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Kinetic Isotope Effect in the Homolytic Abstraction of Benzylic Hydrogen by *tert*-Butoxy Radical

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Abstract: The kinetic isotope effect for the abstraction of hydrogen (deuterium) from toluene by *tert*-butoxy radical derived from *tert*-butyl hypochlorite has been determined as a function of temperature. The determinations were made under conditions eliminating chlorine atom chains. The curved Arrhenius-type plot that is observed is discussed in terms of tunneling.

Chlorination of hydrocarbons by *tert*-butyl hypochlorite is known to proceed via a homolytic chain reaction.[2] For the light-initiated reaction, the sequence shown in eq 1–3 is

$$(CH_3)_3COCl \xrightarrow{h\nu} (CH_3)_3CO\cdot + Cl\cdot \quad (1)$$

$$t\text{-BuO}\cdot + RH \longrightarrow t\text{-BuOH} + R\cdot \quad (2)$$

$$R\cdot + t\text{-BuOCl} \longrightarrow RCl + t\text{-BuO}\cdot \quad (3)$$

generally accepted.[2-5]

Extensive data exist on the relative reactivities of a number of organic substrates toward *tert*-butyl hypochlorite. Discrepancies exist in the work of various investigators.[5-10] These difficulties have been resolved by the demonstration of the incursion of chlorine atom abstraction competitive with reaction 2.[5,6,10] Chlorine atom chains have also led to difficulties in interpreting the kinetics of the reaction.[3,4,11,12]

In extending our investigation of the chlorination of toluene,[8,13] we have examined the kinetic isotope effect with toluene-α-d_3. Previous data suggest that chlorine atom abstraction is significant in results that have been reported. Kennedy and Ingold[9] report k_H/k_D as 2.4 at 40°, and Lee and Teo[10] report a value of 2.5 at the same temperature. These results were obtained by direct competition between the deuterated and nondeuterated toluenes. The k_H/k_D value[5] of 5.0–5.5 at 40° obtained indirectly from the *tert*-butyl alcohol:acetone ratio is substantially larger.

We have determined the value of k_H/k_D for the *tert*-butyl hypochlorite reaction using conditions were chlorine atom chains are excluded. This paper describes these deter-

Table I. Relative Rates of *tert*-Butoxy Radical Reactions of Toluene and Toluene-α-d_3 with *tert*-Butylbenzene

T, °C	No. expts	$k_H/k_B{}^a$	No. expts	$k_D/k_B{}^a$
80	3	1.40 ± 0.02	2	0.422 ± 0.023
40	7	2.05 ± 0.12 (2.0)^b	2	0.492 ± 0.031
0	5	3.43 ± 0.07	3	0.667 ± 0.060
−45	2	8.66 ± 0.26	2	0.822 ± 0.004
−61	4	9.55 ± 0.48	2	0.590 ± 0.009

[a] Experimental error represents average deviation of the number of experiments shown. Each experiment represents at least triplicate analysis. [b] Reference 14.

minations over a wide temperature range and reveals yet another anomaly. It leads to the conclusion that tunneling is of considerable importance in the reaction.

Results

The intermolecular isotope effect was studied between −61 and 80° by conducting competitive chlorinations with *tert*-butyl hypochlorite and a mixture of toluene and *tert*-butylbenzene, k_H/k_B, and a mixture of toluene-α-d_3 and *tert*-butylbenzene, k_D/k_B, in chlorobenzene solution. The total hydrocarbon to hypochlorite was in at least a 5:1 molar ratio for all determinations. Walling and McGuinness[5] have demonstrated that the chlorine atom chain dies out above 0.2 M cyclohexane in a mixture of cyclohexane and toluene. These workers state that other systems involving toluene and aliphatic substrates behave similarly. To confirm this, the known chlorine atom trap, trichloroethylene, was added to reaction mixtures of toluene and *tert*-butylbenzene. Results obtained for k_H/k_B at 40, 0, and −61°, in the presence of 0.107 M trichloroethylene, were indistinguishable from the results obtained in the absence of the trap. Also results obtained for the relative rates using 3:1 molar ratio of toluene:*tert*-butylbenzene were indistinguishable from those obtained using a 1:3 molar ratio. Our value for the relative rate of toluene to *tert*-butylbenzene at 40°, see Table I, agrees with the value of 2.00[14] for the direct determination obtained by Wagner and Walling. Their indirect value of 8.3 is strong evidence for the role of chlorine atom in the reaction with benzylic hydrogen alone and is further evidence that we have eliminated the chlorine atom chain using our conditions.

