a solvent zinc chloride appeared to exert no effect on 2-bromo-1-tetralone DNP (VIb).[25]

With one exception (α-bromoacetophenone DNP (IIb)) the halogen in all the α-halo-DNP's studied[26] could be replaced by a methoxyl group upon short boiling in methanol.[27] From the above considerations it appears that the push–pull effect[23] presumably involved in methanolysis is capable of effecting the replacement in all the secondary halo-DNP's studied. A more effective push or pull (acetate ion or zinc chloride, respectively) seems, however, necessary for replacement of halogen by acetoxyl group in acetic acid solution. In acetic acid alone, elimination, not replacement, was observed and this only in those relatively more reactive α-halo-DNP's already mentioned.

The scheme shown above suggests that in acetic acid the rapid removal of a proton from D might first yield the unsaturated azo compound[28] F which would then—presumably under the influence of hydrogen halide and subject to thermodynamic considerations—tautomerize to the unsaturated hydrazone H. Ultraviolet and infrared absorption spectra substantiate the α,β-unsaturated hydrazone structure of the products isolated from acetic acid in all cases but one. The exception referred to was found in the reaction of α-bromopropiophenone DNP (IIIb) in hot acetic acid. The resulting substance IX of empirical formula $C_{16}H_{12}O_4N_4$, showed an abnormal spectrum in the ultraviolet with maxima at 305 and 413 mμ unlike any of the substituted or unsubstituted DNP's isolated in this study. Although no directly comparable model was at hand the recorded observations on the ultraviolet absorption spectra of azo compounds[29] point to an α,β-unsaturated azo structure for IX.[30,31] The infrared spectra of the dinitrophenylhydrazones studied exhibited bands at 3.0, 6.18 and 6.25 μ; the spectrum of IX, however, showed no N–H stretching band at 3.0 μ and a marked weakening of the 6.25 μ band relative to the 6.18 μ band, which seems consistent with the azo structure shown.[32]

Acknowledgment.—We thank the Eli Lilly Co., Indianapolis, Ind., for financial assistance in this work.

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[25] V. R. Mattox and E. C. Kendall (*J. Biol. Chem.*, **185**, 601 (1950)), have reported the isolation of appreciable amounts of the 4-acetoxyhydrazone on treatment of methyl 3,11-diketo-4,12-α-dibromocholanate with 2,4-dinitrophenylhydrazine in acetic acid containing large excess of sodium acetate or pyridine.

[26] As reported elsewhere (F. Ramirez and R. J. Bellet, THIS JOURNAL, **76**, Jan. (1954): 2-bromocyclobutanone DNP can be recovered unchanged from hot acetic acid or methanolic solutions.

[27] The methanolyses of *anti*-α-bromopropiophenone DNP (IIIbB) and of *anti*-α-bromobutyrophenone DNP (IVbB), which represent the more stable form of the respective isomeric pairs, gave mixtures of stereoisomeric α-methoxy DNP's. On the basis of interconversions among isomers it appears that members of the A-series (*syn*) are more stable than members of the B-series (*anti*) among α-methoxy DNP's. The same is true for *syn*- and *anti*-α-bromoacetophenone DNP's. These observations are consistent with the geometry of the molecules as revealed by atom models.

[28] Working in the 3-keto-4-bromosteroid series with *p*-nitrophenylhydrazine, W. F. McGuckin and E. C. Kendall (*ibid.*, **74**, 5811 (1952)), have recently mentioned the isolation of a "highly colored. . . α,β-unsaturated azo structure" for which details are promised.

[29] W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **75**, 1856 (1953).

[30] An α,β-unsaturated azo structure ($C_2H_5O_2C—CH{=}C(CH_3)—N{=}N—C_6H_4\cdot NO_2$-*p*) has been assigned (J. van Alphen, *Rec. trav. chim.*, **64**, 305 (1945) to the product isolated from the action of *p*-nitrophenylhydrazine on ethyl α-chloroacetoacetate.

[31] A pyrazoline structure for IX was excluded since phenyl vinyl ketone DNP (IIIe) prepared in two ways (see experimental) was found to be stable in acetic acid solution. Pyrazolines have been postulated, without proof, in several instances involving dinitrophenylhydrazine and α,β-unsaturated ketones (G. Morgan and C. F. Griffith, *J. Chem. Soc.*, 841 (1937); C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937)).

[32] *Cf.* R. J. W. LeFevre, M. F. O'Dwyer and R. L. Werner, *Chemistry and Industry*, 378 (1953).

