

THE MAGNETIC SUSCEPTIBILITIES OF THE METAL KETYLs

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In partial fulfillment of the requirements for
the degree of Master of Science in Chemistry

California Institute of Technology
Pasadena, California

1934

CONTENTS

The dissociations of several metal ketyls into free radicals are found by measuring their magnetic susceptibilities in various solvents. It is found that the solvent has a very great effect upon the degree of dissociation. The metal ketyls are found to be only slightly dissociated, for the most cases, in benzene and diethyl ether.

The preparation of several ketones is discussed briefly.

Evidence of non-dissociation is brought out from boiling-point measurements.

The Magnetic Susceptibilities of the Metal Ketyls

Introduction

It does not seem that the question as to whether the metal Ketyls exist as free radicals has yet been settled. Schlenk and his co-workers seemed satisfied that they are completely dissociated (in particular in diethyl ether solution) when they left the problem about 1914. However, recently, Bachmann has come out with evidence of a chemical nature showing that no dissociation at all exists. It was in an effort to throw some light on the answer to this question by the application of a new method, that of determining the magnetic susceptibilities of the free radicals in various solutions, that the present problem was undertaken.

Apparatus

The metal ketyls are very unstable substances with respect to oxygen or any ionizable hydrogen, such as the hydrogen on the -OH group of alcohols and the enol forms of ketones. They are very highly colored, and traces of oxygen or moisture from the air coming in contact with them is evidenced by immediate disappearance of the color. For this reason manipulation with these substances is somewhat difficult. For the preparation and transfer of the solutions, the apparatus shown in figure 1 was used. B is a ground glass joint, so that the

