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USING ISOTOPE EFFECTS.

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THE ORDERING OF CARBON-HYDROGEN BOND STRENGTHS USING ISOTOPE EFFECTS

BY

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Thesis Director's Signature

A handwritten signature in cursive script, appearing to read "Edward Sheers", is written over a horizontal line.

Houston, Texas

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THE ORDERING OF CARBON-HYDROGEN BOND STRENGTHS USING ISOTOPE EFFECTS

INTRODUCTION

Soddy recognized the existence of isotopes in 1910 during his investigations of natural radioactive elements. Five years later Hevesy attempted the first experiments on chemical isotopic exchange while working with lead. It remained until 1919 before the concept of chemical isotope effects was first introduced by Lindeman.¹

The first experimental isotope effect was observed in 1932, just one year after the first successful laboratory separation of the stable hydrogen isotopes in 1932.² The study of isotope exchange and isotope effects has since become an active field of research.

Isotope effects find use as a powerful tool in the elucidation of mechanisms,³⁻⁵ transition state symmetry studies,⁶ the tunneling phenomenon,⁷ useful industrial applications and possibly as a useful tool for a qualitative ordering of chemical bonds which will be introduced later in the discussion.

The theoretical development of the concept of isotope effects can be attributed to several authors.⁸⁻¹⁰ It should be noted however that this theoretical development was a result of the transition-state theory developed by H. Eyring.¹¹ Eyring's theory assumes that the rate of any chemical reaction can be formulated in terms of an activated complex. The rate of chemical reaction can, therefore, be stated as the number of activated complexes passing per unit time over the top of the potential-energy barrier. The calculations for a particular hypothetical reaction (1) can be greatly simplified if it is assumed

that the activation complex $[AB]^{\ddagger}$ is in equilibrium with the reactants.

From this assumption, the equilibrium constant for the formation of complexes becomes (2)

$$(2) \quad K^{\pm} = \frac{[AB]^{\pm}}{[A][B]}$$

The concentration of complexes thus becomes (3)

$$(3) \quad [AB]^{\pm} = K^{\pm} [A][B]$$

and the rate of reaction becomes (4)

$$(4) \quad -d[A]/dt = [AB]^{\pm} \cdot (\text{rate of passage over barrier})$$

The rate of passage over the barrier is equal to the frequency with which the complex flies apart. This vibrational frequency is equal to ϵ/h where ϵ is the average of the vibration that leads to decomposition having the value RT/N , assuming that this is a thoroughly excited vibration and R/N is Boltzmann's constant. The rate of passage over the barrier thus becomes (5)

$$(5) \quad \nu = \epsilon/h = RT/Nh$$

The rate of reaction is therefore (6)

$$(6) \quad -d[A]/dt = k_1 [A][B] = K^{\pm} [A][B] \cdot RT/Nh$$

which yields the rate constant as (7)

$$(7) \quad k_1 = RT/Nh \cdot K^{\pm}$$

To be more precise, the expression k_1 should be multiplied by a factor κ , the transmission coefficient which is the probability that the complex will dissociate into products instead of back into reactants.¹²

In 1889 Arrhenius proposed the following empirical equation which gives the rate constant as a function of absolute temperature (8)

$$(8) \quad k = A \exp(-\Delta E/RT)$$

This equation is generally used instead of the absolute reaction rate equation because of its simplicity. It is with this equation that most of the remaining discussion will be based. In this equation k is the rate constant, $\exp(-\Delta E/RT)$ equals the fraction of the molecules which are activated and A represents an empirical constant which is related to the PZ factor found in the collision theory. Z represents the number of collisions per second in a given volume. In some reactions involving complicated molecules the rates are smaller than the collision theory predicts and an additional factor P , called the probability or steric factor, must be added to the expression.

A simple approach to the development of the isotope effect expression can be shown without detailed mathematical involvement. By considering reaction (9)

and reaction (10)

and with appropriate labelling of the Arrhenius equation, as to designate isotopic substitution, one can obtain for the proton containing case equation (11)

$$(11) \quad k_H = A_H \exp(-\Delta E^H/RT)$$

and equation (12) for the deuterium case

$$(12) \quad k_D = A_D \exp(-\Delta E^D/RT)$$

The transition states in equations (9) and (10) are only hypothetical and the proton and deuteron are not meant to be in the same position nor is either implied to be symmetrically bonded between atom A and atom S.

By definition, the isotope effect is the rate of reaction of one isotope divided by the rate of the same reaction when a different isotope is substituted in the same position or k_H/k_D in the case of the proton and the deuteron. By dividing equation (11) by equation (12), one obtains equation (13)

$$(13) \quad k_H/k_D = (A_H/A_D) \exp (E_D-E_H)/RT$$

At this point, it seems appropriate to discuss the principal factors which influence the magnitude of the isotope effects, namely the stretching frequency, bending frequency and tunneling. Each topic will be discussed and its importance to equation (13) weighed.

From classical mechanics, the stretching frequency of a chemical bond may be compared to the behavior of a spring. If one extends this analogy, the chemical bond, like the spring, obeys Hooke's law, $\underline{f} = -\underline{k}\underline{r}$, where $\underline{f}$ is the restoring force, $\underline{k}$ the force constant and $\underline{r}$ the inter-nuclear distance. The energy curve is parabolic represented by the equation, $E = \frac{1}{2} k(r-r_{eq})^2$. If one plots the energy vs. bond length of a molecule, A-B, the form will be that represented in Figure 1.

Figure 1. Potential-Energy curve of a harmonic oscillator, molecule $A-B$.

At $E = 0$, it is seen that $r = r_{eq}$. Any energy in excess of this for a harmonic oscillator arises because of extensions and compressions of the bond. Considering a hypothetical bond between two atoms A and B , Figure 1 shows that if atom A is held stationary on the $r = 0$ axis, the other atom will oscillate between B and B' . By increasing the energy of the bond from E_1 to E_2 , the oscillation will become more vigorous with the vibrational frequency remaining unchanged.

A true chemical bond has a certain vibrational frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion. The classical oscillation frequency is:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

where μ is the reduced mass of the system, k is the force constant and

c is the speed of light.

Vibrational energies are quantized and the allowed vibrational energies for any particular system may be calculated from the Schrödinger equation. For the simple harmonic oscillator these turn out to be:

$$E_n = (n + \frac{1}{2}) h \bar{\nu} \quad \text{cm}^{-1}$$

where n is referred to as the vibrational quantum number. This equation predicts that the atoms of a diatomic molecule can never be completely at rest. Even when n = 0, there remains a residual amount of energy known as the zero-point energy. The prediction of this residual zero-point energy is one basic difference between the wave mechanical and classical approaches to molecular vibrations.¹³

The importance of zero-point energies can best be described by considering the proton transfer in reaction (14).

