[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

A Correlation between Molar Polarizability and the Effect of Halogen Substituents on the Energy of the Principal Electronic Transitions of Benzene Derivatives[1,2]

BY W. M. SCHUBERT, JAMES M. CRAVEN[3] AND HARVEY STEADLY

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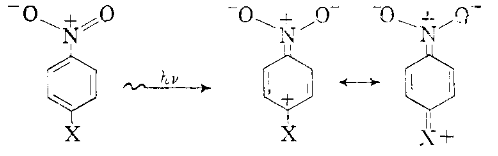
In the principal ultraviolet electronic transition of nitrobenzenes and acetophenones in the gas phase and in heptane solution the order of net electron *release* by a *p*-substituent is: I > Br > Cl > F > H. In the principal electronic transitions of anisoles in the gas phase, the order of net electron *acceptance* by a *p*-substituent is: I > Br > Cl > H > F. In heptane the bromine–chlorine order is inverted. The decrease in gas phase excitation energy is paralleled by an increase in molar refraction for each of the three series of compounds, suggesting that the excitation energy order is governed by the "polarizability" of the substituent. The substituent effects are difficult to rationalize in terms of a mixture of mesomeric release of electrons in the order F > Cl > Br > I and inductive acceptance in the same order.

The electronic effect of a halogen substituent attached to a π-electron system is generally considered to be a combination of inductive and resonance effects.[4] The inductive effect is one of electron withdrawal, presumably in the electronegativity order: F > Cl > Br > I. The resonance effect is an electron release mechanism in the presumed order: F > Cl > Br > I. For most systems, the halogens have an apparent net electron-withdrawing effect. This is reflected in the positive Hammett sigma (σ) values for these substituents.[5] Conclusions regarding the electronic effect of halogen substituents have been based largely upon solution data. Because of the possibility that inherent substituent effects may be masked or at least modified by solvent effects, it was considered desirable to study the effect of halogen substitution in a polar transition *in the gas phase*. Thus the effect of *p*-halogen substitution upon the so-called principal electronic transition of nitrobenzenes, acetophenones and anisoles has been determined in the gas phase as well as in heptane. For nitrobenzenes this transition is approximately represented by the valence bond equation 1, which conveys the idea that a large demand for electron *release* is placed upon the *p*-substituent in the excited state.[6,7] For acetophenones, the transition is similar, though presumably less electron demanding on the *p*-substituent.[8] By contrast, in the principal electronic transition of anisoles, represented approximately by equation 2, a large demand for acceptance of negative charge is placed upon the *p*-substituent.[9]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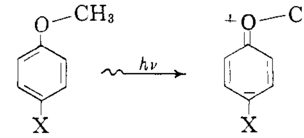
(2)

It has been suggested recently that an important factor in the behavior of a halogen substituent is its "polarizability."[10-12] Therefore, the molar refractions of the nitrobenzenes, acetophenones and anisoles have been determined, for comparison with the spectral results.

Experimental

Compounds.—Commercially available compounds were used, with the exception of *p*-fluoroacetophenone, *p*-iodoacetophenone and *p*-fluoroanisole. *p*-Fluoroacetophenone and *p*-iodoacetophenone were made by a Friedel–Crafts synthesis from fluorobenzene and iodobenzene, respectively.[13] *p*-Fluoroanisole was made by the Schiemann reaction from *p*-anisidine.[14] Final purifications were achieved by several low temperature crystallizations from methanol or pentane. The solvents pentane and heptane were purified as before.[8] N-Methylmorpholine was fractionally distilled from calcium oxide.

Spectral Measurements.—Gas phase measurements were made in a calibrated Aminco 20-cm. quartz cell to the opening of which was sealed a side tube. The cell was swept out with nitrogen, about 0.1 ml. of a pentane solution of the compound was introduced (sufficient to give an optical density reading of 0.3–0.4) and the side tube sealed. The spectrum was measured and λ_{max} determined as before,[8] in an air-thermostated cell compartment. The Beckman DU was equipped with a special fused quartz prism and a photomultiplier, extending the range of the instrument down to 185 mμ. Solution spectra were determined at room temperature as previously described.