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

Derivatives of Sulfenic Acids. XIII. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Styrene[1]

BY WILSON L. ORR AND NORMAN KHARASCH

RECEIVED JUNE 8, 1953

The structure of the adduct of 2,4-dinitrobenzenesulfenyl chloride to styrene is shown by alternate synthesis to be 2-chloro-2-phenylethyl 2′,4′-dinitrophenyl sulfide. This is in accord with the anticipated structure, assuming ionic addition of the sulfenyl chloride, $(NO_2)_2C_6H_3S\delta^+Cl\delta^-$. Formation of the adduct in dry acetic acid follows the rate expression $-dArSCl/dt = k[ArSCl][styrene]$; Ar = 2,4-dinitrophenyl. The reaction is homogeneous, is not sensitive to ordinary illumination, and shows a positive salt effect with lithium chloride and sodium perchlorate. Values of k (min.$^{-1}$) at 25, 35 and 45°, respectively, were 0.0442, 0.0889 and 0.174, corresponding to $E_a = 12.9 \pm 0.3$ kcal./mole. The rate of disappearance of ArSCl was followed by an iodimetric method, within the accuracy of which (*ca.* 1%), the addition of ArSCl to styrene is quantitative. The rate of addition in acetic acid is very much greater than in carbon tetrachloride. The kinetic data are consistent with the postulation that the addition of ArSCl to olefins involves initial formation of a cyclic sulfonium ion, followed by addition of Cl^- to yield the β-chloro sulfide. The formation of the cyclic ion is considered to be the most likely rate-determining step.

Introduction

In other papers of this series[2] the reaction of sulfenyl halides with olefins and alkynes has been described, with particular emphasis on the use of 2,4-dinitrobenzenesulfenyl chloride (I) for the characterization of these substances. Since this reaction is of general interest, investigations concern-

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[1] This study was carried out under the sponsorship of the Office of Ordnance Research, United States Army, Contract Da-O4-495-Ord. 306, and represents a portion of the dissertation to be presented by W. L. Orr in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] (a) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); (c) N. Kharasch, C. M. Buess and S. I. Strashun, *ibid.*, **74**, 3422 (1952); (d) N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).

ing the precise stereochemistry[3] and kinetics of these additions have been undertaken. The major purpose of the present work was to carry out a kinetic study of the addition of I to styrene. This system was selected for initial investigation, since it offers an opportunity—in continuing the work with *p*-substituted styrenes—to relate the electronic character of the substituents to the effects which they may exert on the reaction rates.

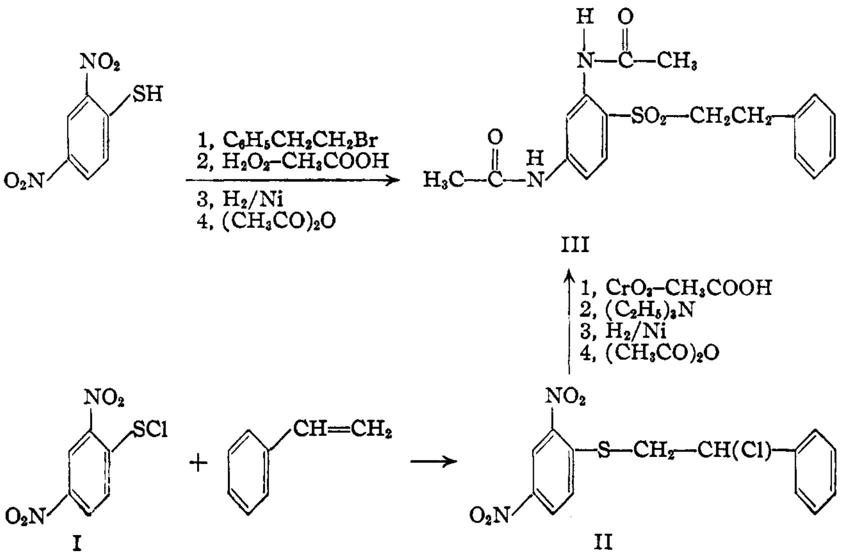

Fig. 1.

Dry acetic acid was selected as the reaction medium. This choice was made because this solvent is suitable for conducting the reaction; and also because acetic acid has frequently been used in kinetic studies involving additions of halogens to olefins,[4] so that comparisons between these related reactions may be anticipated when sufficient cases of the sulfenyl halide–olefin reaction will have been studied.

In dry acetic acid, I reacts with styrene to form a previously tabulated adduct.[2a] It has now been shown that this product can be isolated in over 90% yield; and that the addition of I to styrene is quantitative, as shown by titration of excess I remaining after complete reaction with a known quantity of styrene. While only a single product appears to be formed in this reaction, the demonstrated formation of two distinct adducts in the reaction of I with propene,[2b] and the lack of structure proofs for products closely related to the styrene adduct suggested the need to confirm the structure of this product. This was accomplished by the sequence of reactions shown in Fig. 1, establishing the structure as II. The identical final product, III was obtained from either route.[5]

Because of the easy hydrolytic loss of the chlorine atom in II, the usual method of oxidation of a sulfide to a sulfone with 30% hydrogen peroxide in glacial acetic acid was not suitable for converting II into the corresponding β-chlorosulfone. The desired reaction was, however, readily effected by the procedure recently described by Truce and coworkers.[6,7]

Kinetic Data.—The reaction of I with styrene was followed by determining the rate of disappearance of the sulfenyl chloride *via* the reaction

$$2ArSCl + 2I^- \longrightarrow ArSSAr + I_2 + 2Cl^-$$

This analysis was shown to be quantitative, and sufficiently more rapid than the reaction of I with styrene to permit its use in the kinetic study. The details of the method of analysis are given in the Experimental part.

