

**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reaction was then initiated by turning on the light, and in many cases the reaction was followed by loss of olefin in withdrawn samples by gas chromatography.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.<sup>7</sup> 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<sup>4</sup> 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%.

**Acknowledgment.** The support of this work by the Robert A. Welch Foundation is gratefully acknowledged.

## References and Notes

- (1) From the Ph.D. Thesis of M. M. Butler, Rice University, 1974. A portion was published in preliminary form: E. S. Lewis and M. M. Butler, *Chem. Commun.*, 941 (1971).
- (2) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).
- (3) R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y., 1973, p 265.
- (4) W. A. Pryor and K. G. Kneipp, *J. Am. Chem. Soc.*, **93**, 5584 (1971).
- (5) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y., 1960, p 57.
- (6) S. H. Wiley and E. L. Eliel, *J. Am. Chem. Soc.*, **80**, 3309 (1958).
- (7) E. S. Lewis and M. M. Butler, *J. Org. Chem.*, **36**, 2582 (1971).
- (8) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
- (9) E. S. Lewis and S. Kozuka, *J. Am. Chem. Soc.*, **95**, 282 (1973).
- (10) A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, **94**, 7390 (1972).
- (11) W. A. Pryor, W. H. Davis, Jr., and J. P. Stanely, *J. Am. Chem. Soc.*, **95**, 4754 (1973); R. W. Henderson and R. D. Ward, Jr., *ibid.*, **96**, 7556 (1974); W. A. Pryor and W. H. Davis, Jr., *ibid.*, **96**, 7557 (1974).
- (12) Reference 3, p 270.
- (13) T. Kametani, K. Fukumato, Y. Satah, T. Teshigawa, and O. Umezawa, *Bull. Chem. Soc. Jpn.*, **33**, 1678 (1960).

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

E. S. Lewis\* and K. Ogino<sup>1</sup>

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.  
Received June 6, 1975

**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<sub>6</sub>H<sub>5</sub>SH\* and RH\*. Azo compounds of the form (CH<sub>3</sub>)<sub>2</sub>CXN=NCX(CH<sub>3</sub>)<sub>2</sub> also yield RH by a disproportionation; in these cases *k*<sub>D</sub>/*k*<sub>T</sub> was measured after correction for contamination of RD\* by RH. In these examples, covering X = C<sub>6</sub>H<sub>5</sub>S, CH<sub>3</sub>OC(=O), N≡C, and C<sub>6</sub>H<sub>5</sub>, there was good correlation between *k*<sub>D</sub>/*k*<sub>T</sub> and *k*<sub>H</sub> (measured by others); both are related to the stability of the radical R·. The isotope effects are rather small. Aryl radicals, from Ar-N=NC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, were also studied. The values are quite small (*k*<sub>H</sub>/*k*<sub>T</sub> = 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,<sup>2</sup> 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.<sup>3</sup> Thus, for a single thiol, in a series of exothermic reactions, the isotope effect should fall monotonically as *D*<sub>RH</sub> increases. The radicals studied<sup>2</sup> were all those involved in the addition of mer-

captans 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<sub>3</sub>)<sub>2</sub>CXN=NCX(CH<sub>3</sub>)<sub>2</sub>.

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

nol with a tritium label, and comparing the activity of RH\* to that of C<sub>6</sub>H<sub>5</sub>SH\*. However, with AIBN and related compounds, there is a possible alternate source of unlabeled RH, which would lead to an apparent exaggeration of the isotope effect. This arises from the disproportionation reaction 1. The extent of this reaction (probably almost exclu-



sively a cage reaction) might be measured by the yield of the alternate product, methacrylonitrile, except that this will rapidly add thiol under these conditions, to give a rather difficultly determined product. We therefore chose an alternate way to avoid this complication. If the thiophenol used is mostly deuterated, but with a tritium label, the product of the desired reaction is (CH<sub>3</sub>)<sub>2</sub>CDCN, trace labeled with tritium. The disproportionation product is (CH<sub>3</sub>)<sub>2</sub>CHCN, and the amount of this can be determined in the product by an NMR analysis. The protium product is also formed from protiated thiophenol, contaminating the deuterated material, thus the yield of protiated product is only a high upper limit for the extent of disproportionation, and we chose therefore to ignore this figure.

