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Cage Return and Solvent Viscosity and Their Importance in Determining the Kinetic Deuterium Isotope Effect Observed during Benzylic Bromination

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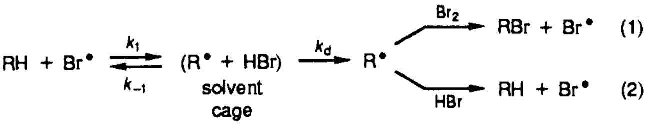
Abstract: The abstraction of a benzylic hydrogen by a bromine atom yields a benzyl radical–hydrogen bromide, radical–molecule pair. Reversal within the solvent cage, internal return, and reversal by the reaction of cage escaped pairs, external return, dominate the kinetics of the bromination. External return can be eliminated by using *N*-bromosuccinimide or molecular bromine and ethylene oxide as the brominating agents. Since internal return is competitive with diffusion, which is viscosity dependent, the solvent viscosity controls the amount of internal return. The viscosity dependence of the kinetic deuterium isotope effect for benzylic bromination at a constant temperature has been determined. As the relative viscosity decreases, the deuterium isotope effect increases. Since the viscosity decreases as the temperature increases, the magnitude of the TDKIE was determined at constant viscosity. The mechanistic interpretation of the TDKIE for these brominations is therefore subject to modification. In the liquid phase the relative rates of bromination of 4-chlorotoluene and toluene (k_{ct}/k_t) increase in magnitude as the temperature decreases and approach 1 at low temperatures. However, at constant viscosity the observed values of k_{ct}/k_t are essentially invariant at 0.58 ± 0.03 from −19 to 70 °C.

A number of years ago we reported that the intermolecular deuterium isotope effect, determined for the photoinitiated bromination of cyclohexane and perdeuteriocyclohexane, when carried out under conditions where the radicals formed do not transfer with the free hydrogen bromide produced in the reaction (eq 2), was different in the vapor and solution phase.[6] It was suggested that this observation was the result of a cage reversal reaction between the radical–hydrogen bromide pair. It was proposed that internal return (k_{-1}) was competitive with diffusion (k_d) (see Scheme I).

Scheme I



When the reaction was carried out in solvent liquid bromine, the vapor phase and solution phase values (k_H/k_D) were the same. Under these conditions the caged radicals could be scavenged by reaction with molecular bromine which made up the cage walls.

These results were used to rationalize the reported differences found between the intramolecular deuterium isotope effect reported for the solution-phase[7] and vapor-phase[8] photobromination of toluene. Unfortunately, cage scavenging by liquid bromine could not be used to eliminate internal reversal with toluene and α,α,α-trideuteriotoluene since high concentrations of liquid bromine undergo ionic reaction with toluene.[6] A kinetic expression, eq 3,

$$\left(\log\frac{[\mathrm{RH}]^0}{[\mathrm{RH}]^f}\Bigg/\log\frac{[\mathrm{RD}]^0}{[\mathrm{RD}]^f}\right)^{\mathrm{sol}} = \left(\frac{k_1^{\mathrm{H}}}{k_1^{\mathrm{D}}}\right)^{\mathrm{vp}}\left(\frac{k_{-1}^{\mathrm{D}}[\mathrm{DBr}]+k_d}{k_{-1}^{\mathrm{H}}[\mathrm{HBr}]+k_d}\right) = \left(\frac{k_1^{\mathrm{H}}}{k_1^{\mathrm{D}}}\right)^{\mathrm{sol}} \quad (3)$$

was derived which accounted for cage reversal during the determination of the deuterium isotope effect,[6] where $[...]^0$ is the initial concentrate, $[...]^f$ is the final concentration, k_1^H/k_1^D is the relative rate of abstraction of hydrogen vs deuterium in the vapor (vp) or solution (sol) phase and k_{-1}^D and k_{-1}^H are the reverse rates in the solvent cage. Using the steady-state approximation for the concentration of the radicals in the cage and assuming that both benzyl radicals and monodeuterated benzyl radicals diffuse at the same rate and that the bulk concentrations of caged hydrogen bromide, [HBr], and deuterium bromide, [DBr], are the same, a relationship for the cage effect was obtained (eq 3). This derivation further assumes that solvent effects play a negligible role in determining the relative rates of abstraction of deuterium or hydrogen, i.e. $(k_1^H/k_1^D)^{\mathrm{sol}} = (k_1^H/k_1^D)^{\mathrm{vp}}$.

