Propane and Normal Pentane.—Since isopropyl bromide was produced from the exchange reaction of propane with *t*-butyl bromide and aluminum bromide, hydrogen–halogen exchange can take place directly at a secondary carbon atom in a normal paraffin. The additional evidence obtained with normal pentane is complicated by the occurrence of side reactions. The product from the reaction of this compound with aluminum bromide and *t*-butyl bromide consisted mainly of *t*-amyl bromide and *s*-amyl bromides in the ratio of 1 to 1.4, respectively. The tertiary bromide comes either from isopentane formed by isomerization, or from isomerized secondary bromides, but the large proportion of secondary bromides found indicates that considerable hydrogen–halogen exchange has taken place directly at secondary carbon atoms, since the reverse isomerization of the *t*-amyl bromide by aluminum bromide yields only 15 to 20% of the secondary isomer.[5] The direct reaction mechanism is also supported by the results previously obtained with cyclopentane, cyclohexane and propane. Attempts to effect an exchange with ethane and *t*-butyl bromide–aluminum bromide were unsuccessful.

These experiments show that direct hydrogen–halogen exchange takes place with normal paraffins or unsubstituted cycloparaffins by removal of a hydride ion from a secondary carbon atom. Therefore, these important types of hydrocarbons can react directly, and in the same manner as saturates containing a tertiary carbon atom, with an alkyl halide or an olefin and hydrogen halide. The results thus support the theory that the first step in the acid-catalyzed reactions of paraffins and cycloparaffins is the formation of a carbonium ion or "polarized complex" from these hydrocarbons. Validation of this type of reaction in terms of another system may be obtained from work in these laboratories[11] on the aluminum halide catalyzed hydrogen–deuterium exchange reactions of propane and the two butanes in which hydrogen and deuterium were transferred between secondary positions and between primary and secondary positions in both propane and *n*-butane, and between primary and tertiary positions in isobutane. The unreactivity of ethane also was demonstrated by this work. Furthermore, great differences in the relative rates of isomerization and hydrogen exchange were noted, corresponding to our findings on the lack of isomerization of cyclohexane.

No evidence has been obtained by us for the direct reaction of a proton with a paraffin or cycloparaffin to yield hydrogen and the corresponding carbonium ion. Much evidence has been presented, however, that acid-catalyzed reactions involving only paraffins, such as isomerization, are strongly accelerated by the presence of very small amounts of olefins[12] which provide initiatory carbonium ions by the addition of protons. Studies in these laboratories with butanes and sulfuric acid again indicate the important effect of small amounts of olefin both on the initiatory step and rate of hydrogen and deuterium exchange.[13] Thereafter the reaction may proceed chain-wise without further supply of olefinic promoter. In the catalytic cracking of saturates,[1] the small amounts of olefin required can be supplied readily by incipient thermal cracking of saturates at the high temperatures (400 to 550°) ordinarily employed in this process.

[11] Wagner, Beeck, Otvos and Stevenson, *J. Chem. Phys.*, **17**, 419 (1949).

[12] Pines and Wackher, THIS JOURNAL, **68**, 595 (1946).

[13] Beeck, Otvos, Stevenson and Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

EMERYVILLE 8, CALIF. RECEIVED JULY 10, 1950

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Determination of Dissociation Constants in a Mixture of Two Weak Acids by Electromotive Force Measurements

BY ROGER G. BATES

The simultaneous dissociation of two weak acids in a mixture is considered. An electromotive force method that permits the determination of the product of the two dissociation constants when one is known is described. This method can be applied advantageously in the study of moderately strong acids. To illustrate the procedure, the dissociation constant of acetic acid at 25° is evaluated from e.m.f. data for five mixtures of sodium acetate, formic acid and potassium chloride. The result is in agreement with accepted values.

