[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

A Hammett Equation Correlation for *trans*-3-Substituted Acrylic Acids

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Second-order rate constants were determined for the reaction of a number of organic acids with diphenyldiazomethane in ethanol at 30°. A linear relationship was found between the values of log k for *trans*-3-substituted acrylic acids and the Hammett *para* σ constants for the same substituents. From this relationship σ-constants were determined for the trichloromethyl and dichloromethyl groups. Data on both acrylic and saturated carboxylic acids were used with the earlier data of Taft and Smith to determine Taft σ^*-constants for six new groups. The effect of acidity on the reaction rates is discussed briefly.

Introduction

In quantitative discussions of the electronic properties of substituent groups in organic molecules the most useful relationships are the equations of Hammett[1,2] and Taft.[3,4] For the determination of Hammett σ-constants and Taft σ^*-constants, measurements on the rates of reaction of acids with diphenyldiazomethane have been found to be useful.[5-7] The previous workers had employed different sets of reaction conditions, of which those of Roberts and Regan, 30° in an absolute ethanol solvent, seemed most convenient for us. The data of Taft and Smith, obtained at 25° in ethanol, should be easily corrected for the 5° temperature difference, especially since the activation energy of the reaction appears to be quite low. Comparison with the experiments of Hoefelmeyer and Hancock, carried out in toluene, would require a somewhat less reliable extrapolation.

Results and Discussion

The rate constants obtained from the reaction of various acids with diphenyldiazomethane in absolute ethanol at 30° are listed in Table I. In each case the value shown is the mean of those obtained in several runs and in no case was the average deviation from the mean as much as 2.5%. In the only direct comparison that can be made with published work our rate constant for benzoic acid is 4% lower than that reported by Roberts, McElhill and Armstrong[8] which in turn is 4% lower than the value of Roberts and Regan.[5] Errors of this order of magnitude would have no effect on any of the conclusions that have been reached in this investigation.

Hammett Substituent Constants.—Determination of Hammett σ (substituent) constants by the ordinary methods was made impractical by the inaccessibility of the properly substituted aromatic acids. Charton has reported that *trans*-3-substituted acrylic acids follow the Hammett equation.[9] According to Charton there is a good relationship between the dissociation constants of these acids and Hammett's *para* σ-constants. A similar relationship is said to exist for *trans*-3-substituted maleic and 3-methylacrylic acids. Aside from a few cinnamic acid derivatives, however, it is not clear just what compounds were studied. In Fig. 1 is a plot of log k for six of our 3-substituted acrylic acids[10] *versus* the appropriate *para* σ-constants (values taken from the collection by Jaffé[2]). The point for the acetyl compound deviates considerably from line A, which was determined to be the best line through the other points by the method of least squares. In the Hammett equation

$$\log k = \log k_0 + \rho\sigma \qquad (1)$$

the values 0.072 for log k and 1.623 for ρ give line A. From the equation and these two values σ-constants were calculated for the other groups studied. Line B was calculated by the least squares method using all of the data (including that for the acetyl compound), and corresponds to a log k_0 value of 0.056 and a ρ-value of 1.495. The new σ-values calculated from lines A and B are listed in Table II.

TABLE I

RATE CONSTANTS FOR REACTION OF ACIDS WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

Acid[a]	k, l. mole^{-1} min.$^{-1}$	log k
$CH_3CH{=}CHCO_2H$	0.61	−0.215
$CH_2{=}CHCO_2H$	1.27	.104
$ClCH{=}CHCO_2H$	2.48	.394
$CH_3COCH{=}CHCO_2H$	4.03	.605
$HO_2CCH{=}CHCO_2H$	6.71	.826
$Cl_2CHCH{=}CHCO_2H$	2.36	.373
$Cl_3CCH{=}CHCO_2H$	5.39	.732
$O_2NCH{=}CHCO_2H$	21.8	1.338
$C_6H_5CO_2H$	1.00	0.000
Saccharin	19.1	1.282

[a] All of the acrylic acids except the acetyl compound are believed to be *trans* (see exptl.).

