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Isotope Effects in Hydrogen Atom Transfers. 9.[1] Neighboring Group Participation

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Abstract: The tritium isotope effects in hydrogen abstraction by bromine atoms from $HC(Me)_2CH_2X$ have been measured in the photobromination reaction by a technique which measures the specific activity of the HBr product. At 1 °C and with the reverse reaction suppressed or irrelevant the values for k_H/k_T are 3.9, 8.2, and 11.6 for X = CH_3, Cl, and Br, respectively. An isotope effect of 3.5 for X = H was also measured, but the contribution of the reverse reaction was not established. The relatively large isotope effect for X = Br is interpreted in terms of a weakening of the CH bond by neighboring bromine participation. The smaller effect of chlorine may correspond to a minor participation, but the unfavorable inductive effect of the chlorine is also a factor. The case of X = Br is the microscopic reverse of the addition of HBr to 2-methylpropene, and the results are compared with isotope effects in the addition to HBr to olefins. The measurement of isotope effect is, within some described limitations, a convenient and general method for detecting neighboring group participation in hydrogen atom abstractions.

Hydrogen atom transfer isotope effects have been proposed as a means of determining bond energies to hydrogen, for example, D_{CH}.[3,4] This is based on the observation that in the reaction

$$A\cdot + HC \rightarrow AH + \cdot C \qquad (1)$$

the isotope effect appears to be maximum in the case of $D_{AH} = D_{HC}$, i.e., for $\Delta H^\circ = 0$. The correlation with ΔH is imperfect,[5,6] but still appears to be useful with a single A· as long as steric effects are constant and there is no major variable contribution of polar structures to the transition state. In this paper we address the problem of whether or not D_{CH} is sensitive to various β substituents. This problem is equivalent to asking whether there is any special stabilization of the radical $R_2\dot{C}CR'_2X$ by interaction between the X group and the singly occupied orbital of the radical. For the case X = Br, considerable evidence for interaction has been collected based on regiospecificity[7] (favoring substitutions on the carbon adjacent to that bearing the bromine), on a favored trans stereochemistry,[7a,8] on enhanced rates,[9] and on some rearrangements accompanying the chlorination of alkyl bromides.[10] The isotope effects in the addition of hydrogen bromide[11] to olefins were considered anomalous unless there was considerable radical stabilization by β-bromine, but the arguments were based on radicals all containing the β-bromine. Without controls lacking the bromine, the arguments lacked strength. The interaction of radicals with β atoms of various sorts, including bromine, has been studied by ESR; interaction is observed, but the consequent stabilization is obscure.[12] Thus the evidence for participation is very stong, although not yet universally accepted.

The photobromination of alkanes is a reaction of considerable generality with a hydrogen atom transfer as one step of the chain. Photobromination is selective (favoring tertiary substitution) so that in a series of compounds, **1**, $CH(CH_3)_2CH_2X$ the major reaction is bromination of the tertiary position for several different X groups. The reaction showing the isotope effect is

$$\mathrm{Br}\cdot + \mathrm{H^{*}C(CH_3)_2CH_2X} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{BrH^{*}} + \cdot\mathrm{C(CH_3)_2CH_2X} \tag{2}$$

The isotope effect is conveniently measured by comparing the specific molar activity of the HBr and the starting 1-X-2-methylpropane-*2-t*, using the equation

$$\frac{k_\mathrm{H}}{k_\mathrm{T}} = \frac{\log (1 - x_\mathrm{H})}{\log (1 - x_\mathrm{H}/r)} \tag{3}$$

or its linear approximation for small extents of reaction

$$\frac{k_\mathrm{H}}{k_\mathrm{T}} \simeq \frac{a_\mathrm{RH}}{a_\mathrm{HBr}} \equiv r \tag{4}$$

where x_H = fraction of RH reacted, a_RH = the specific molar activity of the reagent RH, a_HBr is the specific molar activity of the product HBr, and r is defined in eq 4. The equation is correct if reaction 2 is the only source of HBr and neither RH nor HBr are consumed in other reactions. If HBr is formed by attack of Br· at some other position, then an isomeric bromination product will result, but it was not detected by GC of the product. The only reaction consuming HBr that is not detected by the product analysis is the reverse of reaction 2. The extent of this thermodynamically favorable reverse reaction is determined by the relative values of the rate constants k_{-2} and k_5,[13] the constant for the reaction

$$\cdot\mathrm{C(CH_3)_2CH_2X} + \mathrm{Br_2} \xrightarrow{k_5} \mathrm{BrC(CH_3)_2CH_2X} + \mathrm{Br}\cdot \tag{5}$$

(the alternate fate of the radical), and the relative amounts of HBr and Br_2.

