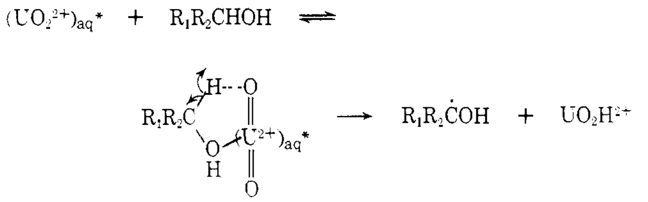
Table IV. Comparison of the Rate Parameters of Deuterated Alcohols and *tert*-Butyl Alcohol with Those of the Corresponding Nondeuterated and Isomeric Alcohols[a]

Alcohol	ϕ	K_q, M^{-1}
C_2H_5OH	0.31	62.5
C_2H_5OD	0.30	
C_2D_5OD	0.14	29
$(CH_3)_2CHOH$	0.34	113
$(CD_3)_2CDOD$	0.18	41
n-Butyl alcohol Isobutyl alcohol *sec*-Butyl alcohol	0.36	130–174
tert-Butyl alcohol	0.02	5

[a] Same conditions as in Table III.

Such special geometrical configuration, needed for the chemical quenching, may be partly responsible for the relatively small quenching constants of aliphatic alcohols (having neither halogen atoms nor a phenyl group). However, this point needs further clarification.



As a summary, quenching of the uranyl fluorescence by aromatic quenchers and aliphatic alcohols involves nonelectronic–electronic energy transfer; quenching by aromatic molecules proceeds through physical radiationless decay of an excited state π complex, while quenching by aliphatic alcohols proceeds through chemical decay (*via* hydrogen abstraction) of an exciplex or collision complex.

Polar Electrophilic Additions to Styrene. Secondary Deuterium Isotope Effects[1a–c]

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Abstract: α-Secondary deuterium isotope effects for polar additions of electrophiles to styrene, *trans*-1-phenylpropene, *p*-bromo-, *p*-chloro-, and *p*-nitrostyrene have been measured. The reactions were carried out at 40° in dry acetic acid using bromine, chlorine, and 2,4-dinitrobenzenesulfenyl halides as the electrophiles. Very small isotope effects (k_H/k_D = 0.97–1.00) were found for bromine and chlorine additions to all but *p*-nitrostyrene. In that case, k_H/k_D values of 0.95 and 0.96, respectively, were found. For the additions of 2,4-dinitrobenzenesulfenyl halides, k_H/k_D values in the range of 0.94–0.97 were found for all the styrenes examined. These results are interpreted with the help of stereochemical and kinetic data.

Since Lewis'[2] and Shiner's[3] pioneering work in the 1950's, secondary deuterium isotope effects have proven to be an invaluable aid in the elucidation of reaction mechanisms. To date, investigations of a wide range of reactions have employed this tool in probing transition state chemistry.[4]

Surprisingly, secondary deuterium isotope effects have been little used to study polar electrophilic additions to olefins. In an early qualitative study, Denney and Tunkel,[5] testing the suggestions of Streitwieser,[6] found inverse isotope effects for the reactions of *trans*-stilbene-d_2 with a variety of reagents. The isotope effects for two known polar electrophilic reagents, bromine (k_H/k_D = 0.91) and 2,4-dinitrobenzenesulfenyl chloride (k_H/k_D = 0.87), were measured, but these data were said to be qualitative. The conclusion of that study was that inverse isotope effects predominate in addition reactions of olefins. More recently, Schubert and Lamm[7] have reported a k_H/k_D of 0.97 ± 0.03 for the acid-catalyzed hydrolysis of styrene-α-d_1. This value is consistent with a mechanism involving carbonium ion formation by solvolytic proton transfer to styrene during the rate-determining step. Since much of the previous work has been qualitative, it was our hope in the present investigation to make quantitative measurements of these effects.

Most previous evidence for the reaction mechanisms of polar electrophilic additions to olefins is based largely on data such as reaction stereochemistry.[8–10] More evidence, such as the direction and magnitude of secondary deuterium isotope effects, is highly desirable. It has been pointed out by Wolfsberg[11] that determination of transition state geometry cannot be

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Partial support was also received from the University of Nebraska Research Council. (c) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-094. (d) Abstracted from the Ph.D. Dissertation of T. W. Regulski, The University of Nebraska at Lincoln, 1971.

