Method D. N-Methyl-N-(*n*-nonyl)-glycineamide Hydrochloride.—N-Methyl-N-(*n*-nonyl)-glycinenitrile (4.4 g.) was added dropwise with shaking to 9 ml. of concentrated sulfuric acid at −10°, the mixture stored at room temperature for 72 hours and subsequently poured into cracked ice. The resulting mixture was basified, extracted with ether, and the extract dried over anhydrous potassium carbonate. Potassium carbonate was separated and the benzene solution evaporated to dryness. The residue, a waxy, white solid, melted at 59–62°, crude, and at 63–63.5° after two recrystallizations from an alcohol-water mixture; yield 3.5 g. after recrystallization. A portion (1.7 g.) of the amide, dissolved in ethanol was converted to the amide hydrochloride in a quantitative yield.

YONKERS 2, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XXIII. The Effects of *para*-Substituents in Styrene on the Kinetics and Mechanism of the Reaction with 2,4-Dinitrobenzenesulfenyl Chloride[1]

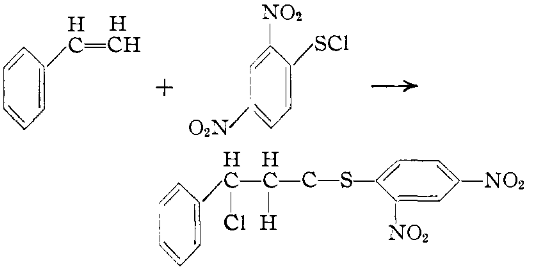
BY WILSON L. ORR AND NORMAN KHARASCH

RECEIVED JULY 5, 1955

The effects of the *para*-substituents, Cl, $-CH_3$ and $-NO_2$, in styrene, on the measured second-order rate constants for the reaction of 2,4-dinitrobenzenesulfenyl chloride with the respective olefins, in dry acetic acid, fit the Hammett equation excellently, with *rho* being −2.20 at 25°. The differences in rates are determined mainly by differences in the activation energies, but significant variations in the entropies of activation occur. The reaction with *p*-methoxystyrene was too fast for rate measurements at 25°, was complicated by polymerization, and the vinyl sulfide $CH_3O—C_6H_4—CH=CH—SAr$ (Ar = 2,4-dinitrophenyl), rather than the 1:1 adduct was formed. At 10–13°, however, up to 86% of the 1:1 adduct, together with the vinyl sulfide and 3–6% of the β-acetoxy sulfide was formed. The 1:1 adduct is not the intermediate whereby the vinyl sulfide forms, at 25°, as shown by studies of the rate of dehydrohalogenation of the adduct into the vinyl sulfide at this temperature. The vinyl sulfide probably arises directly by loss of proton from the intermediate sulfonium ion.

Introduction

A previous paper[2] reported a detailed study of the kinetics and mechanism of the reaction of 2,4-dinitrobenzenesulfenyl chloride (I) with styrene (eq. 1)



(1)

The purpose of the present work was to evaluate the effects of *para*-substituents, in the styrene, on the reactions corresponding to equation 1. Such a study was desirable, since it could clearly demonstrate the relation of electron density, *i.e.*, nucleophilic character, of the carbon–carbon double bond on the rate and course of the olefin–sulfenyl halide reaction and would also test whether the well-known[3,4] Hammett rho–sigma equation applies to this reaction. A negative reaction constant, rho, was anticipated on the basis of a previous proposal[2] for the reaction mechanism, which suggested electrophilic attack by I on the olefin bond, *via* a cyclic sulfonium ion, as the rate-determining step.

When this work was begun, the Hammett equation had not been applied to an "ionic addition reaction" at the olefinic bond.[5] In the interim, however, Overberger and co-workers[6] have reported on the stannic chloride-catalyzed copolymerization of styrene and *para*-substituted styrenes, and correlated their rate data by the Hammett equation. As noted below, their results relate interestingly to the present study.

Kinetic Data.—*p*-Nitro-, *p*-chloro-, *p*-methyl- and *p*-methoxystyrene were selected for study. Rates were measured as described previously,[2] using dry acetic acid as solvent to allow comparisons with the earlier rate data for styrene itself. The rates with *p*-nitro-, *p*-chloro- and *p*-methylstyrenes were measured, and satisfactory second-order rate constants were established for these reactions. All the determinations were carried to 80–90% completion and the products were the 1:1 adducts of I and the particular styrene, in each case. As discussed below, however, the reaction of I with *p*-methoxystyrene was complicated, and only an approximate estimate of the rate constant, at 25°, could be made in this case.

