5d, 110118-06-4; **5e**, 110118-07-5; **5f**, 110118-08-6; **5g**, 110118-09-7; **6a**, 71699-34-8; **6d**, 110118-10-0; **6e**, 110118-11-1; **7a**, 110142-60-4; **7b**, 110142-61-5; **7c**, 110142-62-6; **7d**, 110142-63-7; **7e**, 110142-64-8; **7f**, 110142-65-9; **7g**, 110142-66-0; **8d**, 110118-12-2; **8e**, 110118-13-3; **9a**, 110118-15-5; **9b**, 110118-16-6; **9c**, 110118-17-7; **9d**, 110118-18-8; **9e**, 110118-19-9; **9f**, 110118-20-2; **9g**, 110118-14-4; **10a**, 110172-21-9; **10b**, 110172-23-1; 10c, 110172-25-3; **10d**, 110172-27-5; **10e**, 110172-29-7; **10f**, 110172-30-0; **10g**, 110172-19-5; **11a**, 110172-22-0; **11b**, 110172-24-2; **11c**, 110172-26-4; **11d**, 110172-28-6; **11e**, 110221-06-2; **11f**, 110172-31-1; **11g**, 110172-20-8; **12**, 110118-26-8; **13**, 110118-27-9; **14**, 110172-41-3; **15**, 110172-42-4; **16**, 110172-43-5; **17**, 110118-28-0; **18**, 110172-44-6; **21a** (isomer 1), 110118-22-4; **21a** (isomer 2), 110172-34-4; **21a** (isomer 3), 110172-35-5; **21b** (isomer 1), 110118-23-5; **21b** (isomer 2), 110172-36-6; **21b** (isomer 3), 110172-37-7; **21c** (isomer 1), 110118-24-6; **21c** (isomer 2), 110172-38-8; **21c** (isomer 3), 110172-39-9; **21d** (isomer 1), 110118-25-7; **21d** (isomer 2), 110172-40-2; **21d** (isomer 3), 110221-00-6; **21e** (isomer 1), 110142-57-9; **21e** (isomer 2), 110221-07-3; **21e** (isomer 3), 110142-58-0; **21f** (isomer 1), 110142-59-1; **21f** (isomer 2), 110221-08-4; **21f** (isomer 3), 110267-52-2; **21g** (isomer 1), 110118-21-3; **21g** (isomer 2), 110172-32-2; **21g** (isomer 3), 110172-33-3; 3-pentanone, 96-22-0; isobutyraldehyde, 78-84-2; (methoxethoxy)methyl chloride, 3970-21-6; (benzyloxy)methyl chloride, 3587-60-8; *tert*-butyldimethylsilyl triflate, 69739-34-0; trimethylsilyl triflate, 27607-77-8; triethylsilyl triflate, 79271-56-0.

Role of Cage Return and Solvent Viscosity in the Temperature-Dependent Kinetics of Benzylic Bromination

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The effect of temperature on both the kinetic isotope effect in the homolytic abstraction of benzylic hydrogen by bromine and the competitive brominations of toluene and a ring-substituted toluene was interpreted as being due not only to the activation parameters involved in abstraction but upon the viscosity dependence of the kinetic results. Internal cage return was shown to be viscosity dependent, and the resultant kinetic isotope effect was corrected to account for cage reversal. The viscosity dependence in the relative rates of competitive bromination of toluene and *p*-chlorotoluene showed an inverse correlation to that obtained with temperature. The nonmonotonic Arrhenius plot previously reported could be explained on the basis of these two opposing effects, as well as the fact that over the range of temperature previously reported the reaction mixtures became nonhomogeneous.