The relative rates of toluene-α-d_3 to *tert*-butylbenzene were determined as with undeuterated toluene. Mass spectral analysis of the toluene-α-d_3 available to us revealed that it was composed of 80.2% α-d_3, 12.2% α-d_2, and 7.5% α-d_0. Thus the direct measurement of the relative rate of toluene-α-d_3 to *tert*-butylbenzene included an error due to the α-d_2 and α-d_0 species. The results were first treated as if only α-d_3 material were present. Using the value so obtained and the previously measured k_H/k_B, the calculation was repeated correcting for the presence of both toluene-α-d_2 and -α-d_0. The calculation was repeated to self-consistency. Results are given in Table I.

The values of k_H/k_D reported in Table II are obtained by dividing the k_H/k_B value by that of k_D/k_B. The values of k_H/k_D obtained in this work are compared with similar values obtained previously under conditions where chlorine atom chains were not eliminated in Table II. It is apparent that, in the previous work,[15] chlorine atom abstraction played a significant role.

It may be noted, especially in Figure 2, that the k_H/k_D value at −45° is derived from a k_H/k_B value that falls above the least-squares line for the k_H/k_B data and from a k_D/k_B value that falls below the line determined by the high-temperature, 0 to 80°, values. Thus there appears to be a bias for the k_H/k_D value at −45° determined by combined "error". If we assume that the best values of k_H/k_B are those determined by the least-squares line, the values of 7.5 (−45°) and 10.7 (−61°) lead to k_H/k_D values of 9.12 and 18.1 when combined with the observed k_D/k_B values. If it is assumed that the value of k_D/k_B at −45° should fit the line determined by k_D/k_B at the higher temperatures, a k_H/k_D value of 7.62 is obtained at −45° when combined with the "best line" value of k_H/k_B. This value closely fits the high-temperature "best line" in Figure 1. The error suggested by these calculations lies far outside the precision observed in running the experiments. While it appears reasonable to correct the k_H/k_B values, the low-temperature deviation in the k_D/k_B is *not* random, and it is our belief that a correction in these values is not justified. Indeed, a correction of the −65° value for k_D/k_B gives 3.266 as opposed to the observed value of 0.590. The arguments that follow in this paper are based upon the observed values but would not be changed by correcting the −45° value of k_H/k_D; only the point of curvature in Figure 1, not the curvature itself, can be considered to be in doubt.

Table II. Isotope Effect for *tert*-Butoxy Radical Abstraction from Toluene

T, °C	$k_H/k_D{}^a$	$k_H/k_D{}^b$
80	3.32	1.88
40	4.17	2.4,^{c} 2.5,^{d} 1.98 (45°)
0	5.14	3.13
−45	10.5	4.61 (−39°)
−61	16.2	10.5 (−78°)

[a] This work. [b] Reference 15 except as noted. [c] Reference 9. [d] Reference 10.

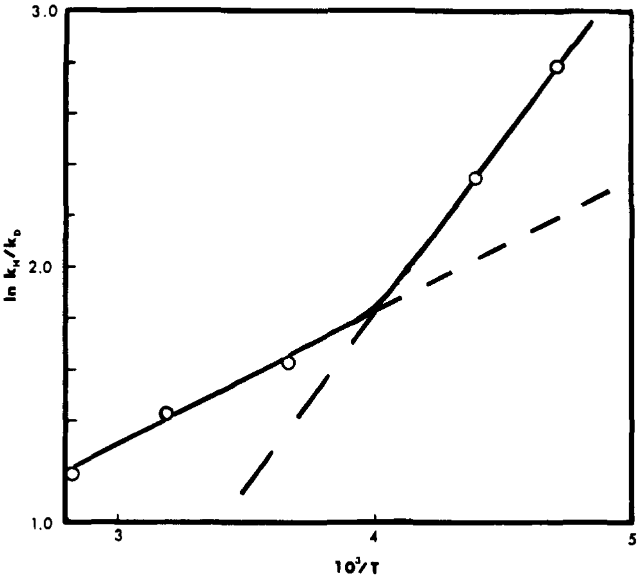

Figure 1. Kinetic isotope effect for *tert*-butyl hypochlorite chlorination of toluene.