[2] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 6306 (1952).

[3] V. J. Shiner, *ibid.*, **75**, 2925 (1953).

[4] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

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

[6] A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[7] W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

[8] R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966).

[9] R. C. Fahey, *J. Amer. Chem. Soc.*, **88**, 4681 (1966).

[10] N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

[11] M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).

made by the use of isotope effects alone, but must be used in conjunction with other stereochemical or kinetic evidence. This type of necessary data is recently available for the polar electrophilic additions of chlorine,[12,13] bromine,[14,15] and 2,4-dinitrobenzenesulfenyl halides[16,17] to a variety of olefins.

The purpose of the present investigation is to examine the use of secondary deuterium isotope effects as a probe of transition state chemistry of polar electrophilic additions and to interpret these effects using available kinetic and stereochemical evidence to ascertain whether or not they are consistent with proposed reaction mechanisms.

Experimental Section

All melting points are uncorrected and were measured using a Mel-temp melting point apparatus. The nuclear magnetic resonance spectra were recorded with Varian A-60 and A-60-D spectrometers. All glpc analyses were performed with a Varian Aerograph Model 90-P3 gas chromatograph. The mass spectral analyses were determined with a Perkin-Elmer Hitachi RMU-6D double focusing mass spectrometer equipped with a Hewlett-Packard integrating digital voltmeter, Model DY-2401C. All calculations were done using the IBM 360/65 computer.

Reagents. Styrene (Aldrich), **bromine** (Mallinckrodt), and **oxygen** (Matheson) were used without further purification. **Chlorine** (Matheson) was passed through a sulfuric acid trap prior to use. **Glacial acetic acid** (Corco) was dried by adding 10% by volume acetic anhydride and 1.0 g of concerted sulfuric acid per liter of this mixture and heating under reflux for 2 days. A forerun was then distilled and dry acetic acid, bp 117–118°, was collected. **2,4-Dinitrobenzenesulfenyl bromide** was prepared by the method of Kharasch[18]; mp 104–105° (lit.[18] 104.5–105.5°). **2,4-Dinitrobenzenesulfenyl chloride** (Aldrich) was recrystallized from carbon tetrachloride; mp 95.0–95.5° (lit.[19] 95.0–95.5°).

***p*-Chloro- and *p*-Bromostyrene.** Para-substituted acetophenone (Aldrich) was reduced with lithium aluminum hydride (Ventron) to the para-substituted 1-phenylethanol in yields of 65.7 (*p*-chloro) and 81.5% (*p*-bromo). The alcohol was dehydrated using catalytic amounts of picric acid (for stabilization) and *p*-toluenesulfonic acid monohydrate[20] to afford a 78% yield of *p*-bromostyrene, bp 113–115° (9 mm) (lit.[21] bp 114–117° (10 mm)), and an 81.3% yield of *p*-chlorostyrene, bp 88–89° (2 mm) (lit.[22] 87–89° (2 mm)).

***p*-Nitrostyrene.** *p*-Nitroacetophenone was reduced to the corresponding alcohol in a 66.5% yield with sodium borohydride (Ventron) in methanol. The alcohol was dehydrated by distillation in the presence of 85% polyphosphoric acid and the crude material was purified by column chromatography (using 96.0 g of Florisil packed in a 40 cm × 3 cm column, and eluting with benzene), giving a 71% yield of *p*-nitrostyrene; mp 25–28° (lit.[23] 29°).

***trans*-1-Phenylpropene.** Propiophenone (Matheson Coleman and Bell) was reduced to 1-phenyl-1-propanol with lithium aluminum hydride in 84.6% yield. Dehydration of the alcohol by distilling it from 85% polyphosphoric acid afforded an 81% yield of *trans*-1-phenylpropene: bp 176° (lit.[24] 73.5° (20 mm)).

