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Electrophilic Bromination of Deuterated Cyclohexenes in Acetic Acid Containing Varying [Bromide]: Kinetics and Product Studies

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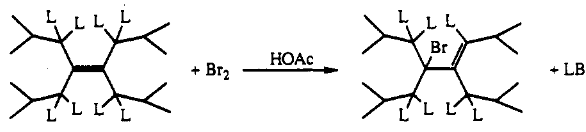
Abstract: The kinetics of bromine addition to various deuterated isotopomers of cyclohexene, namely the parent (**3a**), 3,3,6,6-tetradeuteriocyclohexene (**3b**), and cyclohexene-d_{10} (**3c**), have been determined in HOAc (T = 25 °C) as a function of added [Br$^-$], and the products were determined., The observed kinetic isotope effect for bromination of **3a**/**3b** is $k_H/k_D \simeq 1.0$ with no added salt and indicates that deuteration of the allylic positions does not influence the kinetics. The kinetics of bromination of **3a**/**3c** have been conducted at constant ionic strength (μ = 0.1 LiClO$_4$) as a function of [Br$^-$] to determine the kinetic isotope effect on the Br$_2$ and Br$_3^-$ reactions: (k_{Br_2}) **3a**/**3c** = 1.08 (0.10) × 10^3 M^{-1} s^{-1}/2.15 (0.10) × 10^3 M^{-1} s^{-1} = 0.5; ($k_{Br_3^-}$) **3a**/**3c** = 3.09 (0.11) × 10^2 M^{-1} s^{-1}/3.98 (0.11) × 10^2 M^{-1} s^{-1} = 0.78. The large inverse kinetic isotope effect (KIE) for k_{Br_2} **3a**/**3c** is consistent with a rate limiting step having considerable rehybridization of the olefinic carbons and may also indicate that the partitioning of the bromonium ion between reversal and product formation may be isotopically sensitive. The smaller inverse KIE for $k_{Br_3^-}$ **3a**/**3c** is consistent with a process wherein Br$^-$ nucleophilically captures an olefin/Br$_2$ charge-transfer complex or captures a reversibly formed bromonium/Br$^-$ ion pair. The ratio of the dibromide/bromoacetate products is determined as a function of added Br$^-$ and analyzed by a mechanism wherein the Br$_2$ reaction gives a bromonium ion/Br$^-$ pair that collapses to give a 27:73 mixture of dibromide/bromoacetate, a Br$_3^-$ reaction that gives only *trans*-dibromide, and an additional channel for production of dibromide resulting from external Br$^-$ capture of a bromonium ion. Finally, the kinetics of bromine addition to 1,2-diphenylcyclohexene (**4a**), 3,3,6,6-tetradeuterio-1,2-diphenylcyclohexene (**4b**), 1,2-bis(*p*-chlorophenyl)cyclohexene (**4c**), and 1,2-bis(*p*-methoxyphenyl)cyclohexene (**4d**) have been determined and analyzed in terms of a mechanism involving an open β-bromocationic intermediate. In the case of **4a**/**4b** a k_H/k_D of 1.4 in HOAc suggests that ion formation is reversible in that solvent, and the rate limiting step is Br$^-$ promoted removal of an allylic H(D) from the intermediate. The k_H/k_D determined for **4a**/**4b** in MeOH of 1.0 suggests that in this solvent the rate limiting step is ion formation and that all following steps are fast.

Introduction

Electrophilic bromination has been the subject of intense study and has recently attracted renewed interest.[1] The more recent work has dealt with structural and NMR characterization of a stable bromonium ion,[2] determining the situations where reversible formation of the intermediate ions occurs,[3] investigations of the lifetimes of bromonium ions in MeOH,[4] and investigations of the importance of solvent assistance in olefin bromination.[1a,b,3g] Considering the large number of kinetic studies directed toward this seemingly simple process, it is surprising how few studies dealing with deuterium kinetic isotope effects have been reported. As far as we are aware, the earliest of these concerned the secondary α deuterium KIE for bromination of *trans*-stilbene-d_2 where an inverse value of k_H/k_D = 0.91 was found.[5] Para substituted α-d-styrenes, when brominated in HOAc at 40 °C, were reported[6] to exhibit very small inverse deuterium α KIEs ($k_H/k_D \sim$ 0.95–0.99). Solvent deuterium KIEs have been reported for a variety of olefins in hydroxylic solvents[3e,g,7] and HOAc:[8] the large observed values (k_{SOH}/k_{SOD} = 1.2–1.4) imply considerable H-bonding (electrophilic) assistance in the rate limiting transition states. In chloroform the bromination of cyclohexene by Br$_2$ exhibits a k_{CHCl_3}/k_{CDCl_3} = 1.0, while bromination of the same substrte by tetrabutylammonium tribromide gives k_{CHCl_3}/k_{CDCl_3} = 1.17 (0.03) signifying different reaction mechanisms for each reagent.[9]

Apart from the above few studies, a single example exists wherein a congested olefin, tetraisobutylethylene (TIBE, **1**), when perdeuterated at the allylic positions gives an unusually high KIE (k_H/k_D = 2.2) when brominated in HOAc.[3f] This unusual result is not reconcilable in terms of β secondary deuterium KIEs but stems from the fact that the rate limiting step for this bromination is removal of the allylic L from the bromonium ion to form the double bond rearranged allylic bromide **2**. Although arguments were presented[3f] in support of a negligible effect of the eight β deuteriums on bromonium ion formation, little hard evidence on this point is available. We deal in this report with determining the α and β secondary deuterium KIEs for bromination in HOAc of a typical cyclic olefin, cyclohexene (**3a**), which is specifically deuterated as in **3a**,**c**. Also we report the kinetics and reaction products for the bromination of cyclohexene in HOAc as a function of added [Br$^-$]. Finally, we report the kinetics of Br$_2$ addition



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1 (L = H,D) 2

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(1) For recent reviews and communications see: (a) Ruasse, M.-F.; Motallebi, S. *J. Phys. Org. Chem.* **1991**, *4*, 527. (b) Ruasse, M.-F. *Acc. Chem. Res.* **1990**, *23*, 87. (c) DeLaMare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982, pp 136–197.

(2) (a) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4505. (b) Bennet, A. J.; Brown, R. S.; McClung, R. E. D.; Aarts, G. M.; Klobukowski, M.; Santarsiero, B. D.; Bellucci, G.; Bianchini, R. *J. Am. Chem. Soc.* **1991**, *113*, 8532.

(3) (a) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. (b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988**, *110*, 546. (d) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640. (e) Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298. (f) Brown, R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310. (g) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440. (h) Bellucci, G.; Chiappe, C.; Marioni, F.; Marchetti, F. *J. Phys. Org. Chem.* **1991**, *4*, 387.

