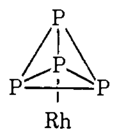
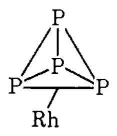
comparison with the spectrum of the $RhClL_3$ starting material and related compounds. The highest energy nonphosphine (arsine) band is assumed to correspond to the 606-cm^{-1} $\nu_1(A_1)$ mode of P_4. The $\nu_2(T_2)$ frequency of free P_4 (465 cm^{-1}) splits into an A_1 and an E mode under C_{3v} symmetry, and we assign the next two lower nonphosphine (arsine) bands to these vibrations. In the triphenylphosphine complex, the lowest of these two vibrations (386 cm^{-1}) has a shoulder, and we therefore attribute it to the E mode split either by solid state effects or reduced molecular symmetry. The $\nu_3(E)$ frequency of P_4 (363 cm^{-1}) remains unsplit under C_{3v} symmetry; we assign the next lower nonphosphine (arsine) band to this vibration. The frequencies assigned to bound P_4 are from 15 to 90 cm^{-1} lower in energy than the corresponding frequency in free P_4.

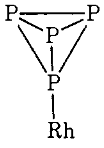
A–D show the possible ways in which P_4 may be linked to the metal atom. We consider D to be unlikely because of the ease with which P_4 is displaced from the complex by CO, and because we expect that breaking one of the edge bonds of the P_4 tetrahedron would give rise to a greater perturbation of the P_4 vibrational spectrum than is observed. We also consider C to be unlikely because the P_4 molecule has no lone-pair p electrons.[3,5,6] Of the remaining two possibilities we favor A, bonding through a face, over B, bonding through an edge. The P_4 valence-shell electrons are in orbitals of symmetry A_1, E, and T_2. Under C_s symmetry (the overall molecular symmetry for A or B) these orbitals become, respectively, A', $(A' + A'')$, and $(2A' + A'')$, all of which can overlap with empty metal orbitals. In addition, the lowest lying empty P_4 orbitals, T_1 and T_2, become, respectively, $(A' + 2A'')$ and $(2A' + A'')$; all of these can overlap with filled metal d orbitals.



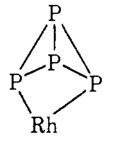
A



B



C



D

Attempts to obtain structural information from ^{31}P nmr spectra have so far been unsuccessful; the *m*-tolyl complex in CH_2Cl_2 at $\sim -60°$ with ^1H decoupling does not show any ^{31}P nmr lines that may be attributed to P_4. At δ −64.8 ppm (relative to $P(C_2H_5)_3$) is an apparently structureless phosphine line which is split into a doublet by coupling with the rhodium (J_{Rh-P} = 112 cps). Each member of the doublet has a width at half-height of ~30 cps. The failure to observe ^{31}P nmr lines due to P_4 in the complex, and the apparent absence of P–P coupling while Rh–P coupling is present, suggests that the P_4 is undergoing either inter- or intramolecular exchange. The nmr results indicate that the phosphine ligands are equivalent.

Acknowledgment. We thank Dr. F. N. Tebbe for arranging to have the ^{31}P nmr spectra determined at the Du Pont Co. Central Research Laboratory.

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Hydrolysis of Acetals and Ortho Esters. Specific Salt Effects Associated with Buffer Experiments in Mixed Solvents

Sir:

We report here some experimental results on specific salt effects which have a close bearing on the study of general acid catalysis in the hydrolysis of acetals and ortho esters.[1] Surprisingly, in this particular context, the presence or absence of the specific effects has not been studied before drawing conclusions.

The inadequacy of the ionic strength principle was clearly demonstrated by Olson and Simonson[2] for equilibria and kinetics of ionic reactions in water. Significant implications for reactions dealt with in this communication follow from the extensive studies of Grunwald and coworkers.[3] They not only derived exact thermodynamic equations for salt effects in mixed solvents, but also devised simple methods, based on linear free energy correlations, for the treatment of experimental data obtained with different salts.

Our point is the following. In order to detect possible involvement of general acid catalysis, one traditionally makes a series of rate measurements in buffer solutions of constant ionic strength and constant buffer ratio, $(HA)/(A^-)$. When varying the concentration of the Brønsted acid, (HA), the ionic strength constancy is maintained with some added electrolyte. Ordinarily, it is thus implicitly assumed that all the activity coefficients involved are influenced by the ions derived from the buffer components in the same way as by those of the added electrolyte. Yet, the validity or invalidity of this assumption, that is, the absence or presence of specific salt effects, can be experimentally established if using different electrolytes to make up the desired overall ionic strength.