Data for a typical rate run at 25° are given in Table I, and these are plotted for a second-order reaction in Fig. 1. The concentrations were varied in different runs, and the data found to conform to the second-order expression

$$-dArSCl/dt = k[ArSCl][styrene]$$

The data of Table I and Fig. 2 also illustrate that the reaction is not sensitive to the effects of diffuse daylight or added glass surface—as shown by the lack of any systematic variation in rates under the different conditions; (*cf.* footnote *a* of Table I). The slight apparent decrease in the calculated rate constants of Table I is caused mainly by the fact that the values are calculated from the initial concentrations, as determined by the preparation of the solutions, rather than from the first analytically determined concentration. This slight discrepancy is magnified in the value of *k* during the first 10% of the reaction because of the sensitivity of the term, log $b(a - x)/a(b - x)$, to small changes in concentration in this region. The per cent. error in the time is also much greater at the start, since the mixing requires finite time. Calculations of *k*, taking the first analytically-determined point as zero time, show that this apparent decrease is not real; and, moreover, the mean value of *k* is not changed significantly by the method of calculation if the values of *k* for less than 10% reaction are neglected. In different experiments the values of *k* for less than 10% reaction were more often higher than the mean value, but in a number of them they were lower, as shown in Table II, illustrating the data for a typical run at 45°, in which the first point (6% reaction) is low. In general, the experi-

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(3) N. Kharasch and A. J. Havlik, THIS JOURNAL, **75**, 3734 (1953).

(4) For a leading reference, *cf.* P. B. D. de la Mare, *Quart. Revs.*, **III**, 126 (1949).

(5) The paper of R. C. Fuson and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1936), and ref. 2b may be consulted for comparable proofs of structure for the adducts of 2-chloroethanesulfenyl chloride and of I to propene. These proofs of structure, of course, depend on the assumption that rearrangement of the β-chloro-substituted sulfide does not occur during oxidation to the sulfone. *Cf.* also, R. A. Turner and R. Connor, THIS JOURNAL, **69**, 1009 (1947).

(6) W. E. Truce, G. H. Birum and E. T. McBee, *ibid.*, **74**, 3594 (1952).

(7) When hydrogen peroxide oxidation was attempted for the conversion of II to its sulfone, a mixture of products was obtained, from which only one compound was isolated in a pure form. The structure of this compound was not established by alternate means, but it did not contain chlorine, and the analyses for carbon and hydrogen were in agreement with the values calculated for the β-hydroxysulfone of II. The product melted (with decomposition) at 162–164°.

TABLE I

DATA FOR A TYPICAL RUN AT 25 ± 0.02°

Conditions[a]	Time, min.	Thiosulfate soln.,[b] ml.	$(a - x)$ concn. ArSCl[c]	$(b - x)$ concn. styrene	$\log \frac{b(a-x)}{a(b-x)}$	k (mole/l)$^{-1}$ min.$^{-1}$
	0		0.07624	0.06374		
L	30	16.48	.06955	.05705	0.00824	0.0506[d]
S	54	15.56	.06566	.05316	.01395	.0465
D	68	14.98	.06321	.05071	.01796	.0487
L	126	13.31	.05617	.04367	.03154	.0461
S	151	12.97	.05473	.04223	.03486	.0425
D	173	12.24	.05165	.03915	.04259	.0454
L	329	9.67	.04081	.02831	.08106	.0454
S	371	9.31	.03929	.02679	.08561	.0425
D	394	9.15	.03861	.02611	.09215	.0431
L	499	8.32	.03511	.02261	.1134	.0419
S	527	8.00	.03376	.02126	.1231	.0430
D	584	7.62	.03216	.01966	.1359	.0429
L	610	7.48	.03157	.01907	.1411	.0426
S	621	7.41	.03122	.01872	.1451	.0431
D	634[e]	7.31	.03085	.01835	.1478	.0430
						Mean: .0441

[a] L = in ordinary light; S = in ordinary light with added glass surface; D = in dark without added surface. [b] The volumes recorded are corrected for a blank of 0.07 ml. on the sodium iodide. The thiosulfate solution was 0.0422 *N*. [c] The initial concentrations are calculated from the weights of reactants and volume of the solution at 25°. [d] The second-order rate constant, k, is calculated from the equation: $k = 2.303/t(a - b) \times \log b(a - x)/a(b - x)$, from the initial concentrations to each point. The dimensions are liters moles^{-1} min.$^{-1}$. The first point was neglected in calculating the mean value of k. [e] Crystals of adduct had begun to precipitate by this time.

