Electrophilic Additions to *anti*-Sesquinorbornene. Br₂ in Methanol and the Addition of Acetic Acid

H. Slebocka-Tilk, D. Gallagher, and R. S. Brown*,†

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

The kinetics and products of addition of Br₂ in MeOH to *anti*-sesquinorbornene (**1**) have been studied at 25 °C in the presence of varying [LiBr]. The products consist of ~10% *cis* dibromide and 90% *cis* methoxy bromide, the amounts of these being independent of the [Br⁻]. The kinetics reveal that the reaction proceeds via the addition of Br₂, and that Br₃⁻ is not a brominating agent for this olefin. Acetic acid is shown to add rapidly to the double bond of **1** in a spontaneous reaction and via an acid-catalyzed process in the presence of HClO₄. For the spontaneous reaction a solvent deuterium kinetic isotope effect (DKIE) of 3.3 is observed. Proton inventory plots of k_{obs} vs atom fraction of deuterium in the medium indicate that the DKIE arises from a transition state for addition involving two or more protons undergoing changes in bonding. The HClO₄-catalyzed addition exhibits a large DKIE of 5.4 and is attributable to a simultaneous attack of HClO₄ or ClO₄⁻ H₂OAc⁺ and HOAc on the double bond. LiClO₄ also catalyzes the addition of solvent through a process exhibiting a DKIE of ~8. Analysis of the various equilibria involved indicates that HClO₄ is produced in appreciable amounts when LiClO₄ is dissolved in HOAc. Analysis of the kinetic dependence of the rate on [LiClO₄] indicates that the active species produced may be the ion aggregate Li⁺/ClO₄⁻/H₂OAc⁺.

Introduction

anti-Sesquinorbene (**1**, ASNB), with its planar olefinic unit,[1] possesses a number of structural properties that make it an attractive substrate for studying the reaction of electrophiles with its double bond.[2] These include (1) the exclusive formation of 1,2-*cis* adducts, and (2) it lacks the proclivity of its parent, norbornene, to undergo extensive Wagner−Meerwein rearrangement.[3]
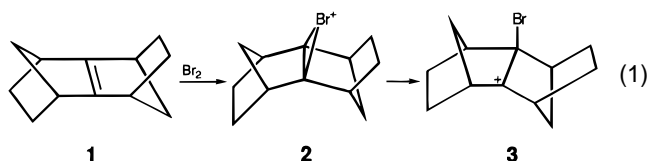
During the course of a program of electrophilic brominations of sterically encumbered olefins[4] we became aware of reports by Bartlett[2,3] and Paquette[5] indicating that, in chlorinated hydrocarbons, Br₂ addition to **1** and its *syn* isomer instantly yielded the corresponding *cis* 1,2-dibromide. The reaction may proceed via the intermediacy of the bromonium ion **2**, and if so, the formation of the *cis* dibromide must require that **2** open to a β-bro-

mocarbocation **3** prior to capture by Br⁻. The fact that Br⁻ capture at the *anti* side is structurally prohibited suggested to us that the bromonium ion might be reversibly formed, a situation akin to that previously demonstrated for bromination of other sterically compressed olefins[4] such as tetraisobutylethylene (**4**), 7-norbornylidene-7-norbornane (**5**), and adamantylideneadamantane (**6**).[4−c]
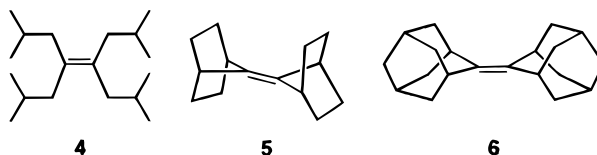
The reported reactivity of **1** toward Br₂ and other electrophiles prompted the investigation described herein, and a detailed mechanistic analysis of the addition of Br₂ in MeOH and HOAc was undertaken. In MeOH, the addition is shown to involve the formation of intermediate ions such as **2** and/or **3** which then evolve to the addition product by ion pair collapse. In HOAc, the situation is far more complicated because of unexpectedly rapid spontaneous and H⁺-catalyzed additions of the solvent and other nucleophiles such as Br⁻.

Experimental Section

a. Materials. *Anti*-Sesquinorbornene (**1**, tetracyclo[6.2.-1.1³,⁶.0²,⁷]dodec-2(7)-ene, or 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanonaphthalene) was prepared by the procedure of Miller and Kopecky[6] and had physical constants identical with those reported.

Acetic acid, methanol, LiClO₄, and LiBr were purified as previously described.[7,4a] Acetic acid-OD, Sigma, 98 atom % D, was purified by the same procedure.

† Address correspondence to this author at: Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6.
⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1996.
(1) Gajhede, M.; Jørgensen, F. S.; Kopecky, K. R.; Watson, W. H.; Kashyap, R. P. *J. Org. Chem.* **1985,** *50,* 4395.
(2) Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985,** *50,* 4093.
(3) (a) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984,** *49,* 1875. (b) Roof, A. A. M.; Ravenscroft, M. D.; Roof, A. A. M. *Ibid.* **1987,** *52,* 1847.
(4) (a) Brown, R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G.; Bianchini, R. *J. Am. Chem. Soc.* **1990,** *112,* 6310. (b) Nagorski, R. W.; Slebocka-Tilk, H.; Brown, R. S. *J. Am. Chem. Soc.* **1994,** *116,* 419. (c) Slebocka-Tilk, H.; Nagorski, R. W.; Motallebi, S.; Turner, P. A.; Brown, R. S. *Ibid.*, in press. (d) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985,** *107,* 4504. (e) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994,** *116,* 2448.
(5) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980,** *102,* 3303.

(6) Kopecky, K. R.; Miller, A. J. *Can. J. Chem.* **1984,** *62,* 1840.
(7) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984,** *106,* 4515.

Table 1. Pseudo-First-Order (k_{obs}) and Second-Order (k_g) Rate Constants for Bromination of 1 in MeOH Containing LiBr, $\mu = 0.3$ (LiClO$_4$), $T = 25$ °C

[LiBr] (M)	k_{obs} (s^{-1})	$10^{-5} k_g$ (M^{-1} s^{-1})[a]
0.05	456 ± 16	9.87
0.07	300 ± 16	6.49
0.1	182 ± 7	3.94
0.15	127 ± 4	2.75
0.20	86 ± 3	1.86
0.25	66 ± 2	1.43
0.30	53 ± 2	1.10

[a] $k_g = k_{obs}/[\mathbf{1}]$; $[\mathbf{1}] = 4.62 \times 10^{-4}$ M.

b. Kinetics. The kinetics of bromination of **1** in MeOH ($\mu = 0.3$ M, LiClO$_4$) were determined at 25 °C under pseudo-first-order conditions of excess olefin and varying [Br$^-$] using an Applied Photophysics SX-17MV stopped-flow spectrometer by observing the rate of loss of the Br$_2$/Br$_3^-$ bands at 410, 290, or 270 nm. The analytical [Br$_2$] varied from 5×10^{-4} to 6×10^{-5} M. The second-order rate constants for the reaction were evaluated as $k_g = k_{obs}/[\mathbf{1}]$. Reported in Table 1 are the average k_{obs} and k_g values as a function of [Br$^-$] (7 to 10 separate determinations per k_{obs}).

