The Abstraction of Hydrogen Atoms from Halomethanes by Recoil Tritium Atoms[1]

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Abstract: Yields of the abstraction reaction by recoil tritium, T + RH → HT + R, have been measured for 14 halomethanes in excess perfluorocyclobutene. The yields per C–H bond, $(HT)_F$, expressed relative to methane as 1.0, range from 1.34 (CHF_3) to 14.6 ($CHCl_3$). Progressive substitution of Cl or Br for H gives steadily higher values, while the fluoromethanes exhibit a maximum: CH_3F, 1.70; CH_2F_2, 2.5; CHF_3, 1.34. These trends are explained by the progressive weakening of C–H bonds with additional halogen substituents, coupled with a strengthening of the C–H bond by polar effects with multiple fluorine atom substituents. Comparison with hydrocarbon values leads to the postulate that residual radicals are more excited for RH = hydrocarbon than for RH = fluoromethane. The values of $(HT)_F$ are postulated to correlate with a combination of the bond dissociation energy of R–H and the excess internal excitation energy of the residual radical R formed by the abstraction reaction.

The varying percentage yields of HT from the abstraction of hydrogen atoms by energetic recoil tritium atoms, as in (1), have been shown to correlate very well with the C–H bond dissociation energies, defined as ΔH for reaction 2, in a variety of hydrocarbons.[3–6] The correlation is sufficiently good that

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

$$RH \longrightarrow R + H \qquad (2)$$

an unknown or an uncertain bond dissociation energy for an alkane can be estimated from the yield of reaction 1 under standardized conditions.[4] Since such measurements can be made rather easily, the valid extension of this procedure to other classes of molecules containing C–H bonds could clearly be of considerable utility. A similar correlation of HT yield with bond dissociation energy has recently been reported for energetic abstraction from N–H bonds.[7]

The chief problem involved in such extensions is the necessarily empirical nature of the observed correlation—the theoretical understanding of the hot abstraction of hydrogen atoms is still without a substantial basis of accepted fact.[5,6,8,9] Indeed, the original experiments which established the correlation[3,5] were undertaken with the purpose of testing the then current hypothesis that the yields of such hot abstraction reactions were completely independent of the identity of C–H bond involved.[10] Thus, while the close correlation can be simply and satisfactorily rationalized for alkanes,[6] the possibility must be kept open that some substituents may affect the bond dissociation energy and the hot abstraction reaction in a different, or at least quantitatively nonproportional, manner. The sole deviation from this correlation thus far reported for C–H bonds has been that observed with isotopic propylene molecules, such as $CH_3CD{=}CD_2$. In this case, the residual $CH_2CD{=}CD_2$ radical requires substantial atomic motion, about 0.1 Å motion of the central C atom, in order to obtain the equilibrium allylic configuration, and the hypothesis has been suggested that the hot abstraction reaction is completed prior to complete relaxation of the residual allyl radical.[11]

A desirable course for further experiments would be the measurement of the hot HT yields from a group of nonhydrocarbon molecules whose bond dissociation energies are well known, thereby making a direct test of the applicability for this new molecular series. However, there is no substantial group of nonhydrocarbons for which any agreed certainty exists concerning the C–H bond dissociation energies.[12] Indeed, even for saturated hydrocarbons, the accuracy of bond dissociation energy measurements is well below that required for a significant test at the level of precision of the HT yield measurements.[6,12]

In our current set of experiments, we have measured the hot HT yields from a large number of halomethanes and have examined the correlation between these values and measurements of their bond dissociation energies where available. The parallel between hot HT yields and bond dissociation energies is generally reasonable, but significant deviations from a monotonic relationship have been found which are consistent with an additional postulate about the mechanism of the hot abstraction reaction. Detailed examination will require more accurate estimates of bond dissociation energies by some other technique consistently applied to a substantial number of halomethanes.

Experimental Section

The tritium atoms have been produced in the usual manner by neutron irradiation of gaseous samples containing a standard composition of 1.5 cm of He^3, 1.5 cm of O_2, 5 cm of RH, and 71

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[2] To whom inquiries should be addressed.

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

[4] J. W. Root and F. S. Rowland, *J. Phys. Chem.*, **68**, 1226 (1964).

[5] J. W. Root, W. Breckenridge, and F. S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965).

[6] E. Tachikawa and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 4767 (1968).

[7] T. Tominaga and F. S. Rowland, *J. Phys. Chem.*, 72, 1399 (1968).

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

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

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

[11] E. Tachikawa, Y.-N. Tang, and F. S. Rowland, *ibid.*, **90**, 3584 (1968).

