J. Org. Chem. 1980, 45, 1401-1406 **1401**

4-methylbenzaldehyde, 104-87-0; trichlorofluoromethane, 75-69-4; 1-(*p*-methylphenyl)-2-bromo-1-methoxy-1,2,3,3,3-pentafluoropropane, 72926-45-5; 1-(*p*-methylphenyl)-2-bromo-1-methoxy-2-chloro-1,2-difluoroethane, 72926-46-6; (*E*)-1-methyl-4-(1-propenyl)benzene, 2077-30-7; (*Z*)-1-methyl-4-(1-propenyl)benzene, 2077-29-4; *erythro*-1-(*p*-methylphenyl)-1,2-dibromopropane, 72926-47-7; *threo*-1-(*p*-methylphenyl)-1,2-dibromopropane, 72926-48-8.

Supplementary Material Available: Table IV (radical bromination reactions) and Table V (^{19}F NMR data of **1b**, **1d**, **1e**, **2b**, **2d**, and **2e**) (2 pages). Ordering information is given on any current masthead page.

Kinetics and Stereochemistry of the Addition of Chlorine to Styrenes

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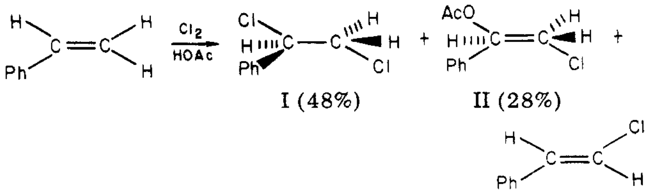
The chlorination of several ring- and side-chain-substituted styrenes has been studied in anhydrous acetic acid, in both the presence and absence of added perchlorate, chloride, and acetate salts. The reactions give three types of product: the 1,2-dichlorides arising from simple addition, 1-acetoxy-2-chloro compounds from addition followed by solvent incorporation, and β-chlorostyrenes from an addition–elimination process. The reactions are completely regiospecific in the Markownikoff sense, and the addition–elimination products are formed with high stereoselectivity. However, both types of addition product are formed nonstereospecifically. Both the product distribution and stereoselectivity are remarkably insensitive to added perchlorate, chloride, or acetate, and very high concentrations of these salts (ca. 1.0 M) are required to produce any significant change in product composition. The results are explicable in terms of a product-determining intermediate which consists of an intimate ion pair between an open β-chlorobenzyl carbonium ion and a tightly held chloride counterion. However, since (*E*)- and (*Z*)-1-phenylpropenes do not give similar product distributions under any conditions used, rotation of the C_α–C_β bond in the carbonium ion must be highly restricted. The rates of reaction have been studied by a combination of potentiometric and stopped-flow spectrophotometric techniques. The reactions are first order in chlorine and first order in olefin and are generally very fast, with most of the rate constants being in the range 10^2–10^5 L mol^{-1} s^{-1}. The rate constants for the ring-substituted styrenes give a good linear correlation against σ^+ with a ρ value of -3.22. This value is less negative than expected from a comparison with other electrophilic additions and is discussed in terms of an earlier transition state with less charge development at C_α than in the analogous bromination reaction. The activation parameters obtained for two of the styrenes support this hypothesis. There is no direct evidence for chlorine bridging at either the transition state or the intermediate stage.

The most thoroughly and systematically studied electrophilic additions of halogens to olefins have involved bromine addition.[1] The kinetics, product distribution, and stereochemistry of bromination of both simple alkenes and alkenes bearing phenyl groups have been investigated by a number of authors.[2] The mechanisms of the corresponding additions of chlorine have been investigated less extensively, largely because the rates of these reactions are much faster than those of the analogous brominations. Most of the mechanistic studies reported so far have dealt with the product distributions and stereochemistry of chlorination of simple alkenes, either involving molecular chlorine[3] or chlorine acetate[4] as the electrophilic species. The rates of these reactions are generally so fast that previous kinetic studies have been restricted either to alkenes containing electron-withdrawing groups[5] or to the determination of relative rates by competition methods.[6] Although the stereochemistry of chlorine addition to various phenyl-substituted olefins has been investigated by several authors,[3] the only kinetic study of the effects of structure on the rates of chlorination involved a limited series of substituted cinnamic acids.[5] It was therefore of interest to investigate more systematically the kinetics and mechanism of chlorine addition to a series of ring- and side-chain-substituted styrenes and to compare the results with directly analogous investigations of similar bromination reactions.[2] These studies have involved both the effects of olefin structure on the rates and the effects of solvent polarity and added nucleophiles on the product distribution and stereochemistry.

