J = 7 Hz), 1.215 (3 H, t, J = 7 Hz); IR of **28** (CCl_4) 1755 cm^{-1}, NMR of **29** ($CDCl_3$) δ 7.8–7.2 (5 H, m), 4.35–3.75 (4 H, m), 2.814 (1 H, d, J = 6 Hz), 2.014 (3 H, d, J = 15.3 Hz), 1.281 (3 H, t, J = 7 Hz), 1.182 (3 H, t, J = 7 Hz), NMR of **30** ($CDCl_3$) δ 7.74–7.64 (2 H, m), 7.42–7.28 (3 H, m), 4.15–3.84 (3 H, m), 3.76–3.61 (1 H, m), 2.286 (3 H, d, J = 15.7 Hz), 1.298 (3 H, doublet of triplets, J = 7.1, 0.5 Hz), 1.145 (3 H, doublet of triplets, J = 7.1, 0.5 Hz).

Acetolysis of Trifluoroacetate 35. A solution of 128 mg of **35** in 8 mL of HOAc was heated at 100 °C for 6 h. A standard workup gave 105 mg (95%) of acetate **18b** which was identical with a sample prepared by acetylation of **15** (R = $CH_3SC_6H_4$) with acetic anhydride in pyridine and the product of acetolysis of mesylate **10b**. NMR ($CDCl_3$) δ 7.6–7.1 (4 H, AA′BB′ quartet), 6.18 (1 H, d, J = 17 Hz), 4.4–3.8 (4 H, m), 2.47 (3 H, s), 2.15 (3 H, s), 1.24 (6 H, overlapping doublet of triplets).

Acetolysis of Mesylate 38. Reaction of 101 mg of **38** in 9 mL of HOAc at 40 °C for 16 h gave, after a standard workup with Na_2CO_3 washing, 85 mg (97%) of PhCH(OAc)CSOMe (**43**), identical with a sample prepared by acetylation of **42** (R = Ph, R′ = H) with acetic anhydride. NMR ($CDCl_3$) δ 7.7–7.3 (5 H, m), 6.21 (1 H, s), 4.05 (3 H, s), 2.16 (3 H, s).

Acetolysis of Mesylate 39. Reaction of 80 mg of **39** in 5 mL of HOAc at 50 °C for 14 h gave, after a standard workup with Na_2CO_3 washing, 59 mg (89%) of a mixture of **48** and **49** in a 61:39 ratio as determined by NMR. Samples of each product were isolated by preparative G.C. NMR of **48** ($CDCl_3$) δ 4.093 (3 H, s), 2.049 (3 H, s), 1.669 (6 H, s); IR of **48** (CCl_4) 1745 cm^{-1}; NMR of **49** ($CDCl_3$) δ 3.735 (3 H, s), 2.276 (3 H, s), 1.578 (6 H, s); IR of **49** (CCl_4) 1743, 1694 cm^{-1}.

Acetolysis of Mesylate (*R*)-(−)-38. Reaction of 369 mg of (*R*)-(−)-**38**, $[\alpha]^{24}{}_{D}$ −15.9°, in 27 mL of 0.05 M NaOAc in HOAc for 6 h 40 min at 40 °C gave, after a workup as described above, with $NaHCO_3$ washing, 295 mg of crude acetate. This product was chromatographed on 13 g of silica gel and eluted with 5% ether in Skelly F. The yield of chromatographed (*R*)-(−)-**43** was 269 mg (85%), $[\alpha]^{24}{}_{D}$ −15.7° (*c* 2.5, CH_2Cl_2). In a run using (*R*)-(−)-**38** with $[\alpha]^{24}{}_{D}$ −22.5°, acetolysis gave (*R*)-(−)-**43** with $[\alpha]^{24}{}_{D}$ −22.0°.

