reference 4. The energy levels between which transitions occur are obtained as eigenvalues of a secular determinant containing both diagonal and off-diagonal terms. If ($\delta_A - \delta_B$), the difference in chemical shift between the interacting nuclei, is much larger than the interaction constant J_{AB}, the off-diagonal terms become negligible; this leads to the simple pattern found for BrF_5 and IF_5, with equally spaced components whose separation is numerically equal to J_{AB}.

In the present problem $|\delta_A - \delta_B| \cong 5J_{AB}$ and the observed pattern can only be accounted for if the off-diagonal terms are included in the calculation. Explicit formulas for the energy levels in terms of δ_A, δ_B and J_{AB} can be derived if a value is assumed in advance for the ratio $|\delta_A - \delta_B| : J_{AB}$. We found such formulas, using the value 5.0 for this ratio. The best fit of the observed spectrum is then obtained with the values $\delta_A = -137.5$ (apex atoms), $\delta_B = -118.7$ (base atoms) and $J_{AB} =$ 145 cycles/second, or 3.63 units of δ under the conditions we used. The actual ratio $|\delta_A - \delta_B|$: J_{AB} is then 5.18, quite near the value taken. The calculated shifts are given in the second column of Table II and the corresponding intensities in the third column. Although intensities are difficult to measure precisely, the agreement both between predicted and observed shifts and intensities is excellent.

The spectrum does not show any additional splitting due to interaction of fluorines in the CF_2 group with those of the SF_5 group. The corresponding interaction parameter must be very nearly zero.

$C_3F_7SF_5$ and $C_4F_9SF_5$.—Chemical shifts for the main resonance peaks of these compounds are included in Table I. The number of peaks depends as expected on the length of the R_F chain, while the spectrum of the SF_5 group is essentially the same as for the perfluoroethyl derivative.

$(C_2F_5)_2SF_4$ and $(C_3F_7)_2SF_4$.—The chemical shifts of the peaks of these materials are given in Table I. The signals from the R_F radicals occur at nearly the same fields as these in the corresponding R_FSF_5 compounds. The fluorines of the SF_4 group give rise to a single resonance (a convenient secondary reference resonance for the SF_x region). This indicates that the four fluorines are equivalent, and is consistent with the supposition that the C–S–C angle is 180° with the fluorines of the SF_4 group in a plane. Again there is no indication of splitting between fluorines in the R_F radical and fluorines bonded to sulfur.

$CF_2CF_2OCF_2CF_2SF_4$.—The peaks found for this cyclic compound are shown in Table I. The two $-CF_2-$ resonances were identified by comparing the shifts with those of the open-chain derivatives. The spectrum of the SF_4 group now consists of two main signals, each of which is split into a triplet by the indirect spin–spin interaction.

This pattern arises because of the fact that the C–S–C angle in this material must be of the order of 90°. The fluorines of the SF_4 group are then no longer equivalent, two of them being approximately in the C–S–C plane, while the other two are above and below it. Each pair will give rise to a signal split into a triplet by the interaction from the other pair. The observed pattern conforms fairly well to the simple form expected when $|\delta_A - \delta_B| >> J_{AB}$; we found $\delta_A = -123.0$, $\delta_B = -94.8$ $J_{AB} = 93$ cycles/sec. (or 2.3 δ-units) so that $|\delta_A - \delta_B| = 12.2 J_{AB}$. The data do not allow one to decide which δ-value corresponds to which pair of fluorine atoms.

The absence of a pattern like the one just described in the spectra of the open-chain $(R_F)_2SF_4$ compounds seems a clear indication that only the 180° form was present in the samples studied.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

A Precise Correlation of Nuclear Magnetic Shielding in *m*- and *p*-Substituted Fluorobenzenes by Inductive and Resonance Parameters from Reactivity

BY ROBERT W. TAFT, JR.

