672. *Nucleophilic Substitution at Silicon and Germanium: Rapid Hydrolytic Reactions of Organo-chlorides.*

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A rapid-reaction technique has been used in studying the rates of hydrolysis in organic solvents of a series of halides R_3MCl, where M is silicon or germanium and R is alkyl or aryl. The effects of water concentration, temperature, solvent composition, and the nature of R have been studied and the course of the reaction at very short time intervals after initiation has been examined for direct evidence of the formation of a 5-co-ordinated intermediate. The mechanism of the hydrolysis is discussed.

THE mechanism of nucleophilic substitution at a saturated carbon atom in halides is well established,[1] but that occurring at the other elements of Group IVb has received much less study. Silicon has received the most attention, and studies of the kinetics and stereo-chemistry of substitution show that usually the process has the characteristics of an S_N2 mechanism although it is possible that the transition state in the reaction may be stable for a short time, constituting an unstable five-fold co-ordinated complex.[2]

The mechanism of substitution at a germanium atom has been the subject of only one research,[3] in which it was claimed that kinetic measurements show that the substitution process at germanium consists of fast formation of a five-fold co-ordinated intermediate and its rate-determining breakdown. This work is unsatisfactory on several grounds, and these conclusions are not justified from the results obtained.*

The rate of substitution in a series of analogous compounds of elements in the same Group should be determined by the size and electronegativity of the central atom, together with the availability of high-energy orbitals which may be used to stabilise transition states during reaction. Accordingly the rate of hydrolysis of trialkyl- and triaryl-chloro-silanes and -germanes was examined. A preliminary report on some of this work has appeared.[5]

* (1) Rate constants were obtained without taking into account the reverse reaction. (2) The rate constants obtained were all very similar—small differences (less than 5% of rate constant values) are used to lead to mechanistic conclusions. (3) It is stated that a synchronous mechanism is not possible if supply of electrons decreases the rate of substitution. This error was made by Swain, Esteve, and Jones [4] and was corrected by Eaborn.[2]

[1] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, Ch. 7.

[2] Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, pp. 103—113, 179—183.

[3] Johnson and Schmall, *J. Amer. Chem. Soc.*, 1958, **80**, 2931.

[4] Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965.

[5] Chipperfield and Prince, *Proc. Chem. Soc.*, 1960, 385.

Experimental

The compounds used were prepared by methods described in the literature, and purified to constant m. p. (for solids) or by fractional distillation (for liquids). B. p.s and m. p.s agreed with those quoted in the literature, and the analyses agreed with the theoretical within experimental error. Solvents were dried before use: ether was dried over sodium wire, and acetone by distillation from magnesium perchlorate or by passage through a 6′ × 1″ column of molecular sieve of grade 4A.

The rates of hydrolysis were measured by mixing solutions of the halide in ether or acetone with an equal volume of aqueous acetone of known concentration. The reactions were rapid ($t_{\frac{1}{2}}$ mostly <1 sec.); the kinetics were measured in a rapid-reaction apparatus (" stopped flow " principle), and the production of hydrogen chloride was followed by changes in electrical conductivity: details of the method are included in the Appendix.

Results.—While the chlorosilanes R_3SiCl (R = Pr^i, Ph, *p*-tolyl) are hydrolysed completely under the conditions stated below (the specific conductivity of a solution of chlorotriphenyl-silane in acetone 2M in water is the same as that of an equimolar solution of hydrogen chloride), chloro-triphenyl- and -tri-*p*-tolyl-germane are incompletely hydrolysed in this medium. The equilibrium constants for the reaction: $R_3GeCl + H_2O \rightleftharpoons R_3GeOH + H^+ + Cl^-$ are: R = Ph, $2 \cdot 2 \times 10^{-6}$, *p*-tolyl $4 \cdot 5 \times 10^{-6}$, and Pr^i $1 \cdot 15 \times 10^{-7}$. Allowance must be made for the reverse reaction in determining the rate constants of hydrolysis (see Appendix).

In all cases there was a simple first-order dependence of the hydrolysis rate on the halide concentration over the range studied (10^{-4}—10^{-2}M). Individual rate constants were repeatable within $\pm 2\%$; the shortest half-life of a reaction examined at room temperature was 0·015 sec. and the longest 20 sec. The apparatus necessary for making observations over this range has been outlined and only modifications to the original apparatus are described in the Appendix.

