lay near the reaction temperature, so that in this case rather lower temperatures were used and the reaction was allowed to run to about 15% of completion. An example of a kinetic run is shown in Fig. 1. The plots generally showed a characteristic sigmoid shape as in Fig. 1. The order of reaction seemed to vary (1.5 to 1.7) from sample to sample. Figure 2 shows the data of Fig. 1 plotted for calculation of the activation energy.

Results

Results are tabulated in Tables I and II. The specific magnetization is designated as σ.

Surface areas were found by B.E.T. nitrogen adsorption. Values obtained on some samples were as follows: N-1, 58 m.^{2}g.$^{-1}$; N-4, 59; N-5, 53. It did not prove possible to prepare samples with more widely varying specific surfaces although this would have been desirable.

Discussion of Results

It has been shown that the activation energy for the gamma → alpha ferric oxide transition decreases with increasing severity of heat treatments. The principal result of heat treatment is to reduce the water content. It may, therefore, be concluded that water stabilizes the gamma ferric oxide lattice as it does the gamma aluminum oxide lattice.

There is no obvious relation between activation energy and particle sizes. This is true because large variations of activation energy occurred with only small variations of specific surface area. But it did not prove possible to prepare samples with large variations in surface area.

It is well known that alumina tends to stabilize the gamma ferric oxide. This has been placed on a quantitative basis, and substantial increases of activation energy have been shown to parallel increases of alumina content. It will be clear that the activation energy will reach a constant value when the ferric oxide becomes saturated with alumina.

Lanthana dissolved in gamma ferric oxide diminished the lattice stability as shown by a decrease of activation energy with increasing lanthana concentration. Gallia appears to be without effect on the stability of the ferric oxide. These results suggest that the stabilizing action of alumina is related to the small size of the aluminum ion. The larger lanthanum ion causes a decrease of stability, while the gallium ion which is almost equal in radius to iron (+3), has no effect on the stability of the gamma ferric oxide.

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The Magnetic Susceptibilities of Some Aromatic Hydrocarbon Anions[1a,b]

BY TING LI CHU AND SHAN CHI YU

RECEIVED DECEMBER 19, 1953

The magnetic susceptibilities of tetrahydrofuran solutions of anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl anions were measured at room temperature by Gouy's method. The results obtained indicate that the monovalent anions under study are monomeric in solution with one unpaired electron and that two unlike monovalent anions exhibit no tendency to associate. Anthracene and phenanthrene also form divalent anions which, however, are diamagnetic.

Introduction

The alkali metals react with a large number of aromatic hydrocarbons in dimethyl ether, 1,2-dimethoxyethane or tetrahydrofuran by transferring one or two electrons to one molecule of hydrocarbon yielding intensely colored anions.[2,3] This reaction involves a measurable equilibrium and it was believed that this equilibrium is determined mainly by the magnitude of the solvation energy of the metal ion and perhaps that of the hydrocarbon anion.[3] In order to obtain information about the general nature of these anions, we have investigated the reaction products formed upon the reaction of sodium with several aromatic hydrocarbons in tetrahydrofuran solution by means of magnetic susceptibility measurements. The hydrocarbons under study consisted of anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl.

Experimental

Materials.—Eastman white label grade anthracene, biphenyl, naphthalene, phenanthrene and *m*-terphenyl, were purified by standard procedures, successive sublimation or fractional distillation under vacuum. Their melting points were 216.5, 69, 80, 99.5 and 87°, respectively.

Tetrahydrofuran was fractionated in a 30- by 2-cm. column of glass helices, b.p. 65–66°, and dried over sodium–potassium alloy.

Magnetic Measurements.—The magnetic susceptibilities of the hydrocarbon anion solutions were measured by the Gouy method at room temperature. The magnetic field was provided by a General Electric Isthmus Electromagnet with conical pole pieces of 5 cm. diameter and 15 mm. pole gap. An Ainsworth microbalance with optical lever was used. Both the magnet and the balance were encased in insulated boxes to minimize air current effects and to maintain constant humidity. Six amperes of current were used in most of the measurements and the field strength was reproducible with respect to the current to 0.1%.

