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.

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[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).

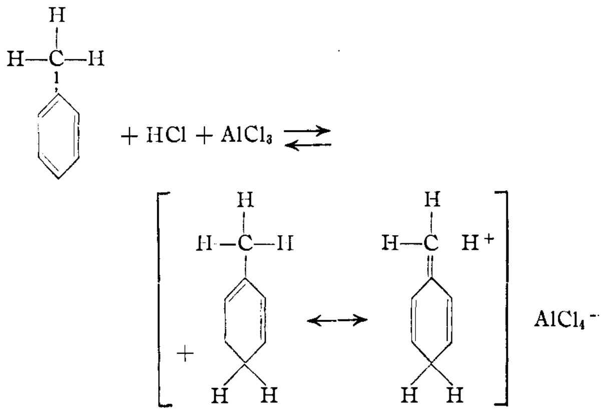
[7] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949). For a discussion of the structure of the complexes of halogen molecules with aromatic compounds, see R. S. Mulliken, *ibid.*, **72**, 600 (1950).

[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.

num chloride and hydrogen chloride react reversibly at −80° to form a deeply colored complex. We interpreted the reaction to involve a transfer of the proton to the aromatic ring to form a carbonium ion salt of the hydrocarbon.[11]



The relative stability of the complexes formed by various aromatic hydrocarbons with aluminum chloride and hydrogen chloride should therefore measure the relative tendency of the aromatic nuclei to accept the protons from the reagents. Therefore the stability of the complex should be directly related to the basic properties of the hydrocarbon and the reaction appeared to offer a promising method for determining the basic strengths of aromatic nuclei.

These experiments[11b] required a determination of the solubility of hydrogen chloride in the aromatic hydrocarbon at a low temperature, followed by a redetermination of the solubility in the presence of a measured quantity of aluminum chloride. In the course of these studies, we observed that the solubility of hydrogen chloride in these hydrocarbons varied markedly, in such a manner as to suggest that increasing basicity of the hydrocarbon solvent resulted in increased solubility of the gas. The phenomenon was interesting; a detailed study of it was therefore undertaken.

The solubility of hydrogen chloride at 25° in several monosubstituted benzenes had been observed previously by O'Brien and his co-worker.[12] However, the number of compounds studied was too few to permit a decision on the utility of the procedure for the comparison of the basic strengths of aromatic nuclei. In order to avoid corrections for the partial pressures of the hydrocarbons and to magnify the interactions between the hydrogen chloride and the aromatic compounds, the solubility of hydrogen chloride was studied at −78.51°. Moreover, it was decided to utilize relatively dilute solutions of the aromatic compounds in a suitable solvent in order to maintain a relatively constant concentration of aromatic nuclei in the solvent and to minimize secondary interactions which might alter the solubility of the gas. Finally, the use of dilute solutions also permitted study of substances with relatively high melting points.

The procedure was applied to 25 aromatic and unsaturated hydrocarbons. An excellent correlation was observed between the observed solubility of hydrogen chloride and the predicted basic strength of the aromatic or olefinic derivative. Moreover, the observed basic properties of the compounds correlate qualitatively with the relative reactivity of these compounds toward electrophilic reagents.[13,14]

McCaulay and Lien[15] have recently described a thorough study of the relative basic strengths of the methylbenzenes, utilizing the interaction of these compounds with hydrogen fluoride–boron trifluoride for the determination of the base strengths. Again the agreement is excellent. It therefore appears that one can use the solubility of hydrogen chloride in aromatic hydrocarbons or the stability of complexes of aromatic hydrocarbons with hydrogen fluoride–boron trifluoride as a measure of basic strength, and there is a close connection between the basic strengths of aromatic nuclei and their susceptibility toward substitution by electrophilic reagents.

Results and Discussion

Representative Aromatics.—Consideration of the effect of the substituent on the electron density of the ring suggests that the basic properties of the following representative benzene derivatives should increase in the order indicated: benzotrifluoride < chlorobenzene < benzene < toluene < *m*-xylene < mesitylene. Solutions in *n*-heptane were made up containing 20 moles of solvent per mole of aromatic (5 mole % solutions in *n*-heptane) and the Henry's law constant ($P_{\mathrm{mm}} = kN_{\mathrm{HCl}}$) at −78.51° was determined. Representative data are reported in Table I and Fig. 1.

It is clear from the data that the increasing solubility of hydrogen chloride correlates well with the predicted increase in basic properties of the aromatic nuclei. No simple correlation with any other property of the compounds is apparent. For example, hydrogen chloride is a polar substance and one might be tempted to attribute the increase in solubility observed in going from benzene to toluene to *m*-xylene to the increasing polar properties of the medium. However, chlorobenzene with still greater polar properties is a poorer solvent than benzene, and mesitylene, a non-polar substance, is the best solvent of the series.

In view of this evidence it appears reasonable to conclude that the solubility of hydrogen chloride in aromatic hydrocarbons and their halogen derivatives is affected by interactions of some kind between the aromatic nucleus and the acid, and that the magnitude of these interactions may be taken as a measure of the basic properties of the nuclei.

It should be mentioned that Rodebush and Ewart[16] pointed out some time ago that the determination of the partial pressure of a volatile acid

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[11] (a) H. C. Brown and H. W. Pearsall, Abstracts, A.C.S. Meeting at New York, Sept. 16, 1947, p. 19-O; (b) H. C. Brown and H. W. Pearsall, THIS JOURNAL, **74**, 191 (1952).

[12] S. J. O'Brien and J. B. Byrne, *ibid.*, **62**, 2063 (1940); S. J. O'Brien, *ibid.*, **63**, 2709 (1941).

[13] P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

[14] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[15] D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[16] W. H. Rodebush and R. H. Ewart, THIS JOURNAL, **54**, 419 (1932).

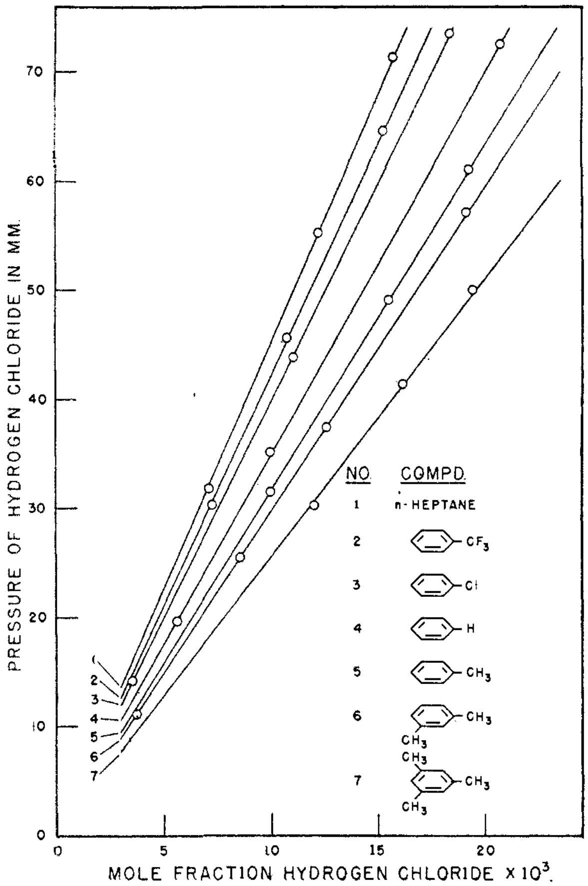

Fig. 1.—Solubility data at −78.51° for hydrogen chloride in *n*-heptane solutions of representative aromatic compounds.

solute permits one to follow the extent of the interaction between the volatile acid and the basic solvent. Moreover, this technique has been extensively applied to a study of the interaction, presumably hydrogen bonding, between the volatile "acid" dichlorofluoromethane, $HCCl_2F$, and a number of basic solvents.[17]

An attempt was made to observe whether a stable 1:1 complex between mesitylene and hydrogen chloride exists at −78° by operating with more dilute solutions (2 and 1%) of the aromatic in the solvent. The observed pressures (Table I) show no inflection at a 1:1 mole ratio of mesitylene to hydrogen chloride, indicating that reactions of the type

$$\text{mesitylene}\cdot\text{HCl} \rightleftarrows \text{mesitylene} + \text{HCl}$$

do not proceed to completion under the conditions of the experiment. However, with the aid of certain assumptions, the data may be used to evaluate equilibrium constants for the formation of a 1:1 complex. Consider the fourth set of data (Table I) for the 2% mesitylene solution: $N = 18.42 \times 10^{-3}$, $p = 65.19$ mm. If no interaction of hydrogen chloride with the aromatic hydrocarbon had occurred, the mole fraction of hydrogen chloride calculated from the Henry's law constant for hydrogen chloride in *n*-heptane should have been 65.19/4520 or 14.42×10^{-3}, instead of the observed value 18.42×10^{-3}. The difference between the observed and calculated values for the mole fraction, 4.00×10^{-3}, may be assumed equal to the actual mole fraction of the complex.