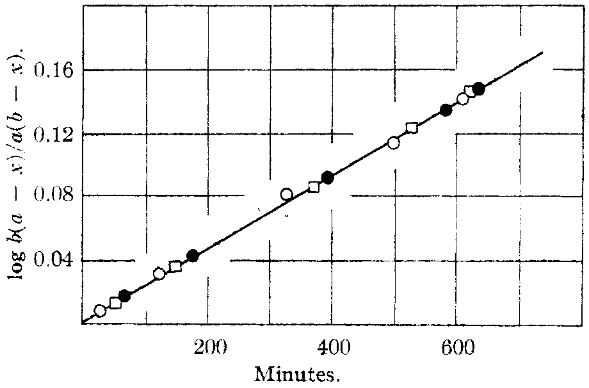

Fig. 2.—The reaction of 2,4-dinitrobenzenesulfenyl chloride with styrene, showing adherence to a second-order rate expression: ○, in ordinary light without added surface; ●, in dark without added surface; □, in ordinary light with added glass surface. Initial concentrations: a = [ArSCl] = 0.07624 *M*; b = [Styrene] = 0.06374 *M*.

TABLE II

DATA FOR A TYPICAL RUN AT 45 ± 0.02°

Time, min.	$S_2O_3^{=}$,[a] ml. *N* 0.0250	$(a - x)$, concn. ArSCl	$(b - x)$, concn. styrene	$\log \frac{b(a-x)}{a(b-x)}$	k, min.$^{-1}$
0	...	0.05009	0.03174	.....	....
10	19.27	.04817	.02982	0.01017	(0.1276)[b]
55	15.62	.03905	.02068	.07793	.1737
157	11.99	.02998	.01163	.21404	.1711
220	10.74	.02685	.00850	.30238	.1725
238	10.44	.02610	.00775	.32920	.1736
406	8.91	.02228	.00393	.55539	.1717
455	8.63	.02158	.00323	.62661	.1729
∞	7.52	.01880	.00045	.....(98.6% reacn.)	

[a] Sample volume was 10.00 ml. [b] Neglecting first point, mean k = 0.1726.

TABLE III

SUMMARY OF RATE CONSTANTS FOR DIFFERENT RUNS

Initial Concn. ArSCl	Initial Concn. styrene	Temp., °C.	k (mole/l.)$^{-1}$ min.$^{-1}$
0.0400	0.0400	25 ± 0.02	0.0437
.0800	.0400		.0459
.0762	.0637		.0441
.0400	.0300		.0439
.0400	.0300		.0436
		Mean =	.0442 av. dev. ± .0007
.0501	.0367	35 ± .02	.0896
.0482	.0213		.0882
		Mean =	.0889
.0501	.0317	45 ± .02	.173
.0481	.0311		.175
		Mean =	.174

TABLE IV

SUMMARY OF RUNS WITH ADDED ELECTROLYTES AT 25 ± 0.02°

Initial Concn. ArSCl	Initial Concn. styrene	Electrolyte, *M* concn.	k (mole/l)$^{-1}$ min.$^{-1}$
0.0400	0.0300	0.0680 $NaClO_4$	0.0552
.0400	.0300	.0200 LiCl	.0463
.0400	.0300	.0600 LiCl	.0509
.0367	.0188	.0920 LiCl	.0566

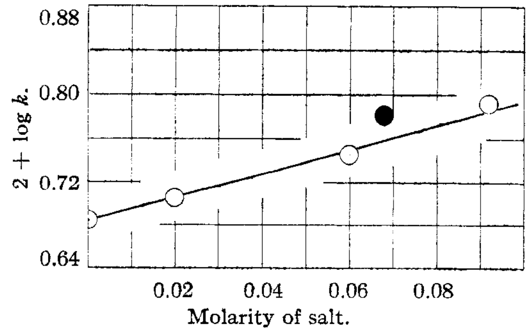

Fig. 3.—Effect of increasing salt concentrations on the rate constant of the reaction of 2,4-dinitrobenzenesulfenyl chloride with styrene: ○, lithium chloride; ●, sodium perchlorate.

mental error was much larger for measurements below 10% reaction; therefore, the mean values of k were determined by using only points from about 10 to 85% reaction.

The rate constants at different temperatures (Table III) lead to a value for the activation energy of 12.9 ± 0.3 kcal./mole; while those in Table IV (*cf.* also Fig. 3) establish that there is a positive salt effect in this reaction. The observation that the effect with sodium perchlorate is of the same magnitude as with lithium chloride indicates that this is a general primary salt effect, rather than a specific effect of chloride ion.

All of the rate measurements reported in this paper refer to dry acetic acid as solvent. One run was attempted in highly-purified carbon tetrachloride, at 25°, but the reaction was far too slow for convenient measurement at that temperature (*cf.* Experimental).

Discussion

The order of the reaction and the effect of added chloride ion seem to rule out any reasonable mechanism involving a preliminary ionization of the sulfenyl chloride. For example (Ar = 2,4-dinitrophenyl; B = styrene)

$$\mathrm{ArSCl} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{ArS^+ + Cl^-}$$

$$\mathrm{ArS^+ + B} \xrightarrow{k_3} [\mathrm{ArSB^+}] \underset{\text{fast}}{\xrightarrow{\mathrm{Cl^-}}} \mathrm{ArSBCl}$$

Such a scheme, depending on the relative magnitudes of k_1, k_2 and k_3, would require either that the rate be independent of the styrene concentration or that the rate be decreased by added chloride ions (mass action effect).