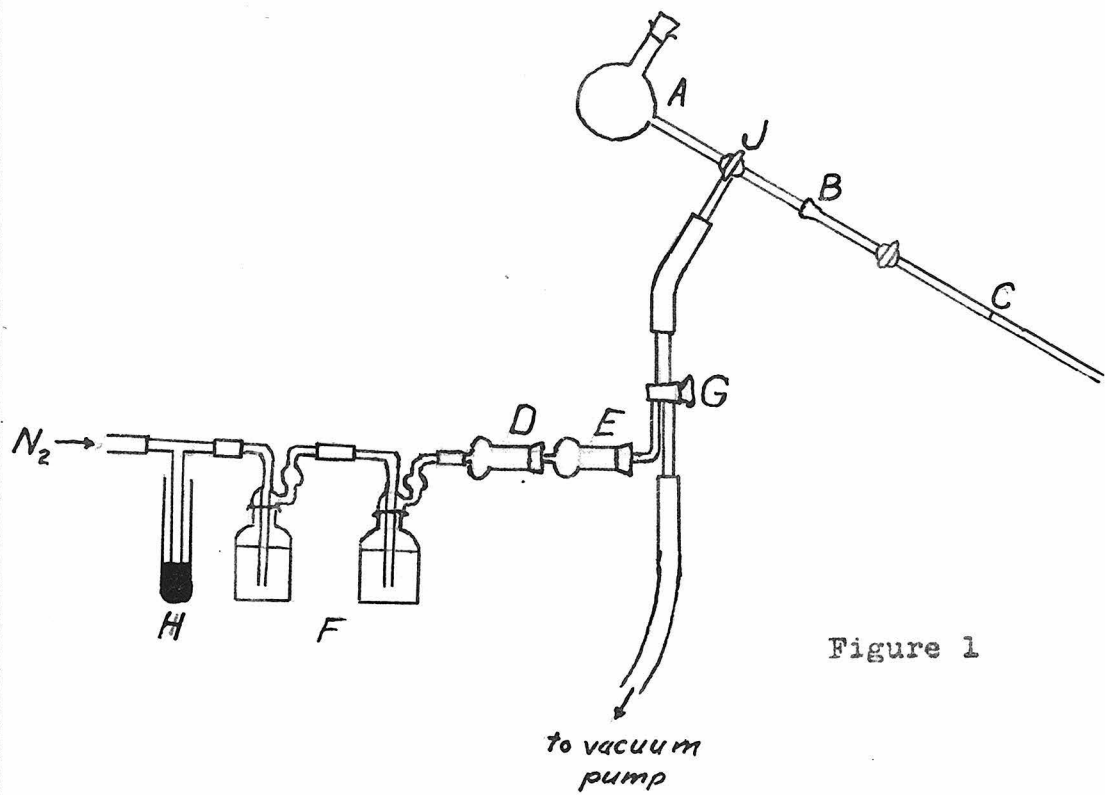


Figure 1

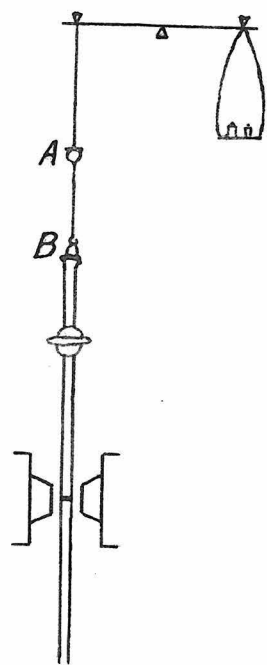


Figure 2

reaction flask A and its 3-way stopcock J may be detached from the rest of the apparatus. The two passages in the core of J meet each other at right angles. C is the tube which is placed between the poles of the magnet. It is divided by a glass partition, the lower half being open to the air; the measurements of magnetic susceptibility are thus made against air at one atmosphere. This tube is closed with a stopcock as shown in the diagram. G is a three-way stopcock arranged so that the tube C can either be evacuated or filled with dry nitrogen from the absorption train. H is a mercury seal for obtaining small pressures in the system. The gas wash-bottles F are filled with a potassium hydroxide solution of potassium pyrogallate to remove any traces of oxygen left in the nitrogen from the tank. D is filled with anhydrous calcium chloride and E with phosphorus pentoxide so that all traces of moisture are removed from the gas.

The apparatus is used as follows: The reaction flask A with its stop-cock J is detached and partially filled with the ketone solution, after which sodium wire is introduced. The flask is then closed and placed in a shaking machine for the proper length of time. Any oxygen initially in the flask is soon removed by the reaction with the metal ketyl, the ketone being regenerated and reacting with more sodium until all the oxygen is gone. After the reaction is complete, the reaction flask is connected with the tube C and the stopcock G, and the whole is allowed to stand until any sediment has

3

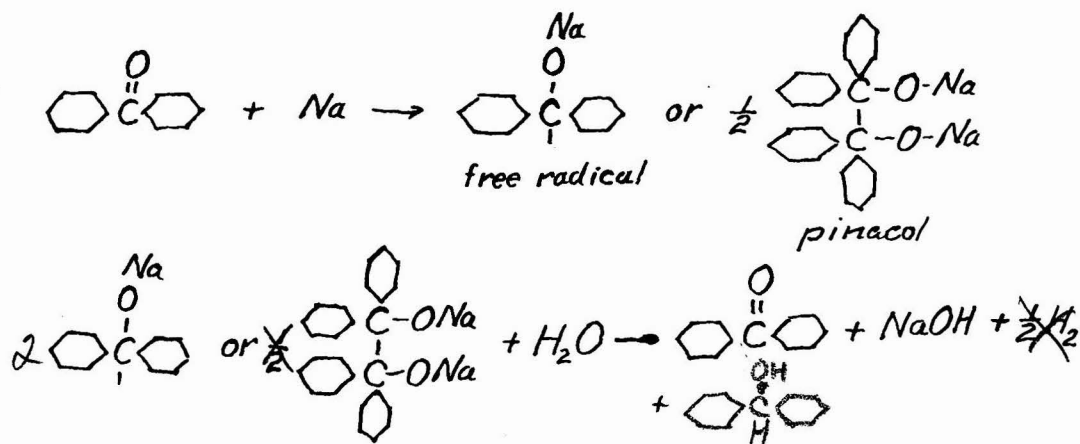
settled. The upper part of the tube C is then filled with nitrogen by alternately evacuating and filling with nitrogen until all traces of oxygen are removed. The tube C is then evacuated once more and the metal ketyl solution drawn in from the upper surface of the liquid in the reaction flask. C is filled to a certain mark, and the space between the liquid and the stopcock is filled with nitrogen.