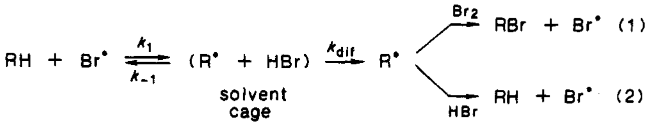
Introduction

A number of years ago we reported that the intermolecular deuterium isotope effect, for the photoinitiated bromination of cyclohexane and perdeuteriocyclohexane, under conditions where the radicals formed do not transfer with the free hydrogen bromide produced (eq 2), was different in the vapor phase and in solution.[1] The difference between the vapor-phase and solution results was shown to result from a cage reversal reaction, between the radical–hydrogen bromide pair, which is competitive with diffusion, see Scheme I.

These results were used to satisfactorily rationalize the reported differences found between the intramolecular deuterium isotope effect reported for the solution[2] and vapor[3] phase photobromination of toluene.

A related phenomena has been recognized for the reaction of radical pairs (*tert*-butyl radicals) in both the vapor phase and in solution. The viscosity of the solvent imposed an anisotropic preference for disproportionation to that of combination, (k_d/k_c), as the viscosity of the solvent increased.[4,5] Prior to these studies the effect of temperature upon the ratio, k_d/k_c, was rationalized as being due to differences in the activation parameters between the two processes.[6] However, the anisotropic phenomena enabled the temperature effect to be explained as a change in the rate ratios, k_d/k_c, as a function of the temperature dependence of the viscosity of the media.[7]

Scheme I



Recently two studies have been reported that involve the temperature-dependent kinetics of benzylic bromination: one measured the temperature dependence of the intermolecular deuterium isotope effect observed for the benzylic bromination of toluene[8] while the other reported the effect of temperature on the relative rates of benzylic bromination for several substituted toluenes.[9] Neither of these studies addressed the question as to whether solvent cage phenomena had an influence on their results.

Deuterium Isotope Effect. The method of determining the temperature dependence of the kinetic isotope effect for the abstraction of a benzylic hydrogen by a bromine atom was an indirect one. The relative rate of hydrogen abstraction from toluene vs. abstraction from

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Table I. Cage Effects for the TDKIE Observed in Benzylic Bromination

temp, °C	$(k_H/k_D)_{vap}$[a]	C	$(k_H/k_D)_{sol}$[c]
0	15.04	0.62	9.27
10	13.70	0.65	8.89
25	12.06	0.60	7.19
40	10.75	0.58	6.21
60	9.36	0.49	4.57
77	8.44	[0.52][b]	

[a] Values calculated from eq 4, ref 3. [b] Value calculated from data given in ref 2 and 3. [c] Values taken from ref 8.

p-chlorotoluene (k_H/k_{ct}) was determined as was the relative rate of abstraction of deuterium from α,α,α-trideuteriotoluene vs. abstraction from *p*-chlorotoluene k_D/k_{ct}); from these, k_H/k_D could be calculated. The reverse reaction of the benzylic radicals with hydrogen bromide was limited by sweeping out, with a stream of nitrogen, the hydrogen bromide as it was formed. The relative rates were compared at five temperatures, from 0 to 60 °C. The kinetic values were used to calculate the activation parameters: $E_D^* - E_H^* = 2.5$ kcal/mol, $A_H^*/A_D^* = 0.188$. At 25 °C, k_H/k_D was found to be 7.2. These parameters were used as a basis in determining, using the criteria given by Bell[10] and more recently by Kwart,[11] the transition-state geometry and whether tunneling affects transport across the activation barrier. The authors[8] concluded that the parameters fell within the range prescribed for a linear H-transfer with tunneling ($k_H/k_D > 9$ at 25 °C; $[\Delta E_a]_D^H \sim$ 1.5–6 kcal; $A_H/A_D < 0.6$); although the k_H/k_D value did not fit the criteria since it was approximately at and not greater than the maximum.

