methylidyne complex has recently been reported,[20] and other binuclear alkylidyne species are known.[7g-i,21] A few metal cluster compounds containing triply and quadruply bridging methylidyne ligands have been synthesized.[11,8,22]

Extensions of the procedure employed for the synthesis of **1** are being explored as possible routes to other homo- and heterobimetallic bridging methylene complexes. In addition, the possibility that the cationic complex **3** might transfer CH^+ to organic substrates is under investigation.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, and the National Science Foundation is gratefully acknowledged.

Registry No. *cis*-**1**, 79839-80-8; *trans*-**1**, 79896-43-8; **2a**, 80461-96-7; **2b**, 80461-95-6; **3**, 80461-93-4; **4**, 12154-95-9; K[CpFe(CO)$_2$], 60039-75-0; CpFe(CO)$_2$CH$_2$O$_2$CCH$_3$, 12244-91-6; CpFe(CO)$_2$CH$_3$, 12080-06-7.

Supplementary Material Available: Synthesis and purification of **1** (4 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Acid–Base Reactions in Water. A Comment on the Eigen Mechanism

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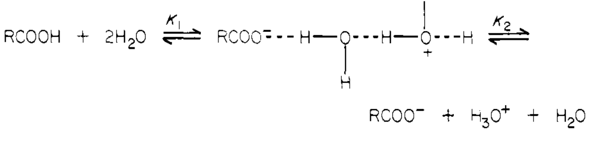
We have shown recently that the large negative heat capacity changes ($\Delta C_p^{\ominus}$) which characterize the ionization of carboxylic acids[1] and amines[2] in water can be understood by postulating that these reactions are not single-stage processes, i.e., they proceed in the sequence suggested by Eigen,[3] namely



$$RCOOH + 2H_2O \overset{K_1}{\rightleftharpoons} RCOO^{-}\cdots H{-}O(H)\cdots H{-}O^{+}(H)\cdots H \overset{K_2}{\rightleftharpoons} RCOO^- + H_3O^+ + H_2O \quad (1)$$

Eigen and co-workers[3,4] have also argued that the rate constants for the diffusion-controlled separation and recombination of the ions in acid–base systems are comparable, and hence K_2 is approximately unity. For our analysis of the temperature dependence of the observed equilibrium constants (K_0) we derive for the coupled equilibria (reaction 1)

$$K_0 = K_1K_2/(1 + K_1) \quad (2)$$

with

$$K_2 = \exp(A/T + B) \quad (3)$$

and

$$K_1 = \exp(C/T + D) \quad (4)$$

Combination of eq 2, 3, and 4 gives

$$K_0 = \exp([A + C)/T] + B + D)/[1 + \exp(C/T + D)] \quad (5)$$

Here we extend the above analysis to fit the data from an extensive study of benzoic acid[5] and that for the autoprotolysis

Table I. Data Related to the Ionization of Benzoic Acid at Various Temperatures

T, °C	$K_{ao} \times 10^5$, (m)[a]	$\Delta K \times 10^7$	K_a(calcd) $\times 10^5$ [b]
5	5.964	2.47	5.936
10	6.100	2.53	6.103
15	6.206	2.28	6.224
20	6.271	2.59	6.298
25	6.331	4.36	6.328
30	6.306	5.10	6.318
35	6.259	4.72	6.272
40	6.193	4.95	6.195
45	6.099	5.15	6.091
50	5.992	5.17	5.965
55	5.838	5.30	5.823
60	5.687	5.54	5.668
65	5.520	5.73	5.504
70	5.341	5.77	5.335
75	5.152	6.01	5.163
80	4.959	6.32	4.990

[a] Data in ref 5 reported on were the "C" scale; the conversion to the "m" scale was made in the usual way–see ref 10. [b] Calculated from eq 5 with values of $A + C$, $B + D$, C, and D given in Table III. The ΔT and ΔK quantities for the Wentworth regression followed the practices established in ref 2. See other references in that communication.

Table II. Data Related to the Autoprotolysis of Water at Various Temperatures[a]

T, °C	$K_{wo} \times 10^{15}$ [a]	K_w(calcd) $\times 10^{15}$	$K_{wo} \times 10^{15}$ [b]	K_w(calcd) $\times 10^{15}$
0	1.139	1.140	1.117	1.120
5	1.846	1.845	1.823	1.819
10	2.920	2.917	2.888	2.881
15	4.505	4.508	4.455	4.450
20	6.809	6.816	6.767	6.717
25	10.08	10.09	9.887	9.921
30	14.69	14.65	14.34	14.36
35	20.89	20.88	20.40	20.39
40	29.19	29.23	28.53	28.47
45	40.18	40.26	39.09	39.11
50	54.74	54.59	53.08	52.94
55	72.96	72.96	70.84	70.70
60	96.14	96.21	92.93	93.24

[a] Data from ref 6, but see also ref 10. [b] Data from ref 7. There is a considerable discrepancy between these two sets of data particularly at the high temperature end. See also footnotes to Table I.