In acetic acid, the kinetic constants for the bromination could not be determined because of a rapid reaction of the olefin with the solvent. The kinetics of reaction of the olefin with the solvent at 25 °C in the absence of Br$_2$ were determined by observing the rate of loss of absorbance of **1** at 254 nm using an OLIS modified Cary 17 UV/vis spectrophotometer. Solutions containing HOAc, DOAc, or MeOH at various concentrations of HClO$_4$, LiClO$_4$, or LiBr (0–0.1 M in the case of acetic acid, or 0–0.30 M in the case of methanol) were placed into 3 mL cuvettes in the spectrophotometer for 15 min prior to the initiation of the kinetics. Reactions were initiated by injection of 30 μL of a 5×10^{-1} M solution of **1** in dry DME or hexane (final concentration of **1** was 5×10^{-3} M). Pseudo first-order rate constants were evaluated by fitting the absorbance vs time data to a standard exponential model via NLLSQ treatment. The reactions generally displayed good first order plots until 90% completion, but after prolonged sitting there were clear drifts in the infinity points. This was more obvious in the cases where mixtures of HOAc and DOAc were employed. Only in the cases where LiBr was employed was the reaction monitored by the increase in absorbance at 254 nm. The so-derived rate constants are presented in Tables 3–7, the reported values being the averages of 3–5 runs.

c. Product Studies. The following two sets of product studies were undertaken for the reaction of **1** with Br$_2$ in MeOH-containing salts. These involved salt concentrations of $\mu = 0.1$ (LiClO$_4$) with [LiBr] = 0, 0.02, and 0.05 M and $\mu = 0.3$ (LiClO$_4$) with [LiBr] = 0.05, 0.20, and 0.30 M. In both sets of experiments, roughly 10 mg of **1** was dissolved in the appropriate solution of salt and then Br$_2$ added dropwise until the color persisted. The volatiles were then removed, and 10 mL of CH$_2$Cl$_2$ was added. This solution was extracted with water to remove the salts and then dried (MgSO$_4$), and evaporated to yield a residue that was analyzed by HPLC under the same conditions as described above. For the set of experiments where $\mu = 0.1$, the products consisted of the expected dibromide **7** and methoxy bromide **8** in a ratio of 8.2 (±0.4) to 91.8 (±0.4), that ratio being independent of the presence of added LiBr. For the set of experiments where $\mu = 0.3$, the same products were produced in a ratio of 10.0 (±0.3) to 90.0 (±0.3) which was also independent of the added [LiBr].

The identities of the dibromide and methoxy bromide were made by comparison of the HPLC retention time, GC-mass spectrum (239, 241, M$^+$ − Br; 211, 212, M$^+$ − Br-C$_2$H$_4$), and ^{13}C spectrum with authentic materials in the case of **7**, and by the GC-mass spectral fragmentation pattern (270, 272, M$^+$; 242, 244, M$^+$ − C$_2$H$_4$) in the case of **8**.

The following isolation experiments were performed for reaction of **1** with HOAc solvent and added salts in the absence of Br$_2$.

(1) Into 50 mL of purified HOAc was placed 18 mg of **1**. The solution was protected from moisture, and 10 mL aliquots were removed after 15, 30, 60, 150 min and finally after 25 h. Each aliquot was worked up by extraction with 25 mL of purified CH$_2$Cl$_2$, which was itself extracted with 2 × 25 mL of water, one 25 mL portion of sat. Na$_2$CO$_3$, and followed again by water. The organic layer was dried (MgSO$_4$), and the volatiles were removed to yield a residue that was analyzed by HPLC (1 mL/min, 88/12, H$_2$O/CH$_3$CN, Waters 8 × 10 C$_{18}$ RCM column, refractive index detection). Only two components were found: one is the starting olefin **1**, and the other is the monoacetoxy derivative **10**. As a function of time, the observed percentages of **1/10** were 15 min, 70/30; 30 min, 20/80; 60 min, 3/97; 150 min, 0/100. In an independent experiment, 18 mg of **1** was reacted for 150 min in HOAc, and an amount of **10** was isolated and identified by the following spectral parameters. ^{13}C NMR (CDCl$_3$) δ 170.6, 96.4, 57.2, 45.7, 40.9, 40.4, 39.8, 36.9, 35.6, 29.9, 25.0, 24.4, 23.3, 21.9; exact mass calcd for C$_{12}$H$_{16}$O$_2$ (M$^+$ − C$_2$H$_4$) 192.1150; found 192.1149, also peaks at 160.1251 (M$^+$ − HOAc), 150.1045, 110.0727, 82.0402, 67.0394; IR (CHCl$_3$ case) 1732 cm^{-1}; ^{1}H NMR (300 MHz) 2.95 (br s, 1 H), 2.76 (br d, 1 H), 2.33 (br t, 1 H), 2.05 (br d, 1 H), 2.00 (s, 3 H), 1.76 (br d, 1 H), 1.57 (m, 4 H), 1.43 (m, 2 H), 1.32 (m, 3 H), 1.12 (m, 3 H).

(2) Into 10 mL of HOAc containing 0.1 M LiClO$_4$ was injected a solution of 9 mg of **1** in 100 μL of hexane. After 1, 2, and 12 min, 3 mL aliquots were removed and quenched with water followed by extraction with CH$_2$Cl$_2$. The organic extracts were subjected to the workup procedure above, dried, and evaporated to give a residue that was subjected to the HPLC analysis above. The analyses showed that the observed percentages of **1/10** at various times were 1 min, 44/56; 2 min, 7/93; 12 min, 0/100.

(3) Into 10 mL of a solution of HOAc containing 0.1 M LiBr was injected 20 mg of **1** in 100 μL of dry DME. After 1 min, the reaction mixture was quenched with water and worked up as above. HPLC analysis showed only one product, namely the monobromide **11**, the identity of which was confirmed by independent comparison of the ^{13}C NMR spectral and mass spectral data reported by Bartlett et al.[3a]

Addition of Br$_2$ to **1** in HOAc was problematic and produced at least four main products. These were, dibromide **7**, monobromide **11**, monoacetoxy **10**, and a fourth component which was identified as acetoxy bromide **9** by GC/MS (peaks at 300, 298 (M$^+$); 272, 270 (M$^+$ − C$_2$H$_4$); 258, 256 (M$^+$ − CH$_2$CO), 230, 229; 219 (M$^+$ − Br)).

Results and Discussion

a. Reaction in MeOH. Given in Table 1 are the rate constants observed for bromination of excess **1** in MeOH as a function of added LiBr, $\mu = 0.3$ (LiClO$_4$). There is a clear diminution in rate as a function of increasing [Br$^-$]. This is attributable to the establishment of the well-known[8–12] Br$^-$ + Br$_2$ ⇌ Br$_3^-$ equilibrium, the association constant of which is[9] $K_{eq} = 177$ M^{-1} in MeOH. For normal olefins, both Br$_2$ and Br$_3^-$ are brominating agents,[8–12] with the former being more effective. Customarily one accounts for the presence of the tribromide equilibrium and the reactivity of both Br$_2$ and Br$_3^-$ by

(8) (a) Ruasse, M.-F.; Aubard, J.; Monjoint, P. *J. Chim. Phys.* **1982**, *82*, 539. (b) Ruasse, M.-F.; Aubard, J.; Galland, B.; Ademier, A. *J. Phys. Chem.* **1986**, *90*, 4382.

(9) (a) Dubois, J. E.; Hegarty, A. F.; Bergman, E. D. *J. Org. Chem.* **1972**, *37*, 2218. (b) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369 and references therein.

(10) DeLaMare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136–197.

(11) Slebocka-Tilk, H.; Zheng, C. Y.; Brown, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 1347 and references therein.

(12) (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.
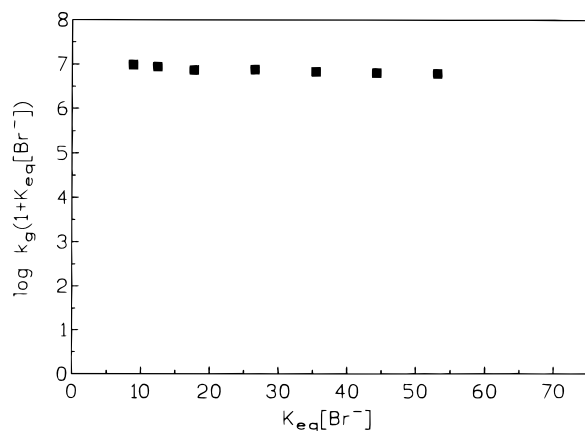
Figure 1. Plot of $k_g(1 + K_{eq}[Br^-])$ vs $K_{eq}[Br^-]$ for bromination of **1** in MeOH; $T = 25$ °C, $\mu = 0.3$ (LiClO$_4$).

invoking the simplified process shown in eq 2 (where ol = olefin), for which can be derived the kinetic expression

$$Br^- + Br_2 \xrightarrow{\text{ol}}_{k_{Br_2}} P$$

$$K_{eq} \updownarrow \qquad\qquad\qquad (2)$$

$$Br_3^- \xrightarrow{\text{ol}}_{k_{Br_3^-}} P$$
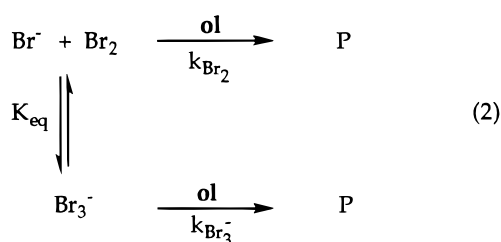
in eq 3.