TABLE I

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN REPRESENTATIVE AROMATICS (*n*-HEPTANE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Millimole, n	Mole fraction $N \times 10^3$	Pressure, mm.	Dissocn. constant[d] K (mm.)	Henry's law constant[e] k(mm.)
n-Heptane	0.217	6.62	29.44		4520
	.402	12.19	55.30		
	.520	15.71	71.28		
Benzotrifluoride	.251	7.28	30.30	2440	4220
	.368	10.64	45.66	3940	
	.529	15.23	64.60	3160	
Chlorobenzene	.117	3.41	13.40	1400	4000
	.346	10.01	39.75	1500	
	.628	18.03	72.32	1600	
Benzene	.344	9.96	35.10	720	3500
	.461	13.30	47.40	740	
	.723	20.70	72.50	650	
Toluene	.343	9.93	31.45	470	3170
	.538	15.49	49.05	450	
	.668	19.16	61.10	450	
m-Xylene	.300	8.69	25.00	350	2980
	.468	13.50	39.99	360	
	.537	15.45	45.95	360	
Mesitylene (5%)	.415	11.99	30.25	240	2550
	.562	16.17	41.46	240	
	.676	19.38	49.92	230	
Mesitylene[b] (2%)	.195	5.83	20.50	290	3510
	.292	8.71	30.79	280	
	.386	11.48	40.55	270	
	.624	18.42	65.19	250	
Mesitylene[c] (1%)	.113	3.42	12.11	150	3910
	.300	9.03	34.64	210	
	.381	11.44	44.79	240	
	.531	15.88	62.83	250	

[a] Unless otherwise indicated: 32.57 mmole of *n*-heptane and 1.629 mmole of aromatic. [b] 32.57 mmole of *n*-heptane and 0.651 mmole of mesitylene. [c] 32.57 mmole of *n*-heptane and 0.326 mmole of mesitylene. [d] $K = N_{Ar}P_{HCl}/N_{Ar\cdot HCl}$. [e] $P_{mm} = kN$. The constants listed were determined graphically (Fig. 1).

The original mole fraction of mesitylene is 0.651/(32.57 + 0.651 + 0.624) or 19.23×10^{-3}. If there is present 4.00×10^{-3} of the 1:1 mesitylene–hydrogen chloride complex, the mole fraction of free mesitylene is 15.23×10^{-3}. The equilibrium constant for the reaction may now be calculated

$$K = \frac{N_{\text{mesitylene}} \times P_{\text{HCl}}}{N_{\text{complex}}} = \frac{15.23 \times 10^{-3} \times 65.19 \text{ mm.}}{4.00 \times 10^{-3}} = 248 \text{ mm.}$$

Calculated in a similar manner, 10 of the 11 sets of data give values of K (Table I) within the range 210–290 mm. (Only the first set of data for the 1% mesitylene solution gives a value of K which is considerably different: $K = 150$ mm. However, with both the mesitylene and the hydrogen chloride being present in such low concentration, there is a possibility that the data could have been seriously affected by a slight trace of a more basic impurity.)

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(17) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938).

It follows that the data strongly support the existence of an unstable 1:1 complex between mesitylene and hydrogen chloride.[18] Dissociation constants for the other aromatic complexes are calculated similarly. The values are given in Table I. The precise nature of the interactions between the aromatic nucleus and the acid will be considered later.

If the solubilities of hydrogen chloride in these solutions really constitute a measure of the relative basic properties of the solute, the same effect should be observed in other solvents. Accordingly, a similar series of measurements was made in toluene as the solvent (10 mole % solutions in toluene). The results are presented in Table II and Fig. 2. It is evident that the order of increasing solubility agrees with that previously noted in *n*-heptane solution.

TABLE II

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN REPRESENTATIVE AROMATICS (TOLUENE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Millimole, *n*	Mole fraction $N \times 10^3$	Pressure, mm.	Henry's law constant,[b] *k*(mm.)
Benzotrifluoride	0.335	6.73	2.24	332
	.530	10.60	3.50	
	.824	16.38	5.43	
Chlorobenzene	.299	6.01	1.88	318
	.555	11.09	3.55	
	.861	17.11	5.53	
Benzene	.313	6.29	1.90	308
	.601	12.00	3.67	
	.947	18.80	5.80	
Toluene	.640	12.78	3.78	299
	.824	16.39	4.87	
	1.061	20.99	6.27	
m-Xylene	.359	7.20	1.99	278
	.542	10.84	2.98	
	.701	13.97	3.92	
Mesitylene	.375	7.52	1.84	254
	.547	10.94	2.78	
	.852	16.93	4.40	

[a] 44.96 mmole of toluene and 4.515 mmole of aromatic. [b] $P_{\text{mm}} = kN$. The constants listed were determined graphically (Fig. 2).

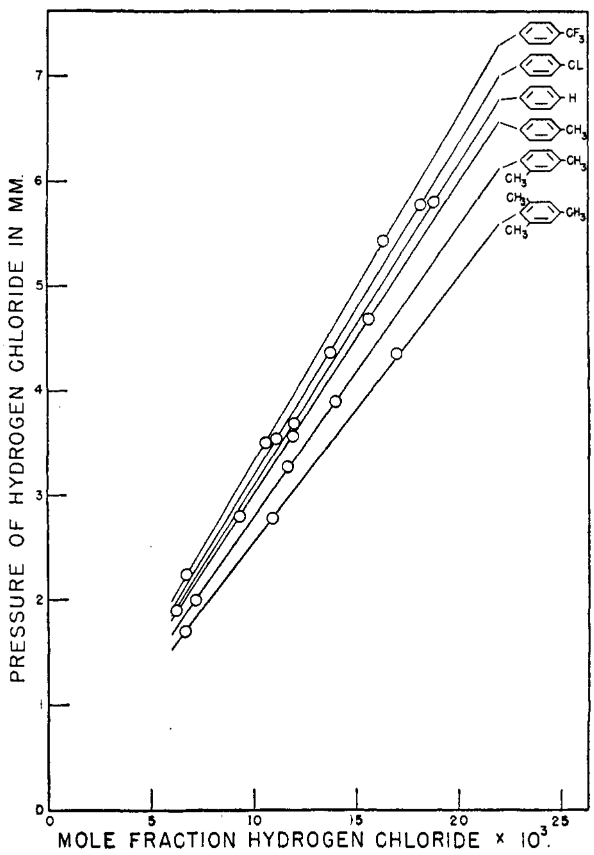

Fig. 2.—Solubility data at −78.51° for hydrogen chloride in toluene solutions of representative aromatic compounds.

If the assumption is made that the solubility of hydrogen chloride in toluene would be that of hydrogen chloride in *n*-heptane except for complex formation, it is possible to calculate a dissociation constant for the toluene–hydrogen chloride complex from the data in Table II. The following values are obtained: 309 (3.78 mm.), 308 (4.87 mm.), 308 (6.27 mm.). These values show a satisfactory constancy, but differ from the average dissociation constant, 460 mm., obtained from the data in dilute *n*-heptane solution (Table I). Either the assumption made in calculating the dissociation constant in pure toluene must be unsatisfactory, or the stability of the complex must be dependent upon the medium. We hope to make a further study of this phenomenon as soon as the pressure of other investigations permits.

In order to obtain an estimate of the dissociation constants for aromatic compounds which were studied only in toluene solution, we adopted the following empirical procedure. The dissociation constants[19] (in *n*-heptane) for benzene (706), toluene (466), *m*-xylene (340) and mesitylene (270) were plotted against the Henry's law constants for the corresponding toluene solutions. The four points define a smooth curve. The dissociation constants for the remaining aromatics were then estimated from their Henry's law constants with the aid of the standard curve. These estimated values are listed in Tables III and VII and designated as "estimated graphically."

Isomeric Methylbenzenes.—It was of interest to observe the various isomeric di-, tri- and tetra-

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[18] The report of O. Maass and J. Russell [THIS JOURNAL, **40**, 1561 (1918)] that they had isolated crystalline complexes of hydrogen bromide and aromatic hydrocarbons stable at very low temperatures led us to anticipate the existence of such complexes in solution at −78°. However, after failing to observe any inflection point in the data, we had concluded that such stable complexes do not exist in solution. We are deeply indebted to Drs. Keefer and Andrews for suggesting the above approach which establishes the existence of unstable 1:1 complexes between hydrogen chloride and aromatic hydrocarbons.

We had originally set ourselves the goal of a precision of 1% in the value of Henry's law constants and data, reported in the Experimental part, indicated that we had actually attained a precision somewhat better than this limit. However, under the conditions of these experiments the complexes are highly dissociated. Relatively small deviations in the pressure readings show up as relatively large changes in the magnitude of the equilibrium constants. We hope in future work to increase further the precision of the measurements and the resulting precision of the dissociation constants at several temperatures in order to determine the heats of formation of the complexes.

[19] The value for benzene is from the data in Table II; the remaining values are based on the data in Table V.