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Table III. Derived Parameters Related to Equation 5 for the Temperature Dependence of the Ionization of Benzoic Acid and the Autoprotolysis of Water

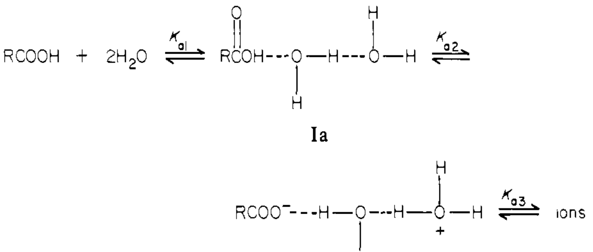
reactant	$A + C^d$	$B + D^d$	C^d	D^d
water[a]	−7966.2 ± 78.22	−5.028 ± 0.314	−3041.7 ± 42.9	9.753 ± 0.059
	−4914.5 ± 117.4	−14.780 ± 0.310	3041.7 ± 42.9	−9.753 ± 0.059
water[b]	−8402.6 ± 158.3	−3.296 ± 0.636	−3088.8 ± 38.1	10.502 ± 0.302
	−5313.8 ± 130.7	−13.797 ± 0.348	3088.8 ± 38.1	−10.502 ± 0.302
benzoic[c]	1386.3 ± 210.5	−13.637 ± 0.536	2834.5 ± 73.3	−9.512 ± 0.552
	−1448.0 ± 267.0	−4.116 ± 1.067	−2834.7 ± 73.7	9.512 ± 0.555

[a–c] Data from ref 6, 7, and 5, respectively. [d] The data in Tables I and II provide two solutions for $A + C$, $B + D$, C, and D. We make no attempt here to decide which of the two alternatives recorded is physically significant. The numbers of significant digits recorded is sufficient to evaluate the K_e(calcd) values to the errors reported (none are available in ref 6), recognizing that the number of digits is greater than that justified by the reported errors in the table.

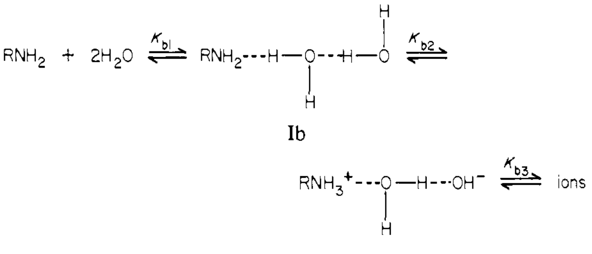
(K_w) of water to eq 5. The result of these calculations are shown in Tables I–III and in each instance the fits to eq 5 are excellent, providing further confirmation as to the suitability of this equation to describe the data.

However, if the heat capacities of ionization are to be related to the stepwise character of the ionization (anomalous heat capacities),[1,2] then the quantity K_1 must likewise be approximately unity. Thus our earlier treatment is in apparent conflict with the Eigen proposals, since for most carboxylic acids K_0 ranges from 1×10^{-3} to 1×10^{-5}, and *hence* K_1 *and* K_3 *cannot both approximate to unity.* The following more elaborate model embraces the Eigen model and removes the apparent contradiction.

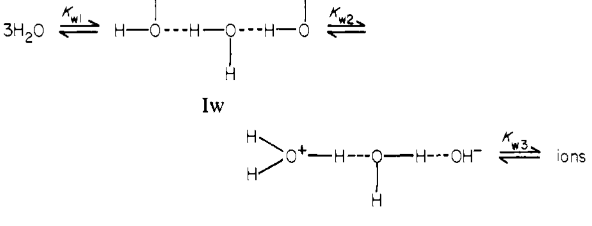
For carboxylic acids and amines we postulate that ionization is preceded by the formation of a hydrogen-bonded complex or aggregate involving the reactant and two water molecules and that in the case of the autoprotolysis of water at least three water molecules are involved. The mechanisms for acids, bases, and water are detailed:



(6)



(7)



(8)

We further postulate the formation and decomposition of the hydrogen-bonded aggregates Ia, Ib, and Iw are diffusion-controlled processes in each direction with the condition that K_{a1}, K_{b1}, and K_{w1} are probably in the range 0.1–10. The subsequent separation of charge then takes place within the aggregates, and it is at this stage differences in the acidity and basicity of the reactant are manifested, i.e., K_{a2} and $K_{b2} \simeq 1 \times 10^{-3} \rightarrow 1 \times 10^{-7}$ and $K_{w2} \simeq 1 \times 10^{-14}$. The ion pairs so formed then diffuse apart according to the Eigen scheme.