RECEIVED AUGUST 29, 1956

Gutowsky's F^{19} nuclear magnetic shielding parameters, δ^F, for *m*- and *p*-substituted fluorobenzenes are precisely correlated by the equations $\delta^F m = (0.583 \pm 0.026)(\sigma_I) - 0.02$ and $\delta^F p = (0.583)(\sigma_I) + (1.880 \pm 0.081)(\sigma_R) - 0.08$. σ_I and σ_R are inductive and resonance parameters, respectively, obtained recently by Taft from a quantitative separation of Hammett σ-values to inductive and resonance contributions. This correlation provides an experimental proof that (1) reaction rates and equilibrium which follow precisely the Hammett equation, $\log (k/k_0) = \sigma\rho$, are determined quantitatively by the effects of the substituent on the electron distribution; and (2) the values of σ_I and σ_R are quantitative and independent measures of the electron-withdrawing effects of substituents through inductive and resonance interactions, respectively.

It has been generally accepted that the σ-values of Hammett (obtained from the ionization constants of *m*- and *p*-substituted benzoic acids) are quantitative free energy measures of the effect of the substituent on the electron distribution (polar effect) in many derivatives of benzene.[1] More recently, it has been proposed that the shielding effects, δ^F, measured by Gutowsky, *et al.*, from the nuclear magnetic resonance lines of *m*- and *p*-substituted fluorobenzenes provide quantitative measures of these effects.[2] Gutowsky, *et al.*, have found, however, that although a plot of δ^F *vs.* σ (*cf.* Fig 1) shows an unmistakable trend toward

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(1) (a) L. P. Hammett, *Chem. Revs.*, **17**, 125 (1953); (b) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York N. Y., 1940, p. 184; (c) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(2) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); (b) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

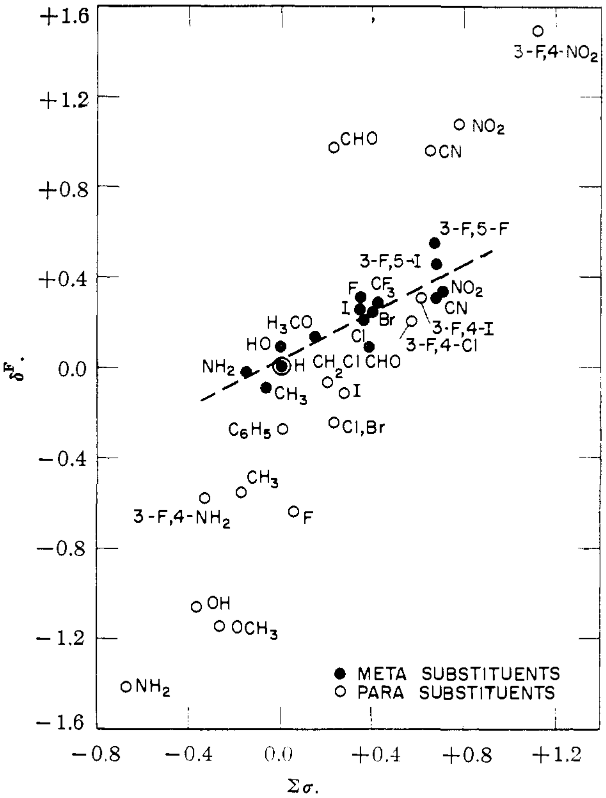

Fig. 1.—Correlation of F^{19} nuclear magnetic shielding effects of *m*- and *p*-substituted fluorobenzenes by Hammett's σ.

correlation, there is no direct relationship of the same order of precision as that very frequently observed in the correlation of reactivity by the Hammett equation.[1] Thus, the question of whether either δ^F- or σ-values (or both) are precise quantitative measures of the electron distribution effects has been left indecisive. Further, it has not been possible to use δ^F-values to empirically predict reliable σ-values.