A Pyrex tube 11 mm. in diameter and 20 cm. long was used for the susceptibility measurements. This tube was calibrated and used for all subsequent measurements. In the Gouy method, the apparent change in weight of the sample on application of the magnetic field, Δw, is measured. The tube calibration was made in terms of $A(H_1^2 - H_2^2)/g$ by measuring Δw of (1) the evacuated tube and (2) the tube filled to a definite height with distilled water, outgassed and sealed off under vacuum. The difference between these two measurements is related to the volume susceptibility of water taken as -0.720×10^{-6} c.g.s. units at

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[1] (a) Taken in part from the Master Thesis of S. C. Yu, Duquesne University, 1954. (b) Presented before the Division of Physical and Inorganic Chemistry at 125th ACS Meeting, Kansas City, Mo., March 1954.

[2] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 442 (1936); A. Jeanes and R. Adams, *ibid.*, **59**, 2608 (1937); J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

[3] D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

room temperature. When the calibration of the tube with water was used to determine the molar susceptibility of $NiCl_2$ in a 20.23% solution (determined by dimethylglyoxime precipitation), the value 4366×10^{-6} was obtained at 26° as compared to the value 4345×10^{-6} interpolated from the results of Nettleton and Sugden.[4] The volume susceptibilities of the hydrocarbon anion solutions were measured in the following manner. The sample tube was outfitted with a ground joint and constricted approximately 20 cm. from the bottom. A weighed amount of the purified hydrocarbon was placed in the tube and a piece of sodium above the constriction. The tube was attached to a vacuum line and thoroughly evacuated. A measured amount of pre-dried tetrahydrofuran was distilled in from a graduated pipet so that the height of the column of solution at room temperature was the same as that of the water used in calibration. The solution was cooled down and the sodium heated to its melting point and carefully worked down to a position slightly below the constriction with a fresh surface. The tube was then sealed off at the constriction while under vacuum. The apparent change in weight of the solution on application of the magnetic field, Δw, was measured before and after the reaction of the solution with sodium. The reaction between sodium and hydrocarbon took place readily.

If we assume that the diamagnetic contribution of the hydrocarbon anion does not differ appreciably from that of the hydrocarbon, the net difference in the two measurements is proportional to the paramagnetic susceptibility of the anion as well as the diamagnetic susceptibility of sodium ion which can be corrected by using Pascal's constant. The paramagnetic volume susceptibilities of anion solutions were obtained by the relation

$$\kappa = -0.720 \times 10^{-6} \frac{\Delta w_{\text{hydrocarbon anion soln.}} - \Delta w_{\text{hydrocarbon soln.}}}{\Delta w_{H_2O} - \Delta w_{\text{evacuated}}}$$

and the molar susceptibilities of the hydrocarbon anions were calculated according to Wiedemann's additivity rule by use of the expression $\chi_m = \kappa w/nd$ where n is the number of moles of hydrocarbon anion present in a solution of weight w and d is the density of the solution.

To determine the quantity of hydrocarbon anion present, the solution was hydrolyzed after the magnetic measurements and the liberated alkali titrated with standard hydrochloric acid. Where the number of moles of sodium reacted was less than that of the hydrocarbon originally used, it was assumed that an amount of monovalent anion equivalent to the liberated sodium was formed. Some hydrocarbons, such as anthracene, form bivalent anions quite readily; the quantity of bivalent anions was determined from the amount of sodium reacted and the hydrocarbon originally used. The amount of reaction between sodium and the aromatic hydrocarbon readily can be controlled, after some practice, by the time allowed for shaking.

The density of the solution was determined by means of an expansion pycnometer of about 5-ml. capacity with expansion neck about 10 cm. fitted to enable measurements under vacuum.

Results and Discussion

The reductions of anthracene, naphthalene, phenanthrene and *m*-terphenyl to the corresponding monovalent anions by sodium in tetrahydrofuran solution proceed readily to completion. However, the reaction between sodium and biphenyl in tetrahydrofuran involves a measurable equilibrium. Monovalent anions of anthracene and phenanthrene can be further reduced although the formation of the divalent phenanthrene anion is very slow.

The molar susceptibilities of various hydrocarbon anions in tetrahydrofuran solution were determined at different concentrations and part of the results are summarized in Table I.