Preparation of (*R*)-(−)-43. A mixture of 249 mg of (*R*)-(−)-**42**, $[\alpha]^{24}{}_{D}$ −52.4°, 210 mg of acetic anhydride, and 0.2 mL of CH_2Cl_2 was stirred at room temperature, and 2 drops of a mixture of 78 mg of H_2SO_4 in 0.35 mL of acetic acid was added. After 2.5 h at room temperature, the mixture was taken up into ether and washed with water and saturated NaCl solution, and dried over $MgSO_4$. After solvent removal using a rotary evaporator, the residue was chromatographed on 15 g of silica gel which gave 297 mg (93%) of (*R*)-(−)-**43**, $[\alpha]^{24}{}_{D}$ −29.3° (c 3, CH_2Cl_2). The NMR spectrum was identical with that of the racemic material. A sample of (*R*)-(−)-**43** in pyridine at room temperature racemized over a period of 18 h. A sample of (*R*)-(−)-**43** in 0.1 M NaOAc in HOAc, after 16 h at 40 °C and 5 days at room temperature, showed a rotation decrease of 10%.

Kinetic Procedures. Rates of most substrates in HOAc were measured using the titrimetric procedures previously described.[1a,b,21] Rates of **10a** and **10b** in HOAc were measured spectrophotometrically by monitoring the absorbance decrease at 257 and 280 nm, respectively. Injection of 15 μL of a solution of the appropriate mesylate in ether into 3 mL of HOAc initiated the kinetic run. Rates of acetolyses of the trifluoroacetates **12** and the *O*-phosphoryl analogue were monitored by gas chromatography using biphenyl as an internal standard using a procedure analogous to that previously described. Methanolysis rates of **10a**, **10b**, and *p*-$MeOC_6H_4CH(OMs)PO(OEt)_2$ were measured spectrophotometrically at 250, 284, and 248 nm, respectively. Rates of reaction of **10e** in ethanol, trifluoroethanol, and formic acid were measured titrimetrically by using previously described procedures. In formic acid and TFE, aliquots were quenched in cold HOAc and rapidly titrated. The rate of **10e** in 97% HFIP was measured spectrometrically at 223 nm.

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Kinetic Isotope Effects in Hydrogen Atom Transfer Reactions between Benzylic Carbons

Bradley C. Bockrath,* Edward W. Bittner,[†] and Thomas C. Marecic

U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania 15236

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The kinetic deuterium isotope effect for transfer of hydrogen from tetralin, dihydroanthracene, fluorene, diphenylmethane, triphenylmethane, and acenaphthene to the benzyl radical was measured at 170 °C. The range of values for the effect was from 6.5 to 8.0. Activation energy parameters were obtained for five of the hydrogen donors. The apparent difference between activation energies for deuterium or hydrogen transfer was ≥2 kcal/mol for triphenylmethane, diphenylmethane, and tetralin. Applications of several tests indicate that a tunnel effect plays a significant role in these hydrogen transfers.

The transfer of a hydrogen atom from a donor to an organic free radical is a fundamental reaction of widespread interest. A particular example is the transfer from a benzylic donor to the benzyl radical. The mechanistic details of such reactions are of special interest because both donor and acceptor are resonance-stabilized at the transition state. The absolute rate for hydrogen transfer must then be heavily influenced by the extensive bond deformations required to achieve resonance stabilization at both benzylic sites.

Kinetic deuterium isotope effects have frequently been used to probe the character of transition states. Jackson and O'Neill measured the deuterium isotope effect for transfer between toluene and benzyl radical.[1] They reported k_H/k_D = 6.7 at 168 °C and suggested that substantial tunneling can account for the large magnitude of

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[†] Department of Chemistry, The Pennsylvania State University, McKeesport, PA 15132.

(1) Jackson, R. A.; O'Neill, D. W. *J. Chem. Soc., Chem. Commun.* **1969**, 1210–1211.

the effect. In earlier work,[2] we measured the isotope effect, $k_H/k_D = 3.9$, for hydrogen transfer from triphenylsilane to benzyl radical at 170 °C. This value is larger than might be expected on the basis of zero-point energy arguments and thus provided further indication that a careful search for a tunnel effect would be worthwhile. Associated cases in which tunnel effects have been documented include the transfer of hydrogen from silane to trifluoromethyl radical,[3] from thiophenol to tris(*p*-*tert*-butylphenyl)methyl radical,[4] and from toluene to triplet diphenylcarbene.[5]

A careful study has also just been completed of rates of hydrogen abstraction by *o*-allylbenzyl radical.[6] This radical is closely related to the benzyl radical used here. The method used by Franz et al.[6] to obtain the isotope effect and the method reported here are different. Isotope effects were measured for hydrogen transfer from diphenylmethane and fluorene in both studies. The values determined by each group for the isotope effects and the derived activation parameters are very similar for these donors.