Figure 2 is a diagram of the apparatus for measuring the magnetic susceptibility of the metal ketyl solutions by the Gouy method. A rod is suspended from the left stirrup of the balance carrying a hook B at its lower end. The rod is broken at A and an arrangement made to use the pan rest. The tube containing the metal ketyl is suspended from the hook B between the poles of the magnet in such a way that the partition is half-way between the upper and lower edges of the pole-pieces. The whole suspended system is enclosed in a carefully constructed wooden box to eliminate air currents. A thermometer is placed in the box for recording temperatures. The door of this box is provided with a window opposite the pole-pieces for observing the tube. The magnet is provided with cooling coils through which water flows. The current is furnished by a direct-current generator and is controlled by means of rheostats. The core is demagnetized by means of a small, gradually-decreased, alternating current. The same cycle

of current changes is repeated each time, so that the same field is reproduced very closely. The field is found to be about 16,500 gauss at 14.0 amperes.

Chemicals

The concentration of metal ketyl in the solution is found by treating the contents of the tube with water and titrating the sodium hydroxide formed with dilute hydrochloric acid. The volume of the tube up to the mark was found by seventeen measurements of the difference in the weight of the tube when filled with water or benzene and when empty, the density of the liquid at the temperature involved being known. The reactions are illustrated for the case of benzophenone below:



The hydrochloric acid was standardized with carefully prepared anhydrous sodium carbonate and with carefully prepared sodium tetraborate. Agreement within 0.2% was obtained between the two methods.

The benzophenone used had a pure white color and melted at 48.0° - 48.5° , the literature value. The p-methoxybenzophenone had a melting-point of 61° - 62° (literature value 62°). The p-biphenyl phenyl ketone was prepared on the basis of the very brief directions in "Beilstein's Handbuch der Organischen Chemie" (vierte auflage), band VII, s. 521. It was crystallized 3 times from alcohol, after which it had a good white color and a melting-point of 101° - 102° (literature value 102°). The yield was about 10%. Three attempts were made to prepare naphthyl phenyl ketone before a successful method was obtained. The first was from benzoyl chloride and naphthalene, anhydrous zinc chloride being used as a catalyst. The second was from α -naphthyl magnesium bromide and benzoyl chloride in anhydrous ether. The successful method was to oxidize α -benzyl naphthalene by refluxing it thirty hours with nitric acid of 36° Be' gravity. References to all these methods will be found in "Beilstein's Handbuch der Organischen Chemie" (vierte auflage), band VII, s.511. The α -benzyl naphthalene was prepared according to directions found in the same reference, band V, s.689. The α -naphthyl phenyl ketone had a fair white color and a melting point of 74.5° - 75.5° (literature value 75.5°). The yield over the two processes (the preparation of the hydrocarbon from naphthalene and benzyl chloride with zinc dust as a catalyst and its oxidation with nitric acid) was about 2%.

Manipulation

The ketone solutions were shaken with sodium wire for a period of four to four and one-half hours, this time being sufficient for complete conversion of the ketone to the metal ketyl in the case of benzophenone, according to Schlenk. It was found by making the ketone solutions up in a definite known concentration and analyzing them for sodium afterwards that this time was sufficient. It was observed that the rate of reaction was much greater in the case of p-biphenyl phenyl ketone. However, the reactivity of p-methoxybenzophenone was much lower than that of benzophenone, there being a certain, (relatively high) concentration of the ketone necessary for the reaction to go at all.. This effect was not observed with either of the other two ketones.