Molar refractions were determined in the usual way.[15] The index of refraction and density measurements were made on the same sample of a compound or solution and at the same temperature, 25 ± 0.1°.

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army.

[2] Presented in part as Paper 69 at the Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[3] National Science Foundation pre-doctoral fellow, 1956–1958.

[4] See, *e.g.*, J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 73.

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[6] See, *e.g.*, A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955); THIS JOURNAL, **77**, 4455 (1957).

[7] W. M. Schubert and J. Robins, *ibid.*, **80**, 559 (1958).

[8] W. M. Schubert, J. Robins and J. L. Haun, *ibid.*, **79**, 910 (1957).

[9] Evidence for the assigned direction of the dipole in the excited state is given in reference 11. Additional evidence is the observation that the principal band shifts to the blue as solvent acidity is increased (J. M. Craven, unpublished results). In view of the Franck–Condon principle, solvent stabilization of the ground state through hydrogen-bonding to the ether oxygen (presumably stronger than to aromatic Cl, Br or I, at least) would lead to destabilization or decreased stabilization of the excited state.

[10] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.*, **22**, 1285 (1957).

[11] A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956).

[12] J. F. Bunnett, THIS JOURNAL, **79**, 5969 (1957).

[13] D. P. Evans, V. G. Morgan and H. B. Watson, *J. Chem. Soc.*, 1167 (1935); W. Kimura, *Ber.*, **67**, 395 (1934).

[14] A. Roe in "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 205.

[15] N. Bauer in A. Weissberger, ed., "Physical Methods of Organic Chemistry," Part II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1160.

Results

The principal band of the compounds studied was in general structureless, quite symmetrical about the peak, and isolated from other bands, except for anisole and *p*-fluoroanisole. The principal band of these compounds was rendered unsymmetrical by the presence of a near-lying band just below 200 mμ. With these exceptions, general band width and shape did not change appreciably as the substituent was changed. Table I lists the values of λ_{max} in the gas phase, and λ_{max} and ϵ_{max} in heptane.

TABLE I[a]

Compound	Gas phase[b] λ_{max}, mμ	Heptane[d] λ_{max}, mμ	Heptane[d] ϵ_{max}
Nitrobenzene	239.1	251.8	8700
p-Fluoro-	245.1	257.1	8400
p-Chloro-	251.3	264.7	12200
p-Bromo-	254.6	269.0	13300
p-Iodo-	264.1	287.6	12400
p-Methyl-	250.2[c]	264.1	10100
Acetophenone	230.1	238.1	12400
p-Fluoro-	233.3	240.3	11900
p-Chloro-	241.3	249.2	17400
p-Bromo-	244.8	252.9	19200
p-Iodo	253.7	263.5	19400
p-Methyl-	238.9[c]	247.2	15600
Anisole	215.0	219.6	8000
p-Fluoro-	214.1	216.9	5600
p-Chloro-	222.8	227.4	11900
p-Bromo-	223.7	226.5	13000
p-Iodo-	229.6	234.0	19000

[a] All values average of at least two determinations; estimated accuracy: ±0.2 mμ for gas phase λ_{max}, ±0.1 mμ for heptane λ_{max}, ±1–2% for ϵ_{max}. [b] The nitrobenzenes and anisoles were measured at 150° and the acetophenones at 100°; λ_{max} values of nitrobenzene and its *p*-fluoro and *p*-chloro derivatives were also measured at 100° and were found to be within experimental error of the 150° values. [c] These values are from ref. 8. [d] Run at room temperature.

The molar refractions, determined at 25.0° for the sodium D line, are listed in Tables II, III and IV. In addition, literature values for the C–X "bond" refractions of the substituents, based largely on measurements on aliphatic compounds,[16] are listed in Table II for comparison. It was found that the results were to some extent dependent on solvent. For example, the values for the liquid compounds differ, by considerably more than the experimental error, from the values obtained in solution. Consequently, the nitrobenzenes and acetophenones were measured in a single solvent, N-methylmorpholine, in order to make the results more strictly comparable. The anisoles were measured as the pure liquids, with the exception of *p*-iodoanisole, a solid, for which anisole was used as a solvent.