In the work described below, a method for determination of deuterium kinetic isotope effects for transfer of hydrogen from various donors to benzyl radical was developed. The method is a simple adaptation of one used previously to measure the relative rate constants for hydrogen transfer to benzyl radical from a series of donors.[2] Kinetic isotope effects were measured for six benzylic donors of different structural type. Large effects were found in all cases. The response of the effect to reaction temperature varied considerably among the different compounds. These results support the suggestion of Jackson and O'Neill[1] and imply that tunneling makes a substantial contribution to the rate of hydrogen transfer between two resonance-stabilized carbon centers.

Results and Discussion

Kinetic deuterium isotope effects were determined by using a method similar to that employed to determine relative rate constants for hydrogen atom transfer from various donors to benzyl radical.[2] The source of benzyl radical was the thermal decomposition of dibenzylmercury. In all cases, the thermolyses were run long enough to completely consume the dibenzylmercury according to a calculation using published rate data[7] for the half-life of the decomposition. In most cases, the decompositions were run in mixtures of the hydrogen donor compound and its deuterated form. In a few cases naphthalene was used as a solvent.

The reactions leading to toluene are given in Scheme I.

Scheme I

$$\mathrm{PhCH_2HgCH_2Ph} \rightarrow \mathrm{2PhCH_2\cdot} + \mathrm{Hg} \quad (1)$$

$$\mathrm{PhCH_2\cdot} + \mathrm{RH} \rightarrow \mathrm{PhCH_3} + \mathrm{R\cdot} \quad (2)$$

$$\mathrm{PhCH_2\cdot} + \mathrm{RD} \rightarrow \mathrm{PhCH_2D} + \mathrm{R\cdot} \quad (3)$$

$$\mathrm{PhCH_2\cdot} + \mathrm{R'H} \rightarrow \mathrm{PhCH_3} + \mathrm{R'\cdot} \quad (4)$$

Competition for benzyl radical by the hydrogen donor, RH, and deuterium donor, RD, determines the relative amount of deuterated toluene formed. This amount is mostly controlled by the relative rates of reactions 2 and 3. These rates depend on the amounts of hydrogen and deuterium donor added to the system. Reaction 4 represents formation of toluene from all other sources of hydrogen in the system and is generally of minor consequence. Hydrogen transfer from radicals formed during the reaction is unlikey to have a significant effect because benzylic radicals have a strong tendency to combine rather than disproportionate. For example, the published value for the disproportionation–recombination rate ratio for the reaction of benzyl radical with tetralyl radical is only 0.021 at 150 °C.[8] With use of this value and the amount of benzyltetralin found among the products in the present experiments, it is estimated that less than 1% of the toluene is formed as a result of disproportionation reactions.

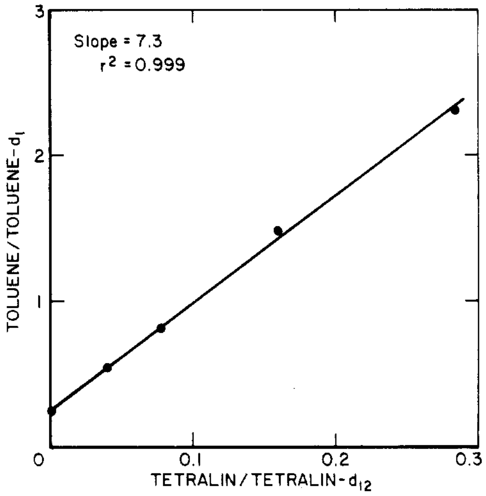
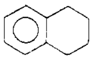
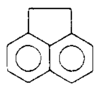
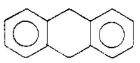
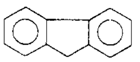
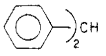
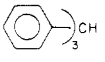


Figure 1. Measurement of the kinetic isotope effect for transfer of hydrogen from tetralin to benzyl radical at 170 °C.

