Nucleophilic Cleavage of the Germanium–Oxygen Bond: Acid-catalysed Hydrolysis of Phenoxygermanes

By **John R. Chipperfield** * and **Geoffrey E. Gould**, Department of Chemistry, The University, Hull HU6 7RX

The acid-catalysed hydrolysis of phenoxygermanes in aqueous dioxan proceeds to a position of equilibrium, and kinetic data show that the reaction is at least second-order with respect to water. Tributylphenoxygermane reacts 5 × 10^5 faster than the analogous phenoxysilane. This result is compared with the relative reactivities of other organosilicon and organogermanium compounds.

THE relationship between the rates of nucleophilic substitution of analogous compounds of silicon and germanium depends upon the nature of the group which is replaced. Alkali-catalysed hydrolytic cleavage of M–hydrogen and M–carbon bonds (M = Si or Ge) occurs more quickly for silicon compounds, whereas hydrolysis of M–acetate and M–halogen bonds is faster for germanium compounds.[1] As there are no reports of the relative rates of acid-catalysed nucleophilic cleavage of bonds in analogous compounds of silicon and germanium, we have measured the rates of acid-catalysed hydrolysis of compounds of the type $R_3GeOC_6H_4X$ (R = $[CH_2]_5CH$, Bu, or Ph; X = H or *p*-Me) for comparison with those measured for silicon compounds.[2]

Solvolytic reactions of the compounds R_3MX (M = Ge or Sn; X = halide, OPh, or OAc) differ from those of the analogous silicon compounds in that they proceed to a position of equilibrium.† Phenoxygermanes react much faster than the analogous silicon compounds. As reactions are fast, and proceed to a position of equilibrium, the rate coefficients found for phenoxygermanes are less accurate than those for phenoxysilanes,[2] but they give a reasonable guide to the behaviour of phenoxygermanes.

By optical density measurements on suitable solutions we confirmed that the compounds R_3GeOPh (R = Bu, Ph, or $[CH_2]_5CH$) are hydrolysed incompletely. For Bu_3GeOPh g.l.c. confirmed Bu_3GeOH and PhOH as the hydrolysis products, and for Ph_3GeOPh t.l.c. confirmed Ph_3GeOH and PhOH as the products [equation (1)].

$$R_3GeOPh + H_2O \underset{k_{-2}'}{\overset{k_1'}{\rightleftharpoons}} R_3GeOH + PhOH \qquad (1)$$

The acid catalytic coefficients, k_a, for the hydrolysis of R_3GeOPh were obtained by calculation of the apparent first-order rate coefficient, k_1', from optical density data (see Experimental section): division by $[HClO_4]$ gives k_a. By analogy with Bu_3SiOPh, the reaction probably proceeds by fast formation of a protonated phenoxide [equation (2)], which is then hydrolysed by reaction

$$H^+ + R_3GeOPh \underset{\text{fast}}{\overset{K_{eq}}{\rightleftharpoons}} R_3GeO(Ph)H^+ \qquad (2)$$

with n water molecules. In the hydrolysis of Bu_3SiOPh, water molecules both act as nucleophiles and also remove a proton from the transition state. The hydrolysis of phenoxygermanes is reversible and the basicity of hydroxides increases in the order $R_3SiOH < R_3GeOH < R_3SnOH$.[6] It is likely that $R_3GeOH_2^+$ is formed in the rate-limiting step [equation (3)] and then quickly loses a proton [equation (4)]. The concentration of $R_3GeOH_2^+$ in the products will be low, as K_p is large, R_3GeOH being a very weak base. The observed value of k_a is given by equation (5).

$$nH_2O + R_3GeO(Ph)H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_3GeOH^+_2 + PhOH + (n-1)H_2O \qquad (3)$$

$$R_3GeOH_2^+ \underset{\text{fast}}{\overset{K_p}{\rightleftharpoons}} R_3GeOH + H^+ \qquad (4)$$

$$k_a = k_2K_{eq}[H_2O]^n \qquad (5)$$

In 1% aqueous dioxan containing $2{\cdot}5 \times 10^{-5}$M-$HClO_4$

---

† Failure to observe this fact invalidates some studies in this field.[3–5] For example the position of equilibrium corresponds to only 50% reaction for Bu_3GeOPh in 5% aqueous dioxan containing 2×10^{-3}M-$HClO_4$.

[1] R. H. Prince, M.T.P. International Reviews of Science: Inorganic Chemistry Series One, ed. M. L. Tobe, Butterworths, London, 1972, vol. 9, p. 353.