TABLE III

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN THE ISOMERIC METHYLBENZENES (TOLUENE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride			Dissocn. constant,[b] K(mm)	Henry's law constant, k (mm.)
	Millimole, n	Mole fraction, $N \times 10^3$	Pressure, mm.[c]		
Benzene[d]				706[e]	308[d]
Toluene[d]				466[f]	299[d]
p-Xylene	0.402	8.06	2.34	430[g]	294
	.885	17.57	5.18		
	1.093	21.61	6.41		
o-Xylene	.245	4.93	1.40	382[g]	286
	.636	12.69	3.65		
	.902	17.91	5.15		
m-Xylene[d]				340[f]	278[d]
Pseudocumene (1,2,4-Me_3)	.623	12.44	3.36	316[g]	272
	.783	15.58	4.24		
	1.011	20.03	5.49		
Hemimellitene (1,2,3-Me_3)	.545	10.90	2.88	294[g]	265
	.838	16.66	4.45		
	1.065	21.07	5.61		
Mesitylene[d] (1,3,5-Me_3)				270[f]	254[d]
Prehnitene (1,2,3,4-Me_4)	.276	5.55	1.34	264[g]	250
	.600	11.98	3.05		
	.777	15.53	3.85		
Isodurene (1,2,3,5-Me_4)	.514	10.28	2.50	258[g]	246
	.733	14.60	3.61		

[a] 44.96 mmole of toluene and 4.515 mmole of aromatic. [b] $K = N_{Ar}P_{HCl}/N_{Ar \cdot HCl}$. [c] $P_{mm} = kN$. The constants listed were determined graphically. [d] Table II. [e] Table I. [f] Table V. [g] Estimated graphically from standard curve.

TABLE IV

RELATIVE BASIC PROPERTIES AND REACTIVITIES (*p*-XYLENE = 1.00)

Compound	Rel. basicity,[a] (HCl)	Relative basicity,[b] ($HF-BF_3$)	Relative reactivity (halogenation)
Benzene	0.61		0.0005[d]
Toluene	.92	0.01[c]	.157[d]
Ethylbenzene	1.06	......	.13[d]
Isopropylbenzene	1.24	......	.080[d]
t-Butylbenzene	1.36	......	.050[d]
p-Xylene	1.00	1.00[c]	1.00[d]
o-Xylene	1.13	2[c]	2.1[d]
m-Xylene	1.26	20[c]	200[d]
Pseudocumene (1,2,4-)	1.36	40	340[e]
Hemimellitene (1,2,3-)	1.46	(*ca.* 40)	400[e]
Mesitylene (1,3,5-)	1.59	2800	80000[d]
Durene (1,2,4,5-)	..	120	1400[e]
Prehnitene (1,2,3,4-)	1.63	170	2000[e,f]
Isodurene (1,2,3,5-)	1.67	5600	240000[e]
Pentamethylbenzene	..	8700	360000[d]
Hexamethylbenzene	..	89000	....

[a] The ratios of the association constants ($1/K_{dissoc.}$) are listed in order to be directly comparable to the $HF-BF_3$ and halogenation data. [b] Except where otherwise indicated, from distribution experiments (ref. 15). [c] From vapor pressure experiments (ref. 15). Since these values appear more precise than those obtained by distribution experiments, they were adopted as standard and the remaining values based on distribution studies were recalculated on the basis *p*-xylene = 1.00, *m*-xylene = 20. [d] Experimental rates of chlorination (ref. 13). [e] Calculated rates of chlorination (ref. 14). [f] Calculated reactivity relative to benzene is 4.4×10^6 and not 4.4×10^7 as reported in ref. 14.

methylbenzenes to determine whether the solubility of hydrogen chloride would be sufficiently affected by the position of the methyl groups to permit comparison of individual isomers. From the results reported in Tables I and II, *n*-heptane appears preferable as a solvent, since it affords larger differences between individual compounds. However, the low solubility of several of the higher melting isomers made it necessary to utilize toluene. Thus, *p*-xylene at −78.51° crystallized from the 5% *n*-heptane solution, but remained soluble in the 10% toluene solution. However, even in toluene the solubility of durene (m.p. 79.5°) was too low for its basicity to be measured.

It is apparent from the results (Table III) that this technique does indeed distinguish between the isomeric di-, tri- and tetramethylbenzenes.

For the most part the results are in good agreement with the order of reactivity toward electrophilic substitution[13,14] and the order of basic strengths of the methylbenzenes, determined with hydrogen fluoride–boron trifluoride[15] (Table IV).

There are, however, two significant discrepancies. In reactivity toward nuclear halogenation and in basicity as determined with $HF-BF_3$, *m*-xylene is markedly different from the other xylene isomers, and mesitylene is also far more reactive and far more basic than the other trimethylbenzenes. Indeed, the reactivity and basicity of mesitylene are so great that it is shifted beyond the range of two of the tetramethylbenzenes (durene and prehnitene) and approaches more closely the properties of isodurene. With the hydrogen chloride technique this greatly magnified effect of meta methyl groups is not observed. An explanation for these differences is offered later.

Monoalkylbenzenes.—When the series methyl-, ethyl-, isopropyl- and *t*-butylbenzene was examined by the usual technique, utilizing 10 moles of toluene as solvent with 1 mole of added aromatic, the solubility of hydrogen chloride proved to be quite high, pointing to an unexpectedly high basicity for these compounds. For example, *t*-butylbenzene yielded a Henry's law constant of 266, a value considerably lower than for toluene, or for that matter, of *m*-xylene (Table II). It appeared possible that the high solubility of hydrogen chloride might in part be due to a defect in the previous experimental procedure. A fixed number of millimoles of a hydrocarbon such as *t*-butylbenzene represents a larger weight and volume of material than the corresponding number of millimoles of a hydrocarbon such as toluene.

In order to avoid the possibility that considerations of this kind were modifying the results, the experimental procedure was altered. A constant quantity of the aromatic compound, 2.5 mmoles, was dissolved in sufficient *n*-heptane to bring the total volume of the solution up to 4.803 ml. However, as seen from the results in Table V and Fig. 3, the apparent high solubility of hydrogen chloride persisted, in spite of the altered technique. Data for *m*-xylene and mesitylene under identical conditions are included in Table V to facilitate comparison.

Because of the altered procedure used in these measurements (Table V), it was more convenient to calculate the dissociation constants utilizing the number of millimoles n, instead of the mole fraction N. It is of interest that the dissociation constants calculated for toluene, *m*-xylene and mesitylene from these data obtained with "molar-type" solutions are in satisfactory agreement with the constants previously reported (Table I) based on data obtained with more dilute "molal-type" solutions.

TABLE V

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN THE MONOALKYLBENZENES (*n*-HEPTANE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Milli-mole, n	Mole fraction $N \times 10^3$	Pressure, mm.	Dissocn. constant,[b] K(mm.)	Henry's law constant,[c] k (mm.)
Toluene	0.140	3.97	11.05	480	2790
	.320	9.04	25.32	470	
	.487	13.69	38.26	450	
Ethylbenzene	.167	4.73	12.22	400	2680
	.328	9.26	24.80	420	
	.537	15.07	40.42	400	
Isopropylbenzene	.217	6.14	15.30	360	2490
	.384	10.82	26.96	350	
	.556	15.60	38.69	330	
t-Butylbenzene	.219	6.20	14.78	330	2380
	.378	10.66	25.15	310	
	.589	16.51	39.56	300	
m-Xylene	.193	5.47	13.53	360	2460
	.441	12.41	30.86	340	
	.678	19.96	46.82	320	
Mesitylene	.126	3.57	7.65	270	2210
	.309	8.73	19.16	270	
	.524	14.71	32.65	260	

[a] 2.5 mmoles of aromatic in sufficient *n*-heptane to make total volume of solution 4.803 ml. [b] $K = n_{Ar}P_{HCl}/N_{Ar\cdot HCl}$. [c] $P_{mm} = kN$. The constants listed were determined graphically (Fig. 3).

McCaulay and Lien[15] observed that hexaethylbenzene is less basic than hexamethylbenzene and therefore concluded that an ethyl group is less effective than a methyl group in contributing to the basic properties of the aromatic nucleus. Furthermore, it is well established that the order of reactivities toward halogenation[13,20] is toluene (100) > ethylbenzene (84) > isopropylbenzene (51) > *t*-butylbenzene (32) ≫ benzene (0.29). (The figures[13] in parentheses give the relative chlorination rates at 25°.) The relative basicities of the monoalkylbenzenes are in conflict with these findings. It follows that a serious discrepancy exists between the effect of the alkyl group on the reactivity of the ring and its effect upon the basic properties of the ring as measured by the hydrogen chloride technique. Fortunately, the explanation to be proposed for the discrepancies previously pointed out also satisfactorily accounts for the present anomaly.

Monohalobenzenes.—The monohalobenzenes were examined by the same technique utilized for the monoalkylbenzenes. The results are summarized in Table VI and Fig. 3.

TABLE VI

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN THE MONOHALOBENZENES (*n*-HEPTANE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Milli-mole, n	Mole fraction, $N \times 10^3$	Pressure, mm.	Dissocn. constant,[b] K(mm.)	Henry's law constant,[c] k(mm.)
Iodobenzene	0.111	3.15	11.58	1250	3750
	.289	8.17	30.58	1310	
	.375	10.57	39.86	1320	
Bromobenzene	.101	2.87	10.50	1240	3660
	.201	5.69	21.30	1340	
	.325	9.18	33.90	1210	
Chlorobenzene	.145	4.11	14.53	1020	3570
	.258	7.30	26.23	1080	
	.413	11.63	41.67	1000	
Fluorobenzene	.162	4.59	14.21	640	3260
	.288	8.14	26.37	720	
	.426	11.99	39.64	750	

[a] 2.5 mmoles of aromatic in *n*-heptane to make total volume of solution 4.803 ml. [b] $K = N_{Ar}P_{HCl}/N_{Ar\cdot HCl}$. [c] $P_{mm} = kN$. The constants listed were determined graphically (Fig. 3).