It will be assumed that groups A and B are heavy relative to the proton. The electronic contributions to the potential energies $[\text{A} \cdots \text{H} \cdots \text{B}]^\ddagger$ and $[\text{A} \cdots \text{D} \cdots \text{B}]^\ddagger$ are assumed to be identical. The difference between the potential energies of the two activated complexes is, therefore, the difference in the mass dependent zero-point vibrational energies.

$$\Delta E^\ddagger = ZPE_{\text{ADB}}^\ddagger - ZPE_{\text{AHB}}^\ddagger$$

The potential energy difference between the reactants is the difference in the vibrational energies in the ground states.

$$\Delta E = ZPE_{\text{AD}} - ZPE_{\text{AH}}$$

The net differences in activation energies is the zero-point energy difference of the ground states minus the difference of the zero-point energy of the transition states.

$$\Delta E = (ZPE_{AD} - ZPE_{AH}) - (ZPE_{ADB}^{\ddagger} - ZPE_{AHB}^{\ddagger})$$

If the molecules A-H and H-B have the same bond strength, the hydrogen atom will occupy the center of mass in the transition state. This condition causes the term $(ZPE_{ADB}^{\ddagger} - ZPE_{AHB}^{\ddagger})$ to vanish because this symmetric vibration is mass independent. If such a case occurs, the difference in activation energies becomes the difference between ground state zero-point energies. This condition would lead to a maximum isotope effect.¹⁴

The idea of bending vibrations in the transition state is usually ignored when speaking in general of isotope effects. It is usually assumed that in a linear three center hydrogen transfer, the bending vibrations for the ground state and the corresponding transition state are similar. Bell's model shows that the contributions of bending frequencies tend to cancel out.¹⁵ Model calculations by More O'Ferrall also show that the effects of bending vibrations cancel and are of little importance in the magnitude of the isotope effect assuming a linear transition state.¹⁶

Previous discussion has assumed the transition state to be linear. Lewis¹⁷ first suggested that a bent transition-state geometry can be responsible for small primary isotope effects. More O'Ferrall, using model calculations, shows that the bent transition-state geometry can lead to small isotope effects.¹⁸

The phenomenon of tunneling is often talked about but is widely misunderstood. The quantum mechanical solution to the "particle in a box" problem gives some insight into tunneling. This solution tells one that

the probability of finding a particle in the classically forbidden region of negative energy is not zero, but a positive number which falls off exponentially with the distance of penetration within the barrier. If the barrier is not infinitely high or infinitely wide there is a certain probability that a particle will leak through. This leakage is referred to as the tunnel effect.¹⁹

Close examination of Heisenberg's uncertainty principle states that the product of the uncertainty in momentum and the uncertainty in position is of the order of Planck's constant or $\Delta y \Delta p \approx h$ in which y is the position of the particle p is the momentum and h is Planck's constant. Since momentum is mass times velocity, one can rewrite the expression as $\Delta y \Delta (mv) \approx h$. Examination of this principle shows that if the velocity remains constant the uncertainty in position is reduced by increasing the mass. In the case of the proton and deuteron, the uncertainty in position will therefore be greater for the proton. If one considers a potential energy barrier, it becomes obvious that as the height and thickness of the barrier increases the degree of tunneling decreases because the greater the uncertainty in position, the greater the chance of finding a particle on the product side of the barrier.

Bell used a parabolic barrier model to illustrate qualitatively how various factors influence tunneling.²⁰ Since data will generally be plotted according to the Arrhenius equation.

$$\ln k_{\text{obs}} = \ln A_{\text{obs}} - (E_{\text{obs}}/RT)$$

Bell has presented the following criteria which enables one to recognize tunneling in a given experimental situation:

1. $A_{\text{obs}} < A$ and temperature dependent.
2. E_{obs} to decrease as the temperature is lowered.
3. $E_{\text{obs}} < E$ because of tunneling.

The following will be expected for H,D,T isotope effects:

1. $k_{\text{H}}/k_{\text{D}} (T)$ larger than classical values.
2. $E_{\text{obs}}^{\text{D}} - E_{\text{obs}}^{\text{H}}$ larger than the zero point energy difference.
3. $A_{\text{obs}}^{\text{H}} < A_{\text{obs}}^{\text{D}}$ (See Figure 2)

Westheimer's²¹ model shows that the magnitude of the primary isotope effect varies with the symmetry of the transition state. A maximum isotope effect should be obtainable when the hydrogen is symmetrically bonded to the atoms between which it is being transferred. Bell²² and Kresge²³ first observed experimentally this isotope maximum suggested by Westheimer in proton exchange reactions.

With some insight into the meaning of kinetic isotope effects coupled with some caution as to their interpretation, it seems appropriate at this point to discuss the research designed to compliment the previous discussion.

A series of hydrogen atom transfer reactions were sought which might give a wide range of isotope effects. If such a range was observed, it was hoped that in some cases the phenomenon of tunneling, transition state symmetry and mechanistic studies would be encountered.

The system chosen was a series of thiol additions to several olefins. Thiols add to olefins under a variety of conditions and mechanisms. The mechanism of greatest interest was that of radical chain addition of a thiyl radical to olefins. The overall reaction is shown in Scheme I.

Figure 2. Arrhenius plot for Proton and Deuteron Transfer Reactions.

Scheme I

Burkhardt²⁴ first suggested that free radicals were involved and Kharasch²⁵ first presented the now accepted chain mechanism. Kharasch, using the methyl mercaptan-ethylene system, found that ΔH for reactions 17 and 18 were both exothermic by 14 and 12 KCal respectively. This point is very interesting and will be dealt with later in the discussion.

Walling and co-workers²⁶ reported the relative reactivities of substituted β -methylstyrenes towards thiyl radicals at 60^o and found that the p-methoxy substituted styrene reacted 100 times faster than the unsubstituted styrene. The enhanced reactivity of the p-methoxy substituted styrene was attributed to polar contributions to the transition state. This point is also interesting and will be dealt with later in the discussion.

Radical additions of thiols to olefins have been reviewed and will not be discussed further.²⁷

METHODS

The tritium isotope effects in radical chain addition of thiols to olefins were studied by a competitive reaction procedure.²⁸ A ten to one hundred-fold excess of thiol, which had previously been exchanged with tritium enriched water, was allowed to react with the appropriate olefin. In the styrene-thiophenol systems all reactions were self-initiating whereas the olefin-benzylthiol system had to be initiated by light. The olefin-mesitylthiol system and olefinbenzylthiol system were also initiated with 2,2'-azobis-(2-methyl propionitrile).

Before any results are presented or discussed concerning this investigation, a brief mention will be made as to possible sources of error.

The usual errors of weights, temperatures, mixing, etc., were held to minimum due to triplicate samples, good temperature control and vigorous stirring.

The major errors were introduced in determination of molar specific activity of reagents and products. This source of error arises not only from weighing, but from statistical errors in the number of counts of each sample. Purity of all samples was checked by tlc, glpc or nmr. All samples showed greater than 99% purity by these methods. Checks showed that extreme deviations were no greater than 1% for each measurement showing that even though these errors are present they are rather insignificant.

During the early stages of the work there was some uncertainty in the rate at which the contents reached bath temperature. This proved a greater problem than first anticipated because at one point

in the p-N,N-dimethylaminostyrene-thiophenol system, the reaction actually took place while the contents were being mixed with a large evolution of heat. This experience lead through a series of modifications to the apparatus described in Figure 4 of the experimental section. The apparatus in Figure 4 allowed the temperature of both reagents to reach bath temperature before being mixed.

The drawbacks to the competitive reaction method for obtaining kinetic isotope effects are numerous and must be considered carefully. The most obvious will now be discussed and will be used when considering the results obtained during this investigation.

In discussing these problems, consider reaction (19) and reaction (20).

The rate equations must be correct as to order in reagents. The adducts XH and XT cannot result from reactions of different order in X. The reactions must be of first order in both RH and RT. In reactions of complexity, the rate constants k_H and k_T must enter into the step which determines the product.

