

glycol column resolved carbon tetrachloride, *t*-butyl alcohol and *t*-butyl acrylate from a mixture of acrolein and acetone. The acrolein-acetone pair was resolved on β,β' -oxydipropionitrile. The blip corresponding to *t*-butyl acrylate was trapped ten times from the triethylene glycol column. Its infrared spectrum was identical with the spectrum of authentic gaseous *t*-butyl acrylate.^{2b}

Acknowledgment.—The authors are indebted to Mr. F. L. Rodgers for patient assistance with the experimentation.

(28) This substance was prepared in poor yield from acrylyl chloride and *t*-butyl alcohol in the presence of Na_2CO_3 ; b.p. 36° (80 mm.), n_D^{20} 1.4102.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

The Effect of Polar Substituents on the Acid-catalyzed Hydrolysis of Organosilicon Hydrides

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The first-order rate constants for the acid-catalyzed hydrolysis of sixteen fluoroalkyl-, ω -cyanoalkyl- and *n*-alkylsilicon hydrides have been determined using aqueous ethanolic hydrochloric acid (1.43 *N*, 95 vol.-% ethanol) at 34.8° . The first-order rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative π -bonding.

Introduction

The polar effect of substituted alkyl groups on the alkali-catalyzed hydrolysis of triorganosilicon hydrides has been reported previously.¹ An excellent correlation of the second-order rate constants was obtained using the Taft equation² for triorganosilicon hydrides containing fluoroalkyl, ω -cyanoalkyl and *n*-alkyl groups.^{1a}

Other linear relationships involving the inductive effect of substituent groups in silicon hydrides have been reported: (a) Hammett's σ -values and modified σ -values *vs.* $\log k$ for the base-catalyzed hydrolysis of triorganosilanes,³ (b) ν SiH (cm.⁻¹) *vs.* empirically determined *E*-values and Taft's σ^* -values,⁴ (c) ν SiH (cm.⁻¹) *vs.* τ (p.p.m.) for a proton attached to silicon,⁵ (d) ν SiH (cm.⁻¹) *vs.* $\log K$ (25°) for the hydrolysis of triorganochlorosilanes.⁶

The acid-catalyzed solvolysis of organosilicon hydrides has been studied by Taketa, *et al.*,⁷ and Baines and Eaborn.⁸ In this paper a study is reported on the effect of polar substituents on the acid-catalyzed hydrolysis of mono-, di- and triorganosilicon hydrides. The first-order rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative π -bonding.

Experimental

Starting Materials.—Trichlorosilane, 3,3,3-trifluoropropyltrichlorosilane,⁹ β -trichlorosilylpropionitrile,^{10,11} β -methyl-

dichlorosilylpropionitrile,^{10,11} chloromethyl dimethylchlorosilane¹² and 3-bromo-1,1,1-trifluoropropane¹³ were available in research quantities. They were fractionally distilled before being used.

Preparation of 3,3,3-Trifluoropropyl-*n*-butyldiethoxysilane and Bis-(3,3,3-trifluoropropyl)-diethoxysilane.—Absolute ethanol (194 g., 4.2 moles) was added to 3,3,3-trifluoropropyltrichlorosilane (463 g., 2.0 moles) over a period of 0.5 hour. Throughout the addition the reaction temperature was maintained between 50 – 60° . After addition was complete, the mixture was heated to 120° and allowed to cool to room temperature. The reaction mixture was then stirred for 16 hours with a slow nitrogen sweep to remove any remaining hydrogen chloride. The material in the flask, 3,3,3-trifluoropropylethoxychlorosilanes (493 g.), analyzed for one chlorine per silicon, a 98% yield.