Para-Substituted Styrenes-α-d_1. Styrene-α-d_1, bromostyrene-α-d_1, *p*-chlorostyrene-α-d_1, and *trans*-1-phenylpropene-α-d_1 were all synthesized using the procedures described for the nondeuterated materials except that lithium aluminum deuteride (Merck Sharp and Dohme, minimum isotopic purity 99%) was substituted for lithium aluminum hydride. For *p*-nitrostyrene, sodium borodeuteride (Merck Sharp and Dohme, minimum isotopic purity 98%) was used in place of sodium borohydride. No absorption by an α-hydrogen could be detected in any of the nuclear magnetic resonance spectra. *trans*-1-Phenylpropene and the para-substituted styrenes, except for *p*-nitrostyrene, were purified by glpc using either a 15 ft × 0.25 in. copper column packed with 3% QF-1 on Chromosorb W, operated at 120° with a carrier gas flow of 60 ml/min, or a 15 ft × 0.25 in. copper column packed with 10% QF-1 on Chromosorb W, operated at 170° with a carrier gas (He) flow of 60 ml/min. All deuterated styrenes were sealed in ampoules and stored in a refrigerator until used. Mass spectral analysis, taken near the appearance potential, indicated an isotope purity of 97 atom % D or greater for each compound.

Kinetic Analysis. The competition method was used in determining the secondary deuterium isotope effects, $k_{\mathrm{H}}/k_{\mathrm{D}}$. Mixtures of deuterated and nondeuterated olefins were made and subjected to mass spectral analysis to determine the starting ratio of the two components. The mixtures were weighed out and diluted to 10 ml with dry acetic acid to make solutions of styrene in approximately onefold excess over the electrophile concentrations used (the method of Kharasch[25] was used to determine the exact concentration of electrophile). A standard electrophile solution was then prepared, also using acetic acid as solvent. The two solutions (a styrene and an electrophile) were equilibrated (40.0°) and rapidly mixed. After reaction was complete, the total amount of reacted electrophile was determined by titration of residual electrophile (if any) by a standard sodium thiosulfate solution. The unreacted olefin was separated by glpc and again subjected to mass spectral analysis.

In the case of polar electrophilic addition of chlorine, the modification of Poutsma[26] was used to inhibit the radical reactions of chlorine, by passing oxygen through the olefin–acetic acid mixture while addition was taking place. The concentrations of all reactants were then determined and the secondary deuterium isotope effects were calculated from appropriate second-order rate equations. For each isotope effect measurement, at least three runs, usually four or more, were performed. Standard deviations for each $k_{\mathrm{H}}/k_{\mathrm{D}}$ were ±0.01 or less. The concentrations of olefins used in the measurements were 0.25–0.35 *M*, with the electrophile solutions varying from 0.1 to 0.2 *M*, depending on the electrophile used.

Deuterium Exchange Experiments. A. Noncatalyzed Reaction. Into a reaction vessel were placed 0.4000 ml (3.48 mmol) of a mixture of styrene and styrene-α-d_1 (exact ratio determined by mass spectral analysis) and 10 ml of dry acetic acid. The vessel was sealed and allowed to stand for 48 hr in a constant temperature bath held at 40.0°. The mixture was quenched with sodium carbonate and extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. After solvent was evaporated, the recovered mixture of deuterated and nondeuterated styrene, isolated by glpc, was subjected to mass spectral analysis to determine the final deuterium content.

Duplicate runs were performed. The starting ratio for the mixture of styrene-α-d_1 to styrene was found to be 1.137 to 1.000. The ratios determined for two samples of the final styrene mixture were 1.138 and 1.141 (an average of 1.140), giving an exchange ratio of 1.002.

B. Acid-Catalyzed Reaction. Into a reaction vessel was placed 0.200 ml (1.74 mmol) of the same starting mixture of styrene and styrene-α-d_1, a catalytic amount of concentrated hydrochloric acid (2 μl) or concentrated hydrobromic acid (3 μl), and 10 ml of dry acetic acid. The vessel was sealed and allowed to stand for 48 hr in a constant temperature bath held at 40.0°. The mixture was quenched with sodium carbonate, extracted with ether, and dried over magnesium sulfate. After evaporation of the solvent, the mixture of deuterated and nondeuterated styrene, isolated by glpc, was subjected to mass spectral analysis to determine the final deuterium content ratio.

