periods of no stirring some fluctuation in temperature will occur.

Applications of the Method.—The results presented here demonstrate that with inside and outside solutions differing in density by 2% or more (the density of 0.5 *M* KCl is 1.02 times that of water at 25°), the diffusion coefficient of the solute can be measured within an accuracy of a few per cent. Obviously wherever the greatest possible precision is desired, as in the determination of the "differential" diffusion coefficients of simple electrolytes, the present method cannot compete with some of the conventional techniques. The principal advantage of our method lies in its combination of speed and simplicity. While it may be no more accurate than other methods of comparable rapidity, such as optical methods which employ an initial discontinuity in concentration, it is certainly simpler, for it requires no special and expensive equipment.

The use of frits in diffusion work has been criticized because of the possibility that adsorption and other effects influence the results. However, the recent work of Stokes on the steady state method[5] indicates that adsorption in the case of simple electrolytes is not an important factor except at low concentrations (for KCl below 0.05 *M*). Experiments in this Laboratory on bovine plasma albumin using the present method are in agreement with the accepted value for the diffusion coefficient. Thus it seems likely that the method in question will be applicable to most substances.

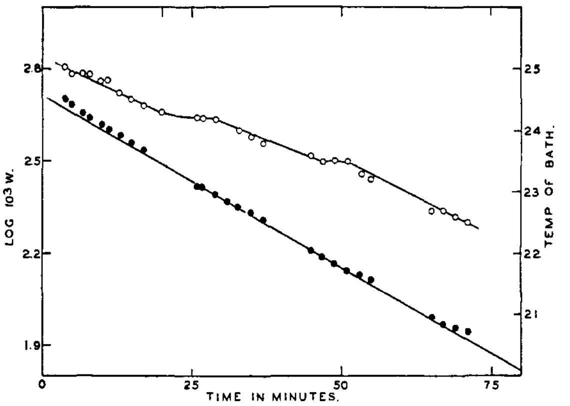

Fig. 5.—Experiment with variable temperature: frit number 1, edges open, C_1 = 0.44 *M* KCl, C_0 = 0: solid circles, corrected for change in density of outside solution; slope of straight line 1.10 × 10^{-2} min.$^{-1}$; open circles, temperature of outside solution, right hand scale.

In principle, the period of diffusion can be made conveniently short for any substance, no matter how small its diffusion coefficient, by decreasing the frit thickness. With frits one millimeter thick, a period of diffusion of about one day is required for polyacrylic acid. For this substance, however, solutions two or three per cent. by weight must be used to attain a maximum *W* of 50 mg. Since the maximum *W* is approximately proportional to thickness, it is apparent that more concentrated solutions would be required if the thickness (and hence the period of diffusion) is to be decreased significantly. Analysis by weighing the frit will then not be equally useful in all cases. For example, it could not be used with success for many long chain electrolytes since the aqueous solution densities of these compounds are nearly the same as that of water.

URBANA, ILLINOIS

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[5] R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Polarographic Behavior of the Nitroanilines in Absolute Ethyl Alcohol[1]

BY MERVIN E. RUNNER[2]

RECEIVED DECEMBER 22, 1951

The reducibilities of the nitroanilines were compared with those for the nitrophenols and nitrobenzene in buffered absolute ethanol solutions. *o*-Nitroaniline (as the free base) was more easily reduced than *p*-nitroaniline, but both were more difficult to reduce than *m*-nitroaniline. The latter exhibited practically the same reducibility as *m*-nitrophenol and nitrobenzene. The influence of the amino and hydroxyl groups on the reducibility of the nitro group was discussed in relation to the acidity of the environment. Diffusion coefficients, separately measured, led to the calculation of 6 electrons involved in the reduction of *o*- and *p*-nitroaniline and 4 to 5 electrons for *m*-nitroaniline.