TABLE II

VALUES OF THE MOLAR REFRACTIONS OF *p*-HALONITROBENZENES

p-Substituent	Concn., mole %	R_D (cm.^{3})[a] soln.	R_D (cm.^{3})[b] pure liq.	R_{C-X}[c] aliphatic
H	4.416	42.43	42.34	1.68
	4.469	42.55		
F	4.573	42.53	42.68	1.55
	5.110	42.44		
Cl	4.539	49.87	...	6.51
	4.389	49.67		
Br	4.962	53.46	...	9.39
	4.548	53.59		
I	3.878	61.48	...	14.61
	4.399	61.53		

[a] Measured in N-methylmorpholine at 25.0°; average deviation 0.06 cm.^{3}. [b] Measured on pure liquid compound at 25.0°; average of two determinations; average deviation 0.01 cm.^{3}. [c] Literature[16] values for the C–X bond refraction.

TABLE III

VALUES OF THE MOLAR REFRACTIONS OF *p*-HALOACETOPHENONES

p-Substituent	Concn., mole %	R_D (cm.^{3})[a] soln.	R_D (cm.^{3})[b] pure liq.
H	9.955	47.48	47.24
	9.998	47.53	
F	10.110	47.44	47.30
	10.096	47.56	
Cl	9.997	54.40	53.87
	9.964	54.65	
Br	9.935	58.19	...
	9.924	58.34	
I	9.990	65.18	...
	10.006	65.18	

[a] Measured in N-methylmorpholine at 25°; average deviation 0.06 cm.^{3} [b] Measured on pure liquid compound at 25.0°; average of two determinations; average deviation 0.01 cm.^{3}

TABLE IV

MOLAR REFRACTIONS OF *p*-HALOANISOLES

p-Substituent	Concn., mole%	R_D (cm.^{3})[b]
H	100	42.95
F	100	42.86
Cl	100	49.22
Br	100	52.73
I	28.228[a]	59.12[a]
	58.995[a]	58.90[a]

[a] Solvent is anisole. [b] Average of two determinations for pure liquids; average deviation 0.01 cm.^{3}

Discussion

In both the gas phase and in heptane solution, the energy of the principal electronic transition of nitrobenzene and of acetophenone is lowered by the substitution of a halogen for hydrogen in the *p*-position. Substitution of a normally electron-releasing substituent such as methyl gives qualitatively the same result (Table I). In view of the electron-demanding nature of the transition, the results of Table I imply a net electron *release* in the order: I (greatest release) > Br > Cl > F > H. Either of two conclusions, each depending on a primary assumption, can be reached. If it is assumed that the predominant mode of electron release in these transitions is electromeric, then it must be concluded that the order of electromeric release is I > Br > Cl > F. This is the conclusion reached by Forbes and Ralph, who suggest that the generally accepted order of electromeric release[4] F > Cl > Br > I is incorrect.[17] On the other hand, if it is assumed that the generally accepted order

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(16) (a) A. I. Vogel, W. T. Crestwell, G. J. Jeffrey and J. Leicester, *Chemistry & Industry*, 358 (1950); (b) G. H. Jeffrey, J. Leicester and A. I. Vogel, *ibid.*, 1045 (1954).

