[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

The Mechanism of Substitution of Some Triarylgermyl Halides

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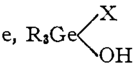
RECEIVED SEPTEMBER 5, 1957

Rate constants were determined for the hydrolysis of several triarylgermyl halides by conductance measurements. Evaluation of the data leads to the conclusion that the reaction proceeds *via* a pentacovalent-germanium derivative,



$R_3Ge\langle^{X}_{OH_2}$,

to the exclusion of the germonium ion, R_3Ge^+. This result is attributed to the ability of the germanium atom to expand its octet, a factor not characteristic of the carbon atom.

The carbonium ion has been accepted as a reality in the mechanistic interpretation of some reactions of carbon compounds. In addition it has been established that this ion increases in stability in the order primary, secondary, tertiary when the substituent is the methyl group. The stabilizing influence of a phenyl group is approximately equal to two methyl groups.[2] Thus it follows that triarylmethyl carbonium ions should be among the most stable.

To establish or verify the existence of the analogous cation of successive elements of Group IVA of the periodic table, it is reasonable to assume that tertiary compounds of these elements are the most likely to form this ion. When carbon, silicon or germanium is bonded to three stable organic groups, it becomes possible to study the properties of the fourth valence of that element. While the remaining valence is influenced to a greater or lesser extent by the nature of the organic substituents, the properties should be largely controlled by the central carbon, silicon or germanium atom.

The reactions of this "isolated" valence bond are included in the general category of substitution or replacement reactions. The substitution reactions of carbon have been well characterized, especially by Hughes, Ingold and collaborators[2-6] and have recently been reviewed by Streitwieser.[7] The characteristics of substitution reactions at a carbon atom are used here as a basis for an interpretation of the mechanism of hydrolysis of some triarylgermyl halides, R_3GeX, in order to obtain evidence for or against the existence of the germanium analog of the carbonium ion.

The ease of ionization of the M–X bond should increase from silicon to germanium. On this basis germanium should have a greater tendency to form a cation analogous to the carbonium ion. However, ionization could involve coördination of the substituting agent in a manner comparable to silicon. Empirically, silicon should be capable of expanding its octet easier than germanium since the smaller silicon atom should have a stronger affinity for electrons. Thus whichever factor is considered, germanium should have a stronger tendency than silicon to form a trivalent cation.

The probability that a germanium analog of the carbonium ion exists may thus be predicted but should not be presumed. The experimental results of this investigation are interpreted by comparison with the accepted mechanism of substitution at a saturated carbon atom, allowing for the possibility of octet expansion by the germanium atom.

Experimental

I. Preparation of Triarylgermyl Halides.—With the exception of tritolylgermyl fluoride, all of the compounds used in this investigation have been previously described and the results are consistent with the literature. In essence, the tetraaryl compound was first prepared by the standard Grignard reaction. The tetraaryl compound was then brominated to obtain triarylgermyl bromide.[8,9,12-15] Found: for $(C_6H_5)_3GeBr$: C, 57.64; H, 4.40; Ge, 19.0; Br, 18.53. Calcd.: C, 56.30; H, 3.94; Ge, 18.95; Br, 20.81. Hydrolysis of the bromide gave the oxide $(R_3Ge)_2O$. With HCl[13,16] the oxide gave $(C_6H_5)_3GeCl$, found: C, 64.76; H, 4.81; Ge, 21.4; Cl, 10.03. Calcd.: C, 63.59; H, 4.45; Ge, 21.53; Cl, 10.43. Treatment of the oxide with HF gave $(C_6H_5)_3GeF$,[9] found: C, 67.12; H, 4.74; Ge, 22.4. Calcd.: C, 66.93; H, 4.68; Ge, 22.48 and $(CH_3C_6H_4)_3GeF$.[10,11,14,15,17] Found: C, 69.23; H, 6.12; Ge, 19.4. Calcd.: C, 69.10; H, 5.80; Ge, 19.89.

