DISSOCIATION CONSTANTS OF AROMATIC POLYNITRO

ADDITION COMPOUNDS WITH BENZENE

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INTRODUCTION

The complexes formed by polynitro compounds with aromatic hydrocarbons are among the best known of the purely organic molecular compounds. They are used as derivatives in the identification of both their component classes of compounds. As interest in the structure of addition compounds has risen, both preparative methods and physical measurements have been applied to determining relative stabilities of the polynitro complexes.

Numerous investigators, (see for example, Baril and Hauber (1), and Pfeiffer and co-workers (2)) have noted the tendency of the mononuclear hydrocarbon picrates to lose the hydrocarbon by efflorescence. Since the salt hydrates have been studied so widely and effectively by vapor pressure measurements, the same method seemed an attractive new approach to measuring heats of dissociation of these addition compounds. It does not indicate the ratio of molecules reacting, but in most cases this is already known to be 1:1 from preparative work or thermal analysis.

HISTORICAL

Very few studies of the aromatic polynitro addition compounds with benzene have been made in the past, probably because of their high degree of instability. Other organic complexes, however, such as the picrates of aromatic hydrocarbons and naphthalene-aromatic polynitro addition compounds, have been studied to some extent by various methods and thus it seems worthwhile to review these methods.

Most work on organic molecular compounds may be classified as (1) investigation of the possible existence of particular combinations and (2) determination of their stabilities. The existence of addition compounds has usually been detected by isolation and analysis of the compounds. However, physical methods have not been neglected. Practically all of them depend on finding and interpreting some deviation from linearity of a measurable property of the binary mixture. Since thermal analysis thus establishes both the ratio of combination and melting point of a possible complex, it has been widely used. (3, 4, 5, 6, 7, 8, 9)

Perhaps the only feature distinguishing qualitative studies of stability from mere tests of existence is the aim of the investigator: by comparison to relate structure to stability. Even quantitative researches, however, are difficult to correlate because in some instances the compounds have been studied in the solid state while in others measurements have been made on them as solutes. As would

be expected, therefore, the dissociation constants reported by various authors vary with the conditions used.

Kendall (10) explained the presence of picrates by the formation of oxonium salts. The existence and stability was determined from the freezing point curve. The melting point was determined by distectic points on the fusion curve.

Kremann (11) in a study on the influence of substitution on binary solution equilibria found the capacity for forming addition compounds not only increases with the number of nitro groups but depends largely on the number of benzene rings in the hydrocarbon.

Drucker (12) in his pycnometric studies of chemical equilibrium established a method of determining the equilibrium constant from the volume of the solution, in the case where there is a measurable difference in the molar volumes of the reactants and products. This was applied to phenanthrene picrate in benzene and xylene.

Bhatnagar, Nevgi, and Tuli (13) measured the diamagnetic susceptibilities of anthracene, naphthalene, and phenanthrene picrates in the solid state and in solution in very pure benzene and found them to be lowered in solution. The values approach those given by the law of mixtures, from which it is concluded that the molecules are dissociated in solution.

Moore, Shepherd, and Goodall (14) in a study of the equilibrium

picric acid + hydrocarbon $\rightleftharpoons$ addition compound
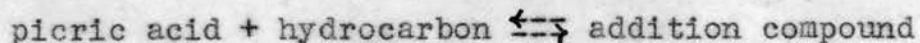
by partition between water and chloroform, assuming 1:1 addition, found the following equilibrium constants: benzene 0.09, toluene 0.12, o-xylene 0.16, m-xylene 0.14, p-xylene 0.16, mesitylene 0.18, naphthalene 2.17, 1-methylnaphthalene 2.76, 2-methylnaphthalene 3.44.

Briegleb (15), from optical data, calculated the heat of dissociation for molecular compounds of o-, m-, and p-dinitrobenzene and sym-trinitrobenzene with naphthalene, biphenyl, and anthracene.

Kremann and Grasser (16), by means of calorimetric studies, found the following degrees of dissociation of the fused complexes of several nitro compounds with naphthalene: m-dinitrobenzene 0.93, p-dinitrobenzene 0.87, 2,4-dinitrotoluene 0.86, 2,4-dinitrophenol 0.83.

Behrend (17) showed that the solubility of anthracene in alcohol was increased by picric acid and found a dissociation constant for the complex of 4.7-5.7 at $25^{\circ}C.$, a value confirmed by Dimroth and Bamberger.

Dimroth and Bamberger (18), through a study of the behavior of a series of hydrocarbons with picric acid in various solvents, found the following relative order of increasing stability of the complex: benzene, fluorene, anthracene, naphthalene, acenaphthene, 1-methylnaphthalene, 2-methylnaphthalene.

Arends (19) studied picric acid compounds of some stilbenes and calculated the equilibrium constant from solubility changes in the heterogeneous systems.

Vanzetti (20) determined the heat of formation of naph-thalene picrate calorimetrically in ethyl alcohol to be 1450 calories.