If the observed equilibrium constants associated with eq 6–8 describe the proportion of the total solute (or water in eq 8) present as free ions, relative to the amount present as other forms in the detailed equations, then it is readily shown that the observed equilibrium constants (K_{eo}) are related to the ancillary constants (K_{e1}, K_{e2}, K_{e3}; e = a, b, and w) by the expressions summarized as

$$K_{eo} = K_{e1}K_{e2}K_{e3}/[1 + K_{e1}(1 + K_{e2})] \tag{9}$$

where e = a (eq 6), e = b (eq 7), and e = w (eq 8).

Since $K_{e2} \ll 1$ for e = a, b, and w, it follows that

$$K_{eo} = K_{e1}K_{e2}K_{e3}/(1 + K_{e1}) = K_{et}/(1 + K_{e1}) \tag{10}$$

where K_{et} is the true equilibrium constant between the neutral species and ions (see below). If the K_{en} quantities (n = 1, 2, and 3) are postulated to have a simple temperature dependence

$$K_{en} = \exp(A_n/T + B_n) \tag{11}$$

then it can be shown that eq 10 gives rise to an equation of the same form as eq 5 but with a different meaning attached to the constant coefficients. The anomalous heat capacities are now related to the existence of labile hydrogen-bonded complexes which precede ionization, i.e., a solvation phenomenon. When considered as real, the $\Delta C_p^\ominus$ changes characteristic of these ionizations are ascribed frequently to solvation phenomena.[9,10] In the present treatment the model is more specific and more chemical in outlook.

The analysis of the temperature dependence presented here raises an important and interesting problem with respect to the elementary equation which relates the K_a and K_b of a conjugate acid base pair to K_w, namely

$$pK_a + pK_b = pK_w \tag{12}$$

The details of this problem are as follows.

When chemists are faced with the task of measuring K_b for an amine, they prefer often to determine the K_a of the conjugate ammonium ion. The relationship given by eq 12 is then used to convert the measured pK_a to the required pK_b.

In terms of the present analysis eq 12 is only valid when applied to the *true equilibrium constants* (K_{et})[11] which are conveniently summarized (see eq 10) i.e.

$$K_{et} = K_{e1}K_{e2}K_{e3} \quad (e = a, b, and w)$$

i.e.
$$pK_{at} + pK_{bt} = pK_{wt} \tag{13}$$

Thus in terms of the present treatment the ratio K_{wo}/K_{ao} is not related simply to K_{bo} for

$$\frac{K_{wo}}{K_{ao}} = \frac{(1 + K_{a1})}{(1 + k_{w1})}\left(\frac{K_{w1}K_{w2}K_{w3}}{K_{a1}K_{a2}K_{a3}}\right) = \left(\frac{1 + K_{w1}}{1 + K_{a1}}\right)K_{bt} \tag{14}$$

The analysis of the temperature dependence of K_{bo} described here allows K_{bt} to be extracted from the variation of K_{bo} on T (see above), and this quantity (K_{bt}) will differ from that found from the variation of the ratio K_{wo}/K_{ao} on T by the factor $(1 + K_{w1})/(1 + K_{a1})$ (see eq 14). Whether such a test of our analysis is possible depends crucially on the precision with which the quantities K_{ao},

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K_{bo}, and K_{wo} are established as a function of temperature and the extent to which the factor $(1 + K_{w1})/(1 + K_{a1})$, in any particular instance, departs from unity. A more detailed account of these and other considerations will appear elsewhere. However, we consider the present treatment of the temperature dependence of these ionogenic reactions to be more informative than that based on empirical equations which are virtually devoid of theoretical content.

Registry No. Benzoic acid, 65-85-0; water, 7732-18-5.

Preparation and Properties of Sterically Unhindered Cis and Trans Dihydrides of Platinum(II)

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Dihydrobis(tertiary phosphine) complexes of platinum(II), PtL_2H_2, undergo a broad spectrum of reactions.[1-17] Examples include insertion,[5-7] dimer formation,[11,12] metallation,[8] formation of platinum(0) compounds,[11,15] oxidative addition,[9,13] and catalysis of the water-gas shift reaction[10] and of alkene hydrogenation.[11] Almost all such dihydrides previously prepared contain bulky tertiary phosphine ligands and assume a trans geometry when L is monodentate. The only known cis dihydrides of this class contain bulky chelating diphosphine ligands.[4,11] In the absence of steric effects, the cis geometry should be electronically favored, since the trans influence of hydride is greater than that of phosphines.[18] The results of a recent ab initio calculation on $Pt(PH_3)_2H_2$ also indicate the cis geometry will be electronically favored.[16]

Previous attempts to prepare platinum(II) dihydrides containing small phosphines have met with limited success, and decomposition often occurs.[1,3,7,11,17] It is generally believed that bulky formation phosphines stabilize" PtL_2H_2 by hindering approach to the PtH_2 moiety.[1,3,11,17] Conversely, analogues which contain small phosphine ligands should be more reactive. We report the synthesis and chemistry of stable but highly reactive unhindered *cis*- and *trans*-PtL_2H_2 complexes and the first examples of cis–trans isomerization of platinum(II) dihydrides. These cis dihydrides are to our knowledge the first examples of four-coordinate d^8 ML_2H_2 in which the cis geometry is not constrained by chelating ligands.