TABLE II

HAMMETT SUBSTITUENT CONSTANTS FROM FIG. 1

Substituent group	σ (*para*) From A[a]	σ (*para*) From B[b]
Cl_3C-	0.407	0.452
Cl_2CH-	.185	.212

[a] Ignoring the point for the acetyl compound. [b] Including the point for acetyl.

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[1] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 2-4e.

[2] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[3] Reference 1, sec. 12-3c.

[4] R. W. Taft, Jr. in M. S. Newman's, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, chap. 13.

[5] J. D. Roberts and C. M. Regan, THIS JOURNAL, **74**, 3695 (1952); **75**, 4102 (1953); **76**, 939 (1954); and earlier references cited therein.

[6] R. W. Taft, Jr., and D. J. Smith, *ibid.*, **76**, 305 (1954).

[7] A. B. Hoefelmeyer and C. K. Hancock, *ibid.*, **77**, 4746 (1955).

[8] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

[9] M. Charton, Abstracts of Papers Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 16-21, 1956, p. 83-O.

[10] For a discussion of whether these compounds were actually *trans* or not see the Experimental section.

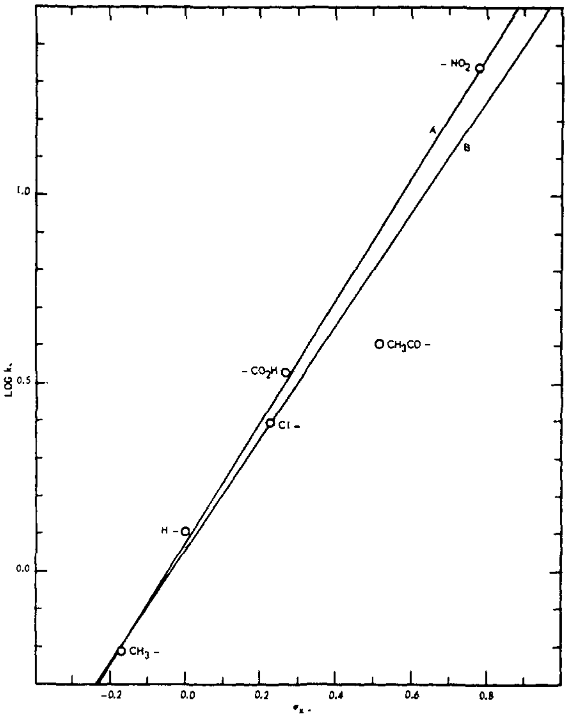

Fig. 1.—Log k for *trans*-3-X-acrylic acids *vs.* σ_4.

The deviation of the acetyl compound might appear to be in the wrong direction to be explained by the suggestion that the acid employed is *cis*, since the usually greater acidity of *cis*-acids would lead one to expect the *cis*-β-acetylacrylic acid to be faster rather than slower than predicted from line A of Fig. 1. However, Shaw has found evidence that the compound exists largely in the pseudoacid form.[11] For this reason we believe that the data obtained by use of line A are more reliable.