II. Kinetic Measurements.—Relative rates of hydrolysis were determined by measuring the change in the ionic conductance of the halide solutions. Titrations of aliquots with KOH, titration of the fluoride ion with Th(IV) and determination of the change in hydrogen ion concentration by e.m.f. measurements were found to be unsuitable.

(1) **Conductivity Bridge.**—The ionic conductance was calculated from the resistance of the halide solution as measured by a Leeds and Northrup conductivity bridge. The input signal for every measurement was a 1000 c.p.s. vacuum tube oscillator. Earphones aided by an amplifier were used to determine the null point. The bridge was capable of a direct reading of resistances up to 60,000 ohms with limiting precision of 0.001 ohm. Where the resistance changed rapidly, that is, 5 ohms or more per minute, the measurement could be made to about ±0.1 ohm. A slower change, 2 ohms or less per minute, permitted measurements within a range of ±0.02 ohm. When resistances greater than 60,000 ohms were measured, a 9000 ohm shunt was used.

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[1] From a thesis submitted by Edwin A. Schmall to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Chap. VII.

[3] E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

[4] E. D. Hughes, *ibid.*, **37**, 603 (1941).

[5] E. D. Hughes, *J. Chem. Soc.*, 968 (1946).

[6] E. D. Hughes, *Quart. Rev.*, **5**, 245 (1951).

[7] A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

[8] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[9] C. A. Kraus and L. S. Foster, THIS JOURNAL, **49**, 457 (1927).

[10] D. L. Tabern, W. R. Orndorff and L. M. Dennis, *ibid.*, **47**, 2039 (1925).

[11] R. Schwarz and M. Lewinsohn, *Ber.*, **64B**, 2352 (1931).

[12] O. H. Johnson and W. H. Nebergall, THIS JOURNAL, **71**, 1720 (1949).

[13] W. R. Orndorff, D. L. Tabern and L. M. Dennis, *ibid.*, **49**, 2512 (1927).

[14] J. K. Simons, E. C. Wagner and J. H. Muller, *ibid.*, **55**, 3705 (1933).

[15] J. K. Simons, *ibid.*, **57**, 1299 (1935).

[16] C. A. Kraus and C. B. Wooster, *ibid.*, **52**, 372 (1930).

[17] H. Bauer and K. Burschkies, *Ber.*, **67B**, 1041 (1934).

(2) **Conductivity Cell.**—A pipet type conductivity cell with 1 cm.² platinized platinum electrodes 1 cm. apart and a capacity of about 15 ml. was used in every case. The temperature of the cell was maintained at 25 or 30 ± 0.05° by a kerosene-bath.

(3) **Chemicals.**—The acetone and *p*-dioxane used as solvents were dried for several hours over anhydrous sodium sulfate and then fractionated through a four-foot column. Acetone, b.p. 56.0° (728.5 mm.); dioxane, b.p. 100.5° (740.5 mm.). These solvents were diluted with conductivity water to prepare the reaction media.

(4) **Procedure.**—The conductivity cell and a glass-stoppered flask equipped with a magnetic stirrer and containing 20 ml. of the selected solvent, were placed in the bath maintained at the chosen temperature. To the solvent in the flask was then added 10 to 15 mg. of the solid halide and the stopwatch started. The conductivity cell was withdrawn from the bath, the solution from the previous run drained out and the cell refilled with fresh solution and returned to the bath. About two minutes generally elapsed from the time the stopwatch was started until the first reading was obtained. Successive readings were usually made at 20 second intervals for 20 minutes.

III. **Conductivity Data.**—The reaction medium was a solution of acetone–water or dioxane–water with the ratios of solvent to water by volume of 5 to 1, 4 to 1, or 3 to 1. The selection of reaction media was somewhat arbitrary but certain factors were considered.

Acetone and dioxane were chosen for two reasons. All of the halides were reasonably soluble in both solvents and there is a rather large difference in the dielectric constant of the two. The particular ratios of solvent to water represented a compromise between rapid solubility of the halides and reasonable conductance of the solutions. In addition, the water content was comparable to systems studied by other investigators. Dilute solutions of the halide were used to ensure a large and essentially constant excess of water throughout the reaction. These conditions permitted a reasonable change in conductivity during the period from 2 to 20 minutes after the time of the addition of the halide.