Results and Discussion

Product Distribution. Since the most commonly used solvent for studying the kinetics of halogen additions is anhydrous acetic acid,[1] the products of chlorination of styrene itself were first determined in this solvent, with as low concentrations of reactants as practical (ca. 0.1 M) in order to approach the conditions under which kinetic measurements were to be made. The reaction gives three products, which are fairly typical of the chlorination of conjugated olefins in hydroxylic solvents. Addition products, including the dichloride I and solvent-incorporated product II, make up the majority of the product. Although no stereochemical information can be obtained with styrene itself, concerning whether the addition mode is syn or anti, the only solvent-incorporated product



I (48%) II (28%)

III (23%)

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(1) G. H. Schmid and D. G. Garratt in "Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1976, Supplement A, Part 2, Chapter 9.

(2) (a) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965); (b) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469, 1477, 1483 (1969); (c) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968); (d) K. Yates and J. A. Pincock, *Can. J. Chem.*, **48**, 2944 (1970).

(3) M. L. Poutsma and J. L. Kartch, *J. Am. Chem. Soc.*, **89**, 6595 (1967); R. C. Fahey, *ibid.*, **88**, 4681 (1966).

(4) P. B. D. de la Mare, M. A. Wilson, and M. J. Rosser, *J. Chem. Soc., Perkin Trans. 2*, 1480 (1973).

(5) P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

(6) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 4285 (1965).

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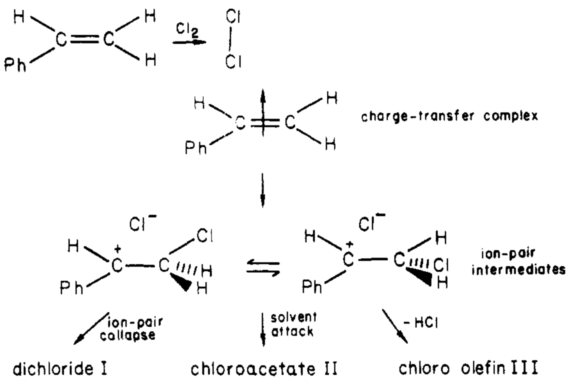
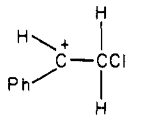
Scheme I



formed is the 1-acetoxy-2-chloro derivative II, so that the reaction is at least regiospecific in the Markownikoff sense. This is in agreement with involvement of a cationic intermediate which is either an open β-chlorobenzyl carbonium ion or at most a highly unsymmetrically bridged chloronium ion. The chloro olefin III, though only a minor product, is by no means negligible. This is in marked contrast to the bromination of styrenes,[2b] where no similar addition–elimination products have ever been reported. The monochloro olefins usually accompanying chlorine addition are most commonly allylic,[3] rather than vinylic as in the present case. This has been interpreted[7] as evidence for chlorine bridging in the cationic intermediate, in the sense that the vinylic hydrogens are thus prevented from attaining a periplanar arrangement with the empty p orbital on the α-carbon and cannot be as easily eliminated as available hydrogens on adjacent (allylic) positions. In the case of styrene there are no allylic hydrogens, but the formation of significant vinylic chloro olefin is in favor of an open benzylic ion intermediate, if the above argument is correct. It is noteworthy that the addition–elimination is stereospecific, in that only the *E* isomer is obtained. This can be understood in terms of steric interactions between the chlorine and phenyl on adjacent carbons in an open β-chlorobenzylic ion intermediate.[8] Conformations which minimize these interactions lead to the *E* isomer by proton loss from the β-carbon.

A proposed reaction pathway which explains the product distribution is shown in Scheme I. That halogens form charge-transfer complexes with olefins is well-known, and in the case of bromination and chlorinations these are believed to lie on the reaction coordinate, from the work of Dubois.[9]

Common though it is, the formation of chloro olefin in reactions of chlorine with olefins has received little attention. It is well established[10] that little elimination usually accompanies solvolysis reactions, especially in less ionizing solvents like acetic acid. Experiments were carried out in attempts to generate the 1-phenyl-2-chloroethyl cation IV under solvolytic and elimination conditions for comparison purposes. These involved the treatment of 2-chloro-1-phenyl tosylate and 1,2-dichloro-1-phenylethane with different solvents, with or without added base. The reactions and the products obtained are summarized in Scheme II. These results demonstrate clearly that the elimination of a proton from the β-carbon is not a facile process from a 2-chloro-1-phenylethyl cation type of intermediate, under solvolytic conditions. Therefore, the ionic intermediate formed during the chlorination of styrene behaves uniquely in its facility for proton loss to give β-chlorostyrene. The results also show that this product is a primary reaction product and does not arise from a secondary reaction of the initially formed 1,2-dichloride I.