Rates of reactions (19) and (20) must not be diffusion controlled for there will be no discrimination between isotopes and the isotope effects will be low.

The adduct obtained from the reaction must not undergo interference such as ionic exchanges which incorporates more tritium into the adduct than normal.

Care must be exercised to assure that rate constants are constant

and are not altered by solvent, temperature, ionic strength, etc.

Careful consideration must also be placed on all proton sources in the system. For example, it was found that thiophenol-t exchanged tritium into the ring upon standing for long periods of time. 2-Mesitylenethiol-t under the same conditions did not. α -Toluenethiol-t was found to exchange tritium into the methylene position during exchange with water but not during reaction with olefins.

Instrumentation:

External temperature was controlled on all reactions by either a Sargent "Thermonitor" controller, Hallikainen "Thermotrol" controller or by a Bailey "Precision Temperature Controller". Gas kinetics were carried out in a standard gas displacement apparatus using silicon oil as the displaced fluid. Glpc analysis where applicable, were carried out on a modified Micro-Tek gas chromatograph using a 6 ft $\frac{1}{4}$ in. column packed with 20% SE-30 on Chromosorb W (60/80). Nmr spectra were run on a Varian Associates A-56/60 and a Perkin-Elmer R-12 spectrometer. Concentrations of nmr samples varied from 1-10% (wt/wt) using CDCl_3 or CS_2 as solvent, depending on solubility of material. Mass spectra were obtained on a Consolidated Electrodynamics Corporation 21-110 mass spectrophotometer.

Apparatus: (Reaction of triphenylmethyl radical with thiols)

The apparatus used was a single unit consisting of three flasks connected in series by appropriate ground-glass joints as shown in Figure 3. The first was a 500 ml. 24/40 one-neck flask. The second was a 500 ml. 24/40 two-neck flask. The third was a 1000 ml. three-neck creased flask. A fritted glass filter was placed between the first and second flask, and two 90° bends with ground-glass 24/40 joints were placed between flask two and three. One of the bends contained a large bore vacuum stopcock. A mechanical stirrer was used for stirring the reaction mixture. The stirring assembly consisted of a stirring rod fitted with a special bushing containing two O-rings. The third flask also contained a small bore vacuum stopcock

used for degassing the system. The entire reaction sequence could, with this device, be executed in the absence of air.

Apparatus: (Thiol addition to various olefins)

The apparatus used in these experiments is shown in Figure 4. The basic assembly consists of a quartz test tube 1.5 x 8 in. fitted with an outer 45/50 joint and a small (2mm) tube entering the bottom of the tube and extending up the outside to the top of the ground-glass joint. The top of the assembly is a 45/50 inner ground-glass joint that has been slightly enlarged at the top. The spacing of the holes in the top is rather critical for it must accommodate a thermistor sealed in glass, a stirring rod, a sample tube and a vent. The thermistor becomes one leg of a Wheatstone bridge assembly, the output of which was connected to a strip chart recorder.

The sample tubes are 2mm glass tubing with a bulb blown in one end. After the ampule is filled with the proper amount of material, it is sealed under vacuum two to four millimeters above the bulb.

Tritium-Labeled Thiophenol:

Reagent grade thiophenol (500 g Eastman), 2 g. of tritium-enriched water (1 mCi/g) and 5 g. of calcium oxide were placed in a 1000 ml flask fitted with a reflux condenser, drying tube and magnetic stirrer, and then heated for 12 hr at 80°. The labeled thiophenol was dried over anhydrous sodium sulfate and distilled. The boiling point was 169° at atmospheric pressure. nmr: (5H)-2.9 τ (s), (1H)-6.7 τ (s). Specific activity of thiol was approx-

Figure 3. Apparatus used for the reaction of triphenylmethyl with various thiols.

Figure 4. Apparatus used in the thiol addition to various olefins.

imately 3×10^8 decomposition/min.mole (0.135 mCi/mole).

Tritium-Labeled α -Toluenethiol:

Same procedure as for labeled thiophenol. Boiling point of α -Toluenethiol was 194-195° at atmospheric pressure. α -Toluenethiol from Matheson-Coleman and Bell. nmr: (5)-5.8 τ (s), (2H)-6.4 τ (s), (1H)-6.55 τ (s). Specific activity of thiol was approximately 5×10^8 decompositions/min.mole (0.225 mCi/mole).

Tritium-Labeled 2-Mesitylenethiol:^{29,30}

Same procedure as for labeled thiophenol. Boiling point of 2-mesitylenethiol was 78°/1.5mm Hg. nmr: (2H)-3.3 τ (s), (6H)-7.8 τ (s), (3H)-7.9 τ (s), (1H)-7.2 τ (s). Specific activity of thiol approximately 2×10^8 decompositions/min.mole (0.090 mCi/mole).

Counting Procedure:

Weighed samples (10-20 mg) were added to 20 ml of a solution containing 5 g of 2,5-diphenyloxazole and 0.1 g of p-bis-2-(5-phenyloxazolyl) benzene per liter of toluene and counted for a period of time to exceed 10^4 counts. Background corrections and efficiency corrections using external standardization were applied to all results. All counting efficiencies were about 28% and no effort was made to maximize the efficiency; no pure compounds quenched badly. Three samples of each reagents were counted and found to have an extreme deviation of less than 1%.

Location of Tritium in Thiophenol:

Tritium-labeled thiophenol (2 g) was oxidized to diphenyl disulfide by hydrogen peroxide in glacial acetic acid. After recrystallization from ethanol, it was counted and found to be inactive. A sample of thiophenol-t that had been standing for 6 months did give a small but detectable count when oxidized in this way, showing that a very slow process did result in the migration of tritium from sulfur to carbon. The activity of this sample was less than 0.1 per cent of the starting mercaptan.

Location of Tritium in 2-Mesitylenethiol:

Same procedure as that used for thiophenol. A sample of 2-mesitylenethiol-t that had been standing for 6 months did not give a detectable count when oxidized in the same manner as thiophenol.

Location of Tritium in α -Toluenethiol:

A different procedure was required to locate the label in α -toluenethiol. The label could either be in the ring, the benzyl position or on the sulfur atom.

α -Toluenethiol (2 moles) was reacted with hydrazine (1 mole) to give benzaldazine after workup with $\text{HCl}/\text{H}_2\text{O}$.³¹ The benzaldazine was then heated on a steam bath with KOH/KMnO_4 to give benzoic acid. The activity of the recovered benzoic acid was indistinguishable from background. By counting the original mercaptan, benzoic acid and disulfide obtained by peroxide oxidation, the location of the label was possible. Results showed that no label was present in the ring

and that less than 0.5 per cent was located in the benzyl position. Oxidation of a sample of α -toluenethiol before and after the reaction showed that the label in the benzyl position occurred during exchange with tritiated water and not during reaction with olefin.

Reaction of Thiols with Olefins:

A typical reaction consists of placing 0.1 mole of mercaptan in the test tube part of the apparatus shown in Figure 4. A 0.001 mole sample of olefin was degassed and sealed in a 1 cm bulb also previously described. The olefin is placed in the top of the apparatus along with the stirrer and thermistor. The entire apparatus after assembly is lowered into a large Dewar beside a quartz well containing a Hanovia mercury lamp. The contents are allowed to attain thermal equilibrium as shown by the strip chart recorder. The bulb containing the olefin is then crushed against a glass spike in the bottom of the apparatus. After the reaction reaches completion, as followed by glpc, the reaction mixture is dissolved into ether and washed three times with 5% sodium hydroxide and twice with water. The ether is removed and the sulfide distilled at reduced pressure. If the sulfone is desired, the sulfide is added to glacial acetic acid and oxidized with hydrogen peroxide yielding white needles.

