

sufficiently large concentration to make the rearrangement competitive with chain reactions of the bromine atom.

The effect of the removal of bromine atoms from the reaction mixture by complexation with olefin (either as a σ - or π -complex) could shift the mechanism for allylic bromination to one involving a slower chain process with succinimidyl radicals acting as chain carriers.²⁷

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(27) This is consistent with the observation that the addition of 2% of norbornene greatly inhibits the benzylic bromination of a mixture of toluenes in benzene solution; unpublished work of Joseph Incremona.

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

Fluorine Nuclear Magnetic Resonance Shielding in *p*-Substituted Fluorobenzenes. The Influence of Structure and Solvent on Resonance Effects¹

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Fluorine n.m.r. intramolecular shielding effects of 63 *p*-substituents in fluorobenzene have been determined at high dilution in a wide variety of solvents. The correlation has been extended between the shielding parameter for a *p*-substituted fluorobenzene relative to its *m*-isomer as internal standard and the reactivity resonance effect parameter, σ_R^0 . The relationship is used both to obtain σ_R^0 values for new substituents and to assess the trends and magnitudes of solvent effects on this parameter. Approximate MO π -electron charge density distributions are also derived. A plot of the shielding parameter for *p*-substituted fluorobenzene relative to internal fluorobenzene, \int_{H^p-X} , vs. the corresponding parameter for the *m*-isomer, \int_{H^m-X} , provides new insight into relationships between the resonance and inductive effects of substituents. Linear σ_R vs. σ_I relationships are shown to be quite special rather than general. A special and well defined class of substituents is recognized by a linear \int_{H^p-X} vs. \int_{H^m-X} plot. These substituents are designated as UAFPD (united atom-like first row pair donor) substituents. The effects of UAFPD substituents on appropriate chemical and physical properties are shown to be quite precisely linear with σ_I in aromatic (or in general, unsaturated) systems, provided that there are essentially no contributing effects of direct charge delocalization interactions between the substituent and the functional group. These remarkably precise relationships, although limited by the number of UAFPD substituents, greatly extend the range of applicability of the relationship $\log(k/k_0) = C_1\sigma_I + C_2$. The effects of polar solvents on fluorine intramolecular shieldings are interpreted as indicating rather distinct categories of solvent dependence on the contributions to the ground electronic state of various types of dipolar resonance forms. Small or undetectable solvent effects are indicated for the contributions of dipolar resonance forms for which at least one of the atomic centers of formal charge is buried within the molecular cavity. On the other hand, with increasing solvent polarity the contributions are generally appreciably increased for those dipolar direct interaction forms in which both of the formal charge centers are on the periphery of the molecule. Some applications to chemical reactivities are considered.

Intramolecular F¹⁹ n.m.r. shielding in the special case of *p*-substituted fluorobenzenes apparently can be directly related, at least approximately, to the π -electron charge density on the fluorine atom^{4,5} or its bonded carbon atom.⁵ Extensive studies⁶ of the solvent effects on the fluorine shielding in *m*-substituted fluorobenzenes suggest that the intramolecular shielding effect of a *p*-substituent in fluorobenzene can be obtained at high dilution in any solvent from the measurement of shielding referred to the standard internal fluorobenzene. The substituted and unsubstituted fluorobenzene present to their environment fluorine atoms which are sufficiently similar that intermolecular shielding cancels with considerable precision in the shielding parameter of the substituted relative to the unsubstituted internal fluorobenzene.

Fluorine shielding is so sensitive to the very small (absolute) intramolecular perturbations in the fluorine atom π -charge density produced by a distant *p*-substituent that this measurement ranks as the most sensitive probe (relative to the experimental error) currently available to investigate such interactions.⁴⁻⁷

Using this distant but very sensitive probe, new and highly instructive investigations of both the effects of substituent structure and of solvent-substituent interactions on the intramolecular shielding effect of *p*-substituents are made possible. In the present paper we report the results of extensive studies of both types.

Solvent-substituent interactions previously investigated by this technique include proton transfer equilibria,⁸ Lewis acid-base equilibria,⁶ hydrogen bonding,⁶ and polar interactions.⁶ This paper reports additional results of the last two kinds, especially the latter. The results can apparently be interpreted in terms of the effects of polar solvents on the relative contributions of various types of dipolar resonance forms to the ground electronic state of the fluorobenzene.

The effects of structure on the intramolecular shielding of $-R$ *p*-substituents have been correlated with the σ_R^0 resonance effect parameter from chemical reactivities.^{7b} The correlation is extended with the present results and is utilized both to obtain σ_R^0 values for new substituent groups and to assess the magnitude of solvent effects on σ_R values. Comparison of the present results with the previously reported corresponding *m*-substituent effect shielding parameters⁶ provides new insight into relationships between the inductive and resonance effects of substituents.

Experimental

Solvents.—Purification of solvents was carried out as previously described.⁹

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TABLE I
 SHIELDING PARAMETERS, \int_{H^p-X} , FOR $-R$ *p*-SUBSTITUTED FLUOROBENZENES^a

Solvent	<i>p</i> -Substituent							
	OCH ₃	OC ₆ H ₅	F	CH ₃	SCH ₃	C ₆ H ₅	Br	OCF ₃
Cyclohexane	11.70	7.45	6.80	5.40	4.40	3.00	2.60	2.25
Benzene	11.45	7.15	6.60	5.40	2.50	2.10
Carbon tetrachloride	11.50	7.40	6.80	5.40	4.30	2.90	2.50	2.10
Diethyl ether	11.65	7.25	6.65	5.45	4.80	..	2.35	1.85
Tetrahydrofuran	..	7.20	6.40	5.40	4.75	..	2.20	..
Dioxane	11.45	7.25	6.60	5.50	4.95	2.90	2.50	2.10
Diglyme	11.40	6.95	6.35	5.30	4.75	..	2.15	..
Diethyl maleate	11.50	7.25	6.30	5.40	4.70	..	2.00	..
Acetic anhydride	11.40	6.95	6.25	5.45	4.70	..	2.00	1.55
Acetone	11.45	6.90	6.30	2.70	2.05	1.60
Pyridine	..	7.00	6.35	5.45	4.75	..	2.25	1.75
Dimethylformamide	11.50	..	6.20	..	4.95	..	2.00	..
Methylformamide	11.55	..	6.35
Benzonitrile	11.45	..	6.35
Nitrobenzene	11.55	7.05	6.30	5.55	4.80	2.10	2.20	1.85
Nitromethane	11.40	..	6.25
Dimethyl sulfoxide	11.35	6.85	6.15	5.30	2.00	..
Methanol	11.45	7.25	6.40	5.55	4.50	2.80	2.10	1.55
75% (vol.) aq. methanol	11.20	I ^b	6.40	5.60	4.40	I	2.10	..
Formic acid	10.70 ^d	..	6.35
Trifluoroacetic acid	6.95 ^d	5.20 ^d	6.40	2.25	2.00
Mean value	11.45	7.15	6.40	5.45	4.70	2.75	2.25	1.85
Av. dev.	±0.08	±0.16	±0.13	±0.07	±0.16	±0.22	±0.16	±0.21

^a In p.p.m. relative to fluorobenzene; exptl. error = ±0.08. ^b I designates insufficient solubility. ^c 1.55 in acetonitrile. ^d Excluded in obtaining mean value.

Fluorobenzenes.—*p*-Fluorotoluene, *p*-fluoroaniline, *p*-fluorophenol, *p*-chlorofluorobenzene, *p*-bromofluorobenzene, *p*-fluorobenzaldehyde, *p*-fluorobenzotrifluoride, *p*-fluorobiphenyl, and *p*-fluoroacetanilide were obtained as previously reported.^{7b} The following compounds were obtained from the Pierce Chemical Co., Rockford, Ill.: *p*-nitrofluorobenzene, b.p. 95° (34 mm.), *n*^{25D} 1.5298 (reported¹⁰ b.p. 86.6° (14 mm.), *n*^{20D} 1.5316); *p*-fluoroacetophenone, *n*^{25D} 1.5120 (reported¹¹ *n*^{25D} 1.5081); and *p*-fluorobenzyl chloride. The following compounds were obtained from L. Light and Co., Ltd., Colnbrook, Eng.: *p*-difluorobenzene, b.p. 87–88° (735 mm.), *n*^{25D} 1.4388 (reported¹² b.p. 88.4° (767 mm.), *n*^{15D} 1.4423); ethyl *p*-fluorobenzoate, *n*^{25D} 1.4842 (reported¹³ *n*^{25D} 1.4707); *p*-fluoro- α,α -trifluoroacetophenone, b.p. 89° (100 mm.) *n*^{25D} 1.4571; *p*-fluorophenylisothiocyanate, b.p. 66° (3 mm.) (reported¹⁴ b.p. 228° (760 mm.), m.p. 12°); *p*-fluorobenzenediazonium fluoroborate, m.p. 162° dec.; 2-methyl-4-fluoro-*N,N*-dimethylaniline, b.p. 78–80° (17 mm.), which was prepared by formyl methylation of 3-fluoro-6-aminotoluene. White Label *p*-fluorobenzoic acid, m.p. 181–183° (reported¹⁵ m.p. 182°); *p*-fluorobenzonitrile, m.p. 35–36° (reported¹⁶ m.p. 34.8°); and *p*-fluoroanisole, *n*^{25D} 1.4851 (reported¹² *n*^{25D} 1.4862) were obtained from Eastman Organic Chemicals.