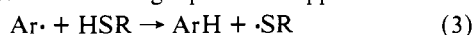
The specific activity of the material divided by the deuterium content is proportional to the tritium:deuterium ratio, and the isotope effect (with a large excess of thiophenol) is given by eq 2, in which  $a_M$  and  $a_P$  are the specific molar ac-

$$k_D/k_T = (a_M/f_D^M)/(a_P/f_D^P) \quad (2)$$

tivities of the thiol (mercaptan) and the product, respectively, and  $f_D^M$  and  $f_D^P$  are the fraction deuterated in the thiol and the product, respectively. The isotope effects found are presented in Table I. The table also presents in the third column the isotope effect  $k_H/k_T$ , calculated from the equation  $k_H/k_T = (k_D/k_T)^{3.262}$  from the equation of Swain and Schaad.<sup>4</sup> In the last column are the relative rates of thermal decomposition of these azo compounds, as given by Timberlake<sup>5</sup> and Ohno.<sup>6</sup>

It is seen that the rate and the isotope effect increase together, although the ordering of the middle two entries in isotope effect is fortuitous, for the experimental error is such that these two are not readily distinguished. Indeed the determination of isotope effects by this method is relatively difficult and tedious, and the accuracy is limited to perhaps  $\pm 3\%$  in  $k_D/k_T$ . The remainder of the isotope effects are concerned with the unsymmetrical azo compounds Ar-N=NC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

The results on derivatives of benzeneazotriphenylmethane are shown in Table II. In this work no disproportionation appeared likely, so that the isotope effects on reaction 3 were directly determined using eq 4 which applies when the



$$k_H/k_T = a_{\text{RSH}}/a_{\text{ArH}} \quad (4)$$

thiol is in large excess (in our cases  $>10\times$ ). In this equation  $a_{\text{RSH}}$  and  $a_{\text{ArH}}$  are the specific molar activities of the reagent RSH\*, and the product ArH. In all cases except where otherwise noted, the other products are triphenylmethane and RSSR. The activity of triphenylmethane might be thought to give the isotope effect in reaction 5, but in fact an isotope effect calculated as in eq 4 is nonreproducible and nearly always smaller than expected by extrapolation of the well-behaved region in a direct measurement of this effect<sup>7</sup> ( $k_H/k_T = 9.3$  calculated at 60 °C). This is exactly what could have been expected, for the reaction is reversible and the phenylthiyl radicals are not effectively scavenged by trityl radicals.<sup>7</sup> This reversal complicates any quantitative treatment of the triphenylmethane activities.



tion of the well-behaved region in a direct measurement of this effect<sup>7</sup> ( $k_H/k_T = 9.3$  calculated at 60 °C). This is exactly what could have been expected, for the reaction is reversible and the phenylthiyl radicals are not effectively scavenged by trityl radicals.<sup>7</sup> This reversal complicates any quantitative treatment of the triphenylmethane activities.

**Table I.** Isotope Effects for the Reaction of (CH<sub>3</sub>)<sub>2</sub>CX with Thiophenol at 103 °C

X	$k_D/k_T$	$k_H/k_T$	$k/k^0$ <sup>a</sup>
CH <sub>3</sub>			1
C <sub>6</sub> H <sub>5</sub> S	1.28	2.24	$6.62 \times 10^3$
CH <sub>3</sub> OC(=O)	1.42	3.14	$2.58 \times 10^5$ <sup>b</sup>
N≡C	1.45	3.36	$2.95 \times 10^5$
C <sub>6</sub> H <sub>5</sub>	1.50	3.75	$4.12 \times 10^6$

<sup>a</sup> Rate of azo compound decomposition relative to that of azo-*tert*-butane.<sup>5,6</sup> <sup>b</sup> The rate is that of the ethyl ester rather than the methyl ester.