The second-order rate constants and the Arrhenius parameters, A and E_a, are given in Table I. Except for the single run at 44.9° for the *p*-methyl homolog, which showed a positive curvature, and the data for *p*-methoxystyrene (*cf.* experimental) all the runs gave excellent, second-order plots, comparable to those obtained earlier[2] for styrene. The complete data for individual runs are not reported here, but are available.[7] The entropies of activation, $\Delta S^{\ddagger}$, calculated from the frequency factors, A, are also tabulated.

The data of Table I show that the rates of addition of the sulfenyl chloride are favored by elec-

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[1] This study was sponsored by the Office of Ordnance Research, United States Army, Contract DA-04-495-Ord. 306.

[2] W. L. Orr and N. Kharasch, THIS JOURNAL, **75**, 6030 (1953).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 186–194.

[4] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[5] The previous non-existence of such studies may be attributed to the fact that many "ionic addition reactions" with suitable olefins are too fast to measure conveniently, and because the reactions are often complicated by side reactions (*e.g.*, substitutions or polymerizations) or they do not clearly involve a single reaction mechanism.

[6] C. G. Overberger, L. H. Arnold, D. Tanner, J. J. Taylor and T. Alfrey, THIS JOURNAL, **74**, 4848 (1952).

[7] W. L. Orr, Doctoral Dissertation, University of Southern California, June, 1954; available in microfilm copy.

TABLE I

RATE CONSTANTS AND ARRHENIUS PARAMETERS FOR THE REACTIONS OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH STYRENE AND *para*-SUBSTITUTED STYRENES

para-Substituent	Temp., °C.[a]	k (moles/l.)$^{-1}$ × sec.$^{-1}$	E_a, kcal./mole[c]	log A[e]	$\Delta S^{\ddagger}$[f]
$-CH_3$	20.0	1.69×10^{-3}			
	25.0	2.43×10^{-3}			
	(30.6)	3.61×10^{-3}	11.98 ± 0.3	6.20 ± 0.22	−32.2 ± 1.0
	35.0	4.67×10^{-3}			
	(44.9)[b]	9.43×10^{-3}			
$-H$	25.0	7.37×10^{-4}			
	35.0	14.8×10^{-4}	12.93 ± 0.3	6.34 ± 0.22	−31.6 ± 1.0
	45.0	29.0×10^{-4}			
$-Cl$	35.0	4.32×10^{-4}			
	(34.6)	4.22×10^{-4}	15.90 ± 0.4	7.91 ± 0.28	−24.4 ± 1.4
	45.0	9.73×10^{-4}			
$-NO_2$	34.0	2.67×10^{-5}			
	45.0	6.93×10^{-5}	16.92 ± 0.3	7.46 ± 0.21	−26.5 ± 1.0
$-OCH_3$	25.0	0.5[d]			

[a] Values in parentheses are for a single run; all others are the mean of two or more runs. [b] This single run showed a positive curvature, the second-order rate constant increasing as the reaction proceeded. The value of k listed is the estimated initial rate. [c] The activation energies, E_a, were calculated in the usual manner from the slopes of $1/T$ *vs.* log k plots. The uncertainties listed are based on the estimated maximum and minimum slopes, which is equivalent, in most cases, to calculation from the maximum to minimum and minimum to maximum values of k at the extreme temperatures. [d] This value is a rough estimate of the minimum value. *Cf.* experimental and discussion of the special features of the reaction with *p*-methoxystyrene. [e] Calculated from the equation, $k = Ae^{-E_a/RT}$. [f] Calculated from the values for A by the equation $A = {}^{kT/h} \times e^{\Delta S^{\ddagger}/R}$.

tron-releasing *p*-substituents in the styrene and that the relative order of reactivities is determined mainly by the activation energy, E_a, or the heat of activation, $\Delta H^{\ddagger}$.[8] However, the variations in the Arrhenius frequency factor, A, or the entropy of activation, $\Delta S^{\ddagger}$, derived from A also have a significant effect on the rates.[9]

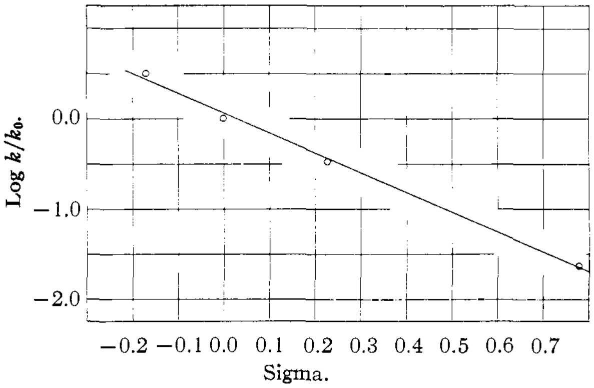

Fig. 1.—The Hammett rho–sigma correlation of rates for the reactions of 2,4-dinitrobenzenesulfenyl chloride with *p*-substituted styrenes, at 45°. The *para*-substituents for the points, from right to left, are: NO_2, Cl, H and CH_3.