The following compounds were prepared as previously described: *p*-fluorostyrene,¹⁷ *p*-fluorophenylmethylcarbinol,¹⁷ *p*-fluorophenylhydrazine,¹⁵ *p*-fluorothiophenol,¹⁹ *p*-fluorophenyl methyl sulfide,²⁰ *p*-fluorophenyl methyl sulfone,²⁰ *p*-fluorobenzenesulfonyl chloride,¹⁹ *p*-fluorobenzenesulfonic acid,¹⁹ *p*-fluorobenzenesulfonamide,¹⁹ *p*-fluoroazobenzene,²¹ *p*-fluoroethylbenzene.²²

The preparation of the following compounds was carried out similarly to that reported⁹ for the *m*-isomer: *p*-fluoronitrosobenzene, m.p. 37.5–39.0° (reported¹⁸ m.p. 39°) in 16% yield; *p*-fluoro-*N,N*-dimethylaniline, b.p. 85–86° (18 mm.) (reported²³ 86–87° (18 mm.)); *p*-fluorotrimethylammonium iodide, m.p. 215–216°; *p*-fluorophenylacetate, b.p. 86° (26 mm.); *p*-fluoro-

diphenyl ether, b.p. 127° (17 mm.) (reported²¹ b.p. 254–255° (860 mm.)); *p*-fluoroiodobenzene, b.p. 65–68° (13 mm.) (reported²⁴ 67–69° (11 mm.)); *p*-fluorobenzoyl chloride, b.p. 85–86° (23 mm.) (reported²⁵ b.p. 104° (38 mm.)); *p*-fluorobenzamide, m.p. 155–156°; *p*-fluorophenyl benzoate, m.p. 63.5–64.5°; *p*-fluorophenyl methyl sulfoxide, b.p. 114–116° (3 mm.); ethyl *p*-fluorobenzenesulfonate, b.p. 123° (2 mm.); *p*-fluoroaniline hydrochloride; *p*-fluorobenzylamine hydrochloride, m.p. 279–281°; *p*-fluorobenzyl cyanide, b.p. 112–114° (14 mm.); *p*-fluorophenylacetic acid, m.p. 83° (reported²⁶ m.p. 85°); *p*-fluorobenzyl alcohol, b.p. 95° (12 mm.); *p*-fluorophenyl sulfur pentafluoride, b.p. 103° (760 mm.); *p*-fluorobenzoyl fluoride, b.p. 148–148.5° (750 mm.); *p*-fluorobenzenesulfonyl fluoride, b.p. 179–180° (745 mm.); 1-(*p*-fluorophenyl)-2-nitroethene, m.p. 100–101°. *Anal.* Calcd. for C₈H₆FNO₂: C, 57.47; H, 3.62. Found: C, 57.23; H, 3.37.

p-Fluorophenyl trifluoroacetate was prepared by Dr. P. E. Peterson from the reaction of equimolar quantities of *p*-fluorophenol and trifluoroacetic anhydride.²⁷ The phenol was heated alone at 100° and the anhydride was added from a dropping funnel cooled with Dry Ice to prevent evaporation of the anhydride. The reaction mixture was stirred and heated to rapid reflux. The trifluoroacetic acid formed was distilled from the reaction mixture and the product fractionated under vacuum in a spinning band column; b.p. 83° (116 mm.). The infrared spectrum in CCl₄ showed the typical strong band at 1780 cm.⁻¹.

p-Fluorophenylacetylene.—Bromine was added dropwise to a solution of *p*-fluorostyrene in carbon tetrachloride until the bromine color persisted. The solution was concentrated *in vacuo* to an oil. Alcoholic potassium hydroxide was added and the mixture refluxed for 1 hr. The mixture was poured onto ice and extracted with three 50-ml. portions of hexane. The organic extracts were washed with a saturated salt solution and dried over Drierite. Solvent was removed and the residue distilled at reduced pressure to give a 19% yield of product, b.p. 64–65° (50 mm.).

p-Fluorophenyltrimethylsilane was kindly prepared by Dr. A. Konstam from the reaction of the Grignard reagent of *p*-fluorobromobenzene with trimethylsilyl chloride.

p-Fluoro- α,α,α -trifluoroanisole was kindly provided by Dr. W. A. Sheppard.

p-Fluorobenzyltrimethylsilane was kindly provided by Dr. A. Konstam.

p-Fluorophenylboronic acid was kindly provided by Prof. H. G. Kuivila.

Procedure.—All measurements (unless otherwise noted) were made with approximately 5% (vol.) solutions of *p*-fluorobenzene. The shielding parameters reported are relative to fluorobenzene

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TABLE II
 SHIELDING PARAMETERS, $-\int_H^{p-X}$, FOR $+R$ p -SUBSTITUTED FLUOROBENZENES^a

Solvent	p -Substituent									
	CF ₃	SF ₃	-CH=CHNO ₂	COCH ₃	CN	NO ₂	NO	COF	COCF ₃	SO ₂ F
3-Methylpentane	4.95	5.20	..	6.05	8.65	9.00
Cyclohexane	5.05	5.35	..	6.10	8.95	9.20	10.50	11.15	12.00	12.20
Benzene	5.15	..	5.80	6.50	9.05	9.45	11.50	11.35	12.45	12.35
Carbon tetrachloride	5.15	5.50	..	6.60	9.20	9.55	11.10	11.40	12.35	12.50
Dioxane	5.15	5.50	5.40	6.15	8.95	9.10	11.60	..	11.80	12.20
Diethyl ether	5.45	5.90	..	6.40	9.20	9.65	11.35	..	12.65	12.70
Tetrahydrofuran	5.65	6.00	..	6.35	9.45	9.75	12.00	12.90
Ethyl acetate	5.80	6.50	9.45	9.85	12.00	11.70	12.85	13.00
Diglyme	5.75	6.55	9.45	10.00
Chlorobenzene	5.50	5.95	..	6.70	9.60	10.05	11.95
Acetic acid	10.00	12.25	11.70	13.00	13.05
Diethyl maleate	5.85	6.35	6.10	6.75	9.70	10.25	12.40	12.00	13.25	13.40
Methanol	5.90	6.35	6.20	7.65	10.25	10.35	12.45	12.10	R	13.50
Acetone	5.80	6.35	5.95	6.55	9.70	10.10	12.45	11.85	12.95	13.35
Acetic anhydride	5.80	6.80	9.75	10.35	12.65	11.95	13.15	13.45
Pyridine	5.70	6.15	6.10	6.80	9.80	10.25	12.55	11.85	12.90	13.55
Dimethylformamide	5.90	6.40	5.95	6.70	9.80	10.30	12.85	11.95	12.95	13.50
Monomethylformamide	5.70	6.25	..	7.00	9.90	10.30	12.75	13.40
Benzonitrile	6.90	9.90	10.45	12.65
Nitrobenzene	5.70	6.25	6.40	6.85	9.90	10.50	12.65	12.05	13.20	13.45
Acetonitrile	5.90	..	6.15	..	9.90	10.35	12.80	12.00	13.10	13.55
Nitromethane	5.75	6.35	6.30	6.95	9.95	10.55	12.90	12.15	13.15	13.60
Dimethyl sulfoxide	5.90	6.40	5.95	6.80	9.85	10.30	13.20	R	12.85	13.55
Methylene chloride	10.85	12.90	13.60
Chloroform	11.05	12.95	12.50	13.45	13.70
Formamide	7.65	10.45	11.00	13.05	13.85
Formic acid	5.35	6.00	6.80	9.55	11.15	11.00	R ^b	12.40	13.55	13.60
75% (vol.) aq. methanol	6.05	I ^b	..	8.50	11.00	11.20	13.70	R	..	14.25
2,2,3,3-Tetrafluoropropanol	5.45	6.05	..	9.30	11.60	11.85	14.80	13.05	..	14.20
Trifluoroacetic acid	5.35	5.95	..	12.80	13.75	14.05	R	15.15	16.80	15.25

^a In p.p.m. relative to fluorobenzene; exptl. error = ± 0.08 . ^b I designates insufficient solubility; R designates that a fast reaction occurs.

as an internal standard. Under these conditions the shielding parameters correspond to the intramolecular effect of the p -substituent at essentially infinite dilution in the indicated solvent.⁹ Detailed procedures and relationships are the same as that previously reported.⁹

Results

Table I lists the results of a nearly complete survey of the shielding parameters for eight $-R$ p -substituted fluorobenzenes relative to fluorobenzene as the internal standard in 20 widely varying pure solvents at high dilution. Table II gives similar results for ten $+R$ p -substituted fluorobenzenes in 30 solvents. Shielding parameters for 23 additional $-R$ p -substituents in four solvents are given in Table III. Tables IV and V lists shielding parameters for 22 additional $+R$ p -substituents in a variety of solvents. All shielding parameters have been rounded to the nearest 0.05 p.p.m. (exptl. error = ± 0.08 p.p.m.).

In the previous paper of this series⁶ it was found that the shielding of fluorobenzene relative to a fixed external standard varies widely with solvent, in part, apparently due to intermolecular dispersion force interactions between the fluorine atom and the solvent. However, the shielding parameters for a wide variety of chemically inert m -substituted fluorobenzenes relative to the standard internal fluorobenzene were found to be solvent invariant to a precision of the same order as the experimental error. This result indicates the considerable precision with which intermolecular shielding cancels in the shielding parameter of the m -substituted fluorobenzene relative to internal fluorobenzene, providing a measure of the intramolecular shielding effect of the m -substituent. Fluorobenzene as an internal reference serves an additional function. Variable physical interactions (or even weak complexing) between the

 TABLE III
 SHIELDING PARAMETERS, \int_H^{p-X} , FOR $-R$ p -SUBSTITUTED FLUOROBENZENES^a

Substituent	Solvent			
	Cyclohexane	Carbon tetrachloride	Methanol	75% (vol.) aq. methanol
O ⁻	19.50	19.30
N(CH ₃) ₂	15.90	15.65	15.05	13.75
NH ₂	14.40	14.20	14.05	13.40
NHNH ₂	I ^b	..	12.25	13.10
OH	10.65	10.85(11.40) ^f	12.95	12.35
CH ₂ Si(CH ₃) ₃	6.95	7.00	7.15	I
C ₂ H ₅	5.05	5.00	5.10	5.10
NHCOCH ₃	I	I ^c	5.15	4.90
CH ₂ CO ₂ ⁻	I	I	4.65	4.55
OCOCH ₃	4.80	4.55	4.15	3.95
CH ₂ NH ₂	3.75	3.60	3.00	3.00
SH	3.50	3.50	4.35	4.20
Cl	3.20	3.10	2.70	2.75
CH(OH)CH ₃	2.75	2.55	2.85	2.80
CH ₂ CO ₂ H	I	2.30	2.75	2.85
CH ₂ OH	2.15	2.05	2.50	2.40
I	1.70	1.55	1.35	1.35
OCOCF ₃	1.60	1.50	R ^d	R ^e
CH=CH ₂	1.45	1.40	1.30	1.30
CH ₂ CN	1.30	1.20	1.35	1.35
CH ₂ Cl	0.50	0.35	0.45	0.35
NCS	..	-0.55
CH ₂ NH ₃ ⁺	-0.85	-1.00

^a In p.p.m. relative to fluorobenzene; exptl. error = ± 0.08 . ^b I designates insufficient solubility; R designates that a fast reaction occurs. ^c 6.85 in dimethylformamide. ^d 1.60 in CH₂NO₂. ^e 0.20 in CF₃CO₂H. ^f In 1% soln. (unpublished results of Mr. M. G. Schwartz).