A mechanism which is consistent with the data involves the initial formation of a cyclic sulfonium ion ($\mathrm{ArSB^+}$), which then adds $\mathrm{Cl^-}$ to give the final product—as has been previously postulated.[2b,8]

$$\mathrm{ArSCl + B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\mathrm{ArSB^+}][\mathrm{Cl^-}] \xrightarrow{k_3} \mathrm{ArSBCl}$$

Depending on the relative magnitudes of the constants, the above formulation leads to two simple, second-order rate expressions.

(a) If $k_3 >> k_1$, assuming a "steady state" in $\mathrm{ArSB^+}$, the rate expression is as shown in 1; and if k_2 is also negligible compared to k_3, this becomes 2.

$$-\mathrm{dArSCl}/\mathrm{d}t = k_3k_1[\mathrm{ArSCl}][\mathrm{B}]/k_2 + k_3 \qquad (1)$$

$$-\mathrm{dArSCl}/\mathrm{d}t = k_1[\mathrm{ArSCl}][\mathrm{B}] \qquad (2)$$

In this case, k_1 is the constant for the rate-determining step.

(b) If k_1 and k_2 are both very much greater than k_3, assuming a sustained equilibrium involving $\mathrm{ArSB^+}$, the rate expression (3) would apply

$$-\mathrm{dArSCl}/\mathrm{d}t = k_1k_3[\mathrm{ArSCl}][\mathrm{B}]/k_2 \qquad (3)$$

Equations 1, 2, and 3 are identical in form, and kinetic measurements cannot distinguish between them unless at least one of the rate constants could be evaluated independently. This type of problem is of general interest with regard to other olefin addition reactions, and therefore merits brief discussion here—even though a definite decision as to whether k_1 or k_3 represents the rate-determining step cannot be reached on the basis of the present evidence. It may be noted that the same uncertainty as to the rate-determining step is found in other olefin-addition reactions, although in a few cases the decision has been clearly made. For example, Bartlett and Tarbell[9] demonstrated unequivocally that the attack of bromine on the double bond of stilbene (in methanol) is rate-determining, whereas in the addition of bromine to a number of weakly-nucleophilic olefins (such as vinyl chloride), in acetic acid, the data were more complex,[10] and the rate-determining step could not be specified with certainty.

In the present study a very marked increase in rate was found with glacial acetic acid, rather than carbon tetrachloride, as solvent. In terms of the qualitative theory of Hughes and Ingold,[11] this would imply that the transition state for the reaction of ArSCl with styrene is more ionic than the original reactants, and that this transition state is therefore more stabilized by the polar medium than are the reactants. On first consideration, this might seem to eliminate case (b)—in which ionic intermediates $(\mathrm{ArSB})^+$ and $\mathrm{Cl^-}$ react—in the rate-determining step—to form the non-ionic products, ArSBCl. This would strengthen the argument for case (a)—leading to the conclusion that k_1 is the rate-determining constant. This argument, however, neglects the fact that even in case (b) the preliminary equilibrium, $\mathrm{ArSCl + B \rightleftarrows ArSB^+ + Cl^-}$, is also involved; and when this is taken into account it can be shown that it is the effects of the medium on the activity coefficients of the reactants and on the transition state for the slow step (whichever it may be) which are the determining factors. In the absence of information as to these influences a definite decision cannot be reached from the effects of medium and added salts. Intuitively, however, we incline to the view that the process which involves breaking of the sulfur to chlorine bond (k_1) would require a higher activation energy, and would be slower than the subsequent step (k_3) which involves union of two oppositely-charged ions. In view also of work such as that of Bartlett and Tarbell,[10] we therefore believe that k_1 represents the more likely rate-determining step. The observations (work in progress) that *p*-chloro and *p*-nitro substituents in styrene decrease the rate of addition of I, while *p*-methoxy greatly increases it, are not in disagreement with this view, but again are not decisive.

It is also interesting to note (Fig. 3) that the plot of log k *vs.* ionic strength, μ, is approximately linear (much more nearly so than is a plot of log k *vs.* $\mu^{1/2}$, or of k *vs.* μ). This indicates that this reaction is another example of the so-called exponential salt effect which Brönsted and Wynne-Jones[12] found for the acid-catalyzed hydrolysis of acetal in aqueous solution. Such a linear dependence of log k *vs.* μ has been observed in a number of reactions of neutral molecules with either an ion or another neutral molecule,[13] an especially interesting example being the hydrolysis of *t*-butyl bromide in acetone–water mixtures (80–90% acetone).[14] In this $\mathrm{S_N1}$ reaction (which is analogous in charge-type of the reactants to the reaction of I with styrene, assuming k_1 to be rate-determining) a positive salt effect of appreciable magnitude was observed, but this de-

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[8] D. J. Cram, THIS JOURNAL, **71**, 3884 (1949).

