[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Reaction of Diazonium Salts with Nucleophiles. VIII. The Formation of Diazosulfones and the Application of Linear Free Energy Equations to Diazonium Salt Reactions[1]

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The reaction of diazonium salts with aromatic sulfinic acids to give diazosulfones in buffered methanol solutions has been studied spectrophotometrically. It was possible to determine both rate and equilibrium constants for the reaction of several substituted diazonium salts and several substituted sulfinic acids. The Hammett equation was successfully applied to rates and equilibria for series in which substituents were varied on either the diazonium salt or the sulfinic acid. The results are discussed in terms of factors determining ρ for these series. The possibility of predicting ρ for other diazo equilibria is examined.

Introduction

The diazosulfones, studied many years ago by Hantzsch,[2] are examples of the covalent diazo compounds. Unlike many other such compounds, there has been no compelling evidence of stereoisomerism in this case,[3] possibly due to the lowering of the barrier to rotation about the $N=N$ bond by contributions of expanded octet structures such as Ib.

Ia   Ib
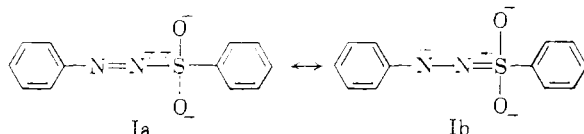
The possibility that the formation of diazosulfones could be studied by the methods previously used to measure equilibrium constants for the formation of other covalent diazo compounds[4-6] was realized.

Methods and Results

The reactions were followed by the change in absorbance of the solutions at a wave length where the diazosulfone absorbed more strongly than did the diazonium ions. In water, solutions 10^{-6} molar in both reactants showed no perceptible change. In 10^{-2} molar solutions, the diazosulfone rapidly precipitated, and the supernatant liquid did not have enough absorbance for accurate measurement. Because of the solubility limitation, methanol was used as solvent. The product precipitated from water dissolved readily in methanol and showed the same absorption spectrum as was obtained by mixing the reagents in methanol solution.

Several complications are present in this system. In unbuffered, or weakly acid methanol solutions, the decomposition of diazonium ions is rapid.[7] It was found that buffers consisting of either trichloroacetic acid or dichloroacetic acid and the corresponding sodium salt inhibited this decomposition while still allowing sufficient ionization of the sulfinic acids for diazosulfone formation to take place at a reasonable rate.

(1) Paper VII, E. S. Lewis and M. D. Johnson, J. Am. Chem. Soc., 82, 5408 (1960).

(2) A. Hantzsch and M. Singer, Ber., 30, 312 (1897).

(3) Cf., however, H. C. Freeman, R. J. W. LeFèvre, J. Northcutt and I. Youhotsky, J. Chem. Soc., 3381 (1952).

(4) E. S. Lewis and H. Suhr, Chem. Ber., 92, 3043 (1959).

(5) E. S. Lewis and H. Suhr, ibid., 91, 2330 (1958).

(6) E. S. Lewis and H. Suhr, ibid., 92, 3031 (1959).

(7) D. F. DeTar, J. Am. Chem. Soc., 78, 3911 (1956).

In solutions much above 10^{-5} molar in diazosulfone, another reaction became important. The incursion of this reaction could be recognized by the fact that the equilibrium solutions no longer gave spectrophotometric analyses which accounted for all of the added diazonium salt. We have made no attempt to isolate the product of this reaction, but it appears possible, in analogy with the reaction of diazosulfonates,[6] that the reaction involves the reduction of the diazosulfone.

Equation 1 describes the formation of diazosulfones. Assuming a second-order forward reaction and first-order reverse reaction, the rate of the reaction is given by eq. 2.