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

Thus, a plot of $k_g(1 + K_{eq}[Br^-])$ vs $K_{eq}[Br^-]$ normally yields a straight line, the intercept of which (k_{Br_2}) refers to the rate constant for free Br$_2$ addition, and the slope of which refers to the tribromide rate constant. Shown in Figure 1 is such a plot for olefin **1**, the important feature of which is the relative invariance[13] of $k_g(1 + K_{eq}[Br^-])$ with varying [Br$^-$]. This suggests that the $k_{Br_3^-}$ term is negligible and can be rationalized as follows.

Several possibilities have been advanced for the mechanism by which Br$_3^-$ adds to the olefinic unit.[8–12] The most recent studies[11,12] favor a process as in eq 4 wherein

$$Br^- + \text{(structure)} \rightarrow Br-Br \longrightarrow \text{(structure)} + Br^- \qquad (4)$$
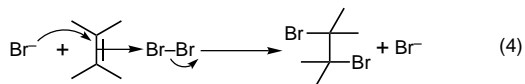
Br$^-$ captures an olefin:Br$_2$ charge transfer complex leading directly to a *trans* 1,2-dibromide plus Br$^-$. Clearly such a process can be ruled out for sterically encumbered olefins such as **5** or **6** and for olefin **1** as well because it cannot form a *trans* adduct. The lack of an observable $k_{Br_3^-}$ term for bromination of **1** therefore supports the process in eq 4.

A second general feature of note for the bromination of **1** in MeOH is the invariance of the product distribution as a function of added [Br$^-$]. HPLC analyses indicated

Table 2. Amounts of *cis*-Dibromide 7 and *cis*-Methoxy Bromide 8 Formed from Bromination of 1 in MeOH as a Function of [LiBr] at Ambient Temperature[a]

[LiBr] (M)	$\mu = 0.1$ (LiClO$_4$)		$\mu = 0.3$ (LiClO$_4$)	
	% **7**	% **8**	% **7**	% **8**
0	8.2	91.8		
0.02	8.4	91.6		
0.05	8.3	91.7	10.4	89.6
0.2			9.8	90.2
0.3			9.7	90.3

[a] Percentages determined by HPLC as described in Experimental Section. Values quotes are averages of 2–3 determinations; errors ±0.4%.

Scheme 1
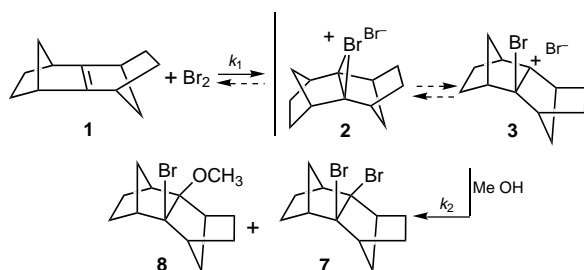
that the only products for this reaction were the *cis*-dibromide **7** and *cis*-methoxy bromide **8**, the relative amounts of which, formed under varying [Br$^-$], are given in Table 2.

Given in Scheme 1 is a mechanism for the bromination of **1** in MeOH that accounts for all observations. That added Br$^-$ does not lead to more dibromide product, nor, from the appearance of the plot in Figure 1, does it lead to a marked common ion rate depression,[14] indicates that any intermediates produced (suggested as **3** and/or **2**) cannot be intercepted by external Br$^-$. Hence product formation must result exclusively from ion pair collapse. Whether bromonium ion **2** is actually produced we cannot say, but if so, because of the unlikeliness of a frontside nucleophilic displacement of the C–Br bond, it must surely open to β-bromocarbocation **3** prior to product formation. Furthermore we cannot say which step, k_1 or k_2, is rate limiting since formation of the ion pair(s) could easily be a reversible or even equilibrium process if internal return is prevalent. We can, however, put some limit on the lifetime of **3** based on the likely rate constant for the capture of an unstable carbocation by a good nucleophile such as Br$^-$ in MeOH. McClelland and co-workers[16a] have shown that Br$^-$ captures cumyl, α-phenylethyl, and benzyl cations at rates approaching the diffusion limit ($10^9–10^{10}$ M^{-1} s^{-1}) in fluorinated alcohols such as trifluoroethanol and hexafluoro-2-propanol. Earlier studies from our laboratories have shown that, in MeOH, anions such as N$_3^-$ and Br$^-$ capture the bromonium ions of cyclohexene and tetramethylethylene as well as the β-bromocarbocation of styrene at the diffusion limit.[16b] Assuming that the cation **3** has a

(13) In actuality, the value of $k_g(1 + K_{eq}[Br^-])$ varies 9.7×10^6 to 6.2×10^6 is from $0.05 \leq [Br^-] \leq 0.3$ M. The origin of this small decrease is unknown but could be due to a specific salt effect in changing from ClO$_4^-$ to Br$^-$.

(14) Were a common ion rate depression, signifying external Br$^-$ capture of an intermediate, in operation, the plot shown in Figure 1 would asymptotically approach the *x*-axis. This has been observed for bromination of **5**,[4b,c] 2-acetoxy-2-cholestene,[15a] and tri-*tert*-butylethylene.[15b]

(15) (a) Calvet, A.; Josefowicz, M.; Levisalles, J. *Tetrahedron* **1983**, *39*, 103. (b) Dubois, J. E.; Loizos, M. C. *C. R. Seances Acad. Sci., Ser. C* **1972**, *274*, 1130.

(16) (a) McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337. (b) Nagorski, R. W.; Brown, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7773.
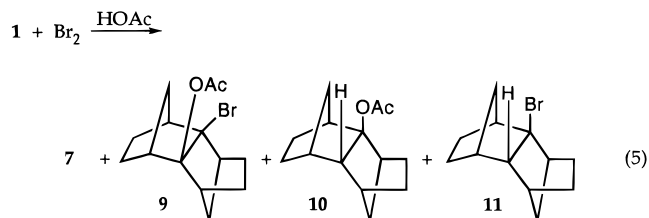
Table 3. Pseudo-First-Order Rate Constants for Reaction of 1 in HOAc and DOAc Containing Varying [LiClO₄], T = 25 °C[a]

[LiClO₄] (M)	k_{obs} (min⁻¹)	
	HOAc	DOAc
0	$(1.40 \pm 0.01) \times 10^{-2}$	$(4.21 \pm 0.02) \times 10^{-3}$
0.025	$(1.92 \pm 0.04) \times 10^{-1}$	
0.05	$(4.09 \pm 0.04) \times 10^{-1}$	
0.075	$(5.67 \pm 0.02) \times 10^{-1}$	
0.10	$(7.75 \pm 0.05) \times 10^{-1}$	$(9.82 \pm 0.21) \times 10^{-2}$

[a] Determined by observing rate of loss of chromophore at 254 nm.

similar reactivity toward external Br⁻, then at [Br⁻] = 0.3 M, the pseudo-first-order rate constant for capture would be roughly 10^9 s⁻¹. That no extra dibromide product is observed under those condition implies that the internal ion pair collapse must occur at least 50 times faster, leading to a lifetime for the ion of 10^{-11} s or less.

b. Reaction in HOAc. Bromine addition to **1** in HOAc initially was problematic because the course of the reaction depended upon the timing in which the reaction components were introduced into the solution. In initial runs, when **1** was added to HOAc, and the mixture allowed to equilibrate by standing for some time, subsequent additions of Br₂ failed to exhibit the expected disappearance of bromine color. When freshly prepared solutions of **1** were treated with Br₂, decolorization was observed to occur, but there were four products produced (**7**, **9**, **10**, **11**, eq 5), the relative amounts of which were

$$1 + Br_2 \xrightarrow{\text{HOAc}}$$

$$7 \ + \ \underset{9}{\text{[structure]}} \ + \ \underset{10}{\text{[structure]}} \ + \ \underset{11}{\text{[structure]}} \qquad (5)$$

highly variable. While products **7** and **9** are easily explained as having arisen via an electrophilic bromination pathway similar to what occurs in MeOH, products **10** and **11** must result from acid-catalyzed additions. In view of the inconsistent behavior of the bromination process, further study of it was discontinued in favour of studies of the acid-catalyzed additions.