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{ClF}_3\text{O}_2\text{Si}$: Cl, 14.15. Found: Cl, 14.4.

n-Butylmagnesium bromide, dissolved in ether (550 ml.), prepared from *n*-butyl bromide (116 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the above prepared 3,3,3-trifluoropropylethoxychlorosilanes (213 g., 0.85 mole), dissolved in ether (200 ml.), over a period of 0.5 hour. Throughout the addition the reaction mixture was cooled in an ice-bath. After refluxing for 16 hours, the reaction mixture was poured onto a mixture of cracked ice and sodium bicarbonate (212 g., 2.0 moles). The ether layer was washed and dried over anhydrous calcium sulfate. After removing the ether, fractional distillation gave: 3,3,3-trifluoropropyltriethoxysilane¹⁴ (33.5 g., 0.13 mole), b.p. 82° (30 mm.), n_D^{20} 1.3650, a 15% yield; 3,3,3-trifluoropropyl-*n*-butyldiethoxysilane (146 g., 0.54 mole), b.p. 105° (30 mm.), n_D^{20} 1.3858, d_4^{25} 0.991, a 63% yield.

Anal. Calcd. for $\text{C}_{11}\text{H}_{23}\text{F}_3\text{O}_2\text{Si}$: C, 48.5; H, 8.51; F, 20.9. Found: C, 49.0; H, 8.65; F, 21.1.

3,3,3-Trifluoropropyl-*n*-butylethoxysilane (5.3 g., 0.019 mole), b.p. 126.5° (30 mm.), n_D^{20} 1.4073, d_4^{25} 0.944, a 2% yield.

Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{F}_3\text{OSi}$: C, 54.9; H, 9.57; F, 20.0. Found: C, 55.8; H, 10.1; F, 19.9.

Using the same procedure described above, 3,3,3-trifluoropropylmagnesium bromide, dissolved in ether (500 ml.), prepared from 3-bromo-1,1,1-trifluoropropane (150 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the 3,3,3-trifluoropropylethoxychlorosilanes (213 g., 0.85 mole). Fractional distillation gave: 3,3,3-trifluoropropyltriethoxysilane¹⁴ (15.4 g., 0.06 mole), b.p.

(10) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(11) G. D. Cooper and M. Prober, *ibid.*, **25**, 240 (1960).

(12) R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945).

(13) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *ibid.*, **77**, 2783 (1955).

(14) O. W. Steward and O. R. Pierce, *J. Org. Chem.*, **26**, 2943 (1961).

(1) (a) O. W. Steward and O. R. Pierce, *J. Am. Chem. Soc.*, **83**, 1916 (1961); (b) **81**, 1983 (1959).

(2) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–675.

(3) (a) H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 3404 (1951); (b) G. Schott and C. Harzdorf, *Z. anorg. u. allgem. Chem.*, **306**, 180 (1960).

(4) (a) A. L. Smith and N. C. Angelotti, *Spectrochim. Acta*, **15**, 412 (1959); (b) H. W. Thompson, *ibid.*, **16**, 238 (1960).

(5) D. E. Webster, *J. Chem. Soc.*, 5132 (1960).

(6) J. F. Hyde, P. L. Brown and A. L. Smith, *J. Am. Chem. Soc.*, **82**, 5854 (1960).

(7) A. Taketa, M. Kumada and K. Tarama, *Bull. Inst. Chem. Research, Kyoto Univ.*, **31**, 260 (1953).

(8) J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 1436 (1956).

(9) P. Tarrant, G. W. Dyckes, R. Dunmire and G. B. Butler, *J. Am. Chem. Soc.*, **79**, 6536 (1957).

82° (30 mm.), n_D^{25} 1.3651, a 7% yield; bis-(3,3,3-trifluoropropyl)-diethoxysilane (120 g., 0.385 mole), b.p. 98° (30 mm.), n_D^{25} 1.3578, d_4^{25} 1.153, a 45% yield.

Anal. Calcd. for $C_{10}H_{18}F_6O_2Si$: C, 38.5; H, 6.13; F, 36.5. Found: C, 38.4; H, 5.86; F, 36.9.