The isotope effects were measured at 1 (± 1) °C. The methods of counting the reagents and the products are described in the Experimental Section. The results are presented in Table I, which shows all the results, except for several similar to the one shown as method A on isobutyl bromide (X = Br) which gave more or less random results leading to $k_\mathrm{H}/k_\mathrm{T}$ varying from 5 to 6.5. Throughout the table, only results using methods B or C can be expected to be free of problems of reversal. The last entry also represents a number of measurements of deuterium isotope effect; a few values are unquestionably slightly low because of a possibility of some reversibility, but analytical precision is also limiting. These measurements then qualitatively agree with the tritium result, as shown by footnote *f*, but cannot stand alone.

Let us first note the values for X = Br, in which experiments with reversal suppressed give a good reproducible isotope effect, substantially larger than the value without efficient trapping of the radical by bromine. There is no reason to question this value of about 11.

Table I. Tritium Isotope Effect in Photobromination of $HC(CH_3)_2CH_2X$ in Carbon Tetrachloride Solution at 1 °C

X	Method[a]	Reversal significant	"$k_\mathrm{H}/k_\mathrm{T}$"[b]
H	A	Yes	3.69
H	A	Yes	3.20
H	A	Yes	3.49
CH_3	A	Yes	4.04
CH_3	B	No	3.75
CH_3	C	No	3.98,[c] 3.82[d]
Cl	B	No	8.14
Cl	B	No	8.18,[c] 8.13[d]
Br	B	No	11.01
Br	B	No	11.1
Br	A	Yes	(5.2)[e]
Br	D[f]	Yes?	5.1 ± 1.4[f] ($k_\mathrm{H}/k_\mathrm{D}$)

[a] Method A uses an insufficiency of bromine, and it is all used up. Reversal can be very serious; the extent depends on the efficiency of removal of HBr from the reaction mixture. Method B and method C stop the reaction by turning off the light and then quenching excess bromine, in B with ethylene, in C with mercury. Method D determined $k_\mathrm{H}/k_\mathrm{D}$ by analysis of deuterium content of unreacted starting material by NMR. [b] These are the values calculated by eq 3 or 4. They are reliable as isotope effects only when the entry in the previous column is No. See text for significance of the first four entries. [c] Result calculated from HBr in the reaction mixture. [d] Result calculated from HBr trapped from exit gases. [e] One of a series not reported, results ranged from 5 to 6.5, and are almost certainly low because of reversibility. The parentheses indicate the unreliability of the results. [f] These four deuterium values suffer from analytical problems as well as possible reversibility. The value calculated from the tritium result by the Swain-Schaad equation is about 5.5: C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).

In contrast are the data for X = CH_3, which show no significant change in the isotope effect whether reversal is suppressed or not. There appear to be only two explanations of this result. One is that reversal is insignificant even though some of the experiments were done without excess bromine. The other is that reversal does occur, but does not influence the calculated isotope effect. This is possible only if $k_{-2}{}^\mathrm{H} = k_2{}^\mathrm{T}$. Although at first sight unreasonable, this is a more defensible explanation than the first. The isotope effects for the forward and reverse reactions are not independent; the ratio is, in fact, the equilibrium isotope effect

$$\frac{k_2{}^\mathrm{H}/k_2{}^\mathrm{T}}{k_{-2}{}^\mathrm{H}/k_{-2}{}^\mathrm{T}} = K_2{}^\mathrm{H}/K_2{}^\mathrm{T} \tag{6}$$

and thus if the reverse isotope effect is unity, the measured isotope effect is the equilibrium isotope effect, which is calculable. The equilibrium isotope effect on reaction 2 reduces to the exchange equilibrium constant for the reaction

$$\mathrm{HR} + \mathrm{TBr} \rightleftarrows \mathrm{TR} + \mathrm{HBr} \tag{7}$$

and the equilibrium constant for reaction 7 can be calculated. The equilibrium constant for reaction 7 can be calculated by the equation

$$K_7 = (1/2.93)\exp[(\Sigma\nu^\mathrm{HR} + \nu^\mathrm{TBr} - \Sigma\nu^\mathrm{TR} - \nu^\mathrm{HBr})/2kT] \tag{8}$$

which neglects the excitation of all relevant vibrational modes. The factor 2.93 is the ratio of the moment of inertia of TBr to that of HBr and the exponential is the zero-point energy term. We use for HBr 2560 cm^{-1}, and for RH we assume[14] a stretching frequency of 2950 cm^{-1} and a doubly degenerate bend at 1350 cm^{-1}. All these frequencies of RT are taken as 0.6202 times the RH frequencies calculated by assuming a reduced mass for a diatomic CH or CT molecule. Similarly, the TBr frequency is 0.5842 times the HBr frequency.