**Table II.** Isotope Effects in Hydrogen Atom Transfer to Ar· from RSH at 60 °C

Ar	R	$k_H/k_T$	" $k_H/k_T$ " Ph <sub>3</sub> CH <sup>a</sup>
<i>p</i> -NO <sub>2</sub> Ph	Ph	1.93	9.85
	Ph	1.90	8.62
	Ph	1.99 <sup>b</sup>	9.44 <sup>b</sup>
<i>p</i> -BrPh	Ph	1.74	9.29
	Ph	1.76	7.04
Ph	Ph	1.66	7.36
	Ph	1.65	7.39
<i>p</i> -CH <sub>3</sub> Ph	Ph	1.63	7.42
	Ph	1.40	7.09
$\alpha$ -C <sub>10</sub> H <sub>7</sub>	Ph	1.43	7.49
	Ph	1.55 <sup>b</sup>	7.97
	Ph	1.56 <sup>b</sup>	7.97
$\beta$ -C <sub>10</sub> H <sub>7</sub>	Ph	1.41	7.11
<i>p</i> -NO <sub>2</sub> Ph	<i>p</i> -ClPh	2.08	9.19
<i>p</i> -ClPh	<i>p</i> -ClPh	1.94	7.01
	Ph	<i>p</i> -ClPh	1.84
$\alpha$ -C <sub>10</sub> H <sub>7</sub>	<i>p</i> -ClPh	1.63	7.02
<i>p</i> -O <sub>2</sub> NPh	<i>t</i> -Bu	3.08	c
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>t</i> -Bu	3.03	c
$\alpha$ -C <sub>10</sub> H <sub>7</sub>	<i>t</i> -Bu	2.75	c

<sup>a</sup> Calculated from the ratio of specific molar activity of thiol to that of triphenylmethane; the number is only a lower limit to the isotope effect. <sup>b</sup> Diluted with benzene. <sup>c</sup> The trityl radical is converted to trityl-*tert*-butyl sulfide, rather than triphenylmethane.

## Discussion

The results in Table I, which show the correlation between the isotope effect and the rate constant  $k_H$ , are entirely consistent with the suggestion of bond-energy isotope-effect correlation. As the radical gets more stable, the forming R-H bond is weaker and closer in dissociation energy to the breaking SH bond, and the transition state for the hydrogen abstraction gets more symmetrical. Thus radical stability is correlated both with ease of decomposition and larger isotope effect.<sup>8</sup> The values of the isotope effects are reasonably consistent with those of the earlier work,<sup>2</sup> but the isotope effects are smaller. This may represent a real difference, perhaps attributable to neighboring group stabilization of the radical by the  $\beta$  sulfur in the olefin addition results, or it may merely be an artifact of the larger experimental error in the current work, compounded by failure of the Swain-Schaad equation, which becomes less useful with small isotope effects.

The results of Table II introduce some new problems. Qualitatively it is still clear that these new forming C-H bonds are stronger than any in Table I, or in the earlier work.<sup>2</sup> Thus the isotope effects, smaller than any studied before, are in the range expected. Table II also shows some duplicate runs, as well as some from experiments with the solvent benzene, instead of thiol as the solvent as in most cases. It is clear that the reproducibility is good, with a de-

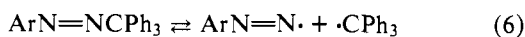
**Table III.** Relative Reactivities for Hydrogen and Chlorine Abstraction by Ar·

Ar·	$k_H/k_{Cl}$	Ar·	$k_H/k_{Cl}$
<i>p</i> -NO <sub>2</sub> Ph·	9.2 (9.3 <sup>a</sup> )	β-C <sub>10</sub> H <sub>7</sub>	1.05
Ph·	1.14 (1.08 <sup>b</sup> )	α-C <sub>10</sub> H <sub>7</sub>	1.03

<sup>a</sup> Reference 17. <sup>b</sup> Reference 16.

viation of <1% from the mean. These isotope effects are different from each other and from unity. Thus, although the hydrogen transfer reactions are probably very fast, they do not occur at every collision, otherwise the reaction rate would be diffusion controlled and the isotope effects would be unity. The possibility exists that the apparent isotope effects are moved closer to unity by close approach to the diffusion-controlled limit, and the variation is due to the remaining rate difference, but it seems improbable that there would be no unit isotope effects among this group which shows such a wide variation. Furthermore, in a different study, a highly exothermic hydrogen transfer with a low intermolecular isotope effect also shows a low intramolecular isotope effect, suggesting that neither process is diffusion controlled.<sup>9</sup> We shall therefore conclude that the low isotope effects imply a very small loss of zero-point energy and a very reagent-like transition state.