(4) Nagorski, R.; Brown, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7773–7779.

(5) Denney, D. B.; Tunkel, N. *Chem. Ind.* (*London*) **1959**, 1383.

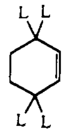
(6) Wilkins, C. L.; Regulski, T. W. *J. Am. Chem. Soc.* **1972**, *94*, 6016.

(7) (a) Ruasse, M.-F.; Motellebi, S. *Bull. Soc. Chim. Fr.* **1988**, 349. (b) Garnier, F.; Donnay, R.; Dubois, J. E. *J. Chem. Soc.* **1971**, 829.

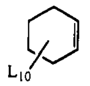
(8) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.

(9) Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, I. *J. Org. Chem.* **1985**, *50*, 3313.

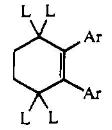
0002-7863/93/1515-1347$04.00/0



3a (L = H)
b (L = D)



3c (L = D)



4a (Ar = C_6H_5; L = H)
b (Ar = C_6H_5; L = D)
c (Ar = C_6H_4Cl; L = H)
d (Ar = $C_6H_4OCH_3$; L = H)

to the more heavily substituted olefins **4a–d**.

Experimental Section

(a) Materials. Acetic acid was purified as described.[3a] LiBr (General Intermediates) and $LiClO_4$ (Alfa) were dried in vacuum at 120 °C over P_2O_5 for 48 h. Br_2 (Aldrich) was used as supplied.

Cyclohexene-*3,3,6,6-d*$_4$ (**3b**) was prepared in 15% yield starting from butadiene sulfone and D_2O (99.9%, Aldrich) according to the published procedure:[10] mass analysis indicated a 98% incorporation of d_4. Cyclohexene-d_{10} (**3c**) was made in 50% yield by dehydration of cyclohexanol-d_{12} (98%, Aldrich) according to a published procedure.[11]

1,2-Diphenylcyclohexene (**4a**)[12] 1,2-bis(*p*-chlorophenyl)cyclohexene (**4c**), and 1,2-bis(*p*-methoxyphenyl)cyclohexene (**4d**) were synthesized by McMurry coupling[13] of the corresponding 1,4-diaroylbutanes which in turn were synthesized in a manner analogous to that reported for 1,4-dibenzoylbutane.[14]

4a:[12] 65% yield; ^{1}H NMR ($CDCl_3$) δ 7.14–6.96 (10 H, m), 2.47 (4 H, m), 1.86 (4 H, m); exact mass calcd for $C_{18}H_{18}$ 234.1408, found 234.1403.

4c: 25% yield; mp 95–96 °C; ^{1}H NMR ($CDCl_3$) δ 6.98 (8 H, AA′BB′ pattern), 2.40 (4 H, m), 1.82 (4 H, m); exact mass calcd for $C_{18}H_{16}{}^{35}Cl_2$ 302.0629, found 302.0631. Anal. C, H.

4d: 30% yield; mp 89–90 °C. ^{1}H NMR ($CDCl_3$) δ 6.80 (8 H, AA′BB′ pattern), 3.72 (6 H, s), 2.40 (4 H, m), 1.80 (4 H, m); exact mass calcd for $C_{20}H_{22}O_2$ 294.1620, found 294.1620. Anal. C, H.

1,1,4,4-Tetradeuterio-1,4-dibenzoylbutane (1,4-dibenzoylbutane-d_4) was made by heating a solution consisting of 25 mL of EtOD, 25 mL of 2 N DCl/D_2O, and 5 g of pure 1,4-dibenzoyl butane[14] at reflux overnight. The cooled mixture was extracted with CH_2Cl_2 which was then dried ($MgSO_4$) and evaporated to yield a residue that was recrystallized from cyclohexane. ^{1}H NMR analysis indicated 80% exchange of the allylic positions. The entire process was repeated two more times to yield material that was >99% (by ^{1}H NMR) exchanged at the α-positions.

1,2-Diphenylcyclohexene-*3,3,6,6-d*$_4$ (**4b**) was synthesized as above from 1,4-dibenzoylbutane[14] which had been perdeuterated at the two α-carbons as described above.

(b) Kinetics. Fast brominations of cyclohexenes **3a–c** and **4d** in purified HOAc at 25 °C were followed at 400–480 nm using a Durrum Gibson stopped-flow spectrophotometer interfaced to a microcomputer system previously described.[15] Digitally stored (TDI 1024 C transient recorder) absorbance vs time traces were analyzed by nonlinear least squares fitting to a standard exponential model to give the pseudo-first-order rate constants, k_{obsd}. Olefin concentrations were varied from 1×10^{-2}–4×10^{-3} M (after mixing) and the [Br_2] was ~2×10^{-4} M. All solutions were prepared and stored with protection from moisture and light. Second-order rate constants (k_{Br_2}) are given as k_{obsd}/[olefin].

Slower brominations (**4a–c**) were determined at 25 °C using a Cary 210 UV/vis spectrophotometer interfaced to a microcomputer as previously described.[3f]

Table I. Rate Constants for Bromination of **3a–c** in HOAc at 25 °C, No Added Salts[a]

olefin	[concn] (M) (×10^3)	k_{obsd} (s^{-1})	k_{Br_2}[b] (M^{-1} s^{-1})
3a	5.3	1.72 (0.09)	324 (17)
3a	8.4	2.71 (0.10)	322 (12)
3b	4.0	1.31 (0.09)	326 (23)
3b	9.6	3.18 (0.11)	332 (11)
3c	4.2	2.60 (0.21)	619 (50)
3c	9.5	5.89 (0.26)	620 (27)
3c	9.5	5.80 (0.33)	607 (35)

[a] [Br_2] = 2×10^{-4} M; followed at various wavelengths from 410–480 nm. [b] k_{Br_2} = k_{obsd}/[ol]; values are an average of 12–16 independent stopped flow determinations; values in brackets are averages of the sums of standard deviations for each determination.

