not show a sharp change in these isomers indicating that $\theta_2$ is similar for each of the molecules.

The line width of the nuclear resonance peaks should be dominated by the Fermi contact interaction and the electron–proton dipole–dipole interaction.[12] The contribution to the line width from both of these interactions should vary as the square of the coupling constant. A plot of the square root of the line widths vs. the coupling constants is shown in Figure 4. Within experimental error the predicted linear relation is observed.

(12) G. W. Canters and E. de Boer, *Mol. Phys.*, 13, 395 (1967); R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *J. Chem. Phys.*, 30, 950 (1959).

## Conclusions

The nmr spectra of a series of phenoxy radicals with cyclic aliphatic substituents have been taken. Coupling constants from two geometric isomers were observed. Some of the coupling constants were found to depend on the geometries of the molecules. The couplings to the $\beta$ protons in the aliphatic rings appear to be dominated by a hyperconjugative interaction while the smaller couplings from the $\gamma$ and $\epsilon$ protons may be due to spin polarization.

# Hydrogen–Deuterium Kinetic Isotope Effects in the Gas Phase Bromination of Monodeuterated Toluene[1]

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**Abstract:** The intramolecular hydrogen–deuterium kinetic isotope effect in the gas phase bromination of monodeuterated toluene has been determined. The ratio of second-order rate constants obtained over the temperature interval of 120–160° can be expressed in terms of the following equation: $k_H/k_D = (1.08 \pm 0.25) \exp(1430 \pm 110)/RT$. The kinetic isotope effect measured in these gas phase experiments is larger than the corresponding values reported in solution studies. A general discussion of the comparison of the solution and gas phase results is presented.

Some of the interesting aspects of comparing reactions in the gas phase to the same reaction in solution have been pointed out by Mayo in a recent article.[2] In the case of free radical hydrogen atom abstraction reactions, the comparison has been limited mainly to the measurement of selectivity ratios for abstraction from various carbon–hydrogen bonds (e.g., primary vs. secondary C–H bonds). For chlorine atom reactions an increased selectivity in the gas phase has been observed.[3] On the other hand, methyl radicals do not exhibit any marked difference in selectivity in comparing gas phase and solution work.[4] In general, differences in selectivity ratios have been explained in terms of cage and solvation effects taking place in the solution reactions.[2]

In our experimental work, the relative rates of abstraction of hydrogen and deuterium atoms by bromine atoms from monodeuterated toluene in the gas phase have been determined. This same kinetic isotope effect was measured previously in carbon tetrachloride solution by Wiberg and Slaugh.[5] The only previous example of the same kinetic isotope effect measured in the gas phase and solution would appear to be the work of Walling and Miller[6] in studying the reaction of chlorine atoms with deuterated toluene.

(1) This research was supported by the National Science Foundation, Research Grant GP-4932.
(2) F. R. Mayo, *J. Amer. Chem. Soc.*, 89, 2654 (1967).
(3) I. Galiba, J. M. Tedder, and J. C. Mattou, *J. Chem. Soc., B*, 604 (1966).
(4) F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, 72, 1265 (1950).
(5) K. B. Wiberg and L. H. Slaugh, *ibid.*, 80, 3033 (1958).
(6) C. Walling and B. Miller, *ibid.*, 79, 4181 (1957).

## Experimental Section

All reactions were carried out in a conventional high-vacuum apparatus. Monodeuterated toluene was synthesized via the reaction of $C_6H_5CH_2MgCl$ with $D_2O$. The extent of deuteration was determined mass spectrometrically using a Hitachi RMU-6 mass spectrometer. Analysis showed the toluene to be 95% $C_6H_5CH_2D$, the remaining 5% being $C_6H_5CH_3$. Reagent grade bromine (stated purity 99.9%, Baker Chemical Co.) was left in contact with potassium bromide for several days. A small amount of this bromine was then distilled from the potassium bromide with only the middle fraction being retained for reaction.

The thermal reactions were carried out over a temperature range of 120–160°. The reaction furnace was equipped with three separate windings of Nichrome wire and, in this way, it was possible to obtain a constant temperature across the reaction cell. The cylindrical reaction cell was made of Pyrex and had a volume of approximately 250 cc.

In an experiment, the desired amount of toluene-$d_1$ was measured in a micropipet and then distilled into the reaction vessel and condensed in a small cold finger at −196°. The bromine was similarly measured in the pipet and then transferred to the cold finger. The stopcock isolating the reaction vessel from the vacuum system (a Kern high-vacuum greaseless stopcock) was then closed. Reaction was initiated by vaporizing the frozen bromine and toluene by warming with hot water; the time required for this was less than 10 sec. The greaseless stopcock plus tubing connecting the reaction cell, cold finger, and stopcock was maintained at 90° by wrapping with insulated heating tape. In this way, condensation of the bromine and toluene was avoided.