Table I. Kinetic Deuterium Isotope Effects Measured at 170 °C for Hydrogen Transfer to Benzyl Radical

donor	k_H/k_D	donor	k_H/k_D
	7.3		8.0
	6.5		
	7.8		7.1
			7.7 ± 0.1[a]

[a] Average of three independent measurements and standard deviation.

Under pseudo-first-order conditions where there is a large excess of hydrogen and deuterium donors over dibenzylmercury, the rate law for appearance of toluene leads to eq 5. Dibenzylmercury was decomposed in a series of

$$\frac{[\mathrm{PhCH_3}]}{[\mathrm{PhCH_2D}]} = \frac{k_2[\mathrm{RH}]}{k_3[\mathrm{RD}]} + \frac{k_4[\mathrm{R'H}]}{k_3[\mathrm{RD}]} \quad (5)$$

reactors, each containing a different ratio of [RH]/[RD]. The amount of RD was held constant in each series. The deuterium kinetic isotope effect, k_2/k_3, was taken to be the slope of the line obtained by plotting $[\mathrm{PhCH_3}]/[\mathrm{PhCH_2D}]$ vs. [RH]/[RD]. Such a plot is shown for tetralin and tetralin-d_{12} in Figure 1. Similar plots using five different ratios of [RH]/[RD] were made for the other donors at various temperatures from 110 to 170 °C. In all cases the

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(2) Bockrath, B.; Bittner, E.; McGrew, J. *J. Am. Chem. Soc.* **1984**, *106*, 135–138.

(3) Jakubowski, E.; Sandhu, H. S.; Gunning, H. E.; Strausz, O. P. *J. Chem. Phys.* **1970**, *52*, 4242–4248.

(4) Colle, T. H.; Lewis, E. S. *J. Am. Chem. Soc.* **1979**, *101*, 1810–1814.

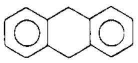
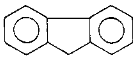
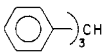
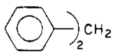
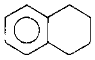
(5) Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 6494–6501.

(6) Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Naushadali, K. S. *J. Org. Chem.*, following paper in this issue. We are indebted to J. A. Franz for sharing these results and his critical comments with us before publication.

(7) Jackson, R. A.; O'Neill, D. W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 509–511.

(8) Manka, M. J.; Stein, S. E. *J. Phys. Chem.* **1984**, *88*, 5914–5919.

Table II. Apparent Deuterium Kinetic Isotope Activation Parameters

	$\Delta E_a^D - \Delta E_a^H$ kcal/mol	A_H/A_D	rel reactivity[a]	reactn enthalpy,[b] kcal/mol
	0.7 ± 0.4[c]	3.1 (4.8, 2.0)[d]	9.3	-13
	1.0 ± 0.25	2.4 (4.4, 1.3)	2.2	
	2.0 ± 0.5	0.76 (1.4, 0.4)	1.2	-10
	2.3 ± 0.6	0.51 (1.0, 0.26)	0.27	-7
	3.0 ± 0.8	0.24 (0.62, 0.09)	0.28	-3

[a] Rate constant per hydrogen relative to triphenylsilane-*d* at 170 °C. Data from ref 2. [b] Values estimated from bond dissociation energies given in ref 8. [c] Uncertainty is based on twice the standard deviation of the slope. An estimate of uncertainty was used for fluorene because the three data points lay very close to the best straight line. [d] Values in parentheses indicate upper and lower limits of uncertainty calculated from twice the standard deviation of the intercept, which gives the value of ln (A_H/A_D).

data were well described by a linear relationship of the form of eq 5.

Isotope effects determined at several temperatures for six donor compounds are gathered in Table I. The compounds were selected to determine the sensitivity of the magnitude of the isotope effect to the structure of the donor. Two of the donors are hydroaromatic compounds. The rest have active benzylic sites with various amounts of resonance stabilization energy available to the transition state and various degrees of freedom of motion available to the adjacent phenyl groups.