A correlation of relatively high precision is now reported between Gutowsky's F^{19} shielding parameter, δ^F, for *m*- and *p*-substituted fluorobenzene derivatives and the inductive and resonance parameters, σ_I and σ_R, obtained recently by Taft from reactivity considerations.[3]

Inductive and Resonance Parameters.—A quantitative separation of the Hammett σ-value to independent inductive and resonance contributions has been proposed according to the equation[3]

$$\sigma \equiv \sigma_I + \sigma_R \qquad (1)$$

σ_I is the inductive contribution, and may be regarded as a measure of the free energy effect of the substituent (relative to the H atom) resulting from its power to attract or repel electrons through space and the sigma bonds of the benzene system. The resonance contribution, σ_R, may be regarded as a measure of the free energy effect resulting from the power of the substituent to attract or repel electrons through resonance interaction with the π-orbital of the benzene system.

The inductive parameter, σ_I, for the substituent X is obtained from the σ^*-values of Taft for XCH_2 groups obtained from aliphatic series reactivities by an empirical adjustment to the scale of Roberts and Moreland (*i.e.*, $\sigma'_X = 0.45, \sigma^*_{XCH_2} \equiv \sigma_I$).[4] The resonance parameter, σ_R, is obtained from eq. 1, *i.e.*, $\sigma_R \equiv p\text{-}\sigma - \sigma_I$, as originally suggested by Roberts and Moreland.[4,5]

A summary of a number of available σ_I- and σ_R-values for substituents is given in Table I. It is apparent that σ_I and σ_R-values are completely different functions of structure. The substituents are listed in Table I according to the order of increasing σ_R-values. The order of increasing σ_I-values is totally different.

TABLE I

TABULATION OF INDUCTIVE (σ_I) AND RESONANCE (σ_R, σ_R^-) PARAMETERS OF SUBSTITUENTS

Substituent	σ_I	σ_R	Substituent	σ_I	σ_R	(σ_R^-)
NH_2	+0.10	−0.76	H	0.00	0.00	(0.00)
OH	+ .25	− .61	$N(CH_3)_3^+$	+ .86	.00	
OCH_3	+ .23	− .50	CH_2Cl	+ .17	+ .01	
F	+ .50	− .44	CN	+ .59	+ .07	(+ .41)
OC_6H_5	+ .38	− .41	$(CH_3)_3Si$	− .12	+ .11	
Cl	+ .47	− .24	CF_3	+ .41	+ .14	
Br	+ .45	− .22	CH_3SO_2	+ .59	+ .14	
CH_3	− .05	− .13	NO_2	+ .63	+ .15	(+ .64)
I	+ .38	− .10	$C_2H_5O_2C$	+ .32	+ .20	(+ .36)
C_6H_5	+ .10	− .09	CH_3CO	+ .27	+ .25	(+ .60)

Qualitative relationships between σ_I-values and the intrinsic electronegativities and other properties of the atoms in the substituent group have been established.[6] The relationship of σ_R-values to structure also has been discussed.[3] Several examples are worthy of specific comment.

The near zero net electron-withdrawing effect of a *p*-F substituent ($\sigma = +0.06$) is the resultant of large but nearly equal and opposed inductive ($\sigma_I = +0.50$) and resonance ($\sigma_R = -0.44$) contributions. The lower halogens, *e.g.*, Cl, have a more net electron-withdrawing effect ($\sigma = +0.23$) because of the greater decrease in magnitude of the resonance ($\sigma_R = -0.24$) than the inductive ($\sigma_I =$

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(3) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956, Chapt. 13, pp. 578–580, 594–597.

(4) Values of σ_I and σ_R are tabulated for a large number of substituents in ref. 3, p. 595. The values of σ_I are listed as σ', and values of σ_R are listed as $\sigma_p - \sigma'$.

The symbolism used in this paper is that agreed to by Brown, Deno, Jaffé, Taft and others in an attempt to provide a more systematic scheme of various sigma values. The system is:

(a) $\sigma = \sigma_I + \sigma_R$; σ is the ordinary Hammett sigma value.

(b) $\sigma^- = \sigma_I + \sigma_R^-$; σ^- is the "dual" sigma value for use with derivatives of phenol and aniline.

(c) $\sigma^+ = \sigma_I + \sigma_R^+$; σ^+ is the Brown sigma value proposed for use in electrophilic reactions of *m*- and *p*-substituted benzene derivatives (H. C. Brown and Y. Okamoto, abstracts of papers presented at the Atlantic City Am. Chem. Soc. Meeting, Sept. 1956, p. 59-O).