4-Triphenylmethyl-1-diphenylmethylene-2,5-cyclohexadiene (I):³²

Mercury (0.1 mole) was added to a solution of triphenylchloromethane (0.021 mole) in 250 ml of dry toluene in the first flask described previously under the topic of apparatus. This procedure is essentially that of Gomberg³³ who believed the product to be hexa-

phenylethane. The system described in Figure 3 was closed, degassed three times and allowed to react at room temperature for 12 hr with vigorous stirring.

Reaction of Triphenylmethyl with Thiols:

The yellow solution of I was filtered from the first flask through a glass wool plug and then through a fritted glass filter into the second flask. To the third flask, 16 g (0.15 mole) of tritium labelled thiophenol was added to 235 ml of dried reagent-grade toluene. The thiophenol-toluene solution was degassed three times. The entire apparatus was then submerged in a bath controlled to within 0.05^o and allowed to attain thermal equilibrium. Compound I was then added dropwise through the stopcock to the thiophenol-toluene solution, which was mechanically stirred as previously described.

Isolation of Triphenylmethane, Trityl Phenyl Sulfide and p-Benzhydryl-tetraphenylmethane II.

The above reaction mixture was dissolved in ether washed with 5% sodium hydroxide and dried over anhydrous sodium sulfate. Toluene was removed by distillation. Three 20 mg samples of toluene were counted and found to be undistinguishable from background. A 3 ft x 1 in chromatographic column packed with neutral aluminum oxide was used to separate the viscous oil. A 2:1 mixture of low-boiling petroleum ether-benzene mixture was used to elute the mixture and obtain complete separation of the triphenylmethane. A 1:2 petroleum ether-benzene mixture was then used to elute the trityl phenyl sulfide. After all trityl phenyl sulfide was removed, methylene chloride was used to elute any

other compounds found. At these low temperatures compound II was found, as shown by its melting point, 226-227^o (lit.³⁴ mp 227^o), mixed melting point and nmr: (1H)-4.45 τ (s), (29H)-2.6-3.0 τ (m). The isolated yields of II were 20 and 15% respectively at -25 and -15^o. The triphenylmethane had mp 93-94^o (lit.³⁵ 93^o), and the nmr showed a singlet at 4.66 τ (1H) and another singlet at 3.02 τ (15H). Trityl phenyl sulfide had mp 100-101^o (lit.³⁶ mp 105-106^o), and the nmr singlet 3.15 τ (5H) and a multiplet between 2.50 τ and 3.10 τ (15H). No attempt was made to determine the exact yields since purity of the products was the main goal. The isolated yields of purified triphenylmethane at -25.0, -15.0, 0.0, 25.0, 40.0 and 60.0^o were 14.0, 40.0, 58.0, 73.0, 82.0 and 90.0% respectively. The low total yields at the lower temperatures do not represent incomplete reaction, for ditrityl peroxide would have been produced on workup and is easily detected. These low yields are attributed to the difficulty of separating triphenylmethane and compound II.

p-Benzhydryltetraphenylmethane II:

The product is made by the reduction of triphenylcarbinol with stannous chloride. A five-fold excess of stannous chloride was added to glacial acetic acid along with the carbinol. Dry HCl was then passed into the solution upon which after a brief reaction time the solution became deep yellow-orange and large crystals began to separate. After the reaction was complete, the solution became colorless and the product was filtered and dried under vacuum. mp 226-227^o (lit.³⁷ mp 227^o). The isolated yield was 60.0 percent.

RESULTS AND DISCUSSION

The addition of thiols to triphenylmethyl followed by the addition of thiols to various olefins will now be discussed.

A toluene solution of "hexaphenylethane", 4-Triphenylmethyl-1-diphenylmethylen-2,5-cyclohexadiene (I), in equilibrium with triphenylmethyl radical, was added with good stirring to a ten-fold excess of thiophenol. The reaction was allowed to stand for ten half-lives for the dissociation process of I.³⁸ Upon workup of the reaction mixture, triphenylmethane and trityl phenyl sulfide were found. Diphenyldisulfide would have been found in the workup procedure if it had been present. It is reported in the literature that disulfides react with triphenylmethyl to yield trityl sulfides, but this reaction requires elevated temperatures.³⁹

From product analysis and tritium content, the mechanism shown in Scheme I is proposed.

Scheme I

Compound I seems free of any induced decomposition because there was still a perceptible color of radical which persisted for several half-lives of the dissociation of I. This also agrees with the absence

of attack of nitric oxide or iodine atoms on I.^{38,40}

With the use of thiophenol-t, the relative specific activity of the triphenylmethane and the thiophenol, which is present in large excess, gives the isotope effect on k_2 if k_{-2} is neglected. The measured isotope effects are presented in Table 1 for various temperatures. The third column in Table 1 is the value of the isotope

Table 1

Isotope Effects Measured by Specific⁴¹
Activity Ratios for Reaction 22

<u>Temp. °C</u>	<u>k_H/k_T^a</u>	<u>k_H/k_T Calcd^b</u>	<u>k_H/k_T^c</u>
-25	27.4	36	27.9
-15	27.4	29	27.4
0	22.3	22.3	
25	14.9	14.8	
40	12.1	12.0	
60	1.9	9.3	

^aMeasured isotope effect for triphenylmethane formation. Each entry represents an average of at least two runs agreeing within 0.3. ^bCalculated from equation 24. ^cMeasured isotope effect for formation of compound II.

effect calculated from the least squares equation (24).

$$(24) \quad k_H/k_T = 0.187 \exp(2590 \text{ cal}/RT)$$

No Arrhenius equation fits all points satisfactorily, however equation 24 fits better than any other over the range 0-40^o as shown by Figure 5.

The failure of the Arrhenius equation to fit all points can be attributed to two sources. The extremely low isotope effect at the highest temperature is almost certainly a result of the reaction rates becoming fast compared to the mixing rates. This condition locally depletes the thiophenol and the assumption of a large excess of thiophenol fails.

The apparently low isotope effects at the lower temperatures can be attributed to neglect in the reversal of reaction (22). When the steady-state concentration of trityl radicals is high, nearly all phenyl thiyl radicals are scavenged by reaction (23), but at the lower temperatures the trityl radical concentration is drastically reduced, enabling the thiyl radicals to abstract hydrogen atoms as they are known to do.⁴² The effect of this reverse reaction, which will also have an isotope effect, will be to reduce the isotope effect measured by the activity of the triphenylmethane, in the limit (which is not approached) to the small value characteristic of an equilibrium isotope effect.

Several observations support this evidence. The first is that at the lower two temperatures a new product is found, namely, p-benzhydrylphenyltriphenyl methane (II). Compound II is an isomer of I, but can-

not result from an intramolecular isomerization, for it contains tritium derived from the thiophenol. The mechanism most probable for formation of II is that shown in Scheme II.

Figure 5. Plot of K_H/K_T vs $1/T$ for the reaction of triphenylmethyl radical with thiophenol.

Scheme II

The measured isotope effect for compound II is also included in Table 1. The closely similar isotope effects suggest a closely similar process, as reactions (22) and (25) certainly are. Compound II has been obtained before from I by an acid-catalyzed process,⁴³ but it seems unlikely that thiophenol is acidic enough to accomplish the reaction at these low temperatures.