Discussion of Results

The Hammett equation, generally applied in the form log $k/k_0 = \rho\sigma$, has been admirably presented by Hammett[3] and reviewed by Jaffe.[4] The data of Table I fit this equation excellently, despite appreciable variations in the values of $\Delta S^{\ddagger}$. As shown in Fig. 1, the log k/k_0 *vs.* sigma plot for the data at 45° gives an excellent linear relation. The line as drawn is the least squares line, minimizing the squares of the deviations along the log k/k_0 axis, and has a slope (ρ) of −2.202. The standard deviation (s) and the correlation coefficient (r), calculated according to Jaffe,[4] have the values 0.807 and 0.997, respectively. Jaffe considers that if r is greater than 0.99 and s is not greater than 0.25 (for a value of ρ in this range) the data fit the Hammett equation excellently. The data for 25° and 35° fit almost as well, as shown in Table II by the values of ρ, s and r at these temperatures. As expected, the value of ρ appears to decrease slightly with increasing temperature, although the recorded variation is only slightly greater than the uncertainty in the value of ρ.

TABLE II

PRECISION OF THE HAMMETT RHO–SIGMA CORRELATION

Temp., °C.	Reaction constant (ρ)	Standard dev., s	Correlation coefficient r
45.0	−2.202	0.087	0.997
35.0[a]	−2.290	.072	.999
25.0	−2.414	.287	.972

[a] To obtain comparable data for this exact temperature, values of k for 35.0° were calculated, as necessary, from the data of Table I, using the Arrhenius equation.

Although the Hammett equation[4] was derived on the basis of a potential energy relation for a reaction series of constant entropy, it is now known to apply on an empirical basis to many reaction series

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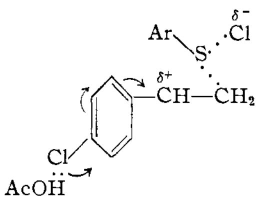
(8) For purposes of discussion and comparisons of the series of reactions, there is little point in distinguishing between the Arrhenius activation energy, E_a, and the heat (or enthalpy) of activation, $\Delta H^{\ddagger}$. By definition, however, they differ by RT; *i.e.*, $\Delta H^{\ddagger} = E_a - RT$. *Cf.* S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417; also, A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 97.

(9) An error in E_a (or $\Delta H^{\ddagger}$) automatically results in a compensating value for A (or $\Delta S^{\ddagger}$)—*cf.* footnotes *e* and *f* of Table I—and it is difficult to obtain these quantities with the desired precision. However, the observed variations are believed to be greater than the experimental errors, as indicated in the estimated uncertainties shown in Table I.

where there are significant variations in entropy. If entropy varies, however, an apparently necessary condition for the equation to apply is a linear relation between entropy ($\Delta S^{\ddagger}$) and heat of activation (enthalpy, $\Delta H^{\ddagger}$). In view of earlier cases of similar nature,[7] it is therefore not surprising that the Hammett equation correlates the present data. A critical evaluation of the often-observed linear relation between enthalpy and entropy, as well as its bearing on the Hammett rho–sigma treatment has been made recently by Leffler.[10]

The large negative entropies of activation are in the range expected for a bimolecular reaction in which there is significant increase in polarity involved in forming the transition state. The increased polarity of the latter requires a greater orientation of the solvent and therefore a large loss of entropy by the solvent.[11,12] When E_a is plotted against log A (or $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$) the plot is approximately linear. Figure 2 shows such a plot, in which the line is drawn through the points for *p*-methylstyrene, styrene and *p*-nitrostyrene, to show the linear relation for these compounds and also the deviation in the case of *p*-chlorostyrene. With only four points, the placement of this line is arbitrary, but the selection is convenient for discussion since the deviation of *p*-chlorostyrene is rationalized, below, on the basis of a specific solvent effect.

With the reaction of styrene as a reference point, the effects of the individual substituents may be considered. Since the postulated transition states for the reactions are more ionic than the reactants (the olefin and I) the large negative values of $\Delta S^{\ddagger}$ may be partially attributed to a greater solvation of the transition state than of the reactants. Because of some functional relation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$,[10] the changes in these quantities are approximately linear (Fig. 2) in the series for the *p*-substituents, methyl, hydrogen and nitro. For the depicted deviation of the *p*-chlorostyrene reaction, it seems reasonable to assume that the *p*-chlorostyrene is more highly solvated than is styrene itself, specifically by hydrogen bonding between acetic acid and the *p*-chloro atom, and that this increment of solvation is lost in the transition state to an extent depending on the degree to which the electromeric effect (+T) of the chlorine atom is called into play by the developing positive center at the olefin bond; *i.e.*, the hydrogen bond is disrupted or weakened, as indicated by the curved arrow, below.



