cm² were used. All studies were in acetonitrile with 0.2 M tetraethylammonium perchlorate as supporting electrolyte. All potentials are referred to the aqueous sce.

9,10-Diphenylanthracene (DPA) was selected as a hydrocarbon whose cation radical is quite stable yet interacts with a variety of nucleophiles at rates which are in a favorable range to demonstrate the ECE process.

In RDE voltammetry, the quantity $(i_L/\omega^{1/2}C)$ is directly related to the number of electrons transferred. As usual, i_L is the limiting current, C is the bulk concentration of electroactive species, and $\omega = 2\pi N$, where N = revolutions per second. The quantity $(i_L/\omega^{1/2}C)$ is independent of ω in the absence of coupled (ECE type) chemical reactions. A plot of $(i_L/\omega^{1/2}C)$ *vs.* $\omega^{1/2}$ is a horizontal straight line corresponding to a n_1 electron process. This is the limiting behavior of DPA in the absence of nucleophiles shown as the lower dotted line of Figure 1 (where DPA acts as a model one-electron oxidation). If an intervening chemical reaction (ECE) is so rapid that it cannot be "outrun" in the range of accessible rotation rates, then $(i_L/\omega^{1/2}C)$ *vs.* $\omega^{1/2}$ will again be a horizontal straight line but limiting proportional to $(n_1 + n_2)$ electrons of the over-all ECE reaction. This is seen in Figure 1 as the upper dotted line corresponding to two-electron behavior.

The quantity n_{obsd} plotted in Figure 1 is given by

$$n_{\text{obsd}} = \frac{(i_L/\omega^{1/2}C)\,(\text{DPA} + \text{nucleophile})}{(i_L/\omega^{1/2}C)\,(\text{DPA alone})}$$

By using the ratio of $(i_L/\omega^{1/2}C)$ for DPA plus nucleophile, compared to DPA alone (which behaves as a one-electron process), n_{obsd} is a direct measure of the average number of electrons transferred and is normalized for solution viscosity, diffusion coefficient, concentration, and electrode area. A more thorough discussion of this and other limiting current comparisons at the RDE is contained in previous literature.[13,17,18]

The experimental points in Figure 1 correspond to the actual behavior of DPA in the presence of the indicated substituted pyridines as nucleophiles. It is clear that the passage of the second electron is competing with the mass transfer since n_{obsd} gradually changes from nearly 2.0 electrons/mole of DPA at low rotation rates to slightly greater than 1 electron/mole at high rotation rates. On the basis of this observation, *the hypothesis that two electrons are transferred as a unit is untenable;* clearly the chemical interaction allowing the second electron to be transferred can be exceeded at high rotation rates.

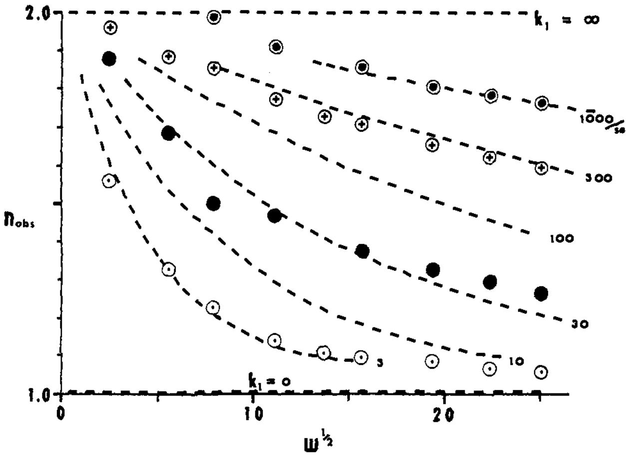

Figure 1. Rate of DPA·⁺ interactions with pyridine nucleophiles: ◉, 0.50 mM 9,10-DPA + 25 mM 4-methylpyridine; ⊕, 0.50 mM 9,10-DPA + 25 mM pyridine; ●, 0.50 mM 9,10-DPA + 25 mM 4-acetoxypyridine; ⊙, 0.50 mM 9,10-DPA + 25 mM 4-cyanopyridine. All solutions were 0.20 M tetraethylammonium perchlorate in acetonitrile plus the constituents given above.