IV

Scheme II

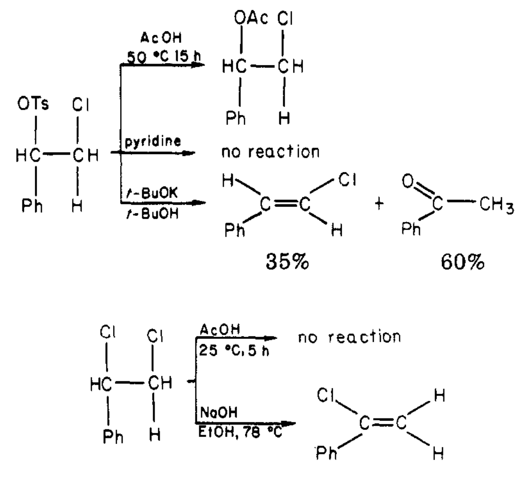
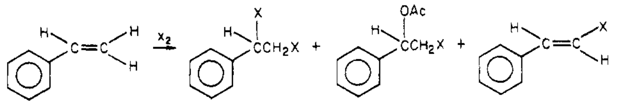


Table I



A B C

halogen	[LiClO$_4$] added, M	% yield A	% yield B	% yield C
Cl$_2$		50	28	23
	0.2	53	24	23
	0.4	53	25	23
	0.8	52	27	19
Br$_2$		80	20	0
	0.1	68	33	0

Since the rates of halogenation of olefins are often measured in the presence of added lithium perchlorate, the product compositions for the chlorination of styrene in the presence of various concentrations of this salt are shown in Table I. It is clear that the product distribution is hardly affected by up to 0.8 M added lithium perchlorate, unlike the corresponding bromination reaction[2b] which shows a marked increase in solvent-incorporated product even with as low as 0.1 M added perchlorate. This indicates that the initally formed (intimate) ion pairs in Scheme I do not as easily go on to form solvent-separated ion pairs (or free ions) as do the corresponding ion pairs in the bromination reaction. Lithium perchlorate, which even at low concentrations is known to stabilize solvent-separated ion pairs[11] and prevent a return to the intimate

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[7] P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, London, 1966, p 102.

[8] H. W. Leung, Ph.D. Thesis, University of Toronto, 1972.

[9] J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965); *ibid.*, 3047 (1966), J. E. Dubois and F. Garnier, *Spectrochim. Acta, Part A*, **23**, 2279 (1967); M. L. Poutsma, *Science*, **157**, 997 (1967).

[10] A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1969.

[11] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

[12] L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, p 356.

[13] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 130 (1963).

Scheme III. Products from Chlorination of Phenylpropenes

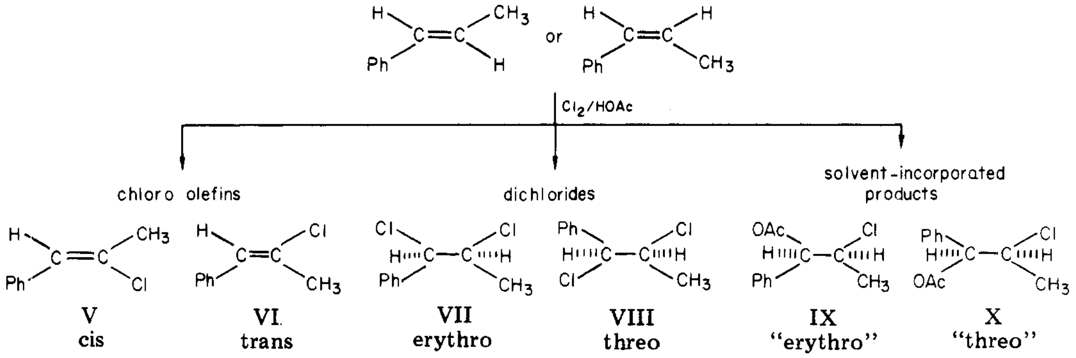

Table II. Salt Effects on the Chlorinations of (*E*)- and (*Z*)-1-Phenylpropene[a]

added salt	concn, M	chloro olefins		dichlorides		chloroacetate	
		cis	trans	erythro (anti)	threo (syn)	"erythro" (anti)	"threo" (syn)
				(*E*)-1-Phenylpropene			
nil		0.8 (±0.2)	6 (±2)	24.5 (±1)	39 (±1)	21.5 (±0.5)	8.5 (±0.5)
NaOAc	0.1	0.7	7	24.5	39	29^b	
LiCl	0.1	0.7	6	25	38	30^b	
LiCl	0.2	0.4	5	26	37	31^b	
LiCl	1.0	0.4	4	31	34	21	8
$LiClO_4$	0.1	0.3	4	22	38	36^b	
$LiClO_4$	1.0	0.4	4	12.8	36	31	15
				(*Z*)-1-Phenylpropene			
nil		7 (±0.2)	1.9 (±0.2)	47 (±1)	14 (±1)	14 (±0.5)	16 (±0.5)
NaOAc	0.1	6.5	1.8	46	15	30^b	
LiCl	0.1	6.5	1.9	45.5	16	30^b	
LiCl	0.2	5.5	2	44.5	15.5	32.5^b	
LiCl	1.0	5	1	42	24	13	15.5
$LiClO_4$	0.1	5.9	1.5	44	13	36^b	
$LiClO_4$	1.0	4.4	1.2	37	13.5	19	25.5

[a] The number under each compound gives the percentage in total product mixture as determined by GLC. [b] In these runs the "erythro" and "threo" diastereomers of the chloroacetate were not separated.

ion pair stage, apparently has little effect on chlorination, as will be seen in the next section.