The above point is illustrated by the results shown in Figure 1. As an example, we have chosen the hydrolysis of triethyl orthobenzoate, as a very similar reaction; the hydrolysis of trimethyl orthobenzoate in 70% methanol–water solvent,[4] has been reported to be subject to general acid catalysis. From the slope of line A alone, $(1.23 \pm 0.13) \times 10^{-2}$ M^{-2} sec^{-1}, obtained with sodium chloride as the added electrolyte, one might be tempted to assume the presence of general acid catalysis by the undissociated acid with a catalytic coefficient of this magnitude. However, as seen from the slopes of lines B and C, quite different results—even of different sign—are obtained when using electrolytes other than sodium chloride.

The observed variations in the hydrolysis rates can be accounted for in terms of specific salt effects on the hydronium ion catalysis. For the second-order rate coefficient of this reaction (first-order coefficient

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(1) (a) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967); (b) T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, **90**, 4081 (1968); (c) R. H. DeWolfe, K. M. Ivanetich, and N. F. Perry, *J. Org. Chem.*, **34**, 848 (1969); (d) A. Kankaanperä and M. Lahti, *Acta Chem. Scand.*, **23**, 2465 (1969); *Suom. Kemistilehti B*, 105 (1970); all these articles contain numerous references to the pertinent literature.

(2) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 348, 1167, 1322 (1949).

(3) (a) E. Grunwald and A. F. Butler, *J. Amer. Chem. Soc.*, **82**, 5647 (1960); (b) R. F. J. Duynstee, E. Grunwald, and M. L. Kaplan, *ibid.*, **82**, 5654 (1960); (c) E. Grunwald, G. Baughman, and G. Kohnstam, *ibid.*, **82**, 5801 (1960), and references to earlier studies therein.

(4) H. Kwart and M. B. Price, *ibid.*, **82**, 5123 (1960).

divided by the hydronium ion concentration) we have

$$k_2 = k_0(\gamma_{\mathrm{H}^+}\gamma_{\mathrm{S}}/\gamma_{\mathrm{X}^+}) \qquad (1)$$

in which the activity coefficients γ refer to the catalyst, substrate, and the critical complex, respectively (defined here to be unity at infinitely dilute electrolyte concentration in the solvent in question). Similarly, we have eq 2 for the dissociation equilibrium of the buffer

$$(\mathrm{H}^+)(\mathrm{A}^-)/(\mathrm{HA}) = K_0(\gamma_{\mathrm{HA}}/\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-}) \qquad (2)$$

acid, HA. From these we obtain eq 3 for the first-

$$k_1 = k_0K_0\frac{(\mathrm{HA})}{(\mathrm{A}^-)}(\gamma_{\mathrm{HA}}\gamma_{\mathrm{S}}/\gamma_{\mathrm{A}^-}\gamma_{\mathrm{X}^+}) \qquad (3)$$

order rate coefficients, k_1, which are measured for the hydronium ion catalyzed reaction in the buffer solutions. As the buffer ratios, $(\mathrm{HA})/(\mathrm{A}^-)$, were the same in all our experiments, the different intercepts in Figure 1 merely reflect differences in the activity coefficient quotient of eq 3, when the ionic strengths of the solutions become made up wholly of the different electrolytes added, *viz.*, sodium chloride, sodium nitrate, and sodium perchlorate. In the same way, the different slopes of the lines in Figure 1 reveal the individual behavior of this quotient when gradually substituting the anions of the above salts by the chloroacetate anions.

The above results provide just another example of "salt-induced medium effects." [3] First, we note that the relative effects of the chloride, nitrate, and perchlorate ions are in the same sequence as in SN1 solvolysis reactions in 50 wt % aqueous dioxane.[3b] This is not surprising, as the critical complexes of the latter reactions involve separation of opposite charges and thus the behavior of the activity coefficient quotient is expected to resemble closely that of eq 3. Second, the effects of various electrolytes are predictable when those for at least two are known (see below).

Conceptually, the treatment of salt effects in mixed solvents by Grunwald and coworkers[3] was to generalize all medium effects, those associated with changes in solvent composition as well as those brought about by added electrolytes. In case of electrolytes in aqueous organic solvents, the derivatives $\mathrm{d}G_t^\circ/\mathrm{d}x_\mathrm{w} = \mu_t$ were shown to be in correlation with the activity coefficients involved. Here G_t° stands for the standard free energy of the electrolyte in question, and x_w is the mole fraction of water. It was demonstrated that, except for some salts with bulky organic ions, the μ_t values for different salts were linearly correlated when going from one solvent to another. Furthermore, in the kinetics of solvolytic reactions, the values of log k, and thus the free energies of activations, were shown to be linearly correlated with the respective μ_t values.