More recently[9] we reported that the effect of temperature on the indirectly determined kinetic isotope effect resulting from the homolytic abstraction of a benzylic hydrogen (or deuterium) by bromine was due not only to the activation parameters involved in abstraction but also to the viscosity dependence of the kinetic results. The method used to determine the isotope effect was an indirect one. By determination of the relative rates of bromination of toluene vs 4-chlorotoluene (k_t/k_{ct}) and α,α,α-trideuteriotoluene vs 4-chlorotoluene (k_{Dt}/k_{ct}) the value of k_H/k_D was obtained: $k_H/k_D = (k_t/k_{ct})/(k_{Dt}/k_{ct})$. The original authors measured the relative rate of bromination of toluene vs 4-chlorotoluene at a number of temperatures (45.0 to −50 °C).[10,11] In our hands, under the conditions previously reported reactions run below −32 °C became nonhomogeneous as the substrates froze out of solution. Consistent results were only obtained above −32 °C.[9] At temperatures above −32 °C abnormal Arrhenius parameters were obtained, since although $k_{ct} < k_t$, as the temperature increased, the ratio of rates k_t/k_{ct} also increased. This observation was rationalized by a process which was entropically controlled[10] ($E_t^\ddagger - E_{ct}^\ddagger = 0.59$ kcal/mol and $\Delta S^\ddagger = -2.47$). An isokinetic temperature was calculated to be −33 °C. Subsequently, internal cage return was used to explain the viscosity dependence of the kinetic results, and it was suggested that the resultant kinetic isotope effect must be corrected to account for cage reversal.[9]

In this paper we report the direct determination of the viscosity dependence of the intermolecular kinetic deuterium isotope effect determined for benzylic abstraction by a bromine atom and

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Table I. The Viscosity Dependence of the Relative Rates of Bromination of *p*-Chlorotoluene vs Toluene

solvent	reagent	temp (°C)	$\eta_i/\eta_{Freon11}$	k_{ct}/k_t
CH_2Cl_2	NBS	10	1.01	0.56[a]
CH_2Cl_2	Br_2, ethylene oxide	10	1.02	0.564 ± 0.001
Freon 11	NBS	10	1.25	0.583[b]
Freon 11	NBS	23	1.01	0.649 ± 0.021
Freon 11/ Freon 113	NBS	23	1.11	0.634 ± 0.012
Freon 113	NBS	23	1.24	0.545 ± 0.005
Freon 113/ Freon 112	NBS	23	1.48	0.622 ± 0.004
Freon 112	Br_2, ethylene oxide	23	1.54	0.643 ± 0.003
Freon 112	NBS	23	1.82	0.683 ± 0.003

[a] Taken from ref 14. [b] Value is extrapolated from the plot of k_{ct}/k_t vs temperature (see Figure 1).

Table II. Relative Rates of Bromination of *p*-Chlorotoluene vs Toluene at Constant Viscosity and Different Temperatures[a]

temp (°C)	k_{ct}/k_t[b,d]	solvent	k_{ct}/k_t[c,d]	solvent
70	(0.595)	–	0.583	Freon 112
23	(0.783)	–	0.545	Freon 113
10	0.823	Freon 11	(0.583)	–
0	0.866	Freon 11	(0.590)	–
–19	0.939	Freon 11	0.606	Freon 11

[a] Relative viscosity $\eta_i/\eta_{Freon11}$ = 1.253 ± 0.009. [b] Taken from refs 10 and 11. [c] This work. [d] Values in parentheses are extrapolated from the plot of k_{ct}/k_t vs temperature (see Figure 1).

demonstrate the viscosity dependence of competitive benzylic bromination. A method is suggested for obtaining the solution-phase rates of bromination in the absence of internal or external reversal.