A second piece of evidence lies in the observation that inactive triphenylmethane, heated with thiophenol-t and azobisisobutyronitrile leads to incorporation of tritium in the recovered triphenylmethane. Because of some uncertainties regarding the molecule initially attacked by the cyanoisopropyl radicals, this evidence is a necessary but insufficient demonstration of attack of the phenylthiyl radicals on triphenylmethane.

2-Mesitylenethiol-t was substituted for the thiophenol-t as previously described and the results are presented in Table II. Least squares equation (26) was used to calculate the isotope effects

$$(26) \quad k_{\text{H}}/k_{\text{T}} = 0.271 \exp(2700 \text{ cal}/RT)$$

in Table II. (See Figure 6).

One may conclude from the large isotope effects listed in Tables I and II that the reactions are not very unsymmetrical and therefore

Table 2

Isotope Effects Measured by Specific
Activity Ratios for Reaction 22
(2-Mesitylenethiol replaced Thiophenol)

<u>Temp. °C</u>	<u>k_H/k_T Exp.</u>	<u>k_H/k_T Calcd.</u>
0.0	41.2	39.3
8.0	36.8	34.1
15.0	29.9	30.3
25.0	25.2	25.9
32.0	21.7	23.3
40.0	20.3	20.8

they have equal barriers in both directions. The value at 25° of $k_H/k_T = \underline{14.8}$ is slightly larger than would be calculated for complete loss of zero-point energy of a harmonic stretching vibration ($\nu = 2575 \text{ cm}^{-1}$) of a typical S-H bond, $k_H/k_T = \underline{11.5}$. This frequency represents an activation energy of 1446 cal/mole, assuming all zero-point energy is lost in the transition state.

The possibility that the high isotope effects arose from the tri-
tyl radicals abstracting a hydrogen from another source other than the
sulfur atom was investigated. The only conceivable source of hydrogen
atoms other than on sulfur was the methyl groups attached to the ring.
For example, if reaction (27) was occurring the triphenylmethane would

have a low activity, thus leading to an isotope effect that was higher than the true one. If the benzyl radical in reaction (27) had been formed it would have abstracted tritium from another molecule of thiol. To test for this reaction, a sample of the recovered 2-mesitylenethiol-t was oxidized to the disulfide and counted. The activity of the disulfide was found to be no greater than background and this possibility of explaining the large isotope effects was discarded.

These large isotope effect values strongly indicate the tunneling phenomenon especially in view of the low pre-exponential factor in equations (24) and (26).⁴⁴ This also suggests a rather symmetric barrier, since tunneling itself seems most associated with symmetric barriers.⁴⁵

A continuation of the previous work was the addition of thiols to various olefins. Since the results are numerous, they will be presented in Tables 3-6. Physical constants and spectra for these compounds are included in the appendix.

Results previously reported from this investigation were found to be in error for the substituted styrenes and diphenylethylenes.⁴⁶ Reasons for the discrepancies are different for the two cases and will be discussed separately.

During the early part of this investigation, the reactions were carried out in a conventional manner by adding all reagents under nitrogen and immersing into an oil bath controlled at the desired temperatures. Results were easily reproducible to within $\pm 5\%$, which is the precision boundaries placed on the competitive method. This work had already been reported, when a very disturbing experience occurred. During the mixing of p-N,N-dimethylaminostyrene with thiophenol, a very vigorous exothermic reaction occurred giving the desired adduct. This experience lead to numerous modifications ending with the one described in Figure 4 of

Figure 6. Addition of 2-Mesitylenethiol to triphenylmethyl radical at different temperatures.

Table 3

Tritium Isotope Effects in the Addition
of Thiophenol to Substituted Styrenes
at 0°.

<u>Styrene</u>	<u>k_H/k_T^a</u>
p-t-butyl	9.73
p-ethyl	10.16
p-methoxy	10.43
p-fluoro	10.53
p-methyl	10.79
m-chloro	10.90
p-chloro	11.01
m-nitro	11.13
m-bromo	11.61
p-hydrogen	12.10

^aThese isotope effects are those obtained in
the modified apparatus discussed in the experimental
section.

Table 4

Tritium Isotope Effects in the Addition of Thiophenol to Substituted Styrenes at 70°.

<u>Styrene</u>	<u>k_H/k_T^a</u>
p-methoxy	6.59
p-hydrogen	6.74
p-chloro	7.13
m-nitro	8.33

Tritium Isotope Effects in the Addition of thiophenol to Substituted 1,1-diphenyl-Ethylenes at 70°.

<u>Substituent</u>	<u>$k_H/k_T^{a,b}$</u>
1,1-p-dichloro	8.93
1,1-p-dihydrogen	10.89
1,1-p-dimethoxy	14.10

^aThese isotope effects are those obtained in the modified apparatus discussed in the experimental section.
^bThese results are corrected for exchange reactions.

Table 5

Tritium Isotope Effects in the Addition
of α -Toluenethiol to $R^1R^2C=CH_2$ at 70°.

<u>R¹</u>	<u>R²</u>	<u>k_H/k_T^a</u>
N-Carbazolyl	H	4.44
PhCH ₂	H	4.81
OAc	H	5.75
CN	H	7.75
CO ₂ Me	H	8.04
CO ₂ Me	Me	9.75
p-CH ₃ OC ₆ H ₄	H	9.43
C ₆ H ₅	H	10.40
p-ClC ₆ H ₄	H	11.26
p-ClC ₆ H ₄	p-ClC ₆ H ₄	8.13
p-CH ₃ OC ₆ H ₄	p-CH ₃ OC ₆ H ₄	--
CH ₃ (CH ₂) ₅	H	6.73 ^b

^aIsotope effects either from modified apparatus
or from paper by E. S. Lewis, M. M. Butler, Chem.
Comm., 941, 1971. ^bAt 0°.

Table 6

Tritium Isotope Effects in the Addition
of 2-Mesitylenethiol to $R^1R^2C=CH_2$ at 70° .

R^1 —	R^2 —	k_H/k_T^a —
CO_2Me	H	3.73
CO_2Me	Me	6.72
CN	H	10.72
$p-CH_3OC_6H_4$	H	7.02
C_6H_5	H	7.15
$p-ClC_6H_4$	$p-ClC_6H_4$	13.05 ^b

^aThese isotope effects are those obtained by merely adding the reagents together and immersing into an oil bath controlled at the desired temperature. ^bIt is assumed that no ionic exchange occurred in the β position of the olefin, since none was detected when thiophenol was used.

the experimental section. This apparatus allowed both reagents to reach bath temperature before being mixed. Results obtained from the new apparatus were of good quality which can be seen from Figures 7 and 8. It was not until a thermistor was placed into the reaction mixture that the culprit was found.

In all reactions of styrene with thiophenol, the reactions were self-initiating and exothermic even at 0^oC. Table 7 shows the temperature rise at various temperatures in this group of reactions along with the molar ratios of reactants.