The Table summarises the kinetic results for the hydrolysis. Not included are results on the opposing reaction: the second-order rate constant of the reaction of hydrogen chloride with triphenylgermanol was determined. Equimolar solutions of this germanol in acetone and of hydrogen chloride in aqueous acetone were introduced into the apparatus, and the

Summary of kinetic data on hydrolysis of chlorides, R_3MCl, in presence of excess of water in acetone and 1 : 1 acetone–ether.

$$R_3MCl + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} R_3M\cdot OH + HCl$$
(Excess)
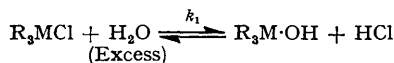
Rate constants, k_1, are expressed in sec.$^{-1}$.

(a) *Reaction of* R_3MCl *with water in acetone:* [H_2O] = 4M.

R	Ph		*p*-Tolyl	Pr^i
Temp.	25	40	25	25
k_1 (Si)	4·03	3·81	1·1	0·038
k_1 (Ge)	0·034	0·036	—	>0·7

(b) *Reaction of* R_3GeCl *with water in 1 : 1 acetone–ether at 25°.*

R	Ph				*p*-Tolyl
[H_2O]	4·06	6·0	7·0	8·0	4·06
k_1 (Ge)	0·06	0·43	0·77	1·15	0·041
k_1 (Si)	2·4				

(c) *Relative rates.** (i) *Effect of medium.* [H_2O] = 4M Temp. = 25°.

$\dfrac{k_1(Si)}{k_1(Ge)}$	Me_2CO	Et_2O–Me_2CO	$\dfrac{k_1(Me_2CO-Et_2O)}{k_1(Me_2CO)}$	Si	Ge
	118	40		0·6	1·8

(ii) *Effect of R.* [H_2O] = 4M.

$\dfrac{k_1(Si)}{k_1(Ge)}$	Ph	Pr^i	$\dfrac{k_1(phenyl)}{k_1(p\text{-}tolyl)}$	Si	Ge
	118	<5·4 × 10^{-2}		3·7 (in Me_2CO)	1·5 (in Me_2CO–Et_2O)

* k_1(Ge) = 0·034 sec.$^{-1}$, taken as unity for Si/Ge comparisons.

decrease of resistance of the mixed solutions due to the fall in acid concentration was measured. The rate constants obtained were $5 \cdot 8 \times 10^3$ l. mole^{-1} sec.$^{-1}$ at 25·0° and $14 \cdot 6 \times 10^3$ l. mole^{-1} sec.$^{-1}$ at 40·0°. Further experiments showed that the reaction between hexaphenyldigerm-oxane proceeded at the same rate as the combination of the germanol with hydrogen chloride. The ratio of rate constants for the forward and the reverse reaction agreed with the experimentally determined equilibrium constants within experimental error.

The kinetics of the initial phase of the (relatively) slow reaction of chlorotri-isopropyl-silane with acetone 2M in water were examined for evidence of the formation of an intermediate.

If an intermediate, C, is formed in the scheme, $A + B \rightleftharpoons C \longrightarrow$ Products, the rate expression for the pre-stationary state of C shows [6] that the formation of the products undergoes acceleration and at sufficiently short time intervals after initiation it is proportional to time squared. Observing the rate of release of hydrogen chloride during hydrolysis thus constitutes a direct test for an intermediate. In fact, the first-order rate constant obtained within 4·5 millisec. to 0·6 sec. was the same as that obtained over 20 sec.

DISCUSSION

We shall consider (*a*) the negative temperature coefficients of these reactions and (*b*) the dependence of the hydrolysis rate order for silicon and germanium on the nature R in R_3MCl.

The plot of log k_1 against log $[H_2O]$ for the hydrolysis of chlorotriphenylgermane in ether–acetone with water in the concentration range 2—4M shows the rate to be given by the expression, $k[Ph_3GeCl][H_2O]^{4\cdot2}$. Measurements of dielectric constant were made on all aqueous ether-acetone solutions: the rapid increase in rate with $[H_2O]$ cannot be accounted for only in terms of dielectric constant.

