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Kinetic Solvent Isotope Effects in the Additions of Bromine and 4-Chlorobenzenesulfenyl Chloride to Alkenes and Alkynes

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The rates of bromination of selected alkenes and alkynes in methanol/methanol-*d*, acetic acid/acetic acid-*d*, and formic acid/formic acid-*d* have a nearly constant value of $k_H/k_D = 1.23 \pm 0.02$. This kinetic solvent isotope effect is attributed to specific electrophilic solvation of the incipient bromide anion by hydrogen bonding in the rate-determining transition state. The rates of bromination were measured in two solvents having the same values of the solvent parameter *Y* but different nucleophilicities in order to assess the importance of nucleophilic solvation. Significant nucleophilic solvent assistance is found for only alkylacetylenes. The kinetic solvent isotope effects of the addition of 4-chlorobenzenesulfenyl chloride to selected alkenes and alkynes in acetic acid/acetic acid-*d* vary from 1.00 to 1.28. These data are consistent with two mechanisms: One involves a tetravalent sulfur intermediate while the second is the sulfur analogue of the S_N2 mechanism.

There have been a number of attempts to draw a parallel between the role of solvents in electrophilic addition and solvolysis reactions. For example, both the Grunwald–Winstein equation[1,2] and the Schleyer[3] approach have been applied to the bromination of alkenes and alkynes. The results of these correlations suggest that the role of the solvent in bromination of alkenes, styrene, and phenylacetylene resembles that which operates in the S_N1 solvolytic process; that is, the leaving anionic groups are electrophilically solvated in both processes. On the other hand, important nucleophilic solvent assistance is found in the bromination of alkylacetylenes, in a manner similar to that in the S_N2 solvolytic process.

A possible probe of the role of solvents in reactions is the kinetic solvent isotope effect (KSIE). Kinetic solvent isotope effects for reactions involving nucleophilic displacement at a saturated carbon have been extensively studied, mostly in H_2O and D_2O.[4]

In these studies the small KSIE's (20–40%) are ascribed to differential transition-state phenomena in which initial-state differences are neglected.[5] Similarly, for electrophilic additions to alkenes and alkynes it seems unlikely that the reaction with virtually nonpolar or weakly polar compounds to form highly polar transition states would be significantly affected by solvent isotope effects upon the initial state.

We report a study of the KSIE on the addition of bromine and 4-chlorobenzenesulfenyl chloride to a selected number of alkenes and alkynes containing terminal and internal double and triple bonds with alkyl and aryl substituents. Our results are compared with the KSIE of solvolysis reactions in order to provide more information about the role of the solvent in the rate-determining transition state of the bromination of alkenes and alkynes.

Results and Discussion

1. Solvent Effects in Bromine Addition to Alkenes and Alkynes. The rates of addition of bromine to model alkenes and alkynes were measured by following the disappearance of electrophilic reagent absorption at 490 nm in acetic acid, deuterated acidic acid (CH_3CO_2D), methanol, and deuterated methanol (CH_3OD) and, for pentyne-1 and hexyne-3, additionally in formic and deuterated formic acid (HCO_2D). The stopped-flow technique was used for all the compounds in all solvents, except for pentyne-1, hexyne-3, and phenylacetylene in acetic acid and deuterated acidic acid. In the latter cases the reaction was monitored by conventional techniques. Reaction rate measurements in an EtOH–2% H_2O mixture were performed by using the same techniques as for acetic acid. The rate measurements were carried out in the absence of added bromide ion and at low bromine concentrations ($<3 \times 10^{-4}$ M) to ensure that only the contribution from the bimolecular process was significant.[6,7] The second-order rate constants and calculated k_H/k_D ratios are given in Table I.

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[1] M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 1977 (1975).

[2] M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **42**, 2689 (1977).

[3] G. Modena, F. Rivetti, and V. Tonellato, *J. Org. Chem.*, **43**, 1521 (1978).

[4] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 822 (1962).

[5] P. M. Laughton and R. E. Robertson, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, p 424.

[6] K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973).