Bronsted (21), by means of E.M.F. studies of the system naphthalene-picric acid-KCl-HCl-H$_2$O, found the heat of formation of naphthalene picrate to be 2050 calories. He also found that the compound becomes more stable with rising temperature.

Brown (22), using nitrobenzene as a solvent, found the following equilibrium constants from the depression of the freezing point: naphthalene picrate 0.228, naphthalene-tri-nitrotoluene 0.464. From these equilibria, the free energy of formation of naphthalene picrate was calculated to be 2083 calories, which agrees well with the value obtained by Bronsted.

Nagornow (23) determined the molecular weight of naph-thalene-m-dinitrobenzene in benzene and found practically complete dissociation. Nevertheless, the heat of solution of the complex was found to differ by 165 gram calories per mole from that of the mechanical mixture.

Halban and Zimpelmann (24), using a photoelectric meth-od, determined the following dissociation constants from extinction coefficients at various concentrations: acenath-thene-sym-trinitrobenzene in tetrachloroethane 0.497, ace-naphthene-m-dinitrobenzene in tetrachloroethane 3.51, ace-naphthene-picric acid in tetrachloroethane 0.524, anthracene-picric acid in chloroform 0.219.

Briegleb and Schachowski (25), using a method similar to that of Halban and Zimpelmann, calculated the heats of dissociation from their results for the trinitrobenzene-naphthalene complex in various solvents: in carbon tetrachloride 3.45, in ether 0.99, in benzene 1.90 calories.

Hammick and Sixsmith (26) found that the initial rate of decomposition of the compound of methyl 4,6,4',6'-tetranitrodiphenate (2 mols.) with indene (1 mol.) corresponds to a unimolecular constant $K_1 = 0.053$ and its formation to a bimolecular constant $K_2 = 1.0$.

A search of the literature revealed no instances in which aromatic hydrocarbon-aromatic polynitro compounds have been studied by vapor pressure methods. However, it was deemed worthwhile to include a few cases in which such methods have been employed to determine stability of other organic molecular compounds.

Rowley (27) measured the vapor pressure of magnesium bromide-diethyl ether solutions by a static method. "Occluded" gases were removed by cooling and continual evacuation until readings were constant.

Gooden and Smith (28) determined the dissociation pressure of the carbon tetrachloride solvate of rotenone and calculated the heat of dissociation from the results obtained.

Davis and Batchelder (29) measured the dissociation pressures of metal pyridine thiocyanates by a static method. Excess pyridine was used to remove air in the system and evacuations were made until constant pressures were reached.

EXPERIMENTAL

Reagents

The chemicals used are listed below with an indication as to their purity. All temperature readings are in degrees Centigrade.

Benzene — Commercial product.

It was dried over sodium for two days, distilled, and the first 50 ccs. of the distillate rejected.

Sulfuric acid — C.P.

Picric Acid — Reagent grade containing an added ten percent of water. It was dried for twelve hours in an oven at 75-80°.

M.P. 121-122°.

2,4,6-Trinitrotoluene — Commercial product.

It was recrystallized from a mixture of carbon tetrachloride and ethylene chloride.

M.P. 80.3-80.8°.

1,3,5-Trinitrobenzene — C.P. M.P. 121-122°.

2,4,6-Trinitro-m-cresol-C.P. M.P. 105-6°

Apparatus

The apparatus used in this study is essentially the same as that of Smith and Menzies (30). The special feature of their method consists in the ease with which, by adding a slight excess of the volatile component, the system may be swept free of foreign gases by repeated evacuations. This expulsion may be continued until a constant pressure indicates that equilibrium has been attained. The apparatus also possesses the advantage of requiring only a small amount of material.

In order to make clear its operation and point out the modifications, it will be necessary to describe fully the more important parts of the apparatus.