To provide a semiquantitative framework for the rates of the chemical interactions, the $n_{\text{obsd}} - \omega^{1/2}$ behavior was calculated *via* Feldberg's digital simulation techniques for an ECE reaction and several finite values for chemical rate constants.[18] For interaction of the cation radical of DPA with various pyridines, the rate expression is of the form

$$-(\text{DPA}\cdot^+)/dt = k_2(\text{DPA}\cdot^+)(\text{pyridine}) = k_1(\text{DPA}\cdot^+)$$

where k_1 is a pseudo-first-order rate constant for excess nucleophile. In order to construct the curves from Feldberg's data, the diffusion coefficient for DPA was taken as 1.76×10^{-5} cm²/sec. The dotted curves of Figure 1 show these calculations for values of k_1 from 3 to 1000 sec^{-1} as indicated on each curve. The experimental points follow the theoretical curves rather closely. More importantly, they are precisely in the order and have roughly the expected magnitudes for interaction of the cation radical with nucleophiles of varying electronegativity. Thus DPA·⁺ interacts most rapidly with 4-methylpyridine and least rapidly with 4-cyanopyridine, as would be expected from linear-free energy relationships of molecular orbital predictions of these substituents. By interpolation of the data of Figure 1, one can easily estimate the magnitude of the pseudo-first-order rate of the chemical interaction.

Many aromatic hydrocarbons and a variety of nucleophiles give similar results at the RDE, and the reaction is a general one for such substitution reactions (cyanation, hydroxylation, etc.). Further studies of this interaction will be reported soon.

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Concurrent General Acid and General Base Catalysis of Esterification

Sir:

In the course of examining the rates of lactonization of a series of phenolic acids (**1**),[1,2] we found the reaction to proceed at a measurable rate in aqueous solution even at pH 7 (30°) and to obey a composite rate

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[1] For the origin of this study, see J. W. Thanassi and L. A. Cohen, *Biochim. Biophys. Acta*, **172**, 389 (1969).

[2] These compounds were prepared by acid-catalyzed alkylation of the corresponding *para*-substituted phenol with methyl 3,3-dimethylacrylate, followed by alkaline saponification of the lactone, according to the general procedure of J. Colonge, E. LeSech, and R. Marey, *Bull. Soc. Chim. Fr.*, 776 (1957). Acceptable elemental analyses were obtained in all cases.

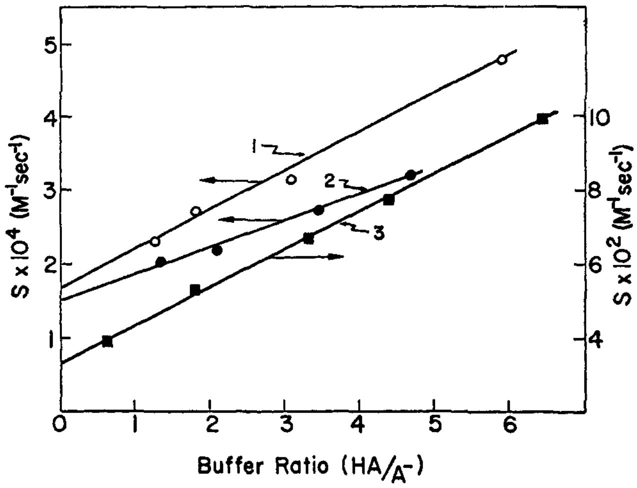


Figure 1. Plots of apparent second-order rate constants *vs.* buffer ratio for compounds **1**, **2**, and **3** (see legend of Table I for derivation of S).

law (eq 1), in which α is the fraction of undissociated

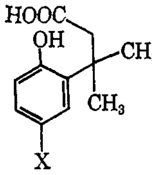
$$k_{\text{obsd}} = \alpha(k_0 + k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{\text{HA}}[\text{HA}] + k_{\text{A}^-}[\text{A}^-]) \quad (1)$$

phenolic acid at a given pH. Independent catalysis by both general acid and general base species was observed in phosphate, imidazole, and Tris buffers, in addition to those of acetate and formate (Table I, Figure 1). Although dihydrocoumaric acid is known to lactonize completely in strongly acidic media,[3] the introduction of the side-chain *gem*-dimethyl substituent increases the rate to such an extent (presumably due to conformational restraint) that the reaction can be studied at pH values at which the contribution to the over-all rate due to buffer catalysis exceeds that due to hydronium ion.