$$ArSO_2^- + ArN_2^+ = ArN_2SO_2Ar' \qquad (1)$$

$$d(ArN_2SO_2Ar')/dt = k_+(ArN_2^+)(Ar'SO_2^-) - k_-(ArN_2SO_2Ar') \qquad (2)$$

Letting a constant in the buffered solutions, and

$$f = \frac{(Ar'SO_2^-)}{(Ar'SO_2^-) + (Ar'SO_2H)}$$

using the subscripts 0 and eq to represent initial and equilibrium concentrations, respectively, routine integration gives

$$fk_+t = \frac{(ArN_2SO_2Ar')_{eq}}{(Ar'SO_2^-)_0 + (Ar^+SO_2H)_0(ArN_2^+)_0 - (ArN_2SO_2Ar')^2_{eq}}\ln g + \text{const.}$$

where

$$g = \frac{(ArN_2SO_2Ar')(ArN_2SO_2Ar')_{eq} - [(Ar'SO_2^-)_0 + (Ar'SO_2H)_0](ArN_2^+)_0}{(ArN_2SO_2Ar')(ArN_2SO_2Ar')_{eq} - (ArN_2SO_2Ar')^2_{eq}}$$

$$(3)$$

Thus, a plot of the logarithmic term, g, versus time allows the calculation of the forward rate constant, k_+, since f may be measured experimentally. A typical plot of the data for diazosulfone formation is shown in Fig. 1. The linearity of the plot shows the applicability of eq. 2. The measurement of $(ArN_2SO_2Ar')_{eq}$ also allows the calculation of the equilibrium constant K_{assoc}, defined in eq. 4

$$K_{assoc} = \frac{(ArN_2SO_2Ar')_{eq}}{(ArN_2^+)_{eq}(Ar'SO_2^-)_{eq}} \qquad (4)$$

and from this, the first-order constant k_-.

The values of these constants for the various diazonium ions and sulfinic acids studied are shown in Table I.

Table I

Constants for the Formation of Diazosulfones

$$XC_6H_4N_2^+ + YC_6H_4SO_2^- \rightleftharpoons XC_6H_4N_2SO_2C_6H_4Y$$

	X =	Y =	$K_{assoc.} \times 10^{-5a}$	$k_+ \times 10^{-5a}$	$k_- \times 10^{5a}$	$pK_a{}^b$	$\sigma_x{}^c$	$\sigma_y{}^c$
1	p-Cl	p-Br	0.350	0.473	1.35	1.09	0.227	0.232
2	..	m-NO₂	....	..	...	0.48	...	.710
3	p-Cl	p-CH₃	2.32	1.84	0.794	1.24	0.227	− .170
4	p-Cl	p-NO₂	0.0240	0.125	5.21	0.64	.227	.778
5	p-Cl	H	1.09	.983	0.901	1.21	.227	.00
6	p-CH₃	H	0.0438	.158	3.62		− .170	.00
7	H	H	0.144	.324	2.23		.00	.00
8	p-Br	H	1.35	.715	0.529		.232	.00
9	m-Cl	H	7.76	3.64	.470		.373	.00
10	m-CF₃	H	13.9	4.72	.354		.43	.00
11	p-CN	H	47.7	14.7	.324		.660	.00
12	p-NO₂	H	103	19.2	.187		.778	.00

[a] Methanol solution, ionic strength $= 2 \times 10^{-3}$; k_+ in units of l.-moles⁻¹.sec.⁻¹; k_- in units of sec.⁻¹; K_{assoc} in units of l.-moles⁻¹. [b] Negative logarithm of the acidity constant of the sulfinic acid measured in 0.090 molar aqueous perchloric acid; uncorrected for ionic strength. [c] D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958).

It is difficult to estimate the errors in these constants. The reproducibility in successive determinations of k_+, with initial concentrations varying by a factor of 2 to 5, was in no case worse than $\pm 20\%$, and was generally better than $\pm 10\%$. The association constants showed an extreme deviation of $\pm 40\%$ for entries number 4 and 12 of
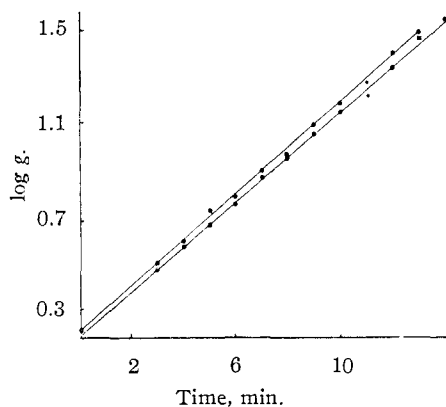

Fig. 1.—Plot of the rate data for the reaction of m-ClC₆H₄N₂⁺ with C₆H₅SO₂⁻ according to eq. 3.

