and the two-step mechanism in which one bond forms directly before the other.[33,34]

For the retrodiene decarboxylation of the maleic anhydride-α-pyrone adduct,[34] it has been shown that the decomposition is probably two step. For decomposition of the adduct of 2-methylfuran and maleic hydride, the reaction has been shown to be one step.[32] Both of these mechanisms are consistent with the proposal of Woodward that a broad spectrum of partial ionic intermediates may be realized between the extreme cases for pure cyclic reactions (little or no polarity in the reactants) and for reactions in which the reaction partners give rise to highly unsymmetrical polar transition states.

The Leffler-type plot of activation energies *vs.* the logs of the frequency factors as mentioned before did not include enough widely spaced points to show a clear-cut relationship. However, when such a relationship is assumed, the *o*- and *p*-nitro esters are far enough removed so that Leffler's treatment[17] would predict a different reaction mechanism for these two esters. It has been shown, however, that the extra resonance stabilization of the transition state can well account for the deviation without having to postulate a change in mechanism. The isokinetic temperature calculated from the slope is 262.2°. This is 86.6° higher than the 175.6° temperature used in the Hammett-type plots. It will be remembered that near or at the isokinetic temperature all the rate constants will tend to be the same and the variations in rate constants will be due to random deviations rather than to kinetically significant results.[35]

From Figure 3 it is clear that the *ortho*-substituted phenylpropiolic esters react at a much faster rate than would be predicted by the corresponding log K/K_0 values for the substituted phenylpropiolic acids. The extrapolation is not entirely valid because of the difference in solvent. Nevertheless, this *ortho* effect has been encountered previously by both Newman[10] and Roberts[11] in reactions catalyzed by bases and by acids, respectively.

That acceleration is observed for *ortho* substituents rules out large steric effects. Furthermore, this is reinforced by the fact that correlation of the rates for the *ortho*-substituted esters is possible on the same plot as that used for *meta*- and *para*-substituted esters when σ^- values are used. We do not clearly understand the *ortho* effects; however, the fact that the σ^- values obtained from the ionization of phenols do correlate our data recognizes Robert's admonition that the correlation of the effect of an *ortho* substituent must be related to the position of the reacting site in the side chain.

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(33) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961), and references cited therein.

(34) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1925, 1933 (1965).

(35) However, see R. C. Petersen, *J. Org. Chem.*, **29**, 3133 (1964).

Organic Reactions and the Critical Energy Density of the Solvent. The Solubility Parameter, δ, as a New Solvent Parameter

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It is suggested that Hildebrand's solubility parameter, δ, provides a measure of the effect of solvent on organic reactions. Quantitative comparisons are made between the use of intrinsic properties of the solvent, such as δ or the dielectric constant, and parameters, such as Y, Ω, Z, S, and E_T, attributable to the interaction of a reference solute with the solvent.

A number of solvent parameters have been introduced recently with the intent of providing an empirical measure of the effect on an organic reaction of changing solvent.[2] Of those available for application at 25°, Y,[3a] Ω,[3b] Z,[3c] S,[3d] and E_T,[3e] S is most inclusive, covering values for 47 pure solvents and the gaseous state. These empirically determined constants relate, each in a different way, to the interaction of a reference solute with an array of solvents. Attempts to demonstrate a relationship between these constants and intrinsic properties of each solvent, such as functions of the dielectric constant like $1/D$,[3a] $(D - 1)/(2D + 1)$,[3a-c,e] or $\rho(D - 1)/M(2D + 1)$,[3b] with D the dielectric constant, ρ the density, and M the molecular weight of the solvent, have been only moderately successful. For example, eq 1 was found to reproduce the data for

$$\Omega_{20} = 0.0251\left[\frac{D-1}{2D+1}\,\frac{10^3\rho}{M}\right] + 0.472 \qquad (1)$$

eight solvents with a correlation coefficient of $r = 0.957$ if the hydroxylic solvents ethanol, methanol, and acetic acid were excluded.[3b]

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[2] For a recent review, see C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

[3] (a) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956); (b) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962); (c) E. M. Kosower, *ibid.*, **80**, 3253 (1958); (d) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960); (e) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).