(c) Product Studies. (i) Bromination of Cyclohexene in HOAc Containing LiBr/LiClO$_4$, μ = 0.1. A typical experiment was performed as follows. Into ~45 mL of purified HOAc containing the appropriate amount of LiBr and/or $LiClO_4$ to give μ = 0.1 and thermostated at 25 °C was placed 40 μL (4×10^{-4} mol) of cyclohexene. To this was added equimolar Br_2 in 5 mL of HOAc. After addition, the colorless solution was poured into 200 mL of H_2O. The resultant mixture was extracted with 3 × 100 mL of CH_2Cl_2, and the combined extracts were washed several times with 10% Na_2CO_3 and then dried over $MgSO_4$. After filtration and removal of the solvent by rotary evaporation with the flask held at T < 20 °C, the residue was taken up in 10 drops of CH_2Cl_2 and then analyzed by GLPC (6′ × 1/8″ 10% OV-1 on 80–100 mesh Chromosorb W; He flow rate = 55 mL/min; T_1 = 120 °C for 2 min followed by a ramp of 5 °C/min to 180 °C). Retention times are as follows: *trans*-1,2-dibromocyclohexane, 6.25 min; *trans*-1-acetoxy-2-bromocyclohexane, 7.3 min.

(ii) 1,2-Diphenylcyclohexene. 3,3,6,6-Tetradeuterio-1,2-diphenylcyclohexene (**4b**) was placed in HOAc along with 1 equiv of Br_2 and the ^{2}H NMR spectrum was monitored. The peak at δ 2.38 attributable to the four allylic D's of **4a** disappeared with the simultaneous appearance of some lower field peaks and a peak at δ 5.36 with a second equivalent intensity peak attributable to DOAc. These observations indicate that the process involves loss of an allylic D^+ concurrent with the attack of Br^+.

1,2-Diphenylcyclohexene was treated with 1 equiv of Br_2 in CH_3OH, and the product was immediately isolated by extraction with CH_2Cl_2. After evaporation of the solvent, the crude residue was subjected to mass spectroscopic analysis which yielded peaks at (mass (% intensity, assignment)) 346.0745 (4.23%, $C_{19}H_{21}O^{81}Br$), 344.0767 (4.28%, $C_{19}H_{21}O^{79}Br$), 265.1585 (4.02%, $C_{19}H_{21}O$), 234.1403 (92.30%, $C_{18}H_{18}$), 233.1317 (40.87%, $C_{18}H_{17}$), 232.1252 (100%, $C_{18}H_{16}$).

Bromination of **4b** was monitored in HOMe by ^{2}H NMR. After the addition of 1 equiv of Br_2, the allylic D's of **4b** at δ 2.36 were replaced by a complex pattern between δ 2.0 and 2.5, along with a peak at δ 4.07 and an increase in the intensity of the resonance at δ 4.86 attributable to *D*OMe.

Results

Given in Table I are the observed pseudo-first-order rate constants k_{obsd} for bromination of excess **3a–c** in HOAc at 25 °C in the absence of added salts. The second-order rate constant, k_{Br_2}, is simply defined as k_{obsd}/[ol]. In Table II are found the kinetic constants for bromination of **3a** and **3c** in HOAc containing various [Br^-] at constant ionic strength (μ = 0.1 $LiClO_4$). Also in Table II are the percentages of the corresponding *trans*-dibromide and bromoacetate addition products formed under the kinetic conditions. The kinetics of bromination of olefins in media containing added [Br^-] are complicated by a rapidly established[16] equilibrium, $Br^- + Br_2 \rightleftharpoons Br_3^-$.[17] In HOAc, the accepted value for the tribromide equilibrium constant is K_{eq} = 92 M^{-1}.[16,17d] Both Br_2 and Br_3^- are brominating agents,[1,17] so that the rate of disappearance of total bromine, or $[Br_2]_t$, is

$$\frac{-d[Br_2]_t}{dt} = k[Br_2]_t[ol]$$

$$= (k_{Br_2}[Br_2]_f + k_{Br_3^-}[Br_3^-])[ol]$$

$$= (k_{Br_2}[Br_2]_f + k_{Br_3^-}K_{eq}[Br^-][Br_2]_f)[ol] \qquad (2)$$

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(10) Wolfe, S.; Campbell, J. R. *Synthesis* **1979**, 117.

(11) Waldmann, H.; Petru, F. *Ber.* **1950**, *287*, 83.

(12) Baumstark, A. L.; Bechara, E. J. H.; Sernigran, M. J. *Tetrahedron Lett.* **1976**, 3265.

(13) Fleming, M. P.; McMurray, J. E. *Org. Synth.* **1981**, *60*, 113.

(14) Fuson, R. C.; Walker, J. T. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. II, p 169.

(15) Brown, R. S.; Ulan, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 3282.

(16) Ruasse, M.-F.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382.

(17) (a) Nakagawa, T. W.; Andrews, L. J.; Keefer, R. M. *J. Phys. Chem.* **1957**, *61*, 1007. (b) Dubois, J. E.; Herzog, H. *Bull. Soc. Chim. Fr.* **1963**, 57. (c) Dubois, J. E.; Hegarty, A. F.; Bergman, E. D. *J. Org. Chem.* **1972**, *37*, 2218. (d) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477, 1483. (e) Kanyaev, N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1959**, *29*, 825. (f) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369 and earlier references therein. (g) Bell, R. P.; Pring, M. *J. Chem. Soc. B* **1966**, 1119. (h) De Young, S.; Berliner, E. *J. Org. Chem.* **1979**, *44*, 1088. (i) Bartlett, P. D.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466. (j) Dubois, J. E.; Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1546.

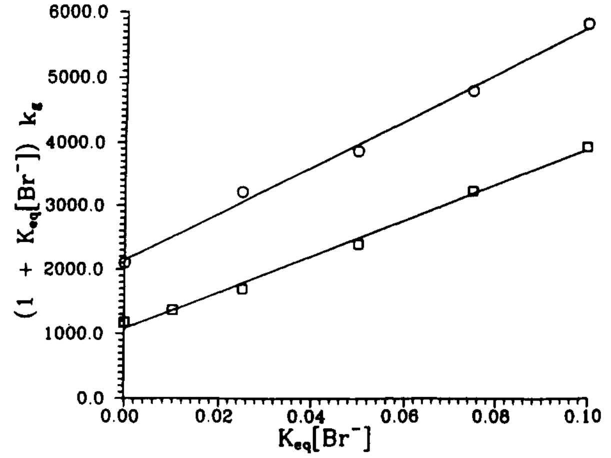


Figure 1. Plot of $k_g(1 + K_{eq}[Br^-])$ vs $K_{eq}[Br^-]$ for bromination of cyclohexene (**3a**, □) and cyclohexene-d_{10} (**3c**, ○) in HOAc at T = 25 °C, μ = 0.1 ($LiClO_4$).