Figure 1 shows an almost actual size drawing of the isotensiscope. The substance to be studied is placed in A, which is a bulb of about 50 ml. capacity sealed to a ground glass connection. This is superior to the older form of apparatus in that it facilitates the removal or exchange of material. As an added precaution to prevent the bath liquid from entering the flask, the ground glass connection was flared to permit use of a mercury seal. On opposite sides of the tubing both above and below the connection are sealed small glass nipples to aid in supporting the flask and contents. Rubber bands hooked over the nipples serve this purpose very well. The upper part of the connection is sealed to pyrex tubing 10 mm. in diameter; this, bent as shown, constitutes the remainder of the isotensiscope. The
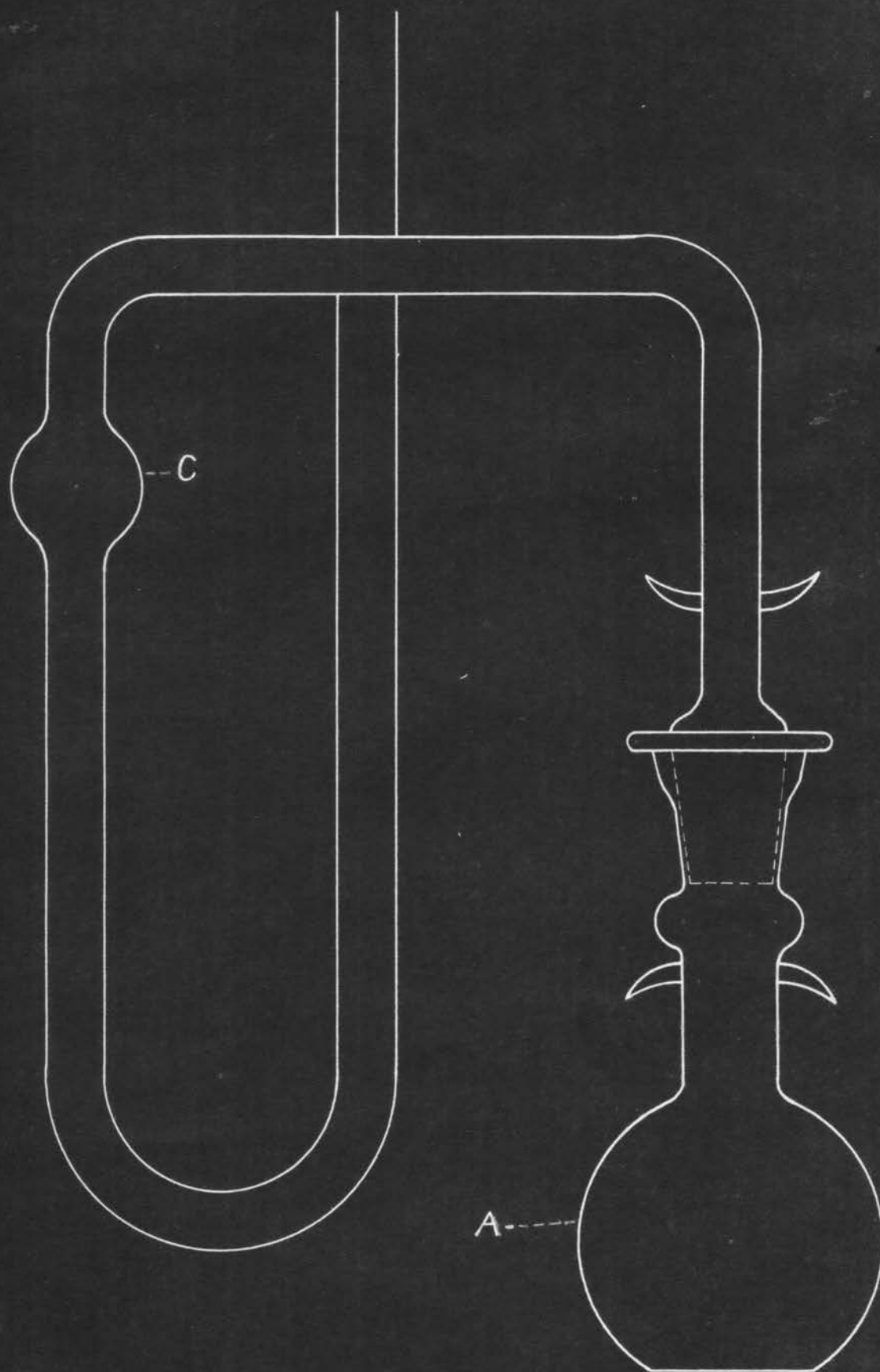
Fig. 1

confining liquid occupies the U-tube, which is about 150 mm. in height, to a height of 40-50 mm. C is an overflow bulb to prevent the confining liquid from being sucked back into A. The vertical tube is about 40 cm. in length so that attachment to the rest of the system may be made sufficiently far above the heated bath.

The bath is a four-liter beaker, which, when filled with water, permits complete immersion of the bulb and U-tube. Heating of the bath is accomplished by means of a micro burner at the lower temperatures and a bunsen burner at the higher ones. In this manner the temperature may be maintained constant to $0.1°$ or even to $0.05°$ with more care. At the higher temperatures, control is more difficult but equilibrium is reached more quickly. Although the amount of absolute error at these high temperatures is probably greater, the pressure being read is likewise higher and the percentage error is no more serious. A mechanical stirrer is used to insure uniform heating of the bath.

A $100°$ thermometer graduated in $0.1°$ is used after having been checked against a thermometer calibrated by the Bureau of Standards. Complete immersion of the mercury column is not possible in a bath of the size used but the same depth of immersion is made during calibration and use.

The manometer is of the open-end type, readings of the mercury levels being made with a cathetometer. Use of a manometer of this type requires frequent readings of the barometer but it was chosen in preference to the closed-end

type in the interests of accuracy. According to Robertson (31), "The short closed-tube manometer, universally sold in the apparatus market, is almost useless in the ordinary laboratory. After a short period of use, air, water, or other volatile material is certain to creep into the closed space and throw all readings into serious error".

General Procedure

Figure II shows a complete drawing of the apparatus to which reference will be made in the following discussion.

