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The Base Catalyzed Exchange of Hydrogen Gas and Protonic Solvents. III. The Catalytic Efficiency of Concentrated Aqueous Alkali^{1,2}

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Studies of the base-catalyzed exchange between water and dissolved molecular hydrogen have been extended to concentrated aqueous KOH, NaOH and LiOH, using parahydrogen and HD as tracers. Rate measurements over a range of concentrations and temperatures have been interpreted in terms of absolute reaction rate theory to yield approximate thermodynamic properties for the activated complex. The results reveal a close thermodynamic similarity between the activated complex and the metal hydroxides. It is suggested that heterolytic cleavage of the bond of the molecular hydrogen is nearly complete at the transition state and that the activated complex at this point closely resembles a solvated hydride ion. The basicity of saturated aqueous KOH is estimated to correspond to an H_+ acidity function value of about 17, based on the kinetic data and an estimated solubility of hydrogen. Although very basic properties have been reported for concentrated aqueous hydrazine and ethylenediamine, only a very slow rate of exchange was found in these solutions.

Introduction

The base catalyzed isotope exchange reactions of molecular hydrogen with dilute aqueous hydroxide solutions^{1a} and with liquid ammonia containing amide ions^{1b} were reported in previous papers. Both reactions were found to be homogeneous, to occur only in the liquid phase, and to follow simple second-order kinetics in the dilute systems, the rate being proportional to the product of the concentrations of hydrogen and the basic ion in each case. Ion pairs were found to be catalytically inactive in the amide-ammonia system.

The extension of this work to the concentrated hydroxide systems was prompted by the fact that the activity coefficients of the alkali metal hydroxides reach very high values in concentrated solution. These high activity coefficients suggest that concentrated alkali may possess an abnormally high basicity, in the same sense that the acidity of aqueous sulfuric acid becomes extremely high as the concentration approaches pure H_2SO_4 . However, the acidity or basicity of such highly non-ideal systems depends upon the activity coefficients of all the species involved in the equilibrium or rate process which is used to evaluate the acidity function and not upon the acid or base alone. The general development of such acidity or basicity functions and their relationship to reaction rates in concentrated acid media have been discussed in detail by several authors and are reviewed in two excellent books.⁴

The properties of all the species involved in the hydrogen exchange reaction are known to vary by large amounts from dilute to concentrated alkali. Therefore it was of great interest to investigate the relationship between the exchange rate and the individual thermodynamic properties of hydrogen, metal hydroxide and water. It was also hoped that some knowledge of the thermodynamic behavior of the activated complex could be obtained through the application of absolute reaction rate

theory and that some conclusions might be drawn regarding the details of the reaction path.

Briefly, the kinetic results show that the concentrated alkali does possess an extreme basicity with respect to the rate of hydrogen exchange and that this unusual basicity arises principally from a large increase in activity coefficient of dissolved hydrogen, which is strongly salted out of the concentrated solutions. By contrast, the thermodynamic behavior of the activated complex was found to be remarkably close to that of the alkali metal hydroxides.

Since this work was started, basicity scales have been proposed for aqueous solutions of hydrazine⁵ and ethylenediamine.⁶ The exchange studies reported below contribute some interesting information about the relative basicities of the aqueous alkali and amine systems, according to indicator measurements and kinetic studies.

Experimental

As in the previous studies, the reaction was carried out in vessels that were about half full of the reacting solution, the remaining volume being filled with excess tracer hydrogen ($p\text{-}H_2$ or HD). Rapid stirring maintained the labelled composition of the gaseous hydrogen essentially the same as that of the dissolved hydrogen at all times during the course of the reaction. With this method the over-all rate of change in the composition of the total hydrogen is proportional to the fraction dissolved in the reactive liquid phase, and the observed rate should be corrected by this factor to obtain the actual exchange or conversion rate in the solution. However, for the purposes of this study, the solubility of hydrogen was not determined in most cases, since it was possible to formulate the rate law in such a way that solubility data were not required for calculation of the desired thermodynamic properties of the activated complex. An approximate determination of the salting coefficient for H_2 by KOH at room temperature was in agreement with the results of Geffcken.⁷

The wide range of alkali concentrations studied prevented the determination of rate constants for all the systems at a single common temperature, since the observed half-lives would vary by a factor of 10^4 in going from the most dilute to the most concentrated alkali solutions. However, all solutions were studied over a range of temperatures, and the data were extrapolated readily to an intermediate reference temperature of 70° when direct observations at that temperature were impractical.

The reaction vessel and the general method for the rate measurements were essentially the same as those reported previously.⁸ Parahydrogen and HD analyses were carried

(1) (a) Paper I, W. K. Wilmarth, June C. Dayton and J. M. Flournoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953); (b) Paper II, W. K. Wilmarth and June C. Dayton, *ibid.*, **75**, 4553 (1953).

(2) This investigation was supported by the U. S. Atomic Energy Commission. Based on the Ph.D. dissertation of John M. Flournoy, Jr., University of Southern California, 1956.