Results

Benzylic Bromination. The brominations were carried out under several conditions which have been shown to proceed without external reversal. In the first experimental procedure the reagent, *N*-bromosuccinimide (NBS) with small amounts of added molecular bromine, was chosen as a constant source of a low-level concentration of molecular bromine. The ability of NBS to rapidly scavenge hydrogen bromide has been substantiated[6] while the addition of small amounts of molecular bromine insured that the photoinitiated reactions proceeds by a bromine atom chain (eqs 1–4).[12]

$$Br_2 \xrightarrow{h\nu} 2Br^\bullet \quad (4)$$

$$ArCH_3 + Br^\bullet \rightarrow ArCH_2^\bullet + HBr \quad (5)$$

$$HBr + NBS \rightarrow NSH + Br_2 \quad (6)$$

$$ArCH_2^\bullet + Br_2 \rightarrow ArCH_2Br + Br^\bullet \quad (7)$$

The brominations were carried out, using the second procedure, with molecular bromine and a large excess of ethylene oxide (an effective scavenger of hydrogen bromide[13]). The results of both methods are consistent (see Table I).

Competitive Bromination of Toluene and a Substituted Toluene. When the competitive bromination of toluene vs 4-chlorotoluene was carried out in solvent Freon 11 at several temperatures, 10, 0, and –19 °C, the resulting rate constants were almost identical with those previously reported;[10] however, when the relative rates were measured over a similar range of temperatures, –19 to 70 °C, but at a constant relative viscosity, $\eta_i/\eta_{Freon11}$ (the ratio of the viscosity of the Freon solvent/the viscosity of Freon 11 at 23 °C, $\eta_i/\eta_{Freon11}$ = 1.253) the ratio of rate constants was almost invariant with temperatures (see Table II). A comparison of these results is displayed graphically in Figure 1. At constant temperature, 23 °C, the viscosity dependence of the relative rates (k_{ct}/k_t) vs T °C was also predictably found to be almost invariant (see Table I and Figure 2). Viscosity at 23 °C or higher was not expected to be a controlling factor in determining the relative rates since at these temperatures the difference in the viscosity dependent reversal becomes smaller (i.e., as the viscosity becomes lower) (see Figure 1).

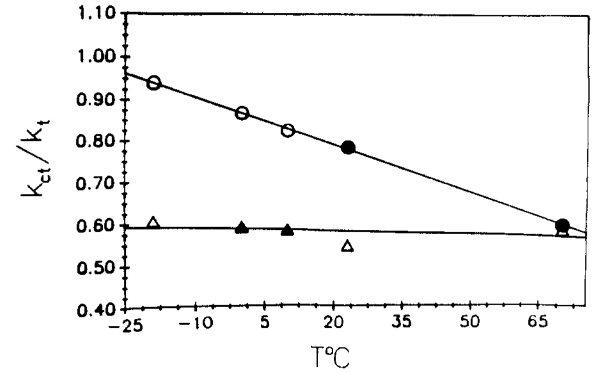

Figure 1. The relative rates of bromination of 4-chlorotoluene/toluene (k_{ct}/k_t) vs temperature (T, °C). Open triangles were determined at constant relative viscosity ($\eta_i/\eta_{Freon11}$ = 1.253). Open circles were taken from ref 11. Filled points are extrapolated values.

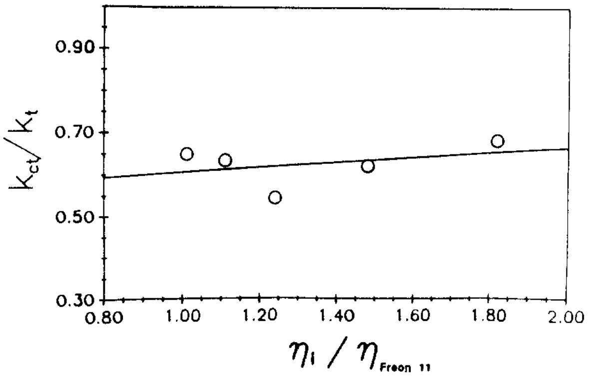

Figure 2. The relative rates of bromination of 4-chlorotoluene/toluene (k_{ct}/k_t, 23 °C) vs the relative viscosity of the Freon solvent ($\eta_i/\eta_{Freon11}$).