Table II. Rate Constants and Product Percentages for Bromination of **3a** and **3c** in HOAc as a Function of Added $[Br^-]$, T = 25 °C, μ = 0.1 ($LiClO_4$)[a]

olefin	LiBr (M)	$LiClO_4$ (M)	k_g[b] ($M^{-1}\ s^{-1}$)	% dibromide[c]	% bromoacetate[c]
3a	0	0.1	1.18×10^3	27.4	72.6
3c	0	0.1	2.10×10^3		
3a	0.01	0.09	7.13×10^2		
3a	0.025	0.075	5.16×10^2	70.6	29.4
3c	0.025	0.075	9.75×10^2		
3a	0.05	0.05	4.30×10^2	82.0	18.0
3c	0.05	0.05	6.92×10^2		
3a	0.075	0.025	4.12×10^2	87.6	12.4
3c	0.075	0.025	6.12×10^2		
3a	0.1	0	3.88×10^2	90.3	9.7
3c	0.1	0	5.76×10^2		

[a] $[Br_2] = 1\text{–}2 \times 10^{-4}$ M; [ol] = 2×10^{-3} M; followed at 410–480 nm. [b] k_g defined as $k_{obsd}/[ol]$; see text; ±5%. [c] Isolated as described in the Experimental Section.

where k_{Br_2} is the second-order rate constant for addition of free Br_2 ($[Br_2]_f$) and $k_{Br_3^-}$ is the rate constant for addition of Br_3^-, or its kinetic equivalent, $Br^- + Br_2$. The observed global second-order rate constant for disappearance of $Br_2(k_g)$ can be expressed[1,17] as

$$k_g = (k_{Br_2} + k_{Br_3^-}K_{eq}[Br^-])/(1 + K_{eq}[Br^-]) \qquad (3)$$

so that a plot of $(1 + K_{eq}[Br^-])]k_g$ vs $K_{eq}[Br^-]$ gives an intercept of k_{Br_2} and a slope of $k_{Br_3^-}$. In Figure 1 is a plot of the data (Table II) for both cyclohexene (**3a**) and cyclohexene-d_{10} (**3c**). The respective k_{Br_2} values are 1.08 (0.10) × 10^3 and 2.15 (0.10) × 10^3 $M^{-1}\ s^{-1}$, while the respective $k_{Br_3^-}$ values are 3.09 (0.11) × 10^2 and 3.98 (0.11) × 10^2 $M^{-1}\ s^{-1}$. Thus, the overall secondary α KIE for the Br_2 addition $(k_{Br_2})_{D/H}$ is inverse at 2.0 as is the one for the Br_3^- addition, $(k_{Br_3^-})_{D/H} = 1.29$.

The second-order rate constants for Br_2 addition to **4a–d** in HOAc or MeOH at 25 °C in the absence of salts are given in Table III.

Discussion

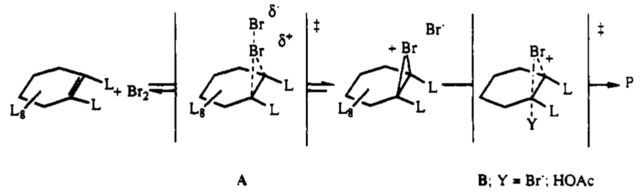
(a) Cyclohexene. (i) Br_2 Reaction. The data of Table I indicate that the β-secondary KIE (k_H/k_D) for Br_2 addition to **3a** and **3b** in HOAc is 1.0 ± 0.1. The products for this reaction are the corresponding *trans*-dibromide and bromoacetate formed in 31% and 69% in the absence of added salts and 27% and 73%, respectively, in the presence of 0.1 M $LiClO_4$ (Table II). The kinetics indicate that substitution of four allylic D's for H's does not affect the reaction rate appreciably when the products are those of addition. This finding experimentally corroborates an earlier interpretation[3f] suggesting that β-isotopic substitution in TIBE (**1**) to give TIBE-d_8 (**1**, L = D) would not generate a significant secondary deuterium β-KIE during reaction with Br_2 if the rate limiting step was simply bromonium ion formation.

Table III. Second-Order Rate Constants for Bromination of 1,2-Diarylcyclohexenes **4a–d** in HOAc and MeOH at 25 °C with No Added Salts[a]

olefin	solvent	k_{Br_2} ($M^{-1}\ s^{-1}$)	method[b]
4a	HOAc	0.131 (0.005)	A
4b	HOAc	0.095 (0.003)	A
4a	MeOH	0.73 (0.03)	A
4b	MeOH	0.69 (0.02)	A
4c	HOAc	0.004 (0.0004)	A
4d	HOAc	2480 (180)	B

[a] $[Br_2] = 1\text{–}2 \times 10^{-4}$ M; [ol] = $2 \times 10^{-3} \rightarrow 5.1 \times 10^{-3}$ M; λ = 410 nm, μ = 0. [b] A, Cary 210 UV/vis spectrophotometer; B, stopped flow.

The data in Table I also show that bromination of cyclohexene-d_{10} (**3c**) leads to an inverse secondary deuterium KIE for k_{Br_2} (**3c**/**3a**) of k_D/k_H = 1.89 (0.19). The dibromide/bromoacetate ratio formed from Br_2 addition to **3c** is 31%/69%, indistinguishable from what is seen for **3a**. The KIE is essentially independent of ionic strength, the value at μ = 0.1 ($LiClO_4$) being 2.0 (0.20) as determined from the intercepts of the plots for **3c** and **3a** shown in Figure 1. The KIE is mostly attributable to the H(D) substitution on the olefinic carbons since substitution of the allylic positions as in **3b** contributes no observable effect to the kinetics. Substitution of the more remote homoallylic ones is also not expected to contribute greatly to the kinetics.[18] The observed inverse KIE is consistent with a rate determining transition state (rdts) in which considerable rehybridization of the olefinic carbons from sp^2 toward sp^3 has occurred,[19] but the size of the KIE is larger than that reported for bromination of styrenes[6] and what is usually observed for addition processes such as Diels–Alder reactions[20] or electrophilic additions of *N*-phenyl-1,2,4-triazoline-3,5-dione to α,β-unsaturated esters[21] in which similar rehybridizations occur. The exact reasons for the large observed value are unclear at present but could result from the major rehybridization effect superimposed upon smaller but cumulative inverse contributions from the eight β and γ deuteria as well as isotopic perturbation of the charge-transfer equilibrium constant. Shown in eq 4 are two possible transition states leading to or away from the bromonium ion that, in principle, are consistent with the KIE:



(4)

In the first, A, if the rdts is formation of the symmetrical bromonium ion, the α-KIE per deuterium is $\sqrt{2.0} = 1.4$ since the extent of rehybridization of each of the carbons is equal. In B, where the rdts is breakdown of the bromonium ion, the observed KIE is a product of two not necessarily equal contributions since the transition state is asymmetric with respect to bond making and breaking. Also consistent with the data would be a virtual

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[18] The best compound for testing this reasonable assumption would be 1,2-dideuteriocyclohexene, but we were unable to prepare this material by the reported[10] route. However, that the γ-deuteria have virtually no kinetic effect can be supported by the fact that γ and δ effects on the solvolyses of various substrates show inverse secondary KIEs of $k_H/k_D \sim 1\%$/D. Shiner, V. J., Jr. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; A.C.S. Monograph 167, Van Nostrand-Reinhold: New York, 1970; pp 151–152.