Taft Substituent Constants.—For the purpose of determining Taft substituent constants our data was combined with that of Taft and Smith.[6] We find benzoic acid to react 1.05 times as fast and Roberts and Regan found it to react 1.13 times as fast at 30° as Taft and Smith did at 25° and Roberts and Regan found acetic acid to react 1.21 times as fast at 30° as Taft and Smith did at 25°. After averaging these data we corrected Taft and Smith's data to 30° by adding 0.051 to log k for each value. While this procedure is not completely rigorous the entire correction is so small that any deviations from it should be very small. The resultant data are plotted against Taft's σ^*-constants in Fig. 2. Since Taft does not appear to have listed a σ^*-value for the n-amyl group, we have used the value (0.162) reported by Hoefelmeyer and Hancock in plotting the data on n-hexanoic acid in Fig. 2. Also plotted are data on the only two other compounds for which we could find both the rate data and the relevant σ^*-constants. These are crotonic acid, which we studied, and phenylpropiolic acid which was studied by Roberts and Carboni.[12] As Taft and Smith have pointed out, benzoic acid reacts much more slowly than would be expected from the polar substituent constant. The point for crotonic acid deviates in the same direction and by almost as large an amount as that for benzoic acid. The point for phenylpropiolic acid also deviates in the same direction, but by a much smaller, though probably significant, amount. As Taft and Smith suggest for the case of benzoic acid, this is probably due to the resonance of the carboxyl group with the group attached thereto. Taft had previously estimated that there is about 700 cal./mole less of such resonance in the benzoate anion than in benzoic acid.[13] From Fig. 3 it may be estimated that 760 cal. of such resonance has been lost in the transition state for reaction with diphenyldiazomethane by benzoic acid, 700 cal. for crotonic acid and 240 cal. for phenylpropiolic acid. The latter factor suggests that α,β-triple bonds enter into much less resonance with carbonyl groups than do α,β-double bonds and directly-attached aromatic rings. From the first two factors it appears, as Kreevoy and Taft have shown more convincingly,[14] that aromatic rings and α,β-unsaturated double bonds resonate about equally well with carbonyl groups. For this reason we have *assumed* that the points for all *trans*-3-substituted acids should fall on a line parallel to that for the unsaturated acids and including as well as possible the points for crotonic and benzoic acids.

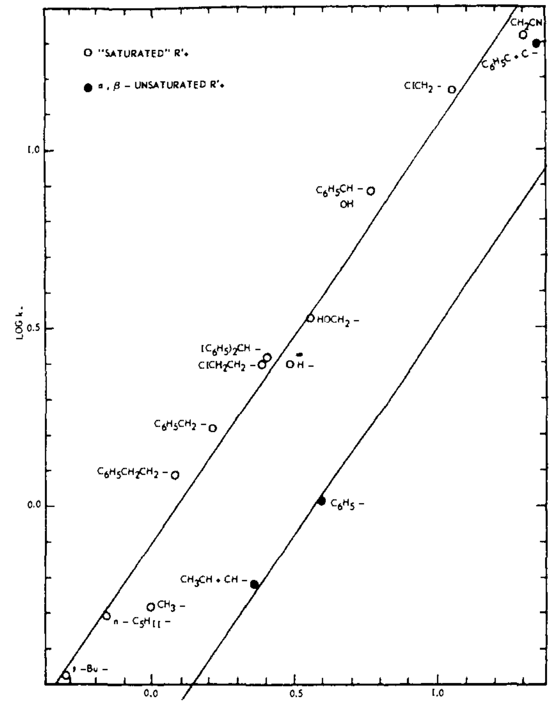

Fig. 2.—Log k for reaction of RCO₂H with diphenyldiazomethane *vs.* σ^* (Taft and Smith).

The Taft equation

$$\log k = \log k_0 + \rho^*\sigma^* \qquad (2)$$

for the upper line has the form

$$\log k = -0.105 + 1.174\ \sigma^* \qquad (3)$$

when the optimum values of log k_0 and σ^* were

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[11] E. Shaw, This Journal, **68**, 2510 (1946).

[12] J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

[13] R. W. Taft, Jr., *ibid.*, **75**, 4237 (1953).

[14] M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **79**, 4016 (1957).

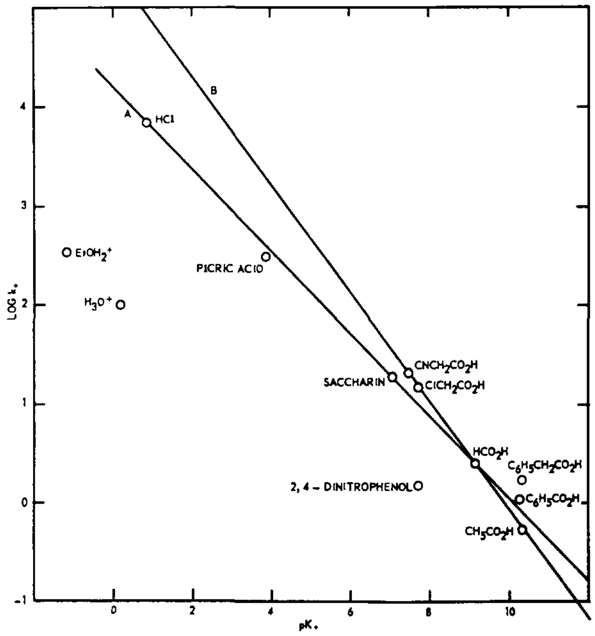

Fig. 3.—Plot of log *k* for reaction of HA with diphenyldiazomethane *vs.* the *pK* of HA.