The electromotive force, E, of the cell

Pt; H_2 (*g.*, 1 atm.), buffer solution, MCl, AgCl; Ag

furnishes the value of $-\log (f_{H}f_{Cl}m_{H})$, for convenience termed *pw*H, in the buffered chloride solution by the equation

$$pw\mathrm{H} \equiv -\log (f_{H}f_{Cl}m_{H}) = (E - E^0)F/(2.3026\ RT) + \log m_{Cl} \quad (1)$$

where E^0 is the standard potential of the cell, m is molality and f is the molal activity coefficient. If the hydrogen ion concentration in the buffer solution is governed by the dissociation of a single weak electrolyte, equation (1) can be combined with the mass law expression for this dissociative equilibrium and the thermodynamic dissociation constant obtained by extrapolation of a function of the e.m.f. to zero ionic strength.[1]

When the hydrogen ion concentration in the buffer solution depends upon the dissociation of more than one acidic or basic group, *pw*H can also be expressed in terms of the dissociation constants for these equilibria. In an earlier contribution,[2] the determination of the product of the dissociation constants for two successive overlapping steps in

[1] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

[2] R. G. Bates, *ibid.*, **70**, 1579 (1948).

the ionization of a polybasic acid from measurements of *pw*H for solutions of the appropriate acid salt was described. It was shown later[3] that similar studies of solutions of a salt of a weak acid and a weak base would yield the product of the dissociation constant of the weak acid and that of the conjugate acid of the base. Best results are obtained if each of the acidic groups is dissociated to the extent of approximately 10 to 90%. Hence, the product of the dissociation constants of a dibasic acid can be determined precisely only when the first group is less than approximately 100 times as strong as the second. Similarly, 5 to 10% of both ions of the weak salt (BH)A should be hydrolyzed if the method is to yield a precise value for the product of the dissociation constants of the acids BH^+ and HA, and again the larger constant should be less than 100 times the smaller.

The hydrogen ion concentration of buffer solutions composed of a moderately strong acid, HA, and its salt, MA, is relatively large and usually cannot be precisely determined. Consequently, the uncertainty in evaluating the ionic composition of the solution may be great enough to limit seriously the accuracy with which the dissociation constant of such an acid can be obtained by the conventional e.m.f. method. It is sometimes advantageous, therefore, to utilize a buffer solution prepared from the salt, MA, and a weak acid such as formic or acetic whose dissociation constant is both well known and not more than a hundred-fold smaller than that of HA. A chloride is added to each buffer solution as usual.

The calculation of dissociation constants in a mixture of two weak acids from *pw*H values derived from e.m.f. measurements is outlined in the following sections. The method was tested by a determination of the dissociation constant of acetic acid from e.m.f. measurements of mixtures of sodium acetate, formic acid and potassium chloride. It has also been applied to a determination of the first dissociation constant of phosphoric acid from e.m.f. measurements of mixtures of potassium dihydrogen phosphate, formic acid and potassium chloride.[4]

Method

The hydrogen ion concentration, m_H, in a buffer solution containing two monobasic weak acids, HA and HB, and their ions, A^- and B^-, is expressed in terms of the two dissociation constants, K_A and K_B, by

$$m_H^2 = K_A K_B \frac{m_{HA} m_{HB}}{m_A m_B} \frac{f_{HA} f_{HB}}{f_A f_B f_H^2} \qquad (2)$$

A relationship between *pw*H and dissociation constants is obtained by combining equations (1) and (2)

$$-{}^1/_2 \log K_A K_B = pw\mathrm{H} + {}^1/_2 \log \frac{m_{HA} m_{HB}}{m_A m_B} + {}^1/_2 \log \frac{f_{HA} f_{HB} f_{Cl}^2}{f_A f_B} \qquad (3)$$

The last term is a linear function of ionic strength at moderate concentrations and approaches zero with dilution. "Apparent" values of log $K_A K_B$ are computed by omission of the last term of equation (3)

$$-{}^1/_2 \log (K_A K_B)' = pw\mathrm{H} + {}^1/_2 \log \frac{m_{HA} m_{HB}}{m_A m_B} \qquad (4)$$

The true log $K_A K_B$ is then evaluated by an extrapolation of 1/2 log $(K_A K_B)'$ to zero ionic strength. Other apparent or inexact quantities will also be identified by placing a prime mark after the appropriate symbol.