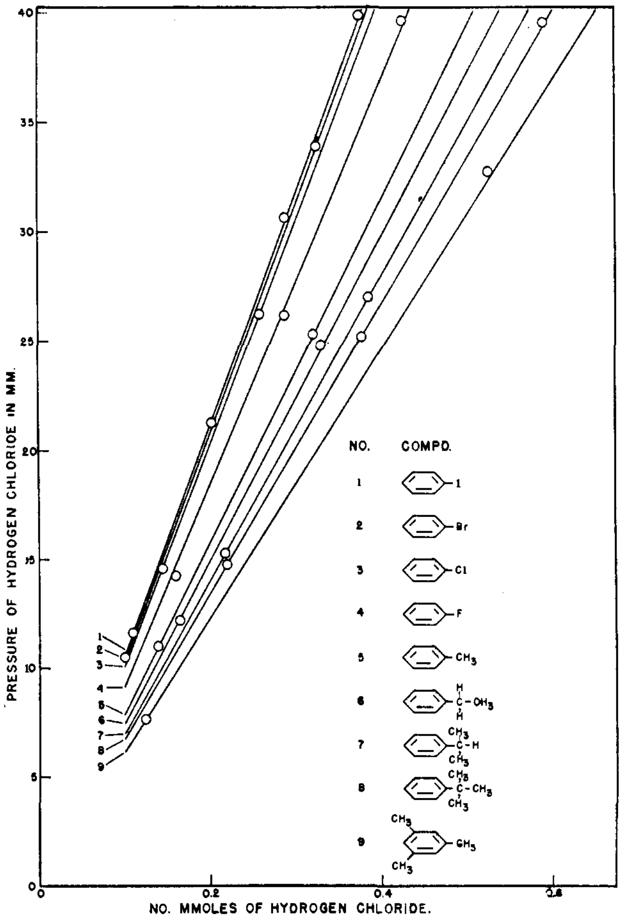

Fig. 3.—Solubility data at −78.51° for hydrogen chloride in toluene solution of monoalkyl- and monohalobenzenes.

The effect of the halogen on the basic properties of the aromatic ring, H > F > Cl > Br > I, is identical with that observed in the monohaloaniline bases.[21] Moreover, the sigma values reported by Hammett[22] (F, +0.062; Cl, +0.227; Br, +0.232;

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(20) E. Berliner and F. Bondhus, THIS JOURNAL, **70**, 854 (1948); E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949).

(21) G. M. Bennett, G. L. Brooks and S. Glasstone, *J. Chem. Soc.*, 1821 (1935).

(22) L. P. Hammett, ref. 5, p. 188.

and I, +0.276) are also in agreement with the observed basicities. Since the order is opposite to that predicted by a consideration of the inductive effect of the halogen, it follows that resonance effects must contribute to the basic properties of the nucleus.

Thiophene.—Because of the high reactivity of thiophene toward electrophilic reagents, it was anticipated that this heterocycle would prove to be an excellent solvent for hydrogen chloride. However, the results in toluene solution lead to a Henry's law constant of 316 (Table VII) as compared with values of 308 for benzene and 318 for chlorobenzene (Table II).

TABLE VII

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN THE THIOPHENE (TOLUENE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Millimole, n	Mole fraction, $N \times 10^3$	Pressure, mm.	Dissociation constant, K(mm.)	Henry's law constant, k(mm.)
Thiophene	0.602	12.02	3.80	1000[b]	316
	.783	15.58	4.92		
	.939	18.63	5.89		

[a] 44.96 mmoles of toluene and 4.515 mmoles of aromatic. [b] Estimated graphically from standard curve.

This discrepancy between the high reactivity and low basicity of thiophene constitutes a fourth anomaly requiring explanation.

Olefins.—A number of representative olefins were examined in toluene solution in order to establish whether the basicity of these compounds agreed with theoretical predictions of base strength. Winstein and Lucas[23] reported a detailed study of the stability of complexes of olefins with silver ion and observed that the stability decreased in the order: n-BuCH=CH$_2$ > Me$_2$C=CH$_2$, EtCH=CHMe > Me$_2$C=CHMe. On theoretical grounds the basicity of the olefins and therefore the stability of the complexes should increase in the opposite order: RCH=CH$_2$ < R$_2$C=CH$_2$ < R$_2$C=CHR. Winstein and Lucas suggested that steric effects were at the basis of the disagreement between the theoretical and observed order. No other experimental procedure has been applied to the determination of the base strengths of a series of olefins.

Experiment revealed that under the conditions employed in the solubility experiments hydrogen chloride neither adds to nor isomerizes olefins, even those distinguished by reactivity and lability of high order. In one experiment involving 2,4,4-trimethyl-2-pentene, hydrogen chloride was maintained in solution at −78.51°. No pressure drop occurred in 24 hours. The hydrogen chloride was removed by distillation at −78°. Recovery was quantitative. The olefin recovered exhibited a refractive index identical with that of the original material. The solubility data are summarized in Table VIII. Data for n-heptane are included to facilitate comparison.

It is evident from the results that the solubility of hydrogen chloride is strongly affected by the structure of the olefin. It was, however, surprising that within the experimental error there appeared to be no difference between the two diisobutylene isomers. Since 2,4,4-trimethyl-1-pentene is a representative of the class R$_2$C=CH$_2$ and 2,4,4-trimethyl-2-pentene is a representative of the class R$_2$C=CHR, an appreciable difference in basicity, and therefore of hydrogen chloride solubility, should be expected.

TABLE VIII

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN REPRESENTATIVE OLEFINS (TOLUENE SOLUTION, −78.51°)

Compound[a]	Hydrogen chloride Millimole, n	Mole fraction, $N \times 10^3$	Pressure, mm.	Henry's law constant,[b] k (mm.)
n-Heptane	0.334	6.71	2.25	335
	.526	10.52	3.50	
	.888	17.63	5.90	
Tetrachloroethylene	.233	4.69	1.54	332
	.403	8.08	2.63	
	.785	15.71	5.15	
1-Octene	.317	6.37	1.95	306
	.487	9.75	3.00	
	.661	13.20	4.11	
Cyclohexene	.303	6.09	1.74	290
	.588	11.74	3.38	
	.995	19.71	5.70	
2,4,4-Trimethyl-1-pentene	.156	3.14	0.901	288
	.574	11.47	3.33	
	.810	16.11	4.75	
2,4,4-Trimethyl-2-pentene	.228	4.59	1.30	288
	.476	9.53	2.75	
	.772	15.37	4.58	

[a] 44.96 mmoles of toluene and 4.515 mmoles of olefin (or n-heptane). [b] $P_{\text{mm}} = kN$. The constants listed were determined graphically.

The freezing points of the two isomeric octenes lie below −78.51°. Accordingly it was decided to measure the solubility of hydrogen chloride in the pure compounds. The results are presented in Table IX.

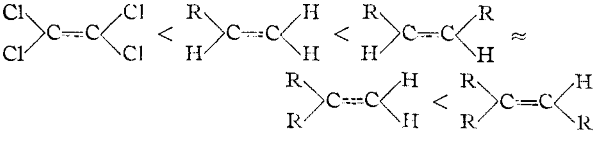
TABLE IX

DATA FOR THE SOLUBILITY OF HYDROGEN CHLORIDE IN 2,4,4-TRIMETHYL-1-PENTENE AND -2-PENTENE (−78.51°)

Compound[a]	Hydrogen chloride Millimole, n	Mole fraction, $N \times 10^3$	Pressure, mm.	Henry's law constant,[b] k (mm.)
2,4,4-Trimethyl-1-pentene	0.325	7.18	3.82	550
	.490	10.78	5.95	
	.840	18.34	10.74	
2,4,4-Trimethyl-2-pentene	.483	10.63	4.49	430
	.774	16.93	7.40	
	.910	19.84	8.72	

[a] 44.96 mmoles. [b] $P_{\text{mm}} = kN$. Estimated graphically. The graphs show a slight curvature, possibly the result of a small quantity of a more basic impurity in the olefin.

The results definitely indicate that the 2-isomer is a considerably better solvent for hydrogen chloride than the 1-isomer and the order of increasing solvent power



is in good agreement both with the predicted effect of

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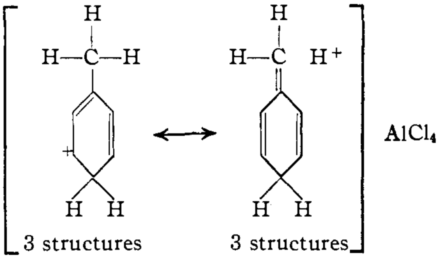
(23) S. Winstein and H. J. Lucas, THIS JOURNAL, 60, 836 (1938).

structure on base strength and the known reactivity of the double bonds toward electrophilic reagents.