Kinetic Deuterium Isotope Effect. Aliquot mixtures of toluene and α,α,α-trideuteriotoluene in Freons of the appropriate viscosity were competitively photobrominated at 23 °C by using NBS and molecular bromine (96:4) as the brominating agent. After completion of the reaction, the product mixtures were analyzed for percent reaction by GLPC and the mixtures of unreacted toluene and deuterated toluene were collected and subjected to mass spectral analysis for the ratio of $PhCH_3/PhCD_3$. The ratio of proteated to deuterated toluenes remaining after the reaction was compared to the same ratio in the reaction mixture before bromination. The absence of appreciable external reversal was confirmed by comparing the ratios of $C_6H_5CD_2H/C_6H_5CD_3$ and $C_6H_5CH_2D/C_6H_5CD_3$ within the limits of experimental error. The relative rates of disappearance of the two substrates allowed the ratio of k_H/k_D to be obtained (eq 8) (see Table III).

$$k_H/k_D = \log([C_6H_5CH_3]^f/[C_6H_5CH_3]^0)/(\log[C_6H_5CD_3]^f/[C_6H_5CD_3]^0) \quad (8)$$

The viscosity dependence of k_H/k_D is displayed in Figure 3. When the correlation from the plot of k_H/k_D vs the relative viscosity, $\eta_i/\eta_{Freon11}$, was extrapolated to the relative vapor-phase viscosity, the calculated isotope effect (k_H/k_D = 12.7, 23 °C) was quite close to that previously reported[8] for the vapor-phase bromination (k_H/k_D = 12.0, 23 °C). At constant viscosity ($\eta_i/\eta_{Freon11}$ = 1.175) the k_H/k_D was found to change very little as the temperature increased (see Table IV and Figure 4).

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Table III. Relative Rates of Bromination of Toluene vs α,α,α-Trideuteriotoluene at 23 °C

solvent	relative viscosity	reagent	$[C_6H_5CH_3]^0$	$[C_6H_5CH_3]^f$	$[C_6H_5CD_3]^0$	$[C_6H_5CD_3]^f$	k_H/k_D[a]
Freon 11	0.996	NBS/Br_2	0.975	0.125	0.916	0.632	5.57 ± 0.17
Freon 11/113	1.070	NBS/Br_2	0.974	0.109	0.926	0.613	5.38 ± 0.32
Freon 113	1.175	NBS/Br_2	0.959	0.107	0.968	0.623	5.30 ± 0.17
Freon 11/112	1.211	NBS/Br_2	0.974	0.195	0.941	0.634	4.10 ± 0.15
Freon 113/112	1.319	NBS/Br_2	0.965	0.153	0.957	0.594	3.91 ± 0.33
Freon 112	1.474	ethylene oxide/Br_2	0.679	0.452	0.671	0.577	2.81 ± 0.49[b]
Freon 112	1.581	NBS/Br_2	0.983	0.352	0.954	0.658	2.78 ± 0.02

[a] Values are the averages of experiments carried out in triplicate. The errors are the average of the deviations from the mean value. [Concentration] = moles per liter; $[...]^0$, initial concentration; $[...]^f$, final concentration. [b] The average of duplicate determinations.

Table IV. Relative Rates of Bromination of Toluene vs α,α,α-Trideuteriotoluene at Constant Viscosity ($\eta_i/\eta_{Freon11} = 1.1750 \pm 0.0002$) and Different Temperatures

solvent	temp (°C)	k_H/k_D	reagent
Freon 11	-8	5.28 ± 0.02	NBS/Br_2
Freon 113	23	5.07 ± 0.23	NBS/Br_2
Freon 112	59.5	4.76 ± 0.20	NBS/Br_2