The polarographic behavior of *o*-, *m*- and *p*-nitro phenols,[3a,4a] N-nitrophenyl-N'-phenylacetamidines,[5] and nitroacetanilides[6] indicate the greatest ease of reduction for the chelated ortho-isomer, with para the most difficult and meta intermediate. The purpose of this investigation was to examine *o*-, *m*- and *p*-nitroanilines in buffered absolute ethyl alcohol solutions for a similar order of reducibility of the isomers and to determine the influence of structure on the half-wave potentials and the generality of the effect of chelation in facilitating reduction of the nitro group. Earlier work[7] on these compounds failed to show this ease of reduction for the ortho compound even though infrared spectrum methods[8] show *o*-nitro-

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[1] Abstracted from a thesis by Mervin E. Runner, presented to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the Ph.D. degree, February, 1950.

[2] Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois.

[3] (a) M. J. Astle and W. V. McConnell, THIS JOURNAL, **65**, 35 (1943); (b) M. J. Astle and W. P. Cropper, *ibid.*, **65**, 2395 (1943).

[4] (a) J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948); (b) *ibid.*, **44**, 683 (1948).

[5] M. E. Runner, M. L. Kilpatrick and E. C. Wagner, THIS JOURNAL, **69**, 1406 (1947).

[6] M. E. Runner and E. C. Wagner, *ibid.*, **74**, 2529 (1952).

[7] M. Shikata and E. Taguchi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **29**, 1 (1934).

[8] W. Gordy and S. C. Stanford, THIS JOURNAL, **62**, 497 (1940).

aniline to be capable of chelation in a manner analogous to *o*-nitrophenol. The reduction potentials reported for the nitroanilines[7] are somewhat in doubt since they were measured by the old tangent method.

Discussion and Results

The effect of hydrogen ion concentration on the reduction of *o*-, *m*- and *p*-nitroaniline is shown in Table I. Single waves were obtained in all experiments. The *o*- and *p*-nitroanilines exhibited 6-electron waves in all media while *m*-nitroaniline gave 4-electron waves at low *pK* values and at higher *pK* values the diffusion currents indicated 5-electron waves (Table III). For the *o*- and *p*-isomers the possibility of quinonization would facilitate reduction to the amine in neutral and alkaline media. The *m*-isomer, however, may yield reduction intermediates subject to rearrangement and condensation. Thus, rearrangement of the phenylhydroxylamine intermediate to a *p*-aminophenol is possible in acid solution. In alkaline aqueous solution phenylhydroxylamine derivatives are converted rapidly to the azoxybenzene derivative and aniline.[9] The former is reducible to hydrazobenzene, requiring four electrons. A similar process in ethanol may account for a wave height approximating five electrons per molecule.

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION ON THE REDUCTION OF 2 × 10^{-4} *M* NITROANILINES IN ETHYL ALCOHOL

	Ortho-		Meta-		Para-	
pK	Diffusion current, μa.	Half-wave potential, volts	Diffusion current, μa.	Half-wave potential, volts	Diffusion current, μa.	Half-wave potential, volts
1	3.88	−0.24	1.98	−0.15	2.89	−0.21
3	3.32	− .41	2.20	− .29	3.12	− .41
5	3.20	− .57	2.58	− .49	3.20	− .60
6	3.23	− .75	2.55	− .70	3.21	− .81
8	3.23	− .80	2.60	− .71	3.40	− .85
9	3.15	− .84	2.62	− .76	3.37	− .88
10	3.00	− .79	2.64	− .69	3.22	− .81
12	3.19	−1.01	2.64	− .93	3.15	−1.04
13	3.16	−0.97	2.64	− .89	3.27	−1.00
17	3.00	−1.05	2.70	− .95	3.09	−1.11

TABLE II

DIFFUSION COEFFICIENT MEASUREMENTS IN ETHYL ALCOHOL[a]

Cell constant *K* = 0.50

Compound	*C*′ (i_d in μa.)	*C* (i_d in μa.)	$t_E \times 10^{-5}$ (sec.)	Temp., (°C.)	$KD \times 10^5$
o-Nitroaniline	11.3	2.2	0.198	25	0.475[b]
o-Nitroaniline	9.2	1.3	.180	30	.369[c]
m-Nitroaniline	5.6	0.9	.252	25	.303[b]
m-Nitroaniline	7.3	2.0	.360	25	.387[c]
p-Nitroaniline	9.0	1.8	.339	25	.286[b]
p-Nitroaniline	10.1	2.2	.288	25	.371[c]

[a] A description of the experimental method appears elsewhere.[6] [b] In medium *pK* 1. [c] In medium *pK* 9.