Preparation of the Organosilicon Hydrides.—The organosilicon hydrides were prepared by the methods given below. Their physical properties and analyses are given in Table II.

a. Tris-(3,3,3-trifluoropropyl)-silane was prepared by the addition of three equivalents of 3,3,3-trifluoropropylmagnesium bromide to trichlorosilane in ether solvent using the procedure of Price.¹⁵ The reaction mixture was refluxed for 16 hours.

b. Chloromethyltrimethylsilane¹⁶ was prepared by the reduction of chloromethyltrimethylchlorosilane with lithium aluminum hydride in ether using the procedure of West.¹⁷

c. β -Methylsilylpropionitrile was prepared by a reverse lithium aluminum hydride reduction of β -methylchlorosilylpropionitrile using the procedure of Steward, *et al.*^{1,18}

d. 3,3,3-Trifluoropropyl-*n*-butylsilane was prepared from 3,3,3-trifluoropropyl-*n*-butyldiethoxysilane as follows: In a 1-liter, 3-necked flask equipped with a stirrer, condenser and dropping funnel, were placed lithium aluminum hydride (9.5 g., 0.25 mole) and ether (400 ml.). The system was vented to the atmosphere *via* a Dry Ice-cooled trap and drying tube. The system was purged with nitrogen, and 3,3,3-trifluoropropyl-*n*-butyldiethoxysilane (109 g., 0.40 mole), dissolved in ether (100 ml.), was added over a period of 1 hour. The reaction mixture was refluxed for 16 hours under a nitrogen atmosphere, and then poured onto a mixture of cracked ice and concentrated hydrochloric acid (200 ml.). The ether layer was dried over anhydrous calcium sulfate, the ether removed by distillation, and the higher-boiling material fractionally distilled. 3,3,3-Trifluoropropyl-*n*-butylsilane (39.4 g., 0.214 mole), was obtained in a 53% yield.

e. Bis-(3,3,3-trifluoropropyl)-silane was prepared by the reduction of bis-(3,3,3-trifluoropropyl)-diethoxysilane with lithium aluminum hydride using the above procedure.

Apparatus and Kinetic Procedure.—For the rate studies, the following apparatus and procedure were used. A 250-ml., three-necked flask was equipped with a Lew magnetic stirrer,¹⁹ a self-sealing rubber stopper, and a glass outlet tube leading to a mercury-filled, 100-cc. gas buret and manometer. The bottom of the gas buret was connected to a balance tube. A stopcock located at the bottom of the buret allowed the system to be adjusted to atmospheric pressure by removing mercury. The flask was maintained at 34.8° by a constant temperature bath. Throughout a single run, the bath temperature was constant within 0.1°; the temperature varied 0.3° from run to run.

Aqueous ethanolic hydrochloric acid (1.43 *N*, 95 vol.-% ethanol)^{19a} was freshly prepared from a stock solution for each run since the acid solution was not stable on standing over a period of days. The standardized acid solution (50 ml.) was placed in the 250-ml. flask, and the system was allowed to reach thermal equilibrium. The silane sample was injected into the reaction flask from a weighed hypodermic syringe. Readings were taken at various times by adjusting the system to atmospheric pressure. The error in the buret reading was approximately 0.1 cc., and the error in timing was about two seconds. During a run, the room temperature was constant within one degree.

The volume of hydrogen evolved was taken as a measure of the amount of silane which had reacted. The rate constants were determined from the slope of the line obtained by plotting $\log [V_\infty - V_t/V_\infty \times 10^2]$ vs. t , where V_∞ = volume of gas evolved at infinite time and V_t = volume of gas evolved at time t . In most cases, the rates of reaction were too slow to determine V_∞ -values experimentally. V_∞ -values were calculated from the weight of the silane and were corrected for the vapor pressure of the solvent. With the two most reactive diorganosilicon hydrides, the

V_∞ -values determined experimentally were within 2% of the calculated values. Straight lines were obtained from 40 to >80% reaction. The less reactive silanes showed the largest deviations, probably resulting from small losses of hydrogen due to diffusion. The data obtained for *n*-propyldimethylsilane tended to give concave-upward curves, probably a result of the slow reaction rate and the volatility of the silane.

Results

The kinetic data for the acid-catalyzed hydrolysis of the organosilicon hydrides are reported in Table I. The physical properties, analytical data and yields of the organosilicon hydrides not reported in the previous papers^{1a,b} are given in Table II.

