be comparable to that observed in the case of the methoxyphenyltrimethylsilanes. To account for the large difference in cleavage of the amines, therefore, one has to assume that the equilibrium between the free *m*-amine and its salt lies largely in the direction of the salt form, while that of the *p*-amine lies principally in the direction of the free base.

In Fig. 1, we have attempted to correlate the ease of cleavage of the aryltrimethylsilanes in an *empirical* manner with a convenient standard of reference, namely, the substituent constants of Hammett.[16,17] Two important deductions can be made from this plot. First, it is obvious that the *m*-dimethylamino group is not in line with the trend of the other groups as has already been discussed. Secondly, if the slope of the line be continued to zero cleavage, it is seen to intersect the abscissa at a σ value slightly greater than +0.4. One might thus predict that it would be possible to carry out side-chain reactions involving electrophilic reagents or in acid media with a minimum of cleavage of the trimethylsilyl group if a substituent is present on the aromatic nucleus the σ-value of which is more positive than +0.4. Some substantiation of this prediction was obtained when we were able to prepare the acid chlorides of both the *m*- and *p*-trimethylsilylbenzoic acids using thionyl chloride with no observable cleavage of the trimethylsilyl group.[8,18,19,20]

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

(17) S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950), pointed out the interesting relationship between the acid cleavage of the aryl C–Si bond and the σ constants of substituents in a benzene ring.

(18) From *p*-trimethylsilylbenzoic acid was obtained *via* the acid chloride, a quantitative yield of *p*-trimethylsilylbenzamide, m.p. 155°. *Anal.* Calcd. for $C_{10}H_{15}NOSi$: N, 7.25; Si, 14.52. Found: N, 7.29; Si, 14.32. R. A. Benkeser and R. E. Robinson, unpublished results.

(19) Work now in progress in this Laboratory involving the successful Friedel–Crafts acylation of aromatic systems with silicon-containing aroyl halides offers further support of the stability of the aryl–C–Si linkage in these cases.

(20) K. C. Frisch and P. D. Schroff, THIS JOURNAL, **75**, 1249 (1953), prepared *p*-trimethylsilylbenzoyl chloride using thionyl chloride in the presence of pyridine as a hydrogen chloride acceptor because they feared that the trimethylsilyl group would be cleaved off; however, we have prepared both the *m*- and *p*-trimethylsilylbenzoyl chlorides in essentially quantitative yields by simply refluxing the silicon-containing acids in excess thionyl chloride for about a 90-minute period. *p*-Trimethylsilylbenzoyl chloride, b.p. 75–76° (1 mm.), $n^{20}D$ 1.5315. *Anal.* Calcd. for $C_{10}H_{15}ClOSi$: Si, 13.19. Found: Si, 13.09.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Alkaline Cleavage of Tetrasubstituted Silanes

BY HENRY GILMAN, A. G. BROOK AND LEWIS S. MILLER

RECEIVED APRIL 17, 1953

A qualitative study of the rate of cleavage of a number of tetrasubstituted silanes by potassium hydroxide in various solvents has been made. The results indicate a relationship between the ease of cleavage of a hydrocarbon radical from silicon and the electron-attracting properties of the radical. The results are consistent with a cleavage mechanism involving a pentacovalent silicon atom in the transition state. (Trichloromethyl)-triphenylsilane has been found to be cleaved by both *n*-butyl- and phenyllithium.

Many investigations have been reported whose ultimate purpose has been to establish a general series by which the relative ease of cleavage of an organic radical from a metal could be predicted. While silicon is not generally considered to be a metal, it has been found to behave in a manner qualitatively analogous to metals in cleavage reactions. Although a comprehensive survey of the cleavage reactions of organosilicon compounds has never been made, numerous isolated examples by both acidic and alkaline reagents have been reported, particularly of the various halogen- and oxygen-substituted alkylsilanes. The purpose of the present study was to extend the realm of these investigations to the field of alkaline cleavage of tetrasubstituted aryl- and mixed arylalkylsilanes, and to attempt to correlate the ease with which a hydrocarbon fragment, as a carbanion, was cleaved from silicon by the nucleophilic reagent with the acid strength of the parent hydrocarbon.