The polynitro compound together with excess benzene is placed in the detached bulb of the isotensiscope and warmed until solution is complete. Upon cooling, the compound crystallizes out. The formation of a solid cake is prevented by shaking the flask during crystallization. By means of a pipette, the confining liquid is introduced through the vertical tube of the isotensiscope into the lower part of the U-tube. Concentrated sulfuric acid was chosen as the confining liquid for this study because it does not possess an appreciable vapor pressure of its own and because its low density, compared to that of mercury, makes its sensitivity to pressure differences high. It does dissolve small amounts of benzene vapor but this solubility is believed to introduce no serious error. Smith and Menzies (32) obtained satisfactory values for the vapor pressure of benzene by a method similar to this in which they used sulfuric acid as the confining liquid. A drying tube containing calcium
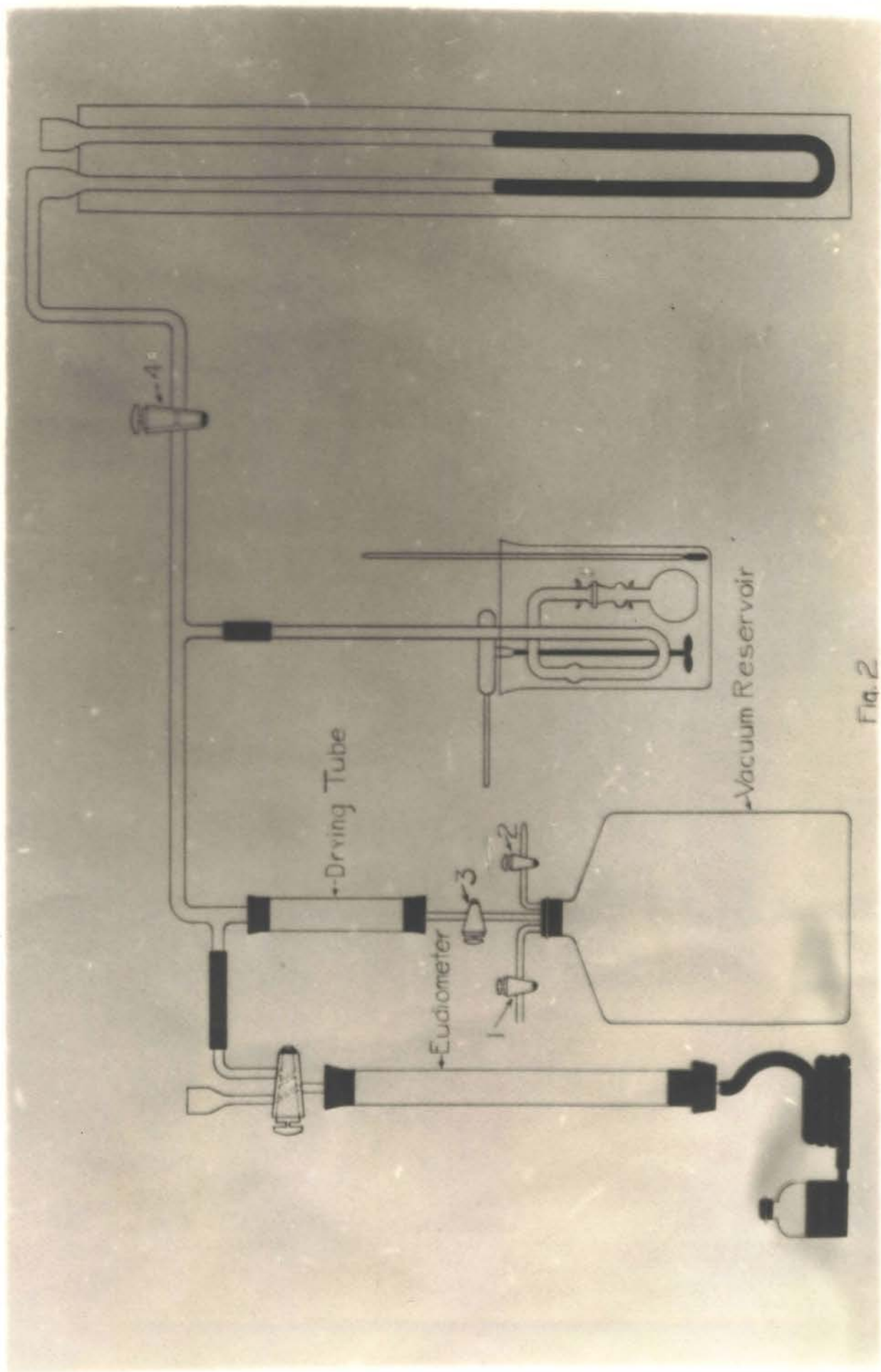
Drying Tube

Eudiometer

Vacuum Reservoir

Fig. 2

chloride was placed just above the vacuum reservoir to min-
imize dilution of the acid by water vapor. In order to test
the apparatus used in this study, the vapor pressure of ben-
zene was again determined and the results obtained checked
very well with those found in the literature.