[12] J. W. Kerr, *Chem. Rev.*, **66**, 465 (1966).

cm of $c\text{-}C_4F_6$. The ultimate analytical measurement has been the ratio of observed HT yield to He^3 content in the same sample aliquot after separation and assay by radio gas chromatography, accurately recording both radioactivity and macroscopic content.[6,13] The He^3 can readily be determined in the presence of excess He^4 (the eluent gas) by thermal conductivity.[14] Equal neutron exposure was ensured for all samples by concentric rotation of all samples through a neutron flux with approximate cylindrical symmetry. In these experiments, absolute evaluations of HT yield have not been emphasized, although the HT yield from CH_4 represents about 2% of the total tritium stopped in the gas phase. The total yield from $CHCl_3$ is about 8% of the total, almost 15 times as great *per bond* as in CH_4.

A detailed description of the radio gas chromatographic apparatus and analytical procedures is available in ref 13.

Materials. Perfluorocyclobutene was obtained from Du Pont and from the Chemical Procurement Laboratories, New York, N. Y. The compound was purified by freeze-pumping several times before introduction into the sample bulb. Its purity was shown to be greater than 99.5% by gas chromatography.

The following compounds were obtained from Matheson Coleman and Bell: CH_3I, CH_2Cl_2, $CHCl_3$. Eastman Organic Chemicals Co. supplied CH_2Br_2 and $CHBr_3$. Methyl fluoride was purchased from the Columbia Chemical Co.; CH_3Cl and CH_3Br came from the Matheson Co. The other fluoromethanes were obtained from Du Pont through the kind cooperation of Dr. Hal Jackson. All gaseous halomethanes were purified by several freezing and pumping cycles. Liquids were purified by freeze-pumping on the small middle cut from a distillation. Measurements were not feasible for the polyiodomethanes because of the low vapor pressures at the ambient temperature (about 20°) of the neutron irradiation facility.

Oxygen gas (Linde Co.) containing less than 1% impurities was used as furnished. The use of He^3 as a tritium source under neutron irradiation has been previously described in great detail.[5,6,13]

Results

The experimentally observed yields of HT from a series of halomethanes are summarized in Table I, corrected for He^3 concentration, ratio of $RH/c\text{-}C_4F_6$, and number of H atoms per molecule. Since the basic purpose of this experiment has been the comparison of the values of the HT yield with the comparable bond dissociation energy and that of $CH_3\text{–}H$ is the most accurately known,[12] we have listed these yields in relative form as an *abstraction parameter*, $(HT)_F$, whose value is normalized to 1.00 per C–H bond in CH_4. The values of $(HT)_F$ and the bond dissociation energies of the hydrocarbons are given in Table II for reference.[6,12]

Table I. Hydrogen Abstraction Parameters, $(HT)_F$,[a] for Recoil Tritium Reactions with Halomethanes in Perfluorocyclobutene

Molecule	$(HT)_F$[a]	Molecule	$(HT)_F$
CH_3F	1.70 ± 0.05	CH_4	(1.00)
CH_3Cl	2.33 ± 0.07	CHF_3	1.34 ± 0.04
CH_3Br	2.00 ± 0.07	CHF_2Cl	3.9 ± 0.6
CH_3I	2.15 ± 0.07	CHF_2Br	3.1 ± 0.1
CH_2F_2	2.5 ± 0.1	$CHFCl_2$	9.1 ± 0.3
CH_2FCl	4.0 ± 0.1	$CHCl_3$	14.6 ± 0.4
CH_2Cl_2	4.1 ± 0.1	$CHBr_3$	9.9 ± 0.5
CH_2Br_2	3.8 ± 0.1		

[a] The hydrogen abstraction parameter, $(HT)_F$, is the yield of HT *per C–H bond* under standard conditions, relative to $CH_3\text{–}H$ as 1.0.

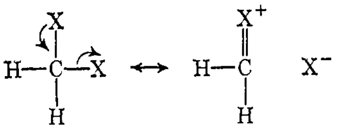
Discussion

The data summarized in Table I represent the relative yields of the energetic abstraction reaction under a particular, closely controlled set of constant experimental conditions. Experiments with a limited number of hydrocarbons have shown that such relative yields have the same qualitative order, and approximately the same quantitative ratios, in the presence of several other molecules as substitute for $c\text{-}C_4F_6$ in its role as major component.[6] The data clearly show substantial variations in the ease of abstraction of H atoms from the halomethanes: the progressive substitution of Cl or Br for H results in a steady increase in the absolute yield of HT *per molecule* of halomethane, and an even more rapid rise in $(HT)_F$, which measures the yield *per C–H bond.* However, the fluoromethanes exhibit an increase from CH_3F to a maximum value of $(HT)_F$ for CH_2F_2 and a marked decrease for CHF_3. The order of reactivity for all halogen substituents is generally comparable to that observed for other systematic measurements of halomethane reactivity in hydrogen-transfer reactions,[12,15–18] *e.g.*, reaction 3 as measured by Raal and Steacie.[19] Steacie has insisted that