It was observed that there were small changes in the field of the magnet (at 14.0 amperes) from day to day, although the same cycle of current changes had been repeated in all the measurements. To eliminate error from this source it was necessary to find the force on the tube filled with the standard substance (benzene) just before or just after each measurement on a metal ketyl solution. For some of the measurements a standard tube filled with benzene was used; this tube was calibrated against the original tube filled with benzene.

The generator would not maintain a very steady voltage at the voltage at which it was necessary to operate it, and this added to the difficulty of the measurements. The balance was not as fine an instrument as should have been used for this work, but by repeating the weighings three to six times, it was possible to eliminate errors. A weighing with "no field" was made both before and after each weighing with the field corresponding to 14.0 amperes, and if there was any difference between the "no field" weighings, the average was taken.

When the electromagnet had not been used for some time, a "drifting" effect was observed, that is, the value for the force on the tube would start high and gradually diminish to a steady value as more weighings were made. The steady value was the one taken. By making measurements with both water and benzene, it was shown that the steady value was the correct one, the susceptibilities for water and for benzene being known.

Formulas

The theory of the Gouy method for magnetic susceptibility gives the following equation:

$$\frac{X_A - X_B}{X_0} = \frac{F_A}{F_0}$$

where X_A is the volume susceptibility to be found

X_B is the volume susceptibility for the substance

B in the lower half of the tube (air, in this case)

X_0 is the volume susceptibility of the substance used
as a standard

F_A is the force when the tube is filled with the
substance the susceptibility of which is desired

F_0 is the force when the tube is filled with the
standard substance.

To find the molal susceptibility of the solute, we must
first calculate its contribution to the volume suscepti-
bility of the solution and then use the following equation:

$$X_M = \frac{X'_A}{C}$$

where X_M is the molal susceptibility of the solute

X'_A is the contribution of the solute to the
volume susceptibility of the solution.

C is the concentration of the solute in moles
per cubic centimeter.

From the Langevin theory we have the following relation:

$$X_M = N\alpha + \frac{Nu^2}{3kT}$$

where α is the diamagnetic susceptibility per molecule

u is the "permanent" magnetic moment per molecule

k is Boltzman's constant

N is Avogadro's number

T is the absolute temperature.

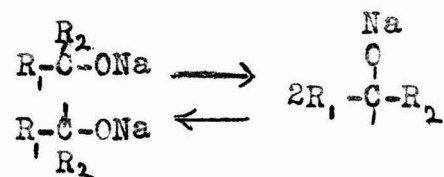
If we solve this last equation for u, we obtain

$$u = 2.83 \sqrt{T(X_M - Na)}$$

in Bohr magnetons. The percentage dissociation into free radicals is given by

$$D = 100 \frac{u^2}{3} \cdot$$

The dissociation is of the following form:



where R₁, R₂, R₃, and R₄ are aryl radicals.

Data

Metal Ketyl	Solvent	Wt. of Solution	Force on solution (mg)	Force on Benzene (mg)	NaOH Found in analysis
<u>p-biphenyl phenyl ketone sodium</u>	<u>benzene</u>	<u>3.334 gm</u>	<u>20.2 (27°)</u>	<u>20.1 (27°)</u>	<u>0.00105 moles in tube</u>
p-biphenyl phenyl ketone sodium	dioxane	3.948	19.6 (26°)	20.9 (26°)	0.000383
# p-methoxybenzophenone sodium	benzene	3.330	20.9 (25°)	21.1 (25°)	0.000147
benzophenone sodium	benzene	3.247	20.5 (25°)	20.4 (24°)	0.000267

Volume of tube (to mark) 371 cc.

The value of $N\alpha$ for the various metal ketyls as calculated according to Pascal's rule from values in the "International Critical Tables" are as follows:

p-biphenyl phenyl ketone sodium	-173 x 10 ⁻⁶ cgs _m . units
p-methoxybenzophenone sodium	141
benzophenone sodium	-124

Specific susceptibility for benzene ("International Critical Tables") -0.712 x 10⁻⁶ cgs_m, units.

