick, 10 ft., 25°	(H_2-CHF_3), CH_2F_2
Hexamethylphosphoramide on firebrick, 10 ft., −10°	H_2, CHF_3, CH_2F_2
Silicone SF-96 on firebrick, 10 ft., −10°	(H_2-CHF_3), CH_2F_2
	$(H_2-CH_3F-CH_2F_2)$, CHF_2Br, CH_3Br, CH_2FBr
Tricresyl phosphate on Chromosorb-P, 10 ft., 25°	(H_2-CH_4), CH_3Br
	H_2, CH_3Cl, CH_3I, CH_2Cl_2
Silicone SF-96 on firebrick, 10 ft., 80°	$(H_2-CH_4-C_2H_6-C_2H_4-CH_3Cl)$, C_2H_5Cl, CH_3I, C_2H_5I
	H_2, CH_3Cl, CH_3Br, CH_2Cl_2, CH_2ClBr
	H_2, CH_3Cl, $(CH_3I-CH_2Cl_2)$, CH_2ClI
Hexamethylphosphoramide on firebrick, 10 ft., −18°	H_2, CH_3F, CH_2F_2
	(H_2-CH_4), CHF_3, CH_3CF_3
Silicone SF-96 on Chromosorb-P, 30 ft., −15°	(H_2-CH_4), CHF_3, CH_3CF_3
Silicone SF-96 on Chromosorb-P, 30 ft., 0°	H_2, CHF_3, CH_2F_2

[a] Compounds grouped within parentheses were not separated from each other.