Table I, but were generally better than $\pm 10\%$. Of the several sources of error present, we feel that the side reaction involving the diazosulfone is the most troublesome. If the measurement of f were a source of error, k_- should have been more reproducible than k_+ or K_{assoc}, since it is independent of the value of f. This was not the case.

Discussion

The Hammett equation was applied to the data of Table I. Least squares treatment of the data produced the following equations.

For the reaction of substituted diazonium ions with benzenesulfinate

$$\log K_{assoc} = 3.76 + 5.26 \tag{5}$$
$$\log k_+ = 2.40 \, \sigma + 2.52 \tag{6}$$
$$\log k_- = -1.36 \, \sigma - 2.74 \tag{7}$$

For the reaction of substituted benzenesulfinates with p-chlorobenzenediazonium ion

$$\log K_{assoc} = -2.07 \, \sigma + 6.02 \tag{8}$$
$$\log k_+ = -1.20 \, \sigma + 3.01 \tag{9}$$
$$\log k_- = 0.87 \, \sigma - 3.01 \tag{10}$$

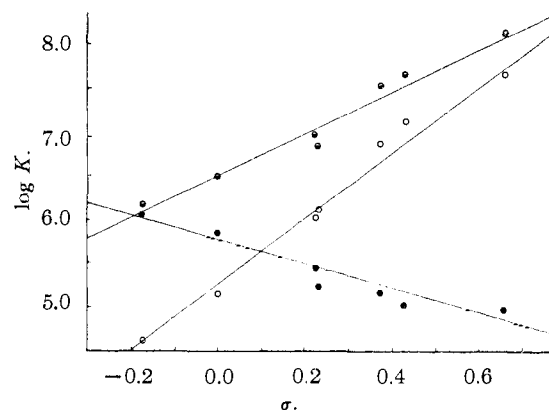Plots of the data are shown in Figs. 2 and 3.

Fig. 2.—ArN₂⁺ + C₆H₅SO₂⁻ = ArN₂SO₂C₆H₅: O = log K_{assoc}; ◐ = log k_+ + 4.00; ● = log k_- + 8.50.

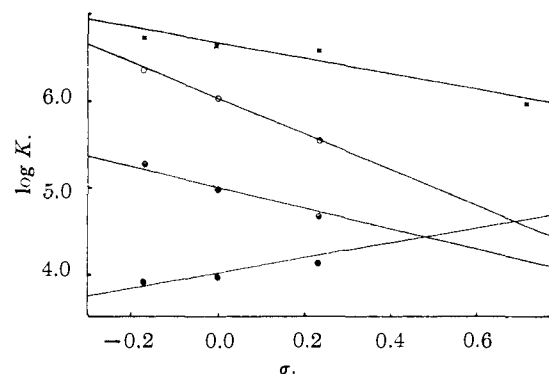Fig. 3.—p-ClC₆H₄N₂⁺ + ArSO₂⁻ = p-ClC₆H₄N₂SO₂Ar. O = log K_{assoc}; ◐ = log k_+ + 2.00; ● = log k_- + 7.00; x = pK_a + 5.50 of sulfinic acids.

The value of ρ in eq. 8 appeared inconsistent with a previously reported ρ of zero for the ionization of sulfinic acids.[8] We therefore determined

(8) R. K. Burkhard, D. E. Sellers, F. DeCou and J. L. Lambert, J. Org. Chem., 24, 767 (1959).

the acidity constants of the sulfinic acids used in this study by a spectrophotometric method. These values are reported in Table I. The previously reported values for all of these acids are $pK = 1.81 \pm 0.1$, corrected to zero ionic strength. We can offer no explanation of these discrepancies, except to note the difficulties attendant in the determination of the acidities of strong acids by the titration method. The values reported here are correlated with fair precision by the eq. 11, as shown in Fig. 3.

$$\log K = 0.976\, \sigma - 1.23 \qquad (11)$$

This ρ is very close to that which would be expected if the proton is lost from oxygen, and the charge remains localized on oxygen. If contributions from structures in which the charge is located on sulfur were important, we should expect ρ to reflect this by being similar to that of the benzeneboronic acids ($\rho = 2.2$) rather than to that of benzoic acids.[9]

In many of the early applications of the Hammett equation to series in which multiple variations in structure could be produced, it was assumed that the $\log K$ surface for the series would be planar.[10] Miller[11] has recently shown that this is not necessarily true, and that, in fact, some of the existing data require a non-planar surface; i.e., ρ for the variation of one substituent is a function of the other substituents, rather than being constant.