TABLE III

THE EXTENT OF REDUCTION AND DIFFUSION COEFFICIENTS IN ETHYL ALCOHOL AT 25°

C = 0.2 millimole, $m^{2/3} t^{1/6}$ = 1.684 mg.$^{2/3}$ sec.$^{-1/2}$

Compound	*pK*	$D_{(\text{found})} \times 10^5$ (cm.²/sec.)	i_d, μa.	*n* (electrons)	$i_d/(Cm^{2/3}t^{1/6})$	$KnD^{1/2}_{(\text{found})}$
o-Nitroaniline	1	0.95	3.88	6	11.52	11.19
o-Nitroaniline	9	.67	3.15	6	9.35	9.40
m-Nitroaniline	1	.61	1.98	4	5.88	5.98
m-Nitroaniline	9	.77	2.62	5	7.78	8.39
p-Nitroaniline	1	.57	2.89	6	8.58	8.67
p-Nitroaniline	9	.74	3.37	6	10.01	9.88

The diffusion current obtained for *o*-nitroaniline in medium *pK* 1 is unusually high relative to meta and para as shown in Fig. 1. Likewise, the diffusion coefficient found for *o*-nitroaniline in this medium is considerably higher than the others (Table III). Catalytic hydrogen waves have been observed for certain amine salts[10] and this may account for the increased wave height of *o*-nitroaniline compared to para; an effect perhaps related to the base strength of the *o*-nitroanilinium ion. In the measurement of the diffusion coefficients,[6] values of *c* and *c*′ were obtained polarographically and reported as diffusion currents (Table II). The exaltation of the diffusion current appears greater for the more dilute solution *c* than for the solution *c*′, hence the diffusion coefficient found for *o*-nitroaniline at this acidity is too large.

In order to facilitate comparison of the half-wave potentials of the nitroanilines they were related to half-wave potentials for nitrobenzene in the manner reported previously for the nitroacetanilides.[6] The difference between the half-wave potentials for each nitroaniline and nitrobenzene was determined for each *pK* value and reported in Table IV. To relate the +T effect of the amino group to the hydroxyl group, the half-wave potentials for *o*-, *m*- and *p*-nitrophenol were determined in similar media. These values, related to the half-wave potentials of nitrobenzene are also shown in Table IV. The data for *o*-nitroaniline show reduction more difficult than for nitrobenzene and *m*-nitroaniline (more negative values). Substituents tending to increase the electron density of the nitro group lead to greater difficulty of reduction compared to nitrobenzene while the opposite is true for substituents tending to decrease the electron density of the nitro group.[6] In acid media the appearance of a formal positive charge on the ammonium group would thus virtually eliminate any electron donating behavior characteristic of the amino group. This agrees

TABLE IV

DIFFERENCE BETWEEN $E_{1/2}$ FOR EACH NITRO-COMPOUND AND NITROBENZENE

	Nitroanilines			Nitrophenols		
pK	Ortho	Meta	Para	Ortho	Meta	Para
1	−0.03	+0.06	0.00	+0.04	+0.02	−0.07
3	− .05	+ .07	− .05	+ .05	.00	− .07
5	− .09	− .01	− .12	+ .04	− .01	− .09
6	− .07	− .02	− .13	+ .09	− .01	− .11
8	− .11	− .02	− .16	+ .08	− .01	− .11
9	− .12	− .04	− .16	+ .04	− .02	− .12
10	− .12	− .02	− .14	+ .04	− .03	− .14
12	− .13	− .05	− .16	+ .01	− .02	− .17
13	− .13	− .05	− .16	− .15	− .18	− .32
17	− .05	+ .05	− .11	− .10	− .07	− .17

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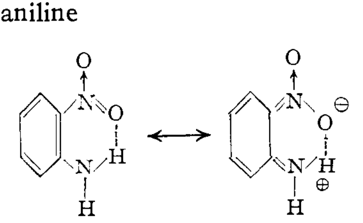
(9) D. Lester and L. A. Greenberg, *ibid.*, **66**, 496 (1944).