It was not possible with this experimental setup to measure the initial amounts of toluene-$d_1$ or bromine to better than ±15%. However, the kinetic isotope effect measurement is not contingent on an exact knowledge of the amounts of starting materials.

The desired kinetic isotope effect was determined by measuring the amounts of HBr and DBr produced from reactions 2a and 2b.

The HBr and DBr formed in these reactions were separated from the reaction mixture via passage through traps at −125° (n-pentane

$$Br + C_6H_5CH_2D \xrightarrow{k_H} HBr + C_6H_5CHD \qquad (a)$$

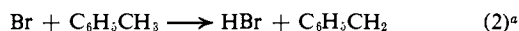$$\xrightarrow{k_D} DBr + C_6H_5CH_2 \qquad (b)$$
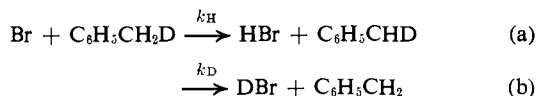
slush). At this temperature the only volatile component is the hydrogen bromide. The HBr and DBr were then converted to isotopic hydrogens ($H_2$, HD, and $D_2$) via passage through an uranium furnace at 550°. The hydrogen was collected by use of a Toepler pump and the ratio of $H_2$ to HD to $D_2$ determined mass spectrometrically. From these ratios and applying the appropriate statistical corrections (including that for the 5% $C_6H_5CH_3$), the ratio $k_H/k_D$ was determined. For example, in a run at 160° the ratio of $H_2:HD:D_2$ determined mass spectrometrically was $151:24.2:1$. From this, one calculates an atom ratio of hydrogen to deuterium of 12.4. Although the sample impurity of $C_6H_5CH_3$ is 5%, this actually represents 7.3% of the abstractable hydrogen atoms. The atom ratio of hydrogen to deuterium is therefore multiplied by 0.927 to correct for this impurity. This gives a corrected hydrogen to deuterium atom ratio of 11.5. Finally, since every $C_6H_5CH_2D$ molecule contains two abstractable hydrogen atoms for each deuterium atom, the ratio of $k_H/k_D$ is obtained by dividing 11.5 by 2 to correct for this statistical factor.

The most difficult problem encountered in this work was to avoid exchange of hydrogen bromide presumably with water absorbed on the walls of the vacuum system. After considerable experimentation it was found that by using greaseless stopcocks and by continuously heating and pumping the reaction vessel, stopcocks, and tubing when not in use this problem was overcome. This was demonstrated by distilling DBr into the reaction cell and then converting this gas to hydrogen via passage through the uranium furnace. From the isotopic composition of the hydrogen obtained, it was shown that exchange had not taken place. In many respects our experimental procedure was comparable to that used by Klein, et al.,[7] in working with HCl and DCl.

## Results and Discussion

The mechanism of the bromine–toluene reaction has been postulated[8] to be similar to other bromine–hydrocarbon reactions, namely

$$Br_2 \longrightarrow 2Br \qquad (1)$$

$$Br + C_6H_5CH_3 \longrightarrow HBr + C_6H_5CH_2 \qquad (2)^a$$

$$C_6H_5CH_2 + Br_2 \longrightarrow C_6H_5CH_2Br + Br \qquad (3)$$

$$C_6H_5CH_2 + HBr \longrightarrow C_6H_5CH_3 + Br \qquad (4)$$

$^a$ Reaction 2 is a combination of reactions a and b previously shown.

followed by the termination steps. In order for the ratio of HBr to DBr to reflect accurately the relative importance of reactions a and b, it is important to make sure that reaction 4 is not occurring to any significant extent. The only reported ratio of $k_3/k_4$ appears to be from the work of Anderson, et al.,[8] which gave the following results

$$\log k_4/k_3 = 3.01 - (1176/T)$$

In the temperature interval from 120 to 160° this predicts a value of $k_4/k_3$ of 1.05 to 1.95. These results have been reconsidered by Benson and Buss,[9] who point out that very possibly a stationary state of bromine atoms was not obtained in the above work and the rate constant ratios obtained may be seriously in error. The kinetic isotope effect measured in our current investigation is a competitive reaction and, as such, is independent of the bromine atom concentration. In order to minimize any complications which might arise from reaction 4, our experiments were carried out

(7) F. S. Klein, A. Persky, and R. E. Weston, Jr., J. Chem. Phys., 41, 1799 (1964).

