Isotope Effects in Hydrogen Atom Transfers. V. The Reactions of Olefins with Mercaptans

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Abstract: Tritium isotope effects have been measured for the hydrogen atom transfer $R_1R_2\dot{C}CH_2SR_3 + HSR_3 \rightarrow R_1R_2CHCH_2SR_3 + \cdot SR_3$ by comparing the tritium content of excess mercaptan with that of its addition product to the olefin $R_1R_2C{=}CH_2$. Several somewhat obscure sources of error in earlier work are uncovered; elimination of these errors results in only minor revision of the values except for the addition of 1,1-diarylethylenes to thiophenol, where two new values of k_H/k_T are much larger than at first thought. The isotope effect in the reaction of mesitylenethiol with trityl radical is also reported; the value of k_H/k_T at 25 °C is 25, almost twice the value in the thiophenol–trityl radical reaction, and a steric enhancement of tunnelling is indicated.

The hydrogen atom transfer is in theory as simple as the proton transfer. In practice the atom transfer is far simpler because neither the reagents nor products are necessarily charged, thus eliminating major solvation effects; it is even practical to work in the gas phase. The isotope effect on this reaction can illuminate various features of the transition state structure and energy, and it is usually easier to measure (by competitive methods) than the actual reaction rate.

Isotope effects in free-radical hydrogen-transfer reactions to or from organic molecules have been frequently measured, but not systematically. This paper is part of a series designed to give the same type of data already available for proton transfers, namely, effects of change in reaction enthalpy on the isotope effect (the "symmetry" effect), effect of temperature, of steric hindrance, and of the nature of the atoms between which the hydrogen is transferred.

The "symmetry" effect, first proposed by Westheimer,[2] suggests that a reaction with $\Delta H° = 0$, that is, for which the forming and breaking bond dissociation energies are equal, should have nearly equal force constants to hydrogen in the transition state and should hence have the largest isotope effect. This is analogous to the maximum in isotope effect in proton transfers when $\Delta pK = 0$.[3] An isotope effect variation of this sort has been observed by Pryor and Kneipp[4] and also in our preliminary communication.[1]

The addition of mercaptans to olefins usually follows the free-radical course of reactions 1 and 2 and the isotope ef-

$$R_3S\cdot + CH_2 = CR_1R_2 \rightarrow R_3SCH_2\dot{C}R_1R_2 \qquad (1)$$

$$R_3SCH_2\dot{C}R_1R_2 + H^*SR_3 \rightarrow \underset{\mathbf{1}}{R_3SCH_2CH^*R_1R_2} + \cdot SR_3 \qquad (2)$$

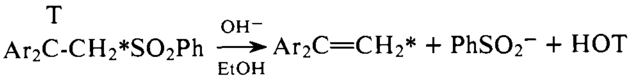
fect in reaction 2 can be measured by comparing the specific activity (a) of H^*SR_3 with that of the adduct **1**; when there is a large excess of mercaptan, eq 3 is a good approxi-

$$k_H/k_T = a_{HSR_3}/a_1 \qquad (3)$$

mation.[5] The sulfides **1** are usually high-boiling oils, and to ensure adequate purity they were usually converted to the crystalline sulfones, $R_3SO_2CH_2C^*HR_1R_2$ (**2**), for counting. The results are reported in Tables I, II, and III. Two errors were discovered in the work reported in the preliminary communication. The major one of these was that there is an extraneous exchange reaction between some 1,1-diarylethylenes and thiophenol, presumably via the ionic mechanism

$$AR_2C{=}CH_2 + PhSH \rightleftarrows Ar_2C^+CCH_3 + PhS^- \qquad (4)$$

and its reverse. Thus a simple counting of the adducts counted more tritium than was introduced by way of the addition reaction, and a low isotope effect would be calculated. The results in Table I were obtained by counting both the sulfone **2** and the 1,1-diarylethylene produced from it by β elimination, as shown in eq 5, where T indicates trace



$$Ar_2\overset{T}{C}\text{-}CH_2{}^*SO_2Ph \xrightarrow[EtOH]{OH^-} Ar_2C{=}CH_2{}^* + PhSO_2^- + HOT \qquad (5)$$

labeling with tritium from the addition and the asterisk shows labeling from the exchange reaction 4. Subtraction of the molar specific activity of the olefin recovered after doing reaction 5 from that of the sulfone gave the activity of the sulfone attributable only to the position labeled T. For thiophenol this error occurred with Ar = Ph and p-$CH_3OC_6H_4$, but not with Ar = p-ClC_6H_4. With benzyl mercaptan $(p\text{-}CH_3OC_6H_4)_2C{=}CH_2$ did exchange, but there was no adduct.