If such an effect occurs, the increase in orientation of the solvent caused by the developing polarity at the reaction site is partially compensated by loss of solvent orientation at the *p*-chlorine atom. The net change in solvent orientation is less than for styrene and the entropy of activation for the *p*-chlorostyrene reaction is therefore less negative than might be anticipated by the reported trend in the series. While the above suggestion is in terms of hydrogen bonding, a similar discussion could be made by using the concept of dipole–dipole interactions.

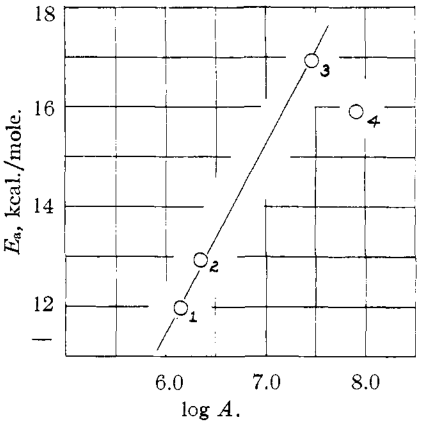


Fig. 2.—Plot of log A *vs.* E_a for the reaction of 2,4-dinitrobenzenesulfenyl chloride with *p*-methylstyrene (1), styrene (2) *p*-nitrostyrene (3) and *p*-chlorostyrene (4). *Cf.* discussion for the placement of the line as shown.

p-Methylstyrene should not, as found, differ significantly from styrene, as regards orientation of the solvent, either in the reactant or transition state. The energy of activation for the reaction with I, for this more nucleophilic olefin, should, however, be lower, and the entropy of activation only slightly lower, as found. In the reaction of *p*-nitrostyrene, the styrene is probably solvated at the substituent, as in *p*-chlorostyrene, but since the nitro group cannot release electrons to the developing positive center at the double bond, this increment of solvation is relatively unchanged in the transition state. The findings with *p*-methoxystyrene, in which case addition of I was very rapid, are presented separately, below.

The general increase in rate of addition with increasing ability of the *para*-substituent to increase the electron availability at the double bond of the styrene is in accord with our earlier considerations of the mechanism of the addition,[2] in which the presumed rate-determining step is formation of a cyclic sulfonium ion (*cf.* eq. 2, below). Electron release from the *para*-substituent would stabilize this sulfonium ion intermediate and favor its rate of formation.

The Reaction Products.—On the basis of the earlier proof of structure[2] for the product from I and styrene, the structures of the adducts (compare eq. 1) with the *p*-substituted styrenes are presumed to be the β-chloro sulfides shown (structure II), while the vinyl sulfide from the reaction of I with *p*-methoxystyrene (*cf.* below) has structure III. The *trans* isomer is most likely for the latter, but this has not been explicitly proved as yet.

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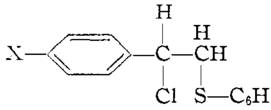
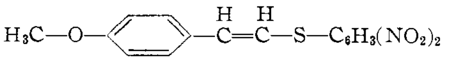
[10] M. L. Leffler, "The Enthalpy–Entropy Relationship and Its Implications for Organic Chemistry," *J. Org. Chem.*, **20**, 1202 (1955).

[11] R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

[12] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 208–218 and 272–284.



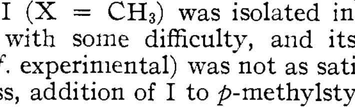
II, X = Cl, NO_2, CH_3



III

The products II, X = Cl and NO_2, were obtained in excellent yields and were easily purified, although a fully suitable elementary analysis for the *p*-nitro compound (a trinitro compound) was not realized. Details of these preparations, with brief comments on observations related to them are given in the experimental part. The *p*-methyl analog of II (X = CH_3) was isolated in 79–89% yield only with some difficulty, and its melting behavior (*cf.* experimental) was not as satisfactory. Nevertheless, addition of I to *p*-methylstyrene was quantitative (as shown by titration for I) and the difficulty in obtaining pure adduct in this case is no doubt caused by a tendency toward vinyl sulfide formation, since this was the predominant behavior found with *p*-methoxystyrene (see below).

The reaction of I with *p*-methoxystyrene was more complex than with the other olefins studied. The product composition was very sensitive to the temperature at which the reaction was carried out and addition of I was accompanied by simultaneous polymerization of the styrene. The extent of polymerization varied appreciably and was sensitive to the particular concentrations and mixing technique employed. At 25°, except for polymeric material, the reaction product was almost entirely the excellently crystalline vinyl sulfide, III; but when the reaction was run near the freezing point of the solution (10–13°), the high yield of crude product obtained consisted of 80–86% of the β-chlorosulfide (II, X = —OCH_3), some vinyl sulfide, III, and 3–6% of the β-acetoxy sulfide, IV.