The hydrogen chloride technique therefore offers promise not only as a method of determining the base strengths of olefins, but also as a means of establishing the degree of substitution of the carbons of a double bond in a complex hydrocarbon. Further study of the basic properties of olefins by this technique is underway.[24]

The Nature of π- and σ-Complexes.—It was previously proposed[11] that the complex formed by the reaction of the catalyst couple, hydrogen chloride–aluminum chloride, with toluene is a carbonium ion salt (I).

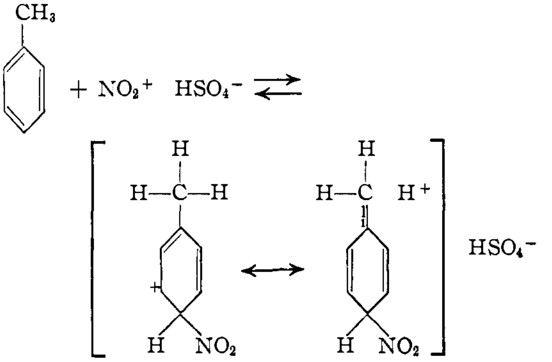
(I)



Presumably isomeric molecules with the proton in the ortho position would be essentially equally probable. A similar structure has been proposed by McCaulay and Lien for the complexes of aromatics with hydrogen fluoride–boron trifluoride.[15]

The structure of these carbonium ion salts is clearly similar to the structure now widely accepted for the intermediate involved in aromatic substitution by electrophilic reagents[25]

(II)

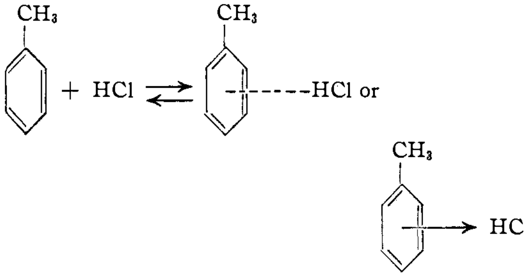


A strong argument that the structures of these aromatic complexes with HCl–AlCl$_3$ and HF–BF$_3$ should be closely related to the structures of the intermediates in aromatic substitution is furnished by the simple quantitative relationship between the relative basicity (HF–BF$_3$) of the methylbenzenes and their relative rates of halogenation (Table IV). A plot of the logarithm of the relative basicity (HF–BF$_3$) *versus* the logarithm of the relative reactivity defines an excellent straight line.

The interaction of hydrogen chloride with aromatic nuclei must be quite different. Whereas the complexes of aromatic hydrocarbons and HCl–AlCl$_3$ or HF–BF$_3$ are deeply colored, conduct the electric current, and readily exchange nuclear hydrogen for deuterium, solutions of hydrogen halides in these hydrocarbons are colorless, the solutions do not conduct the current, and no exchange is observed with deuterium halides. Furthermore, in our experiments on the toluene–HCl–AlCl$_3$ system at −80° we observed that both formation and dissociation of the complex occurred relatively slowly, in a matter of hours; the reaction apparently involves an appreciable energy of activation.[11] In the studies reported in the present paper, equilibrium between hydrogen chloride and the aromatics was established very rapidly—within a matter of a few minutes.

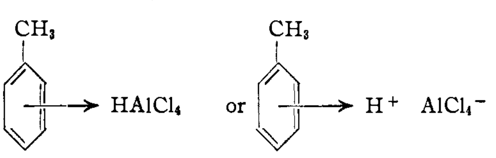
It is therefore proposed that the interaction of hydrogen chloride and aromatic nuclei does not proceed through the formation of similar carbonium ion salts, but instead involves a weak interaction between the π-electrons of the ring and the polar hydrogen chloride molecule (III).

(III)



The latter formulation resembles the π-complexes proposed by Dewar.[26] However, Dewar would prefer to consider all interactions between aromatic nuclei and electrophilic reagents as involving π-complexes of this kind.[27] Thus in contrast to our view, he would formulate the complexes of aromatic hydrocarbons and HCl–AlCl$_3$ or HF–BF$_3$ as not involving the transfer of the proton to any particular carbon atom (IV).

(IV)



In our opinion the experimental evidence favors the view that aromatic complexes are of two distinct types, separated by a significant potential energy barrier. One class consists of the carbonium ion type complexes with the electrophilic atom or group united to a definite carbon atom. The second class consists of complexes of less well-defined structures, involving weak interactions between the electrophilic atom or group and the π-electrons; here there is no definite bond between the electrophilic atom or group and any particular carbon atom.

The benzene molecule is presently pictured as a planar ring with a relatively high concentration of

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[24] Work in progress with L. Domash.

[25] There has been considerable discussion as to whether these should be considered to be transition states in aromatic substitution or intermediates. See L. Melander [*Arkiv for Kemi*, **2**, 213 (1950)] for a critical discussion and pertinent references. The isolation of stable carbonium ion salts with HCl-AlCl$_3$ and HF-BF$_3$, products which must be essentially identical with those involved in the deuteration of aromatic nuclei with DCl-AlCl$_3$ [A. Klit and A. Langseth, *Z. physik. Chem.*, **176**, 65 (1936)], lends strong support to their interpretation as intermediates.

[26] M. J. S. Dewar, *J. Chem. Soc.*, 406, 777 (1946).

[27] Private communication.

electrons on both faces of the plane.[28] An electrophilic atom or group would presumably be attracted to the electron cloud at the positions of greatest density. Since the electron density is postulated to be low near the center of the ring and high immediately above and below the ring of carbon atoms, the electrophilic atom should be associated with the electrons in this position and, presumably, can move readily around this annulus of electron cloud without greatly altering its distribution. An increase in the electrophilic nature of the reagent is considered to result in a penetration of this cloud of π-electrons, with the formation of a covalent σ-bond with one of the six carbon atoms of the ring. This penetration and distortion of the π-electron cloud must involve an appreciable activation energy and accounts for the separation of aromatic complexes into two distinct classes proposed in this paper. It is suggested that the term "π-complex" be restricted to those complexes in which the π-electron cloud is not seriously distorted (*e.g.*, the hydrogen chloride complexes), and the complexes of the remaining class be termed "onium ion-complexes" or, more conveniently, "σ-complexes."

This interpretation affords a simple explanation of the four anomalies observed in this study.

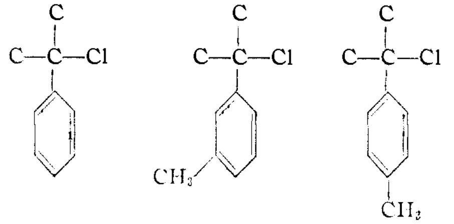
I. The *m*-xylene anomaly
  Relative basicity (hydrogen chloride)
    p-Xylene < *o*-xylene < *m*-xylene
  Relative basicity (HF–BF$_3$)
    p-Xylene < *o*-xylene << *m*-xylene
  Relative reactivity (halogenation)
    p-Xylene < *o*-xylene << *m*-xylene

II. The mesitylene anomaly
  Relative basicity (hydrogen chloride)
    1,2,4-Me$_3$ < 1,2,3-Me$_3$ < 1,3,5-Me$_3$ < 1,2,3,4-Me$_4$
  Relative basicity (HF–BF$_3$)
    1,2,4-Me$_3$ < 1,2,3-Me$_3$ < 1,2,3,4-Me$_4$ << 1,3,5-Me$_3$
  Relative reactivity (halogenation)
    1,2,4-Me$_3$ < 1,2,3-Me$_3$ < 1,2,3,4-Me$_4$ << 1,3,5-Me$_3$

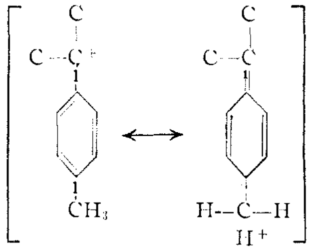
III. The monoalkylbenzene anomaly
  Relative basicity (hydrogen chloride)
    Methyl- < Ethyl- < Isopropyl- < *t*-Butylbenzene
  Relative basicity (HF–BF$_3$)
    Hexamethylbenzene > hexaethylbenzene
  Relative reactivity (halogenation)
    Methyl- > Ethyl- > Isopropyl- > *t*-Butylbenzene

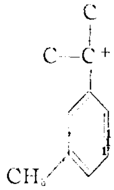
IV. The thiophene anomaly
  Relative basicity (hydrogen chloride)
    Thiophene < benzene
  Relative reactivity
    Thiophene >> benzene

Considerable evidence is now available that the full electron contributing properties of a methyl group can only be realized in an electron deficient system (*e.g.*, carbonium ion) which permits hyperconjugation. Thus a methyl group introduced into the benzoic acid or aniline molecules has only a small effect upon the ionization constant of the acid or base. Moreover, the effect is not very different with the methyl group in either the meta or para position. However, a methyl group introduced into the nucleus of phenyldimethylcarbinyl chloride produces a large effect upon the solvolysis rate in the para position, but only a small effect in the meta position (V).[29] This large effect of the para methyl group is attributed to stabilization of the carbonium ion through hyperconjugation (VI). The meta methyl group cannot stabilize the carbonium ion in this way (VII).