These frequencies lead to $K_7 = 5.7$, but this number is quite sensitive to the frequencies chosen, and to the ratio between the tritium frequencies and the protium frequencies. Thus if instead of using the factor 0.6202 we use the factor 0.5773 ($3^{-1/2}$) which would apply to a harmonic oscillator if the H and T were attached to infinite masses, then we calculate $K = 9.4$. If we include a correction of some sort for the significant anharmonicity of the vibrations, the figure is lower than 5.7. A more precise calculation is not justified, since even the frequencies chosen for RH are more of a guess than firm values. The neglect of vibrational excitation introduces only a few percent error at 1 °C.

We may conclude that a number in the neighborhood of 4–6 is reasonable for K_7. The suggestion that k_2^H/k_2^T for X = CH_3 is close to that equilibrium value is therefore plausible. The isotope effects for X = H are probably too close to the equilibrium value to have major significance. If they are really less than the equilibrium value, they would be taken to mean that $k_{-2}^H/k_{-2}^T < 1$. Such an inverse isotope effect does not need any unprecedented explanation, for with such a large equilibrium isotope effect, a small forward isotope effect is bound to be associated with an inverse effect for the reverse direction.

If we interpret the variation in isotope effect as a variation in transition state symmetry, we must say that the transition state for the case X = Br is more nearly symmetrical than the case X = CH_3. We might then conclude that the ΔH for reaction 2 with X = Br is closer to zero than for X = CH_3, and since the case of X = CH_3 is clearly endothermic, that for X = Br is less so. Hence the tertiary radical is stabilized by the bromine, and participation would be demonstrated.

Such a connection between ΔH and the isotope effect has been shown, however, to be insufficient; it is also necessary to consider the activation energy of the reaction.[6] It will be convenient to use as a measure of TS symmetry the quantity p, defined by the equation:

$$p = E_a/2E_a - \Delta H) \qquad (9)$$

Clearly, $0 \leqslant p \leqslant 1$. For a symmetrical reaction (with $\Delta H = 0$) p has the value ½, for the reaction with very large positive ΔH, the value is nearly unity, and for the highly exothermic reaction with small activation energy, p drops to nearly zero. We shall qualitatively identify p as the fraction of productlike character in the transition state in qualitative agreement with the Hammond postulate.[15] Two simple models which lead to this identification will be described elsewhere.[16] For a series of hydrogen atom transfers the isotope effect can be expected to be maximal for $p = 0.5$, and to be smaller for p near zero or unity.[6]

This measure of symmetry is relevant to the case of the influence by a neighboring chlorine. The increase in isotope effect from X = H or X = CH_3 to X = Cl then *might* be attributable to a fall in p due to a fall in ΔH to a less positive value, but an increase in E_a (due to some kind of unfavorable inductive effect) would also be expected to make p fall to a value closer to 0.5. Thus the value of the isotope effect alone does not tell us that the radical is stabilized.

Indeed, the activation energy for hydrogen abstraction is increased by neighboring chlorine, for chlorine directs bromination to distant positions by an inductive effect.[7a] In accord with eq 9 for an endothermic reaction increasing E_a (without a comparable effect on ΔH) decreases p to a value closer to 0.5 and hence increases the isotope effect. One can then ask to what extent is the isotope effect with X = Br also increased by an inductive effect. The clearly increasing order of isotope effects for changing X, CH_3 < Cl < Br, is not understandable on the inductive effect alone, for bromine should either be about the same as chlorine (based on the nearly identical σ_I values) or in between chlorine and methyl (based on electronegativity). The observed order is readily explained if there are two effects, an increase in E_a due to the inductive effect in the order CH_3 < Cl, Br, and an effect on ΔH by participation in the order Br > Cl.

We conclude that participation by bromine is demonstrated; participation by chlorine, if present, is much less important than that by bromine. It must be stated that the evidence for participation is much more convincing from the other evidence cited; the isotope effect is only a further confirmation. The method has promise for screening large numbers of X groups for participation, however.