In addition to the dielectric constant, which will influence the rate of a reaction through its effect on the electrostatic energy of the reactants and the transition state, the energy necessary to form in the solvent a cavity which can accommodate the transition state must also be considered. This may be done by making use of the cohesive energy density of the solvent.[4] The cohesive energy density, a direct measure of the total molecular cohesion per cubic centimeter of liquid, is measured by the molal energy of vaporization to a gas at zero pressure, $-E$, per molal volume of liquid, V^l: $\delta^2 = -E/V^l$. The square root of the cohesive energy density is termed the solubility parameter, δ, because of its value in correlating and predicting solubility behavior of nonelectrolytes.[4] For solutes in regular solutions, ones in which selective chemical interactions between solute and solvent are absent, it has been shown[4] that with certain simplifying assumptions the logarithm of the activity coefficient of the solute, γ, is directly proportional to the square of the difference between the square roots of the cohesive energy densities of solute, δ, and solvent, δ_s, eq 2. V_1 is the molal volume of the solute and ϕ_s the

$$RT \ln \gamma = V_1 \phi_s^2 (\delta - \delta_s)^2 \tag{2}$$

volume fraction of solvent, which for dilute solutions is equal to unity. Since for reactions in solution $\ln k = \ln k_0 + \ln \gamma_1\gamma_2 \ldots \gamma_i/\gamma^*$ with k the observed rate constant, k_0 the rate constant in ideal solution, and $\gamma_1, \gamma_2 \ldots \gamma_i, \gamma^*$ the activity coefficients for the appropriate species, one may write eq 3 or 4. The assumption may

$$RT \ln \frac{k}{k_0} = V_1(\delta_1 - \delta_s)^2 + V_2(\delta_2 - \delta_s)^2 + \ldots V_i(\delta_i - \delta_s)^2 - V^*(\delta^* - \delta_s)^2 \tag{3}$$

$$RT \ln \frac{k}{k_0} = \delta_s^2(V_1 + V_2 + \ldots V_i - V^*) + (V_1\delta_1^2 + V_2\delta_2^2 + \ldots V_i\delta_i^2 - V^*\delta^{*2}) + 2\delta_s(V^*\delta^* - V_1\delta_1 - V_2\delta_2 - \ldots V_i\delta_i) \tag{4}$$

be made, with some degree of validity, that the volume of the transition state is approximately the sum of the volumes of the reactants,[5] these volumes necessarily including all solvent molecules which interact in any way with the solute or the transition state, so the first term on the right of eq 4 is essentially zero. A further, less-justifiable assumption, that the molal volumes and cohesive energy densities of the reactants and transition states are the same for a single reaction in all solvents under scrutiny, makes the second term on the right in eq 4 constant for all solvents. This leads to a linear relationship, eq 5, between $\ln k$ and δ_s, the solubility parameter of the solvent. Ideally,

$$RT \ln \frac{k}{k_0} = 2\delta_s(V^*\delta^* - V_1\delta_1 - V_2\delta_2 - \ldots V_i\delta_i) + (V_1\delta_1^2 + V_2\delta_2^2 + \ldots V_i\delta_i^2 - V^*\delta^{*2}) \tag{5}$$

a term should be included in eq 5 to accommodate dielectric constant effects, but here solvent effects will be treated as arising solely from the energy necessary for cavity formation. Furthermore, application of eq 5 to systems in which discrete chemical interaction, such as hydrogen bonding, between solute and solvent is significant is not justified except on a pragmatic basis.

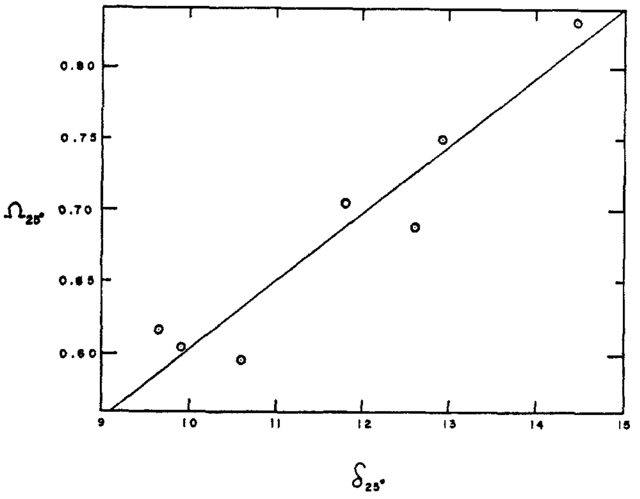

Figure 1.—The relationship between δ, Hildebrand's solubility parameter, and Ω.