calculated by the method of least squares. For the lower line the equation is

$$\log k = -0.663 + 1.174\, \sigma^* \qquad (4)$$

The values of σ^*, the Taft substituent constant, calculated from eq. 4 for α,β-unsaturated groups are listed in Table III. The validity of these values depends on that of the stated assumption, of course.

TABLE III

TAFT POLAR SUBSTITUENT CONSTANTS

R	σ^{*a}
$O_2NCH{=}CH{-}$	1.704
$Cl_3CCH{=}CH{-}$	1.188
$CH_3COCH{=}CH{-}$	1.080[b]
$HO_2CCH{=}CH{-}$	1.012
$ClCH{=}CH{-}$	0.900
$Cl_2CHCH{=}CH{-}$	.882
$CH_2{=}CH{-}$	.653

[a] Calculated from eq. 4. [b] This value is probably unreliable because the acetylacrylic acid appears to have been in the pseudoacid form.

Correlation of Reaction Rates with Acidity.—It is clear that the reactivities of carboxylic acids should be reasonably well correlated with their ionization constants since both the rates and the ionization constants may be correlated well with the Taft substituent constants. It is of interest, however, to see how the reactivities of non-carboxylic acids fit into such a relationship. For this purpose values of log *k* have been plotted against values of *pK* in ethanol in Fig. 3. Much of the available rate data could not be plotted due to the inaccessibility of *pK* values in ethanol. The *pK* values for acetic, formic, benzoic and cyanoacetic acids are those listed by Grunwald and Berkowitz,[15] and those for chloroacetic acid, 2,4-dinitrophenol and picric acid are from the work of Deyrup.[16] The values for the hydronium ion and hydrogen chloride are from Bezman and Verhoek.[17] The value for the ethyloxonium ion follows from a definition of terms, as -log 17, since pure ethanol is about 17 *M*. The *k*-value for ethyloxonium ion is from the work of Roberts and Watanabe,[18] the value for the hydronium ion was estimated as about 100 from their Figs. 2 and 3, and a value of 700 for hydrogen chloride estimated from their footnote 34 and Fig. 5.

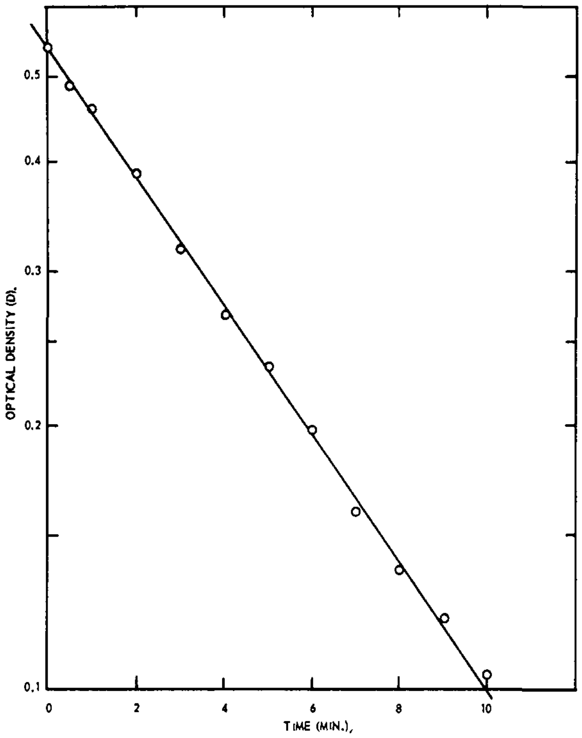

Fig. 4.—Reaction of γ,γ,γ-trichlorocrotonic acid with diphenyldiazomethane in absolute ethanol at 30°.