The bulb is attached to the rest of the isotensiscope
and placed in the bath. Connection to the system is made
with pressure tubing. Stopcocks 2 and 3 are closed immedi-
ately but 1 remains open until the reservoir is evacuated
as completely as possible.

When the bath has reached the desired temperature, stop-
cock 3 is opened slightly until the confining liquid is
pulled to the far side of the U-tube and benzene vapors pass
freely through it. After a short period of evacuation, stop-
cock 3 is closed and 2 is opened. When the pressure in the
reservoir is slightly greater than that of the system, stop-
cock 3 is again carefully opened and air admitted until the
two levels of the confining liquid appear identical to the
eye. Stopcocks 3 and 4 are then closed and the two mercury
levels in the manometer are read. This process of evacua-
tion, leveling, and reading is repeated until constant val-
ues are obtained. Since an excess of benzene is used, one
series of constant values is obtained, (the vapor pressure
of benzene saturated with the molecular compound) followed
by a sudden drop when the excess is removed and then another
set of constant values when only the molecular compound re-
mains. The temperature is then raised to another desired

point and the process of evacuation is again repeated until
constant values are obtained. After the air has once been
displaced and the constant pressure of the molecular com-
pound obtained, it is unnecessary and undesirable to remove
much gas by evacuation. Particularly if readings are to be
made in tandem at several temperatures, there is danger of
exhausting all the benzene from the compound before measure-
ments are complete.

For each compound, one series of determinations is made
in which the temperature is held constant at 30° and evacua-
tions repeated until all benzene is removed. Should a third
set of constant values be obtained, it would indicate the
presence of another compound. The Hulett-type eudiometer,
shown in figure II, is used to secure pressures lower than
those obtainable with the water pump.

Results

In the following tables, the observed pressure in every case is the average of the closely agreeing results of at least two series of determinations. A change of compound and confining liquid was made between each series. At each temperature in each determination, at least five readings of constant pressure were taken.

TABLE I

Vapor Pressures of Benzene

Temp., °C	Observed pressure mm.	Pressure found in literature (33,34)
25.9	97.2	----
29.2	114.2	114.5
30.0	118.2	118.24
33.5	138.3	138.6
35.0	146.6	----
40.0	180.6	181.08
45.0	219.6	----
50.0	268.5	268.97

TABLE II

Dissociation Pressures of Benzene Picrate

Temp.,^{o}C	30.1	40.1	50.05	59.9
Press.,mm.	97.3	167.9	250.1	355.5

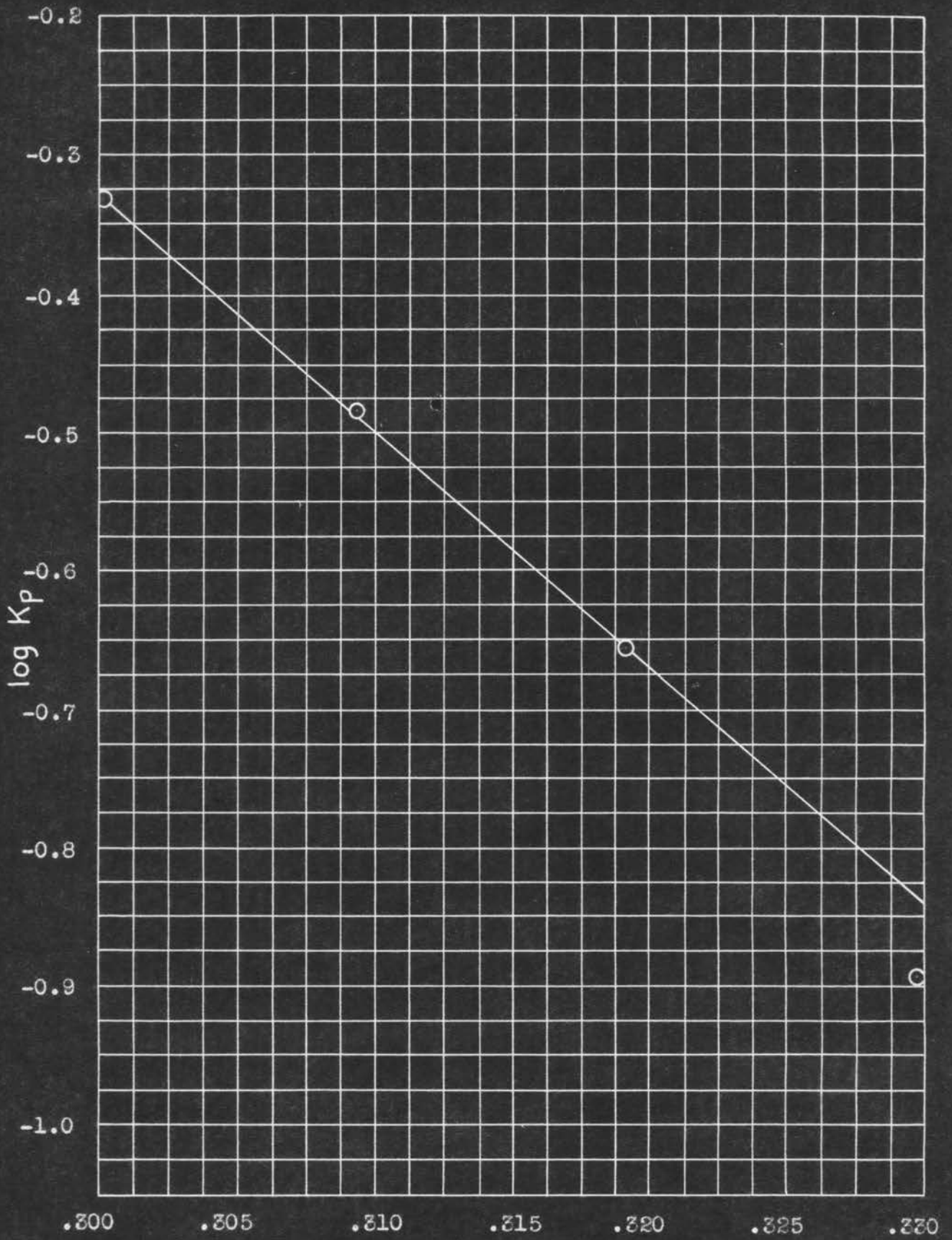| T (abs)	K_p (atm.)	1/T	log K_p
303.2	0.128	0.003298	-0.893
313.2	0.221	0.003193	-0.656
323.15	0.329	0.003095	-0.483
333.0	0.468	0.003003	-0.330