$$CH_3 + RH \longrightarrow CH_4 + R \tag{3}$$

the data of Raal and Steacie are uncertain because of the possible effects of traces of hydrogen halides,[17] and no other widely comparable set of measurements with the halomethanes appears to have been carried out in the past 15 years. Consequently, our detailed comparisons of reactivity will be restricted to the few halomethanes for which specific estimates of the bond dissociation energies are available.

The trend toward increasing $(HT)_F$ by progressive substitution of Cl or Br in halomethanes is semiquantitatively consistent with the weakening of the C–H bond by inductive withdrawal of electrons from the C–H bond by the halogen substituents.[15,16] While the inductive effect is also present in the fluoromethanes, atomic fluorine substituents also introduce partial double-bond character through the tendency toward polar structures such as those indicated in (4).[20] The increasing contribution of such double-bonded structures is shown by the progressive shortening of C–F bond distances with multiple fluorine substituents (C–F distances: CH_3F, 1.385 Å; CH_2F_2, 1.358 Å; CHF_3, 1.332 Å). On the other hand, C–F and C–Cl distances are only slightly affected by additional Cl atom substituents (C–Cl distances in chloromethanes:



(4)

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[13] E. Tachikawa, Ph.D. Thesis, University of California, Irvine, 1967.

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

[15] G. B. Kistiakowsky and E. R. van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

[16] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, translated by M. Boudart, Princeton University Press, Princeton, N. J., 1958.

[17] E. W. R. Steacie, "Atomic and Free Radical Reactions," American Chemical Society Monograph No. 125, Reinhold Publishing Corp., New York, N. Y., 1954.

[18] A. F. Trotman-Dickenson, "Advances in Free-Radical Chemistry," Vol. 1, Logos Press, London, 1965, p 1.

[19] F. A. Raal and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 578 (1952).

[20] L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals," Cornell University Press, Ithaca, N. Y., 1960.

Table II. Hydrogen Abstraction Parameters and Bond Dissociation Energies (kcal/mole) for Saturated Hydrocarbons[6,12]

Molecule	$(HT)_F$	BDE	Molecule	$(HT)_F$	BDE
CH_4	(1.00)	104.0 ± 1	*c*-C_4H_8	2.77 ± 0.10	95 ± 3
c-C_3H_6	1.21 ± 0.03	101 ± 3	*c*-C_6H_{12}	3.21 ± 0.08	94 ± 3
neo-C_5H_{12}	1.54 ± 0.03	99.3 ± 1	*c*-C_5H_{10}	3.41 ± 0.11	93 ± 3
C_2H_6	1.84 ± 0.05	98.0 ± 1			

CH_3Cl, 1.781 Å, to CCl_4, 1.76 Å; C–F distances: CH_2F_2, 1.358 Å; CCl_2F_2, 1.36 Å). Empirically, we conclude that the contribution of polar forms, tending toward stronger C–H bonds, increases with number of fluorine substituents, and finally overcomes the bond weakening trend for all inductive substituents, leading to the decrease in value of $(HT)_F$ from CH_2F_2 to CHF_3.

Comparison of $(HT)_F$ with Bond Dissociation Energies of Halomethanes. While the trends of the values of $(HT)_F$ for halomethanes are certainly in general agreement with the expectations for the corresponding bond dissociation energies, the possibilities for quantitative comparison are not very numerous. The recent compilation by Kerr lists the C–H bond dissociation energies of only four halomethanes (in kcal/mole):[12] CF_3–H, 106 ± 1; CCl_3–H, 95.7 ± 1; CH_2F–H, 101 ± 4; CHF_2–H, 101 ± 4. Only that of CH_3F agrees with the saturated hydrocarbon correlation within its quite broad limit of error; the $(HT)_F$ values of the other three are larger than the expected values from the correlation.

