acid in SO_2ClF at -78 °C. A solution of the dimethylcarbenium ion was prepared by adding 5 mmol of isopropyl chloride in SO_2ClF to 15-20 mmol of SbF_5 in SO_2ClF at -78 °C.

^{1}H NMR spectra of the above solutions showed complete formation of the respective cation.

Ethyl fluoroantimonate complex was prepared, as described,[12] by passing ethyl fluoride through a 15-mmol solution of SbF_5 in SO_2 at -78 °C.

Ozonolysis. The solution of the alkylcarbenium ion to be ozonolyzed was placed in a 15-ml glass reaction tube, fitted with gas inlet and outlet tubes, which was held in a constant-temperature bath. Ozone (5-20 mmol) from a Welsbach T-816 generator was then passed through the solution. After addition of ozone, the solutions were flushed with nitrogen and transferred to ^{1}H NMR and ^{13}C NMR tubes for product analysis.

NMR Spectroscopy. ^{1}H NMR spectra were obtained on a Varian Associates Model A56/60-A spectrometer equipped with a variable-temperature probe. Chemical shifts were measured from external Me_4Si.

^{13}C NMR spectra were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad-band decoupler and variable-temperature probe. Operational parameters were as described previously.[1]

References and Notes

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Isotope Effects in Hydrogen Atom Transfers. IV. Alkyl Halides with Trialkyltin Hydrides

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Abstract: Tritium isotope effects in the transfer of hydrogen atoms from tin to alkyl radicals are reported. Although the isotope effects generally increase as the new CH bond strength weakens, the correlation with bond strength is poor. All the isotope effects are quite small; with alkyl radicals k_H/k_T is in the range 2-3 at 80 °C, increasing to about 4 for benzylic radicals. There is poor agreement with the only published isotope effect on this reaction, and this discrepancy is discussed, with a careful search for possible errors.

The isotope effect in hydrogen atom transfer reactions is sensitive to the relative strengths of the breaking and forming bonds, reaching a maximum when these are roughly equal.[1a,2] This paper represents a study of the extent of this correlation in reaction 1, in which Sn represents alkylated tin, in our case either tributyltin or triphenyltin.[3]

$$R\cdot + SnH \rightarrow RH + Sn\cdot \qquad (1)$$
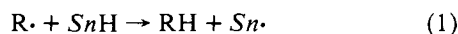
The reaction is especially convenient because it is a step in the very general reduction of alkyl halides by tin hydrides (reaction 2),[4] and hence allows the study of any radical for

$$RX + SnH \rightarrow RH + SnX \qquad (2)$$
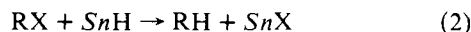
which the corresponding halide is available which does not follow some alternate reaction course with the tin hydrides. When the isotope effect is to be determined competitively, it is further necessary that the product RH be stable in the presence of the excess SnH needed for competition, thus it should not contain double bonds, further reactive halogen, or carbonyl functions.

Isotope effects were determined by adding the alkyl halide to an excess (>2X) of the tin hydride in a solvent containing (as an initiator) azobisisobutyronitrile (AIBN) which was usually decomposed thermally, or in runs below 50 °C, photolytically. The isotope effect was calculated using eq 3[5] in which f is the fraction of hydride consumed,

$$k_H/k_T = \ln(1 - f)/\ln(1 - rf) \qquad (3)$$

and r is the ratio of the specific molar activity of the product RH to that of the reagent SnH. The fraction f was established from the initial number of moles of the tin hydride, SnH_0, and the initial number of moles of alkyl halide, RX_0, by the expression $f = RX_0/SnH_0$. The results are presented in Table I.

The significance of these results is sensitive to their accuracy and we therefore discuss sources of error. A possible major source of error is the purity of SnH and RH, and the estimation of f (eq 3) constitutes another. Impurities influence both the determination of r and of f. Both SnH and RH were distilled before counting, and in most cases the purity was assayed by gas chromatography. Some samples of RH were purified by preparative scale GC, the others were checked for purity by analytical GC, and therefore nonradioactive contaminants can lead to very minor error only. Since the isotope effect is small, contamination of RH* by SnH* below that detectable by gas chromatography will not introduce a detectable error, and there is no other high activity contaminant likely.