In Fig. III values of log K_p for the dissociation of benzene picrate are plotted against 1/T and the best straight line drawn through the points. The following equation relates the pressure expressed in atmospheres with the absolute temperature:

$$\log P = -\ 1870/T + 5.304$$

The heat of dissociation, ΔH, is calculated from the slope of the line as follows:

$$-\Delta H = \text{slope x } 2.303\ R$$

Since the slope is -1870 and R is 1.987 calories, ΔH is found to have a value of 8550 calories.

Fig. 3

TABLE III

Dissociation Pressures of Benzene-sym-Trinitrobenzene Complex

Temp.,°C	30.1	40.1	50.05	59.9
Press.,mm.	112.7	173.0	256.4	363.0

T (abs.)	K_p (atm.)	1/T	log K_p
303.2	0.148	0.003298	-0.829
313.2	0.228	0.003193	-0.643
323.15	0.337	0.003095	-0.472
333.0	0.478	0.003003	-0.321

In Fig. IV, values of log K_p are plotted against 1/T. The equation relating the pressure to the temperature is:

$$\text{Log } P = -1760/T + 4.975$$

The slope of the line being -1760, the heat of dissociation, ΔH, is found to be 8050 calories.
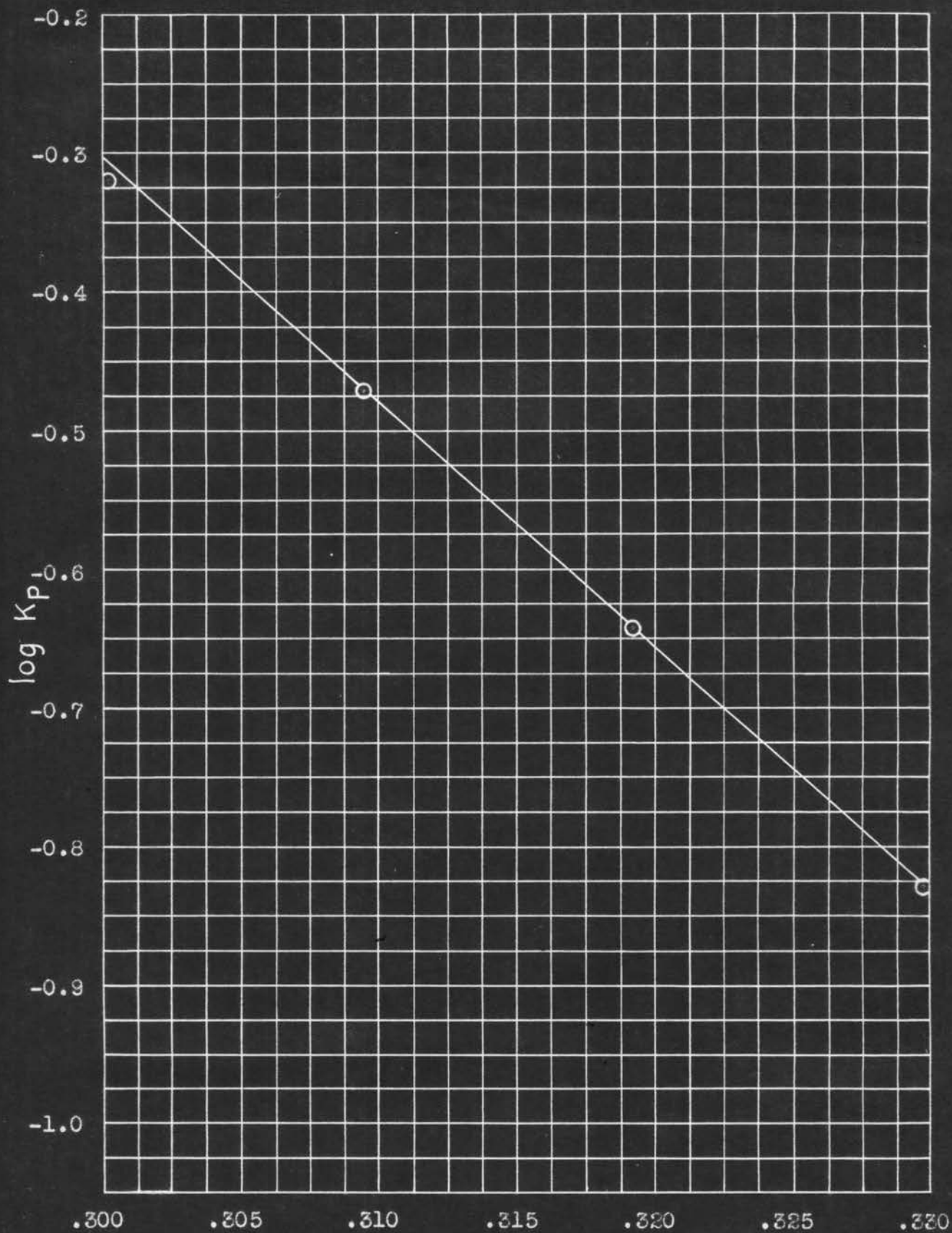
Fig. 4