The occurrence of tunneling in elementary transfer reactions is well recognized as a quite general phenomenon.[9] Several criteria are used to determine those cases where a tunneling effect may play a role. Examination of the kinetic isotope effect is often invaluable because the likelihood of tunneling is strongly related to the mass of the particles in motion at the transition state. The relative magnitude of the isotope effect is often a primary indication that tunneling may be significant. Indeed, at first inspection, the most arresting feature of the data in Table I is that the kinetic isotope effects are larger than might be expected based on the usual assumptions of the classical analysis. In this analysis, the C–H stretching vibration of the donor is transformed into the motion of hydrogen transfer in the transition state. The maximum difference in activation energy between hydrogen and deuterium transfer is taken to be the difference in zero-point energies for bond stretching of the C–H and C–D bonds of the donors. From the frequencies of the appropriate infrared absorption bands, this difference is approximately 1.1 kcal/mol for the donors in question. Assuming the preexponential factors are equal, this difference in activation energy amounts to a maximum expected isotope effect of 3.4 at 170 °C and 4.2 at 110 °C. Thus, for all compounds at all temperatures investigated, the observed isotope effects exceed what might be expected based on simple zero-point energy arguments.

The argument above rests on expected differences in activation energy. A sensible test then is to measure the activation energy difference directly by measuring the isotope effect as a function of temperature. This additional information has also often proved useful as a diagnostic for bent transition states involving C–H bending modes rather than the simple stretching mode usually considered for linear transition states.[10] Temperature-independent isotope effects are associated with bent transition states for hydrogen transfer. In the present case, the isotope effects are clearly not independent of temperature.

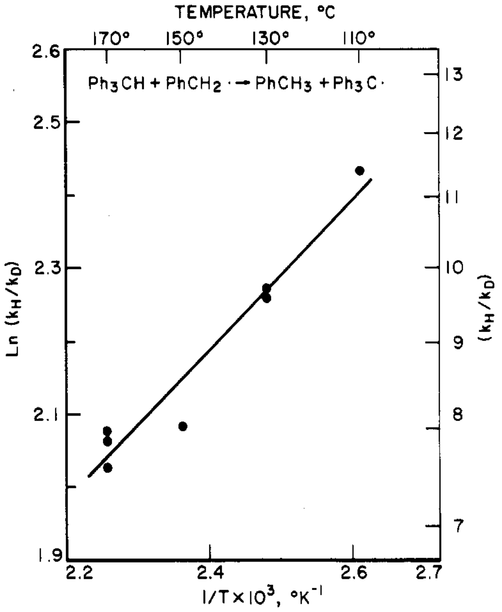


Figure 2. Arrhenius-like plot for the kinetic isotope effect for transfer of hydrogen from triphenylmethane to benzyl radical. From the data, $\Delta E_a^D - \Delta E_a^H = 2.0$ kcal/mol and $A^H/A^D = 0.76$.

An Arrhenius-type plot for the isotope effect for triphenylmethane is shown in Figure 2. Data derived from this and similar plots are gathered in Table II. The range of temperatures covered extended from 110 to 170 °C for all compounds except fluorene, for which it is 130 to 170 °C. The highest effect observed, $k_H/k_D = 13.0$ at 110 °C, was that for tetralin. It is quite evident that there is an effect of temperature on the kinetic isotope effect and that it depends strongly on the structure of the donor compound. For three of the five compounds, the difference in apparent activation energies exceeds 1.1 kcal/mol. These values are clearly above the maximum to be expected on the grounds of classical zero-point energy arguments. Two compounds fall near or below the 1.1 kcal/mol limit. The latter result does not preclude tunneling. However, for fluorene and dihydroanthracene, the large magnitude of the isotope effect remains the primary evidence that a modest tunneling correction factor is necessary.

The derived ratios of preexponential factors, A_H/A_D, are also informative. The values for tetralin and diphenylmethane are below 0.7. The latter value is taken as the lower limit of values that can be reasonably ascribed to processes undergoing strictly classical transfer.[9] Also, the

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(9) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London, 1980.

(10) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401–408.

value for triphenylmethane is near this limit. The values for fluorene and especially that for dihydroanthrecene are unexpectedly high for systems requiring modest tunnel corrections, even considering the relatively high degree of uncertainty associated with this measurement.

