

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

Polar Effects on Rates and Equilibria. VI. The Effect of Solvent on the Transmission of Polar Effects^{1,2}

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Activity coefficients (relative to the gas phase) in water and in decalin were determined for benzene, bromobenzene, nitrobenzene, *m*- and *p*-dibromobenzene, and *m*- and *p*-dinitrobenzene by determination of the solubilities in water, vapor pressures of the pure compounds, and vapor pressures of dilute solutions in decalin. In no case is the ratio $f_{\text{PhH}}f_{\text{PhX}_2}/(f_{\text{PhX}})^2$ larger than 2.1. The observed data agree fairly well with an equation derived previously from the Hammett equation except for the case of aqueous solutions of *m*-dinitrobenzene. The results show that τ , a measure of the efficiency with which substituent effects are transmitted across an aromatic ring in a given medium, has essentially the same value in decalin as in water and is only slightly larger in the gas phase.

Introduction

In a previous paper it was shown that from a modified version of the Hammett equation, in which ρ_m and ρ_p may be equal but do not have to be, and the assumption that σ 's are solvent-independent, it follows that

$$\log \frac{f_{\text{PhH}}^B f_{p-\text{PhX}_2}^B}{(f_{\text{PhX}}^B)^2} = (\tau_p^A - \tau_p^B)(\sigma_{p-X})^2 \quad (1)$$

where f^B 's are activity coefficients in medium B referred to the standard medium A, σ_{p-X} is the *para* substituent constant for the group X, τ_p^A is a measure of the efficiency of transmission of substituent interactions across a *p*-phenylene group in medium A, and τ_p^B is the corresponding constant for medium B.³ An analogous equation may be written for the *meta* case.

Deviations from the Hammett equation have most commonly been attributed to: (1) resonance interactions between substituent groups and reaction centers, (2) solvation of electrically charged groups, (3) hydrogen bonding, and (4) complications peculiar to rate processes such as changes in reaction mechanisms. By determination of activity coefficients of compounds with carefully chosen X groups some of these reasons for deviations may be eliminated and others minimized. Obtaining the data necessary for the application of eq. 1 should give information as to the manner in which substituent influences change with the nature of the reaction medium. It should also furnish a new test of the range of applicability of the Hammett equation, from which eq. 1 was derived.

In the present investigation we have determined activity coefficients for benzene, bromobenzene, nitrobenzene, *m*- and *p*-dibromobenzene, and *m*- and *p*-dinitrobenzene in water and in decalin, with respect to the gas phase.

Experimental

Materials.—Two different batches of decalin (Eastman Kodak Co. White Label <0.01% tetralin) were used, each shown by gas-liquid chromatography to contain $53 \pm 1\%$ *cis*- and $47 \pm 1\%$ *trans*-decalin. Although the first batch absorbed almost negligibly in the ultraviolet at the wave lengths used for analysis, the second batch had to be passed through a 75-cm. column packed with silica gel to remove a small amount of absorbing impurity.

All of the liquid aromatic compounds used were redistilled and shown to be homogeneous by gas-liquid chromatography measurements. All the solids were recrystallized to constant melting point in agreement with literature values.

Determinations of Vapor Pressures.—Our apparatus for vapor pressure determinations was essentially that of Washburn and Heuse,⁴ as modified by Bacarella, Finch and Grunwald.⁵ In it a stream of dry nitrogen is allowed to flow consecutively over

the liquid in a number of saturator tubes which are being continually rocked. The resultant nitrogen stream is then passed through a cold trap to condense the organic vapors from it. In determining the vapor pressure of pure liquids the contents of the cold trap were sometimes weighed and sometimes analyzed spectrophotometrically. In determining the partial pressure of various compounds over dilute solutions in decalin, the spectrophotometric method was used. All measurements were made at $35.0 \pm 0.1^\circ$. The pressure drop across the saturator was less than 0.5 mm.