(17) W. F. Forbes and A. S. Ralph, *Can. J. Chem.*, **34**, 1447 (1956); see also C. N. R. Rao, *J. Sci. Ind. Research (India)*, **17B**, 56 (1958).

of electromeric release is correct, then it must be concluded that electromeric release is not the predominant mode of electron release by the halogens in the principal electronic transitions of the *p*-halo nitrobenzenes and acetophenones. This is the conclusion reached independently by Burawoy and Thompson[11] and by Schubert, Craven, Steadly and Robins.[10]

For the anisoles, the excitation energies in the gas phase are in the order: F (highest energy) > H > Cl > Br > I (Table I). In heptane, the chlorine–bromine order is reversed, illustrating the importance of solvent in modifying apparent substituent effects. Since the principal electronic transition of the anisoles is one in which the *p*-substituent is strongly called upon to accept negative charge,[9] the results imply a net electron *acceptance* by the halogens in the order I > Br, Cl > F. This order is difficult to rationalize in terms of a mixture of resonance and inductive effects alone. The fact that the order of net electron acceptance in the anisoles corresponds to the order of net electron release in the nitrobenzenes and acetophenones suggests an explanation in terms of the polarizability of the substituent. Previously, Burawoy and Thompson have proposed that the polarizability of the C–halogen electrons determines the order of release or acceptance by the substituent.[11] Schubert, Craven, Steadly and Robins have suggested that release or acceptance of electrons by the substituent in a particular state of the molecule is governed both by the polarizability of the bonding electrons and the electronegativity difference between the substituent and the aromatic moiety.[18] Another possible factor may be the direct polarization through space of the substituent by the ring. Such a field effect or internal dispersion force appears to be a factor in the effect of *p*-alkyl substituents in these transitions.[8]

A property which depends upon the polarizability of the electrons of the substituent is the molar refraction. It is true, of course, that the type of internal bond and field polarizability envisioned above is not directly measured by the molar refraction. The molar refraction is instead a measure of the ease with which the electrons are polarized by an external electromagnetic field.[19] However, it seems reasonable to assume that the two types of polarizability are similar. It is therefore of interest to note that for each of the series, nitrobenzenes, acetophenones and anisoles, the order of decreasing excitation energy corresponds to the order of increasing molar refraction.[20] A similar correspondence also is found between the molar refractions and the excitation energies in

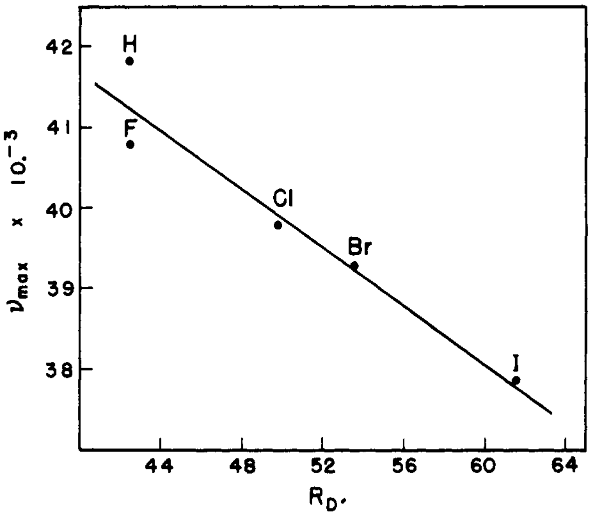

Fig. 1.—*p*-Halonitrobenzenes: plot of molar refraction *vs.* gas phase $\nu_{\max}$; slope, -180 ± 30 cm.$^{-4}$; correlation coefficient, 0.969.

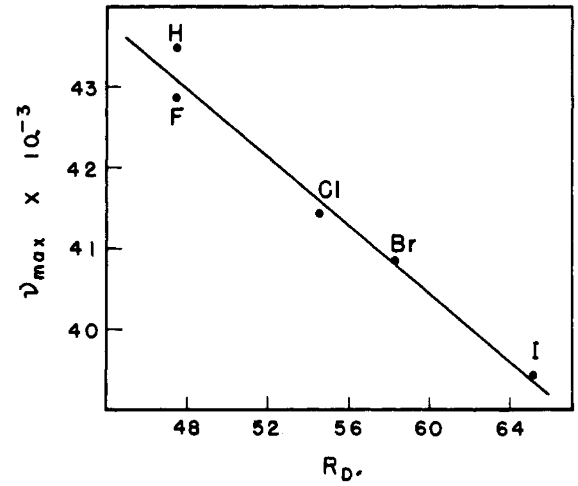

Fig. 2.—*p*-Haloacetophenones: plot of molar refraction *vs.* gas phase $\nu_{\max}$; slope, -210 ± 20 cm.$^{-4}$; correlation coefficient, 0.989.