According to this scheme the symbol σ^* as used by Jaffé (ref. 1c) is replaced by σ^-. The symbol σ^* is retained as used by Taft (ref. 3) for the aliphatic series and for *o*-substituted benzene derivatives. The symbol σ_R as used by Deno (N. C. Deno and A. Schriesheim, THIS JOURNAL, **77**, 3051 (1955)), is replaced by σ^+. The symbol σ' is retained as specifically defined by Roberts (ref. 5), *i.e.*, for 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid derivatives. By the arguments of Roberts and Moreland (ref. 5) and Taft (ref. 3), σ' and σ_I may be equated, *i.e.*, $\sigma_I \equiv \sigma$. The symbols ($p\text{-}\sigma - \sigma' \equiv \chi$) as used by Taft (ref. 3 and abstracts of papers presented at the Atlantic City Am. Chem. Soc. Meeting, Sept. 1956, p. 81-O) are replaced by σ_R.

(5) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

(6) R. W. Taft, Jr., *J. Chem. Phys.*, in press. The discussion is given in terms of σ^*-values, but, of course, applies equally well to σ_I-values.

$+0.47$) parameter. The $N(CH_3)_3^+$ group in accord with its saturated and charged structure has a large inductive electron-withdrawing effect ($\sigma_I = +0.86$) but no resonance effect ($\sigma_R = 0.00$).

Each substituent with a negative value of σ_R is *ortho–para* directing in electrophilic aromatic substitution, and each with a positive value, *meta* directing. Further, substituents with negative σ_R-values are those for which ($\mu_{C_6H_5X} - \mu_{CH_3X}$), the difference in the dipole moment between corresponding phenyl and methyl derivatives, is negative; substituents with positive σ_R-values have positive values of the quantity ($\mu_{C_6H_5X} - \mu_{CH_3X}$). Both the orientation effects and the dipole moment differences are recognized as qualitative measures of resonance interactions.[7]

Two resonance parameters, σ_R and σ_R^-, are listed in Table I for groups such as CN, NO_2 and CH_3CO. The value in parentheses (σ_R^-) is obtained from eq. 1 using the dual sigma constant (σ^-, *cf.* ref. 4) applicable to derivatives of aniline and phenol. The value in the regular column pertains to "ordinary" derivatives of benzene. It is apparent that these groups are not as strongly electron-withdrawing (positive) as groups such as OCH_3 and NH_2 are electron-donating (negative) when the resonance interaction involves only the substituent and the benzene ring (σ_R-value). However, the former groups are strongly electron-withdrawing when the resonance interaction involves substituent, benzene ring, and a strongly electron-releasing functional group (σ_R^--value).

Correlation of Shielding Parameters.—The nuclear magnetic shielding parameters, δ^F, of Gutowsky for *m*-substituted fluorobenzenes are precisely correlated by the equation

$$\delta_m{}^F = (0.583 \pm 0.026)(\Sigma\sigma_I) - 0.02$$

where the summation is used to include 3,5-disubstituted derivatives of fluorobenzene. The probable error of a single point by this equation is 0.03δ unit which is the same as the experimental error reported by Gutowsky, *et al.* The range covered is about 0.7δ unit. The δ^F-values for *m*-substituents are correlated by Hammett σ-values (by the equation $\delta^F = (0.549 \pm 0.045)(\Sigma\sigma) + 0.04$, with a probable error of a single point of 0.05δ unit) with nearly as good precision (as reported by Gutowsky, *et al.*), but this is expected since in many cases σ-values for *m*-substituents are nearly equal to corresponding σ_I values (*cf.* later comment on the relationship of σ_m to σ_I and σ_R). Figures 1 and 2 illustrate the relationship of $\delta^F{}_m$-values to σ- and σ_I-values, respectively.