Table I. Representative Rate Constants for Lactonization[a]

Compound	$10^2k_{\text{H}_3\text{O}^+}$,[b] M^{-1} sec^{-1}	10^5k_{HA},[c] M^{-1} sec^{-1}	$10^4k_{\text{A}^-}$,[c] M^{-1} sec^{-1}	10^5k_0,[d] sec^{-1}
1 (X = H)[e]	2.72	5.10	1.72	3.63
2[f]	6.86[g]	3.45	1.54	
3[h]	3350	1020	337	

[a] All reactions were followed spectroscopically by monitoring the appearance of lactone. [b] Evaluated from the slope of a plot of k_{obsd} *vs.* [H_3O^+]. [c] Evaluated from eq 1 by first obtaining the slopes (S) of plots of k_{obsd} *vs.* buffer anion concentrations at different buffer ratios; k_{HA} and k_{A^-} are obtained from the slope and intercept of a secondary plot of (S) *vs.* the corresponding buffer ratio [HA]/[A^-]. [d] Determined from the intercept of a plot of k_{obsd} *vs.* buffer anion concentration. [e] At 30° in formate buffer, μ = 0.3 M with NaCl. [f] At 60° in formate buffer, μ = 0.3 M with NaCl. [g] Taken from ref 4a; at 60° in 9% ethanol–water, μ = 1.0 M with KCl. [h] At 20° in acetate buffer, μ = 0.3 M with NaCl.



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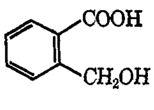

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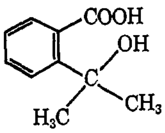

3

The lactonization of 2-hydroxymethylbenzoic acid (**2**) has been reported to be subject to general acid catalysis by phosphate buffer,[4a] and that of **3** by acetate buffer.[4b] In addition to the case of **1**, we have found the lactonizations of **2** and **3** to be subject to concurrent general acid *and* general base catalysis, and to follow the same rate law (eq 1). In Table I are listed the component rate constants for **1** (X = H), **2**, and **3**. A plot of the apparent second-order rate constants (obtained from plots of k_{obsd} *vs.* buffer anion concentration) *vs.* the buffer ratios, for these three cases, is shown in Figure 1.[5] Using four to eight variations of the *para* substituent in **1**, Hammett ρ values were obtained for the several types of catalysis, as shown in Table II, together with activation parameters and solvent deuterium isotope effects.

Table II. ρ Values, Activation Parameters, and Solvent Deuterium Effects

Catalyst	ρ[a]	ΔH,[b] kcal/mol	ΔS,[b] eu	k_H/k_D[b]
H_3O^+	−1.68	14	−20	0.9
HCOOH	−1.50	15	−28	1.9
$HCOO^-$	−0.75	15	−27	2.2
CH_3COOH	−1.50			
CH_3COO^-	−0.80			
H_2O	−0.55			

[a] Based on a least-squares analysis of rate constants, using four to eight variations of X in **1**. [b] Similar values were obtained for several variations of X in **1**.

We consider the observations of concurrent general acid and general base catalysis, in conjunction with the magnitudes of the ρ values and the activation parameters, to be best explained by mechanisms **4** and **5**, in which the rapid, reversible formation of a tetrahedral intermediate (T), from the hydroxy acid (M), is followed by its rate-limiting collapse to lactone (eq 2 and 3).[6] Presumably, the same lactonization mechanism would apply to **2** and **3**.

$$\text{M} \underset{}{\overset{K}{\rightleftharpoons}} \text{T} \xrightarrow{k} \text{lactone} + \text{H}_2\text{O} \quad (2)$$

$$\text{rate} = k_{\text{obsd}}[\text{T}] = Kk_{\text{obsd}}[\text{M}] \quad (3)$$