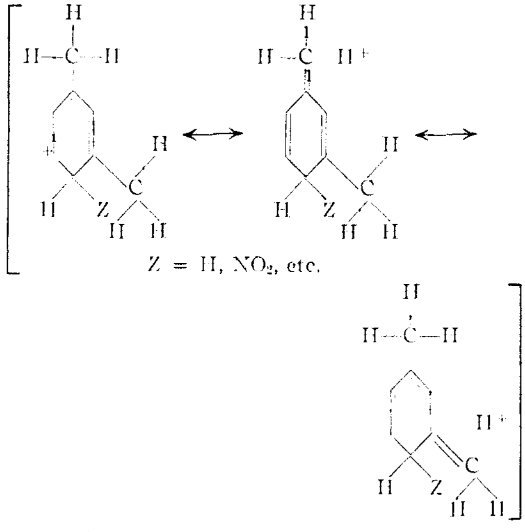
(V)


Rel. rates 1 2 30

(VI)


(VII)


It follows that the remarkably enhanced basicity, as measured by the HF–BF$_3$ technique, as well as the greatly increased reactivity of *m*-xylene over the ortho and para isomers, must be due to the fact that only in the meta isomer can *both* methyl groups contribute to the stabilization of the carbonium ion (VIII).

(VIII)


Z = H, NO$_2$, etc.

In the hydrogen chloride "π-complex" there is only a relatively small distortion of the π-electrons so that the electron releasing qualities of the two methyl groups are only partially realized.

In the same way one can account for the very high basicity and reactivity of mesitylene. Here three methyl groups are in position maximally to stabilize the σ-complex. On the other hand, the other two trimethylbenzenes and both durene and prehnitene have only two methyl groups each in such favored positions. Again in the hydrogen chloride π-complex the methyl groups contribute

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(28) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949.

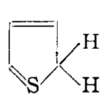
(29) Unpublished work with James D. Brady. Similar effects of methyl substituents in benzhydryl chlorides were observed by J. F. Norris and C. Banta, THIS JOURNAL, **50**, 1804 (1928).

primarily through their inductive effect and the hyperconjugative effect of the methyl groups largely remains latent.

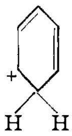
The ease of substitution of the monoalkylbenzenes decreases from Me > Et > *i*-Pr > *t*-Bu, with the decreasing number of α-hydrogen atoms available for hyperconjugation[20,30]; this is in contrast to the order observed by the hydrogen chloride technique. In the latter the alkyl groups must contribute to the electron density of the aromatic ring primarily through their inductive effect.[31]

Finally, the hydrogen chloride technique forces us to conclude that the apparent electron density of the thiophene ring is less than that of the benzene ring. The great reactivity of the thiophene molecule toward electrophilic reagents must be primarily the result of a transition state of low energy. The thiophene ion (IX) must be very stable compared with the corresponding benzene derivative[32] (X).

(IX)



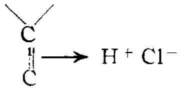
(X)



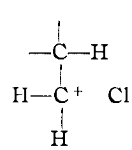
It appears, therefore, that we have two supplementary techniques for investigating electron availability in aromatic nuclei. On the one hand, there is the hydrogen chloride technique which furnishes a measure of the relative electron availability in the ground state of the molecule; on the other hand the HF–BF$_3$ and HCl–AlCl$_3$ technique provides a measure of the relative electron availability in the transition state.

In the case of the olefins, we again appear to be dealing with intermediates of two distinct classes, similar to the π-complexes and the σ-complexes of the aromatic compounds. The hydrogen chloride–olefin complexes presumably involve weak interactions of hydrogen chloride with the π-electrons. The inappreciable conductivity of such solutions, the failure of hydrogen chloride to add to or to isomerize labile olefins, argues against any ionic formulations, such as (XI) or (XII).

(XI)

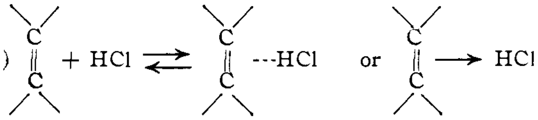


(XII)



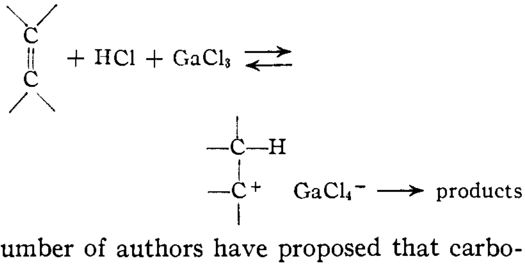
In the presence of small quantities of gallium chloride, hydrogen chloride adds readily to olefins; isomerization and other characteristic reactions of carbonium ions can be observed.[33] It therefore appears that the olefin–hydrogen chloride complex must involve a weak interaction between the π-electrons and the hydrogen chloride (XIII)

(XIII)



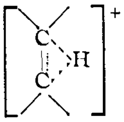
whereas in the presence of gallium chloride carbonium ions are apparently formed as transitory intermediates (XIV).

(XIV)

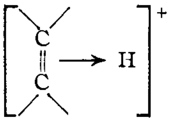


A number of authors have proposed that carbonium ions be formulated as involving a hydrogen bridge or a protonated π-complex[26,28,34,35] (XV) or (XVI).

(XV)



(XVI)



In spite of the fact that no experimental evidence has been advanced which supports such structures for carbonium ions, these formulations have been widely adopted. The results of the present study do not support such formulations for carbonium ions derived from simple olefins. Until sound experimental evidence is available in support of such hydrogen bridged structures in simple systems, the classical formulation is to be preferred.[36]

Finally it may be pertinent to comment on Klatt's study.[4] At 0° he observed the solubility of hydrocarbons in liquid hydrogen fluoride (in weight per cent.) to be: benzene, 2.25; toluene, 1.54; *m*-xylene, 1.17. This leads to an order of basicity in direct contrast to the orders obtained by all other workers. In view of the discussion here presented, it is difficult to account for the observed solubilities if they depend primarily upon the transfer of a proton to the aromatic ring, as postulated by Hammett.[5] However, it is significant that Klatt reports that the benzene solution is colorless, whereas the HF–BF$_3$ and HCl–AlCl$_3$ complexes are all strongly colored. Moreover, McCaulay and Lien[15] report that the toluene–HF–BF$_3$ complex is highly unstable and they were unable to obtain evidence for a corresponding complex with benzene. It follows that the solubility of these simple aromatic hydrocarbons in liquid hydrogen fluoride is probably the result of interactions of the π-rather than those of the σ-type.

As has been pointed out, the π-type interactions in hydrocarbons such as benzene, toluene and *m*-

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(30) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(31) It was pointed out earlier that from the relative electronegativities of the four halogens, one would predict the order of basic properties, $FC_6H_5 < ClC_6H_5 < BrC_6H_5 < IC_6H_5$. Since the opposite order is given by the hydrogen chloride technique (Table VI), it is necessary to consider that resonance effects profoundly modify the electron availability of the aromatic nucleus. This is in sharp contrast to the conclusion reached above that hyperconjugation effects are of relatively minor importance in the ground state of the alkylbenzenes.

(32) We can justify the postulated greater stability of the thiophene ion (IX) by comparing the relatively high stabilities of simple sulfonium ions, R_3S^+, with the much lower stabilities of the corresponding carbonium ions, R_3C^+.

(33) Unpublished work with Miss Martha Havill.

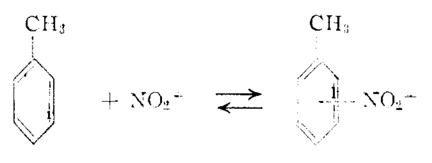
(34) H. Eyring, H. M. Hulburt and R. A. Harman, *Ind. Eng. Chem.*, **35**, 511 (1943).

(35) C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 39-43.

(36) S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952), have reached the same conclusion in the case of the phenylneopentylcarbonium ion.

xylene are relatively small—far smaller than those observed in σ-complex formation—and do not differ greatly with the number and position of the methyl groups, as do the σ-type interactions. Hildebrand[37] has emphasized the importance of correcting for the vapor pressure of the substances being compared when relative reactivities are determined from relative solubilities in a common solvent. Such corrections in the case of benzene, toluene and the xylenes are apparently unimportant in dealing with the large σ-type interactions, such as those observed by McCaulay and Lien.[15] However, they are apparently significant in dealing with the weak π-type interactions, such as are probably involved in Klatt's solubility work. Corrected in this way, Klatt's solubility data give the expected order of basicity.

The Role of π- and σ-Complexes in Aromatic Substitution.—Dewar[28] has proposed that electrophilic substitution of aromatic nuclei involves prior formation of π-complexes.



That such π-complexes are present in reaction mixtures involving aromatic substitution is highly probable. However, Dewar further proposes that the rate-determining step in aromatic substitution will involve the initial formation of the π-complex and that the rate of substitution will parallel the stability of the π-complex. The results and interpretation reported in the present paper suggest that this view cannot be correct.