Solutions of the bromide and of the chloride were relatively good conductors and adequate changes in conductivity occurred under most of the conditions of temperature and reaction media used. Solutions of the fluorides were poor conductors and of the systems studied a usable change in conductivity occurred only in 3:1 and 4:1 dioxane–water solutions at 30°. Under other conditions the change in conductivity was too slow and too small for the determination of the rate constant.

Blank runs with solutions not containing halide were made to determine the effect of temperature variation. In some runs foreign salts were added, principally $NaClO_4$, LiBr, LiCl and LiF in approximately 0.01 *M* concentrations to determine the effect of extraneous salts on the reaction.

The nature of the voluminous data assembled is represented by Table I.[18]

TABLE I

CONDUCTANCE OF $(C_6H_5)_3GeBr$

(10 mg. of $(C_6H_5)_3GeBr$ in 20 ml. of 4:1 dioxane–water solution at 30°, 0.01 *M* with respect to LiBr)

Time	*R*	$C \times 10^9$	Time	*R*	$C \times 10^9$
1:40	4595.2	217571	9:20	4564.72	219071
2:00	4590.5	217801	9:40	4564.60	219077
2:20	4585.6	218074	10:00	4564.48	219083
2:40	4581.7	218260	10:20	4564.38	219088
3:00	4578.5	218412	10:40	4564.30	219092
3:20	4576.1	218527	11:00	4564.22	219095
3:40	4574.2	218617	11:20	4564.22	219095
4:00	4572.65	218692	11:40	4564.22	219095
4:20	4571.3	218756	12:00	4564.28	219093
4:40	4570.1	218810	12:20	4564.23	219095
5:00	4569.1	218861	12:40	4564.18	219097
5:20	4568.3	218900	13:00	4564.12	219100
5:40	4567.6	218933	13:20	4564.08	219102
6:00	4567.0	218962	13:40	4564.10	219101
6:20	4566.5	218986	14:00	4564.13	219100
6:40	4566.15	219003	14:20	4564.22	219095
7:00	4565.75	219022	14:40	4564.18	219097
7:20	4565.38	219040	15:00	4564.13	219100
7:40	4565.08	219054	16:00	4564.05	219104
8:00	4564.85	219065	17:00	4564.18	219097
8:20	4564.72	219071	18:00	4564.08	219102
8:40	4564.67	219074	19:00	4564.22	219095
9:00	4564.68	219073	20:00	4564.02	219105

IV. **Evaluation of Rate Constants.**—In the dilute solutions used the proportion of water in the reaction medium was sufficient to permit the assumption that the HBr and the HCl formed were highly ionized. The low conductivity of the fluoride solutions indicated that the HF was mostly associated as would be expected. To calculate the rate constants, the conductance at any instant was assumed to be a linear function of the concentration of hydrogen halide present at that time.[19] The equivalent conductances were regarded as constant in the dilute solutions of halide, which was justified by the fact that the results consistently adhered to the first-order rate law.

In general the half-life of the reaction under the conditions studied was about one minute. The initial concentration of halide could therefore not be assumed by calculation from the weight of the sample used. In addition a reliable infinite conductance could not always be obtained by extrapolation. Of necessity then the rate constant was calculated from an expression which did not require knowledge of the initial concentration and conductivity or the infinite concentration and conductivity. Use was made only of the data obtained from about the two to six minute interval after zero time. The greatest and fastest change in conductivity occurred during this period.

The method selected for the calculation of the rate constants was a graphical one. The rate constant, *k*, for a first-order reaction is given by the expression

$$k = \frac{2.303}{t_2 - t_1} \log \frac{A - x_1}{A - x_2}$$

where A is the initial concentration of R_3GeX and x_1 is the amount of R_3GeX that has reacted at time t_1.

If t_1 and t_2 are chosen so that $t_2 - t_1$ is always constant, then the ratio $(A - x_1)/(A - x_2)$ also remains constant and is here designated by α.