A number of experiments were conducted to test the reliability of our method. Ordinarily only the first eight of the twelve saturator tubes were filled with liquid, the last four serving as traps for possible spray. In order to learn whether eight tubes are enough to saturate the gas stream a determination of the vapor pressure of benzene was carried out with only five tubes filled. The value obtained was less than 0.15% lower than that obtained using eight tubes. In order to learn whether spray was passing from the saturator into the cold trap a saturated solution (0.1 M) of the relatively non-volatile compound tri-*p*-tolyl phosphate in decalin was placed in the saturator. None of the phosphate could be detected (spectrophotometrically) in the condensate and therefore it was present at a concentration below 10^{-5} M. It follows that there was less than 2×10^{-6} ml. of spray per liter of vapor. This amount of spray would not have an observable effect in any of our experiments. To learn whether the cold trap (cooled in Dry Ice and acetone) was condensing the organic vapors quantitatively, in the case of benzene the effluent gas stream was led to a second Dry Ice cooled trap where it was bubbled through pentane. From the amount of benzene found in the pentane it could be calculated that about 0.3 mm. of benzene passed through the first trap without condensing. This is about 0.2% of the total amount of benzene, a figure that should be smaller with the less volatile compounds, whose vapor pressures decrease more rapidly with decreasing temperature.

Determination of the vapor pressure of benzene in our apparatus gave an uncorrected value of 146.5 ± 0.5 mm. at 34.9° . Correction for the 0.3 mm. that escaped condensation gives 146.8 ± 0.5 mm. Interpolation of the literature values that seem to us to be most reliable gives 147.5 ,⁶ 147.5 ⁷ and 147.7 ⁸ mm., values about 0.6% higher than ours. It may be noted that the literature values were determined by the static method, where the most probable source of error is the incomplete removal of foreign gases from the system, leading to values that are too high, while the most probable errors in our case are loss of the volatile benzene and incomplete saturation of the nitrogen stream, both of which would give too low a value.

To ensure complete flushing of the last four empty saturator tubes and the tube leading to the cold trap by the organic vapor-saturated nitrogen stream, at least 11 liters of nitrogen was passed through the system before a determination was begun. This would cause a significant enrichment or depletion of the concentration of aromatic compound in the decalin solution only in the case of benzene solutions. Therefore for solutions of benzene in decalin a somewhat different technique was used. Ten of the twelve saturator tubes were filled (less protection from spray would be needed in the case of a volatile compound like benzene) and determinations were begun after 3 liters of nitrogen had passed through the system. Even with this precaution the benzene solution in the last saturator was found to be 5.32% depleted after four determinations. It was therefore assumed that this depletion is a linear function of the amount of nitrogen passed through and the observed partial pressure to concentration ratios for benzene were increased by correction factors ranging from 2.00 to 4.63%. In these cases, where relatively small amounts of benzene were condensed in the cold trap, it was found

(1) For paper V in this series see J. Hine and R. P. Bayer, *J. Am. Chem. Soc.*, **84**, 1989 (1962).

(2) Abstracted largely from the Ph.D. thesis of Howard W. Haworth, 1962.

(3) J. Hine, *J. Am. Chem. Soc.*, **82**, 4877 (1960).

(4) E. W. Washburn and E. O. Heuse, *ibid.*, **37**, 309 (1915).

(5) A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

(6) C. B. Willingham, W. J. Taylor, J. M. Pignacco and F. D. Rossini, *J. Research Natl. Bur. Std.*, **35**, 219 (1945).

(7) E. R. Smith, *ibid.*, **26**, 129 (1938).

(8) A. F. Forzaiti, W. R. Norris and F. D. Rossini, *ibid.*, **43**, 555 (1949).

necessary to add known amounts of decalin to the trap before it was permitted to warm to room temperature (with one opening tightly closed and the other loosely corked) to prevent loss of significant amounts of benzene.

The vapor pressures of the pure compounds that are solids at 35°, *p*-dibromobenzene and the dinitrobenzenes, were determined in the same manner as were their partial pressures over decalin solutions, except that enough solid was added to ensure that excess undissolved solid remained present throughout the determination.