Further, this multiple order with respect to the nucleophile is similar to that found for the hydrolysis of benzyl chloride,[7] where between two and six molecules of water participate in the transition state, to the alcoholysis of acid chlorides,[8] where the rate of alcoholysis depended upon the sixth power of the alcohol concentration, and to the alcoholysis of silicon chlorides, where the rate depended upon up to the seventh power of the alcohol concentration.[9]

The structure of water is governed by the extensive hydrogen bonding present. Even when diluted with an organic solvent it is likely that large water-polymer aggregates persist and in the hydrolysis it is the concentration of these polymeric species that determines the rate of hydrolysis (see below). The effect of temperature upon the hydrolysis of chlorosilanes and chlorogermanes is consistent with the breakdown of the water polymer as hydrogen bonds are broken, and thus the decrease in the concentration of the reacting species compensates for the expected Arrhenius dependence of rate upon temperature.

The analogous situation in the alcoholysis of acyl chlorides has been discussed by Hudson and Saville.[8] A simple extension of their treatment to the hydrolyses of organo-silicon and -germanium halides is as follows. Let there be an equilibrium in which the hydrogen-bonded polymer contains n molecules, then we have,

$$nH_2O \rightleftharpoons (H_2O)_n$$
$$c(1-\alpha) \qquad \alpha c/n$$
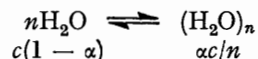
and, if we assume that the relevant activity coefficients are unity, then

$$\alpha/(1-\alpha)^n = nKc^{n-1} \tag{1}$$

The reaction is assumed to occur between the water polymer and the organometallic halide, so that

$$-d[R_3MX]/dt = k_1[(H_2O)_n][R_3MX].$$

If $[(H_2O)_n]$ is sensibly constant over the initial part of the reaction the observed pseudo-unimolecular rate constant, k_{obs}, is given by

$$k_{obs} = k_1[(H_2O)_n] = k_1\alpha c/n,$$

[6] Chipperfield, Thesis, Cambridge, 1961; Gutfreund, *Discuss. Faraday Soc.*, 1955, **20**, 167; Roughton, *ibid.*, 1954, **17**, 116.
[7] Tommila, Paakala, Virtanen, Erva, and Varila, *Ann. Acad. Sci. Fennicæ*, 1959, A2, No. 91.
[8] Hudson and Saville, *J.*, 1955, 4114, 4121, 4130; Hudson and Steltzer, *Trans. Faraday Soc.*, 1958, **54**, 213.
[9] Saville, personal communication.

and so the real and observed activation energies are related by the equation:

$$\frac{E_{obs}}{RT^2} = \frac{E}{RT^2} + \frac{\partial \ln \alpha}{\partial T}, \tag{2}$$

where E is the real activation energy. Logarithmic differentiation of equation (1) and substitution in (2) gives:

$$E_{obs} = E - \Delta H(1 - \alpha)/[1 + (n - 1)\alpha], \tag{3}$$

where ΔH is the heat of association of the water molecules to form the " n-mer." Quite generally, for any hydrolysis where the second term approaches or exceeds the first, small or negative apparent activation energies will be observed: for acyl halides the first term slightly exceeds the first; with the silicon and germanium chlorides studied the second term appears to be slightly the larger, though E_{obs} is close to zero. This is probably the simplest way of regarding the negative temperature coefficients of these reactions. It is almost certainly an oversimplification, because in reality there is probably a range of degrees of polymerisation, each polymeric species having a characteristic reactivity.

Although infrared studies of water in acetone have been reported,[10] there appears to be no quantitative information on the polymerisation of water in these solvents and only a crude estimate of ΔH is possible. It is reasonably certain that the hydrogen bond-energy in water lies within the range 3—5 kcal./mole,[11] and for a tetrameric species ΔH might reasonably be 12—20 kcal. per mole of tetramer. We do not know E, the real activation energy of the reaction, but for reaction with water (apparently in a monomeric state) in a solvent of similar dielectric constant, *viz.*, water in propan-2-ol,[12] the energy of activation is 10 kcal./mole and equation (3) shows that, for such a value of E and α about 0·1, experimental activation energies close to zero will be obtained; if E is smaller, then negative values will be observed. Clearly, negative temperature coefficients for reactions of this kind are not unexpected so long as E is small enough.

In the reaction of triphenylgermanol with hydrogen chloride, the concentrations of the reacting species do not alter with temperature, and a normal temperature dependence is found.