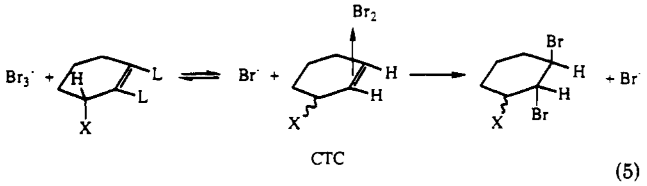
[19] (a) Lowry, T. H.; Richardson, K. S. In *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 232–244. (b) Maskill, H. In *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford, 1985; pp 367–404. (c) Westaway, K. C. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 7, pp 275–392.

[20] Gajewski, J. J.; Peterson, K. B.; Kagel, J. R.; Huang, Y. C. J. *J. Am. Chem. Soc.* **1989**, *111*, 9078.

[21] Elemes, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 8044.

transition state in which product formation and reversion to starting materials are competitive. In this case, the large inverse KIE could in part be due to reversible formation of a bromonium/Br^- ion pair, the partitioning of which could be sensitive to isotopic substitution (i.e., H_{10} cyclohexene reverses more than cyclohexene-d_{10}).[22]

(ii) Br_3^- Reaction. It has long been known that Br_3^- also contributes to the kinetics of bromination.[1,16] In chlorinated hydrocarbons such as $CHCl_3$ or $ClCH_2CH_2Cl$, Bellucci et al.[23] have provided evidence that the tribromide reactions for various 3-substituted cyclohexenes involve product and rate determining attack of Br^- on an olefin/Br_2 charge-transfer complex (CTC, eq 5) to yield the corresponding 3-substituted *trans*-1,2-dibromide.



(5)

In hydroxylic solvents considerably more work has been done, but no one explanation seems consistent with all the experimental data. The three most often cited[17] possibilities are (a) a salt effect that influences the polarity of the medium and hence its ability to support charge developing in the transition state, (b) Br_3^- acting as an electrophile to yield a bromonium ion plus $2Br^-$ ions, and (c) a kinetically equivalent nucleophilic reaction similar to that described by Bellucci[23] where Br^- captures the CTC or some other intermediate having the same stoichiometry, e.g., a bromonium/bromide ion pair. Both Dubois[17f] and Yates[17d] have shown that in MeOH or HOAc the ratio of $k_{\mathrm{Br}_3^-}/k_{\mathrm{Br}_2}$ increases as the olefin reactivity decreases. This seems inconsistent with (b) above since the negatively charged Br_3^- would be anticipated to be a poorer electrophile than Br_2. Also, Yates and Rolston[17d] have shown that in HOAc, the ρ^+ values for the k_{Br_2} and $k_{\mathrm{Br}_3^-}$ reactions for bromination of ring substituted styrenes are −4.21 and −2.02 showing that far less positive charge is generated on the α-carbon atom during the Br_3^- reaction. This is consistent with an asymmetric transition state in which Br^- attacks the α-carbon of the styrene CTC or its ionic equivalent, the cation[24]/Br^- ion pair.

Use of α-deuterium KIEs as in the present study could offer an additional method to probe the Br_3^- reaction with **3a** and **3c**. With respect to mechanistic possibilities a–c above, the expected effects are (a) ($k_{\mathrm{Br}_3^-}$) **3c**/**3a** $\cong$ 1.0 and is insensitive to ionic strength effects, (b) ($k_{\mathrm{Br}_3^-}$) **3c**/**3a** is large, perhaps ~2.0 for Br_3^- acting as an electrophile since the transition state would be similar, in terms of the rehybridization of the olefinic carbons, to the transition state for the Br_2 reaction, and (c) ($k_{\mathrm{Br}_3^-}$) **3c**/**3a** is significantly smaller than that for the Br_2 reaction if Br^- captures the CTC since this would involve not only an asymmetric transition state but also one having far less rehybridization of the olefinic carbons.

The data of Table II and Figure 1 indicate that ($k_{\mathrm{Br}_3^-}$) **3c**/**3a** = 1.29 is significantly lower than noted for the k_{Br_2} reaction (2.0) and suggests far less rehybridization of the olefinic carbons in the Br_3^- transition state than in the Br_2 one. This is likely inconsistent with an electrophilic role for Br_3^- in this case and is more supportive of a nucleophilic role of Br^- on the olefin-Br_2 CTC as in eq 5. A low α-deuterium KIE has been used as a criterion for nucleophilic assistance in substitution reactions, particularly in the case of neighboring group participation.[25] Also, there is a clear distinction between the α-D KIE of k_H/k_D ~ 1.0 for S_N2 reactions and the value of 1.19–1.25 per α C–D(H) for S_N1 reactions of secondary alkyl substrates.[26]

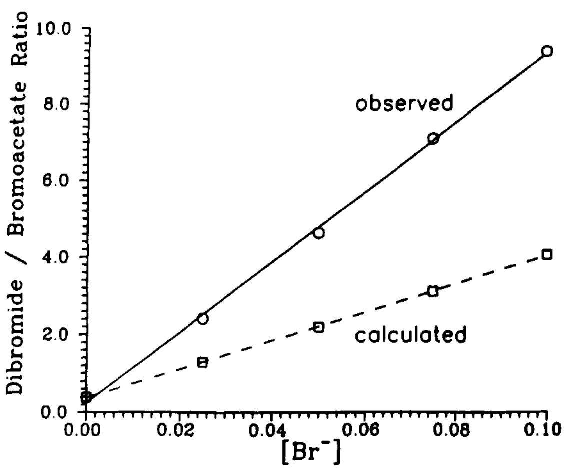


Figure 2. Plot of the dibromide/bromoacetate product ratio obtained from bromination of cyclohexene in HOAc containing varying [Br^-], T = 25 °C, μ = 0.1; ○—○, experimental points; □--□, line computed on the basis of eqs 7 and 8.