In addition to benzene, three of the other compounds that we studied have had vapor pressure determinations reported from which values at 35° may be calculated by interpolation or extrapolation, although in all cases the extrapolation is a fairly lengthy one or the data near 35° are not very precise. The values calculated from literature data are 7.75 mm. for bromobenzene,⁹ 0.14 mm. for *p*-dibromobenzene¹⁰ and 0.56 mm. for nitrobenzene.¹¹

The partial pressure of benzene in decalin was determined at concentrations of 10⁻², 4 × 10⁻² and 10⁻¹ *M*, that of *p*-dibromobenzene at 10⁻², 3 × 10⁻² and 0.979 *M*, that of nitrobenzene at 3 × 10⁻⁴, 10⁻³ and 3 × 10⁻³ *M*, that of bromobenzene at 10⁻² and 10⁻¹ *M*, and that of *m*-dibromobenzene at 10⁻² and 10⁻¹ *M*. For each compound the ratio of the pressure to the concentration remained within 4% of the average value and showed no significant trend. Since the activity coefficients of these compounds are thus seen to remain constant at the concentrations given, the pressure-concentration ratios for *m*- and *p*-dinitrobenzene were determined only on their saturated (but still relatively dilute) solutions. The pressure-concentration ratios (*p*/*c*) obtained are shown in Table I, with the vapor pressures of the pure compounds and the extinction coefficients in decalin used in analysis of the condensates.

TABLE I
EXTINCTION COEFFICIENTS AND VAPOR PRESSURE DATA ON AROMATIC COMPOUNDS AT 35°

Compound	λ , m μ	ϵ , ^a cm. ⁻¹	V.p. (mm.) of pure compound	<i>p</i> / <i>c</i> in dil. decalin soln. ^b
C ₆ H ₆	261	143 ^c	146.8 ± 0.5	31.6 ± 0.4
C ₆ H ₅ Br	272	147	7.48 ± .11	1.846 ± .003
<i>m</i> -C ₆ H ₄ Br ₂	279.5	313	0.428 ± .010	0.126 ± .003
<i>p</i> -C ₆ H ₄ Br ₂	283	266	.134 ± .006	.133 ± .003
C ₆ H ₅ NO ₂	254	8490 ^c	.600 ± .012	.826 ± .037
<i>m</i> -C ₆ H ₄ (NO ₂) ₂	267	5195	(8.15 ± 0.21) × 10 ⁻⁴	.0316 ± .0012
<i>p</i> -C ₆ H ₄ (NO ₂) ₂	255	11050 ^d	(2.25 ± 0.06) × 10 ⁻⁴	.0401 ± .0026
C ₆ H ₅ CH ₃			46.7 ± 0.3 ^e	
<i>m</i> -C ₆ H ₄ (CH ₃) ₂			15.2 ± .1 ^e	
<i>p</i> -C ₆ H ₄ (CH ₃) ₂			15.8 ± .1 ^e	

^a In decalin and, unless otherwise stated, at a slit width of 0.20 mm. ^b Pressure in mm. and concentration in moles/l. ^c 0.28-mm. slit. ^d 0.15-mm. slit. ^e Interpolated from the data of ref. 6, standard deviations estimated.

Solubility Determinations.—Solubilities in water were determined by adding an excess of the aromatic compound to 4.0 ml. of water in a 5.0-ml. ampoule, rotating the sealed ampoule in a constant-temperature bath and analyzing the resultant solution by ultraviolet spectrophotometric measurements using a Beckman DU spectrophotometer. With solids the undissolved solid was removed by filtration, and with liquids a sample of the aqueous layer was taken (after the vial had been kept motionless in the bath for 24 hours to separate the layers) by use of a syringe. All solutions were shaken for at least a week. Several measurements were taken at intervals of at least a day to be sure that equilibrium had been established. Solubilities in decalin were determined by filtration and then analysis of solutions taken from the saturator used for vapor-pressure determinations in those cases in which an excess of aromatic compound was used. The resultant data are listed in Table II. The only comparisons with the literature that seem to be available are in the case of *m*-dinitrobenzene, whose solubility in water at 30° was found to be 3.7 mmoles/l.,¹² and bromobenzene, nitrobenzene and *p*-dibromobenzene for which solubilities of 2.09, 16.6 and 0.0698 mmole/l., respectively, have been reported at 25°. When it is realized that the solubility of the solid compounds increases much more rapidly with increasing temperature than does that of the liquids¹⁴ there is seen to be reasonable agreement between the literature data and those of Table II.

(9) V. R. Dreyer, W. Martin and U. Weber, *J. prakt. Chem.*, [4] 1, 324 (1955).

(10) P. N. Walsh and N. O. Smith, *J. Chem. Eng. Data*, 6, 33 (1961).

(11) E. L. Lynch and C. R. Wilke, *ibid.*, 5, 300 (1960).