Data obtained earlier[2] for the relative reactivity of the donors is also given in Table II along with estimated reaction enthalpies. Comparison of apparent activation energy differences with reactivity data is interesting. Both within the series of fused-ring compounds and between the two methanes, smaller activation energy differences are associated with more reactive donors. Among a group of reactions with very similar transition states, the tunneling correction factor should decrease with decreasing barrier height. It is not possible to directly compare tunneling correction factors here because they are not available from measurement of just the isotope effect. Nonetheless, it is evident that the differences in activation energy between deuterium and hydrogen transfer become smaller as the reactions become more exothermic. This is in accord with a smaller tunnel effect in those cases with a lower activation energy barrier.

In a few experiments, an inert solvent was added to the reaction mixture. Measured values of isotope effects did not change on addition of *tert*-butylbenzene, a solvent used in earlier studies.[2] For example, in the absence of solvent, the isotope effect for triphenylmethane at 170 °C was measured in two experiments as 7.8 and 7.6. When the same compositions were made up with *tert*-butylbenzene to a constant volume about threefold larger, the isotope effect was again 7.8. In a similar comparison, an approximate fivefold dilution with naphthalene was made in an experiment with acenaphthene. In the absence of solvent, the isotope effect was 8.0 at 170 °C. In the presence of naphthalene, it was 7.95. The case for tetralin was somewhat different. In the absence of solvent, isotope effects were 13.0, 9.9, 9.1, and 7.3 at 110, 130, 150, and 170 °C, respectively. With a fivefold dilution with naphthalene, the same series of values was 13.9, 10.7, 9.4, and 7.95. A search of the reaction products obtained in naphthalene was made by gas chromatography for additional hydrogen donors. The amount of the benzyltetralins found was even less than when naphthalene was not used. The amount of benzylnaphthalene formed was negligible. Thus, the small increase in isotope effect observed in naphthalene is not due to the formation of benzylated compounds during the course of the experiment that could serve as more reactive hydrogen donors than tetralin. In any case, the differences are 9% of the value or less in all cases and do not affect the arguments given in the discussion. The activation energy difference given in Table II, 3.04 kcal/mol, is derived from the former data. The experiments with solvent lead to virtually the same value, 3.03 kcal/mol. The ratio of preexponential factors, A_H/A_D, was 0.23 without and 0.25 with solvent.

The fact that a moderate tunneling correction must be considered as a part of the overall rate constant for transfer of hydrogen from donors such as triphenylmethane to benzyl radical must be rationalized with other known facts about this reaction. In earlier work,[2] a linear correlation with a slope of 0.54 was found between the logarithms of relative rates of transfer and the resonance stabilization energies for a series of related benzylic donors, including triphenylmethane. Certainly, the latter fact indicates that the Ph–C–Ph bond angles of triphenylmethane must deform during hydrogen transfer in order to develop resonance stabilization energy. On the other hand, the fact that tunneling is a significant factor in this transfer indicates that the mass in motion along the reaction coordinate must be rather small.

To reconcile these opposing conditions, we propose that the two motions are not synchronous but occur in two stages. In the first stage, the resonance energy available to triphenylmethane is developed through the deformation of the Ph–C–Ph bond angles with the umbrella-like motion of the massive phenyl substituents. In the second stage, the hydrogen atom is transferred between the two benzylic carbons while each maintains a hybridization of considerable sp^2 character that preserves resonance stabilization energy. Dewar has recently discussed the concept of two-stage reactions that are concerted by not synchronous.[11] It is also pertinent that the hybridization of the carbon atom at the end of a breaking or forming bond need not be directly related to the strength or length of that bond.[12] An example given is the attack of methyl radical on ethylene.[12] In the transition state of this reaction, the methyl carbon is rehybridized to near-tetrahedral geometry, while the ethylenic carbon retains mostly sp^2 character. Thus, the most stable bonding situation is maintained for both the developing CC bond and the breaking π bond. In the case of the hydrogen transfer, this same principle is expressed by a transition state in which the benzylic carbons at both the origin and terminus of hydrogen transfer have close to sp^2 hybridization simultaneously.