Table I. Tritium Isotope Effects on the Reaction of RX with R^1_3SnH

R	X	R^1	Temp, °C[e]	k_H/k_T[a]
n-Hexyl	Br	Bu	80	2.65 (5)
2-Hexyl	Br	Bu	80	2.72 (3)
2-Methyl-2-pentyl	Br	Bu	80	2.53 (3)
n-Hexyl	Cl	Bu	80	2.96
n-Hexyl	Cl	Bu	25	3.07[b]
n-Hexyl	I	Bu	80	2.70
2-Hexyl	I	Bu	80	2.73
Cyclopentyl	Br	Bu	80	2.71
Cyclohexyl	Br	Bu	80	2.38[c]
Cyclohexyl	Br	Bu	25	2.60[b,c]
Benzyl	Cl	Bu	80	4.12
Benzyl	Br	Bu	80	4.01
Benzyl	I	Bu	80	3.86
p-Methyl-benzyl	Cl	Bu	80	3.92
m-Methyl-benzyl	Cl	Bu	80	3.82
p-Chloro-benzyl	Cl	Bu	80	3.76
m-Chloro-benzyl	Cl	Bu	80	3.68
Benzyl	Cl	Bu	79	3.90
Benzyl	Cl	Bu	59	4.32
Benzyl	Cl	Bu	21	5.69[b]
Benzyl	Cl	Bu	4	6.32[b]
n-Hexyl	Br	Bu	81	2.56
n-Hexyl	Br	Bu	62	2.71
n-Hexyl	Br	Bu	22	2.95[b]
n-Hexyl	Br	Bu	7	3.06[b]
n-Hexyl	Br	C_6H_5	80	2.55[d]
2-Hexyl	Br	C_6H_5	80	2.30[d]
2-Methyl-2-pentyl	Br	C_6H_5	80	2.14 (2)[d]

[a] Runs were done either in benzene or in 1,2-dimethoxyethane, and often in both, except where otherwise noted. No solvent effects were observed. Parenthetical numbers indicate numbers of runs averaged in the number shown; if not shown, there is only one. [b] Photoinitiated. [c] In toluene solution. [d] In n-decane solution. [e] Runs at 80 °C were done in a bath at this temperature. The temperature in the vessel is within one or two degrees of this temperature. Other temperatures are more accurately controlled.

The determination of f assumes that reaction 2 is quantitative and the only reaction taking place. Because the isotope effect is not very sensitive to f, these assumptions were not rigorously tested, but they nevertheless have some experimental support. The yield of RH from RX was not determined, since the aim was purity, and high yields have been reported, but isolation of RH in high purity would not have been possible with a very small yield. Similarly, small amounts of RX in the volatile products might have been overlooked, but not amounts comparable to the amount of RH. Thus the yield must have been far more than 50%. The side reaction which might (depending on its isotope effect) cause some error is the decomposition of SnH. This was unimportant because SnH was often isolated pure and in usable amount after some reactions and was present in other reaction products as shown by NMR and ir. The reactions carried out in sealed tubes would have developed a significant pressure of hydrogen gas if there had been important decomposition. It was not observed. Figure 1 shows a plot of the calculated values of k_H/k_T for three values of the activity ratio r for various values of f within the experimental range, which shows that an uncertainty in f does not cause a corresponding uncertainty in k_H/k_T. The strongest argument for absence of important error from this source arises from duplicate experiments with various calculated f values. The isotope effects calculated were the same within the experimental error claimed and showed no trend with f.
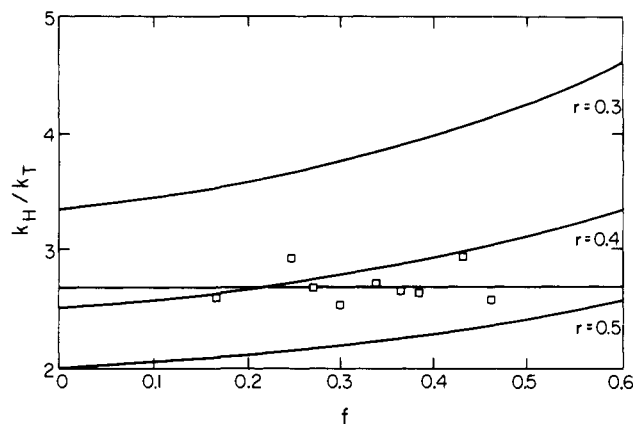

Figure 1. The theoretical dependence of isotope effect on the fraction f of labeled reagent used for various values of the specific activity ratio r from eq 3. Nearly all experimental ratios r were within the limits shown. The squares comprise all points for 1-hexyl halide, and the average value of $k_H/k_T = 2.70$ is shown as the horizontal line. The deviations from the average do not correlate with f.