The magnitude of ρ for the reaction may be considered the sum of two components, ρ_K and ρ_k, in which ρ_K represents the dependence of K on the nucleophilicity (or basicity) of the phenolic hydroxyl group and ρ_k is the ability of the *para* substituent to assist or retard the breakdown of the tetrahedral intermediate. Whereas ρ_K should be negative and independent of external catalysts, ρ_k should be negative only for general acid catalysis, since electron release from X could promote the rate-limiting cleavage of a carbon–oxygen bond (**4**). For general base catalysis, on the other hand, ρ_k should be positive, since electron withdrawal by X would assist in the removal of a proton (**5**). The less negative

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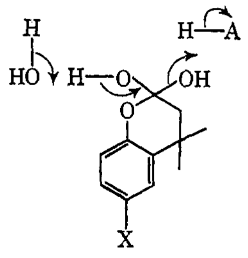
(3) H. Hochstetter, *Ann.*, **226**, 355 (1884).

(4) (a) D. P. Weeks, as cited in J. F. Bunnett and C. F. Hauser, *J. Amer. Chem. Soc.*, **87**, 2214 (1965); (b) D. P. Weeks and X. Creary, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN-64.

(5) In none of the plots was there an indication of a third-order term, which could arise from the concerted action of buffer acid and base.

(6) A mechanism similar to **4** would be applicable to hydronium ion catalysis, the deuterium isotope effect of 0.9 indicating protonation of the tetrahedral intermediate to be more complete prior to its breakdown.

value of ρ, obtained for general base catalysis (Table II), is in accord with these considerations. The proposed mechanisms are supported further by the values of the solvent deuterium isotope effects. The magnitudes of the entropies of activation for hydronium ion catalysis (−20 eu) and for general acid–base catalysis (*ca.* −30 eu) suggest the additional participation of a molecule of water in each case.



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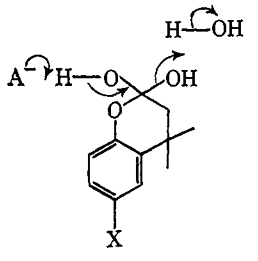

5

Although numerous examples exist of general acid or general base catalysis of reactions of carboxylic acid derivatives,[7] concurrent catalysis by both species is more commonly known at the aldehyde level of oxidation, where tetrahedral intermediates are significantly more stable.[8] An early study of the esterification of acetic acid in methanol has provided the only data suggestive of general acid catalysis of such a reaction.[9] To our knowledge, the lactonizations of **1**, **2**, and **3** constitute the first examples of concurrent general acid and general base catalyzed esterifications.

(7) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).

(8) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

(9) A. C. Rolfe and C. N. Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

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A Novel γ-Induced Reduction with Trichlorosilane. Dialkyl Ether from Alkyl Aliphatic Carboxylate

Sir:

In the course of our study[1] on the γ-induced addition of trichlorosilane to vinyl acetate, we have found that the 1 : 1 adduct (2-trichlorosilylethyl acetate) is reduced to 2-trichlorosilylethyl ethyl ether under the conditions used. This finding indicates the possibility that a carboxylic ester, in general, can be reduced to an ether, the carbonyl group being converted to methylene. Reported here are the scope and sequence of this novel reaction. A degassed mixture of alkyl aliphatic carboxylate and trichlorosilane (1 : 6 molar ratio) in a fused tube was subjected to γ irradiation of 9.6 MR at a dose rate of 0.6 MR/hr at room temperature. After the irradiated product was dissolved in carbon tetrachloride, the ether was identified and estimated by glpc (FID). The results are summarized in Table I. Under the same conditions, however, esters RCOOR′ (R = CH_3; R′ = $CH_2CH_2C_6H_5$, $CH_2C_6H_5$, C_6H_5; or R = $CH_2C_6H_5$, C_6H_5; R′ = C_2H_5) and ethyl thiolacetate ($CH_3COSC_2H_5$) were recovered as such almost quantitatively after the irradiation. Therefore, it can be concluded that only alkyl aliphatic carboxylates can be reduced by this method.