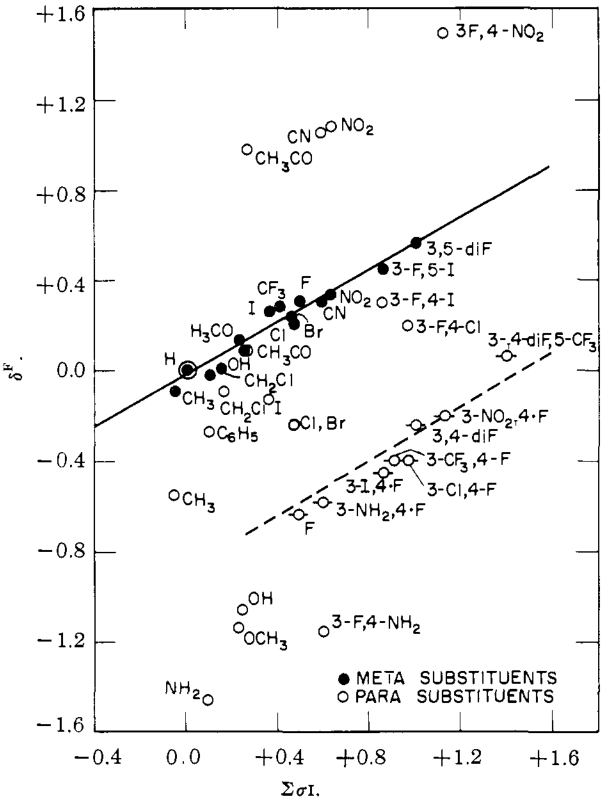

Fig. 2.—Correlation of F^{19} nuclear magnetic shielding effects of *m*-substituted fluorobenzenes by inductive parameter, σ_I.

Figure 2 (for σ_I-values) indicates that δ^F-values for *p*-substituents scatter widely from the correlation line of *m*-substituents. However, the scatter is systematic. Points for *p*-substituents lying above the "*meta* line" are those for groups which are electron-withdrawing by resonance interaction, whereas points lying below are for groups which are electron-releasing by resonance interaction. Further, the points (those with horizontal tails in Fig. 2) for a series of 3-X,4-F-disubstituted fluorobenzenes define a line (the dashed line of Fig. 2) of essentially the same slope as that for *m*-substituted derivatives, but displaced downward by essentially the same distance as for the *p*-F derivative.

If the vertical deviations of the points for *p*-substituents from the "*meta* line" of Fig. 2, *i.e.*, $\delta^F{}_p - (0.583)(\Sigma\sigma_I) - 0.02$ (which is essentially the equivalent of the quantity $\delta_p - \Sigma\delta_m$) are plotted *vs.* corresponding σ_R-values, a precise linear relationship is obtained (Fig. 3). That is, the shielding parameters for *p*-substituted fluorobenzenes are precisely correlated by the equation

$$\delta^F{}_p = (0.583)(\Sigma\sigma_I) + (1.880 \pm 0.081)(\sigma_R) - 0.08$$

The probable error of a single point is 0.07δ unit for a range of about 2.00. Since the ordinate of Fig. 3 presumes to measure the resonance contribution to $\delta^F{}_p$, Fig. 3 illustrates the direct relationship between corresponding resonance contributions to the $\delta^F{}_p$ and to the Hammett σ-values.

The available data provide a rigorous test of the above equation. The series of substituents include those for which inductive and resonance effects are both parallel and opposed. That is, substituents are included within which σ_I- and σ_R-values are totally different functions of structure.

In the case of *p*-NO_2, CN and $COCH_3$ (the $\delta^F{}_p$-value given in Figs. 2 and 3 is that for CHO) fluorobenzenes, the appropriate value of Σ is uncertain in view of the resonance interaction between groups, *e.g.*

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[7] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, p. 216, 477.