The proposed mechanism for the reactions is that of an S_N2 process with a water polymer as a reacting species. In the hydrolysis of chlorosilanes at low water concentrations, a strong autocatalytic effect was noted by Allen and Modena.[13] This was attributed to the necessity for proton removal from the transition state before the products can be formed. Any nucleophile can be the base, including, in essentially non-aqueous media, the displaced chloride ion. Under the conditions used, an excess of water was present and the catalytic effect of the displaced chloride ion is negligible. The efficiency of a hydrogen-bonded attacking water polymer is high because the polymeric unit acts as a base at the same time as providing the nucleophile, *i.e.*, the unit provides the attacking water molecule and a proton switch within the unit provides a means of easy proton removal from that water molecule [see (I), below].

Potentiometric titrations of chlorotriphenyl-silane, -germane, and -stannane with base have shown that it is easier to remove a proton from $R_3Si\cdot OH_2^+$ than from any similar compound of germanium, tin, or lead; the proton becomes harder to remove in that order.[14] Thus the effect of base will be more important at germanium in the removal of the proton than at silicon.

[10] Chulanovsky, *Doklady Akad. Nauk, S.S.S.R.*, 1953, **93**, 25.
[11] Cross, Burnham, and Leighton, *J. Chem. Phys.*, 1937, **59**, 1134; Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 155; Pauling, " Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, New York, 1960, pp. 464 *et seq.*
[12] Prince, *J.*, 1959, 1783.
[13] Allen and Modena, *J.*, 1957, 3671.
[14] Chipperfield, unpublished work; Denison, Thesis, London, 1954.

The solvent effects can be explained in terms of solvent basic strengths. At silicon the rate of hydrolysis is faster in the more polar acetone (as expected for a neutral molecule giving an ion [1]) than in ether–acetone having the same water concentration; at germanium the rate of hydrolysis in ether–acetone is greater than in the polar acetone since the basic nature [15] of the former solvent is the more important factor.

For both silicon and germanium, supply of electrons to the central atom retards the reaction (the effect is greater at silicon), showing that the transition state must be slightly negative, *i.e.*, emphasis must be on the formation of the new bond to oxygen rather than on the breaking of the old bond to halogen.

The inversion of the rate order for silicon and germanium when R is changed from phenyl [$k_1(\text{Ge})/k_1(\text{Si}) = 1 : 120$] to isopropyl [$k_1(\text{Ge})/k_1(\text{Si}) > 20 : 1$] cannot be explained in terms of germanium's larger size, since if bond-making is dominant, as the effect of electron release suggests, then germanium campounds should react faster than their silicon analogues. It is interesting that the rate order depends strongly on the nature of the groups attached to silicon and germanium, two elements having similar tetrahedral radii (1·17 and 1·22 Å) and electronegativities). The experimental determination of activation energies is vitiated by hydrogen-bonding effects, as described above, but to interpret the difference we shall assume that it lies in the activation energies and that the aromatic group is able to lower the activation energy for substitution at silicon more than for substitution at germanium.*

The origin of the activation-energy decrease on introduction of an aryl group is not obvious and it is informative to consider the terms which constitute the activation energy. We may write, remembering that bond-making is important,

$$E_{\text{act}} = \Delta H_{\text{R}_3\text{MCl}} + \Delta H_{(\text{H}_2\text{O})_n} + R + E_{\pi_{\text{tet}}} - E_{\pi\text{TS}} + E_{\sigma_{\text{tet}}} - E_{\sigma\text{TS}} - D_{\text{M-O}} - \Delta H_{\text{TS}},$$

where the activation energy, E_{act}, is expressed in terms of the solvation energy of the chloride, $\Delta H_{\text{R}_3\text{MCl}}$, the solvation energy of a water n-mer, $\Delta H_{(\text{H}_2\text{O})_n}$, the steric repulsive energy arising as $(\text{H}_2\text{O})_n$ approaches M, and the shape of the transition state is attained (R), the change of π-bonding energy in R_3MCl in proceeding from the tetrahedral initial state to the transition state ($E_{\pi_{\text{tet}}} - E_{\pi\text{TS}}$), the corresponding change of σ-bonding energy ($E_{\sigma_{\text{tet}}} - E_{\sigma\text{TS}}$), the M–O bond energy in $\text{H}_2\text{OMR}_3\text{Cl}$, and the solvation energy of the transition state (ΔH_{TS}). It is difficult to obtain accurate estimates of most of these quantities, but the following observations are relevant (where appropriate the rate order expected is given in parenthesis). Since silicon and germanium are so similar in size and the R_3MCl molecules are in any case large, $\Delta H_{\text{R}_3\text{MCl}}$ and ΔH_{TS} will be closely similar for the two elements and can be neglected; the solvation energy of the water polymer is common to both; the steric repulsion energy, R, should be slightly smaller for germanium than silicon [17] since the former is the larger (rate for Ge > rate for Si); the M–O bond energy is larger for silicon than germanium (rate for Si > rate for Ge). Concerning σ-bonding we note that the excitation energy calculated by Gillespie's method [18] for the $sp^3 \rightarrow sp^3d$ promotion is ~0 ev for germanium and ~2 ev for silicon, suggesting that the σ-bond system of the transition state could be established more readily for germanium than for silicon. For π-bonding terms we note that the electron spin resonance spectra of the negative ions of trimethylphenyl-silane and -germane show that silicon is considerably more effective in π-bonding to an aromatic ring than germanium in a tetrahedral environment; [19] the