(iii) Products for Br_2/Br_3^- Reactions with Cyclohexene. Given in Table II are the percentages of dibromide and bromoacetate isolated from the reaction of Br_2 with cyclohexene (**3a**) in HOAc containing varying [Br^-] but at constant ionic strength (μ = 0.1 ($LiClO_4$)). The dibromide/bromoacetate ratio as a function of [Br^-] is plotted in Figure 2. That the intercept of the plot of the dibromide/bromoacetate ratio vs [Br^-] has an intercept of 0.38 (Figure 2) indicates that collapse of the ion pair formed from the Br_2 reaction represents a significant channel to dibromide product. On the other hand, the nucleophilic process which is supported by the low α-D KIE for the Br_3^- mechanism requires that this reaction leads exclusively to trans dibromide. Following approaches used by Kanyaev,[17e] Bell and Pring,[17g] Rolston and Yates,[17d] and De Young and Berliner,[17h] the ratio of the dibromide to solvent incorporated (bromoacetate) product can be calculated once the k_{Br_2}, $k_{\mathrm{Br}_3^-}$, and K_{eq} constants are known. The main difference here from the approach used in the previous works[17d,e,g,h] concerns the 27:73 partitioning of products observed for the k_{Br_2} reaction with cyclohexene in HOAc at μ = 0.1. From the simplified process shown in eq 6 can be derived the expression in eq 7 which gives the predicted dibromide/bromoacetate ratio as a function of [Br^-].

$$\text{dibromide} \xleftarrow{k_{\mathrm{Br}_3^-}} \text{ol} + \mathrm{Br}_3^- \underset{}{\overset{+\mathrm{Br}^-(K_{\mathrm{eq}})}{\rightleftharpoons}} \mathrm{Br}_2 + \text{ol} \xrightarrow{k_{\mathrm{Br}_2}} \underset{27 \quad : \quad 73}{\text{dibromide} + \text{bromoacetate}} \quad (6)$$

$$\frac{[\text{dibromide}]}{[\text{bromoacetate}]} = \frac{0.27k_{\mathrm{Br}_2} + k_{\mathrm{Br}_3^-}K_{\mathrm{eq}}[\mathrm{Br}^-]}{0.73k_{\mathrm{Br}_2}} = 0.38 + \frac{k_{\mathrm{Br}_3^-}K_{\mathrm{eq}}[\mathrm{Br}^-]}{0.73k_{\mathrm{Br}_2}} \quad (7)$$

The calculated dependence, shown in Figure 2 as the dashed line, is seen to lie below the observed line. In other words, based on the simple process shown in eq 6, the predicted dibromide product formed in the presence of added Br^-, is *lower* than observed. This does not necessarily rule out the process given in eq 6, but it does indicate that there must be an additional channel other than the Br_3^- reaction and ion pair collapse of the nascent bromonium ion/Br^- pair for the formation of dibromide in the presence of added Br^-. The most reasonable candidate for this pathway would be capture of a bromonium ion (either a free ion, intimate ion, or solvent separated ion pair) by external Br^-.

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[22] In earlier studies we have shown that solvolysis of *trans*-2-bromocyclohexyl bromobenzenesulfonate in HOAc generates bromonium ions that can be captured by added Br^- to give Br_2 and cyclohexene (Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. *J. Am. Chem. Soc.* **1984**, *106*, 4515).

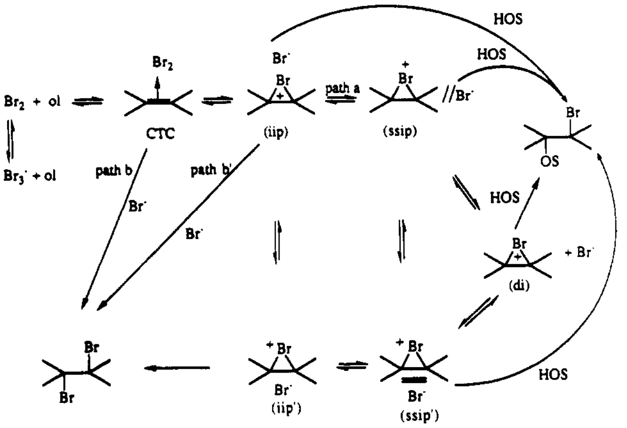
[23] (a) Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, G. *J. Org. Chem.* **1985**, *50*, 3313. (b) Bellucci, G.; Bianchini, R.; Vecchani, S. *J. Org. Chem.* **1986**, *51*, 4224.

[24] In this case the positive counterion could be a partially bridged bromonium ion or a β-bromocation.[1b]

[25] Maskill, H. *J. Am. Chem. Soc.* **1976**, *98*, 8482.

[26] (a) *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; A.C.S. Monograph 167, Van Nostrand-Reinhold: New York, 1970. (b) Harris, J. M.; Hall, R. E.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551 and references therein. (c) Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553.

Scheme I[a]



[a] (iip) and (iip′) are intimate ion pairs; (ssip), (ssip′), and (di) are solvent separated ion pairs and dissociated ions.

(iv) A Scheme Consistent with the Data. Given in Scheme I is a mechanism similar to what we have proposed before[4] that is consistent with the cyclohexene data, and what is generally accepted for the behavior of ions and ion pairs in solution.[27] For the Br_2 reaction in the absence of added salts (labeled path a in Scheme I), ionization of the CTC that is formed in equilibrium with the olefin + Br_2 must generate a nascent intimate ion pair (iip) in which Br^- and the bromonium Br^+ are in close contact. That iip has available to it several potential fates, namely (a) reversal to starting material, (b) rapid backside attack by solvent to give bromosolvate products, (c) translocation of the Br^-/Br^+ ion pair to form a trans disposed intimate ion pair (iip′) perhaps via the involvement of solvent separated ion pairs, and (d) diffusional separation of the intimate pairs to solvent separated and then free ions. At zero added [Br^-], once the iip's undergo diffusional separation, the so-formed Br^- may be considered infinitely diluted so that the major product arising from the free ions would be solvent incorporated. This indicates that at zero added [Br^-], formation of the *trans*-dibromide product can only arise through the fast iip → iip′ conversion followed by ion pair collapse. Solvent incorporated product can arise from capture of any of the iip or the solvent separated/free bromonium ion. In H_2O and hydroxylic solvents of high dielectric constant (e.g., MeOH), the association constants for ions are small ($K_{as} = k_d/k_{-d} \leq 1\ M^{-1}$)[28,29] and are known to increase markedly in passing to solvents of lower dielectric constant. In fact, in glacial acetic acid ($\epsilon = 6.15$),[30] it is generally agreed that acids, bases, and salts are only slightly dissociated:[31] even the strong electrolyte $HClO_4$ has a dissociation constant (here defined as $K_{dis} = k_{-d}/k_d$) of $\sim 10^{-5}$. Since k_d, the rate constant for formation of the ion pairs from free ions can be assumed to be diffusion limited at 10^9–$10^{10}\ M^{-1}\ s^{-1}$ depending on the solvent viscosity, and then variations in the ion pair association constants are easily transcribed into variations in k_{-d}, the rate constant for diffusional separation of the ions.