The experiments with benzene as a diluent were prompted by the observation that the substituent effects on the rates of decomposition of these azo compounds are unusual arising as much from entropy effects as activation energies.<sup>10</sup> This is understandable since the reaction occurs in two steps, rather than one single two-bond cleavage, as in reactions 6 and 7, for then the apparent first-order rate con-



stant (even if the radicals only combined within the cage) would depend on  $k_6$ ,  $k_{-6}$ , and  $k_7$ .<sup>11</sup> If in the thiols ArN=N· gives the diazene by reaction 8, and if this could



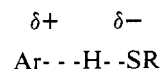
ultimately give ArH<sup>12</sup> by a route not passing through Ar·, then there would be two routes to ArH, possibly with different isotope effects. The intermediacy of the diazene is of course irrelevant if the diazene gives rise ultimately to the aryl radical. If the unimolecular reaction 7 were thus competing with the bimolecular reaction 8, dilution with an inert solvent would relatively favor reaction 7. Although there is a perceptibly but not conspicuously larger calculated isotope effect with the benzene diluent, there is an alternate explanation. A larger isotope effect can be calculated if some ArH gets its H from some source other than RSH. Benzene, although not highly reactive toward free radicals, does act as a H atom source in a reaction accompanying the arylation<sup>13</sup> (by way of the arylcyclohexadienyl radical), so even in the presence of thiols, the apparent increase in isotope effect may be only a manifestation of this familiar reaction. There is therefore no compelling evidence that the true isotope effect is importantly influenced by diluents. Because the effect of this diluent was so small, and because arene from the aryl diazene probably does arise from Ar· in dilute solution, this line was not pursued.

The substituent effects on the isotope effect, both in Ar and in R, are of interest. RS<sup>-</sup> contributions to the transition state must increase in the order *t*-BuS· < PhS· < *p*-ClPhS·, since this is the order of acidities of the thiols. This is not the order of the isotope effects in Table II which increase in

the order PhS· < *p*-ClPhS· < *t*-BuS·. The breaking HS bond dissociation possibly correlates better since the strongest bond is *t*-BuSH, followed by the two aromatic thiols. If we interpret the normally negative  $\rho$  for abstraction of H from toluene as a bond strength effect,<sup>14</sup> then the C-H bond in *p*-chlorotoluene is stronger than that in the parent compound. With this assumption, the bond strength order of *t*-BuSH > *p*-ClPhSH > PhSH and the order of isotope effects is simply another aspect of the symmetry effect. We shall criticize this interpretation after consideration of the Ar substituent effects.

The order *p*-NO<sub>2</sub>Ph· > *p*-ClPh· > Ph· > *p*-CH<sub>3</sub>Ph· > α- or β-C<sub>10</sub>H<sub>7</sub> for the isotope effects appears general for all thiols although supported only by one complete series with thiophenol. If this were entirely a CH bond strength order, this order would be the one of increasing CH bond dissociation energy of the corresponding ArH. These bond energies are not well known; Pryor<sup>3</sup> estimates  $D_{p\text{-NO}_2\text{Ph-H}}$  to be 4 kcal less than  $D_{\text{Ph-H}}$  in accord with our order, but the basis of his estimate is unclear. The rather unreliable use of the rate of decomposition of the arylazotriphenylmethanes to assign relative radical stabilities would make the *p*-NO<sub>2</sub>Ph· the least stable of the aryl radicals studied by Cohen and Wang;<sup>10</sup> activation energy arguments would, however, differ. It is more difficult to believe that the β-naphthyl-H bond is stronger than the phenyl-H bond, so we present an alternative argument in terms of polar effects.

We suggest that in addition to bond strength effects, which we cannot evaluate, there are polar effects in the transition state in the direction shown in 1. This direction is reasonable considering that the thiols are so much more



acidic than ArH. Then the contribution of structures of this polarity to the transition state can reasonably be expected to increase in the order *p*-NO<sub>2</sub>Ph· < *p*-ClPh· < Ph· < *p*-CH<sub>3</sub>Ph·. To the extent that the positive charge is delocalized in the aryl ring, the order Ph· < C<sub>10</sub>H<sub>7</sub>· is also reasonable.<sup>15</sup> There is need, however, for harder evidence than this suggestion of reason, so we have determined variation in polar character of hydrogen abstractions by the method of Bridger and Russell,<sup>16</sup> involving the determination of relative rates of H abstraction from cyclohexane and Cl abstraction from carbon tetrachloride. The results are presented in Table III. The results are in reasonable conformity with those of earlier measurements.<sup>16,17</sup> The fact that the  $k_H/k_{Cl}$  values fall in virtually the same order as the isotope effects in Table II, and also show a significant difference between phenyl and naphthyl, lends substance to the suggestion that the same factor, namely contribution of polar effects, is influencing both results.