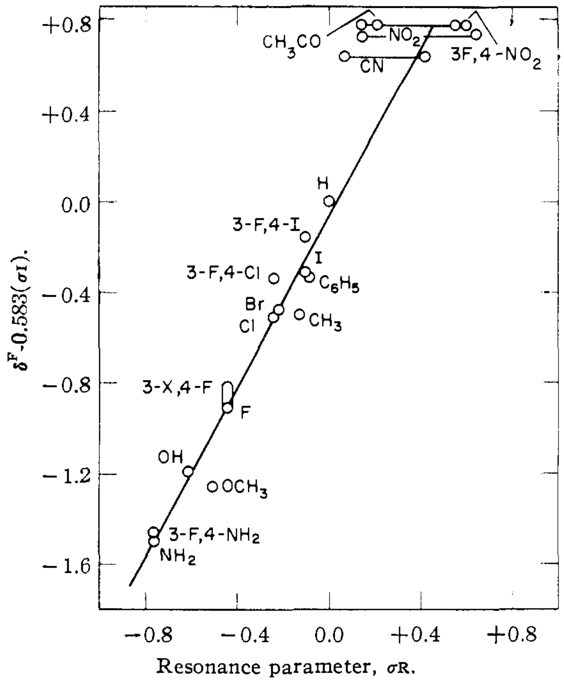

Fig. 3.—Correlation of F^{19} nuclear magnetic shielding effects of *p*-substituted fluorobenzenes by inductive and resonance parameters, σ_I and σ_R.

The sigma-values shown in Fig. 3 for these substituents, for a lower limit, are σ_R and, for an upper limit, σ_R^-. It is apparent that a value intermediate between these two limits would reasonably and precisely correlate the $\delta^F{}_p$-values for these substituents.

Corio and Dailey[8] have recently reported shielding effects for proton magnetic resonance of monosubstituted benzene derivatives, and have attempted to assign the shifts to protons at the *o*-, *m*- and *p*-positions. Although the assignments are open to question (and consequently will not be discussed extensively in this paper), it may be significant that the values assigned to the *p*-protons, $\delta^H{}_p$, are less precisely correlated by σ-values than by the equation

$$\delta^H{}_p = (0.40)\sigma_I + (0.70)\sigma_R$$

For the proton shifts, σ_R values (instead of a value intermediate between σ_R and σ_R^-) are applicable for the $COCH_3$, CN and NO_2 substituents. This correlation provides no evidence that substituent effects are different *in kind* (as suggested by Corio and Dailey) in mono- and disubstituted benzene derivatives, if one allows for resonance interaction between groups. However, in view of the uncertainty in line assignments, no definite conclusions can be drawn from existing data.

The correlation of the nuclear magnetic shielding effects follows an equation of the general form

$$\delta^F = \alpha\sigma_I + \beta\sigma_R \qquad (2)$$

The empirical constants α and β may be regarded as the susceptibilities of the nuclear magnetic shielding to the inductive and resonance interactions of the substituents, respectively. The Hammett sigma values also follow an equation of this form.[3] Specifically

$$\delta m^F = (0.58)\sigma_I + (0.00)\sigma_R;\ \text{and}\ m\text{-}\sigma = (1.00)\sigma_I + (0.33)\sigma_R$$
$$\delta p^F = (0.58)\sigma_I + (1.88)\sigma_R;\ \text{and}\ p\text{-}\sigma = (1.00)\sigma_I + (1.00)\sigma_R$$

The susceptibility constants α and β for *p*-σ values are by definition both unity. In the case of both δ^F and σ-values the susceptibilities to inductive interaction are essentially the same in the *meta* as the *p*-position. However, δ^F-values are only 0.58 times as susceptible to inductive interaction as the σ-values, but 1.88 times more susceptible (for *p*-substituents) to resonance interaction. Thus $\delta^F{}_p$-values are over three times more susceptible to the resonance as the inductive parameters, a result which is in accord with an earlier qualitative conclusion of Gutowsky, *et al.*[2] For $\delta^F{}_m$-values, β is essentially zero in accord with the classical picture of the effect of substituent interaction on the charge distribution in benzene. The markedly different α- and β-values account for the failure of σ-values to correlate precisely the δ^F-values (Fig. 1).