[2] J. R. Chipperfield and G. E. Gould, preceding paper.

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

[4] M. G. Voronkov and L. A. Zhagata, *Zhur. obshchei Khim.*, 1971, **41**, 1776; *J. Gen. Chem.* (*U.S.S.R.*), 1971, **41**, 1784.

[5] S. C. Chan and F. T. Wong, *Z. anorg. Chem.*, 1971, **384**, 89.

[6] R. West, R. H. Baney, and D. L. Powell, *J. Amer. Chem. Soc.*, 1960, **82**, 6269.

at 30°, k_a for the hydrolysis of Bu_3GeOPh is $1{\cdot}05 \times 10^6$ l mol^{-1} min^{-1}. The k_a value for Bu_3SiOPh under analogous conditions is $2{\cdot}87$ l mol^{-1} min^{-1}. The relative reactivity of Bu_3GeOPh in comparison with Bu_3SiOPh is thus *ca.* 5×10^5. This is much greater than the value of 2×10^3 reported by Prince and Timms[7] for the hydrolysis of $([CH_2]_5CH)_3MOAc$ (M = Si or Ge). Although Prince and Timms relied upon an extrapolation to give relative reactivity, their figure is probably correct within a power of 10. The larger relative rate found for acid-catalysed hydrolysis arises from the change of K_{eq} as well as of k_2 when Si is replaced by Ge. The basicities of the compounds Ph_3MOPh (M = Si, Ge, or Sn) are in the order $Ph_3SiOPh < Ph_3GeOPh < Ph_3SnOPh$,[8] and K_{eq} increases in the order Si < Ge < Sn. If k_2 increases by 2×10^3 for germanium compounds (value of Prince and Timms), K_{eq} would need to increase by $2{\cdot}5 \times 10^2$ ($2{\cdot}4$ pK_a units) to give the *ca.* 5×10^5 increase in reactivity observed, which seems reasonable.

As Bu_3GeOPh and Ph_3GeOPh are both hydrolysed very quickly (a stopped-flow spectrophotometer is needed to measure kinetics) we used the less reactive $([CH_2]_5CH)_3GeOPh$ to study the effect of water concentration on k_a. Table 1 shows that k_a varies with water concentration in a similar way to that found for Bu_3SiOPh. It was not possible to measure k_a at higher water concentrations, as $([CH_2]_5CH)_3GeOPh$ is not very soluble. As shown previously,[2] a plot of $\log k_a + H_0$ (k_a values using $2{\cdot}5 \times 10^{-5}$M-$HClO_4$; H_0 for $0{\cdot}1$M-$HClO_4$ in the appropriate solvent) against $\log [H_2O]$ should be linear with slope n. Over the range 1—25% aqueous dioxan $n = 1{\cdot}8$ (Figure), similar to the value found for Bu_3SiOPh.

TABLE 1

Hydrolysis of $([CH_2]_5CH)_3GeOPh$ catalysed by $HClO_4$ in aqueous dioxan at 30·0°: variation of k_a, β, and k_{-2}' with H_2O concentration

$[H_2O]$/% v/v	1	2	3	5	10	15	20	25
$10^{-2}k_a$/l mol^{-1} s^{-1}	2·4	2·5	2·3	1·9	1·5	2·2	2·8	4·8
β	0·73	0·72	0·72	0·61	0·56	0·55	0·53	0·53
k_{-2}'/l mol^{-1} s^{-1}	4·4	6·1	6·1	8·2	9·9	16·3	23·0	32·8
$[HClO_4 = 2{\cdot}5 \times 10^{-5}M]$								

Observed rate coefficients for the reverse reaction, k_{-2}', can be calculated from the experimental data, and values are shown in Table 1. The value of K_p is given by equation (6), where S is R_3GeOH. If acidity

$$K_p = a_{H^+}c_S f_S / c_{SH^+} f_{SH^+} \qquad (6)$$

functions, h_0, are measured using substituted anilines as indicators and $f_{InH^+}/f_{In} = f_{SH^+}/f_{SH}$, K_p can be written as in equation (7). The rate of the reverse reaction

$$K_p = h_0 c_S / c_{SH^+} \qquad (7)$$

is given by equations (8)—(10), leading to

Rate of reverse reaction

$$= k_{-2}[PhOH][R_3GeOH_2^+][H_2O]^{n-1} \qquad (8)$$

$$= k_{-2}[PhOH]h_0 c_S [H_2O]^{n-1}/K_p \qquad (9)$$

$$= k_{-2}'[PhOH][R_3GeOH] \qquad (10)$$

equation (11). A graph of $\log k_{-2}' + H_0$ against $\log [H_2O]$

$$k_{-2}' = k_{-2}h_0[H_2O]^{n-1}/K_p \qquad (11)$$

should be linear with slope $n - 1$. The Figure shows that a good straight line is obtained with $n - 1 = 2{\cdot}3$.