i. Observations. There are several observations of note that need to be explained for the reaction of **1** with HOAc. First, in both the absence or presence of LiClO₄ there is a rapid reaction to yield exclusively a monoacetoxy derivative **10**. Given in Table 3 are the pseudo-first-order rate constants for reaction of **1** in both HOAc and DOAc as a function of increasing [LiClO₄]. The dramatic increase in rate as a function of [salt] is not limited to LiClO₄. Given in Table 4 are the rate constants for disappearance of **1** in HOAc in the presence of increasing [LiBr]. At the highest concentrations, the product of the reaction here is the monobromide **11**. Of note in Table 4 is the fact that in the absence of LiBr, NaOAc at a concentration of 0.1 M does not accelerate the reaction. However, as little as 0.002 M NaOAc can have a profound reduction in the rate in the presence of 0.1 M LiBr. Added NaOAc also causes a significant diminution of the catalytic effect of LiClO₄. Given in Table 5 are kinetic rate constants for reaction of **1** in HOAc containing varying [LiClO₄] and [NaOAc], which shows that adding as little as 3.33×10^{-3} M NaOAc can

Table 4. Pseudo-First-Order Rate Constants for Reaction of 1 in HOAc Containing Varying [LiBr], T = 25 °C

[LiBr] (M)	k_{obs} (min⁻¹)
0	$(1.40 \pm 0.04) \times 10^{-2}$
0	$(1.39 \pm 0.05) \times 10^{-2}$ [b]
0.025	1.62 ± 0.03
0.05	2.48 ± 0.04
0.075	3.22 ± 0.03
0.1	5.65 ± 0.07
0.1	3.50 ± 0.04[c]

[a] Determined by observing rate of change in absorbance of chromophore at 254 nm. [b] Contains added 0.1 M NaOAc. [c] Contains added 0.002 M NaOAc.

Table 5. Pseudo-First-Order Rate Constants for Reaction of 1 in HOAc Containing Varying [LiClO₄] and [NaOAc], T = 25 °C

[LiClO₄] (M)	[NaOAc] (M)	k_{obs} (min⁻¹)
0.1	0	$(7.75 \pm 0.05) \times 10^{-1}$
$0.1-2.5 \times 10^{-4}$	2.5×10^{-4}	$(1.94 \pm 0.01) \times 10^{-1}$
$0.1-1.0 \times 10^{-3}$	1.0×10^{-3}	$(8.38 \pm 0.04) \times 10^{-2}$
$0.1-1.67 \times 10^{-3}$	1.67×10^{-3}	$(6.07 \pm 0.02) \times 10^{-2}$
$0.1-3.33 \times 10^{-3}$	3.33×10^{-3}	$(4.03 \pm 0.01) \times 10^{-2}$
0	0.1	$(1.55 \pm 0.18) \times 10^{-2}$

[a] Determined by observing rate of loss of chromophore at 254 nm.

Table 6. Pseudo-First-Order Rate Constants for Reaction of 1 in Solvent of Varying Atom Fraction D in HOAc/DOAc in Presence and Absence of LiClO₄, T = 25 °C[a]

atom fraction deuterium	k_{obs} (min⁻¹)	
	[LiClO₄] = 0.1 M	[LiClO₄] = 0 M
0	$(7.75 \pm 0.05) \times 10^{-1}$	$(1.40 \pm 0.01) \times 10^{-2}$
0.2	$(5.25 \pm 0.04) \times 10^{-1}$	$(1.15 \pm 0.01) \times 10^{-2}$
0.4	$(3.86 \pm 0.03) \times 10^{-1}$	$(9.10 \pm 0.03) \times 10^{-3}$
0.5	$(2.99 \pm 0.05) \times 10^{-1}$	$(8.10 \pm 0.02) \times 10^{-3}$
0.6	$(2.58 \pm 0.04) \times 10^{-1}$	$(6.95 \pm 0.03) \times 10^{-3}$
0.8	$(1.70 \pm 0.03) \times 10^{-1}$	$(5.60 \pm 0.04) \times 10^{-3}$
1.0	$(9.82 \pm 0.21) \times 10^{-2}$	$(4.21 \pm 0.02) \times 10^{-3}$

[a] Determined by observing rate of loss of chromophore at 254 nm.

cut the catalytic effect of 0.1 M LiClO₄ by ~95%. Once again, these data indicate that NaOAc alone exhibits no acceleration of the rate over what is observed with no added salt.

Second, the reaction with solvent, both in the presence and absence of LiClO₄, exhibits a strong solvent deuterium kinetic isotope effect. Given in Table 6 are kinetic data in HOAc/DOAc mixtures of varying atom fraction of D. The solvent deuterium kinetic isotope effect (DKIE) is 3.3 in the absence of LiClO₄, and ~8.0 in the presence of LiClO₄, signifying differences in the reaction under these two conditions.

Third, since some of the reaction products in the case of bromination of **1** in HOAc arose from an acid-catalyzed electrophilic addition process, the kinetics of reaction of **1** with HOAc containing varying [HClO₄] were determined. Given in Table 7 are the pseudo-first-order rate constants determined in HOAc and DOAc. These data show that the second order rate constant for HClO₄-catalyzed addition of LOAc is $(k_{HClO_4})_{HOAc} = 1.41 \times 10^4$ M⁻¹ min⁻¹ in HOAc, and $(k_{HClO_4})_{DOAc} = 2.57 \times 10^3$ M⁻¹ min⁻¹, the overall DKIE being 5.4. We will deal with the above three points in turn.

ii. Uncatalyzed Rapid Addition of Acetic Acid. Carboxylic acids such as formic and acetic acid are known to add to alkenes,[17] but in the absence of strong acid

Table 7. Pseudo-First-Order Rate Constants for Reaction of 1 in LOAc as a Function of [HClO₄], *T* = 25 °C[a]

HClO₄ (M)	k_{obs} (min⁻¹)	
	HOAc	DOAc
0	$(1.40 \pm 0.01) \times 10^{-2}$	$(4.21 \pm 0.02) \times 10^{-3}$
5×10^{-5}	$(6.45 \pm 0.05) \times 10^{-1}$	
1×10^{-4}	1.39 ± 0.06	
2×10^{-4}	2.83 ± 0.04	$(5.18 \pm 0.04) \times 10^{-1}$

[a] Determined by observing rate of loss of chromophore at 254 nm.

catalysts the reactions are slow. The more acidic trifluoroacetic acid adds to alkenes considerably faster.[18] Fahey and co-workers[19,20] have studied the effects of strong acids in promoting the additions of HOAc and HX to alkenes. Cristol and co-workers[21] have studied the addition of HOAc to norbornadiene and benzonorbornene[21] and concluded that the reaction pathways are complex but might involve bridged carbocationic intermediates or a molecular addition that could be responsible for the observed *cis* exo addition. Subsequently Traylor reviewed the literature up to 1969 dealing with additions of a variety of electrophiles to strained, rigid olefins and advanced his twist strain theory in explaining the propensity of norbornene and similarly strained bicyclic olefins to undergo *cis* addition.[22]

Interestingly, many of the observations made in our study are directly analogous to ones made by Cristol and co-workers[21] in their early study of HOAc addition to norbornadiene. These include the following: (1) a strong catalytic effect of NaClO₄ in promoting the addition of HOAc;[23] (2) the lack of catalysis exhibited by NaOAc. However, when NaOAc was added to mixtures containing NaClO₄, the accelerative effect of the latter was largely eliminated; (3) a strong accelerating effect of HClO₄ for the addition of HOAc. Unfortunately, although these studies included the use of DOAc as a mechanistic probe for the stereochemistry of addition, no solvent DKIE data were reported. However, it might be surmised on the basis of product vs time data presented[21] that $k_{HOAc}/k_{DOAc} \simeq 2$ for the uncatalyzed addition to norbornadiene, and ~1 for the HClO₄-catalyzed addition.[24]

anti-Sesquinorbornene (**1**) has numerous advantages over norbornadiene for study of the electrophilic addition

of HOAc. First, as the data in Tables 3 and 4 show, it is considerably more reactive which must be a consequence of the considerable strain in the Π-system (the angles surrounding each olefinic carbon are 108°, 108°, and 143°, the latter being the angle between the two bridgehead C's and the olefinic C),[1] and lower ionization potential[25] which leads to a marked reactivity toward electrophiles.[1–3] Further, reaction of **1** in HOAc, whether catalyzed by LiClO₄ or HClO₄ gives only the *cis* monoacetoxy product unlike norbornadiene which gives the *cis* adduct and a rearranged nortricyclyl acetate, the relative amounts of which depend on the exact reaction conditions. Finally, **1** exhibits a chromophore at 254 nm which appears as a small shoulder on the HOAc solvent cut-off, making determination of the kinetics of disappearance of **1** by UV/vis spectrophotometry convenient.