It is of interest to inquire, then, of the $\log K$ surface for the present series is planar. The data of Table I do not allow an experimental determination of the curvature of the surface since all of the points fall on two intersecting lines.

In dual substitutions, two sets of Hammett equations are applicable

$$\log K_{ij} = \sigma_i \rho_i{}^I + \log K_{0j} \qquad (12)$$

$$\log K_{ij} = \sigma_j \rho_i{}^I + \log K_{i0} \qquad (13)$$

In these equations, the substituent at position I is identified as i, and that at position J, as j. Thus, σ_i is the substituent constant of substituent i, and $\rho_j{}^I$ is the reaction constant for variation of the substituent at position I while the substituent j is held constant.

Substituting in these equations the values of K_{i0} and K_{0j} given by 12 and 13, respectively, gives 14

$$\log K_{ij} = \sigma_i \rho_i{}^I + \sigma_j \rho_0{}^J + \log K_{00} = \sigma_j \rho_i{}^J + \sigma_i \rho_0{}^I + \log K_{00} \qquad (14)$$

or on rearrangement

$$\frac{\rho_i{}^I - \rho_0{}^I}{\sigma_j} = \frac{\rho_i{}^J - \sigma_0{}^J}{\sigma_i} \qquad (15)$$

In order for the Hammett equation to hold, $\rho_j{}^I - \rho_0{}^I$ must be independent of σ_i, and $\rho_i{}^J - \rho_0{}^J$ must be independent of σ_j. From eq. 15, this condition is fulfilled only if

$$\frac{\rho_j{}^I - \rho_0{}^I}{\sigma_j} = \frac{\rho_i{}^J - \rho_0{}^J}{\sigma_i} = \text{constant} \equiv q^{12} \qquad (16)$$

Sager and Ritchie[13] have developed the equation

$$\rho = (1.8 + 67/e)(\sigma_R{}^* - \sigma_P{}^*) \qquad (17)$$

where the subscript R and P refer to the reaction site group in the reactant and product, respectively, and e is the dielectric constant of the solvent. They have also shown that

$$\sigma^* C_6 H_4 X = \sigma_x + 0.600 \qquad (18)$$

In the present case, R would refer to the $N_2{}^+$ group, and P to the N_2SO_2Ar' group. Thus

$$\rho_j{}^I - \rho_0{}^I = (1.8 + 67/e)(\sigma_{P(0)}{}^* - \sigma_{P(j)})^* \qquad (19)$$

where the 0 and j refer to the unsubstituted and substituted phenyl group of the phenyl sulfinate moiety, respectively.

The difference in σ^*-values in eq. 19 is the effect of the substituent j transmitted through the $C_6H_5N_2SO_2-$ group. The effect up to the nitrogen next to the ring can be calculated from eq. 18, to be σ_j. The effect at the other ring, then, will be this quantity divided by the fall-off factor for the N=N group and the S atom. We may approximate these factors as equal to those of the CH=CH group and the CH_2 group, respectively,[14] 1.5 and 2.8.

The use of these factors, and the combination of eq. 16, 18 and 19 gives

$$q = 0.62 \qquad (20)$$

In the case of the diazosulfones, then, the maximum change in ρ which could be produced by substitution on either the diazo or sulfinate moiety would be 0.4 (for the p-NO_2 group). With the experimental precision realized in this system, this would hardly be distinguishable from the values reported here. The curvature in the surface would be observable, however, in cases where the substituents are not as far separated as in the present case.