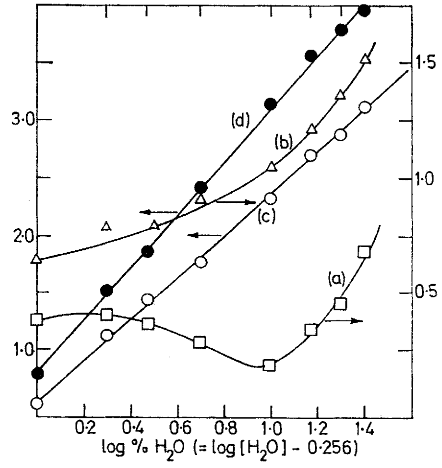
If the principal product were $R_3GeOH_2^+$ rather than R_3GeOH the rate of the reverse reaction would be given by equation (12), where $k_{-2}' = k[H_2O]^{n-1}$, and a plot of

Rate of reverse reaction =

$$k[R_3GeOH_2^+][PhOH][H_2O]^{n-1} \qquad (12)$$

$\log k_{-2}'$ against $\log [H_2O]$ should be linear and not curved as found.

It appears that there are more water molecules participating in the reverse than in the forward reaction. This anomaly probably results from the effects of change of solvent polarity upon k_2 and k_{-2}. Increase in solvent polarity will tend to decrease k_2 and k_{-2} as both refer to (ion + neutral molecule) reactions. As the fraction of reaction, β (Table 1), decreases with rise in water concentration (this is the opposite to the prediction from the law of mass action),



Acid-catalysed hydrolysis of $([CH_2]_5CH)_3GeOPh$ in aqueous dioxan at 30·0°; (a) $\log k_a - 2$; (b) $\log k_{-2}'$; (c) $\log k_a + H_0 - 2$; (d) $\log k_{-2}' + H_0$

---

[7] R. H. Prince and R. E. Timms, *Inorg. Chim. Acta*, 1967, **1**, 129.

[8] N. A. Matwiyoff and R. S. Drago, *J. Organometallic Chem.*, 1965, **3**, 393.

k_2 is lowered more than k_{-2} by increase in the solvent polarity. As shown before[2] the slopes of plots of $\log k_a + H_0$ against $\log [H_2O]$ give the minimum number of molecules of water involved. More water molecules may participate if increase in solvent polarity is considered to decrease k_2. For example to give a slope of **3** for the plot of $\log k_a + H_0$ against $\log [H_2O]$ $k_a^{25\%}/k_a^{5\%}$ should be 16 rather than 2·5 as measured. Retardation of rate by a factor of 6·5 is a reasonable figure for a change in dielectric constant from 3·8 (5% aqueous dioxan) to 14·0 (25% aqueous dioxan).

The relative rate of acid-catalysed hydrolysis, k_a^{rel}, of p-$MeC_6H_4OGeBu_3$ and Bu_3GeOPh is 0·9. For the analogous phenoxysilanes $k_a^{rel} = 1{\cdot}4$. Electron-releasing groups will lower k_2 and increase K_{eq}. As k_a is proportional to k_2K_{eq}, either the two effects almost cancel each other for phenoxygermanes, or k_2 and K_{eq} must be insensitive to electrical effects. Experiments with the compounds R_3GeOPh (R = Bu or Ph) show that k_a is sensitive to the nature of R. Table 2 shows the relative rates of acid-catalysed hydrolysis of Bu_3MOPh in comparison with Ph_3MOPh (M = Si or Ge). Also included is the relative rate of hydrolysis of Bu_3SiOAc in comparison with Ph_3SiOAc. The largest relative rate is found for the germane hydrolysis. It is not easy to explain why the relative rate of hydrolysis of tributyl- and triphenyl-phenoxygermane should be greater than the relative rates of hydrolysis of the analogous acetoxy- and phenoxy-silanes. Changes in the amount of π-bonding present and the altered distribution in phenoxygermanes could alter both K_{eq} and k_2. Detailed discussion of these effects is not profitable without further data.