The question of why increased contributions of polar structures reduces the isotope effect must be attacked. The simplest argument, and the one we believe to be the best, is that in these exothermic atom transfers, stabilization of the transition state by resonance makes these transition states even closer to the reagent in structure, and hence also less symmetric. An interesting corollary is therefore that anything that increases the energy of the transition state without a corresponding change in reagent or product will increase the isotope effect by making the transition state less reagent-like and hence less unsymmetrical. Steric hindrance is such a factor, and the increase in isotope effect in sterically hindered hydrogen transfers has now several examples. Among these, mesitylenethiol gives much higher isotope effects than thiophenol,<sup>2</sup> and proton transfers to 2,6-lutidine have higher isotope effects than to pyridine.<sup>18</sup> Con-

sideration of the potential energy surface in the neighborhood of the transition state as a quadratic surface leads not only to the prediction that steric hindrance will increase the isotope effect by decreasing mass-dependent transition state zero-point energy, but will correspondingly also increase the tunnel correction by increasing the imaginary frequency and its mass dependence.<sup>19</sup>

Although the results of Table III show that  $k_H/k_{Cl}$  are indeed variable, we cannot rigorously conclude that  $k_H$  itself suffers variation, and hence polar character, for it is conceivable (even if implausible) that all the variation lies in  $k_{Cl}$ . We must then reexamine the case for exclusively bond-energy effects, as suggested by Zavitsas.<sup>14</sup> Most of the evidence is based on the reactions of substituted toluenes, and two newer pieces of evidence contradict Zavitsas' suggestions. Tanner<sup>20</sup> and co-workers find that the substituent effect on the rate of abstraction of hydrogen from toluene by trichloromethyl radicals is incompatible with only a bond-energy effect, and more qualitatively convincing, the value of  $\rho$  for attack by tertiary<sup>21</sup> and secondary<sup>22</sup> radicals on toluene is positive, in contrast to the negative values for other radicals. If we are forced to accept polar contributions for abstractions from toluene, it would be unreasonable to ignore them in abstractions from thiophenol.

We conclude that the measurement of these hydrogen atom transfer isotope effects adds to our knowledge of the transition states usefully. The factors controlling the isotope effect are: (1)  $\Delta H_0$ , when  $\Delta H_0$  is small, the isotope effect is large; (2) polar transition state contributions, when these are substantial, exothermic reactions show unexpectedly low isotope effects; (3) steric hindrance, sterically hindered transition states show larger than expected isotope effects. A fourth factor, the nature of the atoms between which the hydrogen is transferred, will be discussed in a subsequent paper.

## Experimental Section

**Materials.** Thiophenol-*t* was made as described before.<sup>2</sup> Thiophenol-*d* was made by a repeated exchange, and by reductions of the disulfide in  $D_2O$ . Both methods gave material only about 90% deuterated; the problem apparently arose during a drying operation with a desiccant containing exchangeable protons. The method is not described in detail because of this difficulty. After tritium exchange, one sample contained  $89 \pm 1\%$  D (by NMR) and had  $4.055 \times 10^8$  dpm/mol. Oxidation gave diphenyl disulfide with a count rate showing that  $0.029 \times 10^8$  dpm/mol had not been on sulfur. Both *p*-chlorothiophenol and *tert*-butyl mercaptan were exchanged with tritiated water as described for thiophenol.<sup>2</sup>

**Azobis(2-phenylthio)-2-propane** was prepared following Benzing.<sup>23</sup> After recrystallization from methanol almost colorless crystals, mp 89–89.5 °C (uncorrected) (lit.<sup>23</sup> 90–90.5 °C), were obtained.

**Azobisisobutyronitrile (AIBN)** was a commercial product recrystallized from ether, mp 104–104.5 °C.

**Dimethyl Azobisisobutyrate.** The methanolysis of AIBN followed the method of Mortimer.<sup>24</sup>

**Azocumene** was kindly given to us by Mr. D. Bishop, of these laboratories.

The substituted areneazotriphenylmethanes were all prepared from the arylhydrazine and triphenylmethyl chloride, followed by oxidation. The aryltritylhydrazine preparation followed that of Cohen and Wang,<sup>8</sup> and the oxidation by hydrogen peroxide followed that of Bridger and Russell.<sup>16</sup> The oxidations of the *N*-*p*-nitrophenyl-*N'*-triphenylmethylhydrazine and the corresponding *p*-chlorophenyl compounds were better accomplished by addition of 1 equiv of bromine to an ethereal solution of the hydrazine.