The reaction constants for all of the diazo equilibria studied thus far are listed in Table III. It is of interest to see how these values compare with those predicted by the relationships recently developed by Sager and Ritchie.[13]

We shall assume that the difference in σ^*-values for the $N_2{}^+$ and the N_2X groups is due to the change in hybridization of nitrogen and to the existence of formal electronic charges. Moffitt[15] has calculated electronegativities of some of the more common elements in various bonding states. Sager and Ritchie[13] have shown that there is a linear relationship between σ^*-values and electronegativities. In order to evaluate the proportionality constant in this relationship for the present case, we have plotted the Moffitt electronegativities of hydrogen and of carbon in sp³-, sp²- and sp-hybridization against the σ^*-values for H, $C_6H_5CH_2CH_2$, $C_6H_5CH=CH$ and $C_6H_5-C\equiv C$, respectively. The pertinent values are shown in Table II. The equation

$$(\sigma_i{}^* - \sigma_j{}^*) = 10(X_i - X_j) \qquad (21)$$

describes the data very well. The σ^*-values for nitrogen in sp- and sp²-hybridization, found from

(9) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(10) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(11) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959).

(12) q is defined by Miller in the general equation: $\log K_{ij} = \sigma_i \rho_0{}^I + \sigma_i\sigma_j q + \sigma_j\rho_0{}^J + \log K_{00}$; cf. ref. 11.

(13) W. F. Sager and C. D. Ritchie, *J. Am. Chem. Soc.*, **83**, 3498 (1961).

(14) The factor 2.8 is taken from ref. 9. The value of 1.5 is from H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

(15) W. Moffitt, *Proc. Roy. Soc. (London)*, **A202**, 548 (1950).

TABLE II

ELECTRONEGATIVITY AND σ^*-VALUES

Group	Moffitt's electronegativity[a]	σ^{*b}
$C_6H_5CH_2CH_2$	0.14	0.080
$C_6H_5CH{=}CH$	.19	0.410
$C_6H_5C{=}C$	.26	1.35
H	.19	0.490
N_{sp}	.38	(2.5)
N_{sp^2}	.33	(2.0)

[a] Ref. 15. [b] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.

TABLE III

RHO VALUES FOR DIAZO EQUILIBRIA

$$ArN_2^+ + X = ArN_2X$$

X =	Obsd. ρ	Calcd. ρ
CN^-	4.7[c]	4.2
O^-	6.3 $(7.2^a)^d$	6.1
SO_3^-	5.1[e]	4.9
$C_6H_5SO_2^-$	3.8	Cf. Disc.

[a] η' value based on m-substituents; cf. R. W. Taft, Jr., J. Am. Chem. Soc., 81, 5343 (1959). [b] The approximate diminution factors for the effect of the negative charge in the product are those given in footnote 14. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6.

the plot of the data, are also shown in Table II. The difference in σ^*-values is -0.5 unit. The change in σ^* due to the neutralization of the unit charge is -1.1.[13] Thus, the total change is -1.6. The values calculated by the use of this number and eq. 17 are shown in Table II. The agreement is surprisingly good considering the crudeness of the method of calculation.

The small ρ observed for the diazosulfone equilibrium is expected from the consideration of structures such as I-b where a partial charge remains localized on the nitrogen. Thus, the absence of stereoisomerism and the small ρ are correlated.

Equation 17 should also be useful for gleaning information about the nature of the transition states of reactions.

Since ρ for the rate of diazosulfone formation (eq. 7) is larger than that for the reverse reaction, we would conclude that the structure of the transition state is closer to that of products than to that of reactants. Quantitatively, two-thirds of the rehybridization, and charge neutralization has taken place in the transition state. The fact that the ratio of ρ for the forward rate constants to that for the equilibrium constants is the same for substituted diazonium ions and for substituted sulfinate ions indicates that no unusual charge distributions exist in the transition state.

Zollinger[16] has found ρ for the coupling of substituted diazonium salts with 2,6-naphthylaminesulfonic acid to be 4.15. Compelling evidence has been offered that the intermediate II lies along the reaction coördinate.[17]

From the arguments presented earlier, we should expect a ρ of 4.0 if the transition state resembles II, assuming for the purpose of calculation that the positive charge is localized between the 2- and 3-position of the naphthalene ring. This value is

(16) H. Zollinger, Helv. Chim. Acta, 36, 1730 (1953).

(17) H. Zollinger, ibid., 38, 1597, 1617 (1955).