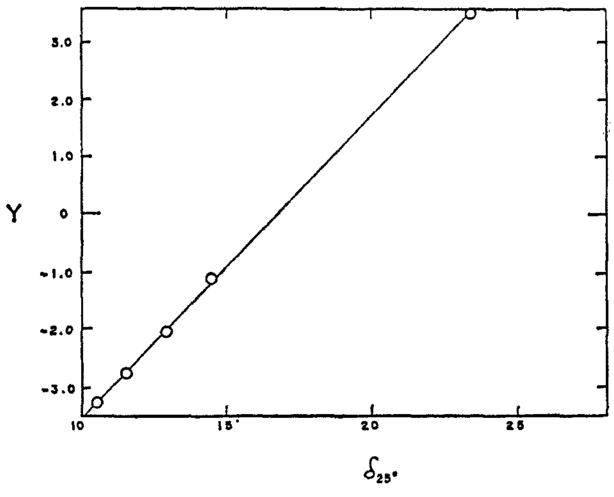

Figure 2.—The relationship between δ, Hildebrand's solubility parameter, and Y for pure solvents.

Values of δ have been determined for more than 150 solvents, many at more than one temperature.[7] A selected list of δ values, together with appropriate Y, Ω, Z, S, and E_T values, is given in Table I.

As mentioned previously, excluding hydroxylic solvents, eq 1 gave the relationship between Ω and the dielectric constant for eight solvents with a correlation coefficient of $r = 0.957$. δ values are available for only seven solvents for which Ω values have been determined, yet now including the solvents methanol and ethanol and excluding none for which data are available eq 6 relates δ and Ω with a correlation coefficient of $r = 0.952$ (Figure 1). Very striking is the

$$\Omega_{25} = 0.133 + 0.471\delta_{25} \tag{6}$$

relationship between Y and δ for which pairs of data are available for five pure solvents, water, and four alcohols (Figure 2). The regression line of eq 7 has a

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[4] J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Edgewood Cliffs, N. J., 1962, pp 88–103.

[5] ΔV^*, the volume of activation, ranges, for many organic reactions with some exceptions, within limits of about ± 10 cc mole^{-1}.[6]

[6] E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964).

[7] (a) Reference 4, pp 171–173; (b) G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958); (c) G. Allen, G. Gee, and G. J. Wilson, *Polymer*, **1**, 456 (1960); (d) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950, pp 435–439; (e) H. Burrell, *Interchem. Rev.*, **14**, 31 (1955).

TABLE I

SOLVENT PARAMETERS δ, Y, Ω, Z, AND S FOR PURE SOLVENTS AT 25°

Solvent	δ	Y^a	Ω^b	Z^c	S^d	$E_{T_{26}}{}^e$	$E_{T_{30}}$
Water	23.4^f	3.493		94.6	0.1540		63.1
Ethylene glycol	14.5^g			85.1	0.0679	51.1	56.3
Methanol	14.45^g	−1.090	0.830	83.6	0.0499	50.8	55.5
Ethanol	12.9^g	−2.033	0.749	79.6	0	46.9	51.9
Nitromethane	12.6^h		0.688		−0.134		46.3
1-Propanol	12.0^g			78.3	−0.0158	45.6	50.7
Acetonitrile	11.8^i		0.703	71.3	−0.1039	41.4	46.0
Methylene iodide	11.8^j				−0.043		
2-Propanol	11.5^f	−2.73		76.3	−0.0413	40.4	48.6
1-Butanol	10.7^g			77.7	−0.0240	45.0	50.2
Methylene bromide	10.7^g				−0.095		
Bromoform	10.6^i				−0.042		
Pyridine	10.6^i		0.595	64.0	−0.1970	37.3	40.2
t-Butyl alcohol	10.5^g	−3.26		71.3	−0.1047	37.4	43.9
Nitrobenzene	10.4^i				−0.218		42.0
Acetophenone	10.4^g						41.3
Carbon disulfide	10.0^j				−0.240		
1,2-Dichloroethane	9.91^i		0.604		−0.151		
Methyl iodide	$9.9^{g,j}$				−0.170		
Methylene chloride	9.88^i			64.2	−0.1890	37.3	41.1
Dioxane	9.73^i				−0.179	34.2	36.0
Acetone	9.66^g		0.616	65.7	−0.1748	37.9	42.2
Chlorobenzene	9.50^i				−0.182	35.0	37.5
Tetrahydrofuran	9.32^i					35.1	37.4
Tetrachloroethylene	9.3^j				−0.263		
Chloroform	9.24^i			63.2	−0.200	36.1	39.1
Benzene	9.15^i				−0.215	33.2	34.1
Ethyl acetate	9.04^i				−0.210	35.4	38.1
Toluene	8.91^i				−0.237	33.0	33.7
Mesitylene	8.8^j				−0.217		
Carbon tetrachloride	8.58^j				−0.245		
Cyclohexane	8.18^i				−0.324		
Ethyl ether	7.74^i				−0.277		
Heptane	7.42^i				−0.337		
Hexane	7.24^i				−0.337		
Isopropyl ether	7.14^k				−0.229		
2,2,4-Trimethylpentane	6.85^i			60.1			
Gas phase	0				−0.556		