(3) Aerojet-General Corp., Azusa, California.

(4) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York, 1959.

(5) N. C. Deno, *J. Am. Chem. Soc.*, **74**, 2039 (1954).

(6) Robert Schaal, *Compt. rend.*, **298**, 2156 (1954).

(7) G. Geffcken, *Z. physik. Chem.*, **49**, 257 (1904).

(8) W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).

out using a Pirani gauge and a mass spectrometer, respectively. All the data presented here were obtained at stirring speeds which were shown empirically to be fast enough so that the diffusion or mixing of hydrogen was not rate-determining.

Although HD or D₂ would, in general, be preferable to parahydrogen as a tracer for an exchange process, the previous work showed that the *p*-H₂, HD and D₂ mechanisms are essentially the same in aqueous alkali, and *p*-H₂ was used for most of the runs, because a mass spectrometer was not directly available to the project. HD was used, however, for the runs in saturated alkali, for two reasons. First, mass-spectrometric analysis of HD-H₂ mixtures was found to be more sensitive than our Pirani-gauge analyses of ortho-parahydrogen mixtures. As a result, the longest runs (in saturated alkali at 10–20°) were shortened to 1–2 days by making measurements over only 10–15% HD exchange, instead of the full half-life which is required for satisfactory analytical accuracy using para-rich hydrogen. Second, in the extremely long runs that were required with saturated NaOH and KOH, there was doubt that non-exchange parahydrogen-conversion processes, such as the diamagnetic and nuclear-spin perturbation mechanisms, could be ruled out as major contributors to the over-all conversion rate. Both the HD exchange and *p*-H₂ conversion rates were determined at 70° in 10.6 molal NaOH; the ratio $k_{HD}/k_{p-H_2} = 0.55$, which was obtained in this experiment, was used to calculate hypothetical *p*-H₂ exchange rates for the saturated systems. It can be shown that, aside from normal isotope effects, the rates of parahydrogen conversion and HD exchange are directly comparable, if each is measured by analysis of gas samples in terms of the degree of enrichment above the natural abundance.

The preparation of para-rich hydrogen and the Pirani gauge method of analysis of ortho-parahydrogen mixtures were generally the same as those described previously.⁸ HD was prepared from LiAlH₄ and D₂O by the method of Fookson, Pomerantz and Rich⁹ and was diluted with tank hydrogen to about 1% HD before use, to facilitate analyses with the mass spectrometer.

Concentrated solutions of sodium¹⁰ and potassium¹¹ hydroxides were prepared according to the method of Åkerlöf and Bender and were stored in polyethylene bottles. These solutions were standardized by weight-titration with normal HCl, and the more dilute solutions were prepared by dilution of weighed amounts of the concentrated alkali. Reagent grade LiOH was found by analysis to be sufficiently pure for direct preparation of LiOH solutions, using boiled, distilled water.

The sodium butoxide solution was prepared from metallic sodium and 1-butanol which was distilled from calcium metal.

The other solutions were prepared directly from the reagents without further purification.

Treatment of the Data

The enrichment of hydrogen in *p*-H₂ or HD was found in all cases to decrease with time according to a first order rate law. A rate constant k can be evaluated from the filament resistance values obtained in the Pirani-gauge analysis of parahydrogen¹² samples removed periodically from the reaction vessel.¹

$$\ln [(R_0 - R_\infty)/(R_t - R_\infty)] = kt \quad (1)$$

To obtain a rate constant k' for the solution phase, it is necessary to multiply k by a factor which is the ratio of the total amount of hydrogen in the vessel to the amount dissolved in the catalytic solution.

$$k' = k \left[\frac{V_g C_g + V_s C_s}{V_s C_s} \right] = k \left[1 + \frac{V_g}{V_s \lambda} \right] \quad (2)$$

In this expression V_g , V_s , C_g and C_s represent the volumes and hydrogen concentrations of the gas phase and of the solution, respectively, and λ is the Ostwald solubility coefficient, C_s/C_g , for hydrogen in the solution.

In the dilute solutions, it was determined that k' for parahydrogen was a sum of two terms, one of which was

(9) A. Fookson, P. Pomerantz and E. H. Rich, *Science*, **112**, 748 (1950).

(10) G. Åkerlöf and P. Bender, *J. Am. Chem. Soc.*, **61**, 1027 (1939).

(11) G. Åkerlöf and P. Bender, *ibid.*, **63**, 1085 (1941).

(12) In the experiments with HD, the comparable expression is $\ln[(HD_0 - HD_\infty)/(HD_t - HD_\infty)] = kt$.

proportional to the concentration of hydroxide from 0.1 to 0.9 molar.

$$k' = k^0 (\text{OH}^-) + k_w \quad (3)$$

In this expression k^0 represents a molar specific rate constant for the basic catalysis and k_w is a background rate for non-exchange conversion by the solvent, water. The quantity k_w was first evaluated by Farkas and Sachsse¹³ as $6.3 \times 10^{-5} \text{ sec.}^{-1}$, essentially independent of temperature. This conversion by the solvent was only a minor term in the studies in dilute solution; it is completely negligible in the studies at hydroxide concentrations above one molar and will be omitted from the treatment which follows.