The π-complex of hydrogen chloride with *t*-butylbenzene is considerably more stable than that with toluene, yet the nuclear halogenation of toluene proceeds at a fivefold faster rate than that of *t*-butylbenzene. The halogenation of mesitylene proceeds at a rate approximately 2,000,000 greater than that of *t*-butylbenzene (Table IV), yet the stabilities of the two hydrogen chloride π-complexes are of the same order of magnitude (Table V).

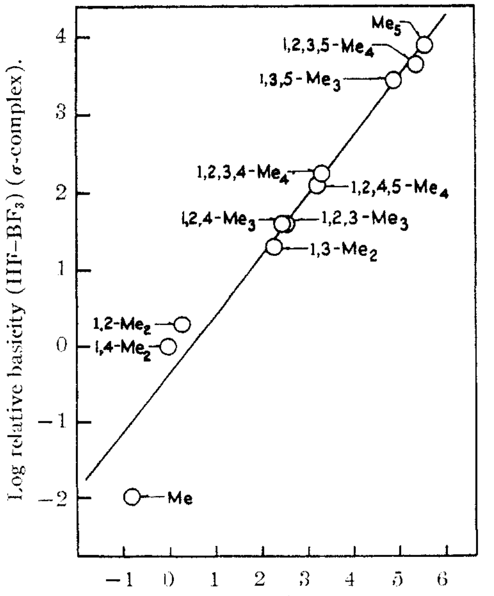


Fig. 4.—Relationship between stability of σ-complex (HF-BF3) and relative rate of halogenation.

It is significant that there is a simple linear relationship (Fig. 4) between the logarithm of the relative rates of halogenation of the methylbenzenes and the logarithm of the relative basicity (HF–BF3) of these hydrocarbons (σ-complexes).[37a] On the other hand, a similar linear relationship (Fig. 5) does not exist between the rate of halogenation and the stability of the hydrogen chloride–aromatic complexes (π-complexes). *It follows that the rate of substitution of aromatic nuclei must be determined not by the stability of the π-complexes, as proposed by Dewar, but must be determined instead by the stability of the σ-complexes.*

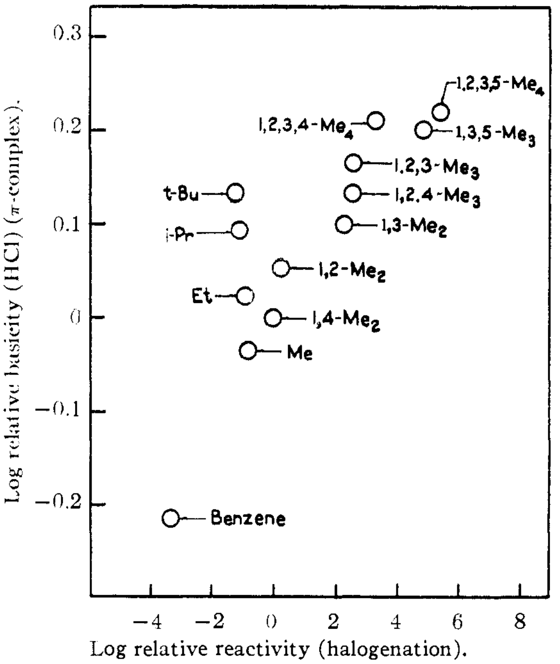


Fig. 5.—Relationship between stability of π-complex (HCl) and relative rate of halogenation.

Experimental Part

Experimental Procedure.—High vacuum equipment and methods[38] were adapted to the determination of the Henry law constants. The portion of the high vacuum apparatus utilized for the solubility studies is shown in Fig. 6.

In a typical determination of the solubility of hydrogen chloride in toluene or *n*-heptane containing dissolved aromatic, where the quantity of solvent was maintained constant, the solvent, which was stored in tube B, was measured out volumetrically in the calibrated bulb C (4.803 ml.) at 25°. The solvent was then transferred to the solubility tube G. The float valve E was closed, dry air admitted to the apparatus to the left of E, and tube D was removed. The aromatic under study was weighed into the tube D (4.515 mmole for toluene as solvent; 1.629 mmole for *n*-heptane as solvent) and connection with the apparatus made through the mercury-sealed greaseless joint. The apparatus was pumped out, trapping the compound at U-tube A

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(37) J. H. Hildebrand, *J. Phys. Colloid Chem.*, **53**, 973 (1949).

(37a) NOTE ADDED TO PROOF.—This relationship has also been noted in a recent publication by F. E. Condon, THIS JOURNAL, **74**, 2528 (1952).

(38) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

with liquid nitrogen. The material was then transferred to the solution tube G, the −78.51° bath placed about the tube, and the solvent and aromatic compound thoroughly mixed with the magnetic stirrer H.

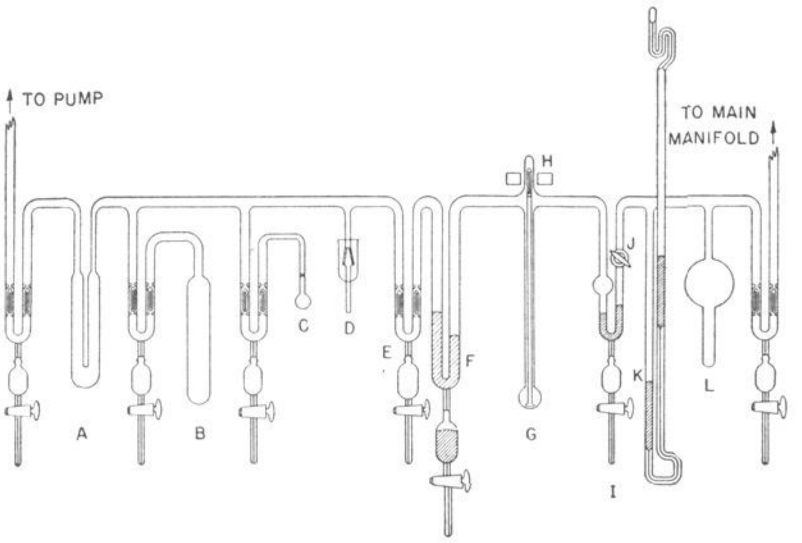

Fig. 6.—Apparatus used for the determination of the solubility of hydrogen chloride at −78.51° in solutions of aromatic compounds.

Where the volume of the solution was maintained constant, the weighed aromatic compound, 2.5 mmoles, in tube D was transferred to the calibrated bulb C. The solvent was then carefully distilled into the bulb until the volume of the solution reached the calibration mark, and the solution was then transferred into the solubility tube G. In this procedure, after the experiment, the hydrogen chloride was separated, and the material was removed and weighed to determine the weight of solvent added.

After sufficient time to permit thermal equilibrium to be attained in tube G (1–2 hours), hydrogen chloride was carefully introduced from the reservoir L through the stopcock J. From the decrease in pressure, as measured on the manometer K with a cathetometer to the nearest 0.05 mm., the number of millimoles of hydrogen chloride introduced was calculated. This was corrected for the small quantity of hydrogen chloride remaining in the vapor space of tube G. The pressure above the solution was measured to 0.01 mm. on the manometer F with a Gaertner 100-mm. micrometer slide cathetometer which reads to 0.001 mm.

The constant temperature bath was constructed of a 1-gal. Dewar vessel, as shown in Fig. 7. It was completely sealed with the aid of a rubber gasket B so that carbon dioxide volatilized from the Dry Ice refrigerant could escape only through the mercury bubbler H. The depth of mercury was maintained at a level, h, such that the pressure in the vessel was precisely 760 mm. The tube E was of glass and was filled with an inert liquid J to facilitate attainment of thermal equilibrium. In operation the vessel was packed almost to the brim with powdered Dry Ice and a temperature of −78.51° was maintained satisfactorily over periods of 30 to 40 hours without difficulty.

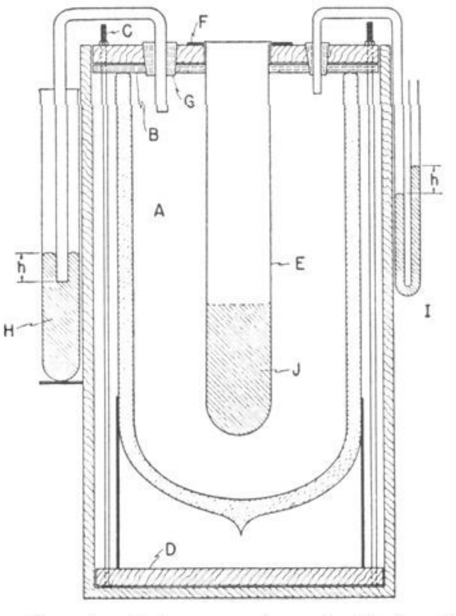

Fig. 7.—Constant temperature bath (−78.51°).