(8) H. R. Anderson, H. A. Scheraga, and E. R. van Artsdalen, ibid., 21, 1258 (1953).

(9) S. W. Benson and J. H. Buss, ibid., 28, 301 (1958).

to very small per cent conversion (usually about 2%) of the bromine. In addition, it was observed that the magnitude of the kinetic isotope effect was independent of the per cent conversion of bromine over the range of 1–4%. Therefore, we assume that under our experimental conditions inhibition by HBr is not observed.

It is also important to assure that no HBr (or DBr) is produced from further bromination of the product benzyl bromide. In order to minimize this effect, reactions were carried out in the presence of a large excess of toluene, usually a tenfold excess of toluene over bromine. Varying the toluene to bromine concentration over a range from 5:1 to 20:1 had no measurable influence on the kinetic isotope effect under our experimental conditions of small per cent conversion of the bromine. Therefore, we assume no complications are introduced from further bromination of the benzyl bromide.

Finally two runs were carried out using $C_6D_5CH_3$ in place of the monodeuterated toluene. Since no DBr was observed in the reaction products we conclude that all of the attack of Br atom on the toluene occurs at the side chain. This result agrees with that of Anderson, et al.,[8] who did not observe any ring bromination of toluene in their experiments.

In this experimental work a secondary kinetic isotope effect is ignored in obtaining the ratio of $k_H/k_D$. However, pervious work on secondary kinetic isotope effects on reactions of this kind shows the magnitude of such effects to be small and negligible in comparison with the primary kinetic isotope effects.

The results of our experiments are shown in Table I. Treatment of the data via the method of least squares

**Table I.** Ratio of Rate Constants for the Reaction of Bromine Atoms with Monodeuterated Toluene$^a$

| $n^b$ | $T$, °C | $10^3/T$ | $k_H/k_D$ | Log $k_H/k_D$ |
|---|---|---|---|---|
| 3 | 121 | 2.54 | 6.69 | 0.825 |
| 3 | 130 | 2.48 | 6.53 | 0.815 |
| 3 | 142 | 2.41 | 6.17 | 0.790 |
| 3 | 150 | 2.36 | 5.93 | 0.773 |
| 3 | 160 | 2.31 | 5.69 | 0.755 |

$^a$ The majority of these runs were carried out with a tenfold excess of toluene over bromine. $^b$ $n$ represents the number of separate experiments at each temperature.

and assuming an Arrhenius-type equation for the rate constant ratios leads to the following results

$$k_H/k_D = (1.08 \pm 0.25) \exp(1430 \pm 110)/RT$$

It should immediately be observed that these results represent a rather large kinetic isotope effect. Following the work of Wiberg and coworkers[10] one might consider that perhaps this large kinetic isotope effect arises from the formation of an unusually symmetrical activated complex in this reaction. A symmetrical activated complex refers to one in which the masses of the end atoms and force constants between the hydrogen (or deuterium) and the end atoms are approximately the same. For example, these requirements were reasonably well met in the $Cl + CH_2D_2$ experiments of Wiberg and Motell[10] in which the C–H bond strength in methane is 108.5 kcal/mol and $D_0$ for HCl is 106.4

(10) K. B. Wiberg and E. L. Motell, Tetrahedron, 19, 2009 (1963).

kcal/mol. Interestingly, the $k_H/k_D$ value obtained in the Cl + $CH_2D_2$ reactions is of about the same magnitude as we observe in our work. In the bromine atom plus toluene reaction the requirements for the formation of a symmetrical activated complex are well met. The H–Br bond energy of 90.3 kcal/mol is close to that of the C–H bond in toluene (~92 kcal/mol). If we consider one end atom to be a benzyl group then the masses of the end atoms are nearly equal. In the measurement of an intramolecular kinetic isotope effect it can be shown that the ratio $k_H/k_D$ calculated from absolute rate theory takes the form[10]

$$k_H/k_D = \frac{(I_A{}^{\pm}I_B{}^{\pm}I_C{}^{\pm})_H{}^{1/2}}{(I_A{}^{\pm}I_B{}^{\pm}I_C{}^{\pm})_D{}^{1/2}} \prod_i^{3N-7} \frac{e^{-1/2u_i(H)}(1 - e^{-u_i(D)})}{e^{-1/2u_i(D)}(1 - e^{-u_i(H)})} \quad (I)$$

where $I_A{}^{\pm}$, $I_B{}^{\pm}$, and $I_C{}^{\pm}$ represent the three moments of inertia of the activated complexes formed for H atom transfer (H subscript) and for D atom transfer (D subscript). The second ratio is temperature dependent ($u_i = h\nu_i/kt$) and represents zero point energy contributions in the two activated complexes. In the case of a symmetrical activated complex, the hydrogen (or deuterium) being transferred is not involved in the symmetrical stretching vibration. Equation I predicts that the loss of this stretching mode in going to activated complex results in an expected kinetic isotope effect of about 7 at room temperature for reactions involving C–H bonds. In view of these considerations, the results obtained in our current study, although representing a very large isotope effect, are not unreasonable.