The conductance C_i at time t_i is assumed to be a linear function of the concentration of HX at time t_i and therefore a linear function of x_i

$$x_i = aC_i + b$$

where a and b are constants. The constant α may therefore be represented by the expression

$$\alpha = \frac{A - aC_1 - b}{A - aC_2 - b}$$

from which the following relation may be derived

$$C_1 = \alpha C_2 + \beta$$

where β is a combination of the constants a, b, A and α.

If C_1 is plotted against C_2 such that $t_2 - t_1$ is a constant, α can be equated to the slope of the line. The rate constant may then be obtained from the relation

$$k = \frac{2.303}{t_2 - t_1} \log \alpha$$

The graphical evaluation of α is illustrated in Fig. 1, where the time interval $t_2 - t_1$ is 20 seconds.[20] The numerical values of the rate constant are summarized in Table II.

V. **Conclusions.**—An interpretation of the kinetics of hydrolysis of the triarylgermyl halides should either (a) substantiate a reaction mechanism involving the germonium ion, R_3Ge^+, or (b) contradict its occurrence and establish more a likely intermediate.

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(18) Table I is Table 54 in the thesis. Microfilm copies of the other 64 tables are available from the University of Minnesota Library.

(19) J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 2412 (1949).

(20) Figure 1 is representative of the six graphs in the original thesis. The numbers refer to the tables of original data mentioned in reference 18. Microfilm copies of the other five graphs are available from the University of Minnesota Library.

TABLE II

SUMMARY OF RATE CONSTANTS

Reaction medium	Ph_3GeBr α[a]	Ph_3GeBr k[b]	Ph_3GeCl α	Ph_3GeCl k	Ph_3GeF α	Ph_3GeF k	Tol_3GeF α	Tol_3GeF k
4:1 Dioxane (25°)	1.228	0.0103	1.203	0.0092	...	....	...	....
	1.218	.0099	1.194	.0089	...	....	...	....
5:1 Dioxane (25°)	1.173	.0091	1.140	.0066	...	....	...	....
	1.186	.0085	1.160	.0074	...	....	...	....
4:1 Acetone (25°)	1.289	.0127	1.263	.0117	...	....	...	....
	1.278	.0123	1.262	.0116	...	....	...	....
3:1 Dioxane (30°)	No data		No data		1.248	0.0111	1.231	0.0104
					1.250	.0111	1.242	.0108
4:1 Dioxane (30°)	1.248	0.0111	1.227	0.0102	1.216	.0098	1.211	.0096
	1.250	.0112	1.231	.0104	1.218	.0099	1.208	.0094
4:1 Acetone (30°)	1.327	.0141	1.310	.0135	No data		No data	
	1.319	.0138	1.314	.0137				
4:1 Dioxane (30°)	No data		No data		1.127	0.0060	1.073	0.0035
0.01 *M* LiF					1.131	.0062	1.078	.0038
4:1 Dioxane (30°)	1.239	0.0107	1.213	0.0096	1.247	.0110	1.260	.0115
0.01 *M* LiCl	1.240	.0107	1.212	.0096	1.265	.0117	1.265	.0117
4:1 Dioxane (30°)	1.232	.0104	1.242	.0108	1.238	.0107	1.258	.0115
0.01 *M* LiBr	1.233	.0104	1.240	.0107	1.244	.0109	1.253	.0113
4:1 Dioxane (30°)	1.206	.0094	1.210	.0095	No data		No data	
0.01 *M* $NaClO_4$	1.200	.0091	1.199	.0091				

[a] $t_2 - t_1 = 20$ sec. [b] Units = sec.$^{-1}$.

A. Possible Mechanisms of Substitution.—A comparison with the chemistry of carbon and the possibility of octet expansion by the germanium atom leads to several possible mechanisms in which the halogen is replaced by the nucleophilic agent, water.

