COMPOSITIONS AND DISSOCIATION CONSTANTS OF

MOLECULAR COMPOUNDS OF OLEFINS WITH PICRIC ACID

By

BILLY G. HARPER

Bachelor of Science

Northeastern State College

Tahlequah, Oklahoma

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Dean of the Graduate School

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INTRODUCTION

The ability of picric acid, like many other polynitro compounds, to form molecular compounds with aromatic hydrocarbons is well known. It is also known that various other agents, especially Lewis acids, which thus associate with aromatic nuclei show the same tendency to associate with olefins: silver ion, aluminum chloride, and sulfur dioxide may be cited as examples. This set of facts suggested that aromatic polynitro compounds, including picric acid, might well form complexes with unsaturated compounds. When preliminary trials had shown that this is indeed the case, experiments were performed to establish the molecular ratios, dissociation constants, and heats of dissociation for several such compounds. The molecular ratio of benzene to picric acid in their complex was also determined at 30° and 10° Centigrade.

The reasons for entering into a study of olefin picrates[*] are both theoretical and practical. Theoretically such work is important because no reference to the study of olefin picrates could be found, and because the structure of molecular compounds in general is not well understood. The practical importance comes from the fact that these complexes might provide a means of separating olefins from saturated hydrocarbons. The formation of picrates has already been used as a method of further separating narrow-boiling fractions of crude petroleum (7).

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[*] This name is used for brevity and by analogy with most nomenclature in the literature, although it incorrectly suggests a salt-like structure.

The earlier workers Nease (40) and Broeg (12) used vapor pressure methods with such success that it was decided to employ the same methods in this study.

HISTORICAL

Since no references could be found to work done on aliphatic olefin complexes with polynitro compounds we will concern ourselves here with a brief history of aromatic polynitro addition compounds with aromatic hydrocarbons and their derivatives.

This type of molecular compound has been prepared for three primary reasons: to help isolate new organic compounds, to identify both classes of substances, and to bring about a better understanding of the structures involved. The latter is done by determining molecular ratios, stability constants, thermodynamic properties, and the effect of substitution on complex formation.

The first two of these reasons are of little importance in the present study; therefore, only the compounds most commonly involved will be mentioned.

The principal polynitro compounds are as follows:
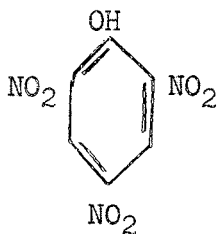
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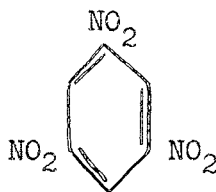
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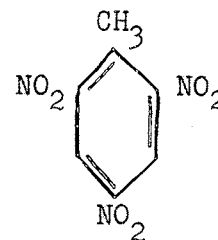
2,4,6-Trinitrotroluene
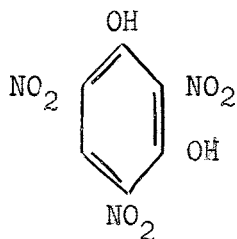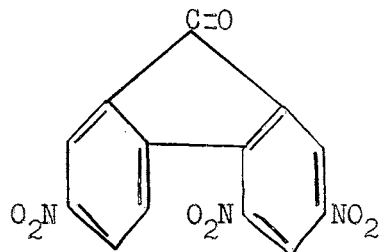
Styphnic Acid   2,4,7-trinitrofluorenone   2,7-Dinitroanthraquinone
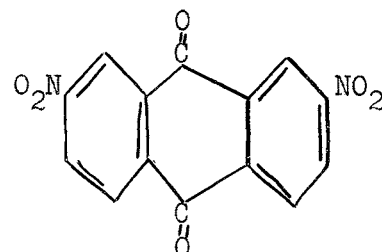
The aromatic hydrocarbons that form complexes stable enough to be used for isolation and identification purposes usually contain two or more condensed benzene rings. These hydrocarbons are most often derived from one of the nuclei shown below:
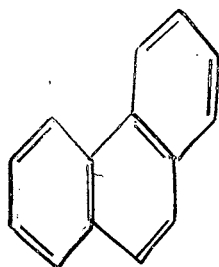
Naphthalene   Phenanthrene   Anthracene   Chrysene
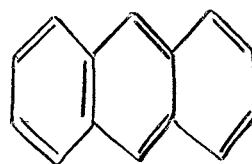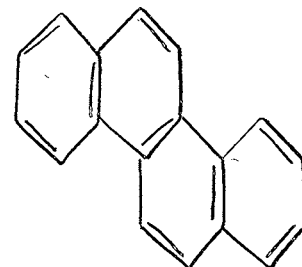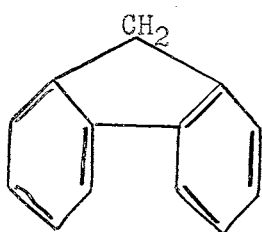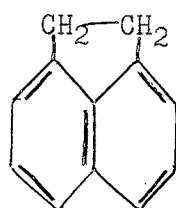
Fluorene   Acenaphthene   Indene   Stilbene
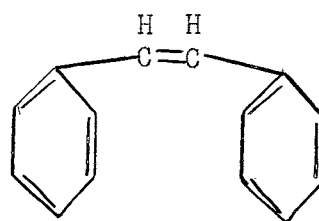
Some of the determinations intended to bring about a better understanding of the structures of these complexes will be briefly considered now.