The second error was less serious, but it does change the order of reactivity from that of the preliminary report. In the early work, a mixture of olefin, a tenfold excess of mercaptan, and azobisisobutyronitrile was plunged into a thermostated bath at 70 or 80 °C. However, it turned out that with thiophenol and substituted styrenes the reaction did not require an initiator, and that the addition reaction was very fast and exothermic. Thus the first results were obtained at a very uncertain temperature. The results in Table I were obtained by breaking a vial of the styrene into the mercaptan after bringing both to thermostat temperature. Temperature uncertainty due to the high exothermicity was minimized by using a 100-fold excess of mercaptan as solvent instead of the tenfold excess used earlier. Temperatures were monitored during the reaction and in no case rose more than 1 °C. Reactions with benzyl mercaptan were never self-initiating and showed no significant temperature rise. These reactions were all photoinitiated and therefore could be studied at any temperature.

Other sources of error were carefully explored and found not to contribute. The position of the label in thiophenol was shown to be on sulfur, except that after standing 6 months, less than 0.1% remained after oxidizing to diphenyl disulfide. After the same time mesityl mercaptan gave a disulfide devoid of activity. Benzyl mercaptan gave a disulfide containing some activity (0.5% of the total), and benzoic acid from further degradation showed no activity, so that there was a little contaminant only in the benzylic position. It arose during the exchange process, for there was no change with time.

The possibility was explored that isotope effects with benzyl mercaptan or mesityl mercaptan were erroneously

Table I. Isotope Effects in Reaction 2 with R_3 = Ph

R_1	R_2	t, °C[a]	k_H/k_T[b]	k_H/k_T (calcd)[c]
p-$CH_3OC_6H_4$	H	70	6.59	
C_6H_5	H	70	6.74	6.78
p-ClC_6H_4	H	70	7.13	
m-$O_2NC_6H_4$	H	70	8.33	
C_6H_5	H	60	7.2	7.25
C_6H_5	H	40	8.4	8.39
C_6H_5	H	20	9.9	9.91
C_6H_5	H	0	12.1	11.99
p-ClC_6H_4	p-ClC_6H_4	70	8.93	
C_6H_5	C_6H_5	70	10.89	
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	70	14.10	
$PhCH_2$	H	70	2.61	
N-Carbazolyl	H	70	2.68	
$OCOCH_3$	H	70	2.67	
CO_2CH_3	H	70	3.89[d]	
CO_2CH_3	CH_3	70	4.42[d]	
CN	H	70	4.96[e]	
n-C_6H_{13}	H	0	4.46	

[a] Temperatures in the bath were controlled to ±0.1 °C, but in the reactions with styrenes, the exothermicity produces uncertainties up to 1 °C in the worst case. [b] Standard errors in isotope effect from counting errors are estimated at ±1.5%. [c] Calculated from eq 8. [d] The possibility of an ionic mechanism exists. [e] The mechanism is probably ionic.

high because hydrogen was abstracted from benzylic positions rather than from sulfur. An error of similar origin, namely, hydrogen derived from extraneous sources, was observed in the isotope effects measured by methane composition in the attack of methyl radicals on toluene.[6] The reaction sequence envisioned was as shown in reactions 6 and 7 leading to a tritium label attached to carbon in the excess mercaptan. However, mesityl mercaptan isolated from the reaction gave a disulfide devoid of detectable activity, and the disulfide from recovered benzyl mercaptan, although perceptibly active as described above, was not more so than that derived from the starting material. Thus the hydrogen in all the adducts is derived virtually exclusively from the thiol group, no exchanges at other positions took place (except where above mentioned), and the reported temperatures are in error by less than 1 °C.