The data of Table 3 indicate that in the absence of added salt, a significant solvent DKIE exists for the uncatalyzed addition of acetic acid. That value, $k_{HOAc}/k_{DOAc} = 3.3$, can be analyzed further in terms of proton inventory experiments given in Table 6. The theory for such analyses is given in several reviews,[26] but the technique is simple and involves measuring the reaction rates in mixtures of HOS and DOS of known isotopic composition. The equation expressing the relationship between the rate constant observed in various mixtures with known atom fractions of D and the fractionation factors (ϕ) for the exchangeable protons responsible for the isotope effect is given in eq 6

$$k_n = k_o \prod_i^{TS} (1 - n + n\phi_i) / \prod_j^{RS} (1 - n + n\phi_j) \qquad (6)$$

where n is the atom fraction of deuterium in the solvent O–L (L = H, D) bonds, and i and j represent the sites undergoing exchange in the transition and reactant sites, respectively. The fractionation factors for the various hydrogens refer to the tightness of their bonding and are significantly less than unity for H's being transferred in the transition state (relating to primary kinetic isotope effects) and also for H's involved in hydrogen bonds where the overall bonding is loose.[27a] The latter relate to secondary deuterium isotope effects of solvation and can contribute significantly to the overall DKIE. Customarily, for reactions where a single step is rate limiting, plots of k_n vs n yield either straight lines, indicating, in the most simplistic analysis, the involvement of a single hydrogen being transferred, or bowed downward lines,

(17) Knight, H. B.; Koos, R. E.; Swern, D. *J. Am. Chem. Soc.* **1953**, *75*, 6213.

(18) (a) Peterson, P. E. *J. Am. Chem. Soc.* **1960**, *82*, 5834. (b) Peterson, P. E.; Allen, G. *J. Org. Chem.* **1962**, *27*, 1505. (c) *Idem. J. Am. Chem. Soc.* **1963**, *85*, 3608. (d) Peterson, P. E.; Casey, C. *J. Org. Chem.* **1964**, *29*, 2325.

(19) (a) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 2445. (b) Fahey, R. C.; Monahan, M. W.; McPherson, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2810. (c) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 3865. (d) Dewar, M. J. S.; Fahey, F. C. *J. Am. Chem. Soc.* **1963**, *85*, 3645. (e) Fahey, R. C.; McPherson, C. A.; Smith, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 4534.

(20) For a detailed compendium of early work see: Fahey, R. C. *Topics in Stereochem.* **1968**, *3*, 237.

(21) Cristol, S. J.; Morrill, T. C.; Sanchez, R. A. *J. Org. Chem.* **1966**, *31*, 2719, 2726, 2733, 2738.

(22) (a) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152. (b) It might be considered that a concerted molecular addition of LOAc to the alkene is the microscopic reverse of the well-known ester pyrolysis involving *syn* elimination of H and OC(O)R. This analogy has been considered as poor by Traylor.[22a]

(23) This effect has also been observed by Monahan wherein LiClO₄ greatly accelerates the reaction of cyclohexene with HOAc containing 0.065 M HCl. In that study, as [LiClO₄] increases, the ratio of chloro to acetoxy cyclohexane products falls from 0.28 to 0.03 as [LiClO₄] passes from 3.9×10^{-4} M to 3.9×10^{-2} M. Monahan, M. W. Ph.D. Thesis, University of California, San Diego, 1968. We thank Professor R. C. Fahey for the loan of a copy of this thesis.

(24) k_{HOAc}/k_{DOAc} calculated on the basis of % ester product formed after reaction of norbornadiene in CH₃CO₂H or CH₃CO₂D for 22.3 h at 188 °C. On the other hand, in the presence of 0.02 M HClO₄, the solvent DKIE on the acid-catalyzed reaction at 50 °C appears to be ~1, since equal amounts of ester (67%) are formed in each medium after 39 min.[21]

(25) Brown, R. S.; Buschek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692 report an ionization potential of 7.90 eV.

(26) (a) Schowen, R. L. In *Isotope Effects on Enzyme-Catalyzed Reactions*; Cleland, W. W., O'Leary, M. H., Northrop, D. B., Eds.; University Park Press: Baltimore, 1977. (b) Schowen, K. B. In *Transition States of Biochemical Processes*; Gandour, R.D., Schowen, R. L., Eds.; Plenum Press: New York, 1978. (c) Venkatasubban, K. S.; Schowen, R. L. *CRC Crit. Rev. Biochem.* **1984**, *17*, 1. (d) Alvarez, F. J.; Schowen, R. L. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 7, pp 1–60. (e) Kresge, A. J.; More-O'Ferrall, R. A.; Powell, M. F. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 7, pp 177–274.

(27) (a) Kresge, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 3065. (b) Chiang, Y.; Kresge, A. J.; Chang, T. K.; Powell, M. F.; Wells, J. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1587. (c) Clark, D. R.; Emsley, J.; Hibbert, F. *J. Chem. Soc. Perkin Trans. II*, **1988**, 919.
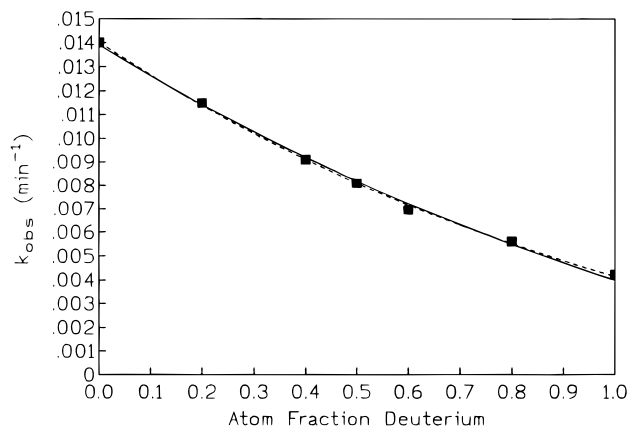
Figure 2. Plot of K_{obs} vs atom fraction of deuterium in solvent for addition of LOAc to 1 in absence of LiClO4; $T = 25$ °C. Solid line through data fit to eq 8, $x = 2$; dashed line through data fit to eq 7, $x = 3$.

indicative of 2 or more H's being transferred or undergoing significant changes in their overall bonding.

Shown in Figure 2 is a plot of the observed rate constant vs n for the reaction of **1** in LOAc (L = H, D) containing no added LiClO$_4$. That the plot is bowed downward is suggestive of a transition state for the reaction where there are two or more protons in flight, or one in which a single proton is in flight and others are involved in developing H-bonds. Almost certainly, the fact that the plot is not a straight line rules out any mechanism such as a concerted addition[22b] of a single LOAc to the double bond as in eq 7.
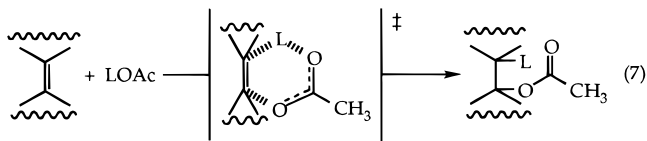
One can consider two possible simple transition states for the addition of LOAc, one being a concerted addition involving two or more molecules of LOAc, and another involving a rate-limiting proton transfer from LOAc to the olefin to generate a protonated olefin/OAc$^-$ ion pair which then undergoes rapid collapse to form the c*is* addition product **10**. We will deal with these in turn.