TABLE IV
 SHIELDING PARAMETERS, $-\int_{\text{H}^{p-X}}$, FOR $+R$ *p*-SUBSTITUTED FLUOROBENZENES^a

Solvent	<i>p</i> -Substituent									
	Si(CH ₃) ₃	C≡C—H	SOCH ₃	CONH ₂	SO ₂ NH ₂	CO ₂ C ₂ H ₅	CO ₂ H	SO ₂ CH ₃	SO ₂ C ₂ H ₅	CHO
3-Methylpentane	0.50	I	I	5.75	I	..	7.70	8.75
Cyclohexane	.50	2.35	I ^b	I	I	5.90	I	I	8.10	9.15
Carbon tetrachloride	.50	2.50	3.00	I	I	6.20	I	8.00	8.30	9.40
Dioxane	..	2.50	2.45	3.50	5.10	6.20	6.20	7.30	8.05	8.90
Diethyl ether	6.25	9.10
Tetrahydrofuran	3.40	..	6.45	6.00	9.15
Diethyl maleate	..	2.80	5.65	6.65	8.90	9.50
Methanol	0.65	2.70	4.80	5.00	6.00	7.15	..	8.85	9.45	R
Acetone	3.80	..	6.60	9.30
Pyridine	3.65	..	6.70	5.55	9.55
Dimethylformamide	0.60	6.05	9.45
Monomethylformamide	0.50	4.15	..	6.70	9.65
Nitrobenzene	..	2.85	..	I	6.45	6.60	9.15	9.55
Acetonitrile	4.25	..	6.70	9.65
Nitromethane	0.55	..	3.35	6.70
Dimethyl sulfoxide	2.75	3.45	..	6.90	9.50
75% (vol.) aq. methanol	I	2.85	5.25	5.55	6.80	7.65	..	9.65	10.15	10.50
Trifluoroacetic acid	R ^c	13.95	..	10.35	11.80	..	12.75	16.10

^a In p.p.m. relative to fluorobenzene; exptl. error = ± 0.08 . ^b I denotes insufficient solubility. ^c R denotes that a fast reaction occurs.

 TABLE V
 SHIELDING PARAMETERS, $-\int_{\text{H}^{p-X}}$, FOR $+R$ *p*-SUBSTITUTED FLUOROBENZENES^a

Substituent	Solvent			
	Cyclohexane	Carbon tetrachloride	Methanol	75% (vol.) aq. methanol
CO ₂ ⁻ Na ⁺	I	I	I	2.30
B(OH) ₂	I	I	2.45	3.05
SO ₃ ⁻ H ⁺	I	I	3.00	3.30
C ₆ H ₅ N=N	3.10	3.25	3.90	I
COSCH ₃	6.0	I
C ₆ H ₅ CO	5.75	6.05	7.25	8.00
CO ₂ C ₆ H ₅	7.45	7.70	8.65	I
COCl	11.20	11.40	R	R
SO ₂ Cl	11.90	12.20	13.35	13.85
N ₂ ⁺	I	27.80 ^b	29.80 ^c	..

^a In p.p.m. relative to fluorobenzene; exptl. error = ± 0.08 . ^b In acetone. ^c In acetonitrile.

solute aromatic ring and solvents of widely varying internal pressure should be essentially equal for substituted and unsubstituted fluorobenzene. Thus little or no effect arising from this source should enter the substituent shielding effects (\int_{H^X} parameters) based upon the internal fluorobenzene standard.

The results in Tables I and III for $-R$ *p*-substituted fluorobenzenes indicate that a similar conclusion can be drawn (although in general somewhat less precisely) regarding the shielding parameters for such compounds relative to internal fluorobenzene.

The *m*-substituents CH₃, C₆H₅, H, Br, F, and OCF₃ were found to be very generally chemically inert in interactions with the solvent. The shielding parameters for these substituents in the *p*-position of fluorobenzene vary in a given solvent over a range of approximately 5 p.p.m. However, the shielding parameters for the given substituent in a wide variety of solvents at high dilution define mean values precise to approximately ± 0.2 p.p.m. (cf. Table I.). Further, the results for the OCH₃ and OC₆H₅ substituents, which extend the range of shielding an additional 5 p.p.m., show a similar solvent insensitivity except in formic and trifluoroacetic acid solutions. It was previously noted that these two substituents (in the *m*-position) act as bases toward these solvents, giving a similar result to that indicated by Table I, namely that resonance occurs at lower field strengths than normal. Table III provides several additional examples of expected variations in shielding

parameters resulting from hydrogen bonding interactions between *p*-substituent and solvent.

In contrast, the results in Tables II, IV, and V for $+R$ *p*-substituted fluorobenzenes show the shielding parameters for these compounds are generally markedly solvent dependent. The nature of the solvent dependence (to be discussed in further detail in subsequent sections), however, shows no resemblance to that for the shielding of internal fluorobenzene relative to a fixed external standard. Thus, for example, the shielding parameters from Table II for one of the *p*-substituted fluorobenzenes plotted *vs.* the shielding parameter for fluorobenzene relative to a fixed external standard⁶ leads to a wide scattering of points. Since the solvent insensitive shielding parameters for *m*-substituted fluorobenzenes and for $-R$ *p*-substituted fluorobenzene cover as wide a range as for most $+R$ *p*-substituted fluorobenzenes (positively charged $+R$ *p*-substituents are exceptions⁸), it may be reasoned that the shielding parameters for $+R$ *p*-substituted fluorobenzenes relative to internal fluorobenzene also involve essentially complete cancellation of intermolecular shielding. The variation of the latter shielding parameters with solvent is then also to be attributed to modification of the intramolecular substituent effect through substituent-solvent interactions (as previously found,⁶ on a much reduced scale, for certain *m*-substituted fluorobenzenes in certain solvents). The nature of the solvent dependence indeed supports this interpretation (cf. subsequent discussion).

Correlation of Shielding Parameters.—The following relatively precise correlation of F n.m.r. shielding parameters for $-R$ *m*- and *p*-substituted fluorobenzenes has been reported^{7c}

$$\int_{\text{H}^{p-X}} = -29.5\sigma_{\text{R}}^0 + \int_{\text{H}^{m-X}} = -29.5\sigma_{\text{R}}^0 - 7.1\sigma_1 + 0.60 \quad (1)$$

where $\int_{\text{H}^{p-X}}$ and $\int_{\text{H}^{m-X}}$ are the shielding parameters for the *p*-substituted fluorobenzene and its *m*-isomer, respectively, relative to internal fluorobenzene (in p.p.m.). The resonance effect parameter, σ_{R}^0 , is obtained by the method of Taft from σ^0 reactivities.^{7b}

The correlation is illustrated in Table VI by comparison of σ_{R}^0 values obtained from reactivities and "normal" values calculated by eq. 1 from the shielding parameters (Tables I and III) in solvents (including hydrocarbon solvents) which define relatively precise mean values of both $\int_{\text{H}^{p-X}}$ and $\int_{\text{H}^{m-X}}$.

TABLE VI
"NORMAL" σ_R^0 VALUES FROM FLUORINE SHIELDING PARAMETERS

Subst.	$-\sigma_R^0$ (reactivity)	$-\sigma_R^0$ (shielding)
O ⁻	0.66 ^a	0.60 ^c
N(CH ₃) ₂	.52	.539 ± 0.006
NH ₂	.48	.481 ± 0.006
NHNH ₂	..	.43 ^c
OCH ₃	0.41	.429 ± 0.003
OH	.40	.427 ± .003 ^d
F	.35	.322 ± .006
OC ₆ H ₅	..	.312 ± .006
OCOCH ₃	..	.21
CH ₂ Si(CH ₃) ₃	..	.20
OCOCF ₃	..	.19
Cl	0.20	.18
OCF ₃	0.17 ^b	.176 ± 0.008
SCH ₃	..	.173 ± .006
Br	0.19	.163 ± .006
SH	..	.15
CH ₂ NH ₂	..	.15
CH ₃	0.10	.146 ± 0.003
C ₂ H ₅	.09	.14
I	.12	.14
C ₆ H ₅	.10	.093 ± 0.008
CH ₂ CN	..	.08
-NCS	..	.06
CH ₂ Cl	..	.03
CH=CH ₂	..	.03
CH ₂ CH ₃ ⁷	..	.00 ^c

^a Based upon σ -values given by J. Hine, *J. Am. Chem. Soc.*, **82**, 4880 (1960). ^b W. A. Sheppard, *ibid.*, **83**, 4860 (1961). ^c In 75% (vol.) aq. CH₃OH solution. ^d In 1% CCl₄ solution.

In Table VII are listed σ_R^0 values obtained from shielding parameters which show the hydrogen bonding solvent effects of 75% (vol.) aqueous methanol and of trifluoroacetic acid on the N(CH₃)₂, OCH₃, OH, OC₆H₅, and SH substituents. The results for the chemically inert substituents, F, Br, and OCF₃, are included for comparison. Although the indicated solvent effects on the σ_R^0 value obtained from the shielding parameters may not be precisely applicable (as previously noted⁶ for the inductive parameters, σ_I) to other systems, it is very probable that they do establish expected general trends and magnitudes.