#

The solution contained excess ketone; this was necessary to make the reaction go at all.

The analysis of the contents of the tube showed 0.1965 gm. total ketone, or 0.1625 gm.

excess ketone. The molal susceptibility of p-methoxybenzophenone as calculated according

to Pascal's rule from values in the "International Critical Tables" is -117 x 10⁻⁶ cgs_m. units.

Results of Magnetic Measurements

The table below gives the calculated percentages of dissociation for the various solutions. In making the calculations, the values for $N\alpha$ were found according to Pascal's rule from values in the "International Critical Tables". The calculated values for $N\alpha$ are accurate to within one or two percent.

Solute	Solvent	Conc.	Temp.	Percentage Dissociation	
				Min.	Max.
p-biphenyl phenyl ketone sodium	benzene	9.4%	27° C	1.7%	3.0%
p-biphenyl phenyl ketone sodium	dioxane	3.0%	26°	36%	41% 45%
p-methoxybenzophenone sodium	benzene	1.0%	25%	17%	33% 42%
benzophenone sodium	benzene	1.7%	25%	0%	1.0%

In the first column under "Percentage Dissociation" are given values calculated under the assumption that the values for the force on the solution and for the force on the standard substance (benzene) are each in error by one-tenth of a milligram, the error being taken with such a sign that the percentage dissociation will be a minimum. In the third column under this same head are given values calculated under the same assumption but with the errors taken with the sign that gives the maximum value for the percentage dissociation.

Perhaps too much weight should not be placed on the values for p-methoxybenzophenone sodium since the solution was necessarily very dilute and the sensitiveness of the method decreases very rapidly with decreasing concentration.

A very remarkable solvent effect is noted in the case of p-biphenyl phenyl ketone sodium. This great increase in dissociation does not seem to be due to the fact that dioxane is an ether since diethyl ether does not have this effect (as we shall see later), nor to the fact that dioxane has a ring structure since benzene also possesses a six-membered ring structure.

When it was observed that benzophenone sodium appeared to be almost completely associated in benzene solution, it was thought profitable to try replacing one of the phenyl groups with a p-biphenyl group since the latter group greatly enhances the dissociation in the case of the ordinary carbon free radicals. For this reason, also, α -naphthyl phenyl ketone was tried, but this ketone resisted all efforts to cause it to form a metal ketyl. Sodium, potassium, and sodium amalgam were all tried, but without effect. This effect may be due to steric hinderance. It could hardly be due to impurities, although impurities do have a great effect, since a metal ketyl was always obtained with the other ketones when in moderate concentration, although the metal ketyl might not go into solution. p-methoxybenzophenone was tried because the p-methoxy group greatly increases the dissociation in the case of the nitrogen free radicals.

It was thought possible that the failure to detect dissociation of the p-biphenyl phenyl ketone sodium in benzene

solution might be due to the diluteness of the solution. A measurement on some of the solid precipitated in the bottom of the tube was accordingly made (the solid is colored), but it was found to be diamagnetic.

It is remarkable how traces of certain impurities will reduce the reactivity of the ketone and especially how they will cause the metal ketyls to coagulate (the solutions are always supersaturated). One of the impurities is thiophene, but there are others. In one case, the thiophene was carefully removed from a certain sample of benzene and the benzene distilled, the portion boiling at a constant temperature being taken. Yet there was some impurity present which caused the metal ketyl to coagulate.

Results from Boiling Point Data

Schlenk performed the following experiment: ("Berichte der Deutschen Chemischen Gesellschaft", V. 46, p. 2840 (1913)). He observed the boiling point of a certain sample of anhydrous diethyl ether; he then introduced a weighed quantity of p-biphenyl phenyl ketone and again observed the boiling point; now he introduced a piece of potassium metal and watched the boiling-point. No change in the boiling point of the solution after the second addition was observed, according to Schlenk. The solution was in contact with an atmosphere of nitrogen. Schlenk uses this as evidence that the metal ketyl is completely dissociated. However,

upon repeating this experiment the following results were obtained;

	I	II
Reading at boiling-point of ether	1.545	1.500
Reading at boiling-point of ketone solution	1.998	1.585
Reading after steady value was reached following addition of potassium	1.737	1.540
Wt. ketone used	1.202gm.	0.293gm.
Wt. ether used (approximate)	21.6 gm.	21.6 gm.