In the case at hand, it may be safely assumed that the ϕ for reactant (solvent) CH$_3$COO$-$L bond is unity[26d,27c] which considerably simplifies the application of eq 6. A modified version of this (eq 8) can be successfully fit to the data of Table 6 (no added LiClO$_4$) where $x = 2$ or 3 signifying two or three protons in flight in the TS having ϕ values of 0.54 and 0.67, respectively.[28]

$$k_n = k_o(1 - n + n\phi)^x \qquad (8)$$

The computed lines based on these fractionation factors are shown in Figure 2 and are seen to fit the data acceptably well. However, the data are not sufficient to distinguish between the two possibilities, and in the

simplest analysis two protons in flight are appropriate. A possible, but not unique, transition state model for such a process in given as **12**.
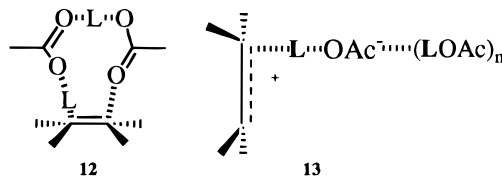
The second possible mechanism, involving the rate-limiting transfer of a proton from solvent to the olefin might, simplistically, proceed through TS **13**. The product of the fractionation factors associated with the proton in flight and the LOAc's solvating the developing OAc$^-$ must be 0.3 in order to account for the observed DKIE of 3.3. Clarke, Emsley and Hibbert[27c] have shown that the ϕ for a fully solvated OAc$^-$ ---(HOAc)$_n$ complex is 0.58 $\pm$ 0.05. The developing OAc$^-$ in **13** cannot by fully solvated, so the appropriate ϕ for this must lie between 0.6 and 1.0. For a TS 50% along the reaction coordinate with a ϕ of 0.8, the required ϕ for the proton in flight would be 0.4, a value that is not unreasonable.[26] Hence we conclude that the stepwise addition of HOAc to this olefin cannot be ruled out on the basis of the proton inventory data although, as discussed later, it is conceptually unsatisfying.

iii. Effect of LiClO$_4$ and HClO$_4$. Added LiClO$_4$ causes significant increases in the rate of addition of LOAc to **1**. The data of Table 2 indicate that the second-order rate constant for this process (defined as the slope of a plot of k_{obs} vs [LiClO$_4$] is 7.58 M^{-1} min^{-1} in HOAc and 0.94 M^{-1} min^{-1} in DOAc which leads to a deuterium KIE of 8.1. That this DKIE is significantly different from the one observed for uncatalyzed solvent addition above ($k_{HOAc}/k_{DOAc} = 3.3$) suggests that the two processes have significant differences and perhaps involve different species. Furthermore, difference in the LiClO$_4$ DKIE and the value obtained for HClO$_4$-catalyzed addition (5.4, Table 7) suggests that the species responsible for catalysis in both cases are slightly different. On the basis of the following we suggest that the species is HClO$_4$ or ClO$_4^-$/H$_2$OAc$^+$ in the case of perchloric acid, and Li$^+$/ ClO$_4^-$/H$_2$OAc$^+$ in the case of LiClO$_4$.

Because of the low dielectric constant of acetic acid (6.2),[29] salts and mineral acids may be substantially ionized into M$^+$X$^-$ pairs, but are largely undissociated even at low concentrations.[30,31] Cristol[21] has reported that NaClO$_4$ has a catalytic effect in promoting the addition of HOAc to norbornadiene (the effect being reversed by the addition of NaOAc) and attributed this to an enhancement of the apparent acidity of weak acids in HOAc. The effect was noted as early as 1934 when the efficacy of H$_3$PO$_4$ or HCl in HOAc in promoting acetylation of cellulose was enhanced by the addition of perchlorate salts.[32] Subsequently Monahan[23] and McPherson[33] in the laboratories of R. C. Fahey noted the ability of LiClO$_4$ to enhance the catalytic effect of HCl in

---

(28) In actuality, unless the 2 or 3 protons in flight have identical fractionation factors, the appropriate fit would be

$$k_n = k_o \prod_{i=1,x}^{TS}(1 - n + n\phi_x)$$

where $x = 2$ or 3. However, such fits have large standard errors since the various ϕ values are heavily correlated.
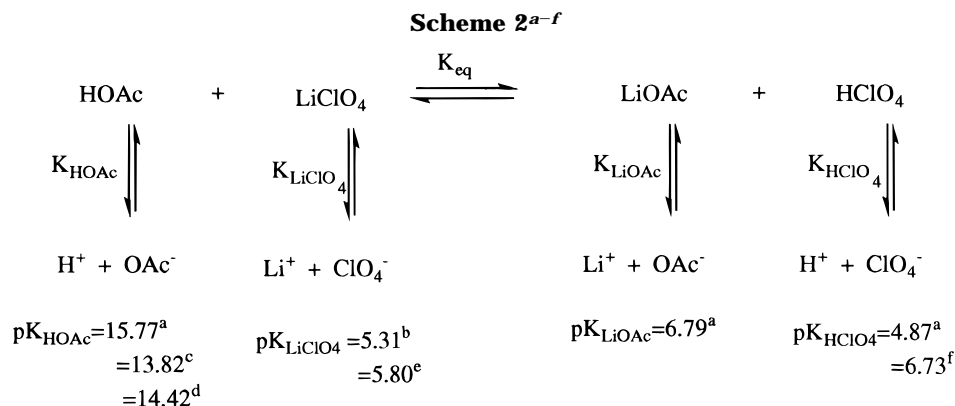
(29) Smyth, C. P.; Rogers, H. E. *J. Am. Chem. Soc.* **1930**, *52*, 1824.
(30) (a) Kolthoff, I. M.; Bruckenstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 1. (b) Bruckenstein, S.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1956**, *78*, 2974.
(31) (a) Poscham, W.; Engelbrecht, A. *Z. Phys. Chemie* (*Leipzig*) **1971**, *248*, 177. (b) Kolling, O. W. *Anal. Chem.* **1968**, *40*, 956.
(32) Krüger, D.; Roman, W. *Angew. Chem.* **1934**, *47*, 58.
(33) McPherson, C. A. Ph.D. Dissertation, University of California, San Diego, 1969.

Scheme 2[a–f]

$$\text{HOAc} \quad + \quad \text{LiClO}_4 \quad \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \quad \text{LiOAc} \quad + \quad \text{HClO}_4$$

$$\downarrow K_{HOAc} \qquad\qquad \downarrow K_{LiClO_4} \qquad\qquad\qquad \downarrow K_{LiOAc} \qquad\qquad \downarrow K_{HClO_4}$$

$$\text{H}^+ + \text{OAc}^- \qquad \text{Li}^+ + \text{ClO}_4^- \qquad\qquad \text{Li}^+ + \text{OAc}^- \qquad \text{H}^+ + \text{ClO}_4^-$$

$$pK_{HOAc} = 15.77^a \qquad pK_{LiClO4} = 5.31^b \qquad\qquad pK_{LiOAc} = 6.79^a \qquad pK_{HClO4} = 4.87^a$$
$$= 13.82^c \qquad\qquad\qquad = 5.80^e \qquad\qquad\qquad\qquad\qquad\qquad = 6.73^f$$
$$= 14.42^d$$

[a] Bruckenstein, S.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1956**, *78*, 1. (Value for pK_{HOAc} based on autoprotolysis constant of $10^{-14.45}$.) [b] Kolling, O. W. *Anal. Chem.* **1968**, *40*, 956. [c] Kolthoff, I. M.; Willman, A. *J. Am. Chem. Soc.* **1934**, *56*, 1007. (Value for pK_{HOAc} based on autoprotolysis constant of $10^{-12.6}$.) [d] Poscham, W.; Engelbrecht, A. *Z. Phys. Chem. (Leipzig)* **1971**, *248*, 177. (Based on autoprotolysis constant for HOAc of $10^{-13.2}$.) [e] Winstein, S.; Kleindinst, P.; Robinson, G. *J. Am. Chem. Soc.* **1961**, *83*, 885. [f] Smith, T. L.; Elliott, J. H. *J. Am. Chem. Soc.* **1953**, *75*, 3566.

promoting the addition of HOAc to various olefins including cyclohexene, *tert*-butylethylene, and styrene. However, despite all of the above observations, to our knowledge, a quantitative analysis of the effect of LiClO$_4$ in HOAc in enhancing the solution acidity has yet to appear.