As a result of our work, we are able to compare the gas phase kinetic isotope effect with the same reaction carried out in solution. The most reliable experimental result in the solution studies appears to be that of Wiberg and Slaugh.[5] They obtain a $k_H/k_D$ ratio of 4.6 at 77° for bromination of toluene-$d_1$ carried out in carbon tetrachloride solution. At 77° our gas phase results calculate to a $k_H/k_D$ ratio of 8.2. Another way of comparing the gas phase results with the solution experiments is to note that the kinetic isotope effect in the gas phase at 225° would be equal to the solution isotope effect at 77°. The explanation of the difference in these two results is not readily apparent. There are a variety of other chemical reactions involving comparison of gas phase and solution results and these appear to be worth discussion.

First, it should be noted that Walling and Miller[6] obtained essentially the same kinetic isotope effect in both the gas phase and solution studies of the $k_H/k_D$ ratio for Cl atom reactions with deuterated toluene. The kinetic isotope effect obtained in the chlorine atom experiments was considerably smaller than the value of the isotope effect measured in the Br atom reactions. However, in terms of a rather unsymmetrical activated complex formed in the Cl atom reactions, the smaller kinetic isotope effect is expected.

The question of relative selectivities of various radicals and atoms is an interesting topic for which some experimental results are available. For example, in the most recent study, Galiba, et al.,[8] report the following ratios for abstraction from primary and secondary C–H bonds of n-hexane in the gas phase.

$$k_s/k_p(\text{gas}) = 2.2 \pm 0.6 \exp(214 \pm 127 \text{ cal})/RT$$

For the same reaction in solution they obtain

$$k_s/k_p(\text{soln}) = 0.8 \pm 0.2 \exp(597 \pm 20 \text{ cal})/RT$$

The much lower preexponential factor in the solution work is postulated to arise from solvent cage effects. It is assumed that the rate constants for the chlorine atom reactions are of the order of diffusion-controlled processes and that solvent cage effects result in a lower selectivity in solution. The reason for the larger temperature dependence of the solution reaction is not at all clear; however, some suggestions have been offered[11] in terms of solvation of the chlorine atom in solution leading to the difference in activation energies.

If cage effects are present in chlorine atom reactions with hydrocarbons such as n-hexane, these same cage effects should appear in the solution reaction of these atoms with monodeuterated toluene. Thus over-all one might have expected a lower $k_H/k_D$ in solution for Cl atom reactions compared to the gas phase result. The fact that this is not observed is puzzling but might conceivably reflect other intrinsic differences in gas phase and solution reactions than have previously been considered. In this connection, it is of interest to point out the recent result of Tedder and Walton[12] in which the recombination rate constants of $CCl_3$ radicals in the gas phase is observed to be two orders of magnitude higher than the corresponding recombination in solution. It is difficult to explain such a large difference in rate constants for a recombination reaction in the two phases.

Selectivity ratios of bromine atom reactions in solution do not appear to have been studied. Since the bromine atom is much less reactive than the chlorine atom it is reasonable to assume that any cage effects (if they do exist) could be less important than in the case of chlorine atoms. Thus in considering both the chlorine atom and bromine atom reactions with monodeuterated toluene there does not appear to be any simple explanation of the $k_H/k_D$ values observed in solution and in the gas phase.

Quite obviously there is a need for more data on reactions of a homologous series, particularly for the same reactions in solution and in gas phase. Whereas our present results support the idea of the importance of a symmetrical activated complex in determining a kinetic isotope effect, there are other results which tend to argue against this point of view.[13] The relationship between the magnitude of a kinetic isotope effect and the activation energy of a reaction or symmetry considerations of the activated complex are fundamental questions which can only be answered with the availability of more experimental data.

(11) C. Walling and M. F. Mayahi, J. Amer. Chem. Soc., **81**, 1485 (1959).

(12) J. M. Tedder and J. C. Walton, Trans. Faraday Soc., **63**, 2464 (1967).

(13) R. B. Timmons and R. E. Weston, Jr., J. Chem. Phys., **41**, 1654 (1964).