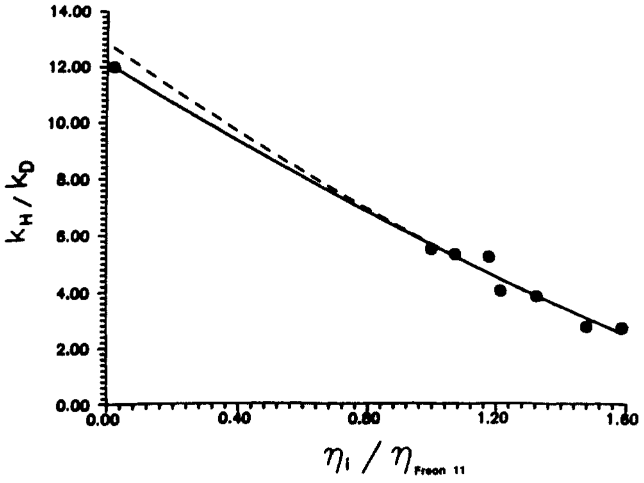

Figure 3. The relative rates of bromination of toluene/α,α,α-trideuteriotoluene (k_H/k_D, 23 °C) vs the relative viscosity of the Freon solvent ($\eta_i/\eta_{Freon11}$). The solid line is the hyperbolic fit of the experimental data which included the vapor-phase value. The dotted line is the least-squares hyperbolic fit of the experimental data extrapolated to the vapor-phase viscosity, $\eta_i/\eta_{Freon11} = 0.02$ (23 °C).

Discussion

The absence of external return during NBS bromination was confirmed by the observation that deuterium for hydrogen, or hydrogen for deuterium, exchange does not take place during benzylic bromination. This observation supported the same conclusion reached previously for the NBS brominations of cyclohexane.[6] In the absence of external return only internal return (cage reversal) can complicate the interpretation of the kinetic results (see Scheme I).

$$RH + Br^{\bullet} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (R^{\bullet} + HBr)_{cage} \xrightarrow{k_d} R^{\bullet} \xrightarrow[Br_2]{k_2} RBr \quad (1)$$

One of the variables limiting the amount of internal return is the rate of diffusion, k_d, of the caged radical–molecule pair. The viscosity of the solvent will be a major factor in limiting the diffusion rate. Although microviscosity should be the controlling parameter, a reasonable approximation using the relative bulk viscosity of similar solvents appears to be a satisfactory way to observe the viscosity dependence.

Since viscosity is directly proportional to temperature, the first viscosity-dependent reactions to be examined are the reactions in which temperature-dependent studies have been reported.

Competitive Bromination of 4-Chlorotoluene vs Toluene. The indirect determination of the temperature dependence of the kinetic deuterium isotope effect for benzylic bromination involved the careful measurement of the relative rates of bromination of 4-chlorotoluene vs toluene (k_{ct}/k_t).

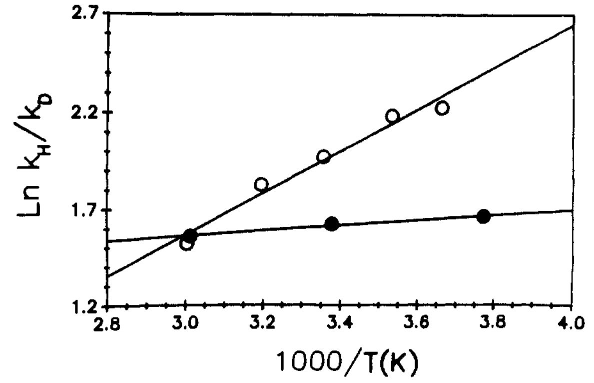

Figure 4. The relative rate of bromination of toluene/α,α,α-trideuteriotoluene [ln (k_H/k_D)] vs $1/T$ (K). Closed circles were carried out at constant viscosity ($\eta_i/\eta_{Freon11} = 1.176$). Open circles were taken from ref 10.

Several values have been reported for the relative rates of NBS bromination of 4-chlorotoluene vs toluene at 10 °C.[11,14] Since the mechanism for benzylic bromination by NBS has been established as proceeding by a bromine atom chain,[12] no clear explanation for this difference has been suggested.[11] In CCl_3F at 10 °C the ratio of rates was reported to be 0.82,[11] (1,2-epoxybutane, Br_2) while a rate ratio of 0.56 was reported for reactions carried out in CH_2Cl_2 (NBS).[14] In our hands the reactions carried out with bromine and 1,2-epoxybutane gave erratic results, since the epoxide appeared to undergo reaction with bromine. When the bromination was carried out in CH_2Cl_2 at 10 °C with ethylene oxide as a scavenger and molecular bromine as the brominating agent ($\eta_i/\eta_{CH_2Cl_2} = 1.10$), the relative rate ($k_{ct}/k_t = 0.56$) was the same as that reported by Kim[14] et al. using NBS in either CH_2Cl_2 ($\eta_i/\eta_{CH_2Cl_2} = 1.08$) or CCl_4 ($\eta_i/\eta_{CCl_4} = 1.07$).