When LiClO$_4$ is dissolved in HOAc, a complex series of equilibria is established as shown in Scheme 2. Fortunately, the equilibrium dissociation constants for the various partners are reported, although there is some disagreement in the exact values.[34] From the process and values given in Scheme 2 it can readily be seen that:

$$K_{eq} = \frac{[\text{LiOAc}][\text{HClO}_4]}{[\text{HOAc}][\text{LiClO}_4]} = \frac{K_{LiClO_4} K_{HOAc}}{K_{LiOAc} K_{HClO_4}} = 2.5 \times$$
$$10^{-6} \text{ to } 1.2 \times 10^{-10} \quad (9)$$

the large uncertainty deriving from the exact values chosen for the various dissociation constants. Further, it can also be shown from the computed K_{eq} in eq 9 that at [LiClO$_4$] = 0.1 M, 5.2×10^{-3} M $\geq$ [HClO$_4$] $\geq 1.4 \times 10^{-5}$ M and that such amounts would be sufficient to account for the rates of the LiClO$_4$ reaction.

The surprisingly large amount of HClO$_4$ produced when LiClO$_4$ is dissolved in HOAc can thus be understood, in terms of Scheme 2, as arising from (a) the large amount of HOAc, and (b) the smaller dissociation constant of LiOAc than of LiClO$_4$, both factors tending to enhance the production of HClO$_4$.

It might therefore reasonably be asserted that LiClO$_4$-generated perchloric acid is responsible for the observed catalysis. Also, the fact that added NaOAc has such a profound diminishing effect on the LiClO$_4$ catalysis (Table 5) is suggestive that some species such as HClO$_4$ or ClO$_4^-$/H$_2$OAc$^+$ is being buffered. However, the following consideration indicates that this explanation is incomplete.

(34) Aside from the disagreement in the exact pK values (see Scheme 2), it should be pointed out that the pK value for HClO$_4$ refers to the dissociation constant for the ion pair ClO$_4^-$ H$_2$OAc$^+$, the relevant equation in operation being

$$\text{HClO}_4 + \text{HOAc} \overset{K_i}{\rightleftharpoons} \text{ClO}_4^- \text{H}_2\text{OAc}^+ \overset{K_d}{\rightleftharpoons} \text{ClO}_4^- + \text{H}_2\text{OAc}^+$$
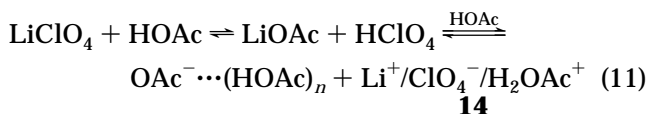
The measured K_i value for HClO$_4$ is reported to be 1.0^{30a} so that the total dissociation constant K given as $K_i K_d/(1 + K_i)$ is, considering the inherent uncertainties, not significantly different from the values quoted in Scheme 2.

From Scheme 2 [HClO$_4$] = [LiOAc] so that LiClO$_4$-generated [perchloric acid] should follow the relationship:

$$[\text{HClO}_4] = \sqrt{K_{eq}[\text{HOAc}][\text{LiClO}_4]} \quad (10)$$

Accordingly, for catalysis arising from such a species, one expects the plot of k_{obs} vs [LiClO$_4$] (Table 3 data) to exhibit a square root and not linear dependence. That the plot is linear can be taken as evidence that the actual catalytic species must contain the elements of Li$^+$ and ClO$_4^-$. Tentatively we suggest the active species to be **14** where Li$^+$ and ClO$_4^-$ are

$$\text{LiClO}_4 + \text{HOAc} \rightleftharpoons \text{LiOAc} + \text{HClO}_4 \overset{\text{HOAc}}{\rightleftharpoons}$$
$$\text{OAc}^- \cdots (\text{HOAc})_n + \text{Li}^+/\text{ClO}_4^-/\text{H}_2\text{OAc}^+ \quad (11)$$
$$\mathbf{14}$$

heavily associated with the acidic species. We have undertaken a proton inventory analysis of the LiClO$_4$-promoted addition of acetic acid to **1** (Table 6 data) and found that the plot of k_{obs} vs atom fraction of D in the medium is bowed downward. This could be a result of a mechanism where there are two or more protons in flight in a concerted transition state involving **14**, **1**, and LOAc. An equally likely possibility is that there is a stepwise addition of proton from **14** to **1** accompanied by a large reorganization of the hydrogen bonding solvent molecules around the ionic species[27c] leading to much reduced values of their ϕ values in the transition state relative to the reactants. Unfortunately, given the paucity of relevant fractionation factor data in HOAc and the unknown nature of the species, we cannot analyze the data further.

iv. Nature of the DKIE for HClO$_4$-Catalyzed Addition of HOAc. That the catalysis afforded by LiClO$_4$ has associated with it a higher DKIE ($\sim$8) than that for HClO$_4$ alone (5.4, Table 7) indicates that somewhat different species are responsible for the catalyzed reaction in each case. The simpler case to analyze is that of HClO$_4$ alone because it avoids the apparent problems of LiClO$_4$ ion pairing described above. Nevertheless, DKIE's of this magnitude are unusually high, particularly for processes involving HX-catalyzed additions to olefins in HOAc. For example, Fahey and Monahan report a DKIE of $k_{HOAc}/k_{DOAc} = 1.3$ for the LCl-catalyzed

Scheme 3[a]
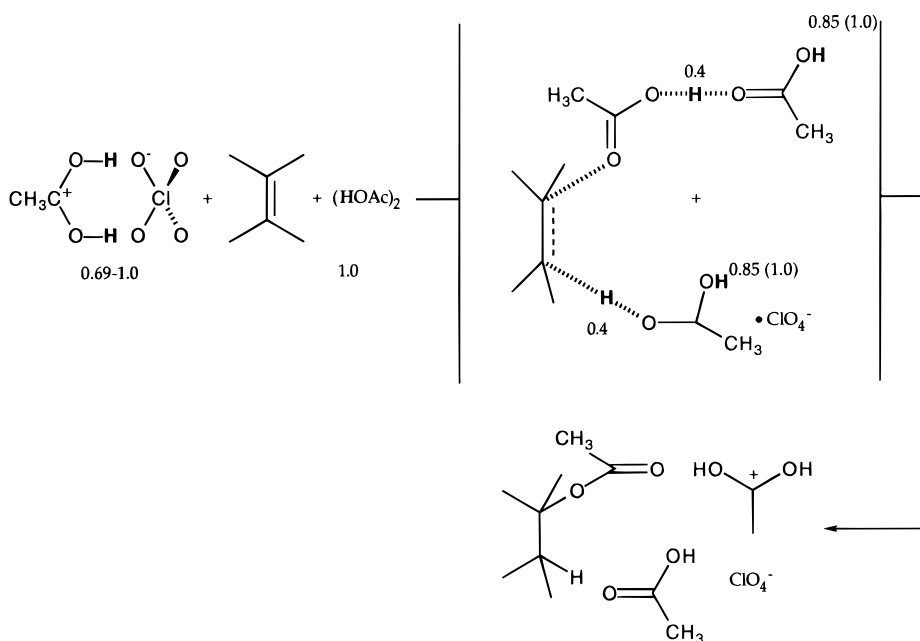
addition of LOAc to cyclohexene, the products being chlorocyclohexane and acetoxycyclohexane.[23] Fahey and McPherson have reported that the k_H/k_D value for LCl-catalyzed addition to 3,3-dimethyl-1-butene in HOAc is ~1.2, while that for the catalyzed addition to styrene is 1.4.[19c,e,33] These results are consistent with a very late transition state where proton transfer occurs in the rate-limiting step.