IV

The structure of III was confirmed by oxidizing it to *p*-anisic acid and by easy formation of III when the 1:1 adduct (II, X = -OCH_3) was treated with triethylamine, in benzene solution, or simply by heating the solutions of the 1:1 adduct (II, X = -OCH_3).

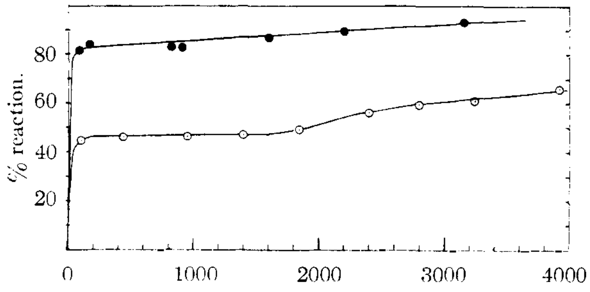
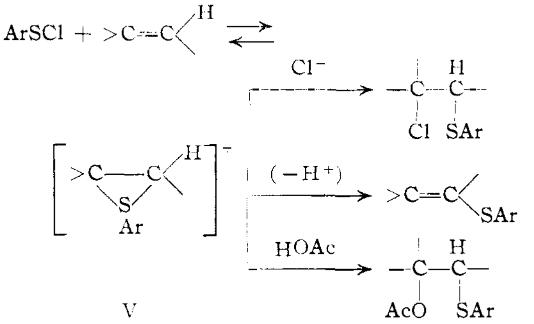


Fig. 3.—Plots of per cent. reaction *vs.* time for the reaction of 2,4-dinitrobenzenesulfenyl chloride and *p*-methoxystyrene.

In the *p*-methoxystyrene reaction, the marked change in product composition for the small change in temperature contrasts interestingly with the other styrenes studied and is suggestive of the reaction path which leads to the vinyl sulfide, III. Kharasch and Buess[13] had suggested, in those cases where vinyl sulfides or β-acetoxy sulfides were found as products from reactions of I and olefins, that these products—as well as the 1:1 adduct—stemmed from the intermediate sulfonium ion, V, eq. 2 (Ar = 2,4-dinitrophenyl). The present study of the reaction with *p*-methoxystyrene lends support to this suggestion by eliminating the possibility that the vinyl sulfide is formed by dehydrohalogenation of the 1:1 adduct. It was found that the rate of dehydrohalogenation of the 1:1 adduct (II, X = -OCH_3), in acetic acid, at 25°, is very slow compared to the rate of formation of III directly from I and *p*-methoxystyrene under the same conditions. The vinyl sulfide, III, which is formed very rapidly in the reaction of I and the olefin, at 25°, therefore does not arise by loss of hydrogen chloride from II (X = -OCH_3), but must be formed directly—presumably from the sulfonium ion, V.



(2)

The fact that II (X = -OCH_3) was sufficiently stable to isolate, in about 86% purity, in a procedure requiring several hours, establishes the above conclusion firmly, since the reaction of I and *p*-methoxystyrene—which yields none of the 1:1 adduct—is essentially complete in a matter of seconds. However, this was also shown in an alternate manner, by taking advantage of the difference in the visible spectra of the vinyl sulfide, III, and the 1:1 adduct, II, X = -OCH_3. The absorption spectra of solutions of the 1:1 adduct in acetic acid slowly change, approaching the spectra of solutions of the vinyl sulfide of corresponding concentrations. The change is essentially complete after 90 minutes at 100° but at 25° is not complete even after 4900 minutes. The detailed curves are available in reference 7.

Data for two runs, at 25°, in dry acetic acid, for the reaction of I and *p*-methoxystyrene appear in the Experimental part and are plotted in Fig. 3. In the first run (open circles), the concentrations of reactants were both 0.03 molar at the start, while in the second run (shaded circles) the initial concentrations were 0.0477 and 0.0200 molar for I and the olefin, respectively. In each run, a very fast initial uptake of I was interrupted by a sharp break

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[13] N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949).

before reaction of I with initially available olefin was complete, and following the break a very slow uptake of I continued. In the second run with a higher ratio of I to olefin the fast reaction corresponds to about 81% reaction in contrast to only 44% in run one where the reactants were at equal concentrations. This suggests that the olefin is being used in some competing reaction, presumably an acid-catalyzed polymerization of the styrene, and the olefin supply is depleted at the sharp break. The slow continued uptake of I which occurred after the fast reaction probably involves a slow substitution of the 2,4-dinitrophenyl group into the aromatic nucleus of the *p*-methoxystyrene polymer since the reaction of I with activated aromatic nuclei (*e.g.*, resorcinol) is known to take place.[14] Product isolation from one of the above runs (no. 37; *cf.* Experimental) agreed well with the amount of adduct expected (44%) from the sharp break in the lower curve of Fig. 3. As required, on the basis of the above suggestion for the continued slow uptake of I, the polymeric product from the reaction contained nitrogen and sulfur, but the nature of this product was not fully investigated.