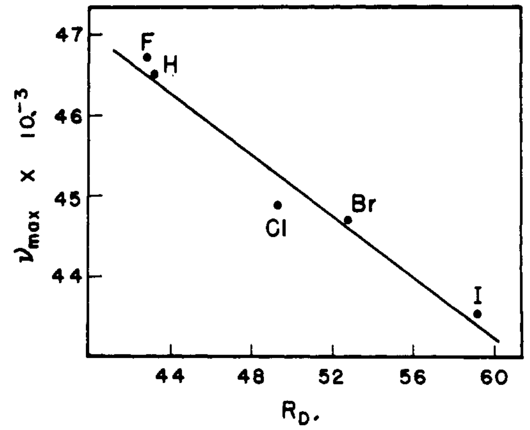

Fig. 3.—*p*-Haloanisoles: plot of molar refraction *vs.* gas phase $\nu_{\max}$; slope -190 ± 20 cm.$^{-4}$; correlation coefficient, 0.984.

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(18) Polarization of the σ-electrons of the bond could be considered synonymous with "inductomeric effect" provided it is recognized that an electronegative substituent may inductomerically release electrons to a more electronegative moiety. A common ground may be found between the viewpoint expressed by Forbes and Ralph and the viewpoints expressed in references 10 and 11, insofar as any π-electrons in the C–halogen linkage may also be polarized in *either* direction.

(19) K. Fajans, in A. Weissberger, ed., "Physical Methods of Organic Chemistry," Part II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1171.

(20) It is to be noted that the molar refractions of the fluorine and hydrogen compounds of the nitrobenzene and acetophenone series do not conform to the order of published atom or "bond" refractions, Table III, as determined largely by measurements on aliphatic compounds.[16] This serves to reaffirm that atom or "bond" refractions are not strictly additive and are somewhat dependent on structure.[19]

heptane, except for the chlorine–bromine inversion in the anisole excitation energies. In Figs. 1, 2 and 3 it is seen that the correspondence between increasing molar refraction and decreasing gas-phase excitation energy is in fact approximately linear. This linearity may be somewhat fortuitous since the two properties were not measured under rigorously identical conditions. Ideally, the molar refractions should also be measured in the gas phase, but this is experimentally impractical. However, there is clearly at least a qualitative parallelism between the two experimental quantities. It is therefore quite possible that the effect of the substituents upon dipolar electronic transitions and upon molar refraction is governed by similar factors.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Hydrolysis of Sultones. The Effect of Methyl Groups on the Rates of Ring-opening Solvolyses

BY F. G. BORDWELL, C. EDWARD OSBORNE[1] AND RICHARD D. CHAPMAN[1]

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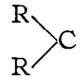
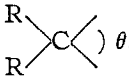
The rates of hydrolysis of eight primary, secondary and tertiary 5-membered ring sultones have been measured. Comparison of these hydrolysis rates among themselves, with those for sultones reported in the literature and with open-chain analogs has brought out a marked retardation effect caused by α- (to oxygen) and β-methyl groups. β-Methyl substitution greatly decreases the hydrolysis rate of these sultones, whereas an acceleration might have been anticipated on the basis of open-chain analogs. Although the net effect of α-methyl substitution is to enhance the rate, the increase in rate is not nearly as great as that expected, and an opposing rate retardation effect is clearly indicated. The effect of γ-methyl groups is less clear-cut, but also appears to be one of rate retardation in hydrolysis. The fact that in ring-openings the atoms formerly bonded cannot separate linearly, as is true in open-chain systems, but must rotate away from one another, is believed to be of fundamental importance in producing unusual and exaggerated effects of substituents in such reactions. The retarding effect of α-, β- and γ-methyl groups on the present ring-opening hydrolyses is believed to be caused by restriction of the required rotation by methyl substitution. The fact that the retardation effects of methyl groups on hydrolysis rates arise chiefly from a decrease in activation entropies is consistent with the idea that they are caused by steric hindrance to rotation. The possible extension of this idea to explain the striking effects of methyl groups on other ring openings is discussed.