Noting that at low salt concentrations molarities and molalities are proportional, the above theory yields the following simple equation for the present case.

$$\log k_1 = a + bc_2(\mu_2 - \mu_1) \qquad (4)$$

Here a and b are empirical parameters, c_2 is the molar concentration of the electrolyte added to the buffer solutions, and μ_2 and μ_1 are the values of $\mathrm{d}G_t^\circ/\mathrm{d}x_\mathrm{w}$ in a reference solvent. The subscript 1 refers to the buffer salt, sodium chloroacetate, and 2 to the added electrolyte. In 50 wt % dioxane–water at 25° the values of μ_t are (kcal/mol): NaCl, −16.6; $\mathrm{NaNO_3}$, −12.6; $\mathrm{NaClO_4}$, −6.8.

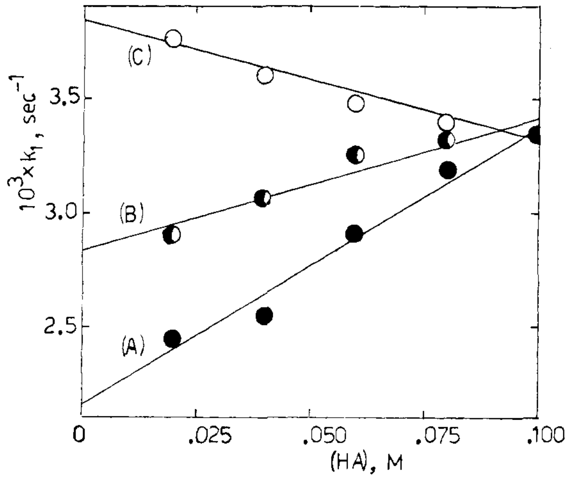

Figure 1. First-order rate coefficients, k_1, for the hydrolysis of triethyl orthobenzoate in 67.4:32.6 w/w dioxane–water solvent in chloroacetic acid–sodium chloroacetate buffers at 45°. Ionic strength = 0.1000 M. The buffer ratio, $(\mathrm{HA})/(\mathrm{A}^-)$, is 1:1 throughout. The ionic strength is maintained constant using the following electrolytes: (A) sodium chloride, (B) sodium nitrate, (C) sodium perchlorate. The slopes and intercepts of the lines are: (A) $(1.23 \pm 0.13) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$, $(2.15 \pm 0.08) \times 10^{-3}\ \mathrm{sec}^{-1}$; (B) $(0.580 \pm 0.105) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$, $(2.83 \pm 0.07) \times 10^{-3}\ \mathrm{sec}^{-1}$; (C) $-(0.515 \pm 0.066) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$, $(3.83 \pm 0.04) \times 10^{-3}\ \mathrm{sec}^{-1}$. (For the experimental technique, see ref 1d.)

With $c_2 = 0$, that is, when no foreign electrolyte has been added to the buffer solution, we obtain, from eq 4, $a = -2.4724$. The values for μ_1 and b are then calculable from any two intercepts in Figure 1, *e.g.*, from those for sodium chloride and sodium perchlorate. In this way, we obtain $b = 0.256$ and μ_1 −9.0 kcal/mol. These values lead, along with the μ_2 value for sodium nitrate, to a value of 2.73×10^{-3} sec^{-1} for the intercept of line B in Figure 1. The experimental intercept for sodium nitrate, $(2.83 \pm 0.07) \times 10^{-3}$ sec^{-1}, shows excellent agreement with the calculated value. Furthermore, the value obtained for μ_1 is of reasonable magnitude when compared with those for various electrolytes.[3]

On the basis of the above results, we suggest that when doing buffer experiments of this kind, one maintain the constancy of the ionic strength with electrolytes of grossly different μ_t values, such as perchlorates and chlorides. For salts of different alkali metals, Grunwald and coworkers showed that the cations had but minor differences in their contribution in μ_t. Consistently, we found that the slopes of Figure 1 were but slightly altered when using lithium salts in place of the corresponding sodium salts.

Finally, as another point, we wish to emphasize that the use of operational pH values is quite irrelevant here, as these values are no measures of the activity coefficient quotient of eq 3. Therefore, the constancy of pH does not guarantee the constancy of this quotient.

Further studies of this and related reactions are in progress.

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