**Isotope Effect Measurement with 2-Substituted 2-Azopropanes.** The methods were all essentially the same, varying only in the work-up which was sensitive to the product volatility. The experiment on azocumene is typical. Azocumene (0.59 g) was dissolved in 4.6 g of thiophenol-*d* (89% deuterated), trace labeled with tri-

tium ( $4.055 \times 10^8$  dpm/mol,  $3.998 \times 10^8$  dpm/mol on sulfur) and heated at  $102 \pm 1$  °C for 1 h. The time chosen for each compound was greater than 7 half-lives; this one is far too long. The solution was then poured into ice and water, and extracted with ether. The ether extract was washed three times with 5% aqueous sodium hydroxide, then with water, and dried over anhydrous magnesium sulfate. The solvent was removed and the residue distilled giving 135 mg of cumene, of >98.2% purity by gas chromatography. The <sup>1</sup>H NMR spectrum (60 MHz) showed that this was 63.3% deuterated, and counting gave a specific molar activity of  $1.889 \times 10^8$  dpm/mol.

The isotope effect is then given by eq 2, as shown in eq 9; the lin-

$$k_D/k_T = \frac{3.998 \times 10^8 \times 63.3}{1.889 \times 10^8 \times 89.3} = 1.50 \quad (9)$$

ear approximation<sup>25</sup> is justified by the ca. 20-fold excess of thiophenol. The reduction in extent of deuteration is in part due to an isotope effect in the atom transfer, and in part due to product contamination by ordinary cumene from the cage reaction. If there were no cage reaction in the isotope effect  $k_H/k_D$  would be about 4.8 (assuming the linear approximation). Applying the Swain-Schaad equation to the  $k_D/k_T$  gives  $k_H/k_D = 2.5$ , and if this were the true isotope effect, then the figures can be reconciled if about 15% of the cumene was formed by cage disproportionation. This number is very high since an estimate of cage recombinations<sup>26</sup> together with the known fraction of disproportionation<sup>26</sup> comes to only about 2% cumene expected. The uncertainties in this calculation are however large. The other cage product,  $XCH_3C=CH_2$ , was not isolated. It presumably would be converted to the thiophenol addition product that escaped isolation.

The residue from the distillation, when worked up, yielded diphenyl disulfide.

In several cases the NMR analysis for deuterated content was checked by a mass spectral analysis at low ionization potential. The results were in good agreement, corresponding to  $\pm 2\%$  in the isotope effect, with no apparent systematic difference.

**Isotope Effects with Substituted Benzeneazotriphenylmethanes.** A typical determination with the unsubstituted compound is described. Benzeneazotriphenylmethane (1.46 g,  $4.18 \times 10^{-3}$  mol) was dissolved in tritium-labeled thiophenol (11.51 g,  $1.05 \times 10^{-1}$  mol,  $4.97 \times 10^8$  dpm/mol) and heated with stirring at  $60 \pm 1$  °C for 4 h. A stream of nitrogen was passed continuously through the solution and then through a dry ice trap. The contents of the dry ice trap were treated with chromium trioxide and iodine to destroy residual mercaptan, dried with magnesium sulfate and distilled. The benzene yield (about 85 mg, 26%) was 97.9% pure by gas chromatography with specific molar activity (corrected for impurity) of  $2.983 \times 10^8$  dpm/mol. The low yield almost certainly is a handling problem rather than a problem of stoichiometry.

The less volatile contents of the reaction vessel were poured into 5% sodium hydroxide solution, extracted with ether, and the ether extract was further washed with sodium hydroxide solution and then water. The ether extract was then dried over magnesium sulfate and the solvent was removed. On addition of methanol crystals formed, and recrystallization yielded triphenylmethane: mp 92.5–93.5 °C; specific activity  $6.74 \times 10^7$  dpm/mol. Thus the isotope effect for benzene formation is  $k_H/k_T = 1.66$ , that for triphenylmethane calculated from this experiment is 7.36, and there is no important side reaction such as abstraction of the aromatic hydrogens by the phenyl radicals, as shown by the very small activity of the recovered diphenyl disulfide,  $1.07 \times 10^6$  dpm/mol.