The abstraction of hydrogen by a bromine atom with X = Br is the microscopic reverse of the hydrogen atom transfer step in the radical addition of HBr to isobutylene. Using eq 6, and our estimate of about 5 for K_7, we deduce $k_{-2}^H/k_{-2}^T = 11/5 = 2.2$ in CCl_4 at 1 °C. This corresponds to a deuterium effect of 1.7, in agreement with the estimate of about 1.5 by Shea and Skell[17] for almost the same radical in CCl_3F. For the reaction of $R_1\dot{C}HCH_2Br$ with HBr the corresponding isotope effect in ether solution at 0 °C varied from 1 to 4 depending on R.[11] The values thus are comparable, but a quantitative comparison is not justified because of the gross solvent difference.

The rather unusual difference between the forward and reverse isotope effects is of course due to the diatomic nature of the product HBr. Thus the hydrogen-containing reagent of reaction 2 has the usual C–H stretching mode and two bending modes, and its moment of inertia is nearly independent of the hydrogen isotope present. The linear transition state likewise can be adequately described as having the isotopic sensitivity of reagent stretching vibration divided between a real linear mode and the imaginary vibration; it also contains two bending modes which to a first approximation resemble the reagent bending modes. The moments of inertia are also insensitive to the hydrogen mass. In contrast, although the product HBr also has an ordinary stretching vibration, because it is diatomic it has no bending modes, and the moments of inertia are almost proportional to the hydrogen mass. Thus although the familiar three-particle one-dimensional model (which depends on cancellation of bending vibrations in the transition state with those of the reagent) works adequately for the forward reaction, it is quite inadequate for the reverse reaction where no cancellation is possible and where the usual assumption of negligible isotopic sensitivity of moments of inertia is grossly in error. This effect has been considered for the proton transfer reactions of HF by Kresge and Chiang,[18] for ionic reactions of all the hydrogen halides by More O'Ferrall and Kouba,[19] and for the radical reactions of hydrogen bromide.[11]

Experimental Section

2-Methylpropane-*2-t* was prepared by the reaction of *tert*-butylmagnesium chloride in tetrahydrofuran with tritiated water. 2-Methyl-2-chloropropane (55 mL, 0.5 mol) in 300 mL of tetrahydrofuran (THF) was added dropwise with stirring in a conventional apparatus to 13 g of magnesium turnings and 30 mL of dry THF, containing a crystal of iodine. After the reaction was started, the flask was cooled in an ice bath. One-half hour after all the *tert*-butyl chloride addition was complete, 0.5 mL of water containing 0.5 mCi of tritium was added, then 10 mL of ordinary water. The flask was then heated on the steam bath and volatile products collected in a trap cooled in dry ice and acetone. The crude volatile product contained some 2-methylpropene, which was destroyed by addition of a small excess of bromine in the dark. Repeated bulb to bulb distillation gave 2-methylpropane-*2-t* which showed only one peak on the gas chromatograph; it assayed (as described later) 1.36×10^9 dpm/mol.

This method was unsuitable for preparation of 2-methylpropane-*2-d*, since the same reaction which gives isobutylene also yields 1 equiv of isobutane, not deuterium labeled. 2-Methylpropane-*2-d* was prepared by the radical chain reaction of *tert*-butyl mercaptan-*d* and tributyl phosphite, as described in the literature.[20]

1-Bromo-2-methylpropane-*2-t*. 3-Methyl-2-butanone was exchanged with tritiated water under reflux in the presence of a trace of concentrated sulfuric acid. The product was dried with molecular sieve and distilled. Oxidation to 2-methylpropionic acid-*2-t* by alkaline bromine followed a published procedure.[21] The acid was reduced with lithium aluminum hydride to 2-methyl-1-propanol-*2-t*[22] and converted to the bromide with phosphorus tribromide.[23] The raw product contained about 1.8% 2-bromo-2-methylpropane by GC analysis. A somewhat shorter route to the tritiated isobutyric acid via hydration of dimethylketene was less useful. The same route made 1-bromo-2-methylpropane-*2-d* when the first exchange was done repeatedly with D_2O instead of tritiated water.

2-Methylbutane-*2-t*. 2-Methyl-2-chlorobutane[24] was converted via the Grignard to 2-methylbutane-*2-t* using the same method used for 2-methylpropane-*2-t*, except that purification was accomplished by fractional distillation in a spinning band column.

1-Chloro-2-methylpropane-*2-t*. The treatment of 2-methyl-1-propanol with thionyl chloride and pyridine gave a sample of chloride pure by GC analysis.