Stereochemistry. The chlorination of (*E*)- and (*Z*)-1-phenylpropene can be used to distinguish between the syn and anti modes of addition to the styrene system, and Fahey and Schubert[2a] have already studied the stereochemistry of these reactions in several solvents. We have confirmed and extended their results, particularly by examining the effects of added salts on the stereochemistry.

In general, chlorination of the phenylpropenes gives the same classes of products as with styrene, i.e., chloro olefins, dichlorides, and solvent-incorporated products. The third type is, of course, only present when nucleophilic solvents are used. Now that different isomers are obtained from different modes of addition (as well as from addition–elimination), a more complicated product composition is obtained. Structures of the isomeric products derived from chlorination of (*E*)- and (*Z*)-1-phenylpropene are shown in Scheme III. It is to be noted for example that syn addition to the *Z* olefin gives the erythro dichloride or the corresponding 1-acetoxy-2-chloro derivative (which is referred to as "erythro" for ease of comparison), whereas anti addition gives the corresponding threo diastereomers. As in the case of styrene, the only solvent-incorporated products found under all conditions studied were formed regiospecifically in the Markownikoff sense.

The product stereochemistry in acetic acid is given in Table II, along with the effects of adding acetate, dichloride, and perchlorate to the system. As reported by Fahey and Schubert[2a], the reactions are clearly nonstereospecific. Although (*Z*)-1-phenylpropene gives predominantly anti addition to form the dichloride, the *E* isomer gives more syn than anti addition. Similar lack of stereospecificity is shown in the solvent-incorporated products, with the *E* isomer now tending to give more anti than syn addition, whereas the *Z* isomer gives almost equal amounts of both diastereomeric acetoxy chlorides. The chloro olefins formed as minor products show more stereoselectivity in that the *E* olefin gives mainly the *E* chloro olefin, and the *Z* olefin mainly the *Z* chloro olefin. Although these addition–elimination products are not formed as stereospecifically as in the case of styrene itself, the results have been explained reasonably by Fahey and Schubert[2a] in terms of the dominance of the initially formed ion pair, arguing that the chloride counterion which remains on the same side of the carbonium ion center acts as the specific proton acceptor in the elimination step.

The two most striking aspects of the results in Table II are that in no case do the starting *E* and *Z* olefins give anything approaching the same distribution of products and that both the product distribution and stereochemistry are remarkably insensitive to the effects of external nucleophiles or perchlorate ion. The first observation means that although the lack of stereoselectivity clearly indicates an open rather than a bridged chlorocarbonium ion intermediate, there cannot be anything like free rotation about the bond between the carbonium ion center and the β-carbon bearing the initially added chlorine atom, since this would lead to a common intermediate from either the

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[14] S. L. Gupta and R. N. Soni, *J. Indian Chem. Soc.*, 42(6), 377 (1965).

(*E*)- or the (*Z*)-1-phenylpropene and similar if not identical product distribution.

The second observation is even more striking in the sense that in the analogous bromination reactions,[2b] even low concentrations (ca. 0.1 M) of acetate or perchlorate produce significant increases in solvent-incorporated product, presumably in the first instance by direct trapping of the intermediate by nucleophile and in the second by promoting solvent-separated ion-pair formation and trapping by solvent. Also, similarly low concentrations of added bromide cause significant increases in dibromide formation, again presumably by direct trapping of the intermediate by nucleophile. In the case of chlorination, however, it requires very high concentrations (1 M) of added salt to produce any significant change in product composition. Even with 1 M $LiClO_4$ the percentage of solvent-incorporated product is only increased from about 30 to 45%.

All of these results strongly indicate a product-determining intermediate which is best represented as a very tight ion pair between an open β-chlorocarbonium ion and its chloride counterion,[8] in which rotation of the C_α–C_β bond is difficult. This ion pair tends to react most easily by ion-pair collapse, although C_α solvent attack and C_β proton abstraction by the chloride counterion are also significant product-forming steps. Interaction with, or trapping by, external anions appears to be very difficult.

We have extended Fahey and Schubert's work[2a] on the effects of solvent polarity on product distribution and stereochemistry by investigating the chlorination of (*E*)- and (*Z*)-1-phenylpropene in acetic anhydride (ϵ 31) and nitrobenzene (ϵ 35). However, the results are somewhat inconclusive and will not be presented here. Even with a range of solvent dielectric constant now extending from 2 to 35, there are no significant trends in product composition with solvent polarity. The only marked effect of changing solvent is that the more nucleophilic solvents produce larger percentages of solvent-incorporated products. These solvent studies, although inconclusive, are not inconsistent with the above tight ion-pair hypothesis.