Evaluation of the Molality Term

Let HA represent the acid of unknown dissociation constant. The cell solutions are prepared by dissolving a salt, MA, of this acid together with chloride, MCl, in a solution of the other acid, HB, whose dissociation constant is known. If the stoichiometric molalities of MA and HB are designated m_1 and m_2, respectively, we have at equilibrium[5]

$$m_{HA} = m_B - m_H \qquad (5a)$$

$$m_{HB} = m_2 - m_B \qquad (5b)$$

and

$$m_A = m_1 + m_H - m_B \qquad (5c)$$

Hence, the molality term in equations (3) and (4) can be written

$${}^1/_2 \log \frac{m_{HA} m_{HB}}{m_A m_B} = {}^1/_2 \log \frac{(m_2 + m_H - m_B) - (m_2 m_H / m_B)}{(m_1 + m_H - m_B)} \qquad (6)$$

Certain activity coefficients are needed to compute m_H and m_B exactly, and these are usually unknown. Estimated activity coefficients will yield apparent values, m_H' and m_B', of these quantities. The uncertainty introduced with this approximation lessens as the ionic strength decreases and disappears in the extrapolation to infinite dilution. The Debye–Hückel equation[6] is used to estimate $f_H f_{Cl}$ for the computation of m_H'

$$-\log m_H' = pw\mathrm{H} - 2A\sqrt{\mu}/(1 + Ba^*\sqrt{\mu}) \qquad (7)$$

where μ is the ionic strength and A and B are constants of the Debye–Hückel theory. Values of 4 to 6 for the ion size parameter, a^*, are most common.

The apparent molality of the ion B, m_B', is readily computed from *pw*H and the known K_B, provided $f_H f_{Cl}$ is taken equal to $f_H f_B / f_{HB}$

$$m_B' = m_2 y/(1 + y) \qquad (8a)$$

where

$$\log y \equiv pw\mathrm{H} + \log K_B \qquad (8b)$$

The ionic strength is given by

$$\mu = m_1 + m_H + m_{MCl} \qquad (9)$$

Dissociation Constant of Acetic Acid

In order to illustrate the application of the equations of the foregoing section in a specific

---

(3) R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **43**, 519 (1949).

(4) R. G. Bates, unpublished work.

(5) These relationships also apply to solutions prepared from the acid HA and the salt MB, provided $m_1 = m_2$. However, if the molality of HA (m_1) does not equal that of MB (m_2) equations (5a) and (5c) become

$$m_{HA} = m_1 - m_2 + m_B - m_H \qquad (5a)'$$

and

$$m_A = m_2 + m_H - m_B \qquad (5c)'$$

Equations (6) and (9) must also be made consistent with (5a)' and (5c)'.

(6) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

case, the dissociation constant of acetic acid was calculated from e.m.f. measurements at 25°. Formic acid was chosen as the acid of known strength. The buffer solutions were composed of sodium acetate and formic acid, each at molality *m*, and each solution was 0.005 molal with respect to potassium chloride. The calculation of $-1/2$ log K_AK_F, where A represents acetic acid and F formic acid, is summarized in Table I. The extrapolation is shown in Fig. 1.

TABLE I

PRODUCT OF THE DISSOCIATION CONSTANTS OF FORMIC AND ACETIC ACIDS

		$-{}^1/_2 \log (K_AK_F)'$	
m	$p w\mathrm{H}$	$a^* = 4$	$a^* = 6$
0.04669	4.2384	4.2362	4.2363
.02993	4.2451	4.2419	4.2420
.02203	4.2490	4.2448	4.2450
.017426	4.2522	4.2471	4.2472
.014414	4.2522	4.2462	4.2463

$(\mu = 0)$; $-{}^1/_2 \log K_AK_F = 4.254$

The value of $-\log K_F$ is 3.751_5 at 25°.[7] Combination with the value of $-{}^1/_2 \log K_AK_F$, namely, 4.254, obtained by extrapolation gives 4.756_5 for $-\log K_A$ (acetic acid) at 25°. This result is in close agreement with 4.756 obtained by Harned and Ehlers[1] and with 4.755 from the conductance measurements of MacInnes and Shedlovsky[8] converted to the molal scale.