(10) E. Knobloch, *Coll. Czech. Chem. Commun.*, **12**, 407 (1947).

with the observation that the half-wave potentials of both *o*- and *p*-nitroaniline become more negative in going from strongly acid media toward the neutral range (Table IV). *p*-Nitroaniline is more easily reduced than ortho at *pK* 1, becomes equal in reducibility at *pK* 3, and more difficult above this value. In medium *pK* 1 the half-wave potential for *o*-nitroaniline relative to para is more negative by 0.03 volt and indicates a stabilization of the nitro group. It was at first thought that the formal positive charge on the adjacent ammonium group and hence its inductive effect might account for the stabilization, but the observation of similar magnitudes of difference in half-wave potentials between nitrobenzene and *o*-nitrotoluene (0.06 v. at *p*H 1.7),[4b] 5-nitro-*o*-cresol and 6-nitro-*m*-cresol (0.05 v. at *p*H 2.2),[3b] 4-nitro-*o*-cresol and 2-nitro-*p*-cresol (0.05 v. at *p*H 2.2),[3b] places the emphasis elsewhere. Approximately the same effect on the half-wave potential is produced by either an *o*-methyl group or an *o*-ammonium group even though the inductive effect of both makes them oppositely orienting. The ammonium group being of approximately the same bulk as the methyl group appears to exert a slight but definite steric effect on the nitro group to decrease its coplanarity with the aromatic ring and hence resonance with it.[11] This trend is even more definitely shown for nitromesitylene, a case where the nitro group is flanked on both sides by methyl groups. At *pK* 5, the half-wave potential is −0.67 volt, approaching the value for nitromethane which is −0.86 volt in the same medium. Amine salt formation in the case of the meta-isomer caused the greatest ease of reduction relative to ortho and para as well as nitrobenzene. At *pK* 3 reducibility of *o*- and *p*-nitroaniline is the same showing the effect of the presence of a smaller amount of anilinium ion. At *pK* 5 and above, *o*-nitroaniline is more easily reduced than para. This behavior is due to the effect of hydrogen bonding involving the nitro and amino groups. The tendency to decrease the resonance energy of the conjugated system involving the nitro group and *o*-amino group through electrostatic attraction between induced terminal charges tends to make the nitro group more easily reduced. In general, the strength of an unsymmetrical hydrogen bond A–H···B is increased by increasing the resultant positive charge of A and the negative charge of B.[12] This can be shown for *o*-nitroaniline



In this case the stronger the hydrogen bond the greater the decrease of resonance energy of the conjugated system involved. The voltage differences between *o*- and *p*-nitroaniline are not as great as those between *o*- and *p*-nitrophenol (Table IV) where the same order of reducibility between the two isomers is found. The fact that oxygen is more electronegative than nitrogen accounts for stronger hydrogen bonds with hydroxyl compounds than with amino compounds. For a similar reason the electron donating capacity of an amino group on an aromatic nucleus is greater than that of a hydroxyl group. This is reflected in the greater difficulty of reduction of *p*-nitroaniline compared to *p*-nitrophenol, if a comparison is made between *pK* 5 and *pK* 10 where only neutral molecules exist. Above *pK* 10 reduction of *p*-nitrophenol becomes more difficult than for *p*-nitroaniline apparently due to an increasing amount of phenolate ion. The other isomers evidence similar behavior above *pK* 12. The reducibility of *m*-nitroaniline compared to *m*-nitrophenol shows very little difference; both are slightly more difficult to reduce than nitrobenzene. The reducibility of ortho- and para-isomers is much more sensitive to the effect of substituents than that of the meta-isomer due to inability of the latter to enter into resonance with the nitro group.