It has been recognized for many years that methyl substitution promotes the formation or "stability" of ring compounds. Evidence for an effect of this kind was collected by Thorpe and Ingold and their students in the period 1915–1930.[2] An early explanation was offered[2b] that *gem*-dimethyl groups by mutual repulsion (B-strain in current terms) would cause an increase in the  $^{R}_{R}\!\!>\!C$ bond angle and a decrease in the θ bond angle of  $^{R}_{R}\!\!>\!C\!<\,)$ θ. If θ is part of a small ring this effect would result in ring stabilization ("Thorpe–Ingold effect"). However, the fact that the effect is by no means confined to small rings or to *gem*-dialkyl groups indicates that this factor is probably of minor importance. Furthermore, measurements of bond angles in open-chain systems have failed to confirm the decrease in θ predicted by the theory.

It is still uncertain as to whether or not methyl substitution leads to a greater thermodynamic stability for ring compounds than for open-chain analogs. However, there is abundant evidence that methyl substitution can lead indirectly to "stabilization" by accelerating the rate of ring closure.[3] A particularly striking example is the observation of Nilsson and Smith[4] that the rate of ring closure of chlorohydrins to epoxides is accelerated from 5- to 20-fold per methyl group, as the hydrogens of ethylene chlorohydrin are successively replaced by methyl groups.

It does not appear to have been generally appreciated that methyl groups may also "stabilize" the cyclic forms by retarding the rates of ring opening. However, the fact that methyl substituted glutaric anhydrides[2b] and methyl substituted cyclic adipic anhydrides[2i] are more stable to hydrolysis than the parent anhydrides clearly suggests this possibility.

The ability of methyl substituents to stabilize the cyclic form in systems where this form is believed to be in equilibrium with an open-chain isomer was the subject of many of the earlier papers.[2,5] It is evident that methyl substitution in such equilibrium systems may favor the cyclic form by increasing the rate of ring closure and/or by decreasing the rate of ring opening.

Several years ago T. Nilsson[6] made a careful

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[1] Abstracted in part from the Ph.D. Dissertations of Richard D. Chapman (June, 1954) and C. Edward Osborne (June, 1956). Presented at the 7th Conference on Reaction Mechanisms at Chicago, Ill., Sept., 1958.

[2] (a) R. M. Beesley, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); (b) C. K. Ingold, *ibid.*, **119**, 305, 951 (1921); (c) G. A. R. Kon, A. Stevenson and J. F. Thorpe, *ibid.*, **121**, 650 (1922); (d) S. S. Deshapanda and J. F. Thorpe, *ibid.*, **121**, 1430 (1922); (e) C. K. Ingold, *ibid.*, **121**, 2676 (1922); (f) L. Bains and J. F. Thorpe, *ibid.*, **123**, 1206 (1923); (g) E. W. Lanfear and J. F. Thorpe, *ibid.*, **123**, 1683 (1923); (h) I. Vogel, *ibid.*, 594 (1927); (i) E. H. Farmer and J. Kracovski, *ibid.*, 580 (1927); (j) A. M. Quadrat-I-Khuda, *ibid.*, 201, 713 (1929).

[3] See, for example, (a) G. W. Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 373; (b) E. L. Eliel, Chapter 2 of "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 119.

[4] H. Nilsson and L. Smith, *Z. physik. Chem.*, **166A**, 136 (1933).

[5] Data on these equilibria recently have been summarized and ably discussed by G. S. Hammond in Chapter 9 of ref. 3b, pp. 460–470.

[6] T. Nilsson, Ph.D. Dissertation, University of Lund, Sweden, 1946.