Previously, for the reaction of Br_2 with cyclohexene in MeOH, we have shown[4] that the dibromide/methoxy bromide product ratio tends to zero as [Br^-] → 0. Within the context of Scheme I, that observation requires that solvent capture of the iip and/or diffusional separation of the first formed iip followed by solvent capture of the free bromonium ion is faster than iip → iip′ interconversion followed by ion pair collapse. In the case of HOAc which has a lower dielectric constant[30] and is less nucleophilic than MeOH, both the diffusional separation of the iip's and solvent capture should be retarded so that ion pair collapse is a more prominent pathway. This expectation is borne out by the observed dibromide/bromoacetate ratio of 0.38 at zero added [Br^-].

Added Br^- introduces at least two additional pathways for the bromination. One of these, labeled path b in Scheme I, involves a tribromide reaction for which the present cyclohexene data suggest that involvent of Br^- attack on the CTC or its kinetic equivalent. One possible kinetic equivalent could involve external Br^- capture of the reversibly formed iip (path b′ in Scheme I). These paths, leading exclusively to dibromide, cannot account for the full [Br^-] dependence of the latter product. However, as in Scheme I, added Br^- could intercept the free ion and through formation of iip′ could lead to dibromide.

The Br_3^- data for cyclohexene in HOAc invite comparison with those reported[17d] for styrene in the same solvent.[32] The reported k_{Br_2} and $k_{Br_3^-}$ values,[17d] if analyzed in terms of a mechanism where Br_2 addition gives bromoacetate and the Br_3^- reaction gives only dibromide, were suggested to give a predicted dibromide/bromoacetate ratio of 11.3 at 0.1 M added Br^-.[32] Experimentally, the observed value is 5.3 which implies there is some component of the Br_3^- reaction that does not generate dibromide product. Recognizing this, Yates and Rolston[17d] suggested a modification of the scheme proposed by Bell and Pring[17g] whereby the Br_2 and Br_3^- reaction generated two different carbonium ions that did not necessarily react with Br^- or HOAc in the same proportions. The kinetic data for substituted styrene[17d,f] indicate the $k_{Br_3^-}/k_{Br_2}$ ratio increases as the olefin becomes deactivated, increasing from 1.2 for styrene to 12 for 3-nitrostyrene. This seems inconsistent with any electrophilic route that leads to fully developed carbocationic intermediates even though, as evidenced by $\rho_{Br_3^-} = -2.02$, some (+) may be developing on the benzylic C. To account for all these facts, we suggest that there are two parallel kinetically important transition states, each having the stoichiometry Br^-, Br_2, ol. One of these leads to dibromide, but the other, in which Br^- acts as a base at the stage of the solvent separated ion pair to assist in the delivery of solvent to the bromonium ion (β-bromocation[1b] or its kinetic equivalent, the CTC), leads to bromoacetate as in eq 8. In either event, Br^- would influence the kinetics of disappearance of Br_2, but, depending on the olefin, the dibromide/bromoacetate ratio would be influenced by the relative amounts of Br^- induced nucleophilic capture vs solvent delivery. In the styrene case,[17d] the data can be fit by a modification of eq 7 in which 85% of the $k_{Br_3^-}$ reaction leads to dibromide and 15% leads to bromoacetate.

(8)

$$\frac{[\text{dibromide}]}{[\text{bromoacetate}]} = \frac{0.675k_{Br_2} + 0.85k_{Br_3^-}K_{eq}[Br^-]}{0.325k_{Br_2} + 0.15k_{Br_3^-}K_{eq}[Br^-]} \qquad (9)$$

(v) Br_2 Reaction with 1,2-Diarylcyclohexenes 4a–d. The kinetic data of Table III reveal two major findings for the Br_2 reaction with **4a–d** in HOAc at 25 °C, $\mu = 0$. First, the k_{Br_2} values for

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(27) March, J. *Advanced Organic Chemistry*, 3rd ed.; J. Wiley and Sons: New York, 1985; pp 263–268, and references therein.

(28) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.

(29) (a) Davies, C. W. *Ion Association*; Butterworths: London, 1962; pp 88–101. (b) Davies, C. W. *Ion Association*; Butterworths: London, 1962; pp 150–161.

(30) *CRC Handbook of Chemistry and Physics*, 48th ed.; Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1967–1968; p E-58. ϵ HOAc = 6.15 (20 °C); ϵ MeOH = 32.6 (25 °C).

(31) (a) Bruckenstein, S.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1956**, *78*, 2974 and references therein. (b) Kolthoff, I. M.; Bruckenstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 1.

(32) In fact the so-calculated[16d] dibromide/bromoacetate ratio for styrene underestimates the ratio predicted on the basis of the mechanism supported by the data obtained by Rolston and Yates. Their data indicate that the Br_2 reaction with styrene in HOAc, 25 °C, $\mu = 0.1$ ($LiClO_4$) at low [Br_2], conditions comparable to those used here, gives 32.5% acetoxy bromide and 67.5% dibromide. The dibromide must arise from ion pair collapse since there is no external Br^- present. Therefore, given the fact that the Br_2 reaction cannot yield exclusively acetoxy bromide, the correct expression for the predicted dibromide/acetoxy bromide ratio at any [Br^-] is

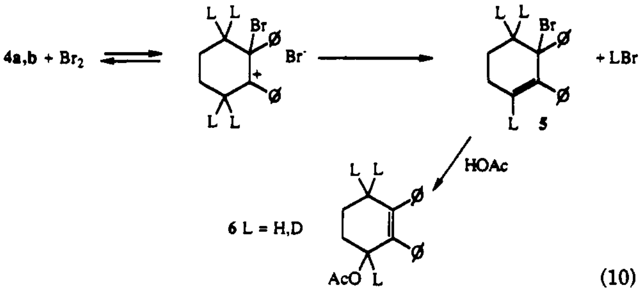
$$\frac{\text{dibromide}}{\text{acetoxy bromide}} = \frac{0.675k_{Br_2} + k_{Br_3^-}K_{eq}[Br^-]}{0.325\ k_{Br_2}}$$

where $K_{eq} = 92\ M^{-1}$ and k_{Br_2} and $k_{Br_3^-}$ are 89 and 109 $M^{-1}\ s^{-1}$, respectively.[16d] The calculated ratio using these values and [Br^-] = 0.1 M is 36.8.