The various possible bromination products of the various reagents were made for identification of the bromination products but only the tertiary position was detectably brominated in all cases except 2-methylbutane, which yielded about 5% by GC of 2-bromo-3-methylbutane. Gas chromatography of the tertiary bromides was difficult but could be accomplished using glass rather than metal in the vaporizer and column, and keeping column temperatures below 90 °C.

Counting. Tritium was counted by solution scintillation spectrometry, and all count rates were converted to absolute disintegration rates using standards and external standardization, although quenching was never a serious problem. Special methods for counting hydrogen bromide and isobutane are described below.

Specific Activity of Isobutane. This determination was based on the fact that at the refrigerator temperature, the partial pressure of a dilute solution of isobutane in toluene is low enough so that counting can be completed without serious vaporization loss. A weighed capillary tube sealed at one end was partially filled with isobutane (either by distillation or with a pipet working inside a freezer at −25 °C). The tube was then immersed in dry ice and acetone and sealed off and the sealed tube and the other fragment were allowed to warm to room temperature and then weighed. The sealed capillary tube was recooled in liquid nitrogen, then placed in the refrigerated counting vial with the toluene-scintillator mixture. Breaking of the capillary with forceps released the isobutane into the counting solution and the capped counting vial in the refrigerated counter was stable for extended periods.

Specific Activity of Hydrogen Bromide. Hydrogen bromide from the reaction mixture collected in the various ways described below was dissolved in enough water to make the handling facile. The tritium content was determined by counting an aliquot of the aqueous solution in a dioxane medium (RPI scintillation grade dioxane containing RPI 2a 80 mixed fluor). The amount of HBr in the aqueous solution was determined by titrating a large aliquot with standard 0.1 N sodium hydroxide solution.

Bromination Method A. A flask C containing a stirring bar was connected by a stopcock A to a vacuum system and by another stopcock B to a second flask D, and both flasks were immersed in a glass ice bath. The flask C could be stirred magnetically and illuminated through the wall of the bottom of the bath by a 275-W "SunLamp". Water was placed in flask D. While kept dark and cold, carbon tetrachloride (ca. 3 mL), the tritiated hydrogen atom source (**1**, X = H, CH_3, or Br), about 0.01 mol, and about 0.0008 mol of bromine (the **1** to bromine ratio was between 10 and 20 to one among the various runs) were placed in C. Air was removed from flask C using freeze-pump-thaw cycles; stopcock A was then closed. After reaching the ice bath temperature the lamp was turned on until the bromine color was gone. The stopcock B was opened to allow hydrogen bromide to pass into the water solution in D, and residual HBr in C was dissolved by adding more water. These two water solutions were usually combined, but sometimes worked up separately without any effect on the results. The water was separated from the carbon tetrachloride solution, and washed with cold pentane to remove the only likely radioactive contaminant, **1**. This washing was conveniently accomplished in a centrifuge tube, the water layer was frozen, and the organic solution was poured off. Repeated washings could be done with minor loss of water, and hence negligible fractionation of the dissolved tritium. Isotope effects were calculated by the linear approximation (eq 4). The results from method A suffer from significant reversal, especially near the end of the reaction where there is very little bromine and a maximum amount of HBr.

Method B. This was identical with method A except that a known excess of bromine was used, and the reaction was controlled by turning off the light after only a small extent of reaction. Then ethylene was passed into the vessel to destroy excess bromine. The extent of reaction was determined by the ratio of brominated **1** to 1,2-dibromoethane. Isotope effects were determined as in method A, except that when the extent of bromination was more than 10%, the exact equation for the isotope effect (eq 3) was used instead of the linear approximation.

Method C was identical with B except that metallic mercury was used to quench excess bromine.

Method D. A mixture of 1-bromo-2-methylpropane-*2-d* with 1-bromo-2-methylpropane in carbon tetrachloride was analyzed for deuterium content by NMR; the amounts of the two species are $a^0{}_H$ and $a^0{}_D$. The mixture in solution in carbon tetrachloride with an insufficiency of bromine was then illuminated while a stream of nitrogen was passed through to remove the HBr. The reaction product was then subjected again to NMR analysis, giving concentrations a_H and a_D for the remaining reagents. The isotope effect was calculated then by the equation

$$k_H/k_D = \frac{\log a_H/a^0{}_H}{\log a_D/a^0{}_D} \qquad (10)$$

The absence of excess bromine makes the values of little more than confirmatory value, even though the nitrogen stream does greatly reduce the HBr concentration, and hence the amount of reversal. The accuracy of the results is also limited by the low precision of the NMR analysis.

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