Discussion

The k_H/k_D values of Table II are plotted as a function of $1/T$ in Figure 1. It will be noted that considerable curvature occurs in this Arrhenius-type plot. From the isotope effect values, the values of $E_D{}^* - E_H{}^*$ and of $A_H{}^*/A_D{}^*$ can be obtained. For the temperature range of 0 to 80°, the plot is linear, and values for $E_D{}^* - E_H{}^*$ of 1.04 kcal/mol and for $A_H{}^*/A_D{}^*$ of 0.77 are obtained. These values are normal. In the temperature range of 0 to −61°, the Arrhenius-type plot is a curve. Using the results at −45 and −61°,

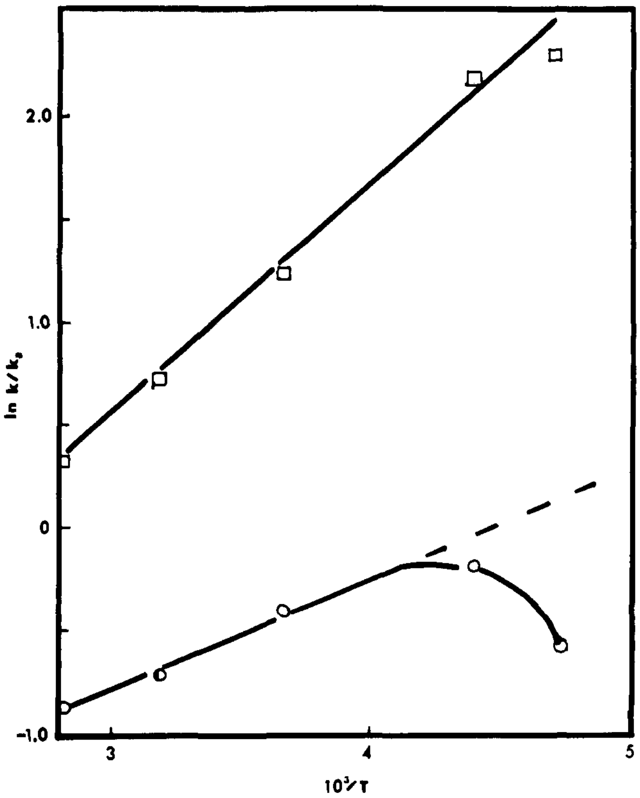

Figure 2. Arrhenius-type plot for the competitive reaction of *tert*-butyl hypochlorite with *tert*-butylbenzene and toluene (□) or toluene-α-d_3 (○).

values for $E_D^* - E_H^*$ of 2.6 kcal/mol and for A_H^*/A_D^* of 0.034 are obtained. These values are anomalous. The explanation of such anomalies, given by Bell,[16] expanded and reviewed by Caldin,[17] and most recently examined by Stern and Weston,[18] involves quantum mechanical tunneling. Specifically Caldin notes four consequences of proton tunneling upon kinetic isotope effects. These are (i) abnormally high values of k_H/k_D, (ii) $E_D^* - E_H^*$ values larger than the difference of zero-point energies for the stretching of C–D and C–H bonds, (iii) values of A_H^*/A_D^* below 0.5, and (iv) an anomaly of the rate constants for hydrogen, deuterium, and tritium transfer. Stern and Weston[18] have since shown that there is no direct general correlation between the extent of tunneling and the relative magnitude of the ratio [ln (k_H/k_T)]/[ln (k_H/k_D)]. There remain three criteria for experimentally demonstrating the presence of tunneling in a reaction system using kinetic isotope effects as a probe.

The criterion for tunneling that abnormal isotope effect values be obtained is not applicable to this study. At the present time, it is not possible to compute exact kinetic isotope effect values for our system.[19,20] Clearly the high-temperature values are in the expected range and cannot be considered anomalous. If one assumes that our high-temperature values are normal, one obtains values of the isotope effect of 9.0 at −61° and of 7.6 at −45° using the Arrhenius-type plot for the high-temperature values, see Figure 1. While the observed values are higher, this is not evidence in the spirit of criterion i.