A relationship has been proposed to link the solution and vapor-phase isotope effects (eq 3).[1] The derivation

$$(k_1^H/k_1^D)_{vap}\underset{(C)}{\left(\frac{k_{-1}^D[\mathrm{DBr}] + k_{dif}}{k_{-1}^H[\mathrm{HBr}] + k_{dif}}\right)_{sol}} = (k_H/k_D)_{sol} \qquad (3)$$

uses the steady-state approximation for the concentration of the radicals in the cage and assumes that both benzyl radicals and deuteriated benzyl radicals diffuse at the same rate, k_{dif}, and that the bulk concentrations of caged hydrogen bromide, [HBr], and deuterium bromide, [DBr], are the same. The original expression, eq 3, can be put in the general form given in eq 4,[12] where C is defined as

$$(k_2/k_1)_{sol} = (k_2/k_1)_{vap}(x + (1/\alpha x) + 1) = (k_2/k_1)_{vap}C \qquad (4)$$

$$x = k_{-1}[\mathrm{HBr}]/k_d \text{ and } \alpha = k_{-2}/k_{-1}$$

the ratio of the fraction of cage escape radicals (f_1/f_2) and α is the ratio of the reverse rate constants for the reactions of radicals 1 and 2 with hydrogen bromide. With increasing viscosity C approaches $1/\alpha$ but its temperature dependence is determined by the effect of temperature on both α and x.

The temperature dependence of the kinetic isotope effect (TDKIE) has been reported for the vapor-phase bromination of toluene (eq 5).[3] Using these parameters

$$k_H/k_D = (1.08 \pm 0.25) \exp{(1430 \pm 110)/RT} \qquad (5)$$

and the values reported for the solution-phase determinations,[8] a table can be constructed comparing the solution-phase and vapor-phase isotope effects. The relative importance of cage reversal can also be calculated for the rate ratios at each temperature, see Table I.

The model, eq 4, predicts that the value of C increases with temperature, since as the temperature increases α, k_{-2}/k_{-1}, approaches 1 while the ratio of $k_{-1}[\mathrm{HBr}]/k_d$ also approaches unity. At this range of temperature the observed value of C was relatively insensitive to temperature. The values of C calculated from the data reported by Timmons[3] and Wiberg[2] are in quite good agreement with those calculated from the data given by Gilliom,[8] especially since these values for k_H/k_D must be corrected to a larger value for an added secondary deuterium isotope imposed from the difference in determining an intermolecular isotope effect using α,α,α-trideuteriotoluene[8] compared to the intramolecular isotope effect obtained from the bromination of α-deuteriotoluene.[2,3]

From the above equations an alternative relationship for C can be derived, eq 6. For the values for the TDKIE

$$1/C = \alpha + f_1 - \alpha f_1 \qquad (6)$$

listed in Table I $C \cong 0.6$, representative values of f_1's for different α's, (k_{-1}^H/k_{-1}^D), can be calculated. In the case of relatively high values of α comparable in the size to k_H/k_D, only a few of the radicals have to be trapped in order to effect a quite noticeable change in the ratio of cage escape radicals, i.e., the observed changes in the solution-phase isotope effects.

The vapor-phase data are clearly much better suited as indicators to describe the transition state. Timmons's results, $(k^H/k^D)^{25\,°C} = 11.19$; $[\Delta E_a]_D^H = 1.43 \pm 0.11$; and $A_H/A_D = 1.08 \pm 0.25$, are in reasonable agreement with the assignment[11] made for a linear H-transfer which involves tunneling.

Temperature Dependence for Homolytic Abstraction. The relative rates of benzylic bromination of toluene and 4-chlorotoluene have been reported for reactions carried out at several temperatures (45 °C, 25 °C, 10 °C, 0 °C, −18.5 °C, −32 °C, −42 °C, and −50 °C).[9] The reverse reaction of the benzylic radicals with the hydrogen bromide produced in the reaction was limited by the addition to the reaction mixture of an epoxide, propylene oxide, which acts as a scavenger for hydrogen bromide. A peculiar Arrhenius plot was reported, showing a change in the sign of its slope at −32°. A Hammett plot for the relative rates of four substituted toluenes vs. toluene was given for brominations at −50.0°. The ρ value, −0.376, was obtained by using σ substituent constants.[9] The photobrominations were carried out in carbon tetrachloride or for the reactions carried out at 0 °C or below in Freon 11.