4a,c,d cannot be fit by any single Hammett $\rho\sigma$ or $\rho^+\sigma^+$ correlation. Ruasse and Argile[33] and Ruasse et al.[34] have presented convincing evidence that α-methylstilbenes[33] and α-methylstyrenes[34] react with Br_2 in MeOH via open β-bromocarbonium ion intermediates. Since it has been established that the relative magnitude of the bromonium and carbonium ion pathways does not change in passing from MeOH to HOAc,[34] it is probably safe to say that **4a–d** react via open cationic intermediates. The kinetic data of Table III can be correlated satisfactorily by a Yukawa–Tsuno plot, $\log k_{Br_2} = -5.51(\sigma_x + 0.65\sigma^+)$, $r = 1.0$, similar to that used to correlate the kinetics of bromination of α-methylstyrenes in MeOH.[34] The slope of this plot is somewhat greater than the −4.59 and −4.26 noted for the α-methylstilbenes[33] and the α-methylstyrenes in MeOH[34] and probably signifies a greater development of (+) charge developing on the benzylic C of **4a–d** in the less polar solvent HOAc.

Second, there is a kinetic isotope effect of 1.38 (0.10) for (k_{Br_2}) **4a**/**4b** in HOAc, but a value of 1.05 (0.05) in MeOH. In S_N1 reactions where the rate limiting step is substantially ion formation (e.g., $(CL_3)_3C\text{-}Cl \rightarrow (CL_3)_3C^+$) the β-secondary KIEs are large and normal, being generally $k_H/k_D = 1.10$ (0.05)/β-CD.[35] The origin of the effect is hyperconjugation and this is known to be dependent upon the amount of (+) charge and the interorbital angle between the developing electron deficient pseudo-Π orbital and the adjacent C–L bond.[36] If ion formation were entirely rate limiting in the case of bromination of **4a,b** and hyperconjugation was the origin of the isotope effect, the observed KIE of 1.4 in HOAc seems too large for only two β-CL bonds which cannot both be optimally aligned with the developing electron deficient p-orbital. In addition, the value in HOAc is not easily reconcilable with the much lower (1.05) value observed in MeOH since it is expected that if ion formation is rate limiting in both cases, the influence of the β-CL bonds should be similar.

In the case of TIBE (**1**, eq 1) we have shown[3f] that deuteration of all eight allylic positions gives a k_H/k_D of 2.2 for the bromine reaction in HOAc. This was attributed to a primary KIE in which the removal of an allylic C–L bond from a reversibly formed bromonium ion was rate limiting or partially rate limiting. In that case, it was shown that the Br_2 reaction led to a double-bond rearranged allylic bromide, and one of the allylic deuteriums was lost to the solvent. In the present case, when a 10 mM solution of **4a** in CD_3COOD is treated with 1.0 equiv of Br_2, the ^1H NMR spectrum shows evidence of a proton being released to the solvent and the formation of an apparent doublet peak at δ 5.37 (J = 3.5 Hz) that we believe is attributable to the allylic acetate **6**, possibly formed from the transient, unstable tertiary allylic bromide **5** as in eq 10. A similar sequence of events is observed in the case of bromination of **4b** which, when monitored by ^2H NMR loses one deuterium to the solvent (CH_3COOH) and exhibits an ^2H resonance at δ 5.30.



(10)

Unfortunately, with the exception of the above facts, unambiguous identification of the products of these reactions has alluded us, and it is of note that the reaction products, as monitored by ^1H or ^2H NMR change as a function of time in the reaction medium. Similar observations have been made by others concerning the stabilities of products derived from Br_2 addition to tetrasubstituted alkenes.[3g,37] In the case of reaction of **4a** in CH_3OH with Br_2, isolation experiments have provided mass spectrometric evidence for some products that arise from the addition of Br and OCH_3, and fragments having the mass of $C_{18}H_{16}$ (**4a**-2H) which could have arisen from loss of HBr, HOME from the former, HBr from an allylic bromide, or HOMe from the allylic methoxy complex. ^2H NMR experiments on bromination of **4b** in CH_3OH indicate that deuteron is released to the solvent, and there is a new deuterium resonance at δ 4.07 that we attribute to the methoxy analogue of **5**.

The larger observed KIE for the bromination of **4a,b** in HOAc (1.4) relative to MeOH (1.05) suggests but does not prove different rate limiting steps for the process in the two solvents. By analogy with the reaction of TIBE, we suggest that in the case of bromination of **4a,b** in HOAc the KIE arises from a partially rate limiting step in which the allylic C–L bond of the open ion is being removed by Br^- at the stage of the intimate or solvent separate ion pairs in competition with reversal of these ions back to Br_2 + **4a,b**. The value of 1.4, which is lower than what is customarily observed for a primary kinetic isotope effect[19-21] could be a consequence of very nearly matched transition-state energies for the forward and reverse reactions in HOAc and a very early transition state for deprotonation. In the more polar and more nucleophilic MeOH, the low KIE of 1.05 suggests that whatever the product forming steps are, they are fast relative to the formation of the ion.

As a final point, we note there is a strong analogy for the above processes in the electrophilic bromination[38] and iodination[39] of certain substituted aromatics which also show primary kinetic isotope effects. This is interpreted[38,39] in terms of rapid and reversible formation of an intermediate bromocyclohexadienyl cation, followed by rate limiting or partially rate limiting proton loss to form halogenated products.

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(33) Ruasse, M.-F.; Argile, A. *J. Org. Chem.* **1983**, *48*, 202.

(34) Ruasse, M.-F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645.

(35) Shiner, V. J. in ref 7, pp 90–159.

(36) (a) Shiner, V. J., Jr.; Jewet, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 1382. (b) Shiner, V. J., Jr.; Humphrey, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 2416.

(37) (a) Meijer, E. W.; Kellogg, R. M.; Wynberg, H. *J. Org. Chem.* **1982**, *47*, 2005. (b) Mayr, H.; Will, E.; Heigl, U. W.; Schade, C. *Tetrahedron* **1986**, *42*, 2519. (c) Lenoir, D. *Chem. Ber.* **1978**, *111*, 41. (d) Andersen, L.; Berg, U.; Pettersson, I. *J. Org. Chem.* **1985**, *50*, 493.

(38) (a) Nilsson, A.; Olsson, K. *Acta Chem. Scand.* **1969**, *23*, 7. (b) Helgstrand, E.; Nilsson, A. *Acta Chem. Scand.* **1966**, *20*, 1463. (c) Schubert, W. M.; Gurka, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 1443 and references therein.

(39) (a) Pradham, D. G. *Ind. J. Chem.* **1973**, *11*, 894. (b) Grovenstein, E., Jr.; Aprahamian, N. S.; Bryan, C. J.; Gnanapragasam, N. S.; Kilby, D. C.; McKelvey, J. M.; Sullivan, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 4261.