(a) The initial step in the reaction could be the dissociation of the Ge–X bond. This process would involve the germonium ion. Two mechanisms may be written, depending upon the relative rates of the successive steps

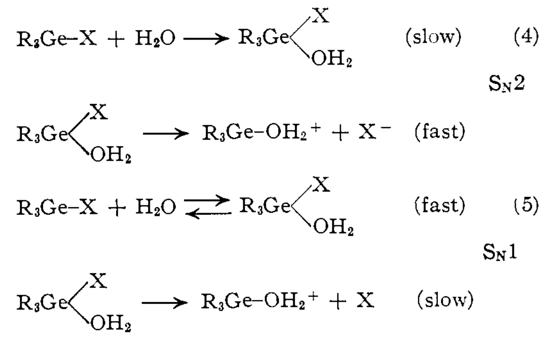
$$R_3Ge\text{–}X \longrightarrow R_3Ge^+ + X^- \quad \text{(slow)} \quad S_N1 \qquad (1)$$
$$R_3Ge^+ + H_2O \longrightarrow R_3Ge\text{–}OH_2^+ \quad \text{(fast)}$$

$$R_3Ge\text{–}X \rightleftharpoons R_3Ge^+ + X^- \quad \text{(fast)} \quad S_N2 \qquad (2)$$
$$R_3Ge^+ + H_2O \longrightarrow R_3Ge\text{–}OH_2^+ \quad \text{(slow)}$$

(b) Replacement of the halogen by the substituting agent could occur as a one-step reaction

$$R_3Ge\text{–}X + H_2O \longrightarrow R_3Ge\text{–}OH_2^+ + X^- \text{ (slow) } S_N2 \quad (3)$$

(c) The ionization of the halide could be preceded by coordination with water. There are two possible mechanisms depending upon which step is rate determining



$$R_3Ge\text{–}X + H_2O \longrightarrow R_3Ge\left\langle\begin{smallmatrix}X\\OH_2\end{smallmatrix}\right. \quad \text{(slow)} \qquad (4)$$
$$S_N2$$
$$R_3Ge\left\langle\begin{smallmatrix}X\\OH_2\end{smallmatrix}\right. \longrightarrow R_3Ge\text{–}OH_2^+ + X^- \quad \text{(fast)}$$

$$R_3Ge\text{–}X + H_2O \rightleftharpoons R_3Ge\left\langle\begin{smallmatrix}X\\OH_2\end{smallmatrix}\right. \quad \text{(fast)} \qquad (5)$$
$$S_N1$$
$$R_3Ge\left\langle\begin{smallmatrix}X\\OH_2\end{smallmatrix}\right. \longrightarrow R_3Ge\text{–}OH_2^+ + X \quad \text{(slow)}$$

The logical mechanism is indicated by the experimental data.

B. Reaction Kinetics.—Ideally, two of the suggested mechanisms should be eliminated by the observed kinetics. Mechanisms 1 and 5 being of the S_N1 type, should exhibit first-order kinetics. Mechanisms 2, 3 and 4 should follow second-order kinetics, S_N2. However, under the experimental conditions the hydrolysis was essentially a solvolytic reaction. The concentration of water was approximately 10^4 times greater than that of the halide. Under these conditions first-order kinetics would be expected regardless of which mechanism was operating and therefore is not sufficient to distinguish between S_N1 and S_N2.

C. Relative Rates.—In a particular solvent with no extraneous salt present, the observed rate constants decrease in the order $R_3GeBr > R_3GeCl > R_3GeF$. Accordingly the ease of substitution appears to vary inversely as the electronegativity of the halogens. From this it may be