In all reactions of substituted styrenes with thiophenol, the reactions were self-initiating and exothermic. A plot of temperature rise of each reaction vs time required for contents to return to the external bath temperatures are superimposed in Figure 9. In these reactions, a 1:100 dilution of four substituted styrenes to thiophenol was used. The purpose of the dilution was to reduce the temperature jump by allowing the solvent (thiol) to act as a heat sink. An interesting feature of this graph is that m-nitro, p-chloro and p-methoxystyrene reached a maximum temperature rise in the same amount of time. However, styrene reaches its maximum temperature rise in approximately one-half the time required by the substituted styrenes. The significance of this difference may or may not be important, but could possibly arise from the fact that styrene is readily available and easily distilled thus lowering the possible number of inhibitors.

Temperature problems of the magnitude encountered were not foreseen because a search of the literature made no mention of any spontaneous reactions. In fact, all discussions of thiol additions to olefins indicated that either light or peroxides were required to initiate the

Figure 7. Thermal addition of thiophenol to styrene.

Figure 8. Photochemical addition of α -toluenethiol to styrene.

Table 7

Bath Temp ($\pm 0.05^\circ\text{C}$)	Temp. Rise	k_H/k_T	mole thiophenol mole styrene
70.0	0.86	6.8	103
60.0	0.43	7.2	102
40.0	0.27	8.4	114
20.0	0.27	9.9	101
0.0	0.10	12.1	104

Temperature rise observed in reaction between styrene and thiophenol.

Figure 9. Temperature rise observed in reaction mixture between substituted styrenes and thiophenol at 70.00°.

reactions.^{47,48} It should be mentioned that the earlier work was not quantitative in nature but was concerned with exploring the chain mechanism of free radical addition to olefins.

The magnitude of the temperature problem is not apparent unless one calculates the possible temperature rise from heat capacity data. If one assumes the hypothetical reaction (28) to have a heat of reaction

of 13 KCal/mole, the following temperature rises can be calculated at 25.0°.

First, consider a ten-fold excess of thiophenol to styrene (0.01 mole styrene: 0.10 mole thiophenol) assuming that ΔH for the overall reaction is on the order of 13 KCal/mole. By comparisons of similar compounds of known heat capacities, and neglecting heat loss and container heat capacity, one can show that a 35.0° rise in temperature is possible under these conditions. With a one hundred-fold excess of thiophenol to styrene (0.001 mole styrene : 0.10 mole thiophenol), the temperature rise is similarly calculated as 3.5°.

The discrepancies in isotope effects for the 1,1-diphenylethylenes were not attributed to temperature problems. They resulted from an acid catalyzed exchange between the ethylene and thiol as shown in reaction (29). This problem was first observed during the attempt to add α -toluenethiol to p,p'-1,1-dimethoxydiphenylethylene. The addition was unsuccessful; however, the recovered ethylene contained tritium. The extent of this problem was found by treating the sulfone of the adduct with potassium hydroxide in absolute alcohol and isolating the starting ethylene. p,p'-1,1-Dichlorodiphenylethylene upon recovery

gave no detectable count showing that reaction (29) did not occur.

However, in the case of 1,1-diphenylethylene and p,p'-1,1-dimethoxy-diphenylethylene a substantial amount of tritium was found. By allowing for the tritium found in the recovered ethylenes, the isotope effects were found to be those given in Table 4 rather than those previously reported.⁴⁶

Tables 3 and 4 show the results obtained in the modified apparatus in which a one hundred-fold excess of thiophenol to styrene was used. These results show some correlation with the Hammett σ 's. (See appendix).

Tables 5 and 6 show the results in which α -toluenethiol and 2-mesitylenethiol respectively were reacted various olefins. These results roughly parallel those of thiophenol.

When speaking of the Hammett functions, it should be pointed out that we are looking at a difference in ρ 's rather than a true ρ value. This relationship is easily shown from the Hammett relationship in the following manner. If one labels the Hammett equation as to isotopic content, equations (30) and (31) result. Upon subtraction of equation

$$(30) \quad \ln k_{\text{H}}/k_{\text{H}}^{\circ} = \sigma\rho^{\text{H}}$$

$$(31) \quad \ln k_{\text{T}}/k_{\text{T}}^{\circ} = \sigma\rho^{\text{T}}$$

(31) from equation (30) and rearranging, one obtains equation (32).

$$(32) \quad \ln k_{\text{H}}/k_{\text{T}} = \sigma(\rho^{\text{H}} - \rho^{\text{T}}) + \text{constant}$$

If one plots $\ln k_H/k_T$ vs σ , the slope obtained will be $(\rho^H - \rho^T)$ as shown in Figure 10. This hypothetical plot encompasses a wide range of sigmas. Since ΔH approaches zero as the isotope effect reaches

Figure 10. Hypothetical plot of isotope effect values vs σ over a very wide range of σ values.

a maximum and $(\rho^H - \rho^T)$ also approaches zero at an isotope maximum, Figure 10 relates isotope effect to the exothermicity or endothermicity of the reaction. At the isotope maximum as shown by the solid and broken lines in Figure 10, the heat of the atom transfer step would become zero because $D_{C-H} - D_{S-H} = 0$. Any value above this maximum will have contributions other than complete loss of zero-point energy in the transition state. Any value below the minimum

will be due to some complication other than zero-point energy differences such as a rapid pre-equilibrium before the rate determining step which could cause an inverse isotope effect.

Referring back to Figure 10, consider the reaction of another mercaptan of different bond strength reacting with the same series of compounds. If this second mercaptan had a stronger bond strength, one would expect a higher isotope effect which also calls for a new k_H/k_T maximum. Pursuing this idea further, consider two symmetrical curves overlapping by some arbitrary amount shown in Figure 11. The degree of overlap can be contributed to energy differences between the bonds of the two mercaptans. The ordinate will be the isotope effect. The abscissa will be the bond energy of the new C-H bond since $\Delta H = D_{C-H} - D_{S-H}$.

From Figure 11, one obtains k_H/k_T for one thiol and another k_H/k_T for the second thiol at each value of (D_{C-H}) . If these values are plotted against one another, a plot such as Figure 12 will be obtained. By following this closed loop from the origin, one will be looking at the increasing or decreasing C-H bond strengths depending on which coordinate is chosen for the strongest thiol bond. Data in Table 8 has been subjected to this treatment resulting in Figure 13. These compiled results are corrected data from the earlier work⁴⁶ along with new data. As can be seen some points lie above or below the curve. It is known that these compounds undergo both ionic and free radical reactions, which have been confirmed in this work. Also, one of the substituted styrenes is below the curve and this can be contributed to ionic contributions such as in reaction (33), which contributes to increasing the rate and lowers the isotope effect. The reverse reaction in equation (34) lowers the isotope effect by incorporating more tritium into the adduct than is

Figure 11. Isotope effects vs bond energies of forming C-H bond.

Figure 12. Isotope effects obtained from figure 11.

Figure 13. Plot of data from table 8.

Table 8

Tritium Isotope Effects in the Addition
of R^1SH to $R^2R^3C=CH_2$ at 70.0° .

