Figure 1. Gain spectrum of 7-hydroxy-4-methylcoumarin (5 × 10^{-3} M in ethanol); HCl concentration ≈ 0.15 N.
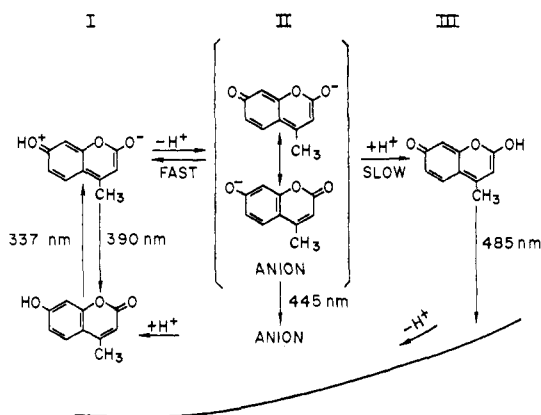

Figure 2. Excited state reactions of 7-hydroxy-4-methylcoumarin.

occurs in two distinct consecutive steps, each of which is an excited-state reaction in which the *products* are also in excited states.

It was found, somewhat unexpectedly, that the shape of the gain spectrum[7] of an acidified solution of I depended on the pump power of the nitrogen laser (Figure 1). There was relatively less gain at high pump power in the region near 400 nm. This observation suggests that an absorbing species is being produced which could account for the decrease in gain in the 400-nm region. Since one would expect I to become both a stronger acid (at the hydroxyl group) and a stronger base (at the carbonyl group) in the excited state I*[8] (see Figure 2), the first excited-state reaction would be a rapid reversible loss of a proton to form the excited anion II* (this is a unimolecular reaction and would be expected to be relatively independent of hydrogen ion concentration). This rapid step is then followed by a proton transfer from the solvent to the excited anion II* to form the phototautomer, III*. (Previous studies[3] showed that the rate of producing III* is dependent on the acid concentration.) The fluorescence of III* at 485 nm leads to the ground state, III, which is "unstable" in this solvent environment. The ground state of the anion, II, is also "unstable" in this solution (no absorption due to II

(7) The apparatus and procedure for obtaining gain spectra are described by C. V. Shank, A. Dienes, and W. T. Silfvast, *Appl. Phys. Lett.*, 17, 307 (1970).

(8) A. Weller, *Progr. React. Kinet.*, 1, 188 (1961); E. Vander Donckt, *ibid.*, 5, 273 (1970).

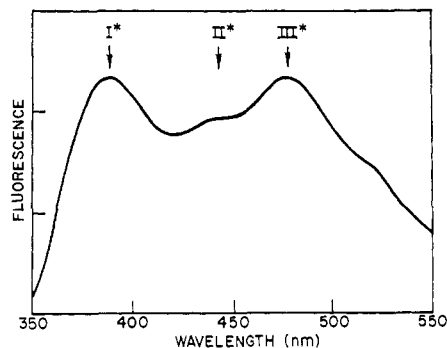Figure 3. Spontaneous fluorescence spectrum of I (2.5 × 10^{-5} M) in slightly acidified (2.0 × 10^{-5} M HClO₄) aqueous 95% methanol.

could be detected by spectrophotometry). However, the reaction II + H⁺ → I should proceed more slowly than the ionization of III (the former reaction is bimolecular, the latter is unimolecular), and, at higher pump power, there would be a transient accumulation of ground state anions II which absorb beyond 400 nm and thus the gain would be decreased in that region.

Further evidence for this scheme was obtained from the spontaneous fluorescence spectrum of I in very weakly acidic media (see Figure 3) where it was found that I*, II*, and III* all emit from the same solution. In this case, presumably, the water and acid concentrations are sufficiently low so that the fluorescence from I* and II* compete successfully with the deprotonation and protonation reactions, respectively.

It should be noted that this example of a two-step phototautomerism is to be distinguished from the cooperative one- or two-proton transfers found in the prototropy of the excited state of salicylic acid derivatives[8] and 7-azaindole,[9] respectively. The utility of gain spectroscopy in probing other adiabatic photoreactions[10] is currently being investigated in related systems.