The first-order rate constants were determined using 1.43 *N* aqueous ethanolic hydrochloric acid (95 vol.-% ethanol) at 34.8° so they could be compared with the data of Baines and Eaborn.⁸ The rate constant obtained for triethylsilane is within one standard deviation of the value reported by Baines and Eaborn.⁸

The rate constants for the reaction of the first and second hydrogens of the diorganosilicon hydrides can be determined from a single run as reported by Baines and Eaborn.⁸ In each of the compounds studied, the rate constant for the reaction of the first hydrogen is from 10 to 15 times greater than the rate constant for the reaction of the second hydrogen. The nature of the species from which the second hydrogen is removed is not known.

The rate constants for the reaction of the first and second hydrogens of β -silylpropionitrile are approximately equivalent. A first-order plot which assumes equal rates for the reaction of the first and second hydrogens (72% reaction) is slightly concave-upward, indicating the rate constant for the reaction of the second hydrogen might be slightly greater. The rate of reaction of the first and second hydrogens is approximately 72 times faster than the initial rate of reaction for the third hydrogen. The reaction rate of the third hydrogen decreases rapidly with time, probably a result of formation of a three-dimensional polymer.

With cyclohexylsilane, Baines and Eaborn⁸ observed a constant rate of hydrogen evolution during the first 20% of the reaction and suggested that all of the hydrogens have similar reactivities. They observed the initial rate was proportional to the concentration of the cyclohexylsilane. However, from the rate data for β -silylpropionitrile, it would seem likely that the rate constant for removal of the third hydrogen of cyclohexylsilane would also be much smaller than the rate constant for removal of the first and second hydrogens.

The rate constants were correlated using the Taft equation²

$$\log k_1 = (\Sigma\sigma^*)\rho^* + C$$

Three linear correlations were obtained (Fig. 1): the triorganosilicon hydrides (13 points), the diorganosilicon hydrides (rate constants for the first hydrogen, 4 points), and the monoorganosilicon hydrides (rate constants for the first hydrogen, 2 points). The correlation data are given in Table III.

(15) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).

(16) L. H. Sommer, W. P. Barie, Jr., and D. R. Weyenberg, *ibid.*, **81**, 251 (1959).

(17) R. West, *ibid.*, **76**, 6012 (1954).

(18) O. W. Steward, Ph.D. Thesis, The Pennsylvania State University, 1957, pp. 132-134; *Dissertation Abstr.*, **17**, 2827 (1957).

(19) Scientific Glass Apparatus Co., Bloomfield, N. J.

(19a) The 95 vol.-% ethanol (sp. gr. $\frac{25}{25} = 0.806$) was prepared by mixing 50 ml. of water with 950 ml. of absolute ethanol.

TABLE I
RATE DATA FOR THE ACID-CATALYZED HYDROLYSIS OF ORGANOSILICON HYDRIDES AT 34.8° IN 95 VOL.-% ETHANOL
(1.43 N IN HYDROGEN CHLORIDE)