Direct interpolation, using the correlation of $(HT)_F$ with saturated hydrocarbon bond dissociation energies, leads to an estimate of 100.5 kcal/mole for CF_3–H.[6] The bond dissociation energy of CF_3–H has been the subject of several investigations with results which, while not entirely consistent, are uniformly higher by several kcalories/mole than 100.5.[12,21–24] Measurement of the activation energies of (5) and its reverse (−5)

$$CH_3 + CF_3H \longrightarrow CH_4 + CF_3 \qquad (5, -5)$$

provides a direct estimate of the difference in bond dissociation energies between CH_3–H and CF_3–H, and indicates that these bond dissociation energies are essentially the same within a few tenths of a kilocalorie/mole; *i.e.*, both are about 104 kcal/mole.[12,21] On the other hand, the atomic reactions of bromine[22] or chlorine[23] with CHF_3, as in reaction 6, are much more

$$X + RH \longrightarrow HX + R \qquad (6)$$

difficult than with CH_4, and comparison of the endothermicities of these reactions leads to the estimate of 106 ± 1 kcal/mole for the bond dissociation energy of CF_3–H. Equilibration with CF_3I, HI, and I_2 also leads to an estimate of 106 ± 1 kcal/mole,[24] and we have used this value in Figure 1.

Excitation Energies of Residual Radicals Left by Abstraction of H. We believe that the "high" $(HT)_F$ value for CHF_3 relative to the saturated hydrocarbon curve of Figure 1 is quite significant, since it indicates that abstraction of H by energetic T atoms proceeds more readily from CHF_3 than it would from an alkane of comparable bond dissociation energy. We believe that this difference in reactivity is correlated with a difference in the residual excitation of the CF_3 or hydrocarbon radical formed in reaction 1 with CHF_3 or alkane. The equilibrium configuration of CF_3 is quite nonplanar and is rather similar to the CF_3 structure already existing in HCF_3.[25,26] Consequently, the energetic abstraction of the H atom need not be accompanied by appreciable changes in the geometry of the CF_3 residue, and the radical is presumably not very internally excited following reaction 1. The CHF_2 radical is also nonplanar[25] and need not be highly excited either, consistent with an estimate of 96 kcal/mole from the $(HT)_F$ value and the hydrocarbon correlation *vs.* the measured bond dissociation energy of 101 ± 4 kcal/mole.[12]

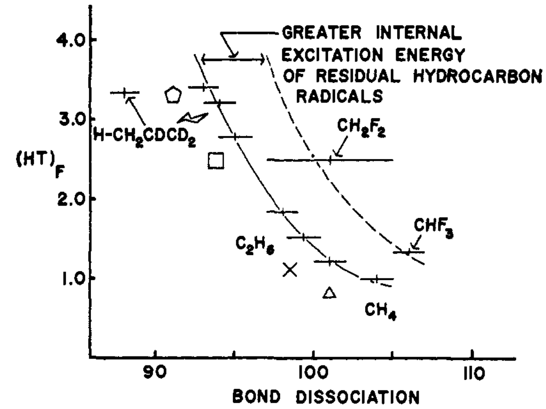

Figure 1. Postulated correlations of $(HT)_F$ with bond dissociation energy of C–H bonds: -----, fluoromethane correlation, little excitation of residual radical; ——, saturated hydrocarbon correlation (ref 6), assumed greater excitation of residual radicals.

The residual radical left after abstraction of H from methane, however, is essentially planar in the minimum energy state and requires appreciable geometrical alteration from the relative atomic positions in the original molecule.[27] Observations of the infrared spectrum of CH_3 in a solid argon matrix have permitted the identification of ν_2, the out-of-plane bending force constant, at 1383 cm^{-1} thereby leading to an estimate of 4.7 kcal/mole for the energy required to convert planar CH_3 (0 ± 3°) into tetrahedral CH_3—in effect, for the out-of-plane displacement of the central C atom by 0.36 Å.[27] Information about the planarity of the

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(21) G. O. Pritchard and R. L. Thommarson, *J. Phys. Chem.*, **68**, 568 (1964).

(22) A. M. Tarr, J. W. Coomber, and E. Whittle, *Trans. Faraday Soc.*, **60**, 2039 (1964); J. C. Amphlett and E. Whittle, *ibid.*, **64**, 2130 (1968).

(23) J. C. Amphlett, J. W. Coomber, and E. Whittle, *J. Phys. Chem.*, **70**, 593 (1966).

(24) C. A. Goy, A. Lord, and H. O. Pritchard, *ibid.*, **71**, 1086 (1967).

(25) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(26) D. E. Milligan and M. E. Jacox, *ibid.*, **48**, 2265 (1968). Infrared measurements of CF_3 in an argon matrix lead to an estimate of 13° for the angle between C–F and the F_3 plane, stated as being in "quite reasonable agreement" with a measurement of 18° from the esr experiments of ref 25. This angle is 19.5° in tetrahedral structures.