TABLE IV

### Dissociation Pressures of Benzene-2,4,6-Trinitro-m-cresol Complex

Temp., °C	30.1	40.1	50.05	59.9
Press., mm.	107.0	163.6	237.5	323.1

T (abs.)	K_p (atm.)	1/T	log K_p
303.2	0.141	0.003298	-0.851
313.2	0.215	0.003193	-0.667
323.15	0.313	0.003095	-0.505
333.0	0.425	0.003003	-0.371

In Fig. V, the values for log K_p are plotted against 1/T and the slope of the best line found to be -1630. The heat of dissociation was calculated to be 7460 calories. The equation relating the absolute temperature to pressure in atmospheres is as follows:

$$\log P = -1630/T + 4.529$$

Since the ratio of combination had not been determined for this compound, an equimolecular mixture was investigated by the cooling curve method. The melting point was found to be about 70° but the plateau on the cooling curve diagram was a very short one.
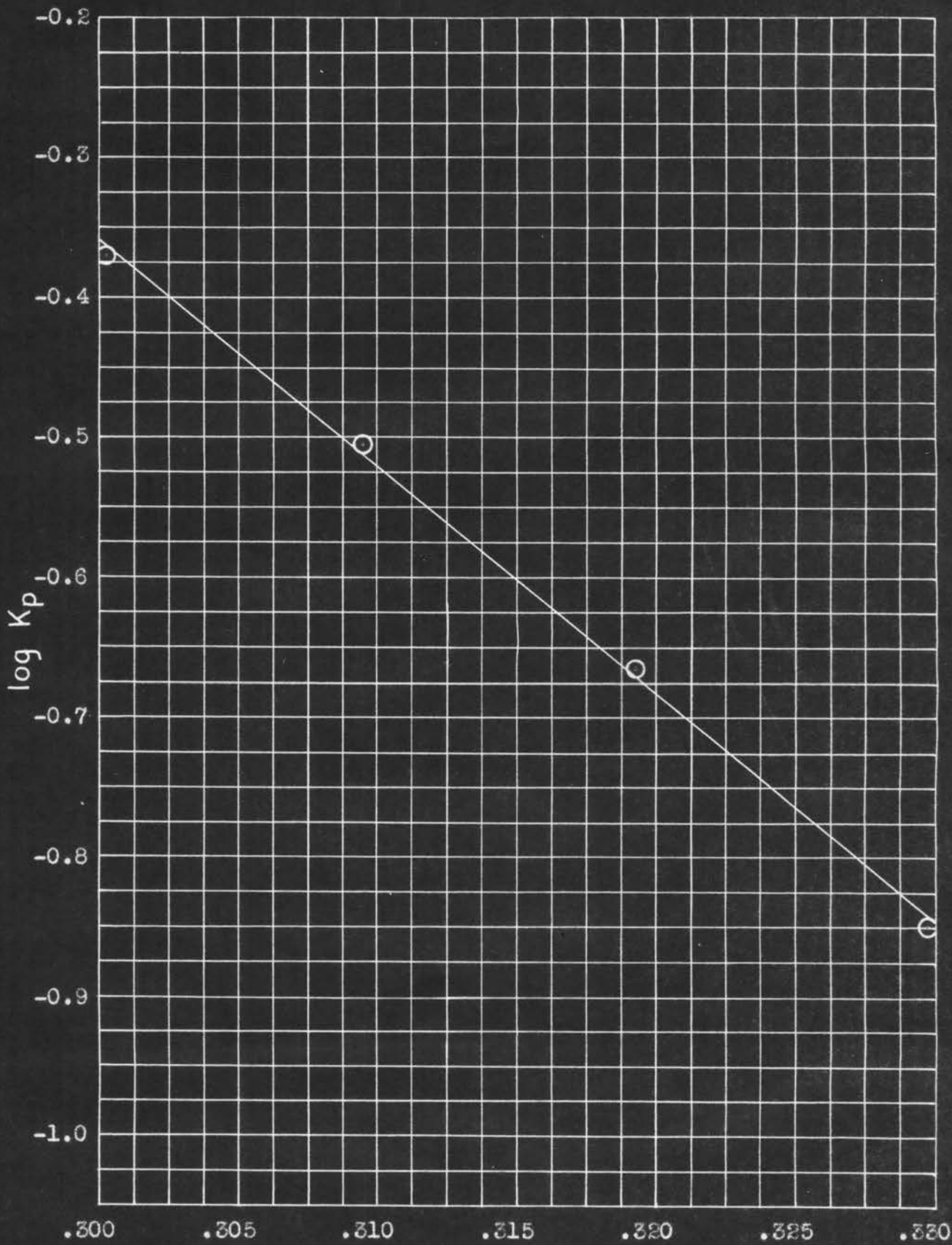
Fig. 5