[7] J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

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Table I. Rates of Bromination and Kinetic Solvent Isotope Effects at 25 °C

compd	solvent	k_2, M^{-1} s^{-1}	k_H/k_D	solvent	k_2, M^{-1} s^{-1}	k_H/k_D	solvent	k_2, M^{-1} s^{-1}	k_H/k_D
pentene-1				CH_3CO_2H	16.5 ± 0.2	1.25 ± 0.02	CH_3OH	421 ± 8	1.21 ± 0.03[a]
				CH_3CO_2D	13.2 ± 0.1		CH_3OD	348 ± 7	
cis-hexene-3				CH_3CO_2H	2830 ± 30	1.23 ± 0.03			
				CH_3CO_2D	2290 ± 40				
styrene				CH_3CO_2H	11.2 ± 0.12	1.22 ± 0.01	CH_3OH	1370 ± 12	1.21 ± 0.02
				CH_3CO_2D	9.2 ± 0.01		CH_3OD	1126 ± 10	
pentyne-1	HCO_2H	0.229 ± 0.00056 × 10^{-4}	1.26 ± 0.01	CH_3CO_2H	3.00 × 10^{-4} ± 2.9 × 10^{-6}	1.28 ± 0.02	CH_3OH	0.0913 ± 0.0019	1.22 ± 0.03
	HCO_2D	0.182 ± 0.00060 × 10^{-4}		CH_3CO_2D	2.33 × 10^{-4} ± 2.0 × 10^{-6}		CH_3OD	0.0751 ± 0.0020	
hexyne-3	HCO_2H	15.5 ± 0.067 × 10^{-2}	1.24 ± 0.01	CH_3CO_2H	5.84 × 10^{-3} ± 1.0 × 10^{-4}	1.23 ± 0.02	CH_3OH	0.849 ± 0.011	1.20 ± 0.02
	HCO_2D	12.5 ± 0.082 × 10^{-2}		CH_3CO_2D	4.73 × 10^{-3} ± 4.0 × 10^{-5}		CH_3OD	0.710 ± 0.010	
phenylacetylene				CH_3CO_2H	4.33 × 10^{-3} ± 6.0 × 10^{-5}	1.20 ± 0.05	CH_3OH	1.22 ± 0.013	1.23 ± 0.002
				CH_3CO_2D	3.60 × 10^{-3} ± 1.5 × 10^{-4}		CH_3OD	1.08 ± 0.011	

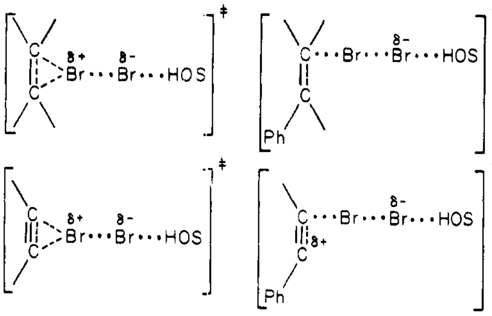
[a] Although the previously reported value[6] k_H/k_D = 1.40 ± 0.20 for pentene-1 is higher than "normal" for electrophilically solvated transition states of bromination, the standard deviation of this determination is 10 times higher than those obtained in our measurements. Taking this fact into account, there is a good agreement between this reported value and our data.

Table II. Rates of Bromination in EtOH-2% H_2O at 25 °C

compd	k_2, M^{-1} s^{-1}	$k_{aq\ EtOH}/k_{aq\ CH_3CO_2H}$[a]
pentene-1	21.6 ± 0.03	1.3
pentyne-1	3.19 × 10^{-2} ± 2.1 × 10^{-4}	106
hexyne-3	0.268 ± 0.003	46
phenyl-acetylene	5.20 × 10^{-3} ± 2.1 × 10^{-4}	1.2

[a] These ratios parallel the behavior of log k vs. Y plots for these substrates. Pentene-1 and phenylacetylene give the linear pattern of the Winstein-Grunwald equation,[1,2] while for hexyne-3 and pentyne-1, marked scatter is observed.[3]

For all compounds studied, a nearly constant value of k_H/k_D (1.23 ± 0.02) was obtained in the three solvents. This value is in good agreement with that found by Dubois (k_H/k_D = 1.40 ± 0.2) for the bromination of pentene-1 in methanol/methanol-*d*.[8] This result has been attributed to the specific electrophilic solvation of the leaving bromide ion regardless of the nature of the cationic part of the rate-determining transition state, with insignificant secondary contributions from nucleophilic solvent assistance. Thus, Br^-, a common anionic leaving group for all brominations, generates an almost constant KSIE.