To summarize briefly the work previously reported, it has been found that silicon–halogen bonds are readily cleaved by nucleophilic reagents,[1,2] silicon–hydrogen,[2] silicon–oxygen,[1a,2] and silicon–silicon bonds[2] are less readily cleaved and silicon–carbon bonds are least readily cleaved by these reagents. In particular, it has been observed that alkylsilanes are quite stable in the presence of alkali,[3] but substitution by halogen leads to less stable compounds more easily cleaved by base, particularly when highly substituted.[4] Unsaturated alkylsilanes such as allyltrimethylsilane appear to be less stable than the saturated analogs.[5]

When unsaturation in the form of phenyl groups is introduced, the tetrasubstituted silanes become quite susceptible to cleavage by nucleophilic reagents. Thus benzyl-, benzhydryl- and triphenylmethyltrimethylsilane are smoothly cleaved by potassium or sodium amide, or by the alkali alkoxides,[6] and both trimethyl- and triethyl-1-indenylsilane are cleaved by alkali, although the related trimethyl-1-indanylsilane is quite stable.[7] The

(1) (a) F. S. Kipping, *Proc. Roy. Soc.* (*London*), **159**, 139 (1937); S. R. Robinson, *Sci. J. Roy. Coll. Sci.*, **15**, 24 (1945); (b) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

(2) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951.

(3) C. Pape, *Ann.*, **222**, 354 (1884).

(4) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945); R. H. Krieble and J. R. Elliott, *ibid.*, **68**, 2291 (1946); F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 485 (1946); E. Larsson and L. O. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947) [*C. A.*, **42**, 5416 (1948)].

(5) Yu. N. Vol'nov and A. Reutt, *J. Gen. Chem. U.S.S.R.*, **10**, 1600 (1940) [*C. A.*, **35**, 2853 (1941)]; L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948).

(6) C. R. Hauser and C. R. Hance, THIS JOURNAL, **73**, 5846 (1951); see also, L. S. Miller, Doctoral Dissertation, Iowa State College, 1950.

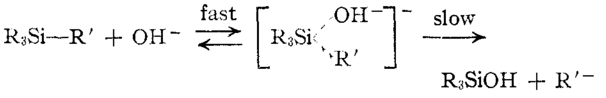
(7) L. H. Sommer and N. S. Marans, THIS JOURNAL, **73**, 5135 (1951).

p-sulfobenzyl group has also been found to be cleaved by base from trimethyl-(*p*-sulfobenzyl)-silane.[8]

Silanols and disiloxanes have been found to be cleaved by *n*-butyllithium,[9] but most unsubstituted tetraaryl- and arylalkylsilanes appear to be stable to this reagent, although triphenyl-(phenylethynyl)-silane is partially cleaved.[10]

In the present study a number of tetrasubstituted aryl- and arylalkylsilanes have been treated with potassium hydroxide in various solvents under a variety of conditions, and the extent of cleavage ascertained together in certain cases with the products formed by the cleavage.

The greater susceptibility of a silicon atom to nucleophilic attack as compared with carbon in the corresponding carbon compound can be attributed to several factors. The larger size and extra electron shell of the silicon atom screen its nuclear charge and make it more polarizable than carbon. An electron-attracting group attached to silicon is able to withdraw electrons from the valence shell, inducing a positive charge on the silicon atom, thus making nucleophilic attack on the silicon atom more favorable. Furthermore, silicon, in contrast to carbon is capable of expanding its valence shell to become penta- or hexacovalent.[11] Hence, a tetrasubstituted silane is able to form a more or less stable coördination complex with the nucleophilic reagent, and thus, any of the groups orginally bonded to the silicon atom have a relatively greater chance of being expelled in place of the attacking group than if no such complex was possible. Recent studies on the rate of hydrolysis of triphenylfluorosilane[1b] have indeed indicated that such a pentacovalent complex is an intermediate in this reaction, and a mechanism for the nucleophilic cleavage of silanes has similarly been proposed.[6,10]



$$R_3Si{-}R' + OH^- \underset{}{\overset{\text{fast}}{\rightleftarrows}} \left[R_3Si\begin{smallmatrix} OH \\ R' \end{smallmatrix} \right]^- \xrightarrow{\text{slow}} R_3SiOH + R'^-$$

$$R'^- + H_2O \xrightarrow{\text{fast}} R'H + OH^-$$

From such a mechanism it follows that electron-attracting substituents should increase the rate of the reaction, and further that the strongest electron-attracting substituent should be that which is cleaved by the hydrolysis.