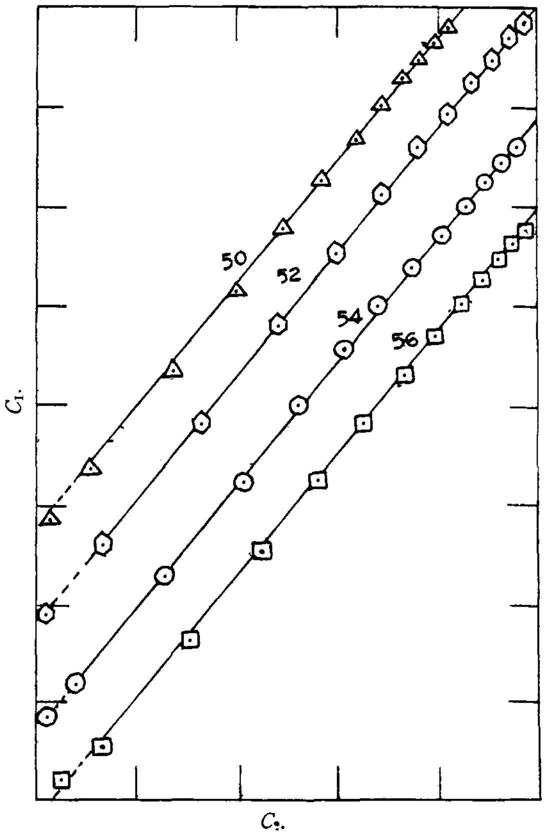


Fig. 1.—Graphic evaluation of rate constant: 50, $(C_6H_5)_3GeF$; 52, $(CH_3C_6H_4)GeF$; 54, $(C_6H_5)_3GeBr$; 56, $(C_6H_5)_3GeCl$. All solutions made with 10 mg. substance in 20 ml. of 4:1 dioxane at 30°. No. 50 and 52 are 0.01*M* with added LiCl, No. 54 and 56 are 0.01 *M* with added LiBr.

concluded that the rate-determining step involves the displacement or the rupture of the Ge–X bond since the observed rates of hydrolysis vary indirectly with the strength of the Ge–X bond.

It was also found that $(C_6H_5)_3GeF$ reacted faster than $(p\text{-}CH_3C_6H_4)_3GeF$. Since the addition of a methyl group in the *para* position would not be expected to exert any steric influence it is concluded that the rate retardation is due to the effect of the more electron-releasing *p*-tolyl group on the transition state in the rate-determining step.

D. **Solvent Effect.**—Two variables were especially considered so far as the solvent was concerned: (a) water was diluted with two organic solvents of widely differing dielectric constants, acetone and *p*-dioxane, and (b) the organic solvent was mixed with varying percentages of water.

The ionizing power of the reaction media used in this investigation has been evaluated[21] for the hydrolysis of *t*-butyl chloride. The ionizing power of a solvent is defined as the log of the rate of solvolysis in that particular solvent relative to the rate of solvolysis in 80% aqueous ethanol. The ionizing power of aqueous acetone is only slightly greater than that for aqueous dioxane at the same concentration even though the dielectric properties of the comparable mixtures differ widely. For example, at 20 volume % water the dielectric constant for the acetone solution is 32 while that of the dioxane solution is only 11. The ionizing power of the reaction medium obviously depends more on the water content than on the dielectric constant.

TABLE III

EFFECT OF EXTRANEOUS SALTS ON RATE OF HYDROLYSIS

Salt added	Halide $(C_6H_5)_3GeBr$	$(C_6H_5)_3GeCl$	$(C_6H_5)_3GeF$	$(p\text{-}CH_3C_6H_4)_3\text{-}GeF$
Br^-	Decrease (A)	Increase (B)	Increase (B)	Increase (B)
Cl^-	Decrease (C)	Decrease (A)	Increase (B)	Increase (B)
F^-	....	....	Decrease (A)	Increase (A)
ClO_4^-	Decrease (C)	Decrease (C)	....	....

That the experimental rates of hydrolysis vary with the reaction medium leads to the following conclusions; (a) the transition state of the rate-determining step involves an increase in the magnitude of charges relative to the reactant and (b) the transition state does not involve the distribution of a given charge, or a decrease in charge relative to the reactant. Either S_N1 or S_N2 is consistent with the observed solvent effect.

E. **Effect of Foreign Salts.**—The effect of the presence of extraneous salts on the rate of hydrolysis is summarized qualitatively in Table III.

In Table III the letter (A) denotes the fact that the salt effects are attributed to the common-ion effect, (B) the ionic strength effect, and (C) to "compound-formation."