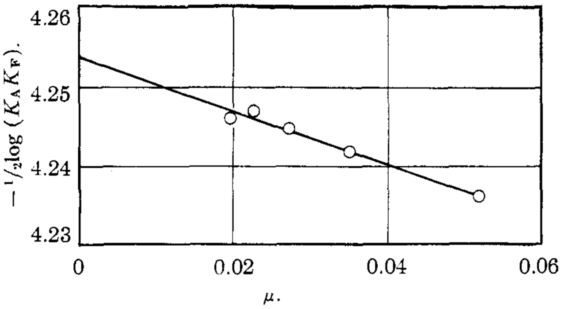

Fig. 1.—Extrapolation of $-{}^1/_2 \log (K_AK_F)'$ to zero ionic strength.

The results given in the last two columns of Table I show only a small uncertainty due to arbitrary choice of the ion size parameter in mixtures of formic and acetic acids. The error from this source increases, however, with the mean strength of the two acids concerned. If the two acids are phosphoric ($-\log K_1 = 2.14$) and formic ($-\log K_F = 3.75$) and $m_1 = 5m_2$, the value of $-{}^1/_2 \log K_1K_F$ in the limit is shifted by 0.0025 unit when $a^* = 6$ is chosen instead of $a^* = 4$. Hence, with increasing acid strength a threshold is reached, as also in the conventional method, above which this procedure is incapable of yielding accurate results.

---

[7] H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1042 (1934).

[8] D. A. MacInnes and T. Shedlovsky, *ibid.*, **54**, 1429 (1932).

WASHINGTON 25, D. C. RECEIVED DECEMBER 9, 1950

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF INTERIOR]

The Heats of Combustion and Formation of Titanium Nitride (TiN) and Titanium Carbide (TiC)

BY GEORGE L. HUMPHREY

The heats of combustion of titanium nitride and titanium carbide were determined by burning the materials in a bomb containing oxygen. The standard heats of formation, calculated from the combustion data, are: TiN, $-80.4_7 \pm 0.2_7$; TiC, $-43.8_5 \pm 0.3_9$ kcal./mole. Free energies of formation also are listed.

Introduction

In continuation of a program of study of the thermodynamic properties of titanium compounds, the heats of combustion and formation of titanium nitride (TiN) and titanium carbide (TiC) were ascertained. This completes the basic information necessary for free energy calculations, since the entropies and high-temperature heat contents of these substances were reported in earlier publications[1-3] from this Laboratory.

The heat of combustion of titanium nitride was determined previously by Neumann, *et al.*,[4] resulting in -80.3 kcal. per mole for the heat of formation. No previous heat of combustion data for titanium carbide have been reported.

Experimental

The Calorimeter and Its Calibration.—The calorimeter and its general operation have been described[5] previously. A recalibration of the calorimeter was made using National Bureau of Standards benzoic acid, Standard Sample 39g, having for its isothermal heat of combustion per gram mass under standard conditions, at 25°, the value $-\Delta U_B/m$ = 26,433.8 ± 2.6 abs. joules. Under the conditions of the calibration experiments (volume of bomb, 355 ml.; water added, 1 ml.; oxygen pressure, 30 atm.; weight benzoic acid, 1.090 g.; temperature, 30°) $-\Delta U_B/m$ is 26,427.8 abs. joules. Conversion to calories was made by taking 1 cal. = 4.1840 abs. joules. The value obtained for the energy equivalent of the calorimeter was 32,369.5 cal./ohm, with an average deviation of ±0.02% and a maximum deviation of 0.03%, in good agreement with previous calibrations.[5]

Materials.—The titanium nitride and carbide were part of the samples used earlier[3] in the high-temperature heat-capacity measurements. The samples were reheated *in vacuo* at 325° and analyzed: (a) TiN, 99.60%; SiN, 0.40%; (b) TiC, 99.00%; Ti, 0.40%; Si, 0.26%; other impurities, 0.34%. The other impurities in the titanium carbide

---

[1] K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

[2] C. H. Shomate, THIS JOURNAL, **68**, 310 (1946).

[3] B. F. Naylor, *ibid.*, **68**, 370 (1946).

[4] B. Neumann, C. Kröger and H. Kunz, *Z. anorg. Chem.*, **218**, 379 (1934).

[5] G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).