Kinetics. The rates of chlorination of a series of ring-substituted styrenes were found to obey a simple rate

$$v = -d[Cl_2]/dt = k_2[Cl_2][\text{styrene}] \qquad (1)$$

equation (eq 1) as reported by other workers.[15] No evidence was found of higher order kinetic terms in chlorine, nor were the rates dependent on chloride ion, except for a small salt effect which was corrected for in the rate constants determined by the previously described[2b] potentiometric method. Since chlorination rates for a given olefin are usually of the order 10^2–10^3 times those of bromination, most of the rate constants had to measured by the stopped-flow technique. The second-order rate constants for the substituted styrenes in acetic acid at 25 °C are given in Table III along with several values for other olefins. Although the rate of chlorination of (*Z*)-1-phenylpropene was accessible by the stopped-flow technique, that of the *E* isomer was too fast to be measured, and it is estimated that both styrenes and alkenes bearing electron-releasing groups have rate constants of at least 10^5 L mol^{-1} s^{-1} at 25 °C.

Table III. Second-Order Rate Constants for the Chlorination of Olefins in Acetic Acid at 25 °C

olefin	$10^{-2}k_2$,[a] L mol^{-1} s^{-1}	method	σ[b]	σ^+[c]
styrene	72.1	stopped-flow	0	0
p-chlorostyrene	18.6		0.227	0.114
m-fluorostyrene	4.06		0.337	0.352
m-chlorostyrene	3.75		0.373	0.399
p-fluorostyrene	65.6		0.062	−0.073
m-nitrostyrene	0.45	potentiometric	0.71	0.674
p-nitrostyrene	0.21		0.778	0.790
3,5-dinitrostyrene	0.081		1.22[d]	1.22[e]
(*Z*)-1-phenylpropene	145	stopped-flow		
(*E*)-1-phenylpropene	>1000			
1-hexene	76.7			
3-hexene	>1000			

[a] Based on 2–4 duplicate runs in each case. Error estimated to be less than 5%. [b] Taken from ref 12. [c] Taken from ref 13. [d] Based on the ionization constant of 3,5-dinitrobenzoic acid from ref 14. [e] Assumed to be as σ.

Linear Free-Energy Relationships. For the ring-substituted styrenes, a good linear plot of log k_2 can be obtained by using either the σ or the σ^+ set of substituent constants. The correlation is marginally better with the σ^+ scale ($r = 0.999$) than with the σ scale ($r = 0.997$), but the difference is not as large as in the case of the corresponding bromination reactions, where log k_2 clearly followed σ^+ better than σ.[2b] The ρ values for chlorination were found to be −3.22 with σ^+ and −3.41 with σ. Although these ρ values are significantly negative, as expected for an electrophilic reaction, the relatively small absolute magnitude of ρ is somewhat surprising. The magnitude of the ρ value has been frequently accepted as a reliable gauge for the degree of charge development at the reaction center, other conditions such as location of substituents and the channels that transmit their effects being equal. Such prerequisities are obviously satisfied in the comparison between the reactions of chlorine and bromine with similar styrene systems under closely comparable reaction conditions (i.e., solvent and temperature). Thus a smaller negative ρ value implies less charge development in the transition state at the benzylic carbonium ion center for chlorination than for bromination. Such a phenomenon is usually associated with charge delocalization by bridging. However, all previous evidence clearly supports the idea that chlorine is a much weaker participant in bridging than bromine,[16] and the product studies discussed in the previous sections demonstrate unequivocally that an open carbonium ion of the ion-pair type of intermediate is responsible for product formation in the reactions of styrene and the 1-phenylpropenes. If one compares the four known electrophilic reactions of the styrene system, namely, sulfenation, bromination, chlorination, and hydration, the reported ρ values[2b,17,18] are in the order $\rho_S <$

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(15) K. Yates, G H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973); P. B. D. de la Mare, *Q. Rev., Chem. Soc.*, 3, 126 (1948).

(16) G. A. Olah and M. Bollinger, *J. Am. Chem. Soc.*, **90**, 947 (1968); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 826 (1948); G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *ibid.*, **96**, 3565 (1974); J. H. Wienga, J. Strating, and H. Wynberg, *Chem. Commun.*, 907 (1968).

(17) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956); K. Izawa, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47**, 1480 (1974).

(18) W. M. Schubert and J. R. Keefe, *J. Am. Chem. Soc.*, **94**, 559 (1972).