TABLE VII
HYDROGEN BONDING SOLVENT EFFECTS ON σ_R^0 VALUES FROM FLUORINE SHIELDING^a

Subst.	Normal	$-\sigma_R^0$ value	
		75% aq. MeOH	CF ₃ CO ₂ H
N(CH ₃) ₂	0.54	0.47	..
OCH ₃	.43	.42	0.34
OH	.43	.45	..
F	.32	.32	0.33
OC ₆ H ₅	.31	..	.27
OCF ₃	.18	..	.18
Br	.16	0.16	.16
SH	.15	0.17	..

^a Exptl. error = ±0.01.

The σ_R^0 values of Table VI may be combined with σ_I values of the previous paper⁶ to obtain σ^0 values. These values are potentially applicable *via* the modified Hammett equation, $\log(k/k_0) = \sigma^0\rho$, to the side-chain reactivities of benzene which are uncomplicated by the effects of direct interaction structures (between substituent and side-chain function) and polarization effects.^{7b,c}

$$\sigma^0(\text{meta}) = \sigma_I + 0.50\sigma_R^0$$

$$\sigma^0(\text{para}) = \sigma_I + \sigma_R^0$$

A discussion of the relationship of σ_R^0 and structure is presented in the following sections.

π -Electron Charge Densities.—Approximate localized MO π -electron density changes produced by the various *p*-substituents may be estimated from the σ_R^0 values given in Table VI through relationships derived previously^{5a,b} between charge density changes and the quantity $\int_{H^p-X} - \int_{H^m-X}$. The resulting relationships are

$$\text{for the fluorine atom, } \Delta q_{(F)} = 0.025\sigma_R^0 \quad (2)$$

$$\text{for the attached (} p\text{-) carbon atom, } \Delta q_{(C)} = 0.133\sigma_R^0$$

where $\Delta q_{(F)}$ is the difference in the π -electron charge density of the fluorine atom of fluorobenzene and that for the *p*-substituted fluorobenzene, and $\Delta q_{(C)}$ is the corresponding difference in the π -electron charge density at the aromatic carbon to which the fluorine atom is bonded. These relationships, in addition to other uncertainties, are based upon the assumption of a fixed ΔE parameter^{5a} for all *p*-substituted fluorobenzenes, and consequently must be accepted with reserve (*cf.*, however, subsequent discussion).

We have made (at the suggestion of Professor Lionel Goodman) an independent test of eq. 2, which is based upon the steric inhibition of resonance effect of a 2-methyl substituent on the *p*-dimethylamino substituent.^{27a} In cyclohexane solution, the shielding parameter for 3-methyl-4-dimethylaminofluorobenzene relative to internal *m*-methylfluorobenzene is +7.05 p.p.m. (we are indebted to Mr. John Carten for this determination). From Table III the normal *p*-dimethylamino shielding effect is found to be +15.90 p.p.m., indicating that the 2-methyl substituent produces a 56% steric inhibition of the resonance effect (note that $\int_{H^p-N(CH_3)_2} - \int_{H^m-N(CH_3)_2} = \int_{H^p-N(CH_3)_2} - \int_{H^m-N(CH_3)_2}$; *cf.* Table VIII). This is essentially the same figure as reported earlier^{27b} based upon σ_R values and upon extinction coefficients for 3-methyl-4-dimethylaminoethyl benzoate.

From eq. 1, one obtains $\sigma_R^0 = -0.24$ for the twisted *p*-dimethylamino substituent. From eq. 2 then we obtain for the *p*-carbon atom a π -electron charge density 0.040 greater in the *p*-dimethylaminofluorobenzene. This is essentially the same figure (0.046) obtained by Lauterbur^{27c} from the C¹³ n.m.r. shieldings of the *p*-carbon atoms in N,N-dimethylaniline and N,N-dimethyl-*o*-toluidine and is in satisfactory agreement with the theoretically calculated value of McRae and Goodman^{27d} of 0.031. Also in quite satisfactory agreement are $\Delta q_{(C)}$ values calculated from eq. 2 for the *p*-NH₂ and *p*-N(CH₃)₂ substituents and corresponding values listed by Lauterbur^{27c} obtained from C¹³ n.m.r. shieldings and from theoretical calculations.

From the largest $-\sigma_R^0$ value (0.60 for O⁻) of Table VI, we find the greatest increase in fluorine atom π -charge density is on the order of 0.02 electron, supporting the earlier assumption that the substituted and unsubstituted compounds present to the solvent nearly identical fluorine atoms. The *p*-carbon atom of the phenoxide ion (in aq. CH₃OH) has an increased π -electron density on the order of 0.1 electron, sufficient to account for the highly activating influence of the O⁻ substituent in electrophilic substitution reactions at the *o*- and *p*-positions.

Equation 2 provides a basis for direct association of the reactivity resonance effect parameter, σ_R^0 , with the π -charge density localized at the *p*-carbon atom in the ground electronic state of a benzene derivative (of the

(27a) B. M. Wepster, "Progress in Stereochemistry," Vol. 2, edited by W. Klyne and P. B. D. de la Mare, Butterworths, London, 1958.

(27b) R. W. Taft and H. D. Evans, *J. Chem. Phys.*, **27**, 1427 (1957).

(27c) P. C. Lauterbur, *ibid.*, in press.

(27d) E. G. McRae and L. Goodman, *ibid.*, **29**, 334 (1958).

TABLE VIII
TYPICAL FIT OF DATA TO EQ. 3 FOR UAFPD SUBSTITUENTS

UAFPD sub- stituent	σ_I	Shielding, F-n.m.r. \int_{H^p-X} , p.p.m.		Parameters \int_{H^m-X} , p.p.m.		C-1 ioniz. ArOH, H ₂ O, 25° log (K^m/K_0)		A-15 sapon. rate, ArCO ₂ Et, aq. acetone, 25° log (k^m/k_0)		A-13 ion-pair formation, ArCO ₂ H, DPG, benzene, 25° log (K^m/K_0) log (K^p/K_0)				Ioniz. 6X- quinolines, H ₂ O, 25° log (K/K_0)	
		Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
O ⁻	-0.15 ^a	19.4	19.3 ^a	+1.7	+1.6 ^a	-0.31	-0.83	-0.90	-1.57	-1.54
NMe ₂	+ .05	15.6	15.8	+0.2	-0.1	+ .03	+0.10	- .36	-0.36	.42	-0.37	-0.98	-0.88
NH ₂	+ .10	14.6	14.1	- .1	+ .3	+ .11	+ .11	- .25	-0.24	- .30	-0.33	- .84	-0.81	- .70	-0.69
NHNH ₂	+ .15	13.7	13.1 ^a	- .5	- .4	+ .20	- .13	- .18	- .69	- .53
OCH ₃	+ .26	11.6	11.6	-1.3	-1.2	+ .38	+ .35	+ .13	+0.13	+ .09	+0.12	- .36	-0.34	- .16
OH	+ .27	11.4	11.4	-1.3	-1.2	+ .40	+ .42	+ .15	+ .11	+ .09	- .34	- .32	- .13	-0.24
F	+ .51	6.8	6.8	-3.0	-3.0	+ .80	+ .79	+ .71	+0.72	+ .69	+ .68	+ .37	+ .35	+ .68	+0.69
C-1		-19.10				+1.69		+2.32		+2.40		+2.94		+3.36	
C-2		+16.55		+0.60		-0.06		-0.48		-0.54		-1.13		-1.04	

^a In 75% (vol.) aq. CH₃OH.

σ^0 type^{7b}). Since σ_R^0 parameters come from measurements of chemical equilibria, a linear relationship (or an approximate one) between the localized *p*-carbon atom π -charge density and the change in this charge density between initial and final electronic ground states (of the σ^0 type) is implied. Equation 2 serves as an empirical relationship which demonstrates that the molecular orbital theory concept of localized π -charge density is a useful one in the interpretation of observed effects of *p*-substituents on chemical reactivities.

Regarding σ_I - σ_R Relationships.—The inductive parameter σ_I and the resonance parameter σ_R have been proposed as independent parameters, *i.e.*, parameters which *in general* are not directly related to one another.^{7c} Recently, Bauld^{28a} and McDaniel^{28b} have made limited comparisons of σ_I and σ_R and have suggested that linear relationships exist between these parameters for all substituents having a common first atom.

Since σ_I is linearly related to \int_{H^m-X} and σ_R^0 is linearly related to $\int_{H^p-X} - \int_{H^m-X}$ (for -R substituents), plots of \int_{H^p-X} vs. \int_{H^m-X} are highly instructive regarding σ_I - σ_R relationships.^{7b,c} In Fig. 1 such a plot has been constructed from all of the available data in cyclohexane solution (a few data in other solvents for substituents not soluble in cyclohexane are also included).

It is abundantly clear from Fig. 1 that *in general* there is no direct relationship between σ_I and σ_R , even for substituents having a common first atom (designated by the set of distinguishing symbols listed under Fig. 1). This result holds for both -R and +R substituents. Rather similar scatter patterns are obtained in plots of substituent effects on aromatic series reactivities, *i.e.* plots of log (k/k_0) vs. σ_I ; *cf.*, for example, Fig. 3, ref. 29. It will be noted from Fig. 1, however, that for substituents with a common first atom there are generally rough trends for σ_R (or $-\int_{H^p-X}$) to increase (become more positive) as σ_I (or $-\int_{H^m-X}$) increases. In general, such trends are very crude, however, and frequent exceptions are to be noted. For example, σ_I is substantially greater for the NO₂ group (normal value,⁶ +0.56) than for the NO group (normal value,⁶ +0.34), while σ_R is appreciably greater for NO (in cyclohexane solution, +0.30) than for NO₂ (in cyclohexane solution, +0.20).³⁰ Several additional examples of pairs of sub-

stituents which show this inverse order behavior include: OC₆H₅ and OCOCH₃; SOCH₃ and SO₂NH₂; C₆H₅ and CH=CH₂; CF₃ and CH₃CO; CN and COF; NCS and N=NC₆H₅.