The ratio found for duplicate samples of the final styrene mixture for the hydrochloric acid catalyzed experiment was 1.132 and for the hydrobromic acid catalyzed experiment was 1.133. The exchange ratio for the HCl-catalyzed experiment was, therefore, 0.996 and for the HBr-catalyzed experiment was 0.997. This suggests that, within the limitations of our measurements, no exchange of deuterium had occurred between styrene-α-d_1 and acetic acid with or without strong acids present in the reaction mixture.

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(12) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4285 (1965).

(13) R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).

(14) J. H. Rolston and K. Yates, **91**, 1469 (1969).

(15) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964).

(16) D. S. Campbell and D. R. Hogg, *J. Chem. Soc. London*, 5887 (1965).

(17) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1201 (1956).

(18) N. Kharasch, C. M. Buess and S. J. Strashun, *ibid.*, **74**, 3422 (1952).

(19) N. Kharasch, *ibid.*, **72**, 1796 (1950).

(20) I. A. Berstein, W. Bennett, and M. Field, *ibid.*, **74**, 5763 (1952).

(21) V. Braun and J. Nelles, *Ber.*, **66**, 1468 (1933).

(22) L. A. Brooks, *J. Amer. Chem. Soc.*, **66**, 1295 (1944).

(23) W. Saunders and R. Williams, *ibid.*, **79**, 3712 (1957).

(24) R. Y. Mixer, W. G. Young, R. F. Heck, and S. Winstein, *ibid.*, **75**, 4094 (1953).

(25) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

(26) M. L. Poutsma, *ibid.*, **87**, 2161 (1965).

Product Distribution from Electrophilic Additions to Styrene and *trans*-1-Phenylpropene in Acetic Acid at 40.0°. A. Bromine Additions. Into a reaction vessel were placed either 0.146 g (1.40 mmol) of styrene or 0.164 g (1.40 mmol) of *trans*-1-phenylpropene and 10 ml of acetic acid. The vessel was equilibrated to 40.0° and 10 ml (1.40 mmol) of bromine solution in acetic acid (equilibrated to 40.0°) was added slowly. After 24 hr, the solution was quenched with sodium carbonate, extracted with ether, and dried with magnesium sulfate. After evaporation of the solvent, nuclear magnetic resonance spectra of the styrene and *trans*-1-phenylpropene 1:1 adducts were determined.

For the bromination of styrene, 28–29% of the 1-acetoxy-2-bromo adduct was formed, the remainder being the 1,2-dibromo adduct. In the case of *trans*-1-phenylpropene, 31–33% of the 1-acetoxy-2-bromo adduct, along with 67–69% of the dibromo compound, was found. No 2-acetoxy-1-bromo adducts were detected for any of the additions. The observed percentages of 1-acetoxy-2-bromo-1-phenylethane are in the range found by Yates[14] (20.2–32.4%, depending on the method of addition used), but are larger than that observed for the *trans*-1-phenylpropene addition (21–23%). The nmr spectrum for each compound is as follows: (1) 1-acetoxy-2-bromo-1-phenylethane (CCl_4) δ 2.02 (s, 3, acetoxy protons), 3.54 (d, 2, CH_2Br), 5.93 (t, 1, $CHOAc$), 7.32 (s, 5, aromatic protons); (2) 1,2-dibromo-1-phenylethane (CCl_4) δ 3.96 (d, 2, CH_2Br), 5.08 (m, 1, CHBr), 7.32 (s, 5 aromatic protons); (3) 1-acetoxy-2-bromo-1-phenylpropane (CCl_4) δ 1.46–1.55 (d, 3, CH_3), 2.10 (s, 3, acetoxy protons); (4) 1,2-dibromo-1-phenylpropane (CCl_4) δ 1.60–2.00 (d, 3, CH_3), 4.60 (m, 1, $CHCH_3$), 5.05 (m, 1, CHC_6H_5), 7.27 (s, 5, aromatic protons.)