It is clear from our Fig. 3 that the oxonium (hydronium) ion and its ethyl derivative are much less reactive than would be expected from their acidities. This may be in some way related to the fact that these two acids are of a different electrical charge type from the others. The reactivity of 2,4-dinitrophenol is also low although by a smaller amount, and the related compound, picric acid, while in reasonable agreement with line A, deviates almost as much as the dinitrophenol from B, a line through the best points for aliphatic carboxylic acids. Perhaps this deviation results from the internal hydrogen bonding between the phenolic hydrogen atom and the nitro group *ortho* to it.

Experimental

Reagents.—Diphenyldiazomethane was prepared by the method of Smith and Howard[19] and stored as the ethanolic solution in low-actinic glassware in a refrigerator. Ethanol was dried by repeated treatment of commercial absolute ethanol with diethyl phthalate and sodium ethoxide followed by fractionation into 500-ml. vessels from which ethanol was removed only three times before the remainder was

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(15) E. Grunwald and B. J. Berkowitz, THIS JOURNAL, **73**, 4939 (1951).

(16) A. J. Deyrup, *ibid.*, **56**, 60 (1934).

(17) I. I. Bezman and F. H. Verhoek, *ibid.*, **67**, 1330 (1945).

(18) J. D. Roberts and W. Watanabe, *ibid.*, **72**, 4869 (1950).

(19) L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 351.

re-dried. The β-acetylacrylic acid,[20] γ,γ,γ-trichlorocrotonic acid,[21] β-chloroacrylic acid[22] and γ,γ-dichlorocrotonic acid[23] were prepared by methods described in the literature. The other materials used were of the best commercially available grade, purified until their m.p.'s agreed with those in the literature.

Stereochemistry of the Acrylic Acids.—The *trans* nature of fumaric acid is too well known to require comment. The crotonic acid isomer that we used (m.p. 72°) has also been fairly convincingly shown to be *trans*,[24] by an argument that also supports the *trans* structural assignment for the γ,γ-dichlorocrotonic acid and the γ,γ,γ-trichlorocrotonic acids that we used. Backer and Beute[22] have given the evidence for the structure of *trans*-β-chloropropionic acid which includes its higher melting point, lower acidity and lower solubility. According to Shaw, the ultraviolet spectrum of solutions of β-acetylacrylic acid is like that of an α,β-unsaturated lactone, showing that the compound must exist almost entirely as the pseudo acid.[11] The nitroacrylic acid used was kindly supplied for us by Dr. Lloyd A. Kaplan of the Naval Ordnance Laboratory.

Technique of Rate Determination.—The technique used in carrying out the rate determination is most easily described in terms of a representative sample.[25]

To about 40 ml. of absolute ethanol in a 50-ml. volumetric flask was added 0.9855 g. of γ,γ,γ-trichlorocrotonic acid. This solution was placed in a 30° thermostated bath with an ethanolic solution about 0.035 *M* in diphenyldiazomethane and a number of 25-ml. low-actinic volumetric flasks. When thermal equilibrium had been reached the acid solution was brought up to 50 ml. with ethanol at 30°. Then 2.00 ml. of the diphenyldiazomethane solution, 5.00 ml. of ethanol and 3.00 ml. of trichlorocrotonic acid solution was pipetted into a 25-ml. flask, where the solutions were mixed and transferred immediately to a thermostated cell in the Beckman DU spectrophotometer. From 15 to 30 seconds elapsed between the start of acid addition and the initial optical density reading (at 525 μ). The time of this reading was defined as "zero" time and subsequent readings were taken during at least two half-lives of the reaction. A plot of time *vs.* the logarithms of the optical density readings (including any necessary cell correction) is shown in Fig. 4. The second-order rate was calculated from the slope of this line and the trichlorocrotonic acid concentration.