[9] P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).

[10] K. Nozaki and R. A. Ogg, *ibid.*, **64**, 697 (1942).

[11] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 608 (1941), and references there cited. *Cf.* also, A. E. Remick, "Electronic Interpretations of Organic Chemistry," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1949.

[12] J. N. Brönsted and W. K. F. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[13] S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand, Inc., New York, N. Y., 1940, p. 1115 ff.; R. P. Bell, "Acid-Base Catalysis," Oxford University Press, New York, N. Y., 1941, especially pp. 21–35; Moelwyn-Hughes, "Kinetics of Reaction in Solution," Oxford University Press, New York, N. Y., 1933, pp. 187–193; E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, pp. 153–177.

[14] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979–1011 (1940), and preceding and later papers of this group relevant to this reaction.

creased as the ratio of water in the solvent was increased. In general, it appears that salt effects of this type become smaller as the solvating power of the solvent is increased, and may not be observed at all in highly aqueous solutions. While the system I and styrene cannot be studied in aqueous media (because of the rapid hydrolysis of I), the observed positive salt effect for the reaction in glacial acetic acid is not unexpected.

The possibility that acid catalysis is operating in the reaction of I and styrene should not be overlooked. This effect would presumably involve hydrogen bonding with the chlorine atom, and facilitate rupture of the sulfur–chlorine bond in the transition state. The lithium and sodium ions of the salts studied could function similarly by electrostatic attraction.

Acknowledgment.—We wish to express our appreciation to the Office of Ordnance Research for financial support, to the Allan Hancock Foundation of the University of Southern California for their kindness in furnishing facilities for conducting this study and to Milton M. Wald for developing the method of analysis for 2,4-dinitrobenzenesulfenyl chloride.

Experimental[15]

Adduct of 2,4-Dinitrobenzenesulfenyl Chloride to Styrene. II.—Reaction of 7.49 g. of I and 5.00 g. of styrene, in 150 ml. dry acetic acid for two days at room temperature, precipitated crude II, which after recrystallization from absolute alcohol gave 8.59 g. of product, m.p. 142.5–143.5° (79%). Concentration of the mother liquor, and dilution with water, gave 1.42 g. of less pure II (m.p. 139–142°); total yield 92%.

2-Chloro-2-phenylethyl 2′,4′-Dinitrophenyl Sulfone.—To a solution of II (4.00 g. in 150 ml. of dry acetic acid) was added a solution of 3.30 g. of chromic anhydride in 100 ml. of acetic acid. After heating 35 min. on the steam-bath, the mixture was poured into 1800 ml. of ice-water, and the resulting precipitate quickly collected, washed with cold water on the filter plate, and dried over sulfuric acid at 2 mm. pressure. The dry product (3.85 g., m.p. 116–119°) was recrystallized from a hot mixture of 43 ml. of ethylene chloride and 75 ml. of Skellysolve B, using decolorizing charcoal. This gave pale-yellow crystals (2.90 g., 66%), which melted at 119–122°. The m.p. was not raised by further recrystallization.

Anal. Calcd. for $C_{14}H_{11}ClN_2O_6S$: C, 45.35; H, 2.99. Found: C, 45.60; H, 3.20.

2,4-Dinitrophenyl Styryl Sulfone.—To 0.50 g. of the above sulfone, dissolved in 20 ml. of dry benzene, 2.0 g. of triethylamine was added. Some amine hydrochloride precipitated immediately, and after 3 hr. the amine salt was collected, using benzene to effect a quantitative transfer and to wash the salt. The desolvated salt weighed 0.18 g. (equiv. to 97% dehydrohalogenation) and was entirely water soluble. The benzene filtrate was extracted with 10% hydrochloric acid, and then with water, dried (Na_2SO_4) and the solvent was removed *in vacuo*. The residue consisted of pale-yellow crystals, which were transferred by means of 10 ml. of ethanol to a filter plate. The product was washed with Skellysolve A and dried *in vacuo;* 0.415 g. (92%); m.p. 165–166° (unchanged by further recrystallization).

Anal. Calcd. for $C_{14}H_{10}N_2O_6S$: C, 50.30; H, 3.01. Found: C, 50.38; H, 3.17.

2,4-Diacetaminophenyl 2′-Phenylethyl Sulfone. III.—This product was obtained by both routes shown in Fig. 1.

(a).—The above sulfone (*m*.p. 165–166°); 0.50 g., in 50 ml. of ethyl acetate, was shaken on the hydrogenator for 14 hr., using *ca.* 0.2 g. of Raney nickel, and an initial pressure of 0.37 lb./sq. in. of hydrogen. The catalyst was collected and washed with 50 ml. of ethyl acetate. The filtrate and washings were refluxed for one hour with 5 ml. of acetic anhydride, and the solution then concentrated to *ca.* 15 ml. at reduced pressure. About 5 ml.of water and 20 ml. of ethanol were added, and the solution again concentrated to *ca.* 10 ml. Cooling to 5° led to a heavy deposit of white crystals, which were collected, washed successively with 50% aqueous alcohol, dilute sodium carbonate, dilute hydrochloric acid, and water; and then dried at 76° (2 mm.). The product (288 mg.) melted at 169.5–171°, after recrystallizing from an ethylene chloride–Skellysolve B mixture. The melting point varied somewhat with the rate of heating, but the above value was consistently obtained if the bath was preheated to 140° and the temperature then raised 3°/min.