This point is illustrated for the n-hexyl radical in Figure 1. This varied evidence does not eliminate incomplete reaction as a source of error in isolated cases, but it can never be a large error.

Measures of accuracy include reproducibility, within about 3% of the mean on all multiple runs not individually presented in the table, and results using different halides; the table shows one such result 10% different from the mean of the others (n-hexyl chloride), one 5%, one 4%, and eleven 3% or less from the mean for that particular radical. We estimate a standard random error of about 3–4% on this basis. Part of this error may have come from temperature uncertainty. The runs establishing the temperature dependence are better in this respect. The hexyl bromide results fit the equation $k_H/k_T = 1.374e^{448/RT}$ with the worst point deviating only 1.3% from the calculated, and for the benzyl case the worst fit is 1.9% from the equation $k_H/k_T = 0.634e^{1270/RT}$. In this latter case the exponential term is larger than can be accounted for by loss of the stretching vibration alone.

The most disturbing suggestion of systematic error is in the cyclohexyl bromide at 25 °C, where our value $k_H/k_T = 2.60$ is to be compared with Carlsson and Ingold's[6] value $k_H/k_D = 2.7$. This discrepancy (their value corresponds to a tritium isotope effect of 4.2 using the relation[7] $k_H/k_T = (k_H/k_D)^{1.442}$, which is seldom far wrong;[8] ours predicts $k_H/k_D = 1.9$) is especially difficult to understand since the two experiments are so similar; both were competitive with excess tin hydride, both initiated by photolysis of an azonitrile, and done on the same compound at the same temperatuere. It appears that reasonable accumulations of random errors are not enough to reconcile the numbers. We therefore repeated the determination of the deuterium isotope effect by essentially the same methods that were used by Carlsson and Ingold. A mixture of 8.86 mmol of tributyltin hydride, 8.42 mmol of tributyltin deuteride, 6.15 mmol of cyclohexyl bromide, 0.019 mmol of AIBN, and 20 ml of dodecane was sealed in an evacuated Pyrex tube; it was placed in a bath at 25 ± 1 °C and irradiated with the high-pressure mercury lamp. The cyclohexane was isolated by preparative scale GC and analyzed by mass spectrometry, giving 33.5 ± 1% cyclohexane-d, giving an isotope effect of 1.6 ± 0.1. We believe that the discrepancies between this result, and the tritium result, and that of Carlsson and Ingold probably arise mostly from error in the mass spectrometric analysis, since in neither study was there a careful study of pressure and ionization potential effects.

The isotope effects in Table I are small. This is largely because the tin–hydrogen stretching frequency (1815 cm^{-1} in Bu$_3$SnH[3b]) is small and the complete loss of this vibration alone in the transition state gives a "maximum" effect of $k_H/k_T = 4.7$ at 80 °C. Furthermore, the hydrogen transfer reactions are all quite exothermic, since the tin–hydrogen bond dissociation energy has been very roughly estimated[3] at 70 kcal/mol, and even for the benzylic CH bonds, $D_{CH} = 87$ kcal/mol. Thus we can expect that all the transition states will be unsymmetrical and hence all the effects should be less than the "maximum". Since real isotope effects are frequently larger than this "maximum" effect calculated from stretching vibration only[1b,8] (through tunnel corrections, and bending vibration contributions), we need not assume that the transition state is quite symmetrical in the benzylic cases and can certainly attribute the difference between the aliphatic cases and the benzylic cases to differences in the forming CH bond strength. We can not see the primary–secondary–tertiary difference, in which we would expect the isotope effect in the tertiary case to be the largest. In fact the observed effect, possibly insignificant, is in the other direction. Similarly, substitution in the benzyl radical appears to produce a difficultly interpretable result, and is probably insignificant. The difference between tributyltin hydride and triphenyltin hydride seems real, and suggests a weaker tin–hydrogen bond in this latter compound, in agreement with its generally higher reactivity.[3]

A factor which seems likely to disrupt a smooth bond-energy isotope effect correlation is the stabilization of the transition state by the contribution of polar structures. These polar structures, often called upon to explain reactivities in free-radical reactions,[9] have been the subject of renewed interest and controversy.[10] In the present work only the largest bond-energy differences result in significant changes in the isotope effects, and the further subdivision of the isotope effects to allow for polar effects appears unfruitful. We therefore do not believe that these results contribute to this problem.