R^2	R^3	$(R^1 \text{ Ph})$ k_H/k_T	$(R^1 \text{ PhCH}_2)$ k_H/k_T
PhCH ₂	H	2.61	4.81
N-Carbazolyl	H	2.68	4.44
OAc	H	2.67	5.75
CO ₂ Me	H	3.89	8.04
CO ₂ Me	Me	4.42	9.75
CN	H	4.96 ^a	7.75 ^a
m-NO ₂ C ₆ H ₄	H	8.33	11.3
p-ClC ₆ H ₄	H	7.13	10.4
Ph	H	6.74	10.4
p-MeOC ₆ H ₄	H	6.59	9.43
p-ClC ₆ H ₄	p-ClC ₆ H ₄	8.93	8.13 ^d
Ph	Ph	10.9	
p-MeOC ₆ H ₄	p-MeOC ₆ H ₄	14.1	--- ^b
CH ₃ (CH ₂) ₅	H	4.46 ^c	6.73 ^c

^aThese isotope effects may be those for an ionic process rather than free radical. ^bNo product isolated; 1,1-di-p-anisylethylene was recovered. ^cAt 0° . ^dIt is assumed that no ionic exchange occurred since none was found in the thiophenol cases.

normal, thus lowering the isotope effect. Reaction (34) does not occur in the case of the styrene-thiophenol system. When this system was interrupted at approximately half completion the recovered styrene contained no excess tritium over background. Interrupting these reactions proved extremely difficult and only the styrene-thiophenol system proved successful.

If the idea that isotope effects are orderable in the manner suggested, it also seems that an added bonus to this idea is that any point lying greatly above or below the curve in Figure 13 is the result of either a different or competing mechanism, assuming that all other variables are constant.

The limited data presented does in fact show that the basics behind the idea of bond ordering are adhered to. However, for this idea to be more acceptable a series of compounds should be used and the mechanism of each should be fully understood.

Summary

There is a wide range of isotope effects in the hydrogen atom transfer in the olefin-thiol system. From this range of isotope effects, a qualitative method for bond ordering has been suggested which offers a possible mechanistic check for a given series of reactions.

Evidence for the tunneling phenomenon has been presented in the triphenylmethyl reaction with thiophenol and 2-mesitylenethiol. The large isotope effects in these reactions also indicates that the transition state is not very unsymmetrical.

The isolation of p-benzhydryltetraphenylmethane (II) from the reaction of thiophenol with 4-triphenylmethyl-1-diphenylmethylene-2,5-cyclohexadiene (I) adds more evidence to the now accepted structure of (I).

The most useful outcome of this investigation has been finding and overcoming the problems associated with the competitive method of obtaining isotope effects. Without knowing the pitfalls of this method, one can be lead to incorrect conclusions even though the incorrect data can be reproduced. In particular, the temperature problems encountered in this investigation leads one to consider a critical evaluation on any previously reported rate data or mechanistic studies done on similar systems.

Most of the time applied to this investigation was in the design, modifications and building of apparatus to overcome the problems encountered in the competitive method.

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APPENDIX

Physical Constants Obtained for Olefin-Thiophenol Adducts
 $(R_1R_2C=CH_2 + C_6H_5SH)$

R_1	R_2	<u>B. P. Sulfide</u>	<u>M. P. Sulfone</u>	<u>Spectral Data (Nmr)</u>
$m-CH_3CO_2C_6H_4$	H	-	84-5	τ 1.8-3.2 (m, 9 H), τ 6.4-7.2 (m, 4 H), τ 7.75 (s, 3 H).
$m-ClC_6H_4$	H	-	69.0	τ 1.8-3.1 (m, 9 H), τ 6.4-7.3 (m, 4 H).
$m-BrC_6H_4$	H	-	60.0	τ 1.7-3.0 (m, 9 H), τ 6.4-7.3 (m, 4 H).
$p-CNC_6H_4$	H	-	123.0	τ 1.9-2.9 (m, 9 H), τ 6.4-7.1 (m, 4 H).
$p-HOC_6H_4$	H	-	52-3	τ 1.8-3.3 (m, 9 H), τ 5.8 (s, 1 H), τ 6.4-7.3 (m, 4 H).
$p-FC_6H_4$	H	-	46-7	τ 1.8-3.2 (m, 9 H), τ 6.2-7.2 (m, 4 H).
$p-C_6H_5C_6H_4$	H	-	110.0	τ 1.9-2.9 (m, 14 H), τ 6.5-7.1 (m, 4 H).
$p-CH_3CH_2C_6H_4$	H	-	33.0	τ 1.8-3.1 (m, 9 H), τ 6.4-7.6 (m, 6 H), τ 8.6-9.0 (triplet, 3 H).

$p\text{-CH}_3\text{OC}_6\text{H}_4$	H	-	57-8	τ 1.9-3.3 (m, 9 H), τ 6.3 (s, 3 H), τ 6.5-7.3 (m, 4 H).
$p\text{-(CH}_3)_3\text{CC}_6\text{H}_4$	H	-	69.0	τ 1.9-3.1 (m, 9 H), τ 6.4-7.2 (m, 4 H), τ 8.7 (s, 9 H).
$p\text{-BrC}_6\text{H}_4$	H	-	105.0	τ 1.9-3.1 (m, 9 H), τ 6.4-7.2 (m, 4 H).
$p\text{-CH}_3\text{CO}_2\text{C}_6\text{H}_4$	H	-	96.0	τ 1.9-3.2 (m, 9 H), τ 6.4-7.2 (m, 4 H), τ 7.7 (s, 3 H).
$p\text{-HCC}_6\text{H}_4$	H	-	56-7.5	τ 2.1-2.8 (m, 10 H), τ 6.6-7.4 (m, 4 H).
$m\text{-NO}_2\text{C}_6\text{H}_4$	H	-	100-1	τ 2.0-2.9 (m, 9 H), τ 6.5-7.1 (m, 4 H).
$p\text{-ClC}_6\text{H}_4$	H	-	100-1	τ 1.9-3.1 (m, 9 H), τ 6.4-7.2 (m, 4 H).
$p\text{-CH}_3\text{C}_6\text{H}_4$	H	-	60.0	τ 1.8-2.9 (m, 9 H), τ 6.4-7.2 (m, 4 H), τ 7.7 (s, 3 H).
C_6H_5	C_6H_5	184/.5mm Hg	178-9	τ 2.1-2.9 (m, 15 H), τ 5.2-5.5 (triplet, 1 H), τ 6.0-6.2 (doublet, 2 H).
$p\text{-ClC}_6\text{H}_4$	$p\text{-ClC}_6\text{H}_4$	-	224-5	τ 2.4-3.6 (m, 13 H), τ 5.4-5.7 (triplet, 1 H), τ 6.1-6.3 (doublet, 2 H).

$p\text{-CH}_3\text{OC}_6\text{H}_4$	$p\text{-CH}_3\text{OC}_6\text{H}_4$	-	138-9	τ 2.4-3.6 (m, 13 H), τ 5.4-5.7 (triplet, 1 H), τ 6.1-6.3 (doublet, 2 H), τ 6.35 (s, 6 H).
OAc	H	99/2mmHg	-	τ 2.5-3.0 (m, 5 H), τ 5.8-6.1 (triplet, 2 H), τ 6.8-7.1 (triplet, 2 H), τ 8.1 (s, 3 H).
CO_2CH_3	H	111/0.7mmHg	-	τ 2.6-3.0 (m, 5 H), τ 6.4 (s, 3 H), τ 6.8-7.1 (triplet, 2 H), τ 7.3-7.7 (triplet, 2 H).
CO_2CH_3	CH_3	95/0.7mmHg	-	τ 2.5-2.9 (m, 5 H), τ 6.4 (s, 3 H), τ 6.5-7.5 (m, 3 H), τ 8.6-8.8 (doublet, 3 H).
CN	H	110/0.6mmHg	-	τ 2.5-3.0 (m, 5 H), τ 6.8-7.1 (triplet, 2 H), τ 7.4-7.7 (triplet, 2 H).
$\text{C}_6\text{H}_5\text{CH}_2$	H	139/0.5mmHg	-	τ 2.4-2.9 (m, 9 H), τ 6.9-7.5 (m, 4 H), τ 7.8-8.3 (m, 2 H).