Table IV. Activation Parameters for the Chlorination and Bromination of Substituted Styrenes

substituents	halogen	k_2, M^{-1} s^{-1} [a]	T, °C	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
m-chloro	Cl_2	5.6×10^2	45.2	6.1 ± 0.2	-32 ± 0.8
		4.8×10^2	40.2		
		4.4×10^2	34.9		
		3.4×10^2	30.0		
		2.3×10^2	17.0		
p-nitro	Cl_2	5.82×10	50.0	5.3 ± 0.1	-29.5 ± 0.5
		4.2×10	40.0		
		3.12×10	32.0		
		2.07×10	25.0		
p-nitro	Br_2	3.0×10^{-2} [b]	25	9.0[c]	−38[c]
3,4-dichloro	Br_2	6.5×10^{-1} [b]	25	8.7[c]	−34[d]

[a] All rate constants determined by the potentiometric method in the presence of added LiCl. [b] Values from ref 2b. [c] Values from ref 2d. [d] Values recalculated from data in ref 2d.

$\rho_{Cl} \lesssim \rho_H < \rho_{Br}$ (in terms of increasing negativity). This obviously does not correspond with the expected order of bridging (or neighboring group) ability of these four atoms, which is almost certainly S ≫ Br > Cl ≫ H. The relatively low ρ value obtained for chlorination therefore requires some alternative explanation.

If the rate-determining transition state in chlorination closely resembles the subsequently formed tight ion-pair intermediate, then it could be said that the degree of Cl–Cl bond breaking at the transition state is smaller than that of Br–Br bond breaking in the bromination transition state or that charge stabilization by the incipient chloride counterion at the transition-state stage is more effective than that by bromide ion. These are approximately equivalent statements and are supported by the fact that chlorination reactions of this type are generally much faster than brominations, indicating an earlier transition state for chlorination, in which less bond breaking or charge development has occurred. The fact that chlorine addition to an olefin is much more strongly exothermic than bromine addition is not inconsistent with the idea of an earlier transition state.

Activation Parameters. It is possible to make a semiempirical comparison of the stabilities of the ion pairs formed in the gas-phase additions of chlorine and bromine to ethylene by using available thermochemical data in a Hess's law cycle.[8] This shows that the carbonium ion–chloride ion pair is about 7 kcal more stable than the corresponding carbonium ion–bromide ion pair. However, this analysis rests on several assumptions and totally neglects solvation. A more direct comparison of relative transition-state stabilities can be obtained from measurement of activation parameters. Because of the high rates of chlorine addition, this could only be done for styrenes with strongly electron-withdrawing groups, as shown by the results in Table IV. Fortunately, some corresponding values for bromine additions are available. The results from the Arrhenius plots are shown in Table IV. It is clear from these data that it is mainly the $\Delta H^{\ddagger}$ term which is responsible for the higher rates of chlorination over bromination. It is roughly 3 kcal more difficult to reach the bromination transition state in terms of $\Delta H^{\ddagger}$, with the $\Delta S^{\ddagger}$ terms also being somewhat more unfavorable for bromination.

Conclusion

The major mechanistic conclusions from all of the above results are that unlike chlorine additions to simple alkenes, there is no direct evidence of bridging by chlorine in the rate-determining transition state of the styrene reaction and that the subsequently formed product-determining intermediate is also best represented as an open β-chlorocarbonium ion. This intermediate appears to be a very tight ion pair in which rotation about the C_α–C_β bond is significantly restricted. The ion pair leads to addition products mainly by ion-pair collapse and solvent trapping, which show a low degree of stereoselectivity. The ion pair can also lead to addition–elimination products by abstraction of a proton by the chloride counterion, but these are formed with a higher degree of stereoselectivity. Both types of product are formed completely regiospecifically. The overall reaction as shown in Scheme I can be accommodated within the more general ion-pair scheme reported by de la Mare,[4] which is very similar to the ones which had previously been proposed by us for both bromine[2b] and chlorine additions.[8]

Experimental Section

Materials. Acetic acid was purified by the method previously described.[2b] Chlorine (Matheson) was dispensed through a Monel-metal regulator through an all-glass system and was dried by being passed through concentrated sulfuric acid and calcium sulfate. All operations involving chlorine were carried out in the dark. Analytical grade lithium chloride, lithium perchlorate, and sodium acetate were dried under reduced pressure at 100 °C and stored over P_2O_5. Solutions of the deliquescent lithium salts were prepared under a dry atmosphere. All olefins except 3,5-dinitrostyrene were commercially available, and samples were distilled immediately before use. 3,5-Dinitrostyrene was prepared from 3,5-dinitrobenzoic acid as follows.[8] The acid was reduced to 3,5-dinitrobenzyl alcohol by using diborane in THF [mp 98 °C; IR at 2.76 and 2.95 μm; NMR δ 6.35 (1 H, t), 6.44 (2 H, m), 2.77 (2 H, s)]. The alcohol was oxidized by using activated manganese dioxide in $CHCl_3$ to give 3,5-dinitrobenzaldehyde (mp 70 °C; IR at 5.84 μm) which was then reacted with malonic acid and pyridine in ethanol to give 3,5-dinitrocinnamic acid (mp 227 °C). Anal. Calcd for $C_9H_6N_2O_6$: C, 45.39; H, 2.54; N, 11.76. Found: C, 46.11; H, 2.73; N, 11.53. This was then decarboxylated by heating with quinoline and cuprous oxide to give 3,5-dinitrostyrene, which was purified on a silica gel column: mp 88 °C; NMR δ 9.00 (1 H, t), 8.65 (2 H, d), 6.97 (1 H, dd), 6.16 (1 H, d), 5.75 (1 H, d).