It is reasonable that δ^F- and σ-values should be related to σ_I- and σ_R-values through different functions. Aside from the different functional groups upon which the two parameters are based (COOH for σ-values and F for δ^F-values), δ^F-values are directly related to very small magnetic energies of a single state (the substituted fluorobenzene) in the presence of a large applied field, whereas σ-values are directly related to relatively large free energy differences between two states (reactant and transition (rate), or product (equilibrium)).

Yet, eq. 2 leaves no doubt that both δ^F and σ are determined by the same basic properties of the substituents (σ_I and σ_R parameters). It is thus inferred that the polar effect of a *m*- or *p*-substituent on the free energy of a benzene derivative follows an equation of the form of eq. 2. In this respect eq. 2 provides a rigorous experimental proof that (1) the reaction rates and equilibria which follow precisely the Hammett equation, $\log (k/k_0) = \sigma\rho$, are determined quantitatively by the effects of the substituent on the electron distribution; and (2) the values of σ_I and σ_R are quantitative and independent measures of the electron-withdrawing effects on energy of substituents through inductive and resonance interactions, respectively.[9,10] From a practical standpoint, eq. 2 is of sufficient precision to enable the accurate determination of σ-, σ_I- and σ_R-values from nuclear magnetic shielding measurements.

Since it is proposed that the polar effect of a *m*- and *p*-substituent on the free energy of a benzene derivative is given by $\Delta F = \alpha\sigma_I + \beta\sigma_R$ (α and β are susceptibility factors dependent upon the nature of the benzene derivative and σ_I and σ_R are the potential inductive and resonance factors de-

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[8] P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956).

[9] This conclusion, of course, is subject to δ^F-values having no appreciable contribution from "disturbing" factors. Dr. Richard Glick has kindly pointed out the possibility that Gutowsky's δ-values may contain unknown but measurable solvent effects.

[10] Other instances in which the inductive and resonance contributions to the effect of the substituent on the free energy of activation behave as independent variables has been previously reported: *cf.* ref. 3, and M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 5590 (1955).

pendent upon the nature of the substituent) we have, then, for the ground state of a reaction

$$\Delta F_g = \alpha_g \sigma_I + \beta_g \sigma_R$$

and for the transition (or product) state

$$\Delta F_{\ddagger} = \alpha_{\ddagger}\sigma_I + \beta_{\ddagger}\sigma_R$$

and thus the polar effect of the substituent on the free energy of activation (or reaction), $\Delta F^{\ddagger} - \Delta F^{\ddagger}_0$, becomes

$$\Delta F^{\ddagger} - \Delta F_0{}^{\ddagger} = \Delta F_{\ddagger} - \Delta F_g = \sigma_I(\alpha_{\ddagger} - \alpha_g) + \sigma_R(\beta_{\ddagger} - \beta_g)$$

It is interesting to note that special relationships are required between $(\alpha_{\ddagger} - \alpha_g)$ and $(\beta_{\ddagger} - \beta_g)$ for this equation to reduce to $\Delta F^{\ddagger} - \Delta F^{\ddagger}_0/-2.303RT = \sigma\rho$. (For example, for *p*-substituents $\alpha_{\ddagger} - \alpha_g$ must be nearly equal to $\beta_{\ddagger} - \beta_g$.) If these conditions are not met then log (k/k_0) should be correlated more precisely by an equation of the form of eq. 2 than by the Hammett equation. It is also apparent that the quantities $(\alpha_{\ddagger} - \alpha_g)$ and $(\beta_{\ddagger} - \beta_g)$ will generally be different than α- and β-values for a single state, a condition consistent with different susceptibilities of the magnetic shielding and Hammett parameters, δ^F and σ, to inductive and resonance interactions.

The δ^F-values for *o*-substituted derivatives of fluorobenzene do not follow eq. 2, except within similar types of substituents. The presence of large proximity effects on electron distributions is implied.