(12) I. M. Kolthoff and W. F. Graydon, *J. Phys. Chem.*, 55, 699 (1951).

(13) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 72, 3114 (1950).

(14) R. L. Bohon and W. F. Claussen, *ibid.*, 73, 1571 (1951).

TABLE II
SOLUBILITY OF AROMATIC COMPOUNDS IN WATER AND DECALIN AT 35.0°

Compound	Solubility, millimoles/l.	
	Water	Decalin
C ₆ H ₆	24.2 ± 0.8 ^a	∞
C ₆ H ₅ Br	2.92 ± .06	∞
<i>m</i> -C ₆ H ₄ Br ₂	0.286 ± .016	∞
<i>p</i> -C ₆ H ₄ Br ₂	0.112 ± .007	979 ± 43
C ₆ H ₅ NO ₂	18.35 ± .26	∞
<i>m</i> -C ₆ H ₄ (NO ₂) ₂	4.67 ± .09	25.79 ± 0.64
<i>p</i> -C ₆ H ₄ (NO ₂) ₂	0.617 ± .018	5.60 ± 0.33
C ₆ H ₅ CH ₃	7.13 ± .22 ^a	∞
<i>m</i> -C ₆ H ₄ (CH ₃) ₂	1.92 ± .06 ^a	∞
<i>p</i> -C ₆ H ₄ (CH ₃) ₂	1.94 ± .06 ^a	∞

^a From ref. 14, standard deviations estimated.

Deviations.—The ± figures listed throughout this paper are standard deviations. The standard deviations for the derived data, such as activity-coefficient ratios, were calculated from the primary data using standard calculations of the propagation of errors.¹⁵ The vertical bars leading from the points in Fig. 1 and 2 are measures of these standard deviations. The lines in Fig. 1 and 2 are drawn so as to pass through the origin with the sum of the squares of the positive deviations being equal to the sum of the squares of the negative deviations.

Discussion

We have made measurements in two very different liquid media, water and a saturated hydrocarbon decalin. In addition our measurements give information concerning a third medium, the gas phase. We have defined activities as being equal to pressures (in mm.) in the gas phase. The solubilities of the various aromatic compounds in water are all so low (<0.025 *M*) that we have assumed that the activity coefficients of the materials at saturation are equal to the activity coefficients at infinite dilution. Since the solubility of water in all the aromatic compounds is also very low we have assumed that the activity of the pure aromatic compound is not changed significantly when it is saturated with water. In using vapor-pressure measurements on saturated solutions of the solid aromatic compounds in decalin as measurements of the vapor pressure of the pure solids, we are assuming that it is pure solid aromatic compound that is in equilibrium with the saturated solution in decalin; that is, that the solids do not contain decalin of crystallization. We also assume ideal behavior of the vapors since in no case is the vapor pressure so much as 0.2 atm.

On the basis of these assumptions, if the reference medium (A) is the gas phase and the second medium (B) is water, the activity coefficient ratio of eq. 1 may be written

$$\frac{f_{\text{PhH}}^w f_{\text{PhX}_2}^w}{(f_{\text{PhX}^w})^2} = \frac{p_{\text{PhH}} p_{\text{PhX}_2} (S_{\text{PhX}^w})^2}{(p_{\text{PhX}})^2 S_{\text{PhH}}^w S_{\text{PhX}_2}^w} \quad (2)$$

where the *p*'s are the vapor pressures of the pure materials and the *S*'s are their solubilities in water. For dilute solutions in decalin, pressure-concentration ratios are proportional to activity coefficients and therefore the activity coefficient ratio may be written

$$\frac{f_{\text{PhH}}^D f_{\text{PhX}_2}^D}{(f_{\text{PhX}^D})^2} = \frac{(p/c)_{\text{PhH}}^D (p/c)_{\text{PhX}_2}^D}{[(p/c)_{\text{PhX}^D}]^2} \quad (3)$$

Values of the logarithms of the activity-coefficient ratios from our measurements are listed in Table III for the bromo and nitro substituents and in aqueous solution for the methyl substituents from the measurements listed by Bohon and Claussen.¹⁴

According to eq. 1, a plot of the logarithms of the activity-coefficient terms referring to a given pair of

(15) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y. 1943, pp. 487-502.