Anal. Calcd. for $C_{18}H_{20}N_2O_4S$: C, 59.98; H, 5.59. Found: C, 59.78; H, 5.38.

(b).—Starting with 2,4-dinitrothiophenol (see Fig. 1), 2,4-dinitrophenyl 2′-phenylethyl sulfide was obtained in 68% yield, m.p. 92.6–93.6°,[16] and this was converted to the corresponding sulfone (m.p. 131–132°, lit.[16] 133°) in 86% yield. The hydrogenation and acetylation were carried out similarly as above, but the period used for hydrogenation was 7 hr.

With controlled heating of the bath (see above), the products from routes a and b melted identically and there was no depression in observed m.p. on admixture.

Materials and Methods for the Kinetic Measurements.—Dry acetic acid was obtained by refluxing the 99.5% acid (Baker and Adamson, reagent grade) with acetic anhydride (*ca.* 50 ml./l. of acid) for 15–20 hr., then distilling through a 90-cm. column (packed with glass helices) at the rate of *ca.* 100 ml./day. The middle cut (600–700 ml.) from one liter of distillate was used. The column was protected from moisture by a drying tube, and the receiver was sealed with paraffin when detached from the column. The freezing point of the acid was always checked just before mixing a solution for a rate run; and only acid freezing above 16.6° was used.

2,4-Dinitrobenzenesulfenyl chloride was the commercial reagent, twice recrystallized from carbon tetrachloride, and dried by pumping at 2 mm., with heating for a short period (*in vacuo*) at 76°. This reagent was always so purified not more than 24 hr. preceding its use in a rate run, but the dry reagent appears to keep suitably for a much longer period when stored in a dark bottle at room temperature.

Styrene was the stabilized product (Matheson Co.) redistilled at reduced pressure prior to each run.

Lithium chloride was the C.P. reagent, dried by heating 5 hr. at 130°, and cooled in a desiccator. Sodium perchlorate was also the C.P. reagent, dried at 130° for 5 hr. and then for 20 min. at 190°, prior to cooling in a desiccator.

Rate Run.—A typical rate run was carried out as follows. Stock solutions of the sulfenyl chloride and styrene were prepared by weighing the proper amounts of the freshly-purified materials, and preparing solutions of desired volume with dry acetic acid at 20°. These were then brought to temperature in the constant-temperature bath, and equal volumes were pipetted and mixed for the run. Initial concentrations were corrected for the volume increases incurred in changing from 20° to the temperature of the run. Aliquots of the solution were taken with a 10-ml. pipet (calibrated with acetic acid at the temperature of the run) and drained into a dry, glass-stoppered flask containing 0.5 g. of dry sodium iodide and about 10 ml. of dry acetic acid. The sodium iodide was predried at 105–110° and cooled in a desiccator. Potassium iodide was not as suitable, for it did not give a quantitative release of iodine in the 3-minute period used in the titration—probably because of the solubility difference. The stopper was replaced, the contents of the flask were gently swirled, the flask let stand exactly 3 min., 50 ml. of water was added, and the released iodine was titrated with standard sodium thiosulfate solution. Starch indicator solution was added as the end-point was approached, and the end-point taken when the last trace of blue color disappeared. This end-point is not as sharp as in aqueous solutions, and it is necessary to stopper the flask and shake vigorously near the end of the titration to ensure

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[15] We are indebted to Dr. Adalbert Elek for the microanalyses. Melting points are not corrected.

[16] The procedure followed was that of R. W. Bost, P. K. Starnes and E. L. Wood, THIS JOURNAL, **73**, 1968 (1951), who give m.p. 89.5°. Our crude product was washed with 5% potassium hydroxide, cold 90% ethanol, and then water, prior to recrystallization from absolute alcohol.

complete escape of the iodine from the insoluble organic material. Blanks were taken on the sodium iodide under the same conditions, and the small corrections deducted from the volumes of thiosulfate solution required to titrate the aliquots. The concentration of sulfenyl chloride was calculated from the corrected volume of thiosulfate. Titrations of known weights of the sulfenyl chloride by this procedure were quantitative, with a precision of about 1%. The concentration of styrene in the solution at any time was calculated from the measured concentration of the sulfenyl chloride, and the difference in initial concentrations of the two reactants. The concentration of sulfenyl chloride at infinite time served as a check on the initial concentrations, as well as on the quantitative nature of the reaction. The agreement was always within 1–2%. The specific reaction-rate constants were calculated from the familiar, second-order expression

$$k = \frac{2.303}{t(a - b)} \times \log \frac{b(a - x)}{a(b - x)}$$

One run was attempted to carbon tetrachloride, purified by the procedure of Price,[17] at 25°, and using initial concentrations of 0.0152 and 0.0589 *M*, respectively, for sulfenyl chloride and styrene. Ten-ml. aliquots were titrated for I at intervals up to 8000 min. The precision of the titrations in this solvent were not as good as in the acetic acid runs, but the results were sufficiently accurate to show that the reaction had scarcely proceeded after 8000 minutes.