Experimental Section

Materials. Dibenzylmercury was recrystallized from ethanol before use. The six hydrogen donors were all obtained from Aldrich Chemical Co. Tetralin was passed over a column of alumina just before use. All of the hydrogen donors were determined to be greater than 98.5% pure by capillary gas chromatography. Tetralin-d_{12} (Aldrich, 99 atom % D) and acenaphthene-d_{10} (Columbia Organic Chemicals, >99 atom % D) were used as received. Triphenylmethane-d, mp 92.2–93.6 °C, was prepared by the reduction of triphenylmethyl chloride by lithium aluminum deuteride (Aldrich, >98 atom % D) in refluxing ether. The crude product was recrystallized from hexanes. The deuterium content was greater than 98% by NMR spectroscopy. Diphenylmethane-d_2 was prepared by the reduction of dichlorodiphenylmethane by lithium aluminum deuteride in refluxing ether. The reaction mixture was quenched with saturated sodium sulfate in D_2O, dried, filtered to remove insoluble salts, stripped of ether, and vacuum-distilled to recover the pure product. The deuterium content was estimated to be greater than 99% D by NMR. Fluorene-d_2 and 9,9,10,10-dihydroanthracene-d_4 were prepared by exchange of the acidic protons in dimethyl-d_6 sulfoxide (Aldrich, 99.9 atom % D). The compounds were dissolved in a tenfold excess of Me_2SO-d_6, and an equivalent amount of sodium metal was added. After being stirred at 70–75 °C for 1 day, the mixtures were quenched with a twofold molar excess of acetic acid-d_1. The crude product was recovered by addition of D_2O and filtration. Purified product was obtained by elution from an activated alumina column with hexane. The column was first preconditioned with D_2O. Without this precaution, a considerable amount of deuterium was lost from fluorene on passing through the column. The deuterium content was increased by a second pass through the exchange procedure with Me_2SO-d_6. The final deuterium content was greater than 98% D for dihydroanthracene and greater than 99% D for fluorene.

Measurement of Isotope Effects. The method follows closely that published earlier.[2] All materials were loaded into a microreactor made from $^1/_2$ in. by 2 in. stainless-steel threaded unions fitted with Swagelok caps. In a typical experiment, 0.21 g (1.45 mmol) of tetralin-d_{12} was loaded in each of five reactors along with 0.02 g (0.053 mmol) of dibenzylmercury. Tetralin was added

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to four of the reactors in the amounts of 0.058, 0.114, 0.231, and 0.478 mmol. The closed reactors were immersed in a thermostatic oil bath held at 170 °C for 20 h. Products were washed from the reactors with *tert*-butylbenzene. Capillary gas chromatographic analysis of the products confirmed that the ratios of tetralin to tetralin-d_{12} remained essentially unchanged over the course of the reaction. In this analysis, tetralin was cleanly separated from tetralin-d_{12}. Toluene was isolated from the reaction mixture using preparative packed-column gas chromatography and collected in glass-wool-packed U-tubes immersed in a dry ice/acetone bath. The ratio of toluene to toluene-d_1 was determined by measuring the relative intensities at masses 92.0626 and 93.0689 with a Kratos MS-50 high-resolution mass spectrometer at an ionizing voltage of 70 eV with resoltuion of at least 1:50 000. The method was shown to be precise and accurate by analyzing samples collected from the gas chromatography of authentic toluene-α-d, of known deuterium content. High resolution is necessary to separate the peaks due to toluene and toluene-d, from close lying neighbors. In the spectrometer, the parent ions decompose to form tropylium ion. Monodeuteriotropylium ion has a mass of 92.0608. The parent ion of toluene containing natural abundance ^{13}C has a mass of 93.0659. The results of this experiment are plotted in Figure 1. Experiments at lower temperatures required longer reaction times for complete decomposition of dibenzylmercury. At 110 °C, the time allowed was 67 days.

