Hydrogen Isotope Effect in the Reaction of Trityl Radicals with Thiophenol[1]

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Received February 8, 1971

Excess thiophenol reacts at room temperature with 4-triphenylmethyl-1-diphenylmethylene-2,6-cyclohexadiene (I) to produce triphenylmethane and phenyl triphenylmethyl sulfide. At -20 and $-40°$, *p*-benzhydryltetraphenylmethane (II), an isomer of I, is also formed. When tritium is present in the SH position, both triphenylmethane and II are labeled, and an isotope effect for the hydrogen transfer from sulfur to carbon is found with $k_H/k_T = 14.9$. Between 0 and 40°, the temperature dependence of the isotope effect is normal, but the measured isotope effect is apparently too low both at high temperatures (60°) and low (-20 and $-40°$). An explanation is offered for the high-temperature deviation in terms of failure of the competitive method. We attribute low-temperature deviations to reversibility. An extremely rough estimate of the rate of this nearly thermoneutral hydrogen atom transfer, $k = 1\ M^{-1}\ \text{sec}^{-1}$, is presented.

The nature of the potential energy surfaces in hydrogen transfer reactions are of much interest, and hydrogen isotope effects have contributed to the knowledge of these surfaces. In proton transfers, it is clear that the solvent is intimately involved and may be the only source of the barrier.[2] Hydrogen atom transfers, on the other hand, seem to have significant barriers even in the gas phase, some of which have been calculated with more or less precision.[3] Isotope effects of a magnitude which require the existence of a barrier have also been observed.[3] The limitations of gas-phase methods, primarily those of volatility, have led us to initiate a systematic study of isotope effects in hydrogen atom transfer in solution, with the idea that the solvent effects will be less important than in the ionic proton transfers. In the transfer of hydrogen from sulfur to carbon, the isotope effects are far larger in the reaction reported here than in the reactions with less stable radicals.[4]

Results and Discussion

When a toluene solution of "hexaphenylethane," 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene[5] (I), in equilibrium with triphenylmethyl radicals, was added with good stirring to a tenfold excess of thiophenol, allowed to stand for 10 half-lives for the dissociation process,[6] and then worked up, triphenylmethane and trityl phenyl sulfide were found. Diphenyl disulfide would have been found by the separation procedure used, but was not found.[7]

We propose the mechanism indicated by reactions 1, 2, and 3. We find no evidence of an induced decomposition of I, which agrees with the absence of attack of nitric oxide or iodine atoms,[6,8] but does not agree with the chain process involving attack by tritylperoxy radicals.[9] However, as described later on, only a rather fast induced reaction is rigorously excluded.

$$\text{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(C_6H_5)_3C\cdot \tag{1}$$

$$(C_6H_5)_3C\cdot + C_6H_5SH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (C_6H_5)_3CH + C_6H_5S\cdot \tag{2}$$

$$(C_6H_5)_3C\cdot + C_6H_5S\cdot \xrightarrow{k_3} C_6H_5SC(C_6H_5)_3 \tag{3}$$

With the use of $C_6H_5S^3H$, the relative specific activities of the triphenylmethane and the thiophenol, which is present in substantial excess, then gives[10] the isotope effect on k_2, neglecting for the moment the reverse reaction. These measured effects are given in Table I for various reaction temperatures. The third column is the value of the isotope effect calculated from eq 4, which fits better than any other the range 0–40°. No Arrhenius equation fits all the points satisfactorily.

TABLE I

ISOTOPE EFFECTS MEASURED BY SPECIFIC ACTIVITY RATIOS FOR REACTIONS 2 AND 4

Temp, °C	k_H/k_T[a]	k_H/k_T calcd[b]	k_H/k_T[c]
-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	

[a] Measured isotope effect for triphenylmethane formation. Each entry represents an average of at least two runs agreeing within ±0.3 [b] Calculated from eq 4. [c] Measured isotope effect for formation of compound II.

$$k_H/k_T = 0.187 \exp(2590/RT) \tag{4}$$

We attribute the failure of the Arrhenius equation 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 rate. Hence the thiophenol is locally depleted, and the assumption of a large excess of thiophenol fails.

The apparently low isotope effects at the lower temperatures can be attributed to neglect of the reversal of reaction 2. When the steady-state concentration of trityl radicals is high, nearly all phenylthiyl radicals are scavenged by reaction 3, but at the lowest temperatures the trityl radical concentrations are drastically

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[1] This work was supported by a grant from the Robert A. Welch Foundation. It was presented in part at the fall meeting of the National Academy of Sciences in Houston, Texas, 1970.