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(17) C. C. Price, THIS JOURNAL, **58**, 1834 (1936).

LOS ANGELES, CALIFORNIA

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

Derivatives of Sulfenic Acids. XIV. 2,4-Dinitrobenzenesulfenium Ion

BY NORMAN KHARASCH, CHARLES M. BUESS[1] AND WILLIAM KING

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Several lines of evidence support the conclusion that the interaction of 2,4-dinitrobenzenesulfenyl chloride and sulfuric acid involves the equilibrium: $(NO_2)_2C_6H_3SCl + H_2SO_4 \rightleftarrows [(NO_2)_2C_6H_3S]^+ + HCl + HSO_4^-$.

In connection with an earlier study[2] of the reaction of 2,4-dinitrobenzenesulfenyl chloride, I, with aromatic systems under Friedel–Crafts conditions, it was noted that solutions of I in sulfuric acid are distinctly red. The purpose of the present study was to elucidate the nature of this color.

Because it was suspected that ionization of I—or of the intermediate sulfenic acid, $(NO_2)_2C_6H_3SOH$—was involved (see equation 1, below) the following data were obtained to determine whether such was indeed the case.

(a) The yellow, crystalline sulfenyl chloride dissolves in 96 or 100% acid to form stable bright red solutions.

(b) Solution of I in sulfuric acid is accompanied by evolution of hydrogen chloride, pointing to scission of the sulfur–chloride bond.

(c) The red color migrates to the cathode during electrolysis of solutions of I in 100% sulfuric acid.

(d) Addition of bisulfate ions (fused anhydrous potassium bisulfate) to solutions of I in 96% acid visibly repressed the red color; and this observation was corroborated by the effect of added bisulfate ions on the absorption spectrum of the solution (Fig. 1B). Similarly, addition of excess, dry hydrogen chloride to dilute solutions of I in concentrated sulfuric acid entirely repressed the development of the red color, giving an absorption characteristic of I, rather than of the solutions of I in absence of excess hydrogen chloride (compare Figs. 1A and 1C). As suspected, solutions of I in concentrated sulfuric acid do not obey Beer's law.

(e) Sulfuric acid solutions of I react rapidly with benzene, whereas reaction fails to occur in the absence of sulfuric acid or other Friedel–Crafts catalysts.[2] The expected product, 2,4-dinitrophenyl phenyl sulfide, was isolated in 30% yield—the low yield being associated with difficulties attending isolation of the sulfide from concentrated sulfuric acid.

(f) Cryoscopic measurements of dilute solutions of I in sulfuric acid led to van't Hoff "*i*" factors between 1.6 and 2.6.

(g) The following related observations were also made. (1) While 2,4-dinitrobenzenesulfenyl bromide and thiocyanate also give the same characteristic color as do solutions of I in sulfuric acid, 2,4-dinitrobenzenesulfenamide does not give this color effect. 2,4-Dinitrochlorobenzene, bis-(2,4-dinitrophenyl) disulfide and 2,4-dinitrothiophenol also do not give colored solutions in sulfuric acid. (2) Addition of a variety of other basic substances (besides benzene, *cf.* item e, above) also discharge the red color of I in sulfuric acid solutions. (3) Solutions of I in dry ethylene chloride give typical red colors when treated with aluminum chloride or silver perchlorate. (4) 2-Nitrobenzenesulfenyl chloride (pale yellow) also gives a stable, distinct orange color when dissolved in concentrated sulfuric acid.

In view of the above observations, we believe that the major behavior involved when I dissolves in sulfuric acid may be expressed by equation 1.

$$(NO_2)_2C_6H_3SCl + H_2SO_4 \rightleftarrows [(NO_2)_2C_6H_3S]^+ + HCl + HSO_4^- \quad (1)$$

The red color of the solution is ascribed to the positive ion, for which the name *2,4-dinitrobenzenesulfenium ion* is suggested. The reaction with benzene and other bases is to be expected, as are also the cathodic migration, the effects of added bisulfate ions and of hydrogen chloride, and the values found for the dissociation factors (eq. 1 requires a maximum of 3, assuming non-ionization of the HCl). The related color formation with aluminum chloride probably involves the interaction, $ArSCl + AlCl_3 \rightleftarrows ArS^{+\delta}AlCl_4^{-\delta}$ (Ar =

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(1) XIII, W. L. Orr and N. Kharasch, THIS JOURNAL, **75**, 6030 (1953).

(2) C. M. Buess and N. Kharasch, *ibid.*, **72**, 3529 (1950).