No.	R	RR'R''SiH ^a R'	R''	No. of runs	k ₁ × 10 ⁴ , min. ^{-1b}	Relative rate	Σσ* ^c
1	CH ₃ CH ₂	CH ₃ CH ₂	CH ₃ CH ₂	3	1.16 ± 0.04 1.19 ^d	1.0	-0.30
2	CH ₃ CH ₂ CH ₂	CH ₃	CH ₃	4	1.99 ± 0.08	1.7	-0.115
3	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂	CH ₃	3	1.45 ± 0.02	1.25	-.23
4	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂		0.745 ^d	0.63	-.345
5	(CH ₃) ₂ CH	(CH ₃) ₂ CH	(CH ₃) ₂ CH		.07 ^d	.06	-.57
6	CH ₃ CH ₂ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂		.70 ^d	.59	-.39
7	(CH ₃) ₂ CHCH ₂	(CH ₃) ₂ CHCH ₂	(CH ₃) ₂ CHCH ₂		.20 ^d	.17	-.375
8	CF ₃ CH ₂ CH ₂	CH ₃	CH ₃	3	3.14 ± 0.07	2.7	.32
9	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CH ₃	3	5.01 ± .26	4.4	.64
10	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	3	9.04 ± .39	7.8	.96
11	CF ₃ CH ₂ CH ₂ CH ₂	CH ₃	CH ₃	3	2.98 ± .04	2.6	.12
12	CF ₃ CH ₂ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂ CH ₂	CH ₃	3	3.11 ± .16	2.7	.24
13	CF ₃ CH ₂ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂ CH ₂	3	3.29 ± .12	2.8	.36
14	N≡CCH ₂ CH ₂	CH ₃	CH ₃	3	4.96 ± .10	4.3	.46 ^e
15	N≡CCH ₂ CH ₂ CH ₂	CH ₃	CH ₃	3	3.26 ± .09	2.8	.17 ^e
16	ClCH ₂	CH ₃	CH ₃	3	2.08 ± .09	1.8	1.05
17	C ₆ H ₅	CH ₃	CH ₃		2.13 ^d	1.8	0.60
18	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅		0.40 ^d	0.3	1.80
19	CH ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂	H		26.2 ^d (1.43) ^{d,f}	22 (1.2)	0.26
20	CF ₃ CH ₂ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂	H	3	54.8 ± 0.6	47	0.68
				3	(3.6 ± 0.2) ^f	(3.1)	
21	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	H	5	111 ± 2	96	1.13
				3	(11.2 ± 0.3) ^f	(9.7)	
22	N≡CCH ₂ CH ₂	CH ₃	H	5	106 ± 5	91	0.95 ^e
				3	(9.5 ± 0.4) ^f	(8.2)	
23	Cyclo-C ₆ H ₁₁	H	H		143 ^d	120	0.83
24	N≡CCH ₂ CH ₂	H	H	3	394 ± 12 ^g	340	1.44 ^e
				5	(5.5 ± 0.3) ^h	(4.7)	

^a Concentration of silane, 0.0250–0.0918 mole l.⁻¹. ^b Standard deviation. ^c Ref. 2, p. 619. ^d Rate constants reported by J. E. Baines and C. Eaborn using aqueous ethanolic hydrochloric acid (1.43 N, 95 vol.-% ethanol) at 34.9°, ref. 8. ^e The σ*-values for the ω-cyanoalkyl groups were calculated by dividing the σ*-value for the cyanomethyl group by the factor of 2.8 for each intervening methylene group, ref. 2, p. 592. ^f Rate of hydrolysis of the second Si-H bond. ^g Rate of hydrolysis of the first and second Si-H bonds. ^h Initial rate of hydrolysis of the third Si-H bond.

For the Hammett equation, Jaffé²⁰ considers correlations which have a correlation coefficient of >0.95 as satisfactory. Both of the correlation coefficients in Table III fall in this range.

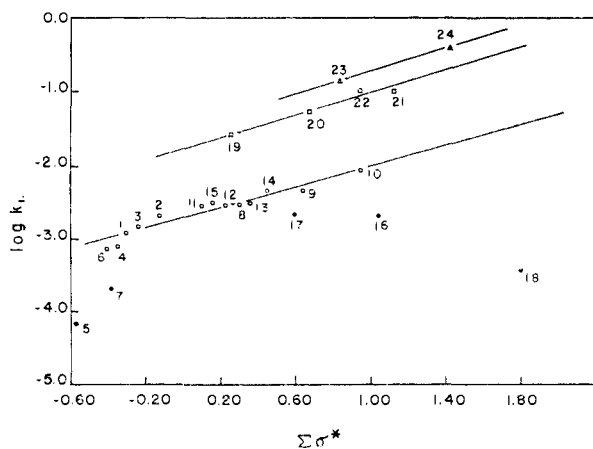


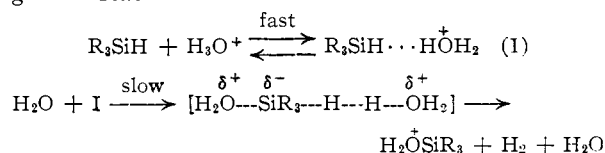
Fig. 1.—Plot of log k_1 vs. $\Sigma\sigma^*$ for the acid-catalyzed hydrolysis of the organosilicon hydrides using aqueous ethanolic hydrochloric acid (1.43 N, 95 vol.-% ethanol) at 34.8°: O, R₃SiH; □, R₂SiH₂; △, RSiH₃; ●, R₃SiH not correlated.