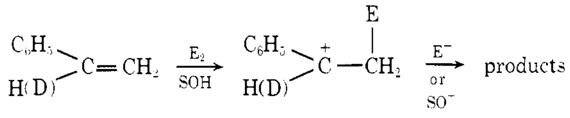
B. Chlorine Additions. Into a reaction vessel were placed either 0.156 g (1.50 mmol) of styrene or 0.176 g (1.50 mmol) of *trans*-1-phenylpropene and 10 ml of acetic acid. The same procedure as in A was followed, except that 10 ml (1.50 mmol) of an acetic acid solution of chlorine was added as a stream of oxygen was bubbled through the reaction flask. After isolation of the products, analysis by nuclear magnetic resonance showed, for the chlorine addition to styrene, that 43–44% of 1-acetoxy-2-chloro-1-phenylethane was formed. For the addition to *trans*-1-phenylpropene, about 32% of the product was 1-acetoxy-2-chloro-1-phenylpropane. The rest of the product was again made up of the 1,2-dichloro adducts. In the latter case, the observed product distribution was near that found by Fahey and Schubert[13] (29% dichloro adduct). The nmr spectra for these compounds were as follows: (1) 1-acetoxy-2-chloro-1-phenylethane (CCl_4) 2.04 (s, 3, acetoxy protons), 3.68 (d, 2, CH_2Cl), 5.91 (t, 1, $CHOAc$), 7.31 (s, 5, aromatic protons); (2) 1,2-dichloro-1-phenylethane (CCl_4) 3.89 (d, 2, CH_2Cl), 4.92 (t, 1, $CHCl$), 7.33 (s, 5, aromatic protons); (3) 1-acetoxy-2-chloro-1-phenylpropane (CCl_4) 1.36–1.49 (d, 3, CH_3), 2.02–2.05 (s, 3, acetoxy protons), 4.30 (m, 1, $CHCl$), 5.78 (t, 1, $CHOAc$), 7.30 (s, 5, aromatic protons); (4) 1,2-dichloro-1-phenylpropane (CCl_4) 1.60–1.72 (d, 3, CH_3), 4.30 (m, 1, $CHCH_3$), 4.86 (t, 1, CHC_6H_5), 7.31 (s, 5, aromatic protons).

C. 2,4-Dinitrobenzenesulfenyl Chloride Additions. Into a reaction vessel were placed either 0.133 g (1.28 mmol) of styrene or 0.150 g (1.28 mmol) of *trans*-1-phenylpropene and 10 ml of acetic acid. The vessel was equilibrated at 40.0° and 10 ml (1.28 mmol) of an acetic acid solution of 2,4-dinitrobenzenesulfenyl chloride (equilibrated at 70.0°) was added. After 24 hr, the procedure outlined in A was followed for the work-up. For the styrene addition, within the limits of the method, no 1-acetoxy-2-(2,4-dinitrobenzenethio)-1-phenylethane could be detected (nmr of the α proton). For the same reaction, but at 25.0°, Kharasch[25] has observed from 6 to 8% of the acetoxy product. For the *trans*-1-phenylpropene reaction, approximately 8–10% of 1-acetoxy-2-(2,4-dinitrobenzenesulfenyl)-1-phenylpropane (determined by observing the α-proton resonance) could be observed. The rest of the product was comprised of the normal addition product, 1-chloro-2-(2,4-dinitrobenzenethio)-1-phenylpropane. The nmr spectra for the adducts are as follows: (1) 1-chloro-2-(2,4-dinitrobenzenethio)-1-phenylethane ($CDCl_3$) δ 3.70 (d, 2, CH_2), 5.10 (t, 1, CH), 7.39 (s, 8, aromatic protons); (2) 1-chloro-2-(2,4-dinitrobenzenethio)-1-phenylpropane ($CDCl_3$) δ 1.35–1.68 (d, 3, CH_3), 3.96 (m, 1, $CHCH_3$), 5.02 (d, 1, CHC_6H_5), 7.28 (m, 8, aromatic protons).

Results and Discussion

In undertaking the investigation, careful consideration was given to the selection of the olefin. First, a clean quantitative reaction was deemed important. For the electrophiles used (chlorine, bromine, and 2,4-dinitrobenzenesulfenyl chloride and bromide) previous studies[13,14,25] have shown that 80–100% yields can be obtained for these additions. Second, orientation of addition was a concern. In this study, α-deuterium isotope effects were to be examined. Therefore, in the first step of the addition, the incoming electrophile (E) must attack the β carbon, yielding an α carbonium ion (Scheme I).