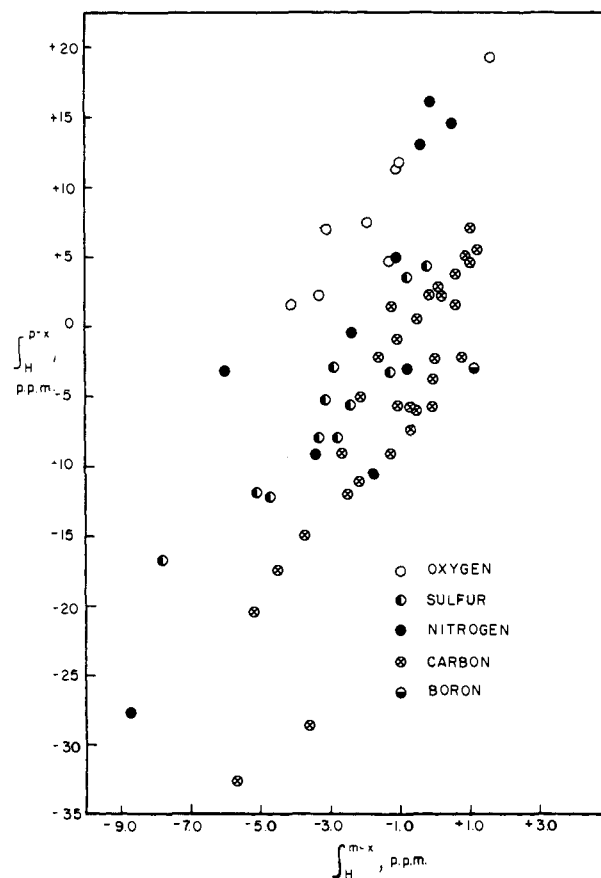


Fig. 1.—Relationship between shielding parameters for *m*- and *p*-substituted fluorobenzenes. First atom of substituent is as designated.

If one restricts comparison to series of closely related structures, relatively precise linear relationships between \int_{H^p-X} and \int_{H^m-X} (and therefore between σ_R or between σ_p and σ_m) do appear. Five such series are illustrated in Fig. 2-4. Figure 2 gives the plot of \int_{H^p-X} vs. \int_{H^m-X} for substituents of the formulas COX SO₂X, both of which generate (separately) relatively precise linear relationships. Points for SOCH₃ and

ments within the series occur so that linear σ_I - σ_R relationships appear. In fact, it may be anticipated that the same structural features which lead to the decay of the linear $\int_{H^p-X} - \int_{H^m-X}$ relationships of the following discussion are also responsible for limitations of direct linear free energy relationships. That is, these structural changes produce reactivity effects which require for description two or more substituent parameters; *e.g.*, σ_I and σ_R^0 or σ_R^+ , etc., rather than the single parameter, σ_I .

(28) (a) N. L. Bauld, Abstracts, 139th National Meeting of the American Chemical Society, March, 1961; (b) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961).

(29) R. W. Taft and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

(30) The larger σ_I value for NO₂ is in accord with the more positive nitrogen atom of this substituent and the predominant role of the first atom in determining the σ_I parameter for the substituent as a whole.⁸ In spite of the larger electron-attracting power of the first atom, σ_R for NO₂ is dramatically less than that for NO. This is apparently to be attributed to the effect of electron repulsion, which is unfavorable to the conjugative accumulation of negative charge on the two oxygen atoms of the NO₂ group. The NO substituent is unencumbered by such a structural feature. It is apparent from the discussion which follows that among structurally similar substituents such factors either do not enter or adjust-

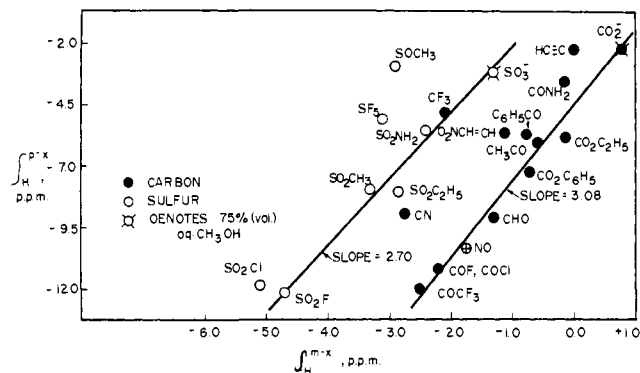


Fig. 2.—Linear \int_H^{p-X} vs. \int_H^{m-X} relationships for $-\text{COX}$ and $-\text{SO}_2\text{X}$ substituents.

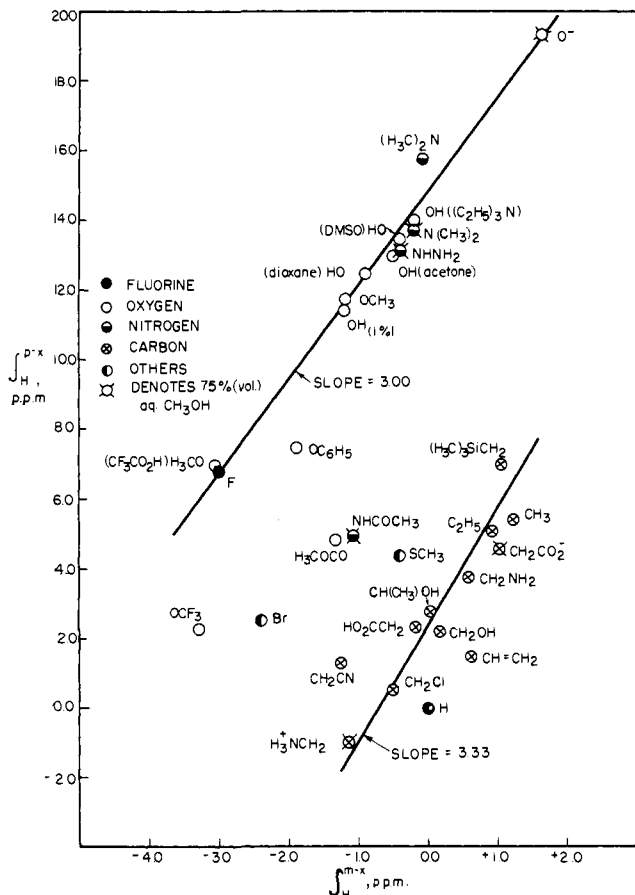


Fig. 3.—Linear \int_H^{p-X} vs. \int_H^{m-X} relationships for UAFPD substituents and for $-\text{CH}_2\text{X}$ substituents.

SF_6 are included to illustrate that these structures do not qualify for the SO_2X line. Similarly it is illustrated in Fig. 2 that the points for CF_3 , $\text{HC}\equiv\text{C}$, $\text{C}\equiv\text{N}$, and $(\text{NO}_2)\text{CH}=\text{CH}$ do not follow the linear relationship defined by COX substituents. Relatively wide variation in the structure of X is apparently permitted, the approximate relationships encompassing $\text{X} = \text{O}^-$, NH_2 , OC_2H_5 , C_6H_5 , CH_3 , OC_6H_5 , H , F , Cl , and CF_3 .

Figure 3 illustrates linear relationships between \int_H^{p-X} and \int_H^{m-X} for substituents of the formula CH_2X and, also for an especially interesting series constituted by the substituents O^- , $\text{N}(\text{CH}_3)_2$, NHNH_2 , OH , OCH_3 , and F . Included in the latter plot are unpublished data of Mr. M. G. Schwartz for the phenols in 1% CCl_4 solutions in the essentially unassociated form⁶ and as 1-1 complexes with several bases (as indicated). A point for the OCH_3 group complexed with trifluoroacetic acid (in this solvent) is also included. Whereas

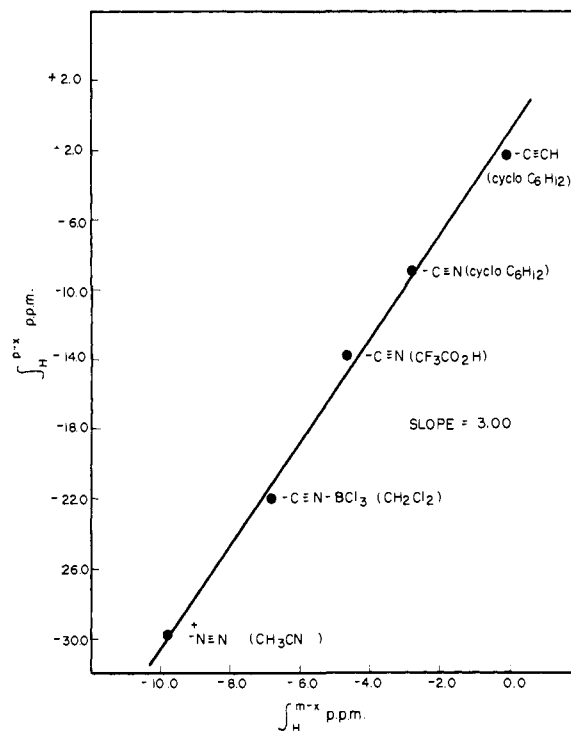


Fig. 4.—Linear \int_H^{p-X} vs. \int_H^{m-X} relationship for "triple bond" substituents; solvent indicated.

the first three series of linear $\int_H^{p-X} - \int_H^{m-X}$ (or $\sigma_R - \sigma_I$) relationships do involve substituents with a common first atom, this last series illustrates the fact that this feature is not a necessary condition for such a relationship. (The fact that the NO substituent fits the line for COX substituents is a further illustration.) It is of further interest to note in Fig. 3 that the substituents OC_6H_5 , OCOCH_3 , NHCOCO_3 , OCF_3 , CH_3 , $\text{CH}=\text{CH}_2$, SCH_3 , Br , and H , for example, do not qualify for this linear relationship.