Because of the above complexities, the rate constant for addition of I to *p*-methoxystyrene cannot be deduced accurately from the present data. On the basis of the first point of the second run (shaded circles), however, the constant must be at least 0.5 (mole/liter)$^{-1}$ sec.$^{-1}$. It could be considerably greater (depending on the competition offered by the effect of the polymerization of the olefin) but it cannot be less. The results obtained do not allow the reaction with the *p*-methoxystyrene to be fitted on the rho–sigma plot together with the other styrenes investigated. Possible reasons for this are noted below.

The *p*-methoxy group is now well known to cause large deviations in rho–sigma correlations. For this reason, numerous revisions of its sigma constant have been suggested and no single value is applicable to all types of reactions. For reactions with large negative values of rho, the *p*-methoxy compound is often more reactive than the correlation predicts and it has been suggested[15] that groups which release electrons very strongly (*e.g.*, $-OCH_3$, $-OH$ and $-N(CH_3)_2$ vary considerably in their electron releasing ability, according to the demand in the given reaction. In the present work, the roughly estimated minimum value of the rate constant for the *p*-methoxystyrene (*cf.* above) is about one hundred and forty times the value expected on the basis of the rho value which fits the other styrenes and the usual value $-(0.268)$ of sigma[3] for the *p*-methoxy group. It does not seem likely, however, that this marked increase in rate is to be ascribed entirely to an unusual electron release by the methoxy group in the reaction of *p*-methoxystyrene and I. A factor which is more likely responsible for the enhanced rate is auto-catalysis by the hydrogen chloride which is released in the reaction of I and *p*-methoxystyrene, for this could promote the rate of addition by helping to polarize the sulfenyl chloride through hydrogen bonding ($ArS^{\delta+}Cl^{\delta-}$-----HCl). While several observations in this Laboratory clearly imply this possibility of acid catalysis for the addition of I to olefins, its full demonstration has only recently been achieved and will be reported in a forthcoming publication. The formation of the vinyl sulfide, III, rather than 1:1 adduct is understandable, however, since the stabilization of the cyclic sulfonium ion, V, by electron release from the *p*-methoxyl group would retard the rate of addition of the chloride ion, so that proton elimination becomes the preferred route for this intermediate ion.

The finding of all three products (compare eq. 2) in the reaction of I and *p*-methoxystyrene shows that the rates of the competing reactions must be reasonably comparable. The large increase in the ratio of vinyl sulfide formed by raising the temperature by only 10° suggests, however, that the energy of activation of the elimination reaction (which leads to the vinyl sulfide) is higher than are those of the reactions which form the β-chloro sulfide or the corresponding acetate, IV. As noted earlier, the initial formation of the cyclic sulfonium ion is probably the rate-determining step in the over-all reaction, followed by the faster competitive steps with the cyclic ion (eq. 2).

The effects of *para*-substituents in the styrene on the rates of additions of I are analogous to those observed by Overberger and co-workers[6] in the stannic chloride-catalyzed copolymerizations of styrene and substituted styrenes. Although the identical series of *para*-substituents was not used, and the solvents and temperatures were also different, the reaction constants, rho, are similar. Overberger and co-workers give rho = -1.7 for the copolymerization of substituted styrenes with (a) styrene, (b) *p*-chlorostyrene and (c) α-methylstyrene. Jaffe[4] has recalculated these data and gives values of rho as -1.932, -1.627 and -2.119 for the three reaction series, respectively. It is also noteworthy that the *p*-methoxystyrene also gave an abnormally fast reaction in the polymerization study. The correspondence in the effects of substituents is suggestive of a parallel between the mechanism of the sulfenyl chloride–styrene reaction and that of the ionic copolymerization reaction, for the rate-determining step in both appears to be an electrophilic attack on the olefinic bond.

Acknowledgment.—We are indebted to Dr. M. L. Leffler, who kindly made his manuscript on the enthalpy–entropy relation available to us, to Dr. Adalbert Elek and Mr. W. J. Schenck for microanalyses, and to the Office of Ordnance Research for support of this study.

Experimental[16]

Starting Materials.—*p*-Chlorostyrene (Monomer–Polymer Corp.) was freshly distilled in all experiments (b.p. 43–43.3° (3 mm.); $n^{19.5}$D 1.5648 (lit.[17] b.p. 38–39°, 2 mm.; n^{20}D 1.5648)). *p*-Nitrostyrene was made from 2-(nitrophenyl)-ethyl bromide[18]; m.p. 21.0–21.4°, after several

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[14] C. M. Buess and N. Kharasch, THIS JOURNAL, **72**, 3529 (1950).