The criterion that the $E_D^* - E_H^*$ values be greater than that predicted from C–D and C–H bond stretching zero-point energy differences, 1.1 kcal/mol, suggests that tunneling is occurring in our system. The value we obtained for $T \geq 0°$ of 1.04 kcal/mol is apparently normal. The value of 2.60 kcal/mol obtained for the temperature interval between −45 and −61° is well beyond the limit expected.

The third criterion of A_H^*/A_D^* values less than 0.5 is also met in our study at temperatures below 0°. The low-temperature value of 0.034 is far below the "minimum" expected value[16-18] of 0.5. Indeed Stern and Weston[18] have shown that tunneling may be important even when "normal" preexponential values are observed. They state that values outside the range of 2 to 0.7 probably cannot be achieved in the absence of tunneling. It should be noted that criteria ii and iii are not experimentally independent of each other. Experimental errors in $E_D^* - E_H^*$ are compensated by errors in the observed A_H^*/A_D^*.

Before tunneling can be used to explain our observations, alternative explanations must be ruled out. Caldin[17] has given five such possible alternatives. The most obvious is a change in mechanism at low temperatures. If there are two concurrent reactions, the one of higher activation energy will predominate as the temperature is increased. This results in Arrhenius-type plot curvature similar to that expected for tunneling. Evidence that we have against this explanation for our system is that chlorine atom abstraction appears to be excluded in our temperature range. This is the most obvious interfering reaction. In addition an Arrhenius-type plot of our k_H/k_B values gives a straight line, see Figure 2. No such straight line should be observed if there is a change in mechanism. The observation of the linear Arrhenius-type plot for k_H/k_B also excludes three other possible explanations for our isotope data given by Caldin.[17] These are a change in solvation as the transition state is formed, a change in solvent structure at low temperatures, and a temperature-independent constant-volume energy of activation. Caldin's fifth alternative explanation involves the reorientation of solvent molecules lagging behind the transfer of hydrogen. Lorand and Wallace have found that the rate constant for hydrogen atom transfer from toluene to *tert*-butoxy radical is of the order of 10^5 M^{-1} sec^{-1} at 25°.[4] It is unlikely that solvent reorientation is slower than this. Indeed it is difficult to imagine any gross reorientation of solvent molecules being required for this relatively nonpolar reaction.

One further difficulty must be examined. The Arrhenius-type plot of k_D/k_B, Figure 2, is nonlinear. The nonlinearity is quite dramatic for temperatures below 0°. Since the k_H/k_B plot is linear, it is reasonable to exclude all of the above possible explanations as cause for the k_D/k_B curve. If H atom tunneling is important in the toluene reaction, it must also be expected to be important in the *tert*-butylbenzene reaction since ln (k_H/k_B) is observed to vary linearly as a function of $1/T$. The curve that we observe in the Arrhenius-type plot of k_D/k_B is in the direction expected if tunneling is important in the *tert*-butylbenzene reaction, the value of k_D/k_B decreases as k_B increases as a result of tunneling.

In this study of the deuterium isotope effect of the reaction of toluene with *tert*-butoxy radical, we have found a curved Arrhenius-type plot leading to a value of $E_D^* - E_H^*$ larger than classical theory predicts and a value of A_H^*/A_D^* outside the limits of classical theory. The only interpretation that seems to explain all of our observations is based upon the quantum mechanical tunnel effect.

Experimental Section

Materials. Reagent grade commercial toluene was distilled on an 8 mm × 24 in. spinning-band (Nester-Faust) distillation column as a constant-boiling heart cut, bp 110.0°. Toluene-α-d_3 was used as obtained from Stohler Isotope Chemicals. Analysis by GLC revealed 2.15% benzene as an impurity. Isotopic analysis was accomplished by mass spectroscopy[21] at an ionization voltage of ca. 10 eV and gave 80.2% α-d_3, 12.2% α-d_2, and 7.5% α-d_0 using the "preference factor" of 3.5 reported by Beynon et al.[22] in the calculation. *tert*-Butylbenzene was prepared by the method of Huston, Fox, and Bender[23] in 70% yield, bp 167.8–170.0°. This was distilled on the spinning-band column to afford a fraction in which no impurities could be detected by GLC. Commercial grade chlorobenzene was distilled in a jacketed Vigreux column and collected as a constant-boiling heart cut, bp 132°. Trichloroethylene was used as supplied as Baker Analyzed Reagent. *tert*-Butyl hypochlorite was prepared as previously described[13] with bp 79.0–80.0°.