$$Cl_3SiCH_2CH_2OCOCH_3 \xrightarrow{Cl_3SiH} Cl_3SiCH_2CH_2OCH_2CH_3$$

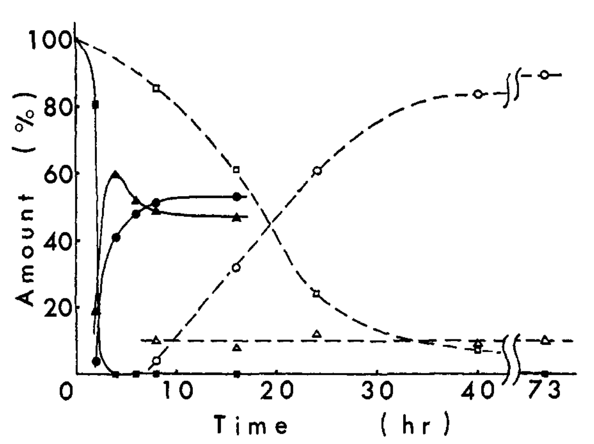

Figure 1. Reduction of ethyl acetate with trichlorosilane for various irradiation times: (- - -) 0.15 MR/hr; (——) 0.45 MR/hr; (□, ■) [ether unchanged]; (○, ●) [ester produced]; (△, ▲) (100 − [ester unchanged] − [ether produced].

Table I. Reduction of RCOOR′ with Trichlorosilane under γ Irradiation

R	R′	Yield of RCH_2OR', %
H	n-C_3H_7	77
CH_3	C_2H_5	85
CH_3	n-C_3H_7	99
C_2H_5	CH_3	100
C_2H_5	C_2H_5	100
C_2H_5	n-C_3H_7	96

To find a clue to the reaction scheme, a mixture of acetone and trichlorosilane (1:1 molar ratio) was irradiated (5.1 MR at 0.3 MR/hr) at room temperature. Distillation of the irradiated mixture gave isopropoxytrichlorosilane [$(CH_3)_2CHOSiCl_3$] in 81.5% yield: bp 115°, $n^{20}D$ 1.4050 (lit.[2] bp 116°, $n^{20}D$ 1.4045); nmr (CCl_4) τ 8.65 (d, 6, J = 11 Hz, CH_3), 5.46 (septet 1, J = 11 Hz, CH). *Anal.* Calcd for $C_3H_7OSiCl_3$: Si, 14.51; Cl, 54.96. Found: Si, 14.87; Cl, 54.87. The same compound was reported[2] to be obtained by uv irradiation of the same mixture. Another series of experiments was run, in which a mixture of 1:2.2 molar ratio of ethyl acetate and trichlorosilane was irradiated for various time periods. Figure 1 shows that yield (*ca.* 50%) of the ether at a later stage using the higher dose rate (0.45 MR/hr) is lower than that (*ca.* 90%) under the lower dose rate (0.15 MR/hr) and that 2 *M* amounts of trichlorosilane is sufficient to reduce the ester with the lower dose rate. The calculated value, 100 − [ester unchanged] (%) − [ether produced] (%), signifies per cent sum of side product and intermediate. These

(1) J. Tsurugi, R. Nakao, and T. Fukumoto, submitted for publication.

(2) (a) R. Calas and N. Duffaut, *Compt. Rend.*, **245**, 906 (1957). Many papers reported the addition of silanes to carbonyl groups, *i.e.*, trichlorosilane to acetaldehyde by uv,[b] trichlorosilane to dialkyl ketones by uv,[c] triethylsilane to ketones by zinc chloride,[d] and triphenylsilane to benzophenone by heat:[e] (b) R. Calas, N. Duffaut, and M. F. Menard, *Rev. Franc. Corps Gras*, **6**, 85 (1959); (c) ref 2a; (d) R. Calas, E. Frainnet, and J. Bonastre, *Compt. Rend.*, **251**, 2987 (1960); (e) H. Gilman and D. Wittenberg, *J. Org. Chem.*, **23**, 501 (1958).