The substituents which do qualify for the linear $\sigma_R - \sigma_I$ relationship include only relatively simple structures in which the first atom of the substituent is from the first row of the periodic table (thus excluding, for example Cl , Br , I , SH , and SCH_3). Further, this first atom bears at least one unshared electron pair (thus excluding, for example, H , CH_3 , and $\text{CH}=\text{CH}_2$) in simple π ($p-p$) conjugation with the benzene ring. This interaction must also be essentially unfettered by further conjugative interactions with the groups bonded to this atom (*i.e.*, the other atoms of groups attached to the first atom are essentially active only by their inductive effect, thus excluding, for example, the substituents OC_6H_5 , OCOCH_3 , NHCOCO_3 , and OCF_3). Quite plainly the substituents which do qualify are those for which the united atom approximation of the substituent in π ($p-p$) conjugation with the ring is most appropriate.

It has been previously demonstrated that the π -electron shielding effect for this simple class of p -substituent is directly related for corresponding X and COX substituents.^{5b} This relationship is anticipated by HMO theory using the united atom model^{5b} (the relationship shows the same structural restrictions given above, which is more restrictive than $\int_H^{p-X} - \int_H^{m-X}$ relationship for COX given in Fig. 2). Employing a similar model, Ehrenson³¹ has shown the HMO π -electron energy changes which are presumably involved in the resonance effects of these substituents in σ^u chemical reactivities are directly related to the effective coul-

(31) S. Ehrenson, unpublished results referred to in ref. 7c.

omb integral of the united atom substituent. It seems abundantly clear for this very special class of substituent that both the inductive and resonance effect parameters σ_1 and σ_R^0 are directly controlled by the effective nuclear charge of the united atom-like substituent. Because of the importance and apparently well defined character of this class of substituent, we propose for them the designation UAFPD (united atom-like first row pair donor) substituents.

The ensuing linearity between σ_1 and σ_R^0 ($\sigma_R^0 = 0.40\sigma_1 - 0.54$) for the UAFPD substituents has important consequences. Consider the very general system X-A-Y, whose appropriate chemical or physical property, P , is measured at Y (X is the UAFPD substituent, A is an intervening molecular cavity, of essentially fixed structure, and Y is some functionality). To the approximation that inductive and resonance effects originating at the X-A bond and transmitted inductively at the A-Y bond can be given by the relationship³²

$$P = \sigma_1 \rho_1 + \sigma_R \rho_R$$

(where ρ_1 and ρ_R are series constants which are dependent upon A and conditions of solvent and temperature and which measure the relative effectiveness of propagation of the inductive and resonance effects of X, respectively, and σ_1 and σ_R^0 are the substituent parameters for X), the property P becomes a function of a single substituent parameter, *i.e.*

$$\text{(for UAFPD substituents)} P = C_1 \sigma_1 + C_2 \quad (3)$$

where C_1 and C_2 are constants.

Equation 3 has previously been demonstrated^{7c,33} for saturated A systems, in which case it is not limited to only the UAFPD substituents. Table VIII lists some typical reactivities (also $\int_{H^{p-X}}$ and $\int_{H^{m-X}}$ values) illustrating the applicability of eq. 3 to systems in which A is unsaturated. The listed reactions are designated by the numbering system employed previously by Taft and Lewis.³⁴ Although eq. 3 is of limited utility (for A unsaturated) because of the relatively few available UAFPD substituents, it is clear from Table VIII that when it is applicable the relationship holds with very high precision (higher, for example, than the Hammett equation, in the original or modified forms). The precision of eq. 3 is all the more remarkable when it is recognized that although the Hammett equation is also a single substituent parameter equation, different values of the substituent parameter are required for the *m*- and *p*-position of benzene. The substituent parameter in eq. 3 depends only upon the character of the substituent and is apparently independent of position of substitution, or of the nature of the molecular cavity A (with the limitation noted below).

Equation 3 can apparently be used as a moderately critical diagnostic tool for detection of the effects of direct conjugative interaction between X and Y (A permitting). Plots of $\log(k/k_0)$ vs. σ_1 for the UAFPD substituents are distinctly nonlinear curves (*i.e.*, $\log(k/k_0)$ is a nonlinear function of σ_1) for the following reactivities (which in each instance include data for N, O, and F substituents); for example: for *p*-substituents, A-1, A-14, A-15, A-16, A-19, D-1, D-10, E-3; for *m*-substituents,³⁴ E-3; for the 7-position, the ionization constants of quinolines,³⁵ and the rates of methoxy-dechlorination of 4-chloroquinolines³⁶; for the 2-position, the rates of sodium borohydride reduction of fluor-

enone.³⁷ For each of these reaction series, direct interaction valence bond forms (between X and Y) can be written and effects on the observed reactivities due to this charge delocalization interaction are anticipated from the nature of the reactivities involved.

Although the number of UAFPD substituents is quite limited, several additional substituents which are presumably of this class could conceivably be investigated under especially favorable circumstances, including $-\text{CH}_2$, $-\text{NH}$, NHOCH_3 , $\text{N}(\text{CH}_3)\text{F}$, OCl , etc.

Figure 3 (or 1 and 2) is unique in regard to the structural distinctions which it makes. The familiar inductive order of charge withdrawal $\text{O}^- < \text{H}$, $\text{N}(\text{CH}_3)_2 < \text{SCH}_3 < \text{OCH}_3 < \text{Br} < \text{F}$ is clearly demonstrated by the $\int_{H^{m-X}}$ values (for the latter four substituents $\int_{H^{m-X}}$ is substantially negative while corresponding $\int_{H^{p-X}}$ values are substantially positive.). Yet, in the linear $\int_{H^{p-X}} - \int_{H^{m-X}}$ relationships it is quite clear that it is the H atom, the conventional standard substituent, which occupies an especially unique position. Perhaps no previous measurements of substituent effects have so clearly placed the hydrogen substituent in a position appropriate to its truly unique structure.

Figure 4 illustrates a linear $\int_{H^{p-X}} - \int_{H^{m-X}}$ relationship for "triple bond" substituents. Again it is clear that the linear relationship is not limited to substituents with a common first atom.

It is not possible at present to specify the detailed structural features which give rise to linear $\sigma_R - \sigma_I$ relationships. Clearly, the nuclear charge of the first atom of the substituent can be varied without destruction of these relationships. It appears that a nearly fixed hybridization state of the first atom of the substituent is a necessary (but not a sufficient) condition. In addition, there must be a fixed number of delocalized electrons and atomic positions within the substituent. If this former criterion is correct, it would mean a nearly common hybridization state for the UAFPD substituents. It should be noted in this connection that data for the NH_2 substituent have not been included (to prevent crowding) in Fig. 3. The data for this substituent including the unpublished results of Mr. M. G. Schwartz for the aniline complexed with dimethylacetamide in 1% CCl_4 solution define a line of essentially parallel slope to that shown in Fig. 3 but apparently displaced by a small amount (1.8 p.p.m.) to the left. This displacement is unexplained, although conceivably it could represent the effect of some small difference in the necessary conditions given above.

As a further criterion of the fundamental character of all five of the linear $\int_{H^{p-X}} - \int_{H^{m-X}}$ relationships illustrated in Fig. 2-4, it is significant that essentially the same slope, 2.70-3.33 (with a mean value of 3.0), is obtained.

The nearly identical slopes may be used as an argument that the ΔE "excitation energy" parameter^{5a} must be approximately constant for most *m*- and *p*-substituted fluorobenzenes. For example, if ΔE were constant for only a given family of closely related substituents in either the *m*- or *p*-position, then linear $\int_{H^{p-X}} - \int_{H^{m-X}}$ relationships of essentially the same slope would not result (as actually observed) among families of substituents of widely different structure, but rather lines of variable slope would be observed. It is, of course, conceivable that deviations from the linear $\int_{H^{p-X}} - \int_{H^{m-X}}$ relationships may arise from variable ΔE , but in view of the nature of structures which do and do not follow the linear relationships this does not appear to be generally the case. The matter, however, does need further theoretical analysis.

(32) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(33) (a) J. D. Roberts and W. T. Moreland, Jr., *ibid.*, **75**, 2167 (1953); (b) S. Siegel and J. M. Komarmy, *ibid.*, **82**, 4547 (1960); (c) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961).

(34) R. W. Taft, I. R. Fox, and I. C. Lewis, *ibid.*, **83**, 3349 (1961).

(35) S. B. Knight, R. H. Wallick, and J. Bowen, *ibid.*, **76**, 3780 (1954); S. B. Knight, R. H. Wallick, and C. Balch, *ibid.*, **77**, 2577 (1955).

(36) E. Baciocchi, G. Illuminati, and G. Marino, *ibid.*, **80**, 2270 (1958).

(37) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962).

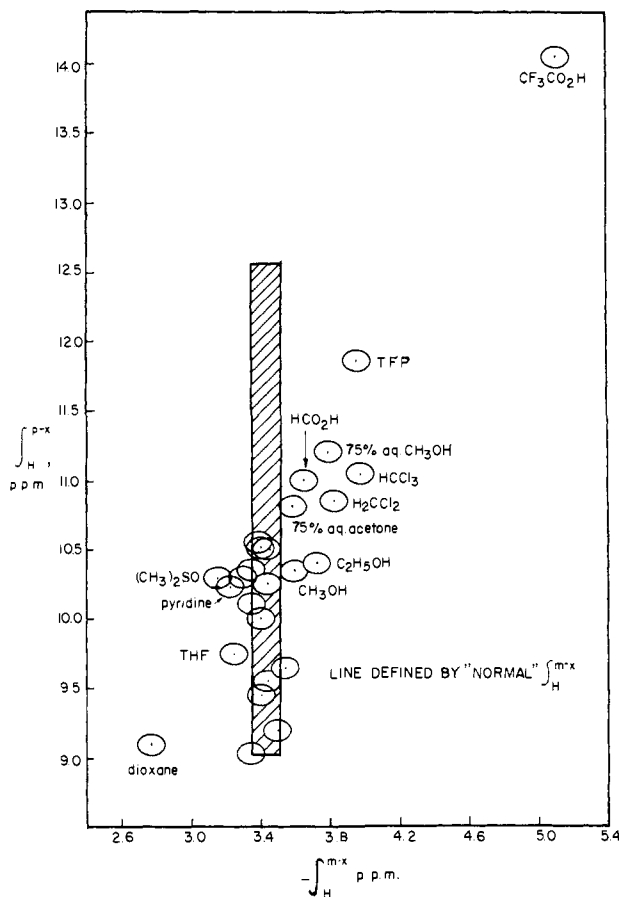


Fig. 5.—Solvent effects on shielding parameters for *m*- and *p*-nitrofluorobenzene.