TABLE I

MOLAR SUSCEPTIBILITIES OF HYDROCARBON ANIONS IN TETRAHYDROFURAN SOLUTION

Hydrocarbon anion	Wt. fraction	Temp., °C.	$\chi_m \times 10^6$
Naphthalene$^-$	0.05499	28	1239 ± 10
	.07631	28	1235 ± 10
Anthracene$^-$	.01679	26	1260 ± 20
	.02021	26	1243 ± 20
Biphenyl$^-$	.02033	26	1242 ± 20
	.03093	26	1250 ± 15
Phenanthrene$^-$	.07754	28	1242 ± 10
	.09758	26	1245 ± 10
m-Terphenyl$^-$	.06485	28	1241 ± 10
	.08039	26	1253 ± 10

Anthracene$^{=}$ diamagnetic
Phenanthrene$^{=}$ diamagnetic

If we assume that the Wiedemann additivity rule is obeyed and that the molecular field constants of the hydrocarbon free radicals are very small, all the monovalent anions under consideration are monomeric in solution. The paramagnetism of these solutions decreases gradually on standing at room temperature, indicating disproportionation. The disproportionation takes place so rapidly in concentrated solutions that attempts to measure the susceptibility of the sodium salt in the solid state were not successful. The monovalent anions of some other hydrocarbons, like di-α-naphthylmethane, were quite unstable even in dilute solution and no satisfactory results were obtained. Divalent anions of anthracene and phenanthrene are diamagnetic as expected because of the lack of degeneracy in the π-orbitals of these hydrocarbons. These divalent anions react reversibly with the corresponding hydrocarbons to form monovalent anions as is evidenced by the susceptibility measurements.

It has been shown[5] that two unlike monomeric triarylmethyls may associate considerably in solution. However, tetrahydrofuran solution of mixtures of monovalent anions of (1) naphthalene and anthracene, (2) naphthalene and *m*-terphenyl and (3) *m*-terphenyl and phenanthrene showed no tendency to associate. The greater stability of the monovalent anions over their dimers may be attributed to delocalization of the $(n + 1)$ electrons in the π-molecular orbitals, formed from the n atomic p-orbitals of the ring carbons.

The extent of reaction between sodium and biphenyl in tetrahydrofuran was further studied quantitatively. A tetrahydrofuran solution of biphenyl of known concentration containing excess sodium was sealed off in a tube under vacuum as in the preparation of a sample for magnetic measurements. The reaction appears to reach equilibrium in about 30 minutes; however, to ensure complete equilibrium, the tube was shaken for six to eight hours at room temperature, 25°. The resulting solution was hydrolyzed and titrated with standard hydrochloric acid. The experimental data which give the number of moles of biphenyl used N_B, the number of moles of tetrahydrofuran N_T and the number of gram atoms of sodium reacted N_S are summarized in Table II.

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(4) H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.* (*London*), **A173**, 313 (1939).

(5) T. L. Chu and S. I. Weissman, THIS JOURNAL, **73**, 4462 (1951)

TABLE II

EQUILIBRIUM DATA FOR THE REACTION BETWEEN SODIUM AND BIPHENYL IN TETRAHYDROFURAN AT 25°

Run	N_B	N_T	N_S
1	0.002774	0.06050	0.0008408
2	.003940	.06033	.0011735
3	.003291	.06057	.0009897

Since the monovalent biphenyl anion is monomeric in solution, we may assume that the following two equilibria are involved.

$$\mathrm{Na(s)} + \mathrm{C_{12}H_{10}} \longrightarrow \mathrm{NaC_{12}H_{10}} \qquad (1)$$

$$\mathrm{NaC_{12}H_{10}} \longrightarrow \mathrm{Na^+} + \mathrm{C_{12}H_{10}^-} \qquad (2)$$