The approximation that the activity coefficients for reactants and activated complex counterbalance each other, an assumption which is inherent in equation 3, cannot be considered valid for the concentrated systems. Therefore, these systems are treated in terms of the Brønsted-Bjerrum equation^{14,15} and the methods of absolute reaction rate theory. In view of the emphasis of this latter theory on thermodynamic concepts, a molality scale of concentration has been used in the equations which follow.

$$k' = k^0 m \frac{(\gamma_{\pm^2})_{\text{MOH}} \gamma_{\text{H}_2}}{[\gamma_{\pm^2}]^*} \quad (4)$$

In equation 4, m represents the molality of the alkali. In dilute solution the molality and molarity scales of concentration become equivalent, except for the slight temperature dependence of the former, and the activity coefficients approach unity; consequently the k^0 of equation 4 may be identified with the same symbol in equation 3.

The molal activity coefficient for hydrogen is defined by equation 5.¹⁶

$$\gamma_{\text{H}_2} = \frac{\lambda_0}{\lambda} \cdot \frac{d}{d_0(1 + 0.001 m M)} \quad (5)$$

where λ_0 and λ are the Ostwald coefficients in pure water and in m molal alkali, respectively, d_0 and d are the corresponding densities¹⁶ and M is the formula weight of the metal hydroxide.

In the development that follows, it is possible to eliminate the dependence upon λ and consequently to remove the necessity of determining the solubility of hydrogen in each of the solutions at each reaction temperature. Since in our experiments $V_g = V_s$, and in the more concentrated solutions $\lambda \ll 1$, then to a very good approximation $k' = k V_g/V_s \lambda$. Equating this expression for k' to that of equation 4 and substituting γ_{H_2} from equation 5, one obtains

$$k \cdot \frac{V_g}{V_s \lambda_0} \cdot \frac{d_0}{d} (1 + 0.001 m M) = k^0 m \frac{(\gamma_{\pm^2})_{\text{MOH}}}{(\gamma_{\pm^2})^*} \quad (6)$$

At this point, in order to simplify the later thermodynamic algebra and as an aid in tabulating the data, it is useful to express the experimental results in a manner which emphasizes only the effects of deviations from ideal behavior. The quantity k_m , defined by equation 7, corrects the observed rate constant k for all the rate-controlling variables, except for the activity coefficients of the activated complex and the alkali.

$$k_m = k \cdot \frac{1}{m} \cdot \frac{V_g}{V_s \lambda_0} \cdot \frac{d_0}{d} (1 + 0.001 m M) \quad (7)$$

The utility of the concept of k_m is that it leads directly to the determination of $(\gamma_{\pm^2})^*$, through the substitution of k_m in equation 6.

$$(\gamma_{\pm^2})^* = \frac{k^0}{k_m} (\gamma_{\pm^2})_{\text{MOH}} \quad (8)$$

At low concentrations, k_m approaches k^0 .

It should also be noted that the appearance of λ_0 , rather than the actual solubility λ , in the formulation of k_m (equation 7), gives k_m the physical significance of a rate constant that is based on the molality of the alkali and the activity of molecular hydrogen. Multiplication of k_m by the activity coefficient of hydrogen would yield a more conventional type

(13) L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933).

(14) J. N. Brønsted, *ibid.*, **102**, 169 (1922).

(15) N. Bjerrum, *ibid.*, **108**, 82 (1924).

(16) The ratio λ_0/λ represents a molar activity coefficient; the remainder of the expression simply converts this quantity to a molal scale. Density values for NaOH and KOH solutions were taken from ref. 10 and 11, respectively.

of rate constant, based on concentrations only. The striking property of k_m is that it does not change very much over a wide range of alkali concentrations at constant temperature (see Table II), showing that the ratio $(\gamma_{\pm}^2)_{\text{MOH}}/(\gamma_{\pm}^2)^*$ is quite insensitive to the salt effect of high alkali concentrations. A purely concentration-dependent rate constant would increase markedly over k_m at high alkali concentrations, due to the strong salting-out of hydrogen.