(27) L. Andrews and G. C. Pimentel, *ibid.*, **47**, 3637 (1967).

other alkyl radicals is not as complete,[28,29] but it is reasonable to suppose that the saturated hydrocarbon radicals require some geometric adjustment from the structure of the hydrocarbon itself. Inasmuch as some adjustment toward the radical structure during reaction seems plausible, while other vibrational modes may also be excited,[5] 4–15 kcal/mole is a reasonable estimate for the excitation energy of residual CH_3 and, by analogy, other hydrocarbon radicals.

We postulate that energetic abstraction is completed for these hydrocarbon molecules on a time scale such that the residual radical has not reached planarity, and is consequently still "hot" with >5 kcal/mole of internal excitation energy in the nonplanar bending modes. The corollary to this postulate is that $(HT)_F$ values will fall to the upper right of this curve in Figure 1 if the residual radical is *less* excited than the alkane hydrocarbon radicals, as for $H-CF_3$ and $H-CHF_2$, and to the lower left if the residual radical is *more* excited, as with the allyl radical from $H—CH_2CD{=}CD_2$. The original excellent correlation found between $(HT)_F$ and bond dissociation energy is thus a special case for molecules with comparable (or smoothly varying) residual excitation energy in the radical. The more general observation is that the value of $(HT)_F$ correlates with an energy parameter representing some combination (perhaps simply the sum) of bond dissociation energy plus residual excitation energy.

This general description is consistent with the "energy cut-off" model of the hot abstraction reaction, as outlined in ref 5 and 6. In this model, the increase in HT yield for lower C–H bond energy is attributed to abstraction by relatively low-energy tritium atoms in the 1-eV range. The velocity of such atoms prior to reaction is $\sim 10^{14}$ Å/sec, and the time of close interaction during abstraction must be $\sim 10^{-14}$ sec.

Expressed in terms of the time scale of the abstraction reaction, the bond dissociation energy measures the weakness of a C–H bond on a time scale that permits continuous adjustment of all bond distances to the minimum energy configuration. However, when the abstraction reaction occurs on the time scale of 10^{-14} sec, the C–H bond may still be considerably stronger than it would be if equilibrated, abstraction itself is therefore less favored, and $(HT)_F$ is lower than predicted from correlations utilizing the equilibrium bond dissociation energy.

Figure 1 is a crude illustration of our present hypothesis for the correlation of $(HT)_F$ with energy; the excitation energies indicated for hydrocarbon radicals and for the allyl radical have only qualitative significance and can have no quantitative significance without much more detailed understanding of the intimate details of these abstraction reactions.[30]

These effects found in the energetic abstraction of hydrogen atoms have a parallel in the photodissociation of RI, for which the residual excitation energy of CF_3 from CF_3I is presumed, on the basis of comparative absence of reactivity, not to be as large as for CH_3 from CH_3I.[31]

Bond Dissociation Energy of $CHCl_3$. The bond dissociation energy of CCl_3–H has often been assigned a value in the vicinity of 91 kcal/mole, but with rather large estimates of error.[16,17,32] The value of 95.7 ± 1 kcal/mole has been calculated by Benson[33] from the earlier measurements of Sullivan and Davidson on the equilibrium among Br_2, $CHCl_3$, HBr, and CCl_3Br.[34] The value of $(HT)_F$ from our experiments with $CHCl_3$ is much higher than the highest on our hydrocarbon correlation curve[35] and disagrees with the bond dissociation energy estimate of 95.7 kcal/mole by an even larger factor than with the fluoromethanes. We do not feel that the evidence for the higher bond dissociation energy of $CHCl_3$ is as strong as for CHF_3, and therefore will not speculate at this time about the significance of the $(HT)_F$ value of $CHCl_3$ *vis-á-vis* the bond dissociation energy correlation.

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(28) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(29) S. Ogawa and R. W. Fessenden, *ibid.*, **41**, 994 (1964).

(30) The implication of Figure 1 is that the excitation energy of all these hydrocarbon radicals is approximately the same, an assumption which has no facts either for or against it. In the absence of such knowledge, the dotted line could equally have been drawn much closer to the three lower bond dissociation energy points (c-C_4H_8, c-C_6H_{12}, c-C_5H_{10} in decreasing order of energy).

(31) C. L. Kibby and R. E. Weston, Jr., *J. Am. Chem. Soc.*, **90**, 1084 (1968).

(32) R. H. Martin, F. W. Lampe, and R. W. Taft, *ibid.*, **88**, 1353 (1966).

(33) S. W. Benson, *J. Chem. Phys.*, **43**, 2044 (1965).

(34) J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).

(35) Values of $(HT)_F$ as high as 50 have been found for haloethylenes; see ref 13.