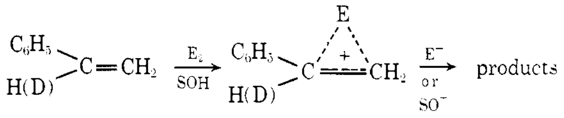
Scheme I



I

If bridging by the electrophile does not occur, a minimal effect should be observed ($k_H/k_D \approx 1.0$), but if the electrophile helps stabilize the carbonium ion through bridging, a maximal effect should be seen ($k_H/k_D < 1.0$) (Scheme II). This is a result of the difference in force constant changes[6] (*i.e.*, in I the deuterium-labeled carbon retains its sp^2 hybridization, while in II the same carbon rehybridizes from sp^2 to a state intermediate between sp^2 and sp^3). For example, Lim solvolyses (which represent an $sp^3 \rightarrow sp^2$ change) show k_H/k_D values of about 1.15.[27] Therefore, a large inverse effect would imply significant bridging in the transition state, whereas a small isotope effect would suggest that partial bond formation to the carbonium ion center from the electrophile was not taking place. Kharasch[17,25] has suggested that sulfonium ion formation occurs for the addition of 2,4-dinitrobenzenesulfenyl chloride to styrene and Yates[14,27,28] has established that only weak bridging, if any, occurs in the addition of bromine to styrene.

Scheme II



II

By studying styrene, not only could the degree of participation of different electrophiles be observed but, in addition, substituent effects might be monitored for the same reactions. Since it was not unreasonable to expect that electron-withdrawing groups would destabilize the carbonium ion, it might be expected that a compensatory increase in bridging would occur and could be observed as a greater inverse isotope effect. If this were true, the magnitude of such effects might provide direct evidence of bridging in those cases where it is possible. It was also necessary that there be significant independent evidence regarding the reaction mechanisms in order that correlation between bridging and observed isotope effects would be established. Kinetic and stereochemical data for reactions of interest were therefore required.

Thus, the styrenes were chosen for the investigation, since they seemed to offer the best hope of meeting these criteria and yielding useful information about the value of α-deuterium isotope effects for studies

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(27) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

(28) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1477 (1969).

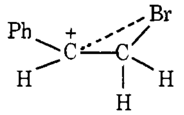
Table I. α-Deuterium Isotope Effects for Polar Electrophilic Additions to Styrene in Acetic Acid[a]

Olefin	Electrophile	$k_H/k_D{}^b$	$s_H/s_D{}^b$	n^c
Styrene	Cl_2	0.99 ± 0.01	0.99	4
	Br_2	0.97 ± 0.01	0.99	5
	2,4-DNBS[d] chloride	0.95 ± 0.01	0.97	4
	2,4-DNBS bromide	0.94 ± 0.01	0.99	4
p-Chlorostyrene	Cl_2	1.00 ± 0.01	0.85	4
	Br_2	0.98 ± 0.01	0.84	4
	2,4-DNBS chloride	0.95 ± 0.01	0.90	3
	2,4-DNBS bromide	0.95 ± 0.01	0.85	4
p-Bromostyrene	Cl_2	1.00 ± 0.01	0.95	4
	Br_2	0.99 ± 0.01	0.95	4
	2,4-DNBS chloride	0.94 ± 0.01	0.86	4
	2,4-DNBS bromide	0.95 ± 0.01	0.86	4
p-Nitrostyrene	Cl_2	0.96 ± 0.01	1.02	3
	Br_2	0.95 ± 0.01	1.04	6
	2,4-DNBS chloride	0.97 ± 0.01	1.01	6
	2,4-DNBS bromide	0.96 ± 0.01	0.94	5
trans-1-Phenylpropene	Cl_2	0.98 ± 0.01	0.90	4
	Br_2	0.98 ± 0.01	0.90	4
	2,4-DNBS chloride	0.94 ± 0.01	0.89	4
	2,4-DNBS bromide	0.96 ± 0.01	0.89	4

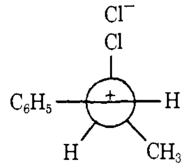
[a] All reactions were carried out at 40.0°. [b] Starting ratio of unlabeled to labeled olefin. [c] Number of separate determinations. [d] 2,4-Dinitrobenzenesulfenyl.

of this kind. Isotope effects, determined by multiple experiments involving three or more separate determinations each, carried out as described in the Experimental Section, are summarized in Table I.