On the other hand, Pasto and co-workers[35] have reported that HBr-promoted addition of HOAc to cyclo-pentene exhibits a DKIE of $k_H/k_D = 0.63$. They explain this result by suggesting that if proton transfer occurs in the rate-limiting step, it must occur from a species where the H–X bond stretching frequency is substantially lower than that for a C–L bond. This suggests proton transfer occurs from undissociated H–Br to the olefin in the rate-limiting step.

Subsequently, Pasto and Gadbury[36] reported that the substantially stronger acid, CF_3SO_3H, gives a k_H/k_D for addition of HOAc to 2-butene of 1.8. This acid, with its poorly nucleophilic counterion, also leads to isomerization of *cis*-2-butene to *trans*-2-butene, the apparent isotope effect on the isomerization process being 2.[35] These results are consistent with at least partially reversible formation of a tight ion pair, with a long enough lifetime for bond rotation, and proton loss to reform starting material. They are also consistent with a pathway involving ion capture by solvent that is competitive with bond rotation.

Apparently, the norm for HX-catalyzed additions to alkenes in HOAc is small DKIE's arising from rate-limiting H-transfer in late transition states forming highly unstable ion-paired intermediates and perhaps larger DKIE's being expected for stronger acids. The situation with $HClO_4$ addition to **1** catalyzed by $HClO_4$ with a high DKIE of 5.4 is unusual and therefore worthy of comment. First, that plots of the $[HClO_4]/k_{obs}$ data of

Table 7 are linear indicates that free ions such as H^+ or H_2OAc^+ are not important for catalysis, and that the catalytically active species is an ion pair, $ClO_4^-H_2OAc^+$,[21,37] or $HClO_4$ itself. Second, although we have not performed the requisite proton inventory plots of k_{obs} vs atom fraction of D in LOAc, the high observed DKIE suggests the involvement of 2 or more protons undergoing changes in bonding for the $HClO_4$-catalyzed reaction.

We suggest, in Scheme 3, a model for the $HClO_4$-promoted reaction consistent with the data. The model involves a concerted addition of the H^+ from H_2OAc^+/ClO_4^- and another molecule of HOAc to the double bond. Given in eq 12 is the equation (a modification of eq 6 where $n = 1$) relating the observed DKIE to the various fractionation factors of the exchangeable protons in the reactant and transition state. For the reactant state we consider that an O-protonated acetic acid has two protons of fractionation factor 0.69–1.0. The lower value is a

$$k_{obs}^D/k_{obs}^H = \prod_i^{TS} \phi_i \Big/ \prod_j^{RS} \phi_j \qquad (12)$$

tenuous estimate based on that of H_3O^+ in H_2O[26] and might be too small since the bulk of the positive charge will be borne by carbon rather than oxygen. We consider the transition state to be 50% along the reaction pathway. The primary DKIE for a proton in flight between oxygens, or oxygen and carbon, is based on a transition state fractionation factor of ~0.4 (with values of 0.3–0.5 used as limits). Such a value for an O····L····C primary DKIE is reasonable considering that proton transfer from H_3O^+ is the rate-limiting step for such reactions as acid-catalyzed alkene hydration[38] and vinyl ether hydrolysis,[39] these processes exhibiting DKIE values ranging from 2–6.

(35) Pasto, D. J.; Meyer, G. R.; Lepeska, B. *J. Am. Chem. Soc.* **1974**, *96*, 1858.

(36) Pasto, D. J.; Gadbury, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 1469.

(37) Homer, R. B.; Moodie, R. B.; Rydon, H. N. *J. Chem. Soc.* **1965**, 4399, 4403.

(38) (a) Gold, V.; Kessick, M. A. *Disc. Faraday Soc.* **1965**, *39*, 84. (b) Chwang, W. K.; Nowlan, V. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 7233. (c) Kabir, S. H.; Seikaly, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 1059.

For the process shown in Scheme 3 with its associated fractionation factors indicated, we calculate a DKIE of 4.1 if the reactant state has a fractionation factor of 0.69, and 6.25 if the value is 1. That these values bracket the observed DKIE of 5.4 suggests that such a simple model is adequate to explain the observations.

Note here that for the simplistic analysis above we have neglected the contribution to the DKIE that would result from changes in the ϕ for the ClO_4^- in passing from the ground to TS. These values are unknown, but it may be surmised that the ClO_4^- will be less well solvated by LOAc in its $CH_3C(OL)_2^+$-associated ground state than it is in the TS. The net effect of this is to decrease the ratio given in eq 12, making the DKIE even larger than that computed above and certainly not smaller.

Finally, we may use the same sort of analysis in assessing the TS involving rate-limiting proton transfer from the $CH_3C(OL)_2^+$ unit to the olefin with generation of a protonated alkene, LOAc, and solvated ClO_4^-. Assuming a limiting case to estimate the maximum expected kinetic isotope effect where ϕ for each O–L bond in the $CH_3C(OL)_2^+$ is 1.0, that for the solvated ClO_4^- in the ground state is unity, and the ϕ for the proton in flight and solvated ClO_4^- in the TS are 0.4 and 0.5,[40] respectively, a DKIE of 5 can be computed. This value is acceptably close to that observed but is probably unrealistically high given that the ϕ for the $CH_3C(OL)_2^+$ O–L bonds and solvated ClO_4^- in the ground state should be lower than unity. For example, if we use values for the former of 0.69 and for the latter of 0.8, a DKIE of 2.2 is computed, far lower than what is observed. For that reason, we tentatively reject the stepwise addition of L^+ and LOAc as a viable process for the $HClO_4$-promoted reaction.

As mentioned previously, we cannot, on the basis of the proton inventory data, rule out a stepwise addition of LOAc to **1**. Conceptually, a stepwise addition might be more likely when the acidic source is a strong one such as $HClO_4$ or $CH_3C(OH)_2^+$. When the acid is much weaker, such as the solvent here, a stepwise addition is less likely since the transition state requires considerable charge separation and the formation of a high energy intermediate. Since the present data suggest the strong acid catalysis does not proceed via a stepwise process, by inference the spontaneous addition reaction with solvent is likely to be concerted.

Conclusions

Sesquinorbornene (**1**) is an unusually informative olefin for study of electrophilic processes because of its chromophore at 254 nm that allows kinetics to be easily monitored, its exhalted reactivity, and its propensity for *cis* addition without Wagner–Meerwein processes. Bromination of **1** in MeOH occurs rapidly, and product formation to generate ~10% dibromide and 90% methoxy bromide results exclusively from ion pair collapse. In acetic acid bromination is more complex and occurs in competition with both spontaneous and $HClO_4$-catalyzed solvent addition. For the spontaneous solvent addition, the observed DKIE of 3.3 is shown to arise from a process involving at least two protons undergoing a change in bonding. The $HClO_4$-catalyzed process probably arises from simultaneous attack of a solvent molecule and H_2OAc^+ proton source on the double bond giving rise to a DKIE of 5.4. $LiClO_4$ is also shown to catalyze the solvent attack on the olefin, and this process exhibits a DKIE of ~8. $LiClO_4$ in HOAc is shown to generate substantial amounts of $HClO_4$, and the observed catalytic effect can be largely eliminated by the addition of small amounts of NaOAc. However, the differences in the DKIE's for the $LiClO_4$- and $HClO_4$-promoted reactions suggests that different acidic species are responsible in each case. A likely source of the difference in the kinetic isotope effects is the change in hydrogen bonds of solvation of the various ionic species in passing from the ground to transition states, thereby contributing secondary DKIE's.

JO951746W

(39) (a) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *J. Am. Chem. Soc.* **1977**, *99*, 7228. (b) Kresge, A. J.; Chiang, Y. *J. Chem. Soc. B* **1967**, *53*, 58. (c) Kresge, A. J.; Yin, Y. *Can. J. Chem.* **1987**, *65*, 1753.

(40) Emsley, J.; Gold, V.; Szeto, W. T. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2641. The authors have strongly shown that a solvated anion such as F^- in HOAc has a ϕ value of 0.55 while a weakly solvated one such as Cl^- has a ϕ of 1.26. On this basis it is difficult to guess what the appropraite value for $ClO_4^-\cdots(HOAc)_n$ would be in the ground and transition state. The values chosen for discussion are those which could generate a maximum computed DKIE.