(9) C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, 63, 253 (1969).

(10) Th. Forster, *Pure Appl. Chem.*, 24, 443 (1970).

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One-Step and Two-Step Displacements at Silicon

Sir:

The hydrolysis of aryloxytriphenylsilanes in 60% acetonitrile–40% water is second order in hydroxide ion at low base concentrations but becomes first order at high base concentrations. This shows that the rate-determining step changes as a function of hydroxide ion concentration. The reaction therefore involves at least two steps and passes through an intermediate, presumably the "expanded octet" adduct.[1,2]

(1) C. G. Swain, R. M. Esteve, and R. H. Jones, *J. Amer. Chem. Soc.*, 71, 965 (1949).
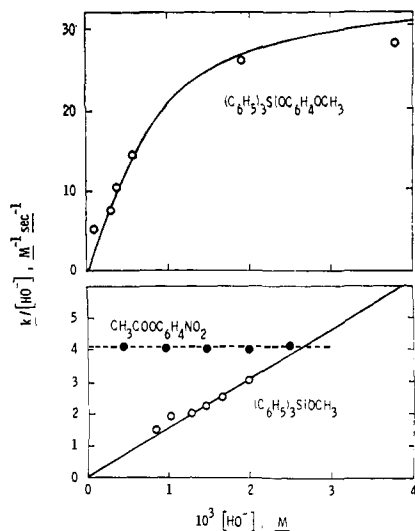
Figure 1. Plots of $k/[HO^-]$ vs. $[HO^-]$ for hydrolysis of p-methoxyphenoxytriphenylsilane (upper part), methoxytriphenylsilane (lower part, open circles), and p-nitrophenyl acetate (lower part, filled circles).

In contrast, the methanolysis of methoxyphenoxymethylphenylsilane proceeds by concerted formation and fission of entering-group and leaving-group silicon–oxygen bonds, rather than through an "expanded octet" intermediate compound, as shown by the observation that formate ion and formic acid buffer components act in combination to catalyze the displacement.
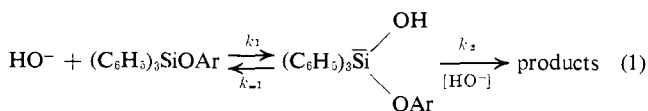
Table I and the upper part of Figure 1 show kinetic

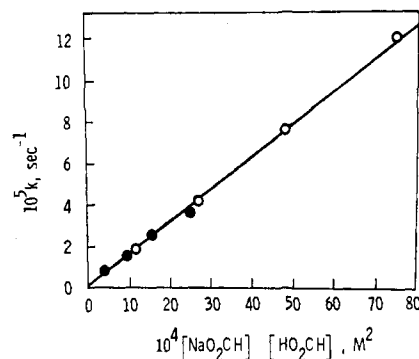**Table I.** First-Order Rate Constants for Hydrolysis of Various Substrates in 60:40 (v:v) Acetonitrile:Water

	10^3k, sec^{-1} $(10^3[HO^-], M)$	
$CH_3OSi(C_6H_5)_3{}^a$	p-$CH_3OC_6H_4OSi$-$(C_6H_5)_3{}^b$	p-$NO_2C_6H_4$-$OCOCH_3{}^c$
0.081 (0.324)	0.584 (0.109)	0.99 (0.24)
1.31 (0.817)	2.10 (0.274)	3.04 (0.74)
2.02 (1.03)	3.98 (0.380)	5.15 (1.24)
2.65 (1.29)	7.97 (0.547)	7.11 (1.74)
3.40 (1.50)	49.5 (1.90)	9.43 (2.24)
4.19 (1.67)	107 (3.80)	
6.08 (1.97)		

^{a} Temperature $20.00 \pm 0.03°$. ^{b} Temperature $26.10 \pm 0.05°$; no effect of added sodium chloride to maintain ionic strength constant at 0.01 M. ^{c} Temperature $25.00 \pm 0.05°$.