This is in accord with the KSIE found in solvolysis reactions. There is no significant difference in the KSIE observed for alkyl halides that react by S_N1 and S_N2 mechanisms.[9] Furthermore, no difference is found in the experimentally measured activation parameters for the hydrolysis of several halides in H_2O and D_2O.[10] Regardless of the size of their alkyl group, alkyl halides that undergo solvolysis by an S_N2 mechanism show no change in the value of their KSIE.[11] The magnitudes of the KSIE's in bromination and in solvolysis are comparable. The specific electrophilic solvation of the leaving bromide ion in bromination of alkenes and alkynes and the solvation of the anionic part of the organic substrate in solvolysis is the prevailing factor that contributes to the KSIE for these reactions. Such a conclusion represents a unified concept of the origin of the KSIE for the reactions under discussion.

The specific nucleophilic solvation of the rate-determining transition states can be conveniently established in terms of the rate ratios in two solvents having the same

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[8] F. Garnier, R. Donnay, and J. E. Dubois, *J. Chem. Soc. D*, 829 (1971).

[9] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **34**, 1714 (1956).

[10] P. M. Laughton and R. E. Robertson, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, p 431.

[11] E. K. Thornton and E. R. Thornton, "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowmann, Eds., Van Nostrand-Reinhold, New York, 1970, p 268.

Table III. Rates of 4-Chlorobenzenesulfenyl Chloride Addition to Alkenes and Alkynes and Kinetic Solvent Isotope Effects in Acetic Acid at 25 °C

compd	solvent	k_2, M^{-1} s^{-1}	k_H/k_D
pentene-1	CH_3CO_2H	15.1 ± 0.06	1.16 ± 0.01
	CH_3CO_2D	13.0 ± 0.08	
cis-hexene-3	CH_3CO_2H	436 ± 2	1.02 ± 0.01
	CH_3CO_2D	425 ± 4	
styrene	CH_3CO_2H	15.9 ± 0.06	1.20 ± 0.01
	CH_3CO_2D	13.3 ± 0.11	
pentyne-1	CH_3CO_2H	0.305 ± 0.001	1.25 ± 0.02
	CH_3CO_2D	0.244 ± 0.003	
hexyne-3	CH_3CO_2H	28.6 ± 0.10	1.00 ± 0.01
	CH_3CO_2D	28.5 ± 0.25	
phenylacetylene	CH_3CO_2H	$9.37 \times 10^{-2} \pm 2.0 \times 10^{-4}$	1.28 ± 0.01
	CH_3CO_2D	$7.32 \times 10^{-2} \pm 3.2 \times 10^{-4}$	

values of the solvent parameter Y but quite different nucleophilicities.[12] Our choice of solvents was acetic acid and EtOH containing 2% of H_2O ($Y = -1.639$ and -1.681, respectively). The appropriate rates of bromination had been measured and are presented in Table II.

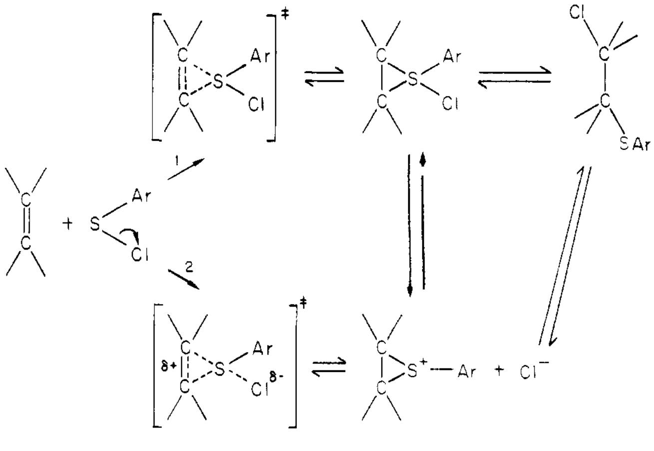
The large rate increase in aqueous EtOH with respect to CH_3CO_2H for hexyne-3 and the even greater one for pentyne-1 demonstrate the presence of significant nucleophilic solvent assistance for these two substrates. The absence of such nucleophilic solvent participation in the bromination of pentene-1 and phenylacetylene is also evident. This is in accord with previous work.[3]

The k_H/k_D ratios from Table I reveal no correlation with the degree of nucleophilic solvent assistance in bromination of alkenes and alkynes. For solvents like methanol and formic acid, considerably different in their nucleophilicities, virtually the same values of k_H/k_D were obtained. This finding is fully analogous to the lack of response of k_H/k_D ratios to nucleophilic solvent assistance in solvolysis.[9]