Taking the standard state for sodium as the metal at 25° and assuming the activity of other molecules or ions equal to the mole fraction, the equilibrium constants, expressed in terms of mole fractions, for equations 1 and 2 may be written as

$$K_1 = \frac{N_S - x}{N_B - N_S}$$

$$K_2 = \frac{x^2}{(N_B + N_T + x)(N_S - x)} \approx \frac{x^2}{(N_B + N_T)(N_S - x)}$$

where x is the number of moles of sodium ion or biphenyl ion present at equilibrium. Eliminating x, we obtain

$$K_1K_2 = \frac{(N_S - K_1N_B + K_1N_S)^2}{K_1(N_B + N_T)(N_B - N_S)}$$

K_1 and K_2 can be evaluated from N_S, N_B and N_T of two different runs. Runs 1 and 2 give $K_1 = 0.367$ and $K_2 = 3.9 \times 10^{-4}$; runs 2 and 3 give $K_1 = 0.360$ and $K_2 = 4.8 \times 10^{-4}$; runs 1 and 3 give $K_1 = 0.370$ and $K_2 = 3.6 \times 10^{-4}$. The average values of K_1 and K_2 at 25° are 0.366 and 4.1×10^{-4}, respectively.

The reaction between sodium and aromatic hydrocarbons in tetrahydrofuran is reversible as indicated by the fact that the intense color of hydrocarbon anion solutions disappears almost completely on shaking with mercury and is restored again by shaking with sodium. Because of the nearly complete removal of sodium by mercury, it was not possible to obtain accurate data by approaching the equilibrium from the other side.

Acknowledgment.—The financial assistance of Research Corporation in carrying out this research is gratefully acknowledged.

PITTSBURGH, PA.

[CONTRIBUTION NO. 1179 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermoelectric Properties of Metal–Ammonia Solutions. I. The Thermoelectric Power of Sodium and Potassium at −33°

BY JACOB F. DEWALD[1] AND GERARD LEPOUTRE[2]

RECEIVED DECEMBER 10, 1953

The thermoelectric properties of sodium and potassium solutions in liquid ammonia at −33° have been studied over the concentration range from 0.002 *M* to saturation. Experimental procedures are outlined, with particular emphasis on methods of preparing solutions of maximum stability. The data for the concentrated solutions are shown to be in strikingly good accord with the predictions based on a degenerate electron gas model. In the dilute range of concentration, where one ordinarily expects the best agreement between theory and experiment, a marked anomaly is observed. The thermoelectric power increases with dilution almost exactly twice as rapidly as theory predicts it should.

Introduction

Investigations of the thermoelectric properties of matter have in the past been primarily concerned with metals and alloys and with electrolytes. In this and subsequent papers we report on our investigations of the thermoelectric properties of metal–ammonia solutions. Such solutions have been extensively investigated in the past and previous work has been reviewed recently.[3,4] Metal–ammonia solutions are unique in allowing one to study the behavior of electrons over an extremely wide range of concentration. Many theories have been presented to account for the observed behavior. The data which we present in this and following papers are in some ways quite anomalous; an understanding of the anomalies should afford additional evidence for a choice between the several models which have been proposed for these solutions.

Experimental

Elimination of Decomposition.—The greatest single difficulty encountered in previous physical measurements on metal–ammonia solutions has been the chemical reactivity of the solute metal with the solvent ammonia. The solutions are thermodynamically quite unstable, decomposing to yield hydrogen and metal amide. In our early work this instability proved troublesome, as it has for others in the past. This was especially true in dilute solution, and since particularly anomalous thermoelectric behavior was observed in this concentration range, considerable time was spent in attempting to minimize the rate of decomposition. Our experience in this regard is worth repeating in detail. Even in our early experiments elementary care was taken. The cells were cleaned with chromic acid solution in standard fashion. The sodium was distilled into the preparation cell under a vacuum of less than 10^{-5} mm.; subsequently sodium-dried ammonia was passed through glass wool and condensed onto the sodium. Although the general trends of the thermoelectric data were apparent (and were subsequently verified by more careful experiments) the scatter of the data was considerable.

To determine the extent of the decomposition reaction and its effect on our data, we then started making conductance measurements immediately before and after the thermoelectric measurements. The kinetics of the decomposition reaction were notably irreproducible at concentrations below 0.1 *M*. One solution would show a change of less than 0.1% per hour and the very next one might be as high as 10% per hour. The largest conductance changes were observed for potassium solutions; for a time we abandoned measurements on these. The figures quoted above represent true bulk decomposition rates, the solutions having been thoroughly mixed just prior to the conductance measurement. The measured resistance was invariably higher

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[3] C. A. Kraus, *J. Chem. Ed.*, **30**, 83 (1953).

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