Viscosity-Dependent Relative Rates. The rate ratio for the direct competitive bromination of toluene vs α,α,α-trideuteriotoluene was determined by measuring the viscosity dependence of the relative rates using NBS. Since the rate of diffusion (k_d) is inversely dependent upon viscosity, the rate of internal return is dependent upon the solvent viscosity. When the kinetic expression derived for the solution-phase deuterium isotope effect (eq 3) was related to the solvent viscosity ($k_d = \alpha/\eta$), a plot of the relative rate expression (k_H/k_D) vs viscosity is that of a hyperbola whose positive cusp is concave up (eq 9). A least-square fit of the

$$\frac{k_H}{k_D} = \frac{k_1{}^H(\alpha + k_{-1}{}^D(DBr)\eta)}{k_1{}^D(\alpha + k_{-1}{}^H(HBr)\eta)} \quad (9)$$

hyperbolic function (eq 10) was obtained by using the experimental data (see Figure 3). A data set was also used that included the

$$\frac{k_H}{k_D} = \frac{k_1{}^H k_{-1}{}^D}{k_{-1}{}^H k_1{}^D} + \left(\frac{\alpha k_1{}^H}{k_{-1}{}^H k_1{}^D}\right)\frac{1}{\eta} + \left(\frac{k_1 k_{-1}{}^D \alpha^2}{k_1{}^D (k_{-1}{}^H)^3} - \frac{k_1{}^H \alpha^2}{(k_{-1}{}^H)^2 k_1{}^D}\right)\frac{1}{\eta^2} + \ldots \text{etc.} \quad (10)$$

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vapor-phase value[8] (k_H/k_D = 12.0, and $\eta_{Vp}/\eta_{Freon11}$ = 0.02).[15] The two curves (Figure 3) are quite similar, and the value of k_H/k_D = 12.7 for the solution-phase data was almost the same as the value calculated for the vapor-phase reactions (eq 11). Over the

$$k_H/k_D = (1.08 \pm 0.25)\ \exp(1430 \pm 110)/RT \qquad (11)$$

range of temperature studied in solution (0–60 °C) the vapor-phase kinetic deuterium isotope effect predicts a change of k_H/k_D of (15.0–9.4)[8] (see eq 11). Over the same temperature range the solution-phase values showed an inverse relationship (9.3–4.6).[10] Clearly the difference between the vapor-phase and solution-phase values is indicative of a remarkable solvent effect. However, since the extrapolated solution-phase value of k_H/k_D (23 °C) at $\eta_i/\eta_{Freon11}$ = 0.02 is very close to that in the vapor, it appears that the hyperbolic extrapolation over the range of viscosity used gives an approximation to the true vapor-phase value. As predicted, the curve (Figure 3) extrapolated to the vapor-phase value of the relative viscosity showed an upward curvature. It is not clear at this time whether the difference (~6%) between the vapor-phase and the extrapolated solution-phase values is in part due to a general solvent effect or entirely due to cage reversal. The discrepancy in the reported values for the solution- and vapor-phase reactions must be assumed to be due primarily to viscosity-dependent internal return. This assumption was substantiated by determining the temperature dependence of the kinetic deuterium isotope effect in solution at a constant viscosity ($\eta_i/\eta_{Freon11}$ = 1.1758) (see Table IV). Arrhenius plot of log (k_H/k_D) vs $1/T$ gave an activation energy difference ($E_D^{\ddagger} - E_H^{\ddagger} = 0.27 \pm 0.04$ kcal/mol) and a ratio for the preexponential factors of $A_H^{\ddagger}/A_D^{\ddagger} = 3.2 \pm 0.2$ eu. A comparison with vapor-phase values of ($E_D^{\ddagger} - E_H^{\ddagger}$ = 1.43 kcal/mol),[8] and $A_H^{\ddagger}/A_D^{\ddagger}$ = 1.08 eu gives an indication of the effect of solvent on the relative rate of abstraction.

The invariance of both k_t/k_{ct} and k_H/k_D with temperature at constant viscosity argues for entropic control of the energetics of the solution-phase bromination. In solution the ordering of the caged products may be responsible for the increased importance of the entropy.