The electron-attracting properties of a group may be evaluated by a study of the acidity of the corresponding hydrocarbon, the more electron-attracting group forming the stronger acid.

$$RH \rightleftarrows R^- + H^+$$

Such studies have been made[12] and a partial series, listed according to decreasing acid strength, was found as follows, compounds of approximately equal strength being inclosed in parentheses. (phenylacetylene, indene); fluorene; triphenylmethane; diphenylmethane; toluene; benzene; alkanes.

While in the present study the rate of cleavage of the silanes has not been evaluated quantitatively, a qualitative determination was possible by comparing the degree of cleavage of the silanes with standard alkaline reagents. From this determination it was possible to draw up a series listing the order of decreasing ease of cleavage of groups from the triphenylsilyl group, under the influence of potassium hydroxide. This series was: (phenylethynyl, 1-indenyl, 9-fluorenyl); benzhydryl; benzyl; (*m*-trifluoromethylphenyl, *p*-chlorophenyl); α-naphthyl; (phenyl, 2-phenylethyl, hexyl). It can be seen that the relative ease of cleavage of these groups from silicon closely parallels the relative acid strength of the corresponding hydrocarbons, and hence tends to substantiate the proposed mechanism which suggests that the stronger the electron-attracting properties of a group (the more acidic the corresponding hydrocarbon), the greater will be its tendency to be cleaved on nucleophilic displacement.

With regard to the actual basic reagents, it was found, as expected, that the most effective reagents for cleavage of carbon–silicon bonds were those which were homogeneous and were good solvents for silanes. It was highly desirable that the reagents contained a small amount of water, so that the polarity of the medium was relatively high. Reagent D, described in detail below, prepared from potassium hydroxide dissolved in a dioxane–ethanol–water mixture, possessed these properties. The dioxane was found to be an excellent solvent for silanes, and the alcohol served to keep the mixture homogeneous.

It has been found that (trichloromethyl)-triphenylsilane is cleaved in ether by both *n*-butyl- and phenyllithium, the products, isolated in low yields, being *n*-butyltriphenylsilane and tetraphenylsilane, respectively.

Experimental[13]

Potassium hydroxide in various solvent combinations was used for the cleavage of the tetrasubstituted silanes, the preparations of which have been reported in the literature. Typical procedures are described below for each reagent, and the conditions and results are listed in Table I, together with references to the preparations of the silanes.

Reagent A. The Cleavage of Trimethylphenylsilane.—Reagent A was prepared from equal volumes of acetone and 50% aqueous potassium hydroxide. In a 100-ml. flask fitted with a reflux condenser and a vapor trap cooled in a Dry Ice–acetone mixture were placed 5.0 g. (0.0333 mole) of trimethylphenylsilane, 10 ml. of acetone and 10 ml. of 50% aqueous potassium hydroxide solution. After refluxing 20 hours the mixture was cooled, poured onto cracked ice containing 3 ml. of concentrated hydrochloric acid, and extracted with ether. The ether layer was dried over sodium sulfate, and carefully fractionated through a column of 15 theoretical plates. No benzene was isolated, and 4.5 g. (90%) of starting material, m.p. 166–169°, was recovered.

Reagent B. The Cleavage of Triphenylbenzylsilane.—Reagent B was prepared from acetone and 20% aqueous potassium hydroxide, the ratio of the volumes used being given in parentheses in Table I. To 10 g. (0.0286 mole) of triphenylbenzylsilane were added 25 ml. of acetone and 10 ml. of aqueous potassium hydroxide. The mixture was refluxed 16.5 hours with the top of the condenser connected to a trap cooled in a Dry Ice–acetone mixture. No liquid

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(8) A. Bygden, *J. prakt. Chem.*, **96**, 86 (1917).

(9) H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 1689 (1950).

(10) H. Gilman and H. Hartzfeld, *ibid.*, **73**, 5878 (1951).

(11) N. V. Sidgwick, "The Electronic Theory of Valency," Clarendon Press, Oxford, 1927, pp. 159–160.

(12) J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(13) Melting points are corrected.