2. Solvent Effects in 4-Chlorobenzenesulfenyl Chloride Addition to Alkenes and Alkynes. We have measured the rates of addition of 4-chlorobenzenesulfenyl chloride to model alkenes and alkynes in acetic acid and deuterated acetic acid by means of the stopped-flow technique. The rate of disappearance of 4-chlorobenzenesulfenyl chloride was followed by measuring the decrease in its absorption at 385 nm. The addition was found to exhibit normal second-order kinetics, first-order in unsaturated substrate and first-order in sulfenyl chloride to at least 80% completion of the reaction. The rate data and calculated k_H/k_D ratios are given in Table III.

The rate of addition of 4-chlorobenzenesulfenyl chloride could be measured only in acetic acid/deuterated acetic acid because water, alcohols, and formic acid all react with arenesulfenyl halides.[13] Therefore, we could not systematically study the effect of solvent polarity on the rate of addition of 4-chlorobenzenesulfenyl chloride. In acetic acid and deuterated acetic acid, the values of k_H/k_D depend upon the structure of the unsaturated compound, varying in the range of 1.00–1.28. Clearly an explanation based on solvent reorganization around the departing chloride ion[14] does not apply since such an effect provides an almost constant value of the KSIE in each case.

Scheme I



There are two possible explanations for the observed variation in the KSIE. It is possible that two reaction pathways exist as shown in Scheme I.[15] Path 1 involves formation of a tetravalent sulfur intermediate which may ionize to the thiiranium ion or may proceed directly to products. Path 2 is the sulfur analogue of the S_N2 mechanism that leads directly to the thiiranium ion.

A second possibility involves a single pathway but a variable transition state structure. Thus bond making would be more advanced than bond breaking for certain substrates. If the rate-determining transition state is reached before the S–Cl bond is significantly broken, only a small or no KSIE will be observed. With substantial S–Cl bond breaking in the transition state, as in bromination, a significant KSIE would be observed. It is impossible to distinguish between these two alternatives from the available data.[16]

Conclusions

The general pattern of solvent polarity effects on rates of bromination reactions seems to be uniform. Thus a change from a less to a more polar solvent results in large increases in the observed rate of bromination.[17,18] This solvent effect consists of contributions from nonspecific solvation (medium effect), in which charge separation in the transition state is facilitated, and from specific electrophilic solvation of the incipient bromide anion by hydrogen bonding. The presence of a sizable and almost constant KSIE, $k_H/k_D \simeq 1.23$, for alkenes and alkynes results mainly from the electrophilic type of solvation, with insignificant nucleophilic solvation contributions in the majority of cases.

Experimental Section

Reagents. The alkenes and alkynes were commercially available (Chemical Samples Corp.) and their purity was verified by GLC and NMR analysis. Acetic acid and acetic acid-*d* (Merck Sharp & Dohme Canada Ltd.) were purified by refluxing for several hours with chromium trioxide and acetic anhydride and then distilled through a column.[19] Commercially available acetic acid-*d* purified by the above method, although pure according

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[12] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

[13] G. H. Schmid and V. M. Csizmadia, *Int. J. Sulfur Chem.*, 8, 433 (1973).

[14] E. M. Arnett and L. E. Small, *J. Am. Chem. Soc.*, **99**, 808 (1977).

[15] G. H. Schmid and D. G. Garratt, "The Chemistry of Double Bonded Functional Groups", Supplement A, Part 2, S. Patai, Ed., Wiley, New York, 1977, p 837.

[16] G. H. Schmid, *Top. Sulfur Chem.*, 3, 100 (1977).

[17] A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977).

[18] F. Garnier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1968).

[19] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 987 (1927).

to GLC standards, was not appropriate for kinetics of bromination (nonreproducible rate constants were obtained). The acetic acid-*d* used for kinetics of bromination was prepared from calculated amounts of acetic anhydride and deuterium oxide by refluxing the reaction mixture for a few hours followed by distilling off the product. Methyl alcohol and methyl alcohol-*O-d* (Merck Sharp & Dohme Canada Ltd.) were refluxed with Br_2 and then distilled twice from bromine and K_2CO_3.[20] Formic acid (>99%) and formic acid-*O-d* (≥98% D) (Merck Sharp & Dohme Canada Ltd.) were fractionally distilled from phthalic anhydride. The EtOH–2% H_2O mixture was prepared from absolute ethanol and distilled water.[21] 4-Chlorobenzenesulfenyl chloride was prepared as previously described.[22]

Kinetics. The rates of bromination of alkenes and alkynes were measured as previously reported.[23,7] The rates of 4-chlorobenzenesulfenyl chloride additions to alkenes and alkynes were determined as previously described.[22] All rates were obtained on a Durrum-Gibson or a Cary 16 spectrophotometer. The reported rate coefficients are the mean values of five to seven independent determinations.