* Measurements of the activation energy of chloride exchange in triorganochlorosilanes, which involves attack of Cl⁻ at silicon, show that aromatic groups in these systems cause substantial decreases of activation energy, compared with aliphatic groups of similar steric effectiveness.[16]

[15] Braude and Stern, *Nature*, 1948, **161**, 169; *J.*, 1948, 1976.

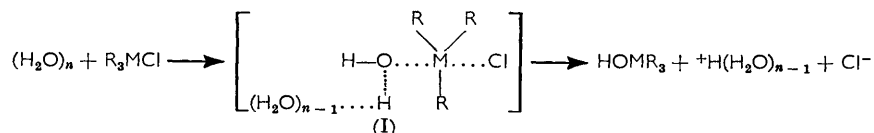[16] Haysom, Thesis, Cambridge, 1962; Haysom and Prince, unpublished work.

[17] Aston, *Chem. Rev.*, 1940, **27**, 59; Aston, Kennedy, and Messerly, *J. Amer. Chem. Soc.*, 1941, **63**, 2343; French and Rasmussen, *J. Chem. Phys.*, 1946, **14**, 389.

[18] Gillespie, *J.*, 1952, 1002.

[19] Bedford, Bolton, Carrington, and Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

transition state which is probably a trigonal bipyramid,[2] is suitable for considerable π-bonding [20] extending over the vacant $3d$-orbitals of silicon and the filled orbitals of π-symmetry on the phenyl group and the oxygen and chlorine atoms. It is interesting that when such π-bonding is eliminated, as in the chlorides $Pr^i{}_3MCl$, the rate order is as expected for stronger transition-state σ-bonds and/or a smaller repulsive term for germanium; and faster hydrolysis then occurs with germanium than with silicon.

We conclude that the balance of evidence favours the hydrolysis mechanism formulated below for silicon and germanium compounds, rearward attack probably occurring,[21] with bond-making dominant.

$$(H_2O)_n + R_3MCl \longrightarrow \left[\begin{array}{c} R \quad R \\ \diagdown \diagup \\ H{-}O \dots M \dots Cl \\ \vdots \qquad | \\ (H_2O)_{n-1} \dots H \quad R \end{array} \right] \longrightarrow HOMR_3 + {}^+H(H_2O)_{n-1} + Cl^-$$

(I)

If species (I) exists as an intermediate it is formed faster than is measurable with our apparatus.

APPENDIX. *Rapid-reaction apparatus for studies with non-aqueous or partly aqueous solvents.* The main performance characteristics of the apparatus have been summarised elsewhere.[22] Points in the present work which were omitted from the previous description are as follows.

(i) The a.c. output signal shown was rectified and this was used to feed the oscilloscope. It is easier to amplify small conductivity changes and thus investigate easily any given stage in the course of a reaction, when a d.c. signal is used.

(ii) The flow was stopped by arresting the motion of the syringe-driving platform: the usual method of arresting the motion of the rear syringe caused the taps in the all-glass apparatus to become unseated. Checks on stopping time showed that flow-stopping with the pushing platform was as efficient as when the rear syringe was stopped (stopping time <3 msec.).

(iii) There is a considerable temperature rise (up to 3°) when dissimilar solvents (*e.g.*, acetone and ether) are mixed in the apparatus. Temperature equilibration with the apparatus occurred within 10 sec. Thus, for fast reactions it is not important as the reaction will be over before the temperature has changed (the actual temperature of reaction is measured with thermocouples placed in the flowing stream). For reactions of greater duration both reactants were dissolved in acetone; there was then only a slight heat of mixing.