Compound-formation is equivalent to the reverse of ionization. Rate retardation would be observed if the ionization of the Ge–X bond led to the formation of the Ge–X′ bond, where the rate of substitution of Ge–X is faster than that of Ge-X′, thus

$$R_3Ge\text{–}X \rightleftarrows R_3Ge^+ + X^-$$
$$R_3Ge^+ + X' \rightleftarrows R_3GeX'$$

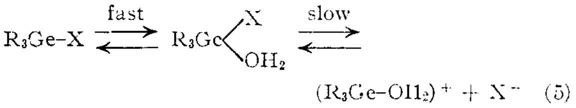
The fact that the observed salt effects do occur is sufficient to establish a unimolecular mechanism, S_N1.

F. **Probable Mechanism.**—From an interpretation of the experimental results it is possible to eliminate all but one of the five reasonable mechanisms of substitution previously suggested. In each of the other four mechanisms there is some aspect which is not consistent with the conclusions cited.

It has been established that substitution occurs by a unimolecular S_N1 type of mechanism. The data effectively eliminate mechanisms 2, 3 and 4. It is necessary then to decide between mechanisms 1 and 5.

Mechanism 1 does not explain the effect of changing the nature of the organic group attached to the germanium atom. As previously described, the ionization of the Ge–X bond is favored by electron-release by the organic group to the germanium atom. If mechanism 1 were valid, $(p\text{-}CH_3C_6H_4)_3GeF$ should hydrolyze faster than $(C_6H_5)_3GeF$ since the *p*-tolyl group is more electron-releasing than the phenyl group. This prediction is contrary to observation.

Mechanism 5 can account for the polar effect of the organic group. In the transition state in the reaction



$$R_3Ge\text{–}X \underset{}{\overset{\text{fast}}{\rightleftarrows}} R_3Ge\begin{matrix}X\\OH_2\end{matrix} \overset{\text{slow}}{\rightleftarrows} (R_3Ge\text{–}OH_2)^+ + X^- \quad (5)$$

the germanium atom is less positive, possibly even negative, relative to the germanium atom in the reactant. The reaction would therefore be inhibited by electron-release to the germanium atom of the reactant. Therefore only mechanism 5 is consistent with all of the experimental observations.

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[21] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Methylene. III. Addition to Carbon Monoxide

BY THÉRÈSE BREMER WILSON AND G. B. KISTIAKOWSKY

RECEIVED DECEMBER 10, 1957

Methylene generated photochemically from ketene reacts with carbon monoxide to re-form ketene. This reaction was studied by determining yields of $CH_2C^{13}O$ when labeled $C^{13}O$ was added, and, independently, by observing the effect of carbon monoxide on the rate of pressure change in irradiated ketene. It is shown to be an association reaction. The ratio of the rates of decomposition and of deactivation of the initially formed energy-rich ketene molecules is 10.5 mm., when the third body is ketene. With the third body efficiency of ketene taken as unity, the deactivation efficiencies of sulfur hexafluoride and nitrogen are found to be 0.8 and of the order of 0.1, respectively. The ratio of rate constants of the reactions of methylene with carbon monoxide and with ketene is found equal to 2.7 by the isotopic measurements and 1.25 by the pressure measurements. The discrepancy between these two values is attributed to the different methods of calculation used and to the assumed mechanism of the reaction of methylene with ketene. Sulfur hexafluoride is found to decrease the rate of pressure change in irradiated ketene.

Introduction

Previous experiments[1] have shown that when ketene is photolyzed in the presence of carbon monoxide ($C^{13}O$), some labeled ketene $CH_2C^{13}O$ is formed; this re-formation of ketene was interpreted as an association reaction of methylene radicals with CO, corresponding to the over-all equation $CH_2 + CO = CH_2CO$. According to Staudinger and Kupfer,[2] ketene is similarly formed when diazomethane is decomposed in the presence of CO.

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[1] G. B. Kistiakowsky and W. L. Marshall, THIS JOURNAL, **74**, 88 (1952).

[2] H. Staudinger and O. Kupfer, *Ber.*, **45**, 508 (1912).