Product Separation and Analysis. Products were separated and analyzed mainly by a combination of GLC and NMR techniques. The GLC apparatus was fitted for flame-ionization detection and mechanical disk integration. The chlorination of styrene was carried out as follows. A 100-mL 0.2 M styrene solution was made up in acetic acid. A saturated solution of chlorine in acetic acid was prepared and its concentration determined.[8,19] This solution was diluted with acetic acid to give 100 mL of an approximately 0.2 M solution in acetic acid. (A solution of accurately predetermined concentration is difficult to obtain due to the volatility of the gas.) To minimize possible further chlorination of primary products, a slight excess of olefin was maintained at the end of the reaction. This applies to styrene as well as to all other systems examined, and hence the results obtained represent the product composition for 90–95% reaction.

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(19) C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, 48, 2045 (1926); N. H. Furman and E. B. Wilson, *ibid.*, 50, 277 (1928).

Two methods were employed in mixing the reactants.

Method A. A 100-mL sample of the 0.2 M styrene solution was placed in a 250-mL three-necked flask fitted with a mechanical stirrer. The vessel was shielded from direct light by aluminum foil and immersed in a bath thermostated at 25 °C. A 100-mL sample of the 0.2 M chlorine solution was pipetted into it through one of the openings. Instant mixing was effected by rapid stirring. Under such conditions the chlorine concentration was kept very low compared to that of the olefin throughout the reaction, similar to conditions maintained in most kinetic experiments.

Method B. Both the styrene and chlorine solutions were introduced at comparable rates through a dropping funnel into a three-necked flask fitted with a mechanical stirrer. Again, precautions were taken to avoid direct light, and the temperature was maintained at 25 °C. Instant mixing was ensured by vigorous stirring. Under such conditions, the concentration of both reactants was maintained at approximately the same level throughout the reaction, thus resembling truly equimolar bimolecular kinetic conditions.

It was found that both methods of addition gave identical product compositions within experimental error.

The reaction between chlorine and styrene was extremely fast and was effectively complete on mixing. In general, the reaction was left for a further 10 min before being worked up. The reaction mixture was then poured into 200 mL of saturated sodium chloride solution. The products were extracted by redistilled pentane (6 × 50 mL). The nonaqueous extracts were combined and washed successively with distilled water, 2% sodium bicarbonate solution, and water. The extract was then dried with sodium sulfate before it was filtered and concentrated under reduced pressure at a temperature below 40 °C. Analytical GLC using a 5 ft × $^1/_4$ in. column of diethylene glycol succinate supported on Chromosorb W showed three main components, which were later shown to be (*E*)-β-chlorostyrene (1 min 25 s), 1,2-dichloro-1-phenylethane (5 min 46 s) (the dichloride), and 1-acetoxyl-2-chloro-1-phenylethane (10 min 22 s) (the chloroacetate). The retention times in parentheses are for a column temperature of 155 °C and a flow rate of 75 mL/min.

A combination of column and preparative GLC was used to separate the product mixture from the chlorination of styrene, and the dichloride was eluted in successive fractions. The remaining chloroacetate was eventually eluted with chloroform. The dichloride and the chloroacetate were obtained in pure form after the removal of solvent. The chloro olefins, however, were mixed with the unreacted styrene and had to be separated with preparative GLC using the same column as that used for analytical purposes. NMR data for the three components were consistent with the assigned structures and with the spectra of unambiguously synthesized or authentic samples, prepared as follows.[8] β-Chloroacetophenone was reduced with sodium borohydride in aqueous methanol to give 2-chloro-1-phenylethanol, which was then acetylated with acetyl chloride to give 1-acetoxy-2-chloro-1-phenylethane. The GLC retention time and NMR spectrum obtained were identical with those obtained for the major component from the chlorination of styrene. A sample of the above 2-chloro-1-phenylethanol was reacted with thionyl chloride to give 1,2-dichloro-1-phenylethane. The GLC and NMR results from this compound were indistinguishable from those of the second component from the chlorination of styrene.

The NMR spectrum of the third product showed very low-field protons only. The pattern of these low-field protons, in fact, provides the strongest evidence that the chloro olefin is the *E* isomer of β-chlorostyrene. The A–B type doublets for the two olefinic protons with coupling constants of 13.8 Hz are consistent with the two protons being located trans to each other in the double bond system, each under comparable deshielding from the geminal phenyl group and chlorine atom, respectively. Comparison with a commercial sample of (*E*)-β-chlorostyrene showed this to be identical with the third product.