Sym-Trinitrotoluene, from the course of the vapor pressure curve, was found to form no addition compound. Consecutive evacuations until all the benzene was removed gave no series of constant pressure readings except that corresponding to the saturated solution.

Further evidence that no compound is formed was given by heating approximately equimolecular quantities until liquid and observing the cooling behavior. Crystallization occurred over a wide range of temperature and the crystals formed were not homogeneous in appearance.

DISCUSSION OF RESULTS

The time spent in finding a suitable method and adapting it to this particular type of work prevented the study of as many compounds as desired. Thus very few conclusions can be made from the results obtained.

Earlier reports (35) that the presence of a methyl group in the polynitro compound decreases the stability of the molecular compound were confirmed. 2,4,6-Trinitrotoluene was found to form no compound with benzene. On the other hand, sym-trinitrobenzene does give a compound stable enough to permit measurement of the dissociation pressures.

The effect of the methyl group was again shown when it was found that picric acid gives a more stable compound with benzene than does 2,4,6-trinitro-m-cresol. The heat of dissociation of the former was calculated to be 8550 calories while the latter had a value of 7460 calories.

A further comparison of the heats of dissociation of the benzene-picric acid complex and sym-trinitrobenzene-benzene complex shows the former to be more stable. This agrees with the report (8) that the presence of the hydroxyl group increases stability of the molecular compound. The question arises here, however, as to whether or not a true comparison can be made since the ratio of combination is different in each case. Two molecules of benzene combine with one molecule of sym-trinitrobenzene (6) while for benzene picrate, the ratio is 1:1 (1). For the 1:1 benzene-

2,4,6-trinitro-m-cresol compound, the unsatisfactory nature of the cooling curve may be attributed to either decomposition of the complex or inadequacy of the apparatus. The latter was not very suitable for the study of complexes in which one of the components is readily volatile.

Observation of Fig. III shows the straight line drawn through the three higher points while the lower point lies below the line. No satisfactory explanation can be advanced for this low value since close agreement of the dissociation pressures were obtained at each temperature in three series of determinations. There is no reason, however, to believe that this dissociation pressure is not the true one. Should a further study of this compound be made, it would be worthwhile to take readings between 30° and 40° and thus determine the course of the curve between these two points.

SUMMARY

The isotensiscope, used in the study of salt hydrates, has been adapted for use in measuring dissociation pressures of aromatic polynitro addition compounds with benzene. The vapor pressures of benzene at various temperatures were determined and found to agree closely with those recorded in the literature.

The dissociation pressures of benzene picrate were measured at 30.1°, 40.1°, 50.05°, and 59.9°. From the results obtained, log K_p was plotted against $1/T$ and the heat of dissociation calculated to be 8550 calories.

The dissociation pressures for the benzene-2,4,6-trinitro-m-cresol complex were determined as before and the heat of dissociation was calculated to be 7460 calories. A cooling curve proved the existence of a 1:1 compound having an approximate melting point of 70°.

From dissociation pressures similarly obtained for the benzene-sym-trinitrobenzene complex, the heat of dissociation was calculated to be 8050 calories.

Sym-trinitrotoluene gave no evidence of an addition compound with benzene by either the thermal analysis or vapor pressure methods.

The comparative stabilities of the compounds studied are found to agree with previous reports as to the effect of the hydroxyl and methyl groups upon compound formation.

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I, Aubrey Hershel Nease, was born at Blair, Oklahoma, August 4, 1916. I attended public school at Blair and Martha, Oklahoma and was graduated from Martha High School in May, 1933.

After attending Oklahoma University one year, I enrolled at Panhandle A. and M. College in September, 1934, and received the Bachelor of Science degree in May, 1937.

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