Experimental Section

Materials. All reagents except Freon 112 and ethylene oxide were obtained as reagent grade (toluene, Phillips research grade) and were distilled before use. Freon 112 was recrystrallized several times before use, while ethylene oxide was used as supplied. *N*-Bromosuccinimide (NBS) (Aldrich Chemical Co.) was recrystallized from hot water and dried over P_2O_5. The reagents were shown to be >99.9% pure by GLPC analysis. Bromine (Chemonics Scientific Ltd., reagent grade) was washed three times with concentrated sulfuric acid and distilled from P_2O_5 through an 18 in. Vigreux column. α,α,α-Trideuteriotoluene (Merck Sharp and Dohme of Canada Ltd., >99.9% D) was used as supplied, after analysis for purity by GLPC and mass spectral analysis.

Viscosity Measurements. The viscosities of all the solvent mixtures reported in this work were determined at the temperatures indicated with an Ostwald viscometer, calibrated using Freon 11 as a standard (23 °C).[9,16]

NBS–Bromine Reactions. Weighed amounts of NBS were placed in Pyrex reaction ampules. A mixture of the toluene substrates, internal standard (*p*-dichlorobenzene), and solvent was prepared and analyzed by GLPC, and its viscosity was measured at 23 °C. In the absence of light, an aliquot of this solution and an aliquot of bromine were added to each ampule. The reaction ampules were degassed by freeze–thaw (three cycles), sealed, thermostated at 23 °C, and irradiated through a Pyrex water bath by using a 300-W incandescent lamp. After the reactions were completed, the mixture was treated with moist potassium iodide and sodium thiosulfate, dried over anhydrous sodium carbonate, and analyzed by GLPC using a 50-m glass capillary column (SE-30). The relative rates of reaction were calculated from the disappearance of reactants.[17] All quantitative values were determined from three or more duplicate experiments and the molar values were determined by using standard calibration curves. The areas were determined by using a HP 5840A GC terminal interfaced to a HP5840A gas chromatograph fitted with an FID detector.

Bromine–Ethylene Oxide Reactions. A mixture of the toluene substrates, internal standard, ethylene oxide, and solvent was prepared, its viscosity was measured at 23 °C, and the mixture was analyzed by GLPC. An aliquot of the mixture and an aliquot of bromine were added to each ampule. The mixtures were then treated as were the reactions with NBS–Br_2, except that the completed reaction mixtures contained no active bromine and were analyzed by GLPC without further workup.

Isotopic Analyses. After the reactions were complete, the unbrominated substrates were collected by preparative GLPC using a 5 ft by $^1/_4$ in. stainless steel column containing 10% Ucon 50 HB 2000 on Chromosorb WAW (60–80 mesh). The collected substrates were analyzed for protium and deuterium content by mass spectrometry on an AEI MS 12 mass spectrometer, 5.6–11 eV. The values reported in Table I are averages of 20 or more mass spectral determinations. All quantitative values were determined from three or more duplicate experiments. The final concentrations of the substrates were determined by GLPC analysis on a 50-m SE-30 capillary column. 1,4-Di-*tert*-butylbenzene or *p*-dichlorobenzene was used as an internal standard.

The viscosity of each solution was determined prior to the addition of the brominating agent.

Solubility of NBS in CH_2Cl_2 Reaction Mixtures at 10 °C. A solution of toluene, substituted toluene, and the internal standard was prepared in dichloromethane. An aliquot of the mixture at 10 °C was mixed with an excess of NBS, and the mixture was mixed thoroughly. The undissolved NBS was removed by filtration, the solvent and substrates were removed by distillation, and the mass of dissolved NBS was determined.

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Registry No. NBS, 128-08-5; D_2, 7782-39-0; *p*-$ClC_6H_4CH_3$, 106-43-4; PhMe, 108-88-3; Br_2, 7726-95-6; ethylene oxide, 75-21-8.

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(15) The value for the relative vapor-phase viscosity for Freon 11 at 30 °C ($\eta_{Vp}/\eta_{Freon11}$ = 0.02) was taken from the Du Pont, Technical Bulletin, *Freon*, B2.

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