data for the hydrolysis of p-methoxyphenoxytriphenylsilane and a plot of $k/[HO^-]$ vs. $[HO^-]$, which should be constant for a reaction which is first order in hydroxide ion and linearly increasing for a reaction which is second order in hydroxide ion. Below about 2×10^{-3} M hydroxide ion, the reaction is second order, but becomes first order in the neighborhood of 3×10^{-3} M hydroxide ion. This behavior is consistent with the scheme of eq

$$HO^- + (C_6H_5)_3SiOAr \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (C_6H_5)_3Si \overset{OH}{\underset{OAr}{\diagup}} \xrightarrow[[HO^-]]{k_2} products \quad (1)$$

Figure 2. Linear dependence of rate constants for methanolysis of methoxyphenoxymethylpenylsilane on acid–base product of formate buffers. The acid/base ratio is 3 for open circles and 1 for filled circles.

1, which yields the kinetic law of eq 2 upon application

$$k = k_1 k_2 [HO^-]^2/(k_{-1} + k_2[HO^-]) \quad (2)$$

of the steady-state assumption to the intermediate. The solid line in the upper part of Figure 1 is a plot of eq 2 with $k_1 = 40$ M^{-1} sec^{-1} and $(k_2/k_{-1}) = 900$ M^{-1}.
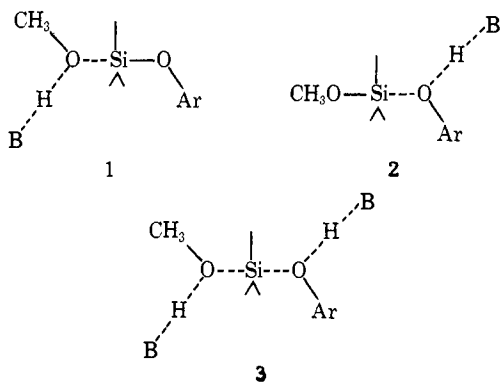
Table I and the lower part of Figure 1 show data for the hydrolysis of methoxytriphenylsilane. This reaction, studied by loss of the tritium-labeled methoxyl group into the solvent rather than by the spectrophotometric technique used above, exhibits a second order in hydroxide ion throughout the range of concentrations studied. The change in rate-determining step should occur only at higher base concentrations because of the poorer leaving group of this substrate.

To ascertain that no characteristics of the medium (hydroxide activities, etc.) were giving rise to the kinetic behavior observed, the rate of hydrolysis of p-nitrophenyl acetate was determined. The behavior is entirely normal (simple first order in hydroxide ion; Table I, lower part of Figure 1).

We conclude that the basic hydrolysis of aryloxysilanes (and probably other Si–O compounds) proceeds through an addition intermediate which requires base catalysis for its decomposition to products.

The *methanolysis* of aryloxysilanes is known to be general-base catalyzed by a protolytic mechanism (the aryloxide leaving group is itself a catalyst, excluding a nucleophilic mechanism).[3] This is consistent with an expanded-octet mechanism having either formation (transition-state structure 1) or decomposition (transition-state structure 2) of the "Si-5" intermediate[2] rate determining. The concerted displacement route (transition-state structure 3) is expected to exhibit simultaneous acid and base catalysis but solvent methanol might compete successfully as an electrophile with a relatively weak acid, so that the observation of simple general-base catalysis in acetate buffers[3] ($pK_a = 9.44$ in methanol) is also in agreement with a concerted mechanism. As a more stringent test, rates of methanolysis of methoxyphenoxymethylphenylsilane were determined in sodium formate–formic acid buffers ($pK_a = 7.75$ in methanol). As the data of Table II show, the rate increases more rapidly than does the concentration of either buffer com-

(2) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(3) R. L. Schowen and K. S. Latham, Jr., *J. Amer. Chem. Soc.*, **88**, 3795 (1966).

1   2

3

Dr. H. Jayaraman for his measurements on *p*-nitro-phenyl acetate.