The products of the chlorination of (*E*)- and (*Z*)-1-phenylpropenes in various solvents, including acetic acid, have already been studied and the products identified by Fahey and coworkers,[2a] and it was only necessary to determine, under conditions similar to the kinetic measurements, whether any change in product composition occurred and also to study the product distribution as a function of added salts and changing solvent. Essentially the same mixing and extracting techniques were used as were used for styrene. Separate solutions which were 0.2 M in the olefin and chlorine were prepared and mixed according to method B. Thus the initial concentrations of both reactants were approximately 0.1 M. The products were isolated by the extraction method used in the case of styrene. The separation and identification of product mixtures were straightforward since they had been worked out previously.[2a] Analytical GLC was carried out by using 5 ft × $^1/_4$ in. column of 20% diethylene glycol succinate on Chromosorb W at a temperature of 150 °C and a helium flow rate of 60 mL/min. The retention times of the six reaction products are as follows: (*E*)-2-chloro-1-phenylpropene (2 min 16 s), (*Z*)-2-chloro-1-phenylpropene (2 min 49 s), *dl-erythro*-1,2-dichloro-1-phenylpropane (7 min 10 s), *dl-threo*-1,2-dichloro-1-phenylpropane (8 min 29 s), *dl*-"*erythro*"- and *dl*-"*threo*"-1-acetoxy-2-chloro-1-phenylpropene (15 min 28 s).

The molar percentages of the components were calculated from integrated areas under the respective peaks. It should be noted that the two diastereoisomers of the chloroacetate were not separated by GLC analysis. The ratio of the two isomers can, however, be deduced from the NMR spectrum of the mixture. Since all the components were characterized, assignment of the various peaks in the analytical GLC was carried out by separating the different components by preparative GLC using a 20 ft × $^3/_8$ in. DEGS column at a temperature of 170 °C and a helium flow rate of 200 mL/min. The NMR spectra of the components were consistent with those reported by Fahey and co-workers.[2a]

Kinetic Measurements. A. Potentiometric Methods. This method has been fully described previously.[2b] It only remained to be established that the Nernst equation was applicable to solutions of chlorine in anhydrous acetic acid, in the presence of lithium chloride as electrolyte. Chlorine solutions were carefully standardized by adding iodide and titrating with freshly prepared thiosulfate.[8,19] Measurements of the electrode potential of these solutions (appropriately diluted) showed[8] that E_{cell} is accurately linear in low [Cl_2] down to 10^{-5} M Cl_2, with a slope of 0.0307 V_1 which is close to the value (0.0295 V) required by the Nernst equation in aqueous solution. Since it is only the change in E_{cell} with time which is required for the rate determinations, this small difference should not significantly affect the accuracy of the rate constants. Since LiCl must be used as supporting electrolyte, the rate constants obtained by this method are subject to a small salt effect. Values of k_2 were thus measured over the range [LiCl] = 0.02–0.12 M and extrapolated to zero chloride concentration, so that they could be compared directly with those obtained by the stopped-flow method.

B. Stopped-Flow Spectrophotometric Method. The rates of reaction were measured by following the decrease in the visible absorption of chlorine at λ = 321 nm with a Durrum-Gibson stopped-flow spectrophotometer. A trace of the reaction progress was stored on the oscilloscope screen and subsequently photographed by using an attached Polaroid camera. Measurements were repeated until successive runs were exactly reproducible. Data taken from the photograph were processed by means of a computer program[8] which calculated the observed rate constants directly. The reactions were all found to be cleanly first order in chlorine and were carried out under conditions of at least 20-fold excess of olefin. Second-order rate constants were obtained from k_{obsd} (the pseudo-first-order rate constants) and the known initial concentration of olefin.

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Registry No. I, 1074-11-9; II, 829-23-2; III, 4110-77-4; V, 21370-53-6; VI, 4541-79-1; VII, 21759-49-9; VIII, 21759-50-2; IX, 21759-51-3; X, 21759-52-4; 1,2-dibromo-1-phenylethane, 93-52-7; 1-acetoxy-2-bromo-1-phenylethane, 5837-69-4; (*E*)-1-phenylpropene, 873-66-5; (*Z*)-1-phenylpropene, 766-90-5; *p*-chlorostyrene, 1073-67-2; *m*-fluorostyrene, 350-51-6; *m*-chlorostyrene, 2039-85-2; *p*-fluorostyrene, 405-99-2; *m*-nitrostyrene, 586-39-0; *p*-nitrostyrene, 100-13-0; 1-hexene, 592-41-6; 3-hexene, 592-47-2; 3,5-dinitrobenzyl alcohol, 71022-43-0; 3,5-dinitrobenzaldehyde, 14193-18-1; 3,5-dinitrocinnamic acid, 72918-17-3; 3,5-dinitrostyrene, 72918-18-4; styrene, 100-42-5.