The quantity $(\gamma_{\pm}^2)^*$ in equations 6 and 8 above is directly related to the free energy change that would accompany the transfer of a mole of activated complex at constant molality from dilute to concentrated alkali.¹⁷

$$(F^{\text{ex}})^* = 2 RT \ln \gamma_{\pm}^* = RT \ln (k^0/k_m) + F_{\text{MOH}}^{\text{ex}} \quad (9)$$

With rate measurements at various temperatures and values for the thermodynamic properties of the alkali at these temperatures, the corresponding heat and entropy of transfer can be calculated for the activated complex. Division of equation 9 by T and differentiation by $1/T$ yields an expression for the enthalpy of transfer in terms of experimental quantities.

$$(H^{\text{ex}})^* = E_a - E_a^0 + \bar{L}_{\text{MOH}} \quad (10)$$

E_a^0 is the activation energy obtained from the temperature dependence of k^0 , dilute solution; E_a is obtained from the slope of a plot of $\ln k_m$ versus $1/T$. An expression for the entropy of transfer can be obtained by combining equations 9 and 10

$$(S^{\text{ex}})^* = R \ln (A^0/A) + S_{\text{MOH}}^{\text{ex}} \quad (11)$$

A^0 and A are the frequency factors obtained from the Arrhenius plots of k^0 and k_m , respectively. To the extent that questionable assumptions and approximations have been incorporated in absolute reaction rate theory, the quantities calculated by equations 9, 10 and 11 cannot be said to have exact thermodynamic significance, in spite of the terminology employed. However, the approximations are only those normally encountered, although some of the equations are not in very general use.

Results

The experimental rate data, expressed in terms of the corrected rate constant k_m , are summarized in Table I. The corresponding experimental activation energies, pre-exponential factors, and values of k_m at the chosen common reference temperature of 70° are listed in Table II. For a complete picture of basicity as a function of concentration, rate data for each alkali concentration should be available at a common temperature. Experimental limitations prevented this, but for the intermediate temperature 70° the extrapolated values of k_m listed in Table II probably are not seriously in error. At 70°, k_m increases with the concentration of KOH, is almost independent of the NaOH concentration and decreases with increasing concentration for LiOH. There are some changes in activation energy, but these are relatively small compared to the large heat of dilution of NaOH and KOH (see Table III). Thermodynamic data for aqueous NaOH and KOH were obtained from the papers of Åkerlöf and Kegeles¹⁸ (NaOH) and Åkerlöf and Bender¹⁹ (KOH). The

(17) The symbolism is that employed by Prigogine and Defay, "Chemical Thermodynamics," Longmans, Green and Co. Ltd., New York, N. Y., 1954, p. 381.

$$F^{\text{ex}} = 2 RT \ln \gamma_{\pm} = (F - F^0) - RT \ln (m_+ m_-)$$

$$H^{\text{ex}} = \bar{H} - \bar{H}^0 = \bar{L}$$

$$S^{\text{ex}} = (\bar{S} - \bar{S}^0) + R \ln (m_+ m_-)$$

The standard state of the alkali is the usual hypothetical one molal aqueous solution. The standard state for the activated complex is the very dilute alkali where k_m reaches a limiting value; consequently, within the limit of error the standard state for the activated complex may also be said to be the same as that of the alkali.

(18) G. Åkerlöf and G. Kegeles, *J. Am. Chem. Soc.*, **62**, 620 (1941).

(19) G. Åkerlöf and P. Bender, *ibid.*, **70**, 2366 (1948).

TABLE I
THE RATE OF CONVERSION OF PARAHYDROGEN IN AQUEOUS ALKALI

Base	m	t (°C.)	$(\frac{k_m \times 10^3}{\text{moles kg. H}_2\text{O sec.}})^{-1}$
KOH	0.1-0.9	100	9.8
	0.1-0.9	80	1.47
	3.00	70	0.56
	5.40	70	.63
	10.6	70	.83
	10.6	60	.310
	10.6	50	.106
	18.0	30	.0118 ^a
	18.0	20	.00314 ^a
	18.0	10	.00069 ^a
NaOH	1.00	100	9.4
	1.00	80	1.32
	3.00	70	0.50
	3.00	70	.226
	4.82	75	.81
	4.82	70	.49
	4.82	60	.176
	10.6	80	.95
	10.6	70	.50
	10.6	65	.298
LiOH	0.235	100	(6.1)
	{ .24 M LiOH } { .66 M LiCl }	100	7.3
	.84	100	8.0
	3.00	70	0.333
	5.2	80	.72
	5.2	60	.098

^a Rate constants for HD exchange.

TABLE II
ACTIVATION ENERGIES, PRE-EXPONENTIAL FACTORS AND SPECIFIC RATE CONSTANTS AT 70° FOR THE CONVERSION OF *p*-H₂

	Molality	E_a	$\log A$	Temp. range	$(\frac{k_m \times 10^3}{\text{moles kg. H}_2\text{O sec.}})^{-1}$	$(\gamma_{\pm}^2)^*$
KOH	0.1-0.9	24.9	12.59	80-100	5.3 ^a	...
	3.00	70	5.9	0.77
	5.40	70	6.6	1.81
	10.6	22.6	11.40	50-60	9.7 ^a	10.1
	18.0	24.2	13.00	10-30	31.0 ^a	42.2
NaOH	1.00	25.6	13.02	80-100	4.7 ^a	0.45
	3.00	70	5.0	.55
	4.82	23.6	11.75	60-75	5.0	.85
	10.6	20.4	9.71	60-70	5.5	4.8
	17.7	22.4	11.26	20-40	8.1 ^a	20.3
LiOH	0.83	4.2 ^a	..
	3.00	3.3	..
	5.2	23.6	11.30	60-80	2.7	..