(iv) The oscilloscope traces were calibrated by using standard " high stability " resistors in place of the cell and recording the deflection obtained. These resistances had a capacity similar to that of the microconductivity cell in the apparatus. The microconductivity cell itself was calibrated in terms of hydrogen chloride concentration by using standard solutions of hydrogen chloride in the appropriate media.

Calculation.—The standard resistor traces were used to construct a calibration graph from which the resistance of the cell at intervals during the reaction could be found. As the specific resistance of hydrogen chloride in the media used is not a linear function of the concentration these specific resistance–conductivity curves for hydrogen chloride were determined and then used to convert the cell resistance into hydrogen chloride concentration.

For halide concentrations $<10^{-3}M$, good first-order plots are obtained (curve II) of log $(\alpha_\infty - \alpha_t)$ against time where α_∞ and α_t are solution conductivity at infinity and time t, respectively. The effect of not taking into account the non-linearity of the relation between hydrogen chloride concentration and conductivity at higher concentrations is also shown (curves Ia and b): different initial slopes are evident. For the hydrolysis of compounds R_3GeCl the rate expression is:

$$k_1 t = \frac{x_e}{2a - x_e} . \ln \frac{ax_e - x(a - x_e)}{a(x_e - x)} = Q,$$

[20] Giacometti, *J. Chem. Phys.*, 1955, **23**, 2068.
[21] Sommer, *Angew. Chem. (Internat. Ed.)*, 1962, **1**, 143.
[22] Prince, *Z. Elektrochem.*, 1960, **64**, 13.

where the symbols have their usual significance, and plots of Q against time are linear over more than 90% of the course of the reaction (curve Ic). Sometimes, as in the curve shown, a small intercept is observed and this is attributable to hydrolysis of the halide before kinetic measurement by traces of water remaining in the solvent, even after intensive drying. The rate expression for the reaction of triphenylgermanol with hydrogen chloride similarly took into account the opposing first-order hydrolysis.
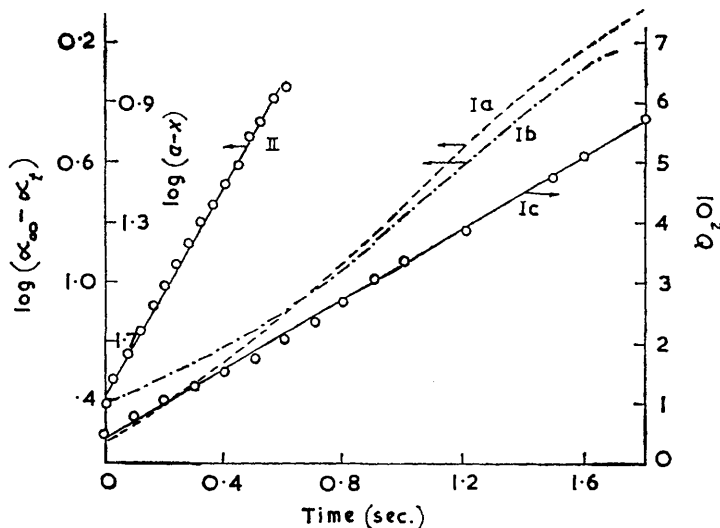
Hydrolysis of chlorotriphenyl-germane (Ia, b, and c) and -silane (II) with acetone ([H_2O] = 2M). Ia, first-order plot [log ($\alpha_\infty - \alpha_t$) against time] with conductivity as a measure of reaction extent; Ib, first-order plot [log (a − x) against time] with hydrogen chloride concentration from conductivity–[HCl] calibration curves; Ic, plot for first-order opposed by second-order reaction, with conductivity–[HCl] calibration curves; II, first-order plot [log ($\alpha_\infty - \alpha_t$) against time] for Ph_3SiCl ([Ph_3GeCl] = 8·65 × 10^{-3}M; [Ph_3SiCl] = 1·87 × 10^{-4}M).

For large numbers of calculations of k_1, time consumption was reduced by electronic digital computing. A programme was prepared which gives k_1 and its standard error and which will vary x_e within narrow limits to maximise the correlation coefficient of the plot; this enables hydrogen chloride concentrations to be determined with greater precision than in a single conductivity measurement at infinite time.

Dielectric constants were measured in the conventional manner by using an RCL bridge and a cell of the Sayce–Briscoe type. The cell and bridge were calibrated with dioxan–water solutions of known dielectric constant.

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