electric moment of acetophenone 2.97 *D*,[12] 2.90 *D*,[13] 2.77 *D*,[14] 2.96.[15] Hassel reported the value 2.97 four separate times. It therefore appears probable that the moment in benzene is in the range 2.90–2.97 *D*. The electric moment value obtained for monoacetylferrocene, 3.02 *D*, is in good agreement with the acetophenone value, indicating once again the aromatic nature of the ferrocene molecule.[16]

TABLE I

DIELECTRIC CONSTANTS, SPECIFIC VOLUMES, POLARIZATIONS AND MOLECULAR REFRACTIONS OF COMPOUNDS STUDIED, DETERMINED IN BENZENE SOLUTION AT 30.0°

w[a]	ϵ	V	$P_{2\infty}$	μ
Monoacetylferrocene, $MR_D = 56.0$, $\alpha = 4.593$, $\beta = -0.4070$				
0.00000	2.2700	1.1508	248.8	3.02
.00619	2.2986	1.1490		
.00705	2.3030	1.1485		
.00729	2.3023	1.1485		
.00768		1.1483		
.00770	2.3051	1.1483		
.00865	2.3094	1.1480		
.00955		1.1478		
.01154	2.3234	1.1466		
.01932	2.3585	1.1433		
Diacetylferrocene, $MR_D = 65.2$, $\alpha = 7.7207$, $\beta = -0.4571$				
0.00000	2.2635	1.1519	424.4	4.23
.00802	2.3216			
.01141	2.3485	1.1465		
.01554	2.3748	1.1449		
.01913	2.3992	1.1432		

[a] The symbols used are; *w*, weight fraction of solute; ϵ, dielectric constant; *V*, specific volume; P_2, solute molar polarization at infinite dilution; MR_D, solute molar refraction for the sodium-D line.

Table I summarizes the dipole moment values of ferrocene and the acetylferrocenes. The zero moment for ferrocene is in accord with the sandwich structure. The equation of Fuchs[17] was developed for the calculation of the resultant moment of compounds with freely rotating angular groups

$$\mu_r = \sqrt{a^2 + b^2 + 2ab \cos \alpha \cos \beta \cos \theta}$$

where α and β are the angles which the resultant of the angular groups make with the axes about which they rotate and θ is the angle between these axes; *a* and *b* are electric moment vectors. Applying this equation

$$\mu = (3.02^2 + 3.02^2 + 2 \times 3.02 \times \cos 90° \cos 90° \cos 180°)^{1/2}$$

The close agreement between the experimental value of diacetylferrocene and that calculated for free rotation is indicative of the probability of free rotation in ferrocene.

If the alternative assumption were made that there was no rotation of the cyclopentadiene groups then the angle between the moment vectors can be calculated from the equation

$$4.23^2 = (3.02^2 + 3.02^2 + 2 \times 3.02 \times \cos \theta)$$

From this it follows that $\theta = 91°$. This result would indicate that the structure of the diacetylferrocene is half-way between the prismatic and the antiprismatic form. A structure intermediate between the prismatic and antiprismatic form would not be centrosymmetrical and hence not in agreement with X-ray data of ferrocene.[18]

Thus the dipole moment data would seem to confirm the free rotation of the cyclopentadiene rings predicted by molecular orbital theory.

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Investigation of Hydrogen Solubility in Molten Alkali Metal Hydroxides

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RECEIVED DECEMBER 6, 1954

Under certain conditions, molten alkali metal hydroxides have been observed to absorb appreciable quantities of hydrogen gas. Thus, if sodium hydroxide or potassium hydroxide contained in a nickel vessel is heated to 500° under vacuum and an hydrogen atmosphere admitted, hydrogen is rapidly absorbed into the melt. This investigation was made, therefore, to determine the solubility of hydrogen in molten sodium hydroxide and potassium hydroxide at 500° and pressures up to 800 p.s.i.a. Since the hydrogen solubility would be expected to be greatest just above the melting point of the hydroxide in question, the solubility in potassium hydroxide was determined also at 410°.

In every case the hydrogen solubility was found to be so small that it was within the experimental error of the measurements involved. The absorption of hydrogen into the melt was found not to depend upon the temperature and pressure, as would be expected if the phenomenon were due to dissolution of hydrogen gas into the molten hydroxide but, rather, was found to be related to the previous treatment of the hydroxide. In the absence of conditions which would cause interaction between the hydroxide and its container, no hydrogen absorption was observed. Conversely, when the hydroxide had been subjected to conditions which caused attack on its container, hydrogen absorption was observed. Thus the observed absorption of hydrogen must be due to its interaction with a corrosion product or products, and not to dissolution of hydrogen gas as such in the molten hydroxide.

In the particular case where nickel containers were used, it has been found that heating the hydroxide to 400° under vacuum does not cause detectable corrosion, while heating to 500° under vacuum introduces a nickel corrosion product into the melt. The exact nature of the corrosion is not entirely certain, but it probably may be represented adequately by the equilibrium[1]

$$2NaOH + Ni \rightleftharpoons Na_2NiO_2 + H_2$$

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[1] D. D. Williams, private communication; to be published by Wright Air Development Center, as Report WADC Tr 54-185, Part 2.

At 400° no detectable reaction occurs even when the system is evacuated. At 500° the corrosion reaction proceeds when the system is under vacuum, but is reversed when hydrogen is admitted.