TABLE 2

Relative rates of hydrolysis of derivatives of silicon and germanium, R_3MX, in aqueous dioxan

M	X	$[H_2O]$/ % v/v	t/°C	Catalyst	$k_a^{Bu_3MX}/k_a^{Ph_3MX}$
Si	OPh	5	30·0	$HClO_4$	3·8 [a]
Si	OAc	5	25·0	None	5·9 [b]
Ge	OPh	1	30·0	$HClO_4$	11·3

[a] Ref. 2. [b] Ref. 6.

EXPERIMENTAL

Tributylphenoxygermane was prepared by stirring tributylgermanol and phenol together at 180° for 4 days. Distillation at 0·2 mmHg yielded tributylphenoxygermane, which was purified by further vacuum distillation. Tributyl-p-methylphenoxygermane was prepared in a similar manner. Phenoxytriphenylgermane was made in a similar manner to triphenoxysilane.[2] Tricyclohexylphenoxygermane was prepared by boiling tricyclohexylgermanol {produced from $([CH_2]_5CH)_3GeCl$ by hydrolysis with KOH in ethanol} with phenol in benzene. Molecular sieves (grade 4A) were added to absorb the water formed.

The purity and identity of all phenoxygermanes was assessed by i.r., u.v., n.m.r., and mass spectroscopy. There were no detectable impurities except sometimes a little (<1%) of the parent phenol. G.l.c. analysis of the liquid tributyl derivatives showed that compounds were >99% pure.

Rate Measurements.—Rate coefficients, k_a, for the acid-catalysed hydrolysis of tricyclohexylphenoxygermane were measured by the spectrophotometric method previously described.[2] Acid-catalysed hydrolysis of tributyl- and triphenyl-phenoxygermanes was rapid, and rate coefficients were obtained by using a stopped-flow spectrophotometer.[9]

Whereas hydrolysis of phenoxysilanes proceeds to completion, phenoxygermanes are only partially hydrolysed and the appropriate rate equation[10] was used to calculate k_a values from spectrophotometric data. These calculations are laborious, and a suitable computer program was written and used. Approximate k_a values can be obtained from spectrophotometric data if the extinction coefficients of reactants and products are known. Consider reaction (13).

$$A \xrightleftharpoons[k_{-2}']{k_1'} B + C \qquad (13)$$

If initially [A] = a, at time t [B] = [C] = x, and finally [B] = [C] = x_e, the integrated rate equation is equation (14).[10] If the overall fraction of reaction,

$$\frac{\ln\{[ax_e + x(a - x_e)]/a(x_e - x)\}}{(2a - x_e)/x_e} = k'_1t \qquad (14)$$

$x_e/a = \beta$, the observed half-life, $t_{\frac{1}{2}}^{obs}$ (when $x = x_e/2$), is given by equation (15). The value of $t_{\frac{1}{2}}^{obs}$ is easily found

$$k_1't_{\frac{1}{2}}^{obs} = \frac{\ln(3 - \beta)}{(2 - \beta)/\beta} \qquad (15)$$

from the observations of optical density as it is the time at which half the change has taken place. The value of β can be calculated from the initial and final optical densities, OD_0 and OD_∞, and the ratio of extinction coefficients of reactant and product, ε_r and ε_p, by equation (16). Molar

$$\beta = (OD_0 - OD_\infty)[1 - (\varepsilon_p/\varepsilon_r)]/OD_0 \qquad (16)$$

extinction coefficients are given in Table 3. Values of k_{-2}' can be calculated from (17). Values of k_a calculated

$$k_{-2}' = k_1'(1 - \beta)/a\beta^2 \qquad (17)$$

by the two methods agreed well. Only the ratio $\varepsilon_p/\varepsilon_r$ is needed to calculate k_a, whereas absolute values are necessary to calculate k_{-2}' as equation (17) includes a (= OD_0/ε_rl, where l = path length).

TABLE 3

Extinction coefficients of phenoxygermanes and of phenol at the same wavelengths

Compound	λ/nm	$10^{-2}\varepsilon_{compound}$/ l mol^{-1} cm^{-1}	$10^{-2}\varepsilon_{phenol}$/ l mol^{-1} cm^{-1}
$([CH_2]_5CH)_3GeOPh$	285·5	6·66	1·28
Bu_3GeOPh	285·5	5·78	1·28
p-$MeC_6H_4OGeBu_3$	293·5	10·0	5·41
Ph_3GeOPh	280	11·5	14·7

We are grateful to the Germanium Research Committee for a gift of $GeCl_4$.

[3/332 *Received*, 13*th February*, 1974]

---

[9] J. R. Chipperfield, *Chem. and Ind.*, 1970, 530.

[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 2nd edn., 1961, p. 186.