II
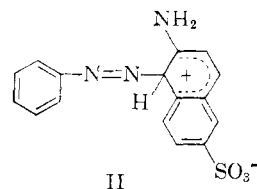
in good agreement with that observed, indicating that the transition state is indeed similar to the intermediate II.

Hammond's discussion of electrophilic aromatic substitution, based on a consideration of the energy of activation of such reactions, leads to approximately the same conclusion.[18]

Rho for the coupling of diazonium salts with 2,6-naphtholsulfonic acid, however, is only 3.5.[16] In this case, the intermediate corresponding to II bears no formal charge except on the distant and unchanging SO_3^- groups. Thus, if the transition state resembles the intermediate, we should predict a ρ of 4.2. Our arguments thus lead us to the postulate that the transition state for this reaction is somewhat closer to reactants than is that for the reaction of naphthylaminesulfonic acid. In terms of Hammond's postulate,[18] this predicts that the intermediate formed from the naphthol derivative is more stable than that from the naphthylamine. This is a pleasingly reasonable prediction.

Experimental

Materials.—All diazonium fluoroborates were prepared by conventional methods and were recrystallized from methanol–acetone mixtures at low temperatures to constancy of their ultraviolet absorption spectra.

Eastman Kodak Co. sodium benzenesulfinate was used without further purification. Eastman Kodak Co. sodium p-toluenesulfinate was recrystallized from water to constancy of the ultraviolet spectrum, and dried under vacuum.

m-Nitro-, p-nitro- and p-bromobenzenesulfinic acids were prepared from the corresponding sulfonyl chlorides by the method of Krishna and Singh.[19] The sulfinic acids were recrystallized several times from water, and dried under vacuum overnight. The acids were stored in a vacuum desiccator, and no changes in their ultraviolet spectra were noted over the period of several weeks. Purity of the compounds was checked by melting point, neutralization equivalent, and constancy of the ultraviolet spectrum.

Reagent grade methanol was used without further purification.

Spectra.—All spectra were measured using a Cary model 14 spectrophotometer with the cell compartment warmed by water circulated from a thermostat at 29.5°. Since the room temperature was not much below this, the cell temperature was not more than 0.5° lower than the thermostat temperature.

In all cases, the sulfinate ions showed absorption at longer wave lengths than did the corresponding acids. It was thus possible to analyze for both components in solutions of the acids, and therefore to determine the fraction in the acid or ionized form.

The diazosulfones all showed absorption in the neighborhood of 320 mμ while the diazonium ions absorbed near 289 mμ. Both of these compounds have extinction coefficients at least twenty times larger than those of the benzenesulfinic acids or sulfinates, with the exception of the p-nitrobenzenesulfinic acid. It was thus possible to make a two-component analysis of the reaction mixtures for the diazosulfone and the diazonium ion. With the p-nitrobenzenesulfinic acid, since the acid was completely ionized in the reaction mixtures, it was possible to make a three-component analyses of the solutions. An analysis accounting for 95–105%

(18) G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

(19) S. Krishna and H. Singh, ibid., 50, 792 (1928).

of the added diazonium ion was used as a criterion for the acceptance of the measurements of the rate and equilibrium constants.

Buffers.—Eastman Kodak Co. trichloroacetic acid was used without further purification. Dichloroacetic acid was distilled at atmospheric pressure through a 50-cm. Vigreux column. The fraction boiling between 193.5 and 194.5° was collected and used for the preparation of buffers.

The buffer solutions were prepared by adding weighed amounts of the acid to a known volume of 2.0×10^{-3} molar sodium hydroxide in methanol, which had been standardized by titration with standard hydrochloric acid.

Rate and Equilibrium Measurements.—The sulfinate or sulfinic acid and the diazonium salts were prepared in separate $ca.$ 10^{-2} molar stock solutions; the diazonium salt solutions were stabilized by the addition of 10^{-3} molar HCl. On further dilution, this amount of acid was neglected. Measured samples of each of the stock solutions were diluted with the buffer solution, mixed, and placed in the absorption cell. The reaction was followed by the change in absorbance of the solutions near 320 μ. When no further change with time was noted, the entire spectrum from 220 μ

to 360μ was recorded. This spectrum was used for the analysis of the reaction mixture for the components.