^a Extrapolated values.

values of E_a in Table II are not believed to be in error by more than ± 0.5 kcal./mole, except possibly in the 18 molal KOH where the longer ex-

trapolation may increase the error to ± 1.0 kcal. In view of the considerable change in \bar{L}_{MOH} with concentration, constancy in E_a is not necessarily to be expected, and the minimum at intermediate alkali concentrations is believed to be outside of the limit of error. The uncertainty in E_a is incorporated in the entropy and enthalpy values which are calculated from equations 10 and 11 and are listed in Table III.

TABLE III

THERMODYNAMIC PROPERTIES OF KOH, NaOH AND THE CORRESPONDING ACTIVATED COMPLEXES AT 70° IN CONCENTRATED HYDROXIDE SOLUTIONS, CORRECTED BY THE IDEAL ENTROPY OF DILUTION^a

	Molality	$F^{\text{ex}}_{\text{MOH}}$	$(F^{\text{ex}})^*$	$H^{\text{ex}}_{\text{MOH}}$	$(H^{\text{ex}})^*$	$S^{\text{ex}}_{\text{MOH}}$	$(S^{\text{ex}})^*$
KOH	3.00	-0.11	-0.2	2.4	..	7.3	..
	5.40	0.56	+0.4	3.7	..	9.0	..
	10.6	1.99	1.6	6.0	3.7	11.6	6.2
	18.0	3.75	2.5	8.6	7.9	13.7	15.4
NaOH	1.00	-0.63	-0.6	1.4	2.1	6.2	8.2
	3.00	-.45	-.4	2.3	..	7.6	..
	4.82	-.15	-.1	2.6	1.3	8.3	4.5
	10.6	1.10	1.1	7.6	3.1	19.4	6.2
	17.7	2.36	2.0	12.6	10.0	30.0	24

^a See footnote 17 for definition of symbols.

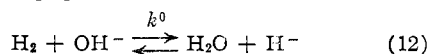
In a few experiments in anhydrous butanol containing 0.26 molal sodium butoxide, the rate of parahydrogen conversion was almost identical with that found in dilute aqueous alkali. Rate measurements at 90° and 100° corresponded to an activation energy of approximately 24 kcal./mole. No great significance can be attached to this figure since sodium butoxide probably is poorly dissociated in this solvent, and the extent of the dissociation would be both temperature and concentration dependent. However, the results do demonstrate that at least for the alkoxide ion the exchange reaction does not require that the oxygen atom of the base be bonded to a proton, as it is in hydroxide ion.

No significant parahydrogen conversion was observed with 100% H_2SO_4 at 140° or with 10 M H_2SO_4 at 120°. Two attempts were made to detect general basic catalysis at 100° in the aqueous system, one with 0.5 M Na_2CO_3 and one with a buffer 0.5 M in PO_4^{-3} and 1.0 M in HPO_4^{-2} . In neither case was there any appreciable catalysis which could not be attributed to OH^- produced by hydrolysis.

Two parahydrogen conversion experiments were conducted in 60 wt. % aqueous solutions of hydrazine and ethylenediamine. In each case the rate was comparable to the rate for about 0.1 molar KOH at the same temperature, in sharp contrast to the extreme basicities that have been reported in these systems from indicator studies.

Discussion

The significance of the present results will be considered in terms of the mechanism formulated in the earlier paper.^{1a} The water molecule and



hydride ion generated in reaction 12 can be visualized as very unstable reaction intermediates

whose properties may not differ markedly from those of the activated complex. As an approximation, it will be assumed that the activated complex consists of a hydride ion and a water molecule. The activity coefficients of the strong electrolytes "NaH" and "KH" can then formally be calculated from the thermodynamic relationship $(\gamma_{\pm}^2)_{\text{MH}} = (\gamma_{\pm}^2)^*/a_{\text{H}_2\text{O}}$ where M in the subscripts refers to either sodium or potassium ion. The quantities $(\gamma_{\pm}^2)_{\text{MH}}$ and $(\gamma_{\pm}^2)_{\text{MOH}}$ have been plotted in Fig. 1 instead of $(\gamma_{\pm})_{\text{MH}}$ and $(\gamma_{\pm})_{\text{MOH}}$, because the rate constant of equation 4 is more closely related to the former quantities. Also, it should be noted that $(\gamma_{\pm}^2)_{\text{MOH}}/(\gamma_{\pm}^2)_{\text{MH}}$ is equal to $\gamma_{\text{OH}^-}/\gamma_{\text{H}^-}$, a quantity which will enter into the discussion below. The behavior of the activated complex is like that of a typical strong electrolyte in that its activity coefficient closely resembles that of the alkali even up to the maximum concentration of $\text{MOH}\cdot 3\text{H}_2\text{O}$. The calculated curves for NaH and KH show no resemblance to the linear curves with zero intercept that are typical of non-electrolytes in ionic solutions; in that sense it may be said that the properties of the hydrogen molecule have disappeared almost completely at the transition state.