The dihydrides *cis*- and *trans*-PtL_2H_2 (*cis*- and *trans*-**1**, L = PEt_3; *cis*- and *trans*-**2**, L = PMe_3) are readily prepared by bubbling hydrogen (1 atm, 25 °C) through solutions of $PtL_2(C_2H_4)$[19] (reaction 1). These reactions proceed to completion in about 15 min as ethylene is swept from the system. Ethane was not detected during the reaction by ^1H NMR spectroscopy in solution nor by gas chromatographic analysis of the gas phase. The ratio of cis and trans isomers formed depends on the solvent (vide infra). All the reactions described here can be conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which shows quantitative conversions to products.

$$PtL_2(C_2H_4) + H_2 \rightleftarrows PtL_2H_2 + C_2H_4 \qquad (1)$$

The dihydride products are readily identified by examination of their ^1H and ^{31}P NMR spectral parameters (Table I). The ^1H NMR spectrum of each trans-dihydride complex exhibits a hydride resonance which is a 1:2:1 triplet arising from coupling to the two phosphines cis to hydride. The hydride resonance of each cis dihydride complex is a second-order doublet of doublets, arising from coupling of each hydride ligand to a cis phosphorus nucleus and to a trans phosphorus nucleus. The spectral parameters in Table I accord well with those of previously reported cis and trans dihydrides of platinum(II).[1-4,8,11,17,20]

Complexes **1** and **2** isomerize in solution to produce an equilibrium mixture of *cis*- and *trans*-PtL_2H_2 (reaction 2). The

$$trans\text{-}PtL_2H_2 \overset{K}{\rightleftharpoons} cis\text{-}PtL_2H_2 \qquad (2)$$

equilibrium constant K depends upon both the solvent and the ligand, L (Table II).[21] Note that, for a given L, the relative concentration of cis isomer increases in going from the nonpolar hydrocarbon solvent to the polar solvent acetone. Since the cis isomer has a dipole moment, it should be better solvated in polar media. Second, in a given solvent, the cis geometry is more favored when L is PMe_3 than when it is PEt_3. Only 3% *cis*-$Pt(PEt_3)_2H_2$ can be detected in toluene, whereas ca. 20% of the PMe_3 dihydride is present in the cis form in this solvent. In acetone *cis*-$Pt(PEt_3)_2H_2$ is still the minor isomer (10%), but upon changing to PMe_3 the cis isomer predominates (70%). Similar results are obtained in other hydrocarbon (benzene) and polar (acetonitrile, methanol, tetrahydrofuran) solvents. These results suggest there is a delicate balance among the steric, electronic, and solvation effects that control the equilibrium between cis and trans isomers.

Analytically pure[22] *trans*-**1** can be isolated as off-white crystals by cooling a concentrated *n*-hexane solution of *trans*-**1** under hydrogen. This hygroscopic solid can be handled briefly in air and is indefinitely stable under 0.5 atm of H_2 at room temperature but decomposes slowly under vacuum. Solutions of **1** under hydrogen in hydrocarbon solvents or in acetone are quite stable. (A

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(20) The dihydride *trans*-**1** has been observed previously in solution.[17]

(21) We are confident that we are observing true equilibrium concentrations in solution since (a) the value of K under a given set of conditions is reproducible among several independently prepared samples, (b) the same value of K is obtained either by dissolving a previously prepared sample of PtL_2H_2 in a given solvent or by generating PtL_2H_2 in that solvent [e.g., by reaction of $PtL_2(C_2H_4)$ and H_2], and (c) after reactions which disturb the equilibrium by partially consuming *cis*- and/or *trans*-PtL_2H_2 (e.g., after adding less than a stoichiometric amount of C_2H_4), the cis–trans ratio returns to its equilibrium value. We have not studied the rates of isomerization of **1** and **2** in detail; however, solutions of **1** reach equilibrium within ca. 15 min at 25 °C, and solutions of **2** equilibrate much faster. We do not yet know the mechanism of isomerization of **1** and **2**, and, for example, whether isomerization could be catalyzed by traces of impurities.

(22) Anal. Calc: Pt, 45.01; P, 14.29; C, 33.25; H, 7.44. Found: Pt, 44.98; P, 14.55; C, 32.74; H, 7.21.

0002-7863/82/1504-1138$01.25/0