Another sample of the same buffer, and another sample of sulfinate solution were mixed alone to determine the fraction, f, in the ionized form.

The spectrum of the diazosulfone was determined from the absorbance of $ca.$ 10^{-2} molar solutions of the reactants in thin cells, so that dissociation would be small. Measurements were made rapidly after mixing in order to eliminate as much as possible the decomposition of the diazosulfone as a factor in the measurement. Although some error could have been introduced from this decomposition, it was possible to obtain reproducible spectra. The minor corrections for dissociation in these solutions were calculated after first tentative association constants were calculated, then the new extinction coefficients were used to calculate refined association constants. Further cycles were not necessary.

[Contribution from the George Herbert Jones Laboratory of the University of Chicago, Chicago 37, Ill.]

Rates, Relative Rates and Product Distributions for the Non-catalytic Chlorination of Benzene, Toluene and t-Butylbenzene in Certain Non-aqueous Non-hydroxylic Solvents. The Influence of Solvent on the Reaction and the Baker–Nathan Effect

By Leon M. Stock and Albert Himoe[1]

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The non-catalytic chlorination of benzene, toluene, t-butylbenzene and p-xylene has been examined in several solvents with particular reference to the influence of the reaction medium on the relative rate: $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$. Certain results for the absolute rates of reaction, competitive measurements of relative rates and product distributions for the chlorination of the aromatics in nitromethane, nitrobenzene, acetonitrile, acetic anhydride and chlorobenzene are presented in this manuscript. In summary, the absolute rate of chlorination of toluene in nitromethane was approximately 10^4 greater than the rate in chlorobenzene. Product distributions were observed to be dependent on the reaction solvent. Moreover, the selectivity of the reagent chlorine was found to be appreciably modified by the solvent. However, the relative rate, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$, was not altered significantly beyond the variation expected for the observed reagent selectivity and was measured to be somewhat larger in these solvents than in aqueous acetic acid media.

Introduction

Considerable interest in the Baker–Nathan effect has led to a number of different views concerning its origin.[2] Of the alternative explanations for the apparent greater electron donor ability of a methyl substituent compared to a t-butyl substituent in certain electron-deficient reactions, two ideas have become familiar. The concept of hyperconjugation[3] as an electrical influence and the suggested steric inhibition of solvation by the t-butyl group have been presented in detail.[2,4] In a recent study, these alternatives have been examined through an investigation of the influence of solvent on reactivity and relative reactivity in a typical electrophilic substitution reaction.[5]

The non-catalytic chlorination reaction of benzene and the alkylbenzenes was selected as the model reaction for the evaluation of substituent effects on the basis of its high selectivity, $\rho = -10$, the relatively simple kinetics and mechanism, the highly electron-deficient transition state and the

dependence of the reaction rate on the composition of the solvent.[6] This reaction was examined in six acetic acid solvents varying in water content from 0.0 to 27.6 M. The absolute rate of chlorination of benzene changed by 6.3×10^3 from the anhydrous to highly aqueous media. However, the relative rates for the alkylbenzenes compared to benzene exhibited only minor changes. Indeed, the quantity log p_f^{Me}/log $p_f^{t\text{-Bu}}$ was 1.10 ± 0.02 among the six solvents. On the basis of these observations, it was concluded that the Baker–Nathan effect did not have its origin in solvation phenomena.[5] It is clear that the results are not decisive as the relative importance of solvation of the electron-deficient aromatic residue and the departing chloride ion has not been assessed. In an attempt to evaluate the importance of solvation as a stabilizing factor on the two fragments of the transition state, it appeared desirable to examine a group of structurally different solvents. In the different reaction media, the degree of solvation of the component parts of the activated complex could be expected to vary according to the properties of the polar and non-polar fragments of the solvent. This approach appeared to offer an opportunity to assess the influence of major structural variations

(1) Research Corporation Fellow, 1959–1961.

(2) For a partial review see, *Tetrahedron*, **5**, 107 (1959).

(3) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959); W. M. Schubert and R. G. Minton, *J. Am. Chem. Soc.*, **82**, 6188 (1960).

(5) L. M. Stock and A. Himoe, *ibid.*, **83**, 1937 (1961).

(6) See ref. 5 for literature citations and a more detailed discussion.