Procedure. Relative reactivities were determined by competitive experiments using solutions of ca. 2 *M* in toluene or toluene-α-d_3, ca. 2 *M* in *tert*-butylbenzene, and 0.7 *M* in *tert*-butyl hypochlorite (plus 0.11 *M* in trichloroethylene in some runs) in chlorobenzene. The solution was placed in an ampoule, degassed by successive freezing in liquid nitrogen, evacuation, and thawing. The sealed ampoule was placed in an appropriate temperature bath and allowed to equilibrate. The solution was irradiated with a 275-W sunlamp, placed externally, and the temperature was followed with a thermocouple and maintained steady by addition of Dry Ice or ice as needed. Upon removal from the bath, completeness of reaction was checked by KI test. Analysis was carried out on an F & M Model 700 gas chromatograph using a 6 ft × ⅛ in. column packed with 5% XF-1150 and 5% Bentone 34 on Chromosorb W. Relative reactivities were obtained as previously described[13] using the chlorobenzene as an internal standard.

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Kinetic Isotope Effects for Nitroalkanes and Their Relationship to Transition-State Structure in Proton-Transfer Reactions[1]

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Abstract: Primary isotope effects, k^H/k^D, have been determined for 1-phenylnitroethane and six of its meta substituted derivatives (pK_a's 6.0 to 7.5) with hydroxide ion, piperidine, diethylamine, and piperazine in water at 25°. A small increase in the ratio (from 7.2 to 9.6) was observed as ΔpK changed from -8.6 to -2.5. A secondary isotope effect of about 15% was observed for $PhCH_2NO_2$. A plot of log k^H/k^D vs. ΔpK using ten of these points and nine literature values gave a bell-shaped curve with gently sloping sides. Solvent isotope effects, k^{DO^-}/k^{HO^-}, were found to range around 1.35 for the parent, *m*-CH_3-, and *m*-$ClArCHMeNO_2$ compounds. Comparison of these values with those of other carbon acids showed that this ratio varied but little over wide ranges of ΔpK. In exoenergetic deprotonations, the k^H/k^D ratio and Brønsted coefficient are larger than expected for a reactant-like transition state while, for endoenergetic reactions, the effect of methyl substitution is generally to retard the deprotonation rate instead of accelerate it, as would be expected for a product-like transition state. These effects can be rationalized, however, by assuming a two-step mechanism, a rate-limiting deprotonation to form a pyramidal nitro carbanion followed by a rapid rehybridization to a planar nitronate ion. This mechanism also can accommodate inverse Brønsted correlations and Brønsted coefficients larger than one.

As part of a general study of the correlation of kinetic and equilibrium acidities of carbon acids, we have been examining various methods for assessing the transition-state structure in the deprotonation of nitroalkanes by bases.[1,3] Reactions of nitroalkanes with strong bases, such as hydroxide ion or methoxide ion, are strongly exoenergetic, which should lead to a "reactant-like" transition-state structure.[4] Evidence that the transition-state structure is not product-like in these instances comes from the finding of several examples of *negative* correlations between kinetic and equilibrium acidities.[3] For example, the increase in acidity (by 2.5 pK_a units in water) from CH_3NO_2 to Me_2CHNO_2 is no doubt caused primarily by the increased stability of the $Me_2C{=}NO_2^-$ ion, yet this stabilizing influence is not felt appreciably in the transition state for deprotonation by hydroxide ion, as may be judged by the 89-fold *slower* rate. Also, nitrocyclobutane is less acidic than nitrocyclopentane,[5] but this destabilizing influence is not felt appreciably in the deprotonation by lyate ion as may be judged by the *faster* rate for nitrocyclobutane.[5] (In 50% MeOH–H_2O, nitrocyclobutane has a 1.9 pK_a unit lower equilibrium acidity but reacts with lyate ion at a four-fold