Some justification for the assumption that the water molecule formed in reaction 12 has become "free" at the transition state is obtained from a consideration of the Åkerlöf-Thomas equation.²⁰

$$\log (\gamma_1/\gamma_2) = \alpha_m \quad (13)$$

In many instances this equation is quite successful in relating the activity coefficients of two electrolytes in a single solution where one electrolyte is present at a fixed, low concentration and the second electrolyte is at a higher, variable molality m ; α is an empirical constant. In applying equation 13 to our data, γ_1 and γ_2 refer to $(\gamma_{\pm}^2)_{\text{MH}}$ and $(\gamma_{\pm}^2)_{\text{MOH}}$, respectively, and m is the molality of the alkali. In Fig. 1 the dotted lines represent $(\gamma_{\pm}^2)_{\text{MH}}$ values calculated using α -values of 12.5×10^{-3} and 3.0×10^{-3} for NaH and KH, respectively. The agreement with experiment is within the limit of error in both cases.²¹ By contrast, if $(\gamma_{\pm}^2)^*$ is used instead of $(\gamma_{\pm}^2)_{\text{MH}}$, the correlation with $(\gamma_{\pm}^2)_{\text{MOH}}$ through the Åkerlöf-Thomas equation is much less satisfactory.

Table III contains the free energy, enthalpy and entropy changes associated with transfer of the activated complex from the very dilute to the more concentrated alkali. For comparative purposes the appropriate thermodynamic properties of the alkali are also listed. Examination of these quantities leads to a further appreciation of the extreme non-ideality of the alkali and the extent to which the activated complex resembles it. As equations 9, 10 and 11 indicate, the variations in k_m , E_a and A of Table II arise from the difference in thermodynamic properties of the alkali and those of the activated complex. The close parallelism

(20) G. Åkerlöf and H. C. Thomas, *J. Am. Chem. Soc.*, **56**, 593 (1934).

(21) In their study of the acid catalyzed hydrolysis of γ -butyrolactone reported in *J. Phys. Chem.*, **55**, 829 (1951), F. A. Long, F. B. Dunkle and W. F. McDevitt found that $\log (f_{\text{H}_3\text{O}^+}/f_{\text{M}^+})$, where M^+ is the activated complex, varied linearly with the ionic strength up to 4.0, the maximum ionic strength studied.

in free energy leads to a cancellation of factors which would have influenced the rate constant by a factor of two hundred. In comparing the enthalpy and entropy of transfer of the two species, it will be noted that while the correlation is less striking than that in free energy, there is an approximate cancellation of factors which, if uncompensated, would have changed the rate one millionfold. Apparently, as frequently happens, the linear correlation in free energy in the system arises from compensating trends in enthalpy and entropy. In fact, this is true for the alkaline solutions themselves; equation 13 can be applied successfully to the activity coefficients of NaOH and KOH, but the other thermodynamic properties in Table III show only an approximate parallelism.²²

In formulating the mechanism there is the possibility that the exchange process would be more accurately represented by a concerted attack of the base and a single water molecule acting as an acid. This mechanism has not been adopted because the concerted path would seem to imply a sensitivity to the acidic properties of the solvent which has not been observed.¹ The failure in the present work to detect an acid catalyzed exchange under rather extreme conditions²³ further emphasizes the dominant role played by the basic ion, and the apparent absence of general basic catalysis perhaps lends some further support to this viewpoint.²⁴

In the absence of a reliable equilibrium basicity scale,²⁵ our kinetic studies represent one of the few sources of information about the basic properties of extremely concentrated alkaline solutions. From the viewpoint of absolute reaction rate theory, reaction 12 may be regarded as a neutralization of molecular hydrogen, with the position of the equilibrium determining k' , the rate constant for the solution phase defined by equation 4. With increasing alkali concentration k' increases, in part because of the increase in m , but principally because of the increase in the ratio $(\gamma_{\pm}^2)_{\text{MOH}} \gamma_{\text{H}_2} / (\gamma_{\pm}^2)^*$. As we have seen, the increase in this quantity arises primarily from the increase in γ_{H_2} , since the activity coefficient of the activated complex and that of the alkali change in a similar fashion with change in medium. In short, when hydrogen is used as a kinetic indicator, the alkali may be regarded as a very basic medium, but only because the low solubility of hydrogen implies a

(22) Equation 13 may also be used to relate the activity coefficients of two different solutions, each containing a single electrolyte at m molal concentration.

(23) The results are in agreement with recently published studies by S. L. Miller and D. Rittenberg, *J. Am. Chem. Soc.*, **80**, 64 (1958).

(24) The absence of basic catalysis implies an α -value approaching unity in the Brønsted equation, $k_{\text{B}} = \text{const.} \cdot K_{\text{B}}^{\alpha}$. An α -value less than unity might be expected in a concerted process where the basic properties of the catalyst might be less important in determining the rate of reaction.