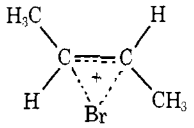
Chlorine and Bromine Additions. As we review the data in Table I, it is apparent that substituent effects on k_H/k_D for these reactions are modest. Only when the most drastic changes in substituent take place are they reflected by a significant change in this ratio. So, for example, when *p*-nitro- ($\sigma^+ = 0.78$) is the substituent, k_H/k_D for both chlorine and bromine addition is lowered to about 0.95. The fact that the range of k_H/k_D found is on the order of 5% tells us that, under the conditions, the α-secondary isotope effect is not a sensitive probe of carbon hydridization. This, of course, may reflect only a small departure from sp^2 hydridization occurring at the transition state. This finding is in full accord with the results of Yates,[14,27,29] who proposed a more open carbonium ion (III) as the intermediate, rather than the symmetrical bromonium ion of Roberts and Kimball[30] (which has often been proposed for brominations of this type). That some weak electrostatic interaction, as in III, exists is further supported by Yates,[14] who observed only about 17% of the cis addition product under similar conditions. Furthermore, if a symmetrical ion were formed, both 1-acetoxy- and 2-acetoxybromo adducts would be expected. That only the 1-acetoxy adduct was found for both styrene and 1-phenylpropene is also in accord with the present model. We could infer that the similarity of isotope effects for chlorination and bromination in all cases constitutes evidence for a similarity in α-carbon hybridization in the transition state (although not necessarily in the details of the ion's structure). There does seem to be a slight, but observable, difference in the k_H/k_D values for bromine and chlorine addition to most of the compounds studied. This is in the direction expected if a more bridged transition state intervenes in the bromine additions. The kinetic and stereochemical evidence supports this interpretation.[13] The stereochemistry observed for the chlorination of *trans*-1-phenylpropene in acetic acid is 27% trans adduct and 39% cis adduct for the dichlorides. For the solvolysis products, substantial amounts of only the 1-acetoxy-2-chloro adduct are obtained. This led Fahey and Schubert to suggest an ion pair IV, which is more freely rotating and is a more fitting representation of the intermediate than a symmetrical chloronium ion. In contrast, the addition of both bromine[14,28,29] and chlorine[13] to *cis*- and *trans*-2-butene gives 99% trans adduct. This suggests that, for these compounds, a symmetrically bridged intermediate V is formed. Clearly the phenyl ring, in the present cases, reduces the need for bridging, due to the ring's ability to disperse the positive charge on a carbonium ion adjacent to it.



III



IV



V

2,4-Dinitrobenzenesulfenyl Halides. Since both 2,4-dinitrobenzenesulfenyl bromide and chloride were easily obtained, the isotope effects for addition of each were measured, to determine the consistency of the measure-

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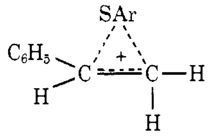
(29) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1483 (1969).
(30) I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

ments. A very similar isotope effect was expected, since the electrophilic species is the same. As can be seen, within the experimental limits of our measurements, both the 2,4-dinitrobenzenesulfenyl bromide and the chloride additions yield the same isotope effect for each reaction. More striking, the k_H/k_D ratio for these additions is virtually insensitive to substituent. Even the para nitro group effects no change. The magnitude and insensitivity are almost certainly due to the greater participation of the sulfur atom which overrides the smaller effects of the electron-withdrawing substituents. Hogg[31] has found this to be the case for the addition of 2,4-dinitrobenzenesulfenyl chloride to a number of α-substituted olefins.