We cannot yet state the size of the isotope effect for a symmetric transition state. The most nearly symmetric transition state is surely that of the benzilic compounds, where the isotope effect approaches 90% of the "maximum" (from complete loss of the SnH stretching vibration). We will either have to assume that there is no important change in the isotope effect over the middle 20–30 kcal difference in bond energies, or that the value attained with more symmetric cases will be substantially in excess of the "maximum". Because the earlier results with mercaptans[1a,1b] found isotope effects much larger than the "maximum", and because the temperature dependence of the isotope effect for the benzyl case is so strong, we believe that tunnel corrections would contribute markedly along with loss of the stretching vibration to achieve rather larger isotope effects.

Experimental Section

Materials. Tributyltin hydride-t was prepared by the reduction of tributyltin chloride with sodium borohydride-t.[11] Tributyltin deuteride was prepared by the reduction of the chloride with lithium aluminum deuteride. Triphenyltin hydride was prepared by the reduction of the commercial triphenyltin chloride with lithium aluminum hydride. It was labeled with tritium by exchange with tributyltin hydride-t. Triphenyltin hydride (30 g) was heated with tributyltin hydride-t (2 g, 3 × 10^6 dpm/mol) to 50 °C for 30 min. Distillation of the product yielded triphenyltin hydride-t: bp 160 °C (0.3 mm); 1.6 × 10^5 dpm/mol.

Procedures. Tritium content was determined by solution scintillation counting and efficiencies were determined by automatic external standardization, calibrated with standard toluene-t samples (with decay corrections). Absolute efficiencies may be in error by as much as 15%, but relative errors are much smaller, especially since there was very little variation in efficiency; no compounds used quenched badly.

Runs to determine the isotope effect were mostly done by the following typical example of procedure A; others were variously modified as described in B, C, or D. Procedures C and D were only used at temperatures below 50 °C.

Procedure A. A 100-ml three-necked flask was equipped with a reflux condenser, an addition funnel, and a nitrogen inlet. In it was placed at room temperature 10 g of tributyltin hydride-t in 40 ml of dry benzene, and nitrogen was passed through to remove air. A solution of alkyl halide (RX) (2 g in 10 ml of dry benzene containing 10 mg of azobisisobutyronitrile (AIBN) as initiator) was placed in the addition funnel. The flask was then immersed in an oil bath at 80 ± 1 °C, and the contents of the addition funnel was added dropwise over a period of 30 min. After another 30 min the mixture was distilled and the product RH was isolated and purified further by preparative scale GC before counting. The excess tributyltin hydride was recovered also by distillation, but this was not very practical for triphenyltin hydride.

Procedure B. The alkyl halide, tin hydride, and AIBN were dissolved in benzene and placed in a flask with a reflux condenser. The flask was then plunged into the hot oil bath to initiate the reaction. Results in two cases using this method were not significantly different from those by procedure A.

Procedure C. The same reagents were sealed in a degassed Pyrex tube, and the tube, immersed in a water bath, was then exposed to the unfiltered radiation from a high-pressure mercury source.

Procedure D. Same as procedure A except that the flask was illuminated by the high-pressure mercury source. The addition funnel was shaded.

Deuterium Isotope Effect. Tributyltin hydride (8.856 mmol), tributyltin deuteride (8.424 mmol), cyclohexyl bromide (6.146 mmol), and AIBN (3.1 mg) were dissolved in dodecane (20 ml) and sealed in a Pyrex tube, then irradiated with a high-pressure mercury source while immersed in a water bath at 24–25 °C. Cyclohexane recovered by distillation was purified by preparative GC and subjected to mass spectrometric analysis using the parent peak intensities. Two analyses gave 32.6 and 34.5% content of C$_6$H$_{11}$D, yielding calculated isotope effects of $k_H/k_D = 1.62$ and 1.52, respectively, using a calculation like that of eq 3 but using isotope ratios.

References and Notes

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