[15] Ref. 4, p. 227 ff.

[16] Melting points are not corrected. Complete details for all experiments are in reference 7, microfilm copies of which are obtainable from the Librarian, University of Southern California, Los Angeles 7, California.

[17] C. S. Marvel and G. L. Shertz, THIS JOURNAL, **65**, 2054 (1943).

[18] R. W. Strassburg, R. A. Gregg and C. Walling, *ibid.*, **69**, 2141 (1947); E. L. Foreman and S. M. McElvain, *ibid.*, **62**, 1435 (1940).

crystallizations from ligroin (b.p. 63–69°). Decarboxylation of *p*-methylcinnamic acid[19] gave *p*-methylstyrene; b.p. 55.7–58.3° (12–13 mm.); $n^{20}\text{D}$ 1.5402 (lit.[20] b.p. 59.6° (13.5 mm.); $n^{20}\text{D}$ 1.5420). *p*-Methoxystyrene was prepared similarly. After usual purification,[20] the product was fractionated and only the middle fraction, b.p. 78–79° (6 mm.), was used. Other reagents were prepared as before[2] or by conventional methods.

Rate Measurements.—These were all made in dry acetic acid. Results are summarized in Table I and discussed above. In all cases, except for *p*-methoxystyrene, which was complicated by polymerization of the olefin and by dehydrohalogenation (*cf.* discussion, and below) the reactions of I and the styrenes was quantitative, as shown by titration[2,21] of excess I remaining after complete reaction. The rate runs were generally followed to at least 80%.

Attempted Rate Runs with *p*-Methoxystyrene.—Stock solutions (0.0600 molar) of the olefin and I were prepared and the concentration of the latter confirmed by titration. These solutions were thermostated to 25° (about 20 min.) and equal concentrations were mixed to start the run (no. 37, ref. 7). Initial concentration of I in the mixture was assumed to be 0.03 molar and 10-ml. aliquots were titrated. The following lists, in order, the time (sec. × 10^{-2}/molar concn. of I/% reaction for each aliquot: 0/0.0300/0; 1.02/0.0167/44.3; 4.38/0.0162/46.0; 9.45/0.0161/46.4; 13.96/0.0159/47.0; 18.40/0.0152/49.3; 24/0.0132/56.0; 27.90/0.0121/59.7; 32.45/0.0117/61.0; 39.20/0.0102/66; 45.20/0.0102/66; 56.50/0.0091/69.5; 71.14/0.0077/74.3; 96.50/0.0069/77.0; 432/0.0054/82.0. Zero time was taken when, in the admixture of I and the *p*-methoxystyrene, about half the latter solution had been added from the pipet (*ca.* 45 sec.). The reaction flask was gently rotated, to mix the reagents, and the first aliquot was withdrawn and half-drained into the titration flask, containing sodium iodide,[2,19] at 102 sec. Figure 3 (open circles) plots the above data and shows the sharp break at 44% reaction.

The similar data for another run (no. 38, ref. 7), at 25°, using excess sulfenyl chloride to minimize polymerization (see Discussion) appear below and are plotted (shaded circles in Fig. 3). Initial concentrations were 0.0477 *M* for I and 0.0200 for the olefin. The values of time (sec. × 10^{-2})/molarity of I/% reaction were: 0/0.0477/0; 0.89/0.03148/81.5; 1.69/0.0309/84.0; 8.20/0.0311/83.0; 9.20/0.0312/82.5; 16.04/0.0303/87.0; 21.94/0.0298/89.5; 31.60/0.0290/93.5; 45.80/0.0291/93.0; 89.80/0.0279/99.0.

Isolation of Products.—Quantities from 0.01–0.03 mole of I and the appropriate olefin were used. I and *p*-chlorostyrene, in dry acetic acid, at room temperature for several days gave the known[22] 1:1 adduct, m.p. 150–151°, in 96% yield. I and *p*-nitrostyrene, in dry acetic acid at 45° for 86 hr., gave 89% of the 1:1 adduct; pale-yellow crystals from chloroform–carbon tetrachloride; m.p. 143.6–144°.

Anal. Calcd. for $C_{14}H_{1}ON_3O_6SCl$: C, 43.82; H, 2.63; N, 10.95. Found: C, 44.29; H, 2.52; N, 11.40.

The *p*-methylstyrene adduct (II, X = CH_3) was obtained, similarly, after 22 hours at 20°, in 85% yield. The product decomposes (presumably loses HCl) on heating and the m.p. depends on rate of heating. Preheating the bath to 130° and raising the temperature 3°/min. gave m.p. 142–145.5° dec. The analytical sample was recrystallized from benzene-ligroin (b.p. 63–69°).