(25) No fully acceptable basicity scale has been published for aqueous alkali, presumably because of the very low solubility of indicators in the concentrated solutions. In an effort to avoid this difficulty, G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 361 (1944), studied the color change of indicators in an organic phase equilibrated with the alkali. Unfortunately, these measurements do not yield a useful basicity scale for the aqueous phase, since they were carried out only in the non-aqueous phase, and the H_{-} scale which was derived refers only to that phase. The H_{-} scale in the aqueous alkali may be very different from that presented, since the ratio of the activity coefficients of the indicator and its conjugate base must be very different in these phases.

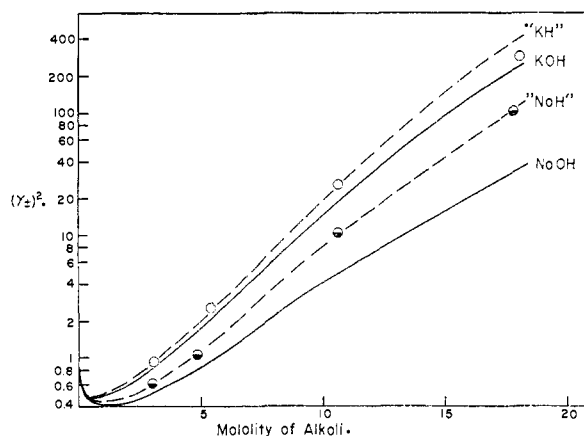


Fig. 1.—Activity coefficients at 70°: the solid lines represent the data for the two alkalis, \ominus and \circ , the experimental points for the activity coefficients of the species "MH" in NaOH and KOH, respectively. The dashed lines represent calculated values for the activated complexes using equation 13.

large activity coefficient and hence a considerable driving force for neutralization. Unfortunately, in the absence of accurate solubility measurement, only approximate values of k' may be obtained, but an illustrative calculation is informative. If a salting-out coefficient of 0.13 is assumed (this is a rough value obtained in the region of 5–10 molal alkali at room temperature), then the rate of hydrogen exchange in 18 molal alkali is approximately five thousand times that in the one molal solution containing parahydrogen at the same concentration. The results would imply an H_{-} value of 17.7 ± 0.7 , the indicated uncertainty representing our estimation of the possible error in the calculation. In an indicator measurement, it would not be surprising if the salting out coefficient of the neutral indicator was as large as or even larger than that for hydrogen, and an H_{-} scale based on indicator measurements should also tend to rise rapidly with increasing alkali concentration because of an increase in γ_{B} , the activity coefficient of the neutral indicator. However, in addition to this factor, the extent of neutralization of the indicator would depend upon the ratio of $\gamma_{\text{OH}^-} / \gamma_{\text{H}^-}$, a quantity which is difficult to estimate and might differ considerably from $\gamma_{\text{OH}^-} / \gamma_{\text{H}^-}$.

Studies of indicator color changes in aqueous solutions of hydrazine⁵ and ethylenediamine⁶ have led the investigators to conclude that these systems are extremely basic, in the Hammett sense, reaching H_{-} values as high as 16–17 at a concentration of 60 weight per cent., the concentration to be considered in the following discussion. To understand the origin of the basicity of these solutions, attention may be focussed on any of the basic species in the solution. The equilibrium involving free hydroxide ion and the neutral indicator HB in the hydrazine solution is of particular interest, because conductivity studies have revealed that the hydroxide ion concentration must be less than 0.01 *M*.²⁶ Further, vapor pressure–composition

(26) L. J. Vieland and R. P. Seward, *J. Phys. Chem.*, **59**, 466 (1955).

measurements indicate that the $\alpha_{\text{H}_2\text{O}}$ is not particularly small, being approximately 0.2 of that in pure water.²⁷ In our experiments it was found that the base catalyzed parahydrogen conversion was very slow, barely exceeding that to be expected for the nuclear moments of the protons in the solvent and certainly not greater than that found in 0.1 M aqueous alkali. These data show that the

(27) J. G. Burtle, *J. Phys. Chem.*, **44**, 1675 (1952).

ratio $\gamma_{\text{OH}}-\gamma_{\text{H}_2\text{O}}/\gamma_{\text{H}}-\alpha_{\text{H}_2\text{O}}$ is not a large quantity in the amine solvents. The result is readily understandable if $\gamma_{\text{OH}}-\gamma_{\text{H}}$ is approximately one, as it is in aqueous alkali, since γ_{H} cannot be very large, the solubility of hydrogen being not unlike that in pure water. By contrast, for the ratio $\gamma_{\text{HB}}\gamma_{\text{OH}}-\gamma_{\text{B}}-\alpha_{\text{H}_2\text{O}}$ to reach so extreme a value in the indicator studies, it is very likely that the ratio $\gamma_{\text{OH}}-\gamma_{\text{B}}$ is a very large number and is responsible for much of the apparent basicity of the medium.