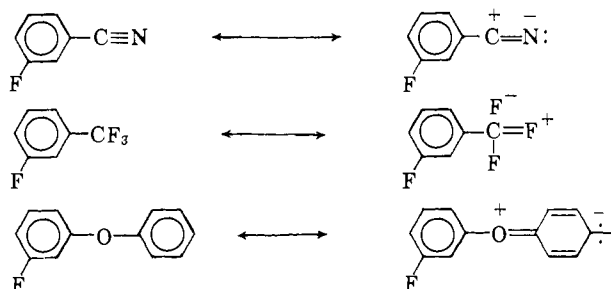
For the CH_2X substituents, the implied linear $\sigma_{\text{R}}^0 - \sigma_{\text{I}}$ relationship leading to the applicability of eq. 3 has been critically tested by Exner.³⁸ The ionization constants for an extensive series of XCH_2 -- CO_2H acids were shown to follow eq. 3.

Our solvent effect studies provide additional evidence that linear $\int_{\text{H}}^{\text{p-X}} - \int_{\text{H}}^{\text{m-X}}$ relationships are not general. Figure 5 gives a plot of $\int_{\text{H}}^{\text{p-X}} - \int_{\text{H}}^{\text{m-X}}$ vs. $\int_{\text{H}}^{\text{m-X}}$ in a wide variety of solvents. Similar results have been obtained with most +R substituents. The unlabeled points, which define a vertical line (a trivial $\int_{\text{H}}^{\text{p-X}} - \int_{\text{H}}^{\text{m-X}}$ relationship) to the precision (essentially the experimental error) indicated by the line breadth shown, correspond to nonprotonic solvents of varying polarity (with increasing polarity $\int_{\text{H}}^{\text{p-X}}$ decreases but $\int_{\text{H}}^{\text{m-X}}$ is unaffected). It will be recognized that all of the labeled solvents which lie to the right of this line are protonic solvents which hydrogen bond with the nitro group.⁶ For these, a very crude linear $\int_{\text{H}}^{\text{p-X}} - \int_{\text{H}}^{\text{m-X}}$ trend does occur. The solvents dioxane, tetrahydrofuran, pyridine, and dimethyl sulfoxide, which lie to the left of the line, are presumably complexed by Lewis acid bonding⁶ to the nitro group.

Qualitative Interpretation of Solvent Effects.—The results of the present and the previous study of solvent effects⁶ can apparently be interpreted conceptually in terms of the solvent susceptibility of the contribution of various (physically insignificant) valence bond structures to the ground (hybrid) electronic state. The very slight (if any) effect of solvent polarity (excluding effects of hydrogen bonding and Lewis acid bonding)

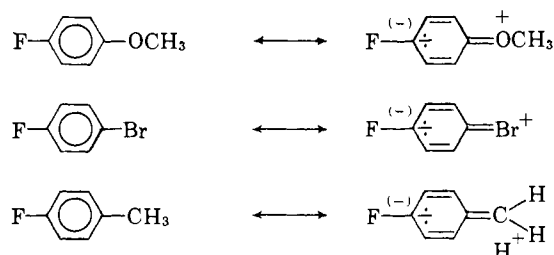
(38) O. Exner and J. Jones, *Collection Czechoslov. Chem. Commun.*, **27**, 2296 (1962).

on the intramolecular shielding effect of most *m*-substituents indicates that there is little or no practical change with solvent polarity in the contribution to the ground electronic state of the right hand ionic valence bond structure such as



Solvent variation from hydrocarbons to N-methylformamide, encompassing a twofold variation in the bulk dielectric constant of the solvent, is accompanied by no practical change in intramolecular shielding of fluorine.⁶ Comparison of the shielding parameters for various *m*-substituents, as well as other properties such as dipole moments and chemical reactivities, leaves no doubt that the ionic structures do make important contributions to the ground electronic state. The contribution simply shows no practical solvent dependence at room temperature.

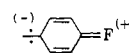
Similarly, the results for -R *p*-substituted fluorobenzenes (excluding again specific solvent-substituent hydrogen and Lewis acid bonding interactions) indicate that with similar gross changes in solvent polarity there is at room temperature little practical change in the contribution to the normal state of the right hand ionic valence bond structures, such as



This conclusion follows from the fact that only relatively small changes in the intramolecular shieldings of -R *p*-substituents with substantial changes in solvent polarity are observed (the effects in general are only slightly beyond the experimental error³⁹). Again, this result cannot be attributed to the fact that the ionic structures make no measurable contributions to the ground electronic states. Comparison of the shielding parameters for various *p*-substituted fluorobenzenes (Table VI) leaves no doubt that the substantial variations in shielding observed can be interpreted in terms of small but measurable contributions to the ground electronic state from the dipolar forms.⁵

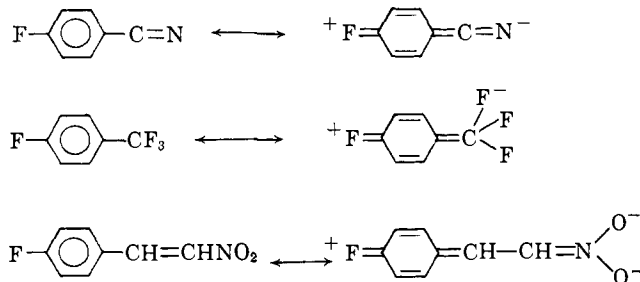
With the sole exception of the *p*- $\text{Si}(\text{CH}_3)_3$ substituent, all of the various +R (electron acceptor) *p*-substituted fluorobenzenes investigated have shielding parameters which are increasingly shifted to lower field strengths with increasing solvent polarity. The present study offers a rigorous confirmation of the early communica-

(39) The small decreases observed in $\int_{\text{H}}^{\text{p-F}}$ (and other) values between hydrocarbon and highly polar solvents (*cf.* Table I) apparently are to be attributed largely to a small increase in polar solvents in the contribution of resonance forms; *e.g.*



of the unsubstituted fluoro benzene reference.

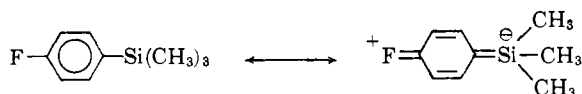
tion of this result.⁴⁰ The measurable variation with solvent of the contribution to the normal state of valence bond structures such as the following is indicated. Further, the magnitude of this effect is such as to indicate in general quite practical consequences.



This interpretation is made more certain when it is borne in mind that the shielding parameters for the *m*-isomers (for which such structures cannot be written) are generally solvent insensitive (*cf.* Fig. 5). The ability of solvent to support the charge-separated direct-interaction paraquinoid forms will be considered in greater detail in a subsequent publication.

The only structural feature in common among the +R *p*-substituents for which shielding parameters are substantially shifted to lower field strengths by polar solvents is the fact that the dipolar direct-interaction resonance forms involve atomic centers of opposite formal charge *both* of which are on the periphery of the molecule. The dipolar resonance forms for -R *p*-substituents do not meet this requirement. Instead, in these structures at least one of the centers of formal charge is buried within the molecular cavity (*i.e.*, is not on an end atom of the molecule). A similar situation prevails for the dipolar forms given above for *m*-substituted fluorobenzenes (with perhaps the special exception of the hyperconjugative form for the CF₃ substituent).

It is apparently not a sufficient condition for the observation of such solvent effects that the substituent be a +R *p*-substituent. The point is well illustrated by the *p*-Si(CH₃)₃ substituent. The shielding parameter for this substituent is negative (that for the *m*-isomer is positive) thus classifying it (consistent with reactivity and dipole moment results)⁴¹ as a +R substituent. There is, however, no measurable solvent dependence of the shielding parameter for this substituent (*cf.* Table IV). Inspection of the dipolar direct-interaction resonance form readily confirms the fact that this form does not meet our necessary condition since the formal charge on the Si atom is buried within the molecular cavity.



These results on the relative susceptibilities of the various vapor base forms to polar solvent effects are qualitatively consistent with the Kirkwood model of electrostatic solvation energy of a dipole in a spherical cavity.⁴² The contribution of a dipolar valence bond form to the resonance hybrid will be enhanced by the lowering of its energy state (relative to that of the other contributing structures) through solvation. The solvation energy given by the Kirkwood model is

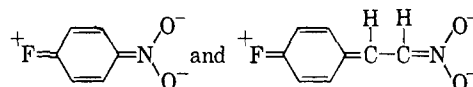
$$\frac{1}{2} \left(\frac{D_i - D}{2D + D_i} \right) \left(\frac{\mu^2}{b^3} \right)$$

(40) R. W. Taft, R. E. Glick, I. C. Lewis, I. Fox, and S. Ehrenson, *J. Am. Chem. Soc.*, **82**, 756 (1960).

(41) *Cf.* R. W. Taft, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 596.

(42) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

where D_i is the internal dielectric constant of the cavity, D is the dielectric constant of the bulk solvent, μ is the dipole moment, and b is the radius of the molecular cavity. For a given increase in dielectric constant of the medium, the greater the distance of separation of the charges in the dipolar resonance form relative to the diameter of the molecular cavity, the greater will be the expected lowering of the energy state of this form and therefore the greater the unshielding of the fluorine atom. This corresponds qualitatively to the observations. Also, if essentially identical dipolar centers are kept at the end atoms and the diameter of the molecular cavity is increased (μ^2/b^3 decreases), the solvation energy of the dipolar form will be decreased. Essentially such a situation prevails in the comparison of the direct interaction forms of *p*-fluoronitrobenzene and *p*-fluorophenyl-*trans*-nitroethylene



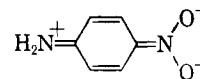
In accord with the expected weaker solvation of the latter form, solvent effects on $\int H^{p-X}$ are appreciably smaller (on either an absolute or a percentage basis) for the latter than the former compound (*cf.* Table II).