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Registry No. 1-Pentene-1, 109-67-1; *cis*-3-hexene, 7642-09-3; styrene, 100-42-5; 1-pentyne, 627-19-0; 3-hexyne, 928-49-4; phenylacetylene, 536-74-3; bromine, 7726-95-6; 4-chlorobenzenesulfenyl chloride, 933-01-7.

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[20] J. E. Dubois and H. Herzog, *Bull. Soc. Chim. Fr.*, 57 (1968).

[21] K. B. Harbison, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.

[22] G. H. Schmid, V. M. Csizmadia, V. J. Nowlan, and D. G. Garratt, *Can. J. Chem.*, **50**, 2457 (1972).

[23] K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, **38**, 2460 (1973).

Methyl Substituent Effects upon the Chemistry of 2-Bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoates

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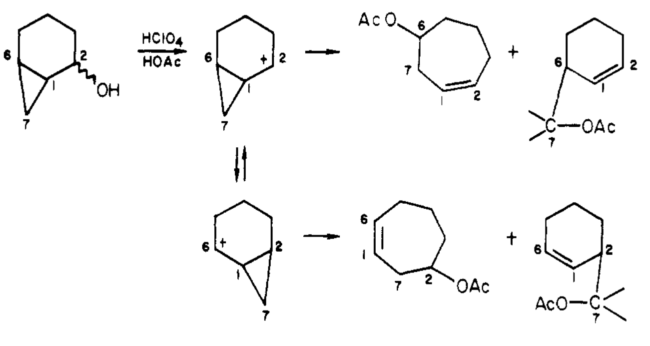
The rates and products of kinetic control in hydrolyses of the unsubstituted and 2-, 6-, and *anti*-7-methyl-substituted 2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates in 80% aqueous acetone have been determined. These are compared with similar data for the 1-methyl-substituted 3,5-dinitrobenzoates reported by Wiberg and Chen. Also, they are compared with the results of our previously reported perchloric acid catalyzed alcohol acetolysis studies for the same systems where the products of thermodynamic control and the percentages of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement occurring prior to their formation were investigated. Several important conclusions regarding the detailed reaction pathway for cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement in the 2-bicyclo[4.1.0]heptyl system have been derived from these comparisons.

Introduction

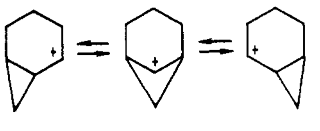
We recently[1] reported a study of the effects of individual 1-, 2-, 6-, or *anti*-7-methyl substitution upon the importance of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements[2] in perchloric acid catalyzed acetolyses[3] of 2-bicyclo[4.1.0]heptanols. This was done, with deuterium labels where necessary, through a determination of the relative amounts of the various possible products formed as depicted in Scheme I. In the scheme the numberings of the carbons in the starting material have been retained throughout to illustrate the consequences of the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement upon the natures of the products.

The perchloric acid catalyzed acetolysis procedure provided primarily the homoallylic acetate products of thermodynamic control via repeated reionization of any initially formed bicyclic acetate products of kinetic control. 1-Methyl substitution increased the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement product formed from about 35% to the theoretical maximum of 50%. However, with 2-, 6-, or *anti*-7-methyl substitution the amount of rearrangement product decreased to less than about 3, 1, and 10%, respectively.

Scheme I



Concerning the 1-methyl substituent effect, this was interpreted as providing possible support for the intervention of a puckered cyclobutyl-type[4] activated complex or intermediate in the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement process.



However, it was not known whether the process is stepwise

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[1] E. C. Friedrich and J. D. C. Jassawalla, *Tetrahedron Lett.*, 953 (1978).

[2] For an excellent source of references, see: G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **98**, 7026 (1976).

[3] E. C. Friedrich and M. A. Saleh, *J. Am. Chem. Soc.*, **95**, 2617 (1973).

[4] K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **92**, 571 (1970).

0022-3263/79/1944-4224$01.00/0