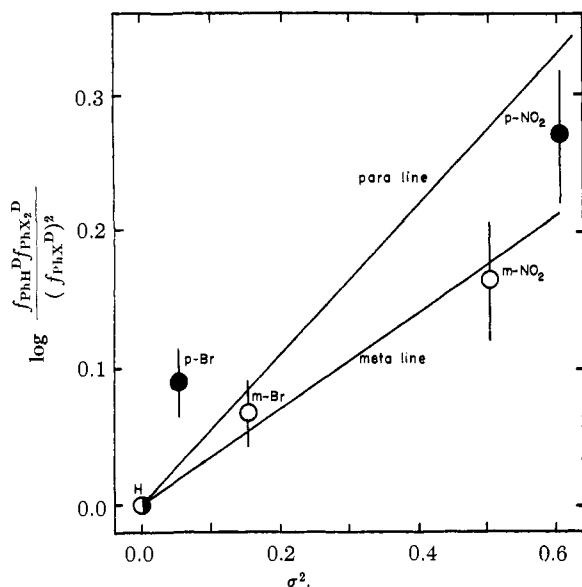


Fig. 1.—Plot of activity coefficients in decalin using eq. 1.

media vs. σ^2 for *p*-substituents¹⁶ should give a straight line of slope $(\tau_p^A - \tau_p^B)$ and a plot vs. σ^2 for *m*-substituents should give a line of slope $(\tau_m^A - \tau_m^B)$.

TABLE III

VALUES OF THE ACTIVITY COEFFICIENT RATIO OF EQ. 1

Substituent	$\frac{f_{PhH}^W / f_{PhX_2}^W}{(f_{PhX}^W)^2}$	$\frac{f_{PhH}^D / f_{PhX_2}^D}{(f_{PhX}^D)^2}$
<i>m</i> -CH ₃	1.11 ± 0.10	
<i>p</i> -CH ₃	1.16 ± .13	
<i>m</i> -Br	1.38 ± .11	1.17 ± 0.07
<i>p</i> -Br	1.10 ± .10	1.23 ± .06
<i>m</i> -NO ₂	0.99 ± .06	1.46 ± .14
<i>p</i> -NO ₂	2.06 ± .12	1.86 ± .21

The points in Fig. 1, referring to activity coefficients in decalin relative to the gas phase, lie fairly near straight lines for both *m*- and *p*-substituents. The plot of the data on activity coefficients in water (Fig. 2) shows that the points for *p*-substituents lie near a straight line, but that those for *m*-substituents do not.

The first important conclusion obtained from these results is that to whatever extent the present data provide a measurement of τ_m and τ_p , the proportionality constants for transmission of substituent effects across a benzene ring, the values of these proportionality constants change relatively little with the nature of the medium that surrounds the molecules bearing the substituents. The slopes of the lines in Fig. 1 and 2 show τ_p differences of 0.53 and 0.60 and τ_m differences of 0.35 and 0.2 between decalin and the gas phase and between water and the gas phase, respectively. These differences are in the direction expected. Substituent effects are larger in the gas phase where the dielectric constant of the medium is lower. However, the differences in τ are no larger than the uncertainty that already exists concerning the value of τ s in aqueous solution, where τ_m values of 2.66, 2.84, 3.53 and 3.57 and τ_p values of 2.87, 2.91, 3.05 and 3.50 have been calculated.^{3,17} Furthermore, a combination of the $(\tau^G - \tau^W)$ and $(\tau^G - \tau^D)$ values gives a $(\tau_p^D - \tau_p^W)$ of 0.07 and a $(\tau_m^D - \tau_m^W)$ of -0.13, values not significantly different from zero, for the differences between τ for water, a solvent of dielectric constant 80, and τ for decalin, whose dielectric constant is 2.2.

(16) The σ -constants used are those listed in J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 87.