[2] See, for example, C. D. Ritchie, *J. Amer. Chem. Soc.*, **91**, 6749 (1969).

[3] Several examples of semiempirical calculations are given in H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.

[4] E. S. Lewis and M. M. Butler, unpublished work.

[5] H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); P. Jacobson, *Chem. Ber.*, **38**, 196 (1905).

[6] K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas, *Justus Liebigs Ann. Chem.*, **551**, 150 (1942).

[7] Although disulfides react with triphenylmethyl to yield trityl sulfides [H. Lecher, *Ber.*, **48**, 524 (1915)], this reaction appears to require a higher temperature. See also W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.*, **86**, 1150 (1964).

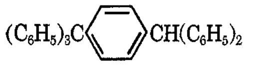
[8] K. Ziegler, L. Ewald, and P. Orth, *Justus Liebigs Ann. Chem.*, **479**, 277 (1930).

[9] K. Ziegler and L. Ewald, *ibid.*, **504**, 162 (1933). It is interesting to note that this induced reaction is much easier to understand in terms of the structure I, than in terms of the hexaphenylethane structure.

[10] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p 58.

reduced, enabling the thiyl radicals to abstract hydrogens, as they are known to do readily.[11] The effect of this reverse reaction (which will of course also have a large isotope effect) will be to reduce the isotope effect measured by the activity of the triphenylmethane, in the limit (which we do not approach) 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*-benzhydrylphenyltriphenylmethane (II). This substance, an isomer of I, cannot result from an intramolecular isomerization, for it contains tritium derived from the thiophenol. We suspect the mechanism of eq 5 and 6, and calculate an isotope effect



II

$$\mathrm{I} + \mathrm{C_6H_5S\cdot} \longrightarrow p\text{-}(\mathrm{C_6H_5})_3\mathrm{CC_6H_4\dot{C}(C_6H_5)_2} + \mathrm{C_6H_5SH} \quad (5)$$

$$p\text{-}(\mathrm{C_6H_5})_3\mathrm{CC_6H_4\dot{C}(C_6H_5)_2} + \mathrm{C_6H_5SH} \longrightarrow \mathrm{II} + \mathrm{C_6H_5S\cdot} \quad (6)$$

for its formation as shown in the last column of Table I. The closely similar isotope effects suggest a closely similar process, as reactions 2 and 6 certainly are. Compound II has been obtained before from I by an acid-catalyzed process,[12] 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.

Finally, we may conclude from the large value of the isotope effect itself that the reaction is not very unsymmetrical, and therefore it has an approximately equal barrier in both directions. The value at 25° of $k_H/k_T = 14.8$ is slightly larger than would be calculated for complete loss of zero-point energy of a harmonic stretching vibration (ν 2575 cm^{-1}) of a typical SH bond, $k_H/k_T = 11.5$. We might be tempted to attribute the observed higher value to tunneling, especially in view of the low pre-exponential factor in eq 4,[13] but this also suggests a rather symmetric barrier, since tunneling itself seems most associated with symmetric barriers.[14] We do not believe that our data are unequivocal evidence for tunneling, but suggest that they do indicate a rather symmetric barrier.

It is of course even more valuable in defining the potential surface of reaction 2 to measure the rate rather than the isotope effect. Our experiments do not allow us to do this with any precision, but one result casts light upon this problem. When the experiment was performed at 0°, it was noted that the color of the trityl radical decreased sharply upon addition of a solution of I to a solution of thiophenol. However, there was still a perceptible color which persisted for several half-lives[6] of the dissociation of I, but the color was not detectable after 10 half-lives. This is the basis of the statement above that there does not appear to be any important induced decomposition of I, but it also allows a very rough estimate of k_2. If we neglect reactions 5 and 6 and the reverse of 2, the steady-state concentration of trityl radicals (T·) can be calculated from eq 7,

$$(\mathrm{T\cdot}) = \frac{-2k_2(\mathrm{C_6H_5SH}) + \sqrt{[2k_2(\mathrm{C_6H_5SH})]^2 + 4k_1k_{-1}(\mathrm{I})}}{2k_{-1}} \quad (7)$$

in which k_1 and k_{-1} are known.[6] If we (rather arbitrarily) assume that perceptible color is one-tenth the color of a solution of I in equilibrium with trityl radicals, then this equation can be solved for k_2, giving the value $k_2 = 1\ M^{-1}\ \mathrm{sec}^{-1}$, which is probably within a few orders of magnitude. This can be compared to the value $k = 60$, estimated from the literature on propagation rates and chain transfer constants for the reaction of radicals in polymerizing styrene with *tert*-butyl mercaptan at 0°.[15] The numbers are close enough so that little can be said about the comparison. It is interesting, however, that the method could in principle be used for measuring k_2 with good precision, although we have not undertaken this experimentally difficult problem.