Acknowledgments.—We wish to acknowledge with gratitute our indebtedness to the Department of the Navy, Bureau of Ordnance, for support of this work; to Dr. Lloyd A. Kaplan for preparing and supplying us with many of the compounds used in this study and for useful discussions of the problems involved in their use. We also wish to thank Dr. D. V. Sickman, Dr. M. J. Kamlet and other members of the staff of the Chemistry Research Department of the U. S. Naval Ordnance Laboratory for intellectual and material assistance during the course of this investigation.

ATLANTA, GA.

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[20] W. G. Overend, L. M. Turton and L. F. Wiggins, *J. Chem. Soc.*, 3500 (1950).

[21] K. von Auwers, *Ber.*, **56B**, 715, 731 (1923).

[22] H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1935).

[23] G. Braun, THIS JOURNAL, **52**, 3167 (1930).

[24] *Cf.* E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., Houston, Tex., Vol. 1A, p. 632.

[25] *Cf.* J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2167 (1953).

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Substitution and Addition Reactions of the Fluoroölefins. III.[1] SN2′ Substitution Reactions of Chlorofluoroallyl Chlorides with Halide Ions[2]

BY JOHN H. FRIED AND WILLIAM T. MILLER, JR.

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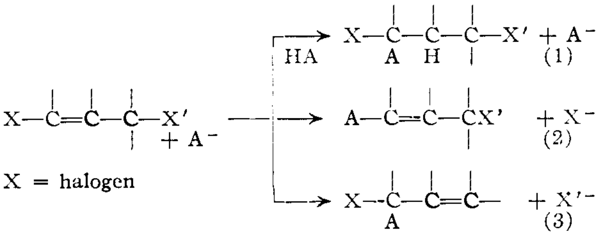
The synthesis of 3,3-dichloro-1,1,3-trifluoropropene and 3,3-dichlorotetrafluoropropene is reported. Both compounds were shown to undergo substitution reactions readily with fluoride, chloride and iodide ions. In all cases only rearranged products were obtained corresponding to the SN2′ type mechanism. The order of nucleophilic reactivity for the halide ions with the above fluoropropenes was shown to be $F^- > Cl^- > I^-$ the reverse of the order for SN2 reactions. The observed order is discussed in terms of the extended SN2′ transition state. Attention is drawn to the great importance to carbon–fluorine chemistry of the high order of nucleophilic reactivity shown by fluoride ion with the fluoroölefins.

Three typical products may be formed by reaction of a nucleophilic anion, A^-, with a fluorinated olefin in solution. These correspond to: (1) addition of HA in the presence of HA or other source of protons, (2) substitution of vinyl halogen, and (3) substitution of allyl halogen.[3] All three type reactions have now been shown to take place with halide ions. For example, 1,1-difluorohaloethylenes and -propenes add HX under mild conditions in the presence of a proton donor.[4] Substitution of vinyl halogen has been shown to take place with olefins of the type $CFX{=}\overset{|}{C}CF_3$.[7] Olefins of the



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[1] This paper is a continuation of the series previously entitled, "Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides"; preceding paper, A. H. Fainberg and W. T. Miller, Jr., THIS JOURNAL, **79**, 4170 (1957).

[2] Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, Abstracts of Papers, p. 18M. Based on the thesis submitted by John H. Fried to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[3] M. D. Hurwitz and W. T. Miller, Jr., Abstracts of Papers, 114th Meeting, Amer. Chem. Soc., Washington, D. C., August, 1948, p. 4L.

[4] The addition of HF to fluoroölefins is brought about by reaction with potassium fluoride in formamide.[5] The addition of HCl, HBr and HI occurs readily in acetic acid solution. The addition of HF occurs with difficulty in acetic acid solution due presumably to the formation of relatively unreactive the HF_2^- ion.[6]

[5] W. T. Miller, Jr., and John Fried, Abstracts of Papers, 132nd Meeting, Amer. Chem. Soc., New York, N. Y., September, 1957, p. 29M.

[6] W. T. Miller, Jr., and H. F. Koch, unpublished work.

[7] For example, substitution of the chlorine in $CClF{=}CFCF_3$ takes place on reaction with potassium fluoride in formamide.[3]