$$PhCH_2SH^* + R\cdot \overset{?}{\longrightarrow} Ph\dot{C}HSH^* + RH \qquad (6)$$

$$\begin{array}{c} Ph\dot{C}HSH^* + PhCH_2SH^* \longrightarrow PhCHH^*SH^* + PhCH_2S\cdot \\ \Big\downarrow (O) \\ (PhCHH^*S{-})_2 \end{array} \qquad (7)$$

In addition to the 70 °C data, the reaction of styrene was followed at temperatures down to 0 °C, and the isotope effects fit with satisfactory precision eq 8, as shown in the last

$$k_H/k_T = 0.738 \exp(1512/RT) \qquad (8)$$

column of Table I (these figures are required to reproduce the calculated data, but are of course not determined to this many significant figures), and in data not shown, the reaction of benzyl mercaptan with styrene fitted about as well eq 9.

$$k_H/k_T = 0.55 \exp(2000/RT) \qquad (9)$$

Table IV shows measurements of another kind, on the transfer of a hydrogen atom from mesityl mercaptan to the trityl radical, following exactly the methods described for the reaction of thiophenol with trityl radical.[7] Unlike that work, the isotope effects are adequately fit by the Arrhenius type eq 10, as shown by the last column in Table IV.

$$k_H/k_T = 0.114 \exp(3200/RT) \qquad (10)$$

Table II. Isotope Effects in Reaction 2 with R_3 = $C_6H_5CH_2$ at 70 °C

R_1	R_2	k_H/k_T[a]
n-C_6H_{13}	H	6.73
$C_6H_5CH_2$	H	4.81
N-Carbazolyl	H	4.44
$OCOCH_3$	H	5.75
CO_2CH_3	H	8.04[b]
CO_2CH_3	CH_3	9.75[b]
CN	H	7.75[c]
p-$CH_3OC_6H_4$	H	9.43[d]
C_6H_5	H	10.40[d]
p-ClC_6H_4	H	11.3
m-$NO_2C_6H_4$	H	11.3
p-ClC_6H_4	p-ClC_6H_4	8.13[e]
C_6H_5	C_6H_5	(6.70)[f]

[a] The standard errors in k_H/k_T due to counting errors are believed to be ±1.5%. [b] An ionic mechanism is possible. [c] An ionic mechanism is probable. [d] These are new results; they differ from those in ref 1, but probably not significantly. [e] No correction for exchange was believed necessary since it was unnecessary with the more acidic thiophenol. [f] No exchange correction was made; the result may therefore be too low.

Table III. Isotope Effects in Reaction 2 with R_3 = 2,4,6-Trimethylphenyl at 70 °C

R_1	R_2	k_H/k_T[a]
CO_2CH_3	H	3.73[b]
CO_2CH_3	CH_3	6.72[b]
CN	H	10.72[b]
p-$CH_3OC_6H_4$	H	7.02
C_6H_5	H	7.15
p-ClC_6H_4	p-ClC_6H_4	13.05[c]

[a] ±1.5% from counting errors. [b] Ionic course possible. [c] No exchange correction made, nor probably required; this value is however a firm lower limit.

Table IV. Isotope Effects in the Reaction of 2,4,6-Trimethylthiophenol with Trityl Radical

t, °C	k_H/k_T	k_H/k_T(calcd)[a]
0.0	41.2	41.5
8.0	36.8	35.1
15.0	29.9	30.5
25.0	25.2	25.3
32.0	21.7	22.3
40.0	20.3	19.5

[a] Calculated from eq 10.

Discussion

Symmetry Effects. The isotope effects presented clearly are largest for the weakest forming CH bond. If the SH bond dissociation energy in thiophenol is about 75 kcal/mol,[8] then only the weakest of the forming CH bonds could give a fairly symmetric transition state, and the increase in isotope effect from R_1 = $C_6H_5CH_2$, R_2 = H, where the radical is a simple secondary radical (D_{CH} = ~95 kcal), k_H/k_T = 2.6, to the case R_1 = C_6H_5, R_2 = H, with a benzylic radical (D_{CH} = ~84 kcal), k_H/k_T = 6.7, and then to R_1 = R_2 = C_6H_5, with a doubly benzylic radical (D_{CH} probably <80 kcal), k_H/k_T = 10.9, is very clear. Good bond dissociation energies do not seem to be available for the Ar_2RC-H bond or Ph_3CH bond; it is possible that this latter bond is actually weaker than the 75 kcal SH bond. We therefore concur with Pryor and Kneipp[4] that the bond-energy difference is the major factor determining the isotope effect.