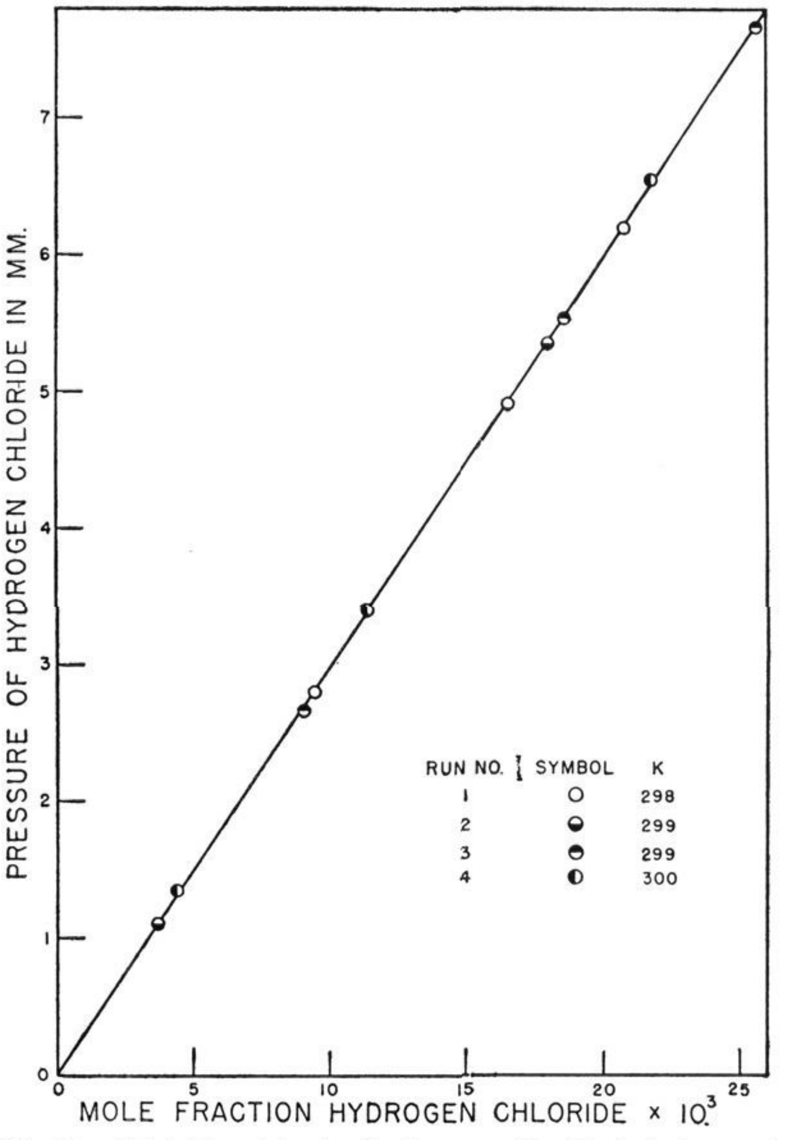

Fig. 8.—Solubility data for hydrogen chloride in toluene at −78.51°.

TABLE X

PHYSICAL PROPERTIES OF COMPOUNDS

Compound	B.p. or m.p. °C.	Mm.	n^{25}_D
Benzene	79.4	745	1.4979
Benzotrifluoride	101		1.4120
Bromobenzene	M. −31.05		1.5569
t-Butylbenzene	168.7	743	1.4899
Chlorobenzene	131.2	743	1.5220
Cyclohexene	81.9	741	1.4442
Durene	M. 79.3–79.7		
Ethylbenzene	135.0	741	1.4931
Fluorobenzene	84.2	742	1.4629
Hemimellitene	170–172	741	1.5109
n-Heptane	97.9	744	1.3853
Iodobenzene	186.9	742	1.6162
Isodurene	84.6–84.7	17	1.5104
Isopropylbenzene	151	744	1.4888
Mesitylene	163.0	742	1.4950
1-Octene	120.5	744	1.4060
Prehnitene	M. 7.5–9.5		
Pseudocumene	64.0–64.5	21	1.5123
Tetrachloroethylene	120.6	747	1.5040
Thiophene	83.2	740	1.5250
Toluene	110.2	746	1.4941
2,4,4-Trimethyl-1-pentene	100.9	742	1.4060
2,4,4-Trimethyl-2-pentene	104.2	743	1.4133
o-Xylene	143.5	740	1.5020
m-Xylene	138.0	741	1.4943
p-Xylene	137.6	741.5	1.4932

Test of Precision.—In order to test the precision attainable, five separate determinations were made for toluene. These yielded values for Henry's law constant at −78.51° of 298, 299, 299, 300, 299 mm. Representative data for four of these determinations are illustrated in Fig. 8. It was therefore concluded that the Henry's law constant could be obtained with a precision of 1 part in 300. Although refinements in technique might have improved the precision, we found it ample to distinguish between the different compounds whose basicities were of interest.

Materials.—The trimethyl- and tetramethylbenzenes were generously supplied by Professor Lee Irvin Smith of the University of Minnesota. The remaining compounds were commercial products, the purest available. Depending upon the quantity available, the compounds were distilled either through a Todd Micro Column (rated efficiency: 50 theoretical plates) or a helices packed column (rated efficiency: 75 theoretical plates). Only materials which boiled constantly and exhibited constant refractive indices were utilized. The bromobenzene was a Bureau of Standards sample for styrene determinations by the freezing point method and was used without further purification. Physical data for these compounds are summarized in Table X.

Acknowledgment.—We wish to acknowledge our indebtedness to the Standard Oil Company (Indiana) for financial support of this investigation and to Professor L. I. Smith for his generous samples of the higher methylbenzenes. We are also indebted to Mr. Lionel Domash and Miss Martha Havill for assistance in calculating the dissociation constants for the aromatic–hydrogen chloride complexes.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Thermal Racemization of Dimethyl (−)-Bromosuccinate

BY LAWRENCE J. ANDREWS AND JAMES E. HARDWICKE

RECEIVED JANUARY 7, 1952

Contrary to a previous report it has been found that no extensive racemization occurs when optically active bromosuccinic acid is converted to its dimethyl ester with diazomethane. The ester does, however, lose activity when subjected to repeated distillation under reduced pressure. To demonstrate the sensitivity of this ester to thermal racemization a series of kinetic measurements of the rate of loss of optical activity of this compound at several temperatures has been made. Kinetic measurements of the dehydrobromination reaction, which occurs simultaneously with racemization, have also been made. Similar kinetic studies have also been carried out using optically active methyl esters of α- and β-bromobutyric acids. The results are of interest as regards the mechanisms of the racemization and dehydrobromination reactions.

It is known that certain esters of optically active bromosuccinic acid undergo slow autoracemization at room temperature.[1] It has also been demonstrated that in acetone solution dimethyl (−)-bromosuccinate can be racemized in the temperature range of 0 to 52° by the addition of inorganic bromides.[2] However, little is known concerning the thermal racemization of pure esters of this type.

Interest in this problem has arisen as an outgrowth of attempts to check the report[3] that a racemic ester is formed when (−)-bromosuccinic acid is treated with diazomethane. All samples of dimethyl bromosuccinate which have been prepared by this method in this Laboratory have retained a high degree of optical activity comparable to that of samples prepared by esterification with methanol in the presence of anhydrous hydrogen chloride. It has, however, been noted that the optical rotation of the ester diminishes appreciably as the material is subjected to repeated distillation.

A series of measurements of the kinetics of racemization and dehydrobromination of dimethyl (−)-bromosuccinate at temperatures in the vicinity of 100° has been made to establish that the racemizations resulting from distillation of the ester are thermally induced. In addition similar studies have been made with the methyl esters of optically active α- and β-bromobutyric acid. These results are of interest in connection with a discussion of possible mechanisms for the racemizations.

The Kinetic Measurements.—In the course of preliminary measurements it was noted that a precipitate was formed in samples of the dimethyl bromosuccinate which had been heated for long periods of time. This precipitate, m.p. 100–101°, was readily identified by mixed melting point determination as dimethyl fumarate. Walden[1] also recognized that this ester showed a tendency to form dimethyl fumarate on distillation, and Olson and Long[4] have observed in studying the halide ion catalyzed racemization of (−)-bromosuccinic acid the simultaneous occurrence of a dehydrobromination reaction.

To study the racemization rates two series of measurements were made at each temperature investigated. In the first series the loss in optical activity of samples of the pure bromoester as a function of the heating time was determined. In a second set of measurements weighed samples of the ester were heated over various time intervals and were then analyzed for hydrogen bromide.

The following reactions have been considered in deriving a rate law for the interpretation of the data taken in following the loss of optical activity of the bromoester

$$l \underset{k_2}{\overset{k_1}{\rightleftarrows}} d \tag{1}$$

$$l \xrightarrow{k_3} \mathrm{U} \tag{2}$$

$$d \xrightarrow{k_3} \mathrm{U} \tag{3}$$

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[1] P. Walden, *Ber.*, **31**, 1416 (1898).

[2] (a) T. Wagner-Jauregg, *Monatsh.*, **53**, 791 (1929); (b) R. Kuhn and T. Wagner-Jauregg, *Naturwiss.*, **17**, 103 (1929); (c) E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937); (d) A. R. Olson, L. D. Frashier and F. J. Spieth, *J. Phys. & Colloid. Chem.*, **55**, 860 (1951).

[3] E. Bergmann and Y. Sprinzak, THIS JOURNAL, **60**, 1998 (1938).

[4] A. R. Olson and F. A. Long, *ibid.*, **56**, 1294 (1934).