UNIVERSITY PARK, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Crystal Structure of Copper(II) Fluoride

BY CLAUDINE BILLY[1a] AND HELMUT M. HAENDLER[1b]

RECEIVED OCTOBER 1, 1956

Introduction

The structures of several simple metallic fluorides are as yet unknown. In general, fluorides of the type MF_2 have been reported with either the cubic fluorite structure or the tetragonal rutile structure. The transition from 8-coördination in the fluorite type to the 6-coördination of the rutile structure has been related to a decrease in radius ratio. As the cation radius becomes still smaller, deviations from the rutile structure might be expected. At the lower extremity, beryllium fluoride has the 4-coördinated β-cristobalite structure.

The crystal structure of copper(II) fluoride has been reported incorrectly as cubic by Ebert and Woitinek.[2] This erroneous conclusion has been previously discussed[3] and corrected on the basis of powder pattern data. It has now been possible to complete a single crystal study of this fluoride, which agrees with our earlier conclusions that the symmetry can be no higher than monoclinic.

Experimental

During a study of the melting of copper(II) fluoride[3a] in an inert atmosphere it was noted that the solidified melt from one run contained several small, apparently crystalline, fragments of colorless material imbedded in the dark red matrix. The sample was transferred immediately to the dry box and the fragments separated by hand from the residual solid. Three or four irregular pieces were obtained. These were coated with Formvar-T (from ethylene dichloride solution) and mounted on glass fibers with R-313 bonding agent.[4] They showed no plane surfaces and were rather poor in quality, with considerable inhomogeneity. It was not certain that they were copper(II) fluoride.

The samples were mounted at random in the goniometer head and oscillation photographs taken at various orientations until recognizable layer lines appeared. In some cases the crystals apparently were multiple, and it was necessary to search for a clear single crystal region. It was not always possible to reorient or remount a specimen without interference by the glass support rod.

Oscillation and Weissenberg photographs were taken with both Cu Kα and Mo Kα radiation. We were able to obtain usable photographs for *hnl* and *nkl* reflections. Intensities of zero layer Weissenberg photographs were estimated by comparison with an intensity scale printed on the same film. An actual reflection was used to imprint the scale. With the traverse of the Weissenberg camera set at the equivalent of 3.5° of crystal rotation, exposure in seconds corresponds to exposure in hours of the usual Weissenberg film (crystal rotation about 200°). The camera was moved 5 mm. between each timed exposure. Both multiple film technique and controlled variation in exposure time were used simultaneously. Because of the poor crystals it was still difficult to obtain as satisfactory intensity data as desired.

It soon became obvious from correlation of powder diffraction data with the single crystal results that the samples were actually copper(II) fluoride. These powder data, from a Philips 114.6 mm. camera, were used to improve the unit cell dimensions. Diffractometer data from one of our samples have been obtained recently.[5] These do not alter the previous dimensions appreciably.

Structure Determination.—The unit cell of copper(II) fluoride is monoclinic with the symmetry of space group $P2_1/c$, but comparison to other AF_2 type fluorides is simplified if a different monoclinic cell is chosen. The structure is then very nearly the rutile type. The space group designation is transformed to $P2_1/n$. This designation has also been used to elucidate the structure of the styrene–palladium chloride complex,[6] and we have followed the terminology suggested in that article.

The dimensions of the new cell are: a = 3.32 Å., b = 4.54 Å., c = 4.59 Å., β = 83° 20′, Z = 2, V = 68.64 Å.^{3}, D_x = 4.91 g./cc., D_{obs} = 4.85 g./cc. The two copper atoms are in the special positions 000 and ${}^1/_2{}^1/_2{}^1/_2$. The fluorine atoms are in the four general positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

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[1] (a) Laboratoires des Services Chimiques de l'Etat, Paris. (b) To whom communications should be addressed. This work was supported in part by the Research Corporation and the Atomic Energy Commission.

[2] F. Ebert and H. Woitinek, *Z. anorg. Chem.*, **210**, 269 (1933).

[3] (a) H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, Jr., THIS JOURNAL, **76**, 2178 (1954); (b) J. M. Crabtree, C. S. Lees and K. Little, *J. Inorg. Nuclear Chem.*, **1**, 213 (1955); (c) H. M. Haendler, *Science*, **123**, 459 (1956).

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