Anal. Calcd. for $C_{15}H_{13}N_2O_4SCl$: C, 51.06; H, 3.71; Cl, 10.05. Found: C, 51.26; H, 3.69; Cl, 9.90.

By reaction of I and *p*-methylstyrene at 13–14° (in dry acetic acid solution), the yield of adduct was 89%; while at 45°, only 73% of product resulted. The starch–iodide test[13] was used to judge completion of reaction.

Reaction of *p*-methoxystyrene and I, at 25°, in dry acetic acid, for 3 hr., using 0.016 mole of each reactant gave 90% of the chlorine-free, red vinyl sulfide (III), m.p. 198.5–200°. Some polymerization of the olefin was also noted.

Anal. Calcd. for $C_{15}H_{12}N_2O_5S$: C, 54.21; H, 3.64. Found: C, 53.92; H, 3.68.

Structure III was confirmed by oxidation, with alkaline permanganate, to *p*-anisic acid (m.p. and m.m.p. 183–184°) and dehydrohalogenating crude II (X = $-OCH_3$) to III (see below).

At 10–13° with I and *p*-methoxystyrene—and with a small proportion of benzene added to allow attaining the lower temperature—a chlorine-containing product resulted. This melted at 84–90°, with evolution of hydrogen chloride and deepening of color, solidified at 100° to a red material (undoubtedly III) which melted at 196–199°. Because of its easy dehydrohalogenation, the pure 1:1 adduct could not be obtained and the content of II (X = $-OCH_3$) was therefore assigned on basis of chlorine analysis of the product mixture; material having 86 ± 3% adduct was obtained. Treatment with the triethylamine, in benzene solution, caused quantitative conversion to III, m.p. 198–200°, which did not depress the m.p. of the vinyl sulfide obtained directly from the reaction mixture, at 25°; *cf.* above.

The reaction mixture from I and *p*-methoxystyrene, at 10–13; also yielded 3–6% of the β-acetoxy compound IV. This was isolated by chromatographing the reaction product on alumina ("Alcoa-F-20") using benzene–ligroin (b.p. 63–69°), with increasing benzene content, for elution. The 1:1 adduct (II, X = Cl) was partially destroyed on the column and preceded the acetate (II, X = OAc) on elution. The final eluates gave, on evaporation, a small amount of yellow oil, which was induced to crystallize from ligroin (b.p. 63–69°), melted at 116–118° and did not decompose on being heated above its melting point (compare the chloride, above). Recrystallization from benzene-ligroin (b.p. 63–69°) raised the m.p. to 117.5–119°.

Anal. Calcd. for II (X = OAc), $C_{17}H_{16}N_2O_7S$: C, 52.04; H, 4.11. Found: C, 51.73; H, 4.15.

Product Isolation from a Rate Run (Run 37, above) between I and *p*-Methoxystyrene.—After four days at 25°, solvent was lyophilized from 360 ml. of solution remaining from the run. The residue was dissolved in benzene and chromatographed on a column of alumina ("Alcoa F-20") 28 × 0.5 inches. Fraction 1 contained most of the orange band, which passed rapidly down the column, as benzene was added. This fraction was concentrated to *ca.* 80 ml., giving a red, crystalline precipitate, which was collected (fraction A). Complete evaporation of the solvent left a similar red residue (B) which could not be "pumped off" at 2 mm. for 24 hours. Eluate 2 left a residue, B′, and further eluates (using benzene, chloroform and finally acetone) left only a pale-orange, viscous oil which was judged to be polymerized olefin which had reacted partly with I (possibly by substitution in the aromatic ring; *cf.* Discussion). The material gave positive tests for nitrogen and sulfur, but was not further investigated.

Continued chromatography of A and combined B and B′ led to 1.39 g. of III (from fraction A), m.p. 198.5–199.5°; and 0.20-g. and 0.17-g. fractions from B and B′, melting, respectively, at 142–184° and 145–182°. The latter were judged to be mostly impure III. The yield of III, on basis of pure product from A, is 39%; and on basis of all three fractions above, the yield of III is 49%. The yield of 39–49% of isolated III corresponds well with the value of 44% III, as estimated from the sharp break in the rate curve (Fig. 3).

UNIVERSITY PARK
LOS ANGELES, CALIFORNIA

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[19] C. Walling and K. B. Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

[20] H. E. Clements, K. V. Wise and S. E. J. Johnsen, *ibid.*, **75**, 1593 (1953).

[21] N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).

[22] N. Kharasch, C. M. Buess and S. I. Strashun, THIS JOURNAL, **74**, 3422 (1952).