The same procedure was used for the *p*-tolueneazotriphenylmethane, but for the others with less volatile products, the nitrogen stream and dry ice trap were omitted, and the entire reaction mixture was partitioned between 5% sodium hydroxide and water, and then distilled. Yields of these less volatile compounds were somewhat better (up to 77% for nitrobenzene). Naphthalene was recrystallized from ether after distillation.

**Relative Reactivities of Cyclohexane and Carbon Tetrachloride Toward Aryl Radicals.** The procedure followed that of Bridger and Russell,<sup>16</sup> and the analyses were all by gas chromatography. Six determinations were done on the unsubstituted compound, yielding an average value of 1.14 for  $k_H/k_{Cl}$ , with a standard deviation of 0.05. Thus the result is not significantly different from the earlier one, with  $k_H/k_{Cl}$  given as 1.08.<sup>16</sup>

**Acknowledgment.** We acknowledge gratefully support of this research by a grant from the Robert A. Welch foundation.

## References and Notes

- (1) Robert A. Welch Foundation postdoctoral fellow, 1973-74.
- (2) E. S. Lewis and M. M. Butler, submitted; see also E. S. Lewis and M. M. Butler, *Chem. Commun.*, 941 (1971).
- (3) W. A. Pryor and K. G. Kneipp, *J. Am. Chem. Soc.*, **93**, 5584 (1971).
- (4) C. G. Swain, E. G. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).
- (5) J. W. Timberlake and M. H. Hodges, *Tetrahedron Lett.*, 4147 (1970).
- (6) A. Ohno, Y. Ohnishi, and N. Kito, *Int. J. Sulfur Chem., Part A*, **1**, 151 (1971).
- (7) E. S. Lewis and M. M. Butler, *J. Org. Chem.*, **36**, 2582 (1971).
- (8) Strictly the rate of the thermolysis of the azo compound is related to  $D_{RN}$ , whereas the isotope effect depends on  $D_{RH}$ , and C. Rüchardt (*Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970)), points out that these may not be parallel. This does not appear to be a case with difficulties of this sort.
- (9) E. S. Lewis and K. Ogino, unpublished work.
- (10) (a) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953); (b) M. G. Alder and J. E. Leffler, *ibid.*, **76**, 1425 (1954).
- (11) Several pieces of evidence point to the perceptible stability of aryl-diazonyl radicals. The diazonium salts  $ArN_2^+$  give a reversible wave on reduction in the polarograph (R. M. Eloffson and F. F. Gadallah, *J. Org. Chem.*, **34**, 854 (1969)), and some aryl allyl azo compounds give a rearranged product apparently of cage recombination still retaining the nitrogen (J. H. Done, J. H. Knox, R. McEwen, and J. T. Sharp, *J. Chem. Soc., Chem. Commun.*, 532 (1974)). W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92**, 5403 (1970), deduce from viscosity-rate relations that the arylazotriphenylmethanes are one-bond cleavage initiators, a conclusion also reached from the pressure dependence (R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972)) and from the nature of the CIDNP signal of the product (K.-G. Seifert and F. Gerhart, *ibid.*, 829 (1974)).
- (12) Aryl diazenes do give ArH, but the radical  $Ar\cdot$  is probably the usual intermediate: P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2367 (1968).
- (13) S. H. Wilen and E. L. Eliel, *J. Am. Chem. Soc.*, **80**, 3309 (1958).
- (14) A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, **94**, 7390 (1972).
- (15) However, the stabilities of the undelocalized aryl cations, as revealed by the rates of hydrolysis of diazonium ions which pass through a transition state strongly resembling the aryl cation (E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Am. Chem. Soc.*, **91**, 419 (1969); H. Zoltinger, *Acc. Chem. Res.*, **6**, 335 (1975); L. Klasinc and D. Schulte-Frohlinde, *Z. Phys. Chem. (Frankfurt am Main)* **60**, 1 (1968)) do not follow this reasonable suggestion, for both naphthyl derivatives react somewhat more slowly than the phenyl (D. F. DeTar and S. Kwong, *J. Am. Chem. Soc.*, **78**, 3921 (1956); D. Schulte-Frohlinde and H. Blume, *Z. Phys. Chem. (Frankfurt am Main)*, **59**, 268 (1969)).
- (16) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3954 (1963).
- (17) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Am. Chem. Soc.*, **88**, 1189 (1966).
- (18) The earliest report is L. Funderburk and E. S. Lewis, *J. Am. Chem. Soc.*, **86**, 2531 (1964).
- (19) E. S. Lewis, "Isotopes in Organic Chemistry", Vol. 2, E. Bunce and C. C. Lee, Ed., Elsevier, in press.
- (20) D. D. Tanner, R. J. Arhart, E. V. Blackburn, N. C. Das, and N. Wada, *J. Am. Chem. Soc.*, **96**, 829 (1974).
- (21) W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Am. Chem. Soc.*, **95**, 4754 (1973).
- (22) R. W. Henderson, *J. Am. Chem. Soc.*, **97**, 213 (1975).
- (23) E. Benzing, *Justus Liebigs Ann. Chem.*, 631, 1 (1960).
- (24) G. A. Mortimer, *J. Org. Chem.*, **30**, 1632 (1965).
- (25) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y., 1960, p 57.
- (26) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966); **88**, 143 (1966); S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).