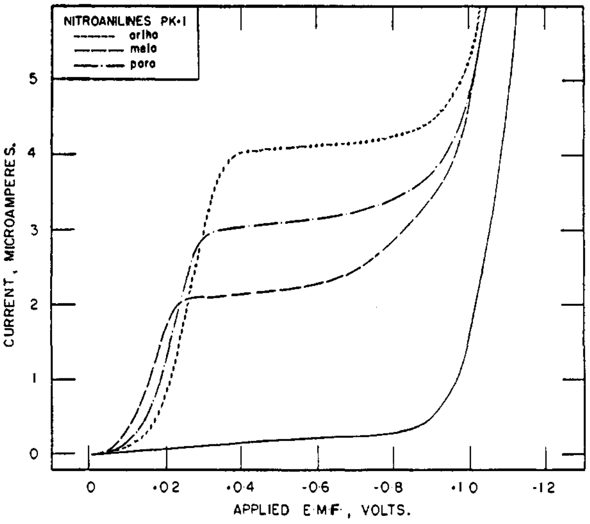


Fig. 1.

Hydrogen bonding tends to lessen the stabilizing effect of electron donating influences (+T effect) exerted by the ortho-substituent. The sum of these influences need not result in a lower half-wave potential for the ortho-compound compared to that of meta or nitrobenzene. In the case of *o*-nitrophenol the hydrogen bonding effect is greater than the +T effect of the hydroxyl group, therefore, this compound is more easily reduced than meta or nitrobenzene. For *o*-nitroaniline the +T effect of the amino group is greater than the effect due to the hydrogen bond and results in more negative half-wave potentials for ortho than for meta. In comparison with the para-isomer the ortho-isomer, where chelation is possible, will in general be more easily reduced in the case of neutral molecules where salt structures do not exist.

Experimental

The diffusion coefficients of the nitroanilines were separately measured in order to use the Ilkovic equation for determining the extent of reduction. The experimental pro-

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[11] The possibility of the *o*-ammonium group exerting a steric effect on the nitro group was suggested by one of the referees.

[12] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 307.

cedures and the ethanol buffers are described elsewhere.[6] The negative logarithm of the dissociation constant (*pK*) for each of the acids used in the buffers serves to describe the acidity of the solution when the buffer ratio is kept at unity.

Materials.—The nitroanilines, nitrophenols and nitromesitylene were commercially available materials and were recrystallized from ethanol. *o*-Nitrophenol was steam distilled before recrystallization. Melting points of the nitro compounds were identical with those reported in the literature. Nitrobenzene and nitromethane, after drying over calcium chloride, were vacuum distilled employing a Widmer fractionating column.

PHILADELPHIA 4, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Solubility of Hydrogen Chloride at Low Temperatures. A Measure of the Basic Properties of Aromatic Nuclei; π- and σ-Complexes and Their Role in Aromatic Substitution[1,2]

BY HERBERT C. BROWN AND JAMES D. BRADY[3]

The solubility of hydrogen chloride at −78.51° in dilute solutions of aromatic compounds in toluene and in *n*-heptane varies in a manner which indicates that the magnitude of the solubility is a measure of the basic properties of the aromatic nuclei. Henry's law constants for these solutions of representative aromatic compounds reveal the following order of increasing solubility: benzotrifluoride < chlorobenzene < benzene < toluene < *m*-xylene < mesitylene. The technique distinguishes between isomeric methylbenzenes: *p*-xylene < *o*-xylene < *m*-xylene < pseudocumene < hemimellitene < mesitylene < prehnitene < isodurene. The monosubstituted benzenes yield the order: iodo- < bromo- < chloro- < fluoro- < benzene- < methyl- < ethyl- < isopropyl- < *t*-butyl-. Thiophene appears less basic than benzene by this technique. Olefins neither add hydrogen chloride nor undergo isomerization under the conditions of the measurements. These compounds modify the solubility of hydrogen chloride in a manner as to suggest the following order of increasing basicity: $Cl_2C{=}CCl_2 < RCH{=}CH_2 < R_2C{=}CH_2, RCH{=}CHR < R_2C{=}CHR$. Equilibrium constants are calculated for the reaction at −78.51°: $Ar{\cdot}HCl \rightleftarrows Ar + HCl$.