For *trans*-1-phenylpropene, Schmid and V. M. Csizmadia[32] have found that the addition of 2,4-dinitrobenzenesulfenyl chloride in 1,2-dichloroethane at room temperature gives a single product, identified by nuclear magnetic resonance to be the trans Markovnikov addition product, with no cis addition detected. Although, in the present case, the solvent medium is changed, it would not be unreasonable to expect the same stereochemistry in acetic acid since either the same amount of trans addition or more would be expected with decreasing dielectric constant ($ClCH_2CH_2Cl$, ϵ 10.4, acetic acid, ϵ 6.2). This has been found to be true for both the brominations of *cis*- and *trans*-1-phenylpropene[29] and *cis*-stilbene.[33] In the present study, 2,4-dinitrobenzenesulfenyl chloride addition in acetic acid gives only the trans Markovnikov adduct with a small amount of another compound, presumably the 1-acetoxy-2-(2,4-dinitrobenzenethio)-1-phenyl propane (judging by the presence of a proton resonance in its nmr spectrum at ~5.80 ppm).

Equally interesting is the comparison of the isotope effects for the sulfenyl halide additions to those found for bromine and chlorine additions. Here, for all the styrenes we examined, excluding the para nitro compound, average values of k_H/k_D of 1.00 for chlorination and 0.98 for bromination are found. For the sulfenyl halide additions, an average k_H/k_D of 0.95 is found. This result suggests significantly more bridging with concomitant loss of sp^2 character for the α-carbonium ion and achievement of sulfonium ion character as in VI.



VI

This is consistent with the ρ values found for the reactions of the electrophiles with meta and para substituted styrenes.[17,34] It may be inferred from our results, and from the fact that the sulfenyl halides give predominately trans addition, that a less open carbonium ion (VI) is formed during the sulfenyl halide reactions in acetic acid. This is not to say that the sulfonium ion is symmetrical, as was the bromonium ion postulated in the original work of Kimball and Roberts.[30] It only suggests that the electrostatic bond formed is of greater strength in the sulfonium ion than for the corresponding bromonium ion in acetic acid.

Finally, it should be noted that a rough trend in the observed isotope effects does exist. From the data, it appears that increasing sp^2 character of the α-carbonium ion is reflected by the effects. With a poorly bridging atom, such as chlorine, essentially no effect is found, the more polarizable bromine atom yields a small, but reproducible, effect, and the sulfur species shows an even larger effect. In the anomalous para nitro case, we postulate that a leveling effect has been exerted by the strongly electron-withdrawing substituent, thus compensating for the poor bridging ability of chlorine and bromine under our reaction conditions.

Conclusion

The secondary deuterium isotope effects presented here for polar electrophilic additions to styrenes and *trans*-1-phenylpropene agree with the postulate that more open carbonium ion intermediates intervene in these reactions, rather than the type represented by the classical symmetrically bridged model where both bonds are equally formed (as for the *cis*- and *trans*-2-butenes). Moreover, these results, together with the stereochemical and kinetic evidence available, suggest that charge dispersal has developed to a greater extent in the transition states for 2,4-dinitrosulfenyl halide additions than in the analogous bromine and chlorine additions.

Although the range of k_H/k_D observed was not large, it does appear to reflect the degree of sp^2 character of the α-carbon at the transition state and, by inference, the importance of bridging as a means of stabilizing the incipient carbonium ions. The results are in full accord with the previous kinetic and stereochemical evidence for the reactions studied. The behavior of *p*-nitrostyrene supports the view that destabilization of the carbonium ion may lead to increased bridging, even by reluctantly bridging groups. In the current study, k_H/k_D was not a sensitive probe of the transition state geometry. However, such measurements show clear promise of being useful in more nearly limiting cases (*e.g.*, for polar electrophilic additions in less nucleophilic solvents, where decreased solvation of the transition state might lead to more bridging or, *e.g.*, in cases where the possibility of stabilization by substituents such as phenyl is not present). Studies of such compounds may be expected to yield minimum values for k_H/k_D effects of the type under consideration. Such work is presently underway.

We therefore conclude that additional evidence for the utility of α-secondary deuterium isotope effects, interpreted with the aid of stereochemical and kinetic evidence, has been adduced. Our results complement and confirm the conclusions of previous workers regarding the nature of the intermediates involved in the polar electrophilic additions we have examined.

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(31) G. M. Beverly and D. R. Hogg, *J. Chem. Soc. B*, 175 (1971).

(32) V. M. Csizmadia, Ph.D. Dissertation, University of Toronto, 1966.

(33) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, 27, 4523 (1962).

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