## Isotope Effects in Hydrogen Atom Transfer. VII. Benzylic Hydrogen Abstraction by *tert*-Butoxy and Other Radicals

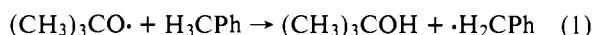
E. S. Lewis\* and K. Ogino

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.  
Received June 6, 1975

**Abstract:** Chlorination of toluene by *tert*-butyl hypochlorite involves the attack of *t*-BuO $\cdot$  on the benzylic hydrogen; isotope effects can be measured by comparing the activity of the product *t*-BuOH with that of PhCH<sub>3</sub>-*t*. At 40 °C,  $k_H/k_T = 11.5$ ; substituted toluenes give similarly rather large values of  $k_H/k_T$ , which increase slightly with  $\sigma$ . In contrast, Cl $\cdot$  attack gives  $k_H/k_T = 3.7$ , in rough agreement with earlier deuterium effects. Literature values for the isotope effect in the nearly equally exothermic attack by CH<sub>3</sub> $\cdot$  and the more exothermic attack by C<sub>6</sub>H<sub>5</sub> $\cdot$  are closer to the *t*-BuO $\cdot$  value than to the Cl $\cdot$  value. Earlier large values of isotope effect in bromination are confirmed with tritium. Secondary effects of tritium in the *t*-BuO $\cdot$  attack were measured, and are undetectable. It is postulated that the symmetry effect on the isotope effect is important only when one of the elements flanking hydrogen in the transition state is in the second row or beyond.

Earlier papers<sup>1</sup> in this series have considered the isotope effect in hydrogen atom transfers as it is influenced by bond dissociation energy or  $\Delta H$  factors, which show, in agreement with Pryor and Kneipp,<sup>2</sup> that large isotope effects are associated with near zero values of  $\Delta H$ . Extension to the much more exothermic reactions of aryl radicals with thiols showed the expected very small isotope effects, but also showed small substituent effects which were most easily interpreted in terms of a polar transition state.<sup>3</sup> We now concern ourselves with hydrogen atom transfers between carbon and other elements, especially with the transfer to the *tert*-butoxy radical.

Toluene is chlorinated by *tert*-butyl hypochlorite in a radical chain reaction where we shall be concerned with step 1. Various methods can in principle be used. The use of



tritium as the hydrogen isotope puts further limitations on the methods that can be used; for example, Wiberg and Slauch<sup>4</sup> measured an intramolecular isotope effect by chlorinating PhCHD<sub>2</sub> or PhCH<sub>2</sub>D, and determining the D content of the benzyl chloride. With trace label tritium the T content of the benzyl chloride is virtually independent of the primary isotope effect until the extent of chlorination is quite large, and the method is quite unsuitable, especially since dichlorination can occur at large conversions. We determined the T content of the Me<sub>3</sub>COH, avoiding problems of exchange and adsorption by dilution with a large excess of water, and counting the water solution. This method does not count methane derived from methyl radicals from the decomposition of the *tert*-butoxy radicals, since it is not water soluble. It does count HCl, which is the product from the chlorine atom chain which sometimes accompanies reaction 1 in the hypochlorite reaction. We therefore added