In order to determine the effect of viscosity on the relative rates of bromination, the viscosities of the reaction mixtures used in the brominations[9] were determined at each of the temperatures reported. When an attempt was made to measure the viscosities of the reaction mixtures at temperatures lower than −32 °C, the temperature at which a break in the Arrhenius plot had been reported,[9] the reaction mixture became nonhomogeneous as the substrates became insoluble in the solvent. An inverse linear dependence of ln of the relative viscosity vs. temperature was obtained, but as expected, although the slopes were similar, since the viscosity was determined by a laminar flow technique, two separate correlations were obtained with temperature, one for CCl_4 solutions and one for Freon 11 solutions. The molecular differences which influence the fluid properties of the solutions appeared to be corrected for by a correlation of the temperature dependence of the viscosity of each solution relative to its

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[12] The authors are indebted to Professor Cheves Walling who suggested putting eq 3 in this form.

Table II. Relative Rates and Viscosities of the Reaction Mixtures Used for the Benzylic Bromination of *p*-Chlorotoluenes vs. Toluene at Various Temperatures

reaction media	*T* (K)	η_i/η_0[a]	k_{ct}/k_H[b]
CCl_4	318	0.752	0.736
CCl_4	298	0.870	0.780
Freon 11	283	1.123	0.823
CCl_4	273	1.063	0.865
Freon 11	273	1.107	0.866
Freon 11	254	1.213	0.939
Freon 11	241	1.485	0.985

[a] Viscosity of each reaction mixture relative to its own solvent. [b] The relative rates were taken from ref 9.

Table III. Relative Rates of Benzylic Bromination of *p*-Chlorotoluene vs. Toluene at 23 °C in Solvents of Different Viscosity

reaction media[a]	η_i/η_a[a]	k_{ct}/k_H[c]
CCl_4	0.815	0.857 ± 0.037 (0.758 ± 0.004)[d]
Freon 11	0.958	0.844 ± 0.003
Freon 11 (0.5 M)[b]	0.970	0.792 ± 0.067
Freon 113 (0.5 M)[b]	1.156	0.758 ± 0.008
Freon 113	1.082	0.718 ± 0.034
Freon 112	1.336	0.627 ± 0.045

[a] Viscosities relative to either pure CCl_4 (entry 1) or Freon 11 (entry 2–6). [b] In these reactions the [toluene] and [*p*-chlorotoluene] were each 0.5 M, while in the others the concentration was 1 M. [c] The values reported are the average of two or more independent experiments. The errors are the standard deviations from the mean value. [d] The relative rates of bromination determined for the mixture which did not contain propylene oxide.

own pure solvent. Although this correction may be fortuitous, it places both solvents on the same plot (see Table II and Figure 1).

The relative rates of competitive bromination are affected in the same manner by both internal cage return and external reversal. When the competitive bromination of *p*-chlorotoluene and toluene was carried out to completion, without added epoxide, the two radicals formed in their kinetic ratio, reacted differentially, with the hydrogen bromide free in the solution, resulting in a lower value of k_{ct}/k_H, see Table III, footnote d. The viscosity dependence of the relative rate ratio is predicted, due to increased internal cage return, to show an inverse relationship. As predicted the relative rate of bromination, k_{ct}/k_H, decreased with increasing viscosity, see Table III and Figure 1. Since the previously reported[9] relative rates of bromination showed an increase in the rate ratio, k_{ct}/k_H, with increasing temperature (or decreasing viscosity), the two effects are seen to be in opposition to each other, and it seems quite risky to give any interpretation to the magnitude of a temperature effect for a reaction which is readily reversible. The break in the Arrhenius plot can be due to the nonhomogeneity of the solution but is without a doubt markedly affected by the viscosity of the solution at the lower temperatures.