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Absolute Rate Constants for Hydrogen Atom Abstraction by Benzyl Radical from Thiophenol, Tributylstannane, Tributylstannane-*d*, and Dicyclohexylphosphine and for the Cyclization of the 2-Allylbenzyl Radical[1]

James A. Franz,* Naushadali K. Suleman, and Mikhail S. Alnajjar

Pacific Northwest Laboratory, Richland, Washington 99352

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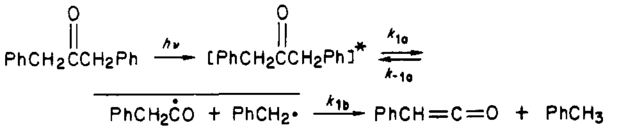
Absolute rate constants for the abstraction of hydrogen atom from thiophenol, tributylstannane, and tributylstannane-*d* in hexane and tributylstannane and dicyclohexylphosphine (DCPH) in cyclohexane were determined by competition of the abstraction reaction of benzyl radical, produced by the photolysis of dibenzyl ketone, with self-termination using termination rate constants of Fischer et al. in cyclohexane. For tributylstannane in cyclohexane, $\log (k_{abs}/M^{-1}\ s^{-1}) = (8.647 \pm 0.172) - (5.584 \pm 0.238)/\theta$, and for DCPH, $\log (k_{abs}/M^{-1}\ s^{-1}) = (8.001 \pm 0.184) - (6.278 \pm 0.26)/\theta$, $\theta = 2.303RT$ kcal/mol. A rate expression for benzyl radical termination in hexane was developed by combining values of $k_{abs}/(k_t)^{1/2}$ from the competition of benzyl abstraction from Bu_3SnH vs. termination using the values of k_{abs} obtained in cyclohexane. The resulting expression for self-termination of benzyl in hexane, $\ln (2k_t/M^{-1}\ s^{-1}) = (25.98 \pm 0.36) - (1803.58 \pm 199.4)/RT$, is in satisfactory agreement with the termination rates predicted by using the Smoluchowski equation for rate control by translational diffusion ($\ln (2k_t) = 26.53 - 2065.6/RT$). For benzyl in hexane, values of $k_{abs}/(k_t)^{1/2}$ combined with the experimental expression for termination gave, for reaction with thiophenol, $\log (k_{abs}/M^{-1}\ s^{-1}) = (8.273 \pm 0.180) - (3.790 \pm 0.24)/\theta$ and, for the reaction of benzyl and tributylstannane-*d*, $\log (k_{abs}/M^{-1}\ s^{-1}) = (8.712 \pm 0.410) - (6.155 \pm 0.56)/\theta$. Relative rate expressions (k_{re}/k_{abs}) for the cyclization of the 2-allylbenzyl radical vs. abstraction from tributylstannane, thiophenol, and DCPH were combined with the absolute rate expressions for abstraction from these donors to give, for the cyclization of 2-allylbenzyl radical to 2-indanylmethyl radical, the expression $\log (k_{re}/s^{-1}) = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$.

The photolysis of dibenzylketone provides a convenient source of benzyl radicals for the study of hydrogen abstraction from reactive hydrogen donors. The excited singlet state of dibenzyl ketone precedes the shorter lived triplet state[2] leading to teh phenylacetyl–benzyl geminate cage pair (eq 1).



$$PhCH_2C(=O)CH_2Ph \xrightarrow{h\nu} [PhCH_2C(=O)CH_2Ph]^* \underset{k_{-1a}}{\overset{k_{1a}}{\rightleftharpoons}} \overline{PhCH_2\dot{C}O + PhCH_2\cdot} \xrightarrow{k_{1b}} PhCH{=}C{=}O + PhCH_3 \quad (1)$$

Ninety-nine percent of the geminate pairs, which do not undergo internal return (k_{-1a}), produce free benzyl radical[3] following the decarbonylation step (eq 2). Less than 0.3%

$$PhCH_2\dot{C}O \xrightarrow{k_2} PhCH_2\cdot + CO \quad (2)$$

of the geminate pairs produce phenylketene and toluene (k_{1b}) in low-viscosity solvents. The decarbonylation rate is represented by $\log (k_2/s^{-1}) = (12.0 \pm 0.3) - (6.9 \pm 0.4)/\theta$, $\theta = 2.303RT$ kcal/mol.[4] In the absence of hydrogen donors, benzyl radicals terminate to form bibenzyl (eq 3) or transient semibenzenes (eq 4).[3] The semibenzenes have

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