(17) J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

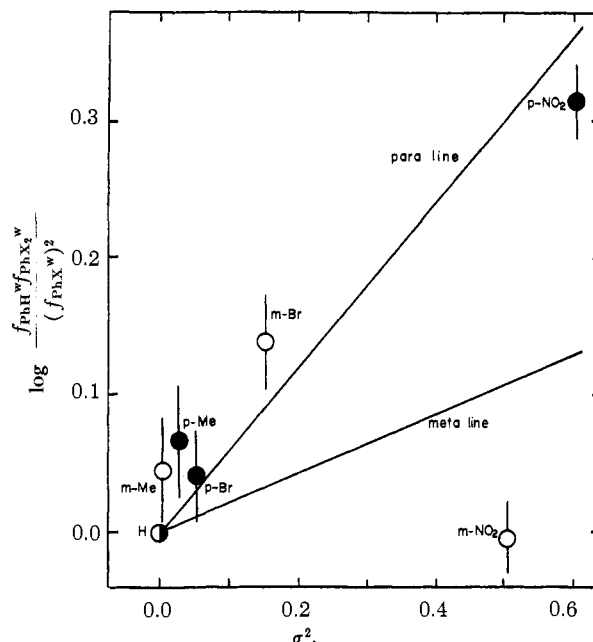
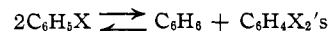


Fig. 2.—Plot of activity coefficients in water using eq. 1.

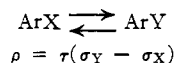
Whether our observations provide any general measure of the effect of solvent changes on the transmission of substituents or not, it is clear that they demonstrate that the equilibrium constants for the disproportionation of toluene, bromobenzene and nitrobenzene



will change by factors equal to the activity-coefficient ratios listed in Table III over the range of media: water, decalin, gas; that is, no change will be more than about twofold.

It is possible that our results are rather generally applicable to interactions between electrically neutral substituents, the only kind that we have studied, but not to charge-dipole or charge-charge interactions. Our approach does not seem applicable to electrically charged substituents, since it appears completely unreasonable to expect the σ -constants for such substituents to be solvent independent.

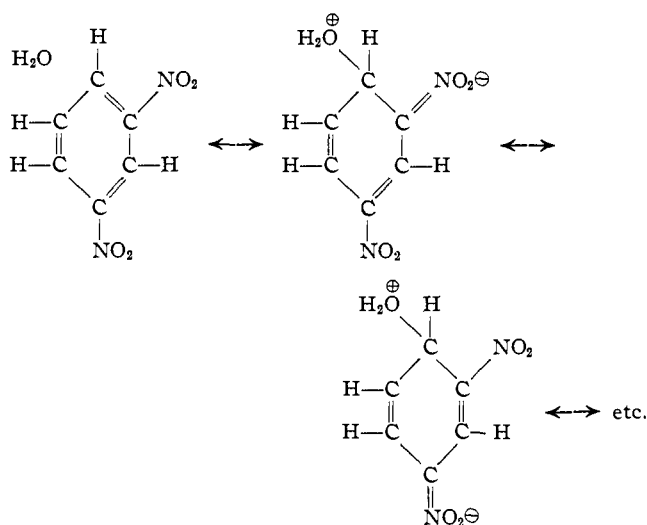
It has earlier been shown that in the reaction



If τ is relatively solvent independent as we have found, the changes in ρ that have been observed to accompany solvent changes must be attributed to changes in σ_X and/or σ_Y . Since in almost all the cases studied either X or Y is an electrically charged group, such a change is not surprising; even with groups capable of entering into hydrogen-bonding interactions with the solvent, considerable changes in σ may be anticipated.

The average deviation of the points in Fig. 1 and 2 (excluding the points for hydrogen, which fit by definition) is 0.052 log unit. This is smaller than that (0.071) found by Hammett for the first 52 reaction series to which the Hammett equation was applied.¹⁸ Nevertheless it seems probable that there are specific solvent-aromatic interactions that result in deviations from eq. 1. The deviation of the point for *m*-nitro in Fig. 2 (omission of this point would reduce the average deviation to 0.036) may be due to such an interaction. Since the only datum used in determining this point

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 192.



that was not used in determining the point for *m*-nitro in Fig. 1 (which falls reasonably near the line) is the solubility of *m*-dinitrobenzene in water, there may be an interaction between the basic oxygen atoms of water and the carbon atoms *ortho* and *para* to the nitro groups in *m*-dinitrobenzene. Such an interaction is somewhat analogous to the reaction that results in a purple solution of *m*-dinitrobenzene in liquid ammonia,¹⁹ but we are not postulating that the contributions of the right-hand structures above are sufficient to make the geometry of the *m*-dinitrobenzene significantly dif-

(19) J. D. Farr, C. C. Bard and G. W. Wheland, *J. Am. Chem. Soc.*, **71**, 2013 (1949).

ferent from that in a solvent with which it has no such interaction.