Conclusions

For radical reactions that are readily reversible, the solvent cage effect must be considered. A study of the effect of temperature on these reactions must also include the viscosity dependence of the kinetics, since internal cage return can be a dominant factor. The results of one such study, the TDKIE for the benzylic bromination of toluene, can be evaluated for its viscosity dependence by considering the activation parameters obtained from its vapor-phase reaction.

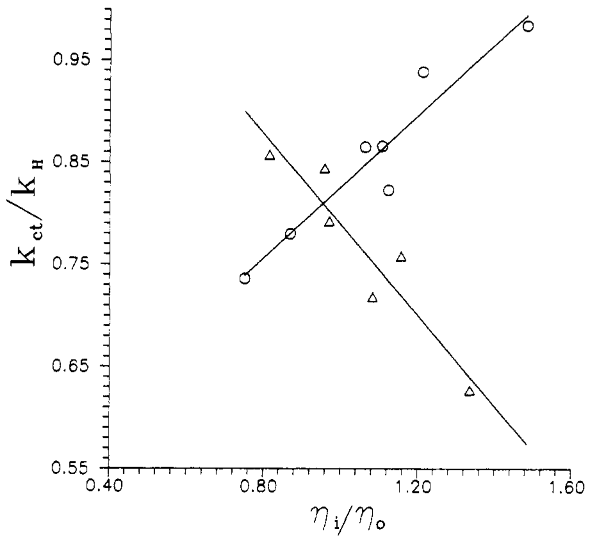

Figure 1. Plot of the relative rates of bromination of *p*-chlorotoluene/toluene, k_{ct}/k_H, at a number of temperatures vs. the viscosity of the reaction mixture relative to its pure solvent at the same temperatures, ○, and a plot of k_{dt}/k_H(23 °C) vs. the viscosity of the reaction mixtures (solvent carbon tetrachloride or Freon 11) relative to the solvents carbon tetrachloride or Freon 11, △.

The relative rates of benzylic bromination of toluene and substituted toluenes are likewise affected by cage return. Since return affects the magnitude of the kinetic ratio, observed as products, or even whether it is greater or less than one, conclusions reached from kinetic parameters derived from such studies are dubious unless the effects of viscosity are considered.

Experimental Section

Materials. All reagents except Freon 112 and 1,2-epoxybutane were obtained as reagent grade [toluene, (Philips research grade)] and were distilled through an 18-in. Teflon spinning band column before use. Freon 112 was recrystallized several times before use, while the epoxide (Aldrich Chemical Co.) was used as supplied. The reagents were shown to be >99.9% pure by GLPC analysis.

Viscosity Measurements. The viscosities of all the solvent mixtures reported in this work were determined at the temperatures indicated in Tables I, II, and III by using an Ostwald viscometer, calibrated using the solvent indicated as a standard.[13]

Procedures. The reaction mixtures were prepared according to the procedures given in ref 8 and 9, and their viscosities were measured at the temperatures indicated in Tables I, II, and III. The photoinitiated bromination reactions were carried out in degassed sealed Pyrex ampules, thermostated at 23 °C, and irradiated through a Pyrex water bath using a 200-W incandescent lamp. After the reactions were completed, mixtures were analyzed by GLPC using a 50-m glass capillary column (SE-30). The relative rates of reaction were calculated from the disappearance of reactants.[14] All quantitative values were determined from two or more duplicate experiments and the molar values were determined by using standard calibration curves obtained by using known mixtures of the authentic materials. The areas were determined by using a HP 5840A GC terminal interfaced to a HP 5840A gas chromatograph fitted with an FID detector.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; Br_2, 7726-95-6; Br, 10097-32-2; toluene, 108-88-3; *p*-chlorotoluene, 106-43-4; benzyl radical, 2154-56-5; *p*-chlorobenzyl radical, 3327-51-3.

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