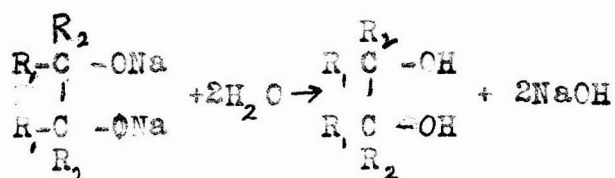
In each case the deep green color of the metal ketyl began to appear about five minutes after the potassium metal had been added. The temperature then gradually fell until the steady value recorded was reached. In I the steady value was reached in about an hour and in II it was reached in about two hours. In each case, to make certain that no further change would take place, the boiling was allowed to go on at the steady value for about an hour. The slowness of the fall in temperature seems to be due to the slowness of the reaction. The solution was such a deep green at the end of both experiments that light could not be seen through it; there was an excess of potassium metal in each case. The fact that the third reading in each experiment was not half-way between the other two is probably due to the fact that a very small ring of precipitated metal ketyl formed on the glass just above

the level of the liquid. This was due to spattering (when the metal ketyl is once precipitated from solution, it will not dissolve). Calculations from the above figures show that the ketone exists as single molecules in the ether solution. These experiments show that the metal ketyl is probably ^{not} dissociated at all in the ether solution.

Certain organic chemists feel that too much reliance can not be placed upon such boiling point evidence. It was from a desire to find out whether such evidence is reliable that experiments similar to the above were tried using dioxane as the solvent. It appears, however, that at the boiling-point of dioxane (101°) the metal ketyl is almost completely coagulated. There is evidence, also, that at this temperature there is considerable breaking up of the ketone into smaller molecules by the alkali metal.

Evidence of a Chemical Nature.

Bachmann has pointed out ("Journal of the American Chemical Society", v.55,p.1179 (1933)) that if the ketone is completely associated, a pinacol should be obtained upon the reaction of the metal ketyl with water, according to the following equation:



where R_1 and R_2 are aryl radicals. However, he also points out that these pinacols are unstable in alkaline solution. He repeats that he obtained good yields of some of the pinacols by pouring the metal ketyl solutions into acid solutions. He closes the argument by pointing out that if a pinacol could be found which is stable in alkaline solution, the corresponding metal ketyl should give a 100% yield of the pinacol. Such a pinacol is 9,10-diphenyl-dihydrophenanthrene-diol, and Bachmann says that he obtained a 100% yield of this pinacol.

It yet remains to explain the color of these metal ketyls in solutions in which they have been found to be almost completely associated. We might say that the free radical is so very highly colored that the small amount present gives rise to the observed color. This is supported by the observation in the case of the p-biphenyl phenyl ketone sodium that the dioxane solution, although only about one-third as concentrated as the benzene solution, was far darker than the latter; the dissociation is quite high in dioxane but only very low in benzene.

Summary

1. A new method, that of magnetic susceptibility, is applied to the determination of the dissociation of the metal ketyls.
2. The preparation of certain aromatic ketones is discussed.

3. The formation and properties of the metal ketyls is discussed.
4. A very remarkable specific solvent effect is noted.
5. Evidence from boiling points in agreement with the magnetic evidence but in disagreement with certain previous work is given.

Literature Reference

Sugden ("Transactions of the Faraday Society," Jan. 1934, p.23) gives the results of some measurements of the magnetic susceptibilities of benzophenone potassium and p-biphenyl phenyl ketone potassium in dioxane. He gives no particulars but says that these are about 85% dissociated in solutions which are more concentrated than those employed here.