The same trends show in Table II for the reactions of benzyl mercaptan in which the isotope effects are mostly larger (in conformity with D_{SH} about 88 kcal/mol, the value for CH_3SH), but are smaller for the diarylethylenes, where the H atom transfer step is now probably endothermic. We assume but cannot prove that the presence of the β sulfur atom does not influence the CH bond energy importantly. This is not general for all β hetero atoms, and an isotope-effect-sensitive influence of β-Br has been detected.[9] However, in addition to the bond-dissociation-energy difference as the major factor in determining these isotope effects, there are further factors, which are now discussed.

Substituent Effects. There is some evidence on the isotope effects with substituted styrenes. The rates of some radical reactions follow the Hammett equation, leading to eq 11, and we can express the substituent

$$\log (k_H/k_H^0) = \rho_H\sigma$$

$$\log (k_T/k_T^0) = \rho_T\sigma$$

$$\log (k_H/k_T) = (\rho_H - \rho_T)\sigma + \log (k_H^0/k_T^0) \qquad (11)$$

effect on isotope effect by the sign of $\rho_H - \rho_T$. For thiophenol with substituted styrene (shown in the first four entries of Table I), $\rho_H - \rho_T$ is apparently positive, as shown by the increase of isotope effect in the sequence p-OCH_3 < H < p-Cl < m-NO_2. However, the reaction of thiophenol with substituted 1,1-diphenylethylenes gives a negative $\rho_H - \rho_T$. For benzyl mercaptan with styrenes it is positive, and also possibly positive for the diarylethylenes. One might try to explain this result by attributing the substituent effects entirely to bond energy effects, as once advocated by Zavitsas.[10] However, this explanation would be highly forced and is no longer necessary since positive values of ρ for abstraction from toluene have been found,[11] which is incompatible with a pure bond-energy effect for abstractions from toluene. These new substituent effects are real (for example in Table I the extreme of the four results with substituted styrenes differs from the mean by more than four estimated standard deviations), but the Hammett correlation is by no means perfect. In a series of measurements on ten monosubstituted styrenes with thiophenol at 0 °C (not here reported) the Hammett plot is poor; it also suggests a positive value of $\rho_H - \rho_D$, not greater than +0.2, using either σ or σ^+. The small range of isotope effects makes the experimental error a major contributor to the quality of the fit, and hence makes extensive analysis fruitless.

Steric Effects. The studies with mesityl mercaptan were aimed at exploring the possibility of steric effects on the isotope effects. The three methyl substituents unquestionably also influence the SH bond dissociation energy, probably in the direction of weakening the SH bond. However, the isotope effects in the reaction with the styrenes lie between the values for thiophenol and the values for benzyl mercaptan, with the highest SH bond dissociation energy. It may be concluded that the high isotope effects relative to thiophenol are probably not due to a very small bond-energy difference. This view is supported by the isotope effects with the trityl radical, which are much higher than the values with thiophenol (for example, at 25 °C $k_H/k_T = 25.2$ with mesityl mercaptan, Table IV, and 14.9 with thiophenol[7]). This enhanced isotope effect is almost certainly in part attributable to a tunnel correction, as suggested by the high isotope effect, the large exponential term in eq 10, and the small preexponential term.[3] The complications in the thiophenol–trityl radical reaction at temperature extremes were not observed here, but the temperature extremes were not approached.

The suggestion of a substantial tunnel correction for the mesityl mercaptan–trityl radical reaction is probably only in part attributable to steric hindrance, since eq 9 also suggests less convincingly a smaller tunnel correction. Similarly, the temperature dependence of the trityl radical–thiophenol reaction,[7] where the steric hindrance must be much less, also is suggestive of a small but perceptible tunnel correction.