TABLE I

CLEAVAGE OF TETRASUBSTITUTED SILANES BY ALKALI

Silane	Silane, mole	Reagent	Vol. reagent, ml.	Time, hours	Temp., °C.	Recovered silane, %	Products[a]
Trimethylphenyl-	0.0333	A	20	20	Reflux	90	0
Triphenylbenzyl-[16]	.286	B(2.5:1)	35	16.5	Reflux	25	33% toluene[b]
Triphenylbenzyl-	.01	C	20	44	70	71	....
Triphenylbenzyl-	.004	C	20	16	70	70	....
Triphenylbenzyl-	.004	D	20	1	60	76	....
Trimethyl-9-fluorenyl-[17]	.42	B(2.5:1)	35	14	Reflux	0	100% fluorene
Trimethyl-9-fluorenyl-	.005	D	25	0.17	25	Trace	88% fluorene
Triphenyl-9-fluorenyl-[16]	.0024	B(3:1)	4	1	Reflux	10	64% hexaphenyldisiloxane
Triphenyl-9-fluorenyl-	.012	B(1.2:1)	22	16	Reflux	0	100% fluorene, 80% hexaphenyldisiloxane
Triphenyl-9-fluorenyl-	.001	D	5	0.167	25	21	....
1,4-Bis-(trimethylsilyl)-benzene	.0045	B(1:1)	10	16	Reflux	100	0
n-Hexyltriphenyl-[16]	.0055	B(1:1)	20	16	Reflux	100	0
Triphenyl-(2-phenylethyl)-[16]	.011	B(2:1)	15	16	Reflux	100	0
Triphenyl-(2-phenylethyl)-	.001	D	5	4	60	86	0
Triphenyl-(2-phenylethyl)-	.001	D	5	23	85	91	0
p-(Trimethylsilyl)-benzoic acid[18]	.0026	B(1:1)	10	16	Reflux	90	0
Phenyltrichloro-	.0643	B	40	24	Reflux	...	No benzene
Triphenylbenzhydryl-[16]	.004	C	20	16	70	20	42% hexaphenyldisiloxane
Triphenylbenzhydryl-	.004	D	20	1	70	0	....
Triphenylbenzhydryl-	.001	D	5	0.5	40	78	....
Triphenylbenzhydryl-	.001	D	5	0.5	60	9	....
Triphenyl-(phenylethynyl)-[16]	.004	C	20	0.5	70	0	Approx. 23% phenylacetylene[c]
Triphenyl-(phenylethynyl)-	.001	D	5	0.17	25	0	....
Triphenyl-(*m*-trifluoromethylphenyl)-[16]	.001	D	5	21	60	65	....
Triphenyl-(*m*-trifluoromethylphenyl)-	.004	D	20	24	85	0	51% benzotrifluoride[d] 48% triphenylsilanol
Triphenyl-(*m*-trifluoromethylphenyl)-	.01	D	50	5	60	85	10% triphenylsilanol
Triphenyl-(*p*-anisyl)-[19]	.001	D	5	24	60	97	0
Triphenyl-(*p*-chlorophenyl)-[21]	.01	D	50	24	85	26	Trace C_6H_5Cl
Triphenyl-(1-naphthyl)-[20]	.001	D	5	5	60	97	0
Triphenyl-(1-naphthyl)-	.001	D	5	24	85	85	Trace naphthalene[e]
Triphenyl-(1-indenyl)-[16]	.001	D	5	0.17	25	0	83% triphenylsilanol
(1,1)-Bis-(triphenylsilyl)-indene[16]	.0005	D	5	0.17	25	0	85% triphenylsilanol
Triphenyl-(trichloromethyl)-[21]	.001	D	5	0.17	25	0	87% triphenylsilanol
Hexaphenyldisiloxane	.001	D	5	0.17	25	93	....
Hexaphenyldisiloxane	.001	D	5	1	60	47	....
Hexaphenyldisiloxane	.001	D	5	5	60	Trace	95% triphenylsilanol
Triphenyl-	.00015	D	0.75	10 sec.	25	0	Theor. H_2 evolved in 10 sec.
Trimethyl-(triphenylmethyl)-[16]	.0015	A(1:1)	20	20	Reflux	0	95% triphenylmethane

[a] A dotted line in this column indicates no attempt was made to isolate any products. [b] Identified by conversion to 2,4 dinitrotoluene, m.p. 70°. [c] Identified by b.p. 140–142° and odor. [d] Identified by b.p. 100–102° and refractive index $n^{18.6}D$ 1.4155. [e] Identified by mixed melting point.