(20) H. H. Jaffé, *Chem. Revs.*, **53**, 236 (1953).

Discussion

Polar Effects.—The effect of polar substituents on the rate of the acid-catalyzed hydrolysis of organosilicon hydrides is quite small ($\rho^* = 0.77$), the reaction being facilitated slightly by electron withdrawal from the silicon atom. Baines and Eaborn⁸ noted the same effect qualitatively from the acid-catalyzed hydrolysis of *p*-substituted phenyldimethylsilanes. This effect is in contrast to the very large increase in rate by electron withdrawal from silicon in the alkali-catalyzed hydrolysis ($\rho^* = 4.27$).^{1a}

The reaction mechanism proposed by Eaborn²¹ involving electrophilic attack by a hydronium ion and nucleophilic attack by a water molecule in the rate-determining step seems reasonable based on the above polar effects since the silicon atom must be more negative in the transition state than the ground state.



(21) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 204–206.

TABLE II
ORGANOSILICON HYDRIDES^a

No. ^b	Yield, %	B.p. ^c		n_D^{25}	d_4^{25}	Mole-% purity ^c	Silane Hydrogen, %		Carbon, %		Hydrogen, %		Fluorine, %	
		°C.	Mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
10	52	89.5	15	1.3528	1.297	>99	0.315	0.32	34.0	34.0	4.1	4.3	53.4	53.4
16 ^d	56	81	741	1.4168	0.892	>99	0.93	0.91	33.2	33.5	8.35	8.4		
20	53	132	743	1.3782	0.941	>99	1.09	1.08	45.6	45.7	8.2	8.3	30.9	31.2
21	49	126	735	1.3423	1.180	>99	0.89	0.89	32.1	32.1			50.9	50.8
22	58	51	15	1.4267	0.841	>99	2.03	1.99	48.4	48.2	9.1	8.7		
24 ^e	41	38	15	1.4255	0.836	>99	3.55	3.55						

^a The organosilicon hydrides not reported in this table have been reported previously, ref. 1. ^b Table I. ^c Determined by vapor phase chromatography. ^d Ref. 16. ^e Ref. 14.

TABLE III
CORRELATION DATA

Correlation	ρ^*	$(\rho^*)^2$	a^b	s_0 (a)	$(\log k_1)$	\bar{r}^c
R ₃ SiH	0.77	0.06	-2.72	0.08	0.09	0.961
R ₂ SiH ₂	.77	0.09	-1.77	0.03	0.06	0.972
RSiH ₃	.72	..	-1.56

^a Standard error. ^b Intercept. ^c Correlation coefficient.

Steric Effects.—The points representing the mono-, di- and triorganosilicon hydrides fall on separate lines with the same slope (within one standard error), and the distance between these lines is smaller as the number of substituent groups on the silicon atom is decreased. All of the organosilicon hydrides included in the correlations have substituent groups which are not branched, except cyclohexylsilane. The above observations suggest that steric effects are important and the linear relationships represent organosilicon hydrides in which the steric effects of the groups around the silicon atom are very similar. The successful correlation of the second-order rate constants for the alkali-catalyzed hydrolysis of triorganosilicon hydrides with the Taft equation was ascribed to constant steric effects.^{1a}

In the correlation of the data for the triorganosilicon hydrides, the points representing the compounds with two methyl groups tend to lie above the regression line, and the points representing the compounds without methyl groups, below. The point representing the diorganosilicon hydride with one methyl group also lies above the regression line. These observations indicate that the methyl group has slightly smaller steric requirements than the larger groups. These differences in steric requirements are probably partly responsible for the observed scattering of the data.