One striking feature of all the isotope effects is the rather large range, for example, with thiophenol from 2.6 to 14 at 70 °C. In contrast to the isotope effects in proton transfers which are within a factor of 2 of the "theoretical maximum" (for loss of all stretching zero-point energy) for a wide range of ΔpK,[3] these radical reactions are more smoothly correlated with $\Delta H°$ and cover a wider range (the "theoretical maximum" of k_H/k_T is 9.2 for an SH bond with ν = 2500 cm^{-1} at 70 °C). Thus Bell's argument,[12] which places the burden of dependence of isotope effect on ΔpK for proton transfer on the tunnel correction, appears less applicable to H atom transfers, and the original Westheimer "symmetry" argument (modified by inclusion of tunnel corrections, which are necessarily absent in Westheimer's artificial surface) with substantial isotope sensitive zero-point energy in the transition state for the highly exothermic reactions is supported. One difference between proton transfers and hydrogen atom transfers is the charge distribution and solvation. Furthermore, virtually all the proton transfers are between atoms in the first row, whereas the atom transfers here involve a second-row element. Because the bonding to second-row atoms is so different there may be a further effect on the force constant symmetry. We cannot directly explore the endothermic region with studies of these chain reactions, simply because chain reactions with very highly endothermic steps are rare, but the potential of studying the reverse reaction and calculating the equilibrium isotope effect brings both branches of the curve in principle within reach.

Conclusion. The isotope effects in the reaction $R\cdot + HSR' \rightarrow RH + \cdot SR'$ are determined by a number of factors. A major factor is the "symmetry" of the reaction, with the largest isotope effects occurring at $\Delta H° = 0$. Steric hindrance enhances the isotope effects as it does in proton transfers. There appear to be effects from charged contributions to the transition states, but these are not yet separated from the two previous effects. Thus we are not quite yet able to use the isotope effect to measure $\Delta H°$, and hence dissociation energies of bonds to hydrogen, but the possibility remains.

Experimental Section

Materials. **Thiophenol-*t*.** Reagent grade thiophenol (500 g) and tritiated water (2 ml, 2 mCi) were heated together, then anhydrous sodium sulfate was added, and the liquid distilled, bp 169 °C, with specific activity 3 × 10^8 dpm/mol. Oxidation of a small sample to diphenyl disulfide with hydrogen peroxide in glacial acetic acid was followed by recrystallization of the disulfide from ethanol. The disulfide was devoid of measurable activity. When this oxidation was repeated after the thiophenol-*t* had been standing at room temperature for about 6 months, the disulfide contained less than 0.1% of the thiophenol activity.

Benzyl Mercaptan-*t*. This was exchanged following the method for thiophenol, starting with Matheson Coleman and Bell α-toluenethiol. Its activity was 5 × 10^8 dpm/mol. Oxidation with hydrogen peroxide gave dibenzyl disulfide with a specific activity of about 4 × 10^6 dpm/mol. Oxidation with hydrazine gave benzalazine[13] and further oxidation with alkaline permanganate gave benzoic acid, which was without measurable activity.

2,4,6-Trimethylthiophenol-*t*. Commercial mesityl mercaptan was exchanged following the method for thiophenol. It boiled at 78 °C at 1.5 Torr, specific activity 2 × 10^8 dpm/mol. Oxidation gave inactive disulfide, even after 6 months standing.

Addition of Thiol to Olefin. The thiol (0.1 mol) was placed in a test tube shaped quartz container, equipped with a sealed stirrer, an inert gas inlet, and a sealed thin-walled bulb containing degassed olefin (0.001 mol) on the end of a movable glass rod located over a spike in the bottom of the tube. A glass-sealed thermistor was also in the solution for measuring temperature. The thiol was largely freed of oxygen by passing nitrogen through, and the whole assembly was placed in a large Dewar flask used as a thermostat. A mercury lamp was placed in a quartz well next to the reaction vessel. When temperature equilibrium was obtained as shown by the thermistor resistance, the glass bulb was broken by pushing it down on the spike. The reaction was then initiated by turning on the light, and in many cases the reaction was followed by loss of olefin in withdrawn samples by gas chromatography. In the case of the reactions of substituted styrenes with thiophenol, the reactions started on mixing without the need for photoinitiation. These fast reactions showed a perceptible temperature rise (about 1 °C for *p*-methoxystyrene, 0.85 °C for styrene, 0.6 °C for *p*-chlorostyrene, and 0.25 °C for *m*-nitrostyrene at 70 °C, less at lower temperatures); these maximum rises were attained within about 1–2 min, and corresponded to a significant but by no means complete reaction, thus the average temperature at which product was formed is much closer to the equilibrium temperature than these peak temperatures.