The hydroxide samples used for the determinations were thoroughly degassed at or slightly above the melting point of the hydroxide being used, 319.1° for sodium hydroxide[2] and 410° for potassium hydroxide.[3] A known amount of hydrogen gas was introduced into the system and, after allowing the system to come to equilibrium, the amount of gaseous hydrogen remaining in the system was calculated. Another increment of hydrogen was then added and the procedure repeated.

Four sets of duplicate experiments were made: two blank runs with empty nickel liners at 500°; two with sodium hydroxide at 500°; two with potassium hydroxide at 500°; and two with potassium hydroxide at 410°. In every case the amount of gaseous hydrogen in the system at equilibrium was found to be the same, within the limits of the experimental error, as the amount of hydrogen added. The difference between the amount of hydrogen added and the amount of gaseous hydrogen found at equilibrium averaged 1.1, 1.0, 1.9 and 1.0% of the amount of hydrogen added for the four sets of duplicate runs in the order mentioned, and varied in a random fashion. The limits of error were such that the hydrogen solubility may be said to be less than 60 mg. hydrogen per 100 g. of hydroxide under all conditions examined.

Experimental

The sodium hydroxide and potassium hydroxide used in these experiments were specially dehydrated, low-carbonate preparations. The apparatus and experimental procedures were similar to those described in previous papers.[4,5] Screw-cap nickel liners for containing the hydroxides were fabricated from International Nickel Company Grade "L" nickel. They were pretreated at 400° by alternate 30-minute periods of hydrogen and vacuum for four hours to remove any surface oxidation and adsorbed gases.

A screw-cap nickel liner was loaded in an inert atmosphere box with approximately 25 g. of hydroxide. The liner was then placed in a stainless steel pressure vessel, which was welded gas-tight. The pressure vessel was connected by means of copper tubing to a calibrated manifold and a pressure recording gage. The volume of the copper line plus the pressure vessel were calibrated by expanding hydrogen from the unknown volume, which included a previously calibrated high-pressure manifold, into the known volume of a low-pressure manifold which had been at a flat vacuum. Corrections were made for the non-ideality of hydrogen at the pressure used.

The pressure vessel was clamped in an upright position in a molten lead-bath inside a muffle furnace. It was then degassed for one hour at or slightly above the melting point of the hydroxide being used, after which it was heated to the temperature desired for the experiment. The temperature was controlled to ±1°.

Solubility determinations were carried out by addition of a known weight of hydrogen from the high-pressure manifold to the pressure vessel system, in which was incorporated a 1000 p.s.i. recording pressure gage. Approximately 15 minutes were allowed for the system to come to equilibrium. (Exploratory experiments showed this to be a sufficient interval to establish equilibrium.) Another increment of hydrogen was then added and the procedure repeated. Hydrogen additions were made in such a way as to increase the pressure in the system by approximately 100 p.s.i. intervals to 800 p.s.i.a.

The calculations were carried out as follows. From the known pressure drop in the high-pressure manifold, the weight of hydrogen added to the system was calculated. The weight of hydrogen gas actually present above the system was then calculated in two parts, the first being the weight of hydrogen gas present in the pressure vessel at the equilibrium pressure and the operating temperature, and the second being the weight present in the copper tubing system at the equilibrium pressure and room temperature. The sum of these two values represented the weight of hydrogen gas above the hydroxide melt at equilibrium. This latter value was subtracted from the weight of hydrogen added to give the hydrogen difference (or "solubility") for the weight of sample used. Corrections for the non-ideality of hydrogen under the various conditions were derived from the data compiled by Deming and Shupe.[6]

After completing a solubility determination, the pressure vessel was cooled under approximately 800 p.s.i.a. of hydrogen, cut open, and the liner unloaded under an inert atmosphere. Samples of the resolidified melt were analyzed for total alkalinity, and a spectrographic analysis was made for trace metals. These analyses proved there had been no interaction between the hydroxide and its nickel container during the solubility determination.

In addition to these routine analyses, quantitative tests for gas evolution on dissolution of the hydroxides in degassed, distilled water were made by a modification of the method of Banus and Vetrano.[7] Because the hydroxides evolved small quantities of gas even prior to being subjected to hydrogen (presumably argon adsorbed while handling the hydroxides in an inert atmosphere box), it was necessary to determine what fraction of the evolved gas was hydrogen. This was done by sealing a platinum wire into the air chamber at the top of the gas buret, and, after the gas evolution for a sample had been completed, sparking the gas mixture with a Tesla coil until there was no further reduction of the gas volume. In every case the hydrogen found was less than 0.5 mg. per 100 g. of hydroxide. It is not known whether this small quantity of hydrogen was dissolved in or occluded by the hydroxide, and it is recognized that there is no definite relationship between this value and the hydrogen solubility under the conditions of the solubility run. It is definitely established, however, that hydrogen was present in the resolidified samples. The hydrogen evolutions are, therefore, consistent with the experimental results, although they do not afford positive confirmation of them.

The sodium hydroxide used in these experiments contained 0.07% sodium carbonate; the potassium hydroxide, 0.12% potassium carbonate. Other impurities were present in trace quantities only.

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Reaction of Dimethyl Ether–Boron Trifluoride with Quaternary Alkyl Ammonium Halides

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RECEIVED NOVEMBER 4, 1954

A consideration of the structure of dimethyl ether–boron trifluoride suggested the possibility of preparing methoxy fluoborates by a metathetical reaction of the etherate and quaternary ammonium halides. Schlesinger[1] has observed that either lithium or sodium fluorides react with diethyl

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