Experimental Section

Apparatus.—The apparatus used was a single unit consisting of three flasks connected in series by appropriate ground-glass joints. 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, 24/40 two-neck 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 flasks two and three. One of these 90° bends contained a large bore vacuum stopcock. 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.

Tritium-Labeled Thiophenol.—Reagent grade thiophenol (500 g), 2 g of tritium-enriched water (1 mCi/g), and 5 g of calcium oxide were placed in a 1-l. 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.

Counting Procedures.—Weighed samples 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 about 40 min. 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. Four samples of thiophenol gave an average specific activity of 4.13×10^8 decompositions min^{-1} mol^{-1} with an extreme deviation of less than 3%.

Location of Tritium Label 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.

Exchange between Thiophenol and Triphenylmethane.—Thiophenol (20 ml, 0.19 mol) (specific activity = 4.13×10^8 decompositions min^{-1} mol^{-1}), 1.5 g (0.006 mol) of reagent grade triphenylmethane, and 0.05 g of azobisisobutyronitrile were placed in a 50-ml flask fitted with reflux condenser and drying tube and then heated at 80° for 18 hr. The mixture was cooled, dissolved

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[11] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959).

[12] F. Ullmann and W. Borsum, *Ber.*, **35**, 2877 (1902); see also A. E. Tschitschibabin, *ibid.*, **37**, 4709 (1904).

[13] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 211.

[14] R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

[15] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 95, 153.

in ether, washed with 5% sodium hydroxide, and dried over anhydrous sodium sulfate. After evaporation of the ether, the triphenylmethane was recrystallized twice from ethanol. Two samples of the triphenylmethane were counted and found to have a specific activity of 1.34 × 10^7 decompositions min^{-1} mol^{-1}. The melting point of the recrystallized triphenylmethane was 93-94°.[16]

4-Triphenyl-1-diphenylmethylene-2,5-cyclohexadiene (I).—Mercury (20 g, 0.1 mol) was added to a solution of 5.78 g (0.021 mol) of triphenylchloromethane in 250 ml of dry toluene in the first flask, following with minor modification the procedure of Gomberg.[17] The system was closed, degassed three times, and allowed to react at 20° for 12 hr with vigorous stirring.

Reaction of Triphenylmethyl with Thiophenol.—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 mol) of tritium-labeled 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° and allowed to attain thermal equilibrium. Compound I was then added dropwise through the stopcock to the thiophenol–toluene solution, which was magnetically stirred.

Isolation of Triphenylmethane, Trityl Phenyl Sulfide, and *p*-Benzhydryltetraphenylmethane (II).—The reaction mixture was washed with 5% sodium hydroxide and dried over anhydrous sodium sulfate. Toluene was removed by distillation, counted, and found to have no tritium. A 3 ft × 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 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 remaining compounds. Only at −25 and −15° were any other compounds found. At these low temperatures compound II was found, as shown by its melting point, 226–227° (lit.[18] mp 227°), and mixture melting point and nmr (singlet, τ 4.45, 1 H; multiplet, τ 2.60–3.00, 29 H). The triphenylmethane had mp 93–94°, and the nmr showed a singlet at τ 4.66 (1 H) and another singlet at τ 3.02 (15 H). Trityl phenyl sulfide had mp 100–101° (lit.[7] mp 105–106°), and the nmr showed a singlet at τ 3.15 (5 H) and a multiplet between τ 2.50 and 3.10 (15 H). No attempt was made to determine the exact yields since purity of the products was our main goal. The isolated yields of purified triphenylmethane at −25.0, −15.0, 0.0, 25.0, 40.0, and 60.0° were 14.0, 40.0, 58.0, 73.0, 82.0, and 90.0%, respectively. The isolated yields of recrystallized II at −25.0 and −15.0° were 24.0 and 22.0%, respectively. The low total yields at the lower temperatures do not represent incomplete reaction, for ditrityl peroxide would have been produced on work-up and is easily detected. We attribute the low yields merely to the difficulty of separating triphenylmethane and compound I.

Registry No.—II, 3416-63-5; triphenylmethane, 519-73-3; trityl phenyl sulfide, 16928-73-7.