[a] Reference 3a. [b] Corrected to 25° from data given in ref 3b. [c] Reference 3c. [d] Reference 3d. [e] Reference 3e. [f] Reference 7e. [g] Corrected to 25° from value in ref 7c. [h] Reference 7d. [i] Reference 7b. [j] Reference 7a. [k] At 20° from ref 7c.

$$Y = -8.75 + 0.524\delta_{25} \qquad (7)$$

correlation coefficient of $r = 0.9998$! The theoretical justification for the application of eq 5 to hydrogen-bonding solvents is tenuous at best, yet the fact that alcoholic solvents do fit this formulation implies that the factors which make δ values questionable for these solvents may largely cancel out in the interaction of reactants and transition states with these solvents.

A simple relationship between δ and E_T, Z, or S, which in part was derived from Z,[3d] should not be expected since the spectroscopically observed transitions used for determination of E_T and Z values would not, from consideration of the Franck–Condon principle, permit reorganization of the solvent to form a new cavity to accommodate the excited state. In agreement with this, only poor linearity results from a plot of $E_{T_{30}}$ *vs.* δ (21 common solvents), of Z *vs.* δ (13 common solvents), and of S *vs.* δ (33 solvents and the gaseous state). Water does not fit, and values for water have been excluded in determining eq 8–10, but an S value has been assigned to the gaseous state[3d] and this has been included (with $\delta_{\text{gas}} = 0$) in deriving eq 10. An $E_{T_{26}}$ value has not been reported for water,

$$E_{T_{30}} = 20.0 + 2.13_5\delta_{25} \quad (r = 0.920) \qquad (8)$$

$$Z_{25} = 32.3 + 3.60\delta_{25} \quad (r = 0.912) \qquad (9)$$

$$S = -0.624 + 0.046\delta_{25} \quad (r = 0.919) \qquad (10)$$

but the data from the 18 solvents for which both δ and $E_{T_{26}}$ are available give eq 11, which has a correlation coefficient of $r = 0.948$.

$$E_{T_{26}} = 5.98 + 3.13\delta_{25} \qquad (11)$$

A straight-line relationship has been demonstrated to exist between Z and Y[3c] and a curvilinear one between E_T and Y.[3e] Since an excellent straight-line relationship exists between Y and δ (eq 7), one would be led to expect good linear relationships between E_T or Z and δ. The correlation coefficients for eq 8 and 9 show the relatively poor straight-line relationships between these values and δ, and plots of the data do not demonstrate any simple curvilinear relationships. This seemingly paradoxical conclusion may be understood if one realizes that the Y, Z, and E_T values which are linearly related were all determined in mixed aqueous solvents, whereas the Y and δ values which are linearly related refer to pure solvents. From this it may be inferred that Y values (and correspondingly the Z and E_T values) as determined in binary solvent mixtures do not relate simply to any intrinsic property of the gross solvent mixture but must be influenced by the microscopic behavior of the two-component solvent mixture in the vicinity of the solute molecules resulting from localized heterogeneities, solvent sorting, and selective hydrogen bonding.

The Preparation and Reactions of Some Silanes Containing the Trifluorovinyl Group

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A series of silanes of the type $CF_2{=}CF(CH_2)_nSiX_3$ where $n = 0, 1, 2$, and 3 and X = alkyl, pentafluorophenyl, hydrogen, or negative groups has been prepared. Some of their chemical properties have been determined.

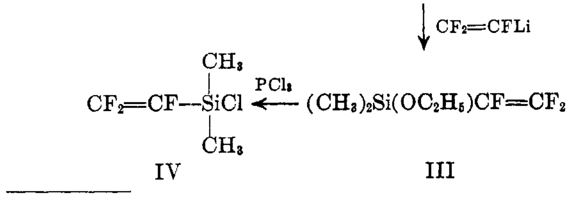
For a number of years interest in this laboratory has been focused on the preparation and reactions of fluoro olefins. As part of this continuing program it seemed desirable to synthesize and study the reactions of silanes containing the trifluorovinyl group separated from the silicon atom by varying numbers of methylene units.