collected in the trap. A considerable amount of white solid precipitated from the reaction mixture during the heating period and on cooling the flask. The product was filtered and washed successively with methanol, water and methanol, leaving 3.7 g. of solid, m.p. 222°, which was shown to be hexaphenyldisiloxane by mixed melting point. The filtrate was acidified with 200 ml. of dilute (1:20) hydrochloric acid, precipitating a solid melting from 80–87°. To separate the starting material from triphenylsilanol, this solid was refluxed for 30 minutes with 98% formic acid, which has been found to convert triphenylsilanol to hexaphenyldisiloxane,[14] and then diluted with water. Extraction of the solid residue with three small portions of acetone left an additional 1.5 g. of hexaphenyldisiloxane, m.p. 220–223°. Removal of the acetone from the three extracts gave 2.5 g. of starting material, m.p. 90–95°, which when crystallized from ethyl acetate melted at 96–97° (mixed melting point undepressed). From the residue obtained by hydrolysis of the original reaction mixture was isolated about 1 ml. (33%) of toluene, identified by conversion to 2,4-dinitrotoluene, m.p. 70°.

Reagents C and D. Cleavage of Triphenylbenzylsilane.—Potassium hydroxide (1.12 g.) was dissolved in 3.6 ml. of water, 50 ml. of anhydrous ethanol and 200 ml. of sodium-dried redistilled dioxane. This mixture (reagent C) was found by titration to be 0.101 *M* in potassium hydroxide and 1.12 *M* in water (Karl Fischer titration).[15] Reagent D was similarly prepared from 20 g. of potassium hydroxide,

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[14] H. W. Melvin, unpublished work in this Laboratory.

[15] H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

[16] H. Gilman, A. G. Brook and L. S. Miller, THIS JOURNAL, **75**, 3757 (1953).

[17] H. Gilman, R. A. Benkeser and G. E. Dunn, *ibid.*, **72**, 1689 (1950).

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

[19] R. A. Benkeser, Doctoral Dissertation, Iowa State College, 1947.

[20] H. Gilman and C. G. Brannen, THIS JOURNAL, **73**, 4640 (1951).

10 ml. of water, 200 ml. of ethanol and 200 ml. of dioxane. Titration with acid and Karl Fischer reagent showed it to be 0.73 *M* in potassium hydroxide and 1.90 *M* in water. The procedures employing these two reagents were identical.

To 1.4 g. (0.004 mole) of triphenylbenzylsilane in a 50-ml. glass-stoppered volumetric flask was added 20 ml. of reagent D. The flask was placed, with occasional shaking, in a constant temperature bath at 60 ± 0.5° for 1 hour. The reaction mixture was then poured into excess cold dilute hydrochloric acid (1:50), and the solid filtered off. It was washed with 35 ml. of 90% aqueous methanol to leave 1.06 g. (76%) of starting material, m.p. 96–97°. No hexaphenyldisiloxane was formed in the cleavages employing reagent D, and it was found that triphenylsilanol is soluble to the extent of 2.5 g. per 100 ml. of 90% aqueous methanol, whereas the silanes themselves were practically insoluble in this solvent. This procedure was therefore used to determine the amount of starting material uncleaved by reagents C and D, and hence the extent of the cleavage.

Cleavage of (Trichloromethyl)-triphenylsilane.[21] **A. With *n*-Butyllithium.**—To a suspension of 10 g. (0.0264 mole) of (trichloromethyl)-triphenylsilane in 100 ml. of ether at 25° was added 0.08 mole of *n*-butyllithium in 90 ml. of ether. A vigorous reaction ensued, during which the reaction mixture became reddish-brown. The mixture was refluxed overnight under nitrogen at which time Color Test I[22] was still positive. The reaction mixture was hydrolyzed with dilute sulfuric acid, the ether layer removed and dried, and the ether distilled. The residue was a viscous oil which was distilled to give 13.5 g. of straw-colored distillate boiling in the range 195–200° (0.25 mm.) and 1.3 g. of amber liquid boiling at 235–240° (0.2 mm.). The former fraction partially solidified to yield crystals melting over the range 68–76°, which after recrystallization from petroleum ether (b.p. 60–70°) gave 1.3 g. (15.5%) of solid melting at 86°. A mixed melting point of this solid with an authentic sample of *n*-butyltriphenylsilane[23] showed no depression.