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[16] W. R. Orndorff, R. C. Gibbs, S. A. McNulty, and C. V. Shapiro, *J. Amer. Chem. Soc.*, **49**, 1543 (1927).

[17] M. Gomberg and C. S. Schoepfle, *ibid.*, **39**, 1659 (1917).

[18] W. Schlenk, E. Marcus, *Ber.*, **47**, 1665 (1914).

Kinetics of the Reaction of Some Trialkyl Phosphites with Benzil

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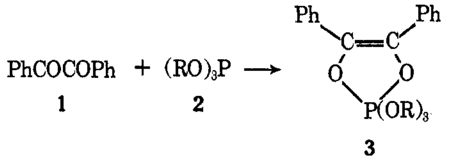
Received October 22, 1970

The effect of substituents on the reaction rates of trialkyl phosphites $[(RO)_3P]$ with benzil has been studied. The rate constant, k, in the rate equation, $v = k[(RO)_3P][PhCOCOPh]$, increases with the change of R in the order of methyl, ethyl, and isopropyl, while a little change of k is observed with R of *n*-propyl, *n*-butyl, *n*-amyl, *n*-octyl, and *sec*-butyl, and the k value decreases by substitution of 2-methoxyethyl for methyl. The relative rates fit the Taft equation, $\log (k/k_0) = -3.28\,\sigma^* + 0.40\,E_s + 0.03$. Both polar and steric effects affect the rate with R of C_nH_{2n+1} ($n \geqq 3$), while polar effect alone is dominant with R of methyl and ethyl. The correlation between the ^{31}P nmr chemical shift relative to $(CH_3O)_3P$, $\Delta\delta\ ^{31}P$, and the relative reaction rate or Taft's σ^* value is discussed. These facts present an additional support for our previous mechanism involving a nucleophilic attack of the phosphorus atom on the carbonyl carbon.

In our previous papers,[1-3] kinetics of the reaction of trialkyl phosphite with benzil and substituted benzils favored a mechanism involving a nucleophilic attack of a phosphorus atom of phosphite on a carbonyl carbon atom of benzil, which is similar to a mechanism proposed by Litt for aliphatic α diketones.[4]

The present paper deals with the kinetic study on the reaction of a number of trialkyl phosphites (**2**) with benzil (**1**) forming substituted 1,3,2-dioxaphospholes (**3**) (eq 1) to clarify the effect of substituents at phosphorus atom. The rate was measured by means of uv spectrophotometry.[5-7]



(1)

Results

The reaction of a number of trialkyl phosphites (**2**) with benzil (**1**) proceeds quantitatively at room temperature to yield 2,2,2-trialkoxy-4,5-diphenyl-1,3,2-dioxaphospholes (**3**). The rate was measured by means of ultraviolet spectrophotometry of the product **3**.

Rate Law. –The rate was measured in dioxane at 20.0, 25.0, 30.0, and 35.0°. The rate law is expressed

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[1] Y. Ogata and M. Yamashita, *J. Amer. Chem. Soc.*, **92**, 4670 (1970).

[2] Y. Ogata and M. Yamashita, *Tetrahedron*, in press.

[3] Y. Ogata and M. Yamashita, *ibid.*, in press.

[4] A. D. Litt, Ph.D. Thesis, Rutgers University, 1968.

[5] (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105*a* (1959); (b) V. A. Kukhtin and K. M. Orekhova, *Zh. Obshch. Khim.*, **30**, 1208 (1960); *Chem. Abstr.*, **55**, 358*h* (1961); (c) V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *ibid.*, **32**, 2333 (1962); *Chem. Abstr.*, **58**, 9127*g* (1963); (d) K. M. Kirillova and V. A. Kukhtin, *ibid.*, **32**, 2338 (1962); *Chem. Abstr.*, **58**, 9128*c* (1963).

[6] (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963); (c) F. Ramirez, N. Ramanthan, and N. B. Desai *ibid.*, **84**, 1317 (1962); (d) F. Ramirez, N. Ramanthan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (e) F. Ramirez, A. V. Patwardhan, N. Ramanthan, N. B. Desai, C. V. Greco, and S. R. Heller, *ibid.*, **87**, 543 (1965).

[7] (a) G. H. Birum and J. L. Dever, U. S. Patent 2,961,455 (1960); *Chem. Abstr.*, **55**, 8292*g* (1961); (b) G. H. Birum and J. L. Dever, U. S. Patent 3,014,949 (1961); *Chem. Abstr.*, **56**, 10191*a* (1962).