The first trifluorovinylsilane was prepared by Knunyants,[1] who obtained $(CF_2{=}CF)_4Si$ as the reaction product of trifluorovinylmagnesium iodide and silicon tetrachloride. Seyferth[2,3] prepared $CF_2{=}CFSi(C_2H_5)_3$ by the Grignard method and $CF_2{=}CFSi(CH_3)_3$ by the reaction of trimethylchlorosilane with trifluorovinyllithium, which was prepared by treating trifluorovinyltin compounds with phenyllithium.

In our laboratory trifluorovinyltrimethylsilane (I) was prepared in 65% yield by a two-step reaction in which bromotrifluoroethylene reacted with methyllithium to give trifluorovinyllithium, which was allowed to react with trimethylchlorosilane.

An attempt was made to prepare trifluorovinyldimethylchlorosilane from the reaction of trifluorovinyllithium and dimethyldichlorosilane in a 1:1 molar ratio, but only bis(trifluorovinyl)dimethylsilane (II) was obtained. This experiment confirms the results of Knunyants in indicating the increased reactivity of the silicon–chlorine bond in silanes containing both this group and a trifluorovinyl group attached to silicon.

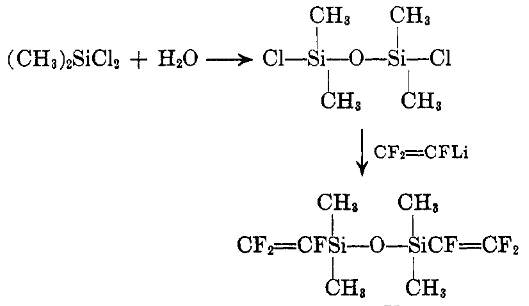
Alkoxysilanes undergo approximately the same reactions as chlorosilanes although they are somewhat less reactive; therefore, a synthetic procedure was devised which led to the formation of trifluorovinyldimethylchlorosilane by the scheme shown in eq 1. The compounds were identified by elemental analysis, MRD, and infrared spectra.



$$(CH_3)_2SiCl_2 + C_2H_5OH \xrightarrow{(C_5H_{11})_3N} (CH_3)_2SiCl(OC_2H_5) \xrightarrow{CF_2=CFLi} \underset{\text{III}}{(CH_3)_2Si(OC_2H_5)CF{=}CF_2} \xrightarrow{PCl_5} \underset{\text{IV}}{CF_2{=}CF{-}\overset{CH_3}{\underset{CH_3}{Si}}Cl} \quad (1)$$

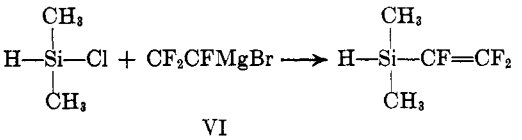
IV III

The *sym*-tetramethylbis(trifluorovinyl)disiloxane was prepared by the route shown in eq 2. Another compound of the series was prepared by allowing dimethylchlorosilane to react with trifluorovinylmagnesium bromide to give trifluorovinyldimethylsilane (eq 3).



$$(CH_3)_2SiCl_2 + H_2O \longrightarrow Cl{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}Cl \xrightarrow{CF_2=CFLi} CF_2{=}CF\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}CF{=}CF_2 \quad (2)$$

V



$$H{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}Cl + CF_2CFMgBr \longrightarrow H{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CF{=}CF_2 \quad (3)$$

VI

Elemental analysis and infrared data were consistent with this structure. When trifluorovinyllithium was used instead of the Grignard reagent, a brown tar was obtained.

Pentafluorophenylmagnesium bromide was prepared and allowed to react with $CF_2{=}CFSi(CH_3)_2Cl$ to give the trifluorovinylpentafluorophenyldimethylsilane (VII). It was of some interest to determine whether one or both fluorine-containing groups would be cleaved by reaction with base. Consequently, a sample of the product was treated with alcoholic potassium hydroxide and a gas, presumably $CHF{=}CF_2$, was obtained. Examination of the liquid products showed that pentafluorobenzene had also been formed, thus indicating the cleavage of both groups.

A different approach was used to prepare $(CH_3)_3SiCH_2CF{=}CF_2$ (VIII). Earlier Tarrant and Warner[4] had shown that Grignard reagents reacted with fluoro olefins to give alkylated or arylated fluoro olefins while Dixon[5] reported that lithium reagents behaved in the same manner. With tetrafluoroethylene, lithium rea-

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(1) R. N. Sterlin, I. L. Knunyants, L. N. Pinkince, and R. D. Yatsenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1492 (1959).

(2) D. Seyferth, K. A. Brandle, and G. Raab, *Angew. Chem.*, **72**, 77 (1960).

(3) D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962).

(4) P. Tarrant and D. A. Warner, *ibid.*, **76**, 1624 (1954).

(5) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).