To express our activity coefficients in terms of contributions for various substituent groups in a manner analogous to that used by Derr and co-workers²⁰ would yield values of 1.0 for the activity-coefficient ratio in eq. 1. Benson and Buss pointed out that if ϕ is a molecular property, then for the disproportionation reaction



$\Delta\phi$ approaches zero as the separation between R and S becomes large compared to their dimensions.²¹ In our case ϕ is the logarithm of the activity-coefficient ratio. The values of ϕ are small, but in several cases significantly larger than zero, showing that for the N groups (*m*- and *p*-phenylene) that we used the interacting substituents are not removed a sufficient distance from each other for ϕ to be a simple additive property of the nature of the groups present. Equation 1 may be thought of as providing the correction for this deviation from simple additivity.

Acknowledgments.—We wish to acknowledge our indebtedness to the National Science Foundation for support of this investigation, to the Rayonier Corporation for the grant of a fellowship to H. W. H., and to Vernon D. Parker, who made preliminary investigations on this problem.

(20) G. J. Pierotti, C. A. Deal and E. L. Derr, *Ind. Eng. Chem.*, **51**, 95 (1959); O. Redlich, E. L. Derr and G. J. Pierotti, *J. Am. Chem. Soc.*, **81**, 2283 (1959); M. N. Papadopoulos and E. L. Derr, *ibid.*, **81**, 2285 (1959); C. H. Deal, E. L. Derr and M. N. Papadopoulos, *Ind. Eng. Chem. Fundamentals*, **1**, 17 (1962).

(21) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

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Polar Effects on Rates and Equilibria. VII. Disproportionation and Isomerization of Alkyl- and Halobenzenes^{1,2}

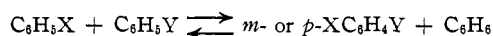
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Equilibrium constants have been determined for the simple disproportionation reactions of bromobenzene and ethylbenzene and the mixed disproportionation reactions of bromobenzene with toluene and with fluorobenzene. Equilibrium constants for the formation of *m*-disubstituted benzene derivatives are correlated satisfactorily by an expression based on the Hammett equation, but equilibrium constants for the formation of *p*-disubstituted benzenes are correlated very poorly by this expression. When the Hammett substituent constants in the expression are replaced by inductive substituent constants the correlation becomes excellent for both *meta* and *para* compounds. The significance of these results is discussed.

Introduction

It has been pointed out earlier that on the basis of the Hammett equation, or of a less restrictive form of the Hammett equation, in which ρ_{meta} and ρ_{para} need not be equal, an equation may be derived to predict the equilibrium constant for such aromatic disproportionation reactions as³



including cases where X and Y are the same. By studying compounds with electrically neutral X's and Y's that are incapable of direct resonance interaction even when *para* to each other, it should be possible to test the disproportionation equation with a minimum of complications due to (1) resonance interactions between groups attached to the aromatic ring, (2) solvation of electrically-charged groups, (3) complications peculiar to rate processes (such as changes in reaction mechanism), and

(if the solvent and substituent groups are carefully chosen) (4) hydrogen bonding. More important, a new test would also be provided for the parent relationship, the Hammett equation, and in this test the effect of the four factors listed above—those most commonly blamed for failure of the Hammett equation—is minimized so that the influence of other factors, such as how near each other the substituent group and the reaction center may be, can be evaluated.

Unfortunately we found in the literature no direct quantitative measurements on aromatic disproportionations of the type needed. The thermochemical data from which equilibrium constants for such reactions could be calculated are not nearly so precise as desired. However, von Dumreicher and subsequent workers showed that halobenzenes disproportionate to benzene and dihalobenzenes in the presence of Friedel-Crafts catalysts,^{4,5} and Heise and others showed that similar reactions occur with alkylbenzenes.⁶ We therefore

(1) For paper VI in this series see ref. 18.

(2) Abstracted largely from the Ph.D. thesis of Henry E. Harris, 1962.

(3) J. Hine, *J. Am. Chem. Soc.*, **82**, 4877 (1960).

(4) O. von Dumreicher, *Ber.*, **15**, 1866 (1882).

(5) F. Fairbrother and N. Scott, *Chem. Ind. (London)*, 998 (1953).