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Table II. First-Order Rate Constants for the Methanolysis of 5×10^{-4} *M* Methoxyphenoxymethylphenylsilane in Buffered Methanol at $25.00 \pm 0.01°$

[HO$_2$CH], *M*	[NaO$_2$CH], *M*	$10^5 k$, sec^{-1}
0.0600	0.0200	1.89 ± 0.09
0.0900	0.0300	4.06 ± 0.08
0.1200	0.0400	7.59 ± 0.19
0.1500	0.0500	12.0 ± 0.04
0.0200	0.0200	0.81 ± 0.02
0.0300	0.0300	1.45 ± 0.05
0.0400	0.0400	2.60 ± 0.06
0.0500	0.0500	3.58 ± 0.26

^{a} Ionic strength maintained at 0.05 *M* with added lithium perchlorate. Error limits are standard deviations.

ponent. Figure 2 shows that the rate law of eq 3 is

$$v = k_{BBH}[R_3SiOAr][NaO_2CH][HO_2CH] \qquad (3)$$

obeyed with $k_{BBH} = 1.62 \pm 0.08 \times 10^{-2}\ M^{-2}\ \text{sec}^{-1}$. This is in agreement with structure **3** and the displacement is therefore concerted.

To reconcile simultaneous acid–base catalysis with an Si-5 intermediate would require either (a) that formic acid interacts with the O of Si–OAr to catalyze nucleophilic attack, in formation of the intermediate, although this oxygen is much less basic than formate ion in both R_3SiOAr and the intermediate[4] or (b) that formate ion removes the proton of a rapidly and reversibly formed methanol adduct of the reactant as the Si–OAr bond breaks. The latter would necessitate that this oxonium-like proton not be rapidly transferred to an adjacent solvent molecule but that it await the arrival of formate ion; this seems quite unlikely. We therefore conclude that this reaction is concerted.

The initially surprising conclusion that the methanolysis and hydrolysis reactions of very similar compounds proceed by different mechanisms is probably related to the equally surprising base catalysis of expulsion of the good leaving group aryloxide in the hydrolysis reaction (eq 1). The base may catalyze a critical pseudorotation of the addition compound. Lack of opportunity for such catalysis in methanol may open the way for competition by the concerted mechanism.

(4) *Cf.* W. P. Jencks, *Chem. Rev.*, 72, 702 (1972).

Trapping of Electrochemically Generated Cyclopropenyl and Cycloheptatrienyl Anions by Charged Reagents

Sir:

We have described[1] the use of electrochemical reduction to generate the cycloheptatrienyl anion and a series of cyclopropenyl anions and the use of the electrochemical data in the determination of their basicities. The anions were generated from the corresponding cations, and two clear waves could be discerned by cyclic voltammetry corresponding to reduction first to the radical and then to the anion. However, controlled potential electrolysis at either the first or second wave afforded only the reductive dimer, a bis(cycloheptatrienyl) or bis(cyclopropenyl). At the first wave this is the expected product from dimerization of the radical, but at the second wave it corresponds to reaction of the anion with the starting cation. Remarkably, this was the only product at the second wave even when hydroxylic solvents, such as acetic acid, were employed in an attempt to capture the anion by protonation.

This result suggested that the trapping of the products occurs in the inner Helmholtz plane of the electrical double layer at the electrode and that solvent is not present in this region. Accordingly, to put an acidic reagent at the electrode surface we have used a novel supporting electrolyte, guanidinium perchlorate,[2] and have found that it is able to trap these anions by protonation even when it is present in low nominal concentration relative to more acidic solvents. Some trapping of the anions by protonation was also observed using triethylamine hydrobromide or dimethylamine hydrochloride as electrolytes, but they were not usable over as wide a negative potential range as is guanidinium ion and were thus not examined further. The result has some general significance for both mechanistic and synthetic organic electrochemistry.
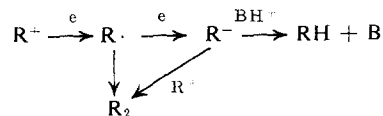
The electrolyte was prepared from guanidine hydrochloride in methanol by reaction with stoichiometric amounts of KOH (filter) and then perchloric

(1) R. Breslow and W. Chu, *J. Amer. Chem. Soc.*, 95, 411 (1973).
(2) K. V. Titova and Y. Ya Rosolovskii, *Zh. Neorg. Khim.*, 10, 446 (1965).