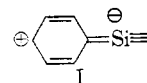
The low reactivity of triisopropylsilane and triisobutylsilane toward the acid-catalyzed hydrolysis of the Si-H bond is undoubtedly the result of increased steric effects due to branching in the attached groups.⁸ As expected, the point for triisopropylsilane shows the largest deviation from the regression line.

Cyclohexylsilane does not appear to show any greater steric effects than β -silylpropionitrile for removal of the first hydrogen. This would indicate that the rate of reaction of the first hydrogen in the monoorganosilicon hydrides is not very sensitive to branching in the organic group.

The points representing the compounds phenyldimethylsilane, triphenylsilane and chloromethyldimethylsilane all fall below the regression line

for the triorganosilicon hydrides. As expected, if steric effects were involved, the point for triphenylsilane shows the largest deviation. However, unusual steric effects would not be expected for chloromethyldimethylsilane. The deviation for chloromethyldimethylsilane is probably due to dative π -bonding which may also be responsible for the deviations of the phenyl-substituted silicon hydrides.

Dative π -Bonding.—There is substantial evidence for dative π -bonding between a silicon atom and an attached atom or group of atoms in which filled p-orbitals are available for bonding.²² Dipole moment²³ and nuclear magnetic resonance⁵ studies have indicated that contributions from structures such as I are important in the ground state of phenyl-substituted silicon compounds. If the



electron release from a phenyl group to silicon by dative π -bonding is important as evidence indicates, it would be in opposition to the electron-withdrawing effect, *i.e.*, $-I$ effect. The net result would be a decrease in the inductive effect of a phenyl group attached to silicon relative to carbon. Since the σ^* -values were determined for substituent groups on carbon, deviations from the Taft equation would be expected for phenylsilicon compounds.

From the above discussion, it would seem that the observed deviations of the phenyl-substituted silicon hydrides from the regression line for the triorganosilicon hydrides are probably partly a result of dative π -bonding, steric effects also being partly responsible.

Recently, Brook, *et al.*,²⁴ have proposed a direct interaction between the filled p-orbitals of an oxygen atom and the vacant d-orbitals of a silicon atom when the oxygen is separated from the silicon by one carbon atom, *e.g.*, α -silyl ketones and α -silylcarbinols. Frye, *et al.*,²⁵ have reported results which indicate that a transannular interaction between the filled p-orbitals of a nitrogen atom and the vacant d-orbitals of a silicon atom

(22) For general reviews on the subject see ref. 21, pp. 94-103, and F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

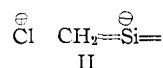
(23) H. Feiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.*, **75**, 2821 (1953).

(24) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz and C. M. Warner, *ibid.*, **82**, 5102 (1960).

(25) C. L. Frye, G. E. Vogel and J. A. Hall, *ibid.*, **83**, 996 (1961).

occurs when the spatial arrangement of the atoms are conducive to bonding.

The point representing chloromethyldimethylsilane falls a substantial distance below the regression line for the triorganosilicon hydrides. In this case, it seems unlikely that steric effects would be responsible. Direct interaction between the filled p-orbitals of the chlorine atom and the vacant d-orbitals of the silicon atom, analogous to the interaction proposed by Brook, *et al.*,²⁴ seems likely for chloromethylsilicon compounds. Resonance structures of the type II cannot be ruled out. Effects of this type would tend to reduce the in-



ductive effect of the chloromethyl group on a silicon atom relative to a chloromethyl group on a carbon atom and cause serious deviations from the Taft equation.

The above postulate for a chloromethyl group on silicon is supported by dipole moment studies. Freiser, *et al.*,²⁶ reported 0.25 D. for the (CH₃)₃-SiC_{aliph} bond moment in chloromethyldimethylsilane. Coleman and Freiser²⁷ reported 0.26 D. for the (CH₃)₃-SiC_{arom} bond moment in *p*-chlorophenyltrimethylsilane. Considerable dative π -bonding between the benzene ring and the silicon atom in *p*-chlorophenylsilicon compounds has been proposed to explain dipole moment data.²⁷ Since approximately the same bond moment for the (CH₃)₃-SiC group is observed in both compounds, it seems reasonable to assume that electron release from the chloromethyl group to the silicon atom is also occurring.