B. With Phenyllithium.—A solution of 0.05 mole of phenyllithium in 80 ml. of ether was added slowly, with stirring, at 0°, to a suspension of 6.2 g. (0.0164 mole) of (trichloromethyl)-triphenylsilane in 100 ml. of ether. After standing overnight under nitrogen, the resulting solution gave a negative color Test I. The solution was hydrolyzed with water, and the ether layer separated and distilled on a water-bath. The residue was heated at 100° and 20 mm. pressure, and was then extracted with petroleum ether (b.p. 79–122°). The 0.3 g. (5.4%) of residue from this extraction melted at 232–234°, and its mixed melting point with tetraphenylsilane showed no depression. The petroleum ether extract was a brown viscous material from which no definite product was isolated.

AMES, IOWA

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[21] H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 968 (1951).

[22] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[23] H. Gilman and H. W. Melvin, *ibid.*, **71**, 4050 (1949).

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

The Separation of Relative Free Energies of Activation to Three Basic Contributing Factors and the Relationship of These to Structure

BY ROBERT W. TAFT, JR.

RECEIVED APRIL 23, 1953

Relative rates for many reactions may be attributed to three basic factors: (1) electrical effects; (2) steric strain effects; and (3) entropy or "steric hindrances to motions" effects. Experimental data are utilized to make this separation for relative rates of hydrolysis (or esterification) of aliphatic esters, RCOOR′, in which structure is varied in the acyl component, R. The effect of structure on factors (2) and (3) is discussed. A working hypothesis called the Strain–Entropy principle is proposed. The steric strains for the formation of the ester transition states are found to be one-fourth that of the strain energies for the formation of the corresponding homomorphic amine–trimethylboron addition compounds. This important linear strain energy relationship has been realized only because of the indicated separation of relative free energies of activation.

The effect of structure on reactivity is properly discussed in terms of the relative free energies, heats and entropies of activation which are thermodynamic functions of the hypothetical equilibrium.[1]

$$\mathrm{A} + \mathrm{A}_0^{\ddagger} \rightleftarrows \mathrm{A}^{\ddagger} + \mathrm{A}_0$$

A is a general reactant of a reaction series and A_0 is the reactant selected as the standard of comparison. The starred terms refer to corresponding reaction transition states. According to basic relations of statistical thermodynamics, the following equations apply[2]

$$\Delta\Delta F^{\ddagger} = -RT \ln k/k_0 = \Delta\Delta E_{\mathrm{p}}^{\ddagger} - RT \ln \Pi\, Q \quad (1)$$

where $\Delta\Delta F^{\ddagger}$ = relative free energy of activation; the free energy change accompanying the above reaction; k/k_0 = relative rate constant; $\Delta\Delta E_{\mathrm{p}}^{\ddagger}$ = relative potential energy of activation, the energy change that would accompany the above reaction if both reactant and transition states were completely deprived of all their energies of motion. $\Pi Q = q_{\mathrm{A}^{\ddagger}} q_{\mathrm{A}_0} / q_{\mathrm{A}_0^{\ddagger}} q_{\mathrm{A}}$, where q's are partition functions involving kinetic energies of motion. These include motions of solvent molecules involved in solvation as well as all motions at absolute zero.

$$\Delta\Delta H^{\ddagger} = \Delta\Delta E_{\mathrm{p}}^{\ddagger} + RT^2 (\mathrm{d}\,(\ln \Pi Q)/\mathrm{d}T) \quad (2)$$

where $\Delta\Delta H^{\ddagger}$ = relative heat of activation, the enthalpy change accompanying the above reaction.

$$\Delta\Delta S^{\ddagger} = R \ln \Pi Q + RT(\mathrm{d} \ln \Pi Q)/\mathrm{d}T \quad (3)$$

where $\Delta\Delta S^{\ddagger}$ = relative entropy of activation, the entropy change accompanying the above reaction.

It has been previously suggested that in many reactions the relative potential energy of activation, $\Delta\Delta E_{\mathrm{p}}^{\ddagger}$, is a composite of two terms, namely[3]

$$\Delta\Delta E_{\mathrm{p}}^{\ddagger} = \Delta\Delta E_{\mathrm{e}}^{\ddagger} + \Delta\Delta E_{\mathrm{R}}^{\ddagger} \quad (4)$$

where $\Delta\Delta E_{\mathrm{e}}^{\ddagger}$ = relative potential energy of activation resulting from electronic energy differences, *i.e.*, a term due to inductive, polarization and resonance effects. Solvent effects which arise from these effects are included. $\Delta\Delta E_{\mathrm{R}}^{\ddagger}$ = relative potential energy of activation resulting from

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[1] F. P. Price, Jr., and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 193.

[3] This is a modified expression of the type given by G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 193.