After reaction the reaction mixture was dissolved in ether, extracted three times with 5% sodium hydroxide and twice with water, and distilled. In most cases the vacuum distilled sulfide was oxidized with hydrogen peroxide in glacial acetic acid to a crystalline sulfone. The properties of the reaction products (NMR and mass spectral data) are summarized in the thesis of ref 1. In no case was an unexpected product encountered.

Correction for Exchange of Starting Olefin. The sulfone from the reaction of thiophenol with the 1,1-diarylethylenes was treated with potassium hydroxide in ethanol, and standard work-up allowed isolation of the reformed diarylethylenes. With *p*-chlorophenyl as the aryl group, the final olefin had no activity, but with *p*-anisyl and phenyl as the aryl group, the olefins were active. The activity used to calculate the isotope effect was the specific molar activity of the sulfone less that of the reformed olefin.

Search for Exchange of Benzyl Mercaptan During Reaction. After reaction of benzyl mercaptan with olefin, the mercaptan was recovered from the alkaline extractions and oxidized to the disulfide. The disulfide was active but indistinguishable from disulfide produced before reaction. Similarly, dimesityl disulfide showed no activity when recovered from the reaction mixture.

Reaction of 2,4,6-Trimethylthiophenol with 4-Triphenyl-1-diphenylmethylene-2,5-cyclohexadiene. This followed exactly the procedure previously described for the reaction with thiophenol.[7] No *p*-benzhydryltetraphenylmethane was found among the reaction products.

Counting. All tritium counting was done by solution scintillation counting in solutions containing 10–20 mg of material in 20 ml of counting solution, containing 5 g of 2,5-diphenyloxazole (POP) and 0.1 g of *p*-bis-2-(5-phenyloxazolyl)benzene (POPOP). At least 10^4 counts were recorded; background corrections were always small; efficiency corrections were made by external standardization, but were never importantly variable, since no compounds quenched significantly. Efficiencies were about 28%.

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Isotope Effects in Hydrogen Atom Transfers. VI. Radicals from Azo Compounds in Thiophenol

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Abstract: Radicals R· derived from azo compounds abstract hydrogen atoms from thiophenol giving RH, and the tritium effect is readily measured by comparing the activity of $C_6H_5SH^*$ and RH^*. Azo compounds of the form $(CH_3)_2CXN{=}NCX(CH_3)_2$ also yield RH by a disproportionation; in these cases k_D/k_T was measured after correction for contamination of RD* by RH. In these examples, covering X = C_6H_5S, $CH_3OC({=}O)$, N≡C, and C_6H_5, there was good correlation between k_D/k_T and k_H (measured by others); both are related to the stability of the radical R·. The isotope effects are rather small. Aryl radicals, from $Ar{\cdot}N{=}NC(C_6H_5)_3$, were also studied. The values are quite small (k_H/k_T = 1.4 to 3.1). Evidence is presented to support an important contribution of polar structures to the transition state. The basis of the influence of these transition state polar contributions on the isotope effect is considered; the same considerations also explain the steric enhancement of isotope effects.

In the previous paper of this series,[2] the isotope effects in some reactions of carbon radicals (R·) with thiols were shown to correlate with the exothermicity of the reaction, a correlation also explored by Pryor and Kneipp.[3] Thus, for a single thiol, in a series of exothermic reactions, the isotope effect should fall monotonically as D_{RH} increases. The radicals studied[2] were all those involved in the addition of mercaptans to olefins, although the work of Pryor covered a far wider range of radicals and thiols. In this paper we explore a wider range of radicals available from the decomposition of azo compounds. The first part describes results with compounds of the form $(CH_3)_2CXN{=}NCX(CH_3)_2$.

In principle, the isotope effect could be determined simply by decomposing the azo compound RNNR in thiophe-