Although the Kirkwood model accounts qualitatively for the observed solvent effects, the shielding parameter data indicate that the bulk dielectric constant is an inadequate *quantitative* measure of the ability of the solvent to support charge separations in solute molecules. A more detailed consideration of this subject will be presented in a subsequent paper.

Applications to Reactivities.—The important consequences on reactivities,^{7c,43} barriers to rotation,^{44a} and infrared frequencies^{44b} of increasing the contribution of dipolar direct interaction forms to the ground electronic state in solvents of increasing polarity have been previously pointed out. We wish to note a further example of a reactivity effect, which apparently has not been previously recognized. The effects of select *m*-substituents on the rate of reaction of aniline with benzoyl chloride in benzene,⁴⁵ 25°, follows the Hammett equation ($\rho = -3.20$) with excellent precision:

<i>m</i> -Substituent	$\log(k/k_0)_{\text{obsd}}$	σ_p
CH ₃	+0.27	+0.22
Cl	-1.23	-1.18
NO ₂	-2.20	-2.24

However, for the *p*-NO₂ substituent $\sigma_p = -4.06$, whereas $\log(k/k_0)_{\text{obsd}} = -3.25$. The discrepancy can be attributed to the fact that $\sigma = +1.27$ for the *p*-NO₂ is applicable only to aqueous solutions.⁴⁶ In benzene solution the direct interaction form



contributes less to the normal state of the reactant molecule than in aqueous solutions. This leads therefore to a reduced σ -value of +1.02, applicable in this solvent. The resulting solvent effect on reactivity amounts to the appreciable decrease in free energy of

(43) (a) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559 (1953); (b) M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **60**, 569 (1958).

(44) (a) J. C. Woodrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962); (b) L. J. Bellamy, *et al.*, *Trans. Faraday Soc.*, 1677 (1959).

(45) F. J. Stubbs and C. Hinshelwood, *J. Chem. Soc.*, 571 (1949).

(46) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

activation (in benzene relative to water) of approximately 1.0 kcal./mole.

Equation 1 may be rearranged to the following form, which may be utilized to obtain the effective $\bar{\sigma}_R$ values for the +R substituents in various solvents from the shielding parameters listed in Tables II, IV, and V of this paper and Tables II-IX of ref. 6.

$$\bar{\sigma}_R = (-0.0339)(\int_{H^p-X} - \int_{H^m-X}) \quad (4)$$

The solvent effects on $\bar{\sigma}_R$ values obtained from eq. 4 may be taken to indicate the expected magnitudes of solvent effects on the reactivity effects of these sub-

stituents, but the precise quantitative applicability of these substituent parameters is questionable.

In a subsequent paper linear relationships generated by plots of \int_{H^p-X} vs. \int_{H^m-X} for pairs of +R substituents (from the data of Tables II and IV) are considered in detail. The effect of solvent on the contribution of dipolar direct interaction forms is used as a model to obtain a generalized scale of solvent polarity; *i.e.*, \int_{H^p-X} values for +R substituents are utilized as measures of the ability of solvent to support charge separation in simple solute molecules. Applications to the effect of solvent on the rates of ion-forming reactions are made.

[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIF.]

The Reaction of Alkanes with Phosphorus Trichloride and Oxygen¹

BY FRANK R. MAYO, LOIS J. DURHAM, AND KYLE S. GRIGGS

RECEIVED OCTOBER 9, 1962

The reaction of phosphorus trichloride and oxygen with alkanes to give alkylphosphonyl chlorides is a free radical chain reaction with chlorine atoms as one chain carrier. The mechanism of chain propagation has been deduced by studies of products of the reaction of cyclohexene and one with styrene are also reported. These studies have shown that phosphorus trichloride is 0.36 times as reactive as cyclohexane toward chlorine atoms, that phosphorus trichloride is half as reactive as oxygen toward cyclohexyl radicals, that $C_6H_{11}PCL_2O$ radicals decompose into $C_6H_{11}POCl_2$ and Cl 3.6 times as often as they decompose into $POCl_2$ and C_6H_{11} , and that cyclohexylphosphonyl chloride is one-third as reactive as cyclohexane toward chlorine atoms and in chlorophosphonation. At relatively high ratios of oxygen to phosphorus trichloride, cyclohexyl phosphodichloridate (found as cyclohexene in our analyses) is produced at the expense of cyclohexylphosphonyl chloride. Reactions of phosphorus trichloride toward free radicals and of other alkanes in chlorophosphonation are discussed.

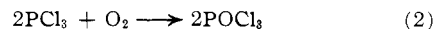
1. Introduction

A remarkable reaction of saturated hydrocarbons with phosphorus trichloride and oxygen was discovered independently some time ago by three groups of workers: by Clayton and Jensen^{2a} in this country; by Soborovsky, Zinovyev, and Englin in the Soviet Union^{3a}; and by Graf in Germany.⁴ The latter was apparently the first to discover the reaction,⁴ but the last to publish on it. Soborovsky and co-workers have extended the reaction to alkyl halides,^{1,3b} ethers,^{3b} and cyanides,^{3k} to unsaturated compounds,^{3a,c,f,g,i,j} and to chlorophosphines.^{3d,e,h,m} The work on alkanes and phosphorus trichloride has recently been reviewed and extended by Isbell and Wadsworth.⁵

To a first approximation, saturated hydrocarbons give alkylphosphonyl chlorides by the over-all reaction^{3a,4}



This reaction is accompanied by a competing oxidation of phosphorus trichloride



Since both reactions occur readily in the absence of light and added catalysts,^{2a,5} and since both are susceptible to similar inhibitors,^{2b,5} they must be closely related.⁵ Reaction 1 has been pushed to about 60% of the theoretical yield with an excess either of phosphorus trichloride^{3a,4} or of hydrocarbon.^{2a,5} Cyclohexane has been most studied because it is one of the few alkanes to give a single, crystalline, monosubstitution product.^{2a,b,4}

The most striking feature of the *chlorophosphonation* reaction (eq. 1) is its high rate at low temperatures. Isbell and Wadsworth⁵ report that the reaction is "virtually instantaneous, the speed being governed only by the rate at which oxygen could be caused to dissolve in the reaction mixture." They found no significant change in products over the range -100° to $+100^\circ$ (vapor phase), and certainly none between -40° and $+70^\circ$. Ethane reacted to -80° without any induction period,⁴ and again the rate depended on the oxygen supply. One object of the present work is to determine the mechanism by which alkanes are so easily involved in reaction 1. Another object is to determine why, in view of the competition between reactions 1 and 2, yields of phosphonyl chloride are insensitive to alkane-phosphorus trichloride feed ratios.⁵

The principal conclusions of this paper are summarized in sections 3, 4, 1, and 5.

2. Experimental and Details

2.1. Materials.—Phosphorus trichloride was reagent quality, obtained in 1-lb. bottles from J. T. Baker and from Mallinckrodt. Each lot of material was distilled in an atmosphere of nitrogen and stored in a glass-stoppered bottle. The material was occasionally redistilled to remove traces of hydrolysis and oxidation products. Cyclohexane, >99 mole %, was obtained from Phillips Chemical Co. Each lot was distilled before use. Melting points were -6.5° . Among the many lots of these reagents which we employed, there was no indication that their sources or histories were important.

(6) F. R. Mayo, E. Acton, and K. Egger, unpublished work.

(1) Preliminary accounts of this work were presented to the Division of Organic Chemistry at the 134th and 140th National Meetings of the American Chemical Society, Chicago, Ill., September 8, 1958, Abstracts, p. 6P, and September 5, 1961, Abstracts, p. 41Q, and to the Division of Petroleum Chemistry at the 137th National Meeting, Cleveland, Ohio, April 14, 1960, Abstracts, p. 17Q.

(2) (a) J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948); (b) W. L. Jensen, Ph.D. Dissertation, Stanford University, 1948; (c) W. L. Jensen and C. R. Noller, *J. Am. Chem. Soc.*, **71**, 2384 (1949).

(3) (a) L. Z. Soborovsky, Yu. M. Zinovyev, and M. A. Englin, *Dokl. Akad. Nauk SSSR*, **67**, 293 (1949); (b) *ibid.*, **73**, 333 (1950); (c) Yu. M. Zinovyev, L. I. Muler, and L. Z. Soborovsky, *J. Gen. Chem. USSR*, **24**, 391 (1954); (d) L. Z. Soborovsky and Yu. M. Zinovyev, *ibid.*, **24**, 527 (1954); (e) Yu. M. Zinovyev and L. Z. Soborovsky, *ibid.*, **26**, 3375 (1956); (f) L. Z. Soborovsky, Yu. M. Zinovyev, and L. I. Muler, *Chem. Abstr.*, **51**, 1825 (1957); (g) *ibid.*, **54**, 20841 (1960); (h) Yu. M. Zinovyev, V. N. Kulakova, and L. Z. Soborovsky, *J. Gen. Chem., USSR*, **28**, 1600 (1958); (i) Yu. M. Zinovyev and L. Z. Soborovsky, *Chem. Abstr.*, **54**, 340 (1960); (j) L. Z. Soborovsky, Yu. M. Zinovyev, and T. G. Spiridonova, *ibid.*, **54**, 1270 (1960); (k) R. I. Bystrova, Yu. M. Zinovyev, and L. Z. Soborovsky, *ibid.*, **54**, 8604 (1960); (l) Yu. M. Zinovyev and L. Z. Soborovsky, *ibid.*, **54**, 10836 (1960); (m) *ibid.*, **55**, 1415 (1961).

(4) R. Graf, *Chem. Ber.*, **85**, 9 (1952).

(5) A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.*, **78**, 6042 (1956).