(26) H. Freiser, R. Charles, J. Speier and M. Eagle, *J. Am. Chem. Soc.*, **73**, 5229 (1951).

(27) A. Coleman and H. Freiser, *ibid.*, **83**, 4127 (1961).

Baney²⁸ has correlated the hydrogen-bonding acidity of various triorganosilanols with the Taft σ^* -values and observed that chloromethyldimethylsilanol and the phenyl-substituted silanols were less acidic than predicted by the σ^* -values for the chloromethyl and phenyl groups. In this study, steric effects of the organic groups bonded to silicon should be of minor importance.

Other atoms in addition to oxygen and chlorine which have filled p-orbitals available for bonding may also interact directly with the vacant d-orbitals of silicon when they are separated from the silicon by one carbon atom. The base strengths of ω -trimethylsilylalkylamines do not decrease regularly as the number of methylene groups between the silicon and nitrogen atoms is increased from one to three; trimethylsilylmethylamine is a slightly weaker base than β -trimethylsilylethylamine.²⁹ These observations are inconsistent with inductive effects. The small K_B -value for trimethylsilylmethylamine could be explained by partial bonding between the nitrogen and silicon atoms.

The proposed intramolecular rearrangement of a fluorine atom from carbon to silicon in the thermal decomposition of α -fluoroalkylsilicon compounds is in agreement with the above postulate.³⁰

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(28) R. H. Baney, private communication.

(29) L. H. Sommer and J. Rockett, *J. Am. Chem. Soc.*, **73**, 5130 (1951). The following values were reported for $K_B \times 10^4$ at 25°: trimethylsilylmethylamine, 9.1; β -trimethylsilylethylamine, 9.7; γ -trimethylsilylpropylamine, 5.6.

(30) R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 394 (1959).

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.]

Interannular Electronic Effects in Ferrocene: Kinetics of Reaction of Substituted Ferrocenic Acids with Diphenyldiazomethane

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The kinetics of the reaction of heteroannular substituted ferrocenic acids with diphenyldiazomethane in toluene were studied under second-order conditions at 30°. For the substituents H, CH₃CO-, C₂H₅-, C₆H₅CO- and C₆H₅CH₂-, the logarithms of the second-order rate constants were correlated with the corresponding acid constants and with Hammett *para* sigma constants. The rate of esterification of 1- α -hydroxybenzyl-1'-ferrocenic acid was much too fast for correlation with its acid constant. This can be ascribed to interannular hydrogen bonding between the α -hydroxybenzyl group and the carboxyl group in the acid.

Interannular transmission of electronic effects through the ferrocene nucleus has been demonstrated in the acid constants of heteroannular ferrocenic acids²⁻⁴ and in the shifts of the infrared

stretching frequencies of substituted ferrocenyl acids and esters.⁵ The acid constants and spectral shifts vary in the direction expected from the electronic effects of the substituent groups.

The reaction of carboxylic acids with diaryldiazomethanes has been thoroughly studied kineti-

(1) This work was taken from the Ph.D. dissertation of Robert Eisenenthal, submitted to the University of North Carolina, January, 1961.

(2) A. N. Nesmeyanov and O. A. Reutov, *Doklady Akad. Nauk, S.S.S.R.*, **115**, 518 (1957).

(3) A. N. Nesmeyanov and O. A. Reutov, *Izvest. Akad. Nauk, S.S.S.R.*, 926 (1959); *C. A.*, **54**, 191 (1953).

(4) W. F. Little and R. Eisenenthal, *J. Am. Chem. Soc.*, **82**, 1577 (1960); and *J. Org. Chem.*, **26**, 3609 (1961).

(5) L. A. Kazitsyna, B. V. Lokshin and A. N. Nesmeyanov, *Doklady Akad. Nauk, S.S.S.R.*, **127**, 333 (1959).