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The Vibrational Spectra and Structure of Bis-cyclopentadienylmagnesium

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A study of the infrared and Raman spectra of bis-cyclopentadienylmagnesium in solution and in the solid state is reported. A comparison of the observed vibrational frequencies with those obtained for ferrocene indicate that the molecular geometry is best represented by a "sandwich" structure. An assignment of frequencies has been made which is quite similar to that reported for ferrocene and related compounds. The results are not in agreement with the early reports of an essentially ionic bonding in bis-cyclopentadienylmagnesium and are better explained by the presence of covalent ring-to-metal bonding, which is weaker than the metal to ring bonding in ferrocene.

Introduction

The discovery of ferrocene has led to the synthesis and characterization of a large number of organo-metallic compounds.²⁻⁴ Physicochemical investigations have reasonably well established the molecular structure and the type of chemical bonding in most of these substances. However, there still exist some doubts regarding the nature of the bonding in metal cyclopentadienyls and their derivatives.

A pentagonal antiprismatic structural configuration has been assigned to ferrocene and similar cyclopentadienyls. Weiss and Fischer⁵ have shown that in the crystal form $\text{Mg}(\text{C}_5\text{H}_5)_2$ has a "sandwich" configuration and proposed a rather weak covalent d^2sp^3 hybridization overlapping the ionic electrostatic binding between the metal and cyclopentadienyl ions. However, based on magnetic, spectral and chemical investigations, Wilkinson, *et al.*,⁶ conclude that the bonding in bis-cyclopentadienyl $\text{Mg}(\text{II})$ and $\text{Mn}(\text{II})$ is essentially ionic. According to these authors, two cyclopentadienide anions are expected on electrostatic grounds to align themselves on opposite sides of the cation with their planes parallel, the structure thus very closely resembling that of "sandwich bonded" molecules, such as ferrocene. The configuration in the case of the ionic molecules (*e.g.*, $\text{Mn}(\text{C}_5\text{H}_5)_2$ or $\text{Mg}(\text{C}_5\text{H}_5)_2$) is thus assumed to be due merely to the geometry resulting from charge distribution, whereas in the case of ferrocene-like

molecules, it is a requirement of the metal-to-ring covalent bonding. This postulation of difference in bond type has been prompted by notable differences in chemical properties, by conductivity measurements in liquid ammonia⁶ and by mass spectra measurements and determination of appearance potentials.⁷ The mass spectra do not provide confirmative evidence regarding the configuration. However, the stability of the parent compound is indicated by the stability of molecule-ions in the mass spectra. In the case of Mg and Mn cyclopentadienides, the parent molecule-ions $\text{C}_{10}\text{H}_{10}\text{M}^+$ are relatively unstable, contributing only 20% to the total ion yield in contrast to the Fe , Co , Cr , etc., compounds, in which the molecule-ion contributes roughly 50% or more of the total ion yield. The instability of the molecule-ions in Mg and Mn compounds again is evidenced by the enhanced yields of $\text{C}_5\text{H}_5\text{M}^+$ and M^+ ions. These observations, along with the chemical properties of the compounds, such as metathetical reactions with ferrous chloride to form ferrocene, hydrolysis with water, etc., have led the previous workers⁵⁻⁷ to reach the conclusion that the metal-to-ring bond in Mn and Mg cyclopentadienyls is of a quite different nature from that of the bonding in ferrocene-type molecules.

The concept of ionic bonding in $\text{Mg}(\text{C}_5\text{H}_5)_2$ has been discussed by Cotton and Reynolds.⁸ The analogy between the spectrum of $\text{Mg}(\text{C}_5\text{H}_5)_2$, especially in the C-H stretching region, and those of ferrocene and nickelocene indicate the sandwich structure in the free state. The existence of the ionic bonding in the magnesium compound has then been evaluated from a consideration of the molecular orbital overlap and on the basis of ionization potentials. Finally, they conclude that the magnesium compound does behave as though

(1) Post-doctoral Research Fellows.

(2) (a) M. Rausch, M. Vogel and H. Rosenberg, *J. Chem. Ed.*, **34**, 268 (1957); (b) E. O. Fischer, *Angew. Chem.*, **475** (1955).

(3) P. L. Pauson, *Quart. Rev. (London)*, **9**, No. 4, 391 (1955).

(4) "Advances in Inorganic Chemistry and Radiochemistry," Editors, H. J. Emeleus and A. G. Sharp, Vol. I, Academic Press, Inc., New York, N. Y., 1959, p. 55.

(5) E. Weiss and E. O. Fischer, *Z. anorg. u. allgem. Chem.*, **278**, 219 (1955); E. O. Fischer and S. Schreiner, *Ber.*, **92**, 938 (1959).

(6) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nuclear Chem.*, **2**, 95 (1956).

(7) L. Friedman, A. P. Irsa and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955).

(8) F. A. Cotton and L. T. Reynolds, *ibid.*, **80**, 269 (1958).