The results obtained by the hydrogen chloride technique agree, for the most part, with the relative basicities established by the use of $HCl-AlCl_3$ or $HF-BF_3$, or deduced from the ease of nuclear substitution by electrophilic reagents. Four discrepancies are noted between the relative basicities established by the hydrogen chloride technique and those established by the other procedures mentioned. These discrepancies are nicely accounted for on the assumption that aromatic complexes exist as two separate species or classes, with distinct chemical and physical properties: π-complexes and onium or σ-complexes. It is further proposed that the hydrogen chloride and $HX-MX_3$ techniques supplement each other—the former furnishing a measure of electron density in the ground state of the molecule, the latter in the transition state.

A linear free energy relationship exists between the rate of halogenation of aromatic compounds and the stability of σ-complexes ($HF-BF_3$). A similar relationship involving the stability of π-complexes (HCl) does not exist. This argues against Dewar's proposal that the rate of aromatic substitution is determined by the rate of formation and the stability of the π-complex. Instead, the rate of aromatic substitution appears to depend primarily upon the stability of the σ-complex.

The observation by Klatt[4] that aromatic hydrocarbons dissolve in liquid hydrogen fluoride was interpreted by Hammett[5] to involve a proton transfer to the aromatic nucleus.

$$C_6H_6 + HF \leftrightarrows C_6H_7^+ + F^-$$

Recently, considerable attention has been devoted to studies of the basic properties of aromatic nuclei. Thus Fairbrother proposed that the change in the dipole moment of iodine dissolved in various aromatic and unsaturated hydrocarbons was related to the postulated basic properties of these substances.[6] Fairbrother also pointed out that the shift in the color of iodine solutions in hydrocarbon solvents from violet to red to brown could also be correlated with the basic properties of the solvents. More recently, Benesi and Hildebrand[7] have demonstrated that the absorption spectra of these iodine solutions show regular changes in the ultraviolet region which can again be correlated with the postulated basic nature of aromatic hydrocarbons. Similar shifts in the spectra of such solutions of bromine[8a] and of chlorine[8b] have also been observed. Finally, Andrews and Keefer have examined the formation of complexes between silver ion and aromatic compounds and have correlated the stability of these complexes with the ability of the aromatic nuclei to function as bases.[9]

While phenomena based upon the absorption spectra of halogen solutions or the stability of silver ion complexes are presumably related to acid–base interactions, it appears desirable to obtain a more direct experimental basis upon which to develop our understanding of the basic properties of aromatic hydrocarbons. For this purpose a study of the proton affinity of aromatic nuclei by the use of methods related to that introduced by Klatt[4] offers more promise.[10]

We had recently observed that toluene, alumi-

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(1) The Catalytic Halides. III. A preliminary Communication appeared in THIS JOURNAL, **71**, 3573 (1949).

(2) This paper is based upon a thesis submitted by James D. Brady in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Company (Indiana) Fellow at Purdue University, 1947–1949.

(4) W. Klatt, *Z. anorg. allgem. Chem.*, **234**, 189 (1937).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 293–294.

(6) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

(7) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949). For a discussion of the structure of the complexes of halogen molecules with aromatic compounds, see R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(8) (a) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950); (b) *ibid.*, **73**, 462 (1951).

(9) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

(10) Unfortunately, Klatt's own results cannot be used without modification to estimate the basic properties of various aromatics. Apparently the solubility of aromatic hydrocarbons in liquid hydrogen fluoride must depend upon factors other than the proton affinity of the ring. Thus Klatt reports that the solubility changes in the order, *m*-xylene < toluene < benzene, whereas there are both theoretical and experimental reasons to believe that the basic properties of these hydrocarbons must vary in the opposite order, with *m*-xylene being much more basic than benzene.