N-Carbazolyl	H	67-8 (solid)	-	τ 1.9-3.1 (m, 13 H). τ 5.5-5.8 (triplet, 2 H), τ 6.8-7.1 (triplet, 2 H).
$\text{CH}_3(\text{CH}_2)_5$	H		165/0.5mmHg	τ 1.8-2.7 (m, 5 H), τ 6.7-7.2 (triplet, 2 H), τ 7.9-9.5 (m, 15 H).

Physical Constants Obtained for Olefin-2-Mesitylenethiol Adducts
($R_1R_2C=CH_2 + RSH$)

R_1	R_2	B. P. Sulfide	M. P. Sulfone	Spectral Data (Nmr)
$p-HC_6H_4$	H	150/0.5mmHg	88-9	τ 2.6-3.0 (m, 7 H), τ 6.4-7.1 (m, 4 H), τ 7.3 (s, 6 H), τ 7.7 (s, 3 H).
$p-CH_3OC_6H_4$	H	-	106-7	τ 2.7-3.3 (m, 6 H), τ 6.2 (s, 3 H), τ 6.5-7.2 (m, 4 H), τ 7.4 (s, 6 H), τ 7.7 (s, 3 H).
$p-HC_6H_4$	$p-HC_6H_4$	-	116	τ 2.8-3.2 (m, 12), τ 5.2-5.5 (triplet, 1 H), τ 6.0-6.2 (doublet, 2 H), τ 7.4 (s, 6 H), τ 7.8 (s, 3 H).
$p-ClC_6H_4$	$p-ClC_6H_4$	-	152-3	τ 2.7-3.1 (m, 8 H), τ 5.2-5.5 (triplet, 1 H), τ 6.1-6.2 (doublet, 2 H), τ 7.4 (s, 6 H), τ 7.7 (s, 3 H).

$\text{CO}_2 \text{CH}_3$	H	125/0.5mmHg	-	τ 3.1 (s, 2 H), τ 6.4 (s, 3 H), τ 6.9-7.7 (m, 4 H), τ 7.5 (s, 6 H), τ 7.8 (s, 3 H).
$\text{CO}_2 \text{CH}_3$	CH_3	127/0.5mmHg	-	τ 3.1 (s, 2 H), τ 6.4 (s, 3 H), τ 6.9-7.4 (m, 3 H), τ 7.5 (s, 6 H), τ 7.8 (s, 3 H), τ 8.6-8.8 (doublet, 3 H).
CN	H	38-9 (solid)	-	τ 3.1 (s, 2 H), τ 7.0-7.8 (m, 4 H), τ 7.5 (s, 6 H), τ 7.8 (s, 3 H).

Physical Constants Obtained for Olefin- α Tolueneethiol Adducts
 $(R_1R_2C=CH_2 + RSH)$

R_1	R_2	B. P. Sulfide	M. P. Sulfone	Spectral Data (Nmr)
$p\text{-HC}_6\text{H}_4$	H	135/0.6mmHg	-	τ 2.6-3.2 (m, 10 H), τ 6.4 (s, 2 H), τ 7.2-7.5 (m, 4 H),
$p\text{-CH}_3\text{OC}_6\text{H}_4$	H	165/0.6mmHg	-	τ 2.3-3.3 (m, 9 H), τ 6.3 (s, 2 H), τ 6.4 (s, 3 H), τ 6.6-7.7 (m, 4 H).
$m\text{-NO}_2\text{C}_6\text{H}_4$	H	-	131-2	τ 2.4-3.2 (m, 9 H), τ 6.4 (s, 2 H), τ 6.7-7.6 (m, 4 H).
$p\text{-ClC}_6\text{H}_4$	H	-	150-1	τ 1.9-3.1 (m, 9 H), τ 6.3 (s, 2 H), τ 6.4-7.2 (m, 4 H).
$p\text{-HC}_6\text{H}_4$	$p\text{-HC}_6\text{H}_4$	-	125-6	τ 2.3-3.2 (m, 15 H), τ 5.3-5.6 (triplet, 1 H), τ 6.2 (s, 2 H), τ 6.4-6.6 (doublet, 2 H).
$p\text{-ClC}_6\text{H}_4$	$p\text{-ClC}_6\text{H}_4$	-	144-5	τ 2.5-3.0 (m, 13 H), τ 5.2-5.6 (triplet, 1 H), τ 6.2 (s, 2 H), τ 6.3-6.5 (doublet, 2 H).

OAc	H	115-6/0.75mmHg	-	τ 2.7 (s, 5 H), τ 5.7-6.0 (triplet, 2 H), τ 6.3 (s, 2 H), τ 7.2-7.6 (triplet, 2 H), τ 8.1 (s, 3 H).
CO ₂ CH ₃	H	143-4/0.8mmHg	-	τ 2.7 (s, 5 H), τ 6.35 (s, 2 H), τ 6.4 (s, 3 H), τ 7.2-7.7 (m, 4 H),
CO ₂ CH ₃	CH ₃	114/015mmHg	-	τ 2.6 (s, 5 H), τ 6.3 (s, 2 H), τ 6.35 (s, 3 H), τ 7.0-7.6 (m, 3 H), τ 8.7-8.9 (m, 3 H).
CN	H	116-7/1.0mmHg	-	τ 2.7 (s, 5 H), τ 6.3 (s, 2 H), τ 7.2-7.7 (m, 4 H).
CH ₃ (CH ₂) ₅	H	124/0.5mmHg	-	τ 2.8 (s, 5 H), τ 6.4 (s, 2 H), τ 7.6-7.9 (triplet, 2 H), τ 8.3-9.5 (m, 15 H).
C ₆ H ₅ CH ₂	H	149/1.0mmHg	-	τ 2.6-3.0 (m, 10 H), τ 6.4 (s, 2 H), τ 7.2-8.4 (m, 6 H).

N-Carbazolyl	H	102 (solid)	-	τ 1.9-3.1 (m, 13 H), τ 5.6-5.9 (triplet, 2 H), τ 6.5 (s, 2 H), τ 7.2-7.5 (triplet, 2 H).
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Mass Spectra Data from Olefin-Thiol Adducts ($R_1R_2C=CH_2 + RSH$)

R_1	R_2	R_3	Mass of Molecular Ion (M/e) (calculated)	Molecular Ion Peak (measured)
C N	H	Ph	163.0455*	163.0429 -
$CH_3(CH_2)_6CH_2$	H	Ph	254.1339	254.1330 -
$CH_3(CH_2)_6CH_2$	H	PhCH ₂	236.1598*	236.1598 -
CO ₂ Me	H	Ph	-	196*
CO ₂ Me	CH ₃	Ph	-	210*
OAc	H	Ph	-	196*
PhCH ₂	H	Ph	-	228*
m-ClPh	H	Ph	280.0324	280.0328 -
p-ClPh	H	Ph	-	280
m-BrPh	H	Ph	325.9798	325.9873 -
p-BrPh	H	Ph	325.9798	325.9853 -
Ph	Ph	Ph	-	290*

(* Represents data on sulfides: Unmarked represents data on sulfones)

Figure 14. Plot of k_H/k_T vs Hammett σ 's for the reactions between thiophenol and several substituted styrenes at 0.0°