Kremann (31), Sinomiya (44-50), Kofler (30), and Dimroth and Bamberger (18) all attempted to compare stabilities and relate them to structure.

Sinomiya's investigations were all qualitative, and his conclusions were based on the existence or nonexistence of complexes between various pairs of molecules as shown by phase diagrams. He found that the decreasing order of activity of hydrocarbons toward polynitro compounds in general is as follows: Naphthalene, pyrene and fluoranthene > acenaphthene > phenanthrene > benzene > fluorene > anthracene > chrysene. For naphthalene alone, the order of decreasing influence exerted by various substituents is as follows: NH_2 > OH > OCH_3 > Cl > Br > H > CO_2H > CO_2CH_3 > CN > COC_6H_5 > NO_2. Kofler's work with α - and β - substituted naphthalenes agrees with the results of Sinomiya in that α derivatives form more stable complexes than β derivatives. Dimroth and Bamberger compared stability constants to give the following quantitative order of decreasing activity: 2-methylnaphthalene > 1-methylnaphthalene > acenaphthene > naphthalene > anthracene > fluorene > benzene. Kremann states that the hydrocarbon capacity for forming complexes depends to some extent upon the number of rings present. As to the nitro component both Sinomiya and Kremann showed that the greater the number of nitro groups present the greater the possibility for complex formation. Sinomiya further showed that symmetrical trinitrobenzene forms more stable complexes than unsymmetrical trinitrobenzene; and that para- and meta-dinitro benzenes yield more stable complexes than the ortho derivative. The order of decreasing influence of a second substituent on the complex-forming

ability of a trinitro compound was given as follows: $H > OH > NH_2 > CH_3 >$ $Cl > OCH_3$; on dinitro compounds the order is $CO_2H > Cl > OH > Br > CH_3 >$ $H > OCH_3 > CHO$.

Several studies have been made in which stability constants were determined. Complexes of polynitro aromatic compounds and their stability constants are listed in the table given on the following pages along with the methods employed to determine them. The only ones excluded are those of polynitro phenols with amines which are of a much higher order of stability and have a different structure.

Structural Theories. --- In spite of the fact that molecular complexes of polynitro compounds have long been known their structures are still relatively obscure. Several investigators have presented ideas concerned with explaining them; a few of these ideas will be outlined here to indicate the complexity of this structural problem.

Three basic conceptions of these compounds seem to exist. They are as follows: (1) A covalent bond exists between the molecules in the complex. (2) There is an electron transfer between such molecules. (3) There is an attraction between such molecules which is due to hydrogen bonding or similar electrostatic forces, van der Waals forces, or polarization forces arising from permanent and induced dipoles.

Some of the early subscribers to covalent-bond ideas were Sudborough (52) and Moore, Shepherd and Goodall (38); more lately Brackman (9) has used them in his theory of complex resonance. This theory states that one of the election configurations is formed by two separate unbound molecules, while in another configuration the molecules are bound by a covalent bond.

DISSOCIATION CONSTANTS OF MOLECULAR COMPLEXES OF POLYNITRO AROMATIC COMPOUNDS

Complex (Molecular ratio 1:1 except as noted)	Reference	K_c	Method of Study	Temp., °C.
m-Bromonitrobenzene – aniline	(38)	16.66	partition between $CHCl_3$ + H_2O	18
p-Chloronitrobenzene – aniline	(38)	33.33	"	"
p-Dinitrobenzene – aniline	(38)	5.55	"	"
p-Dinitrobenzene – aniline	(34)	1.42	spectrophotometry in $CHCl_3$	"
m-Dinitrobenzene – aniline	(34)	1.38	"	"
m-Dinitrobenzene – aniline	(38)	5.58	partition between $CHCl_3$ + H_2O	"
1,5-Dinitronaphthalene – aniline	(38)	1.75	"	"
2,4-Dinitrotoluene – aniline	(38)	6.66	"	"
sym-Trinitrobenzene – aniline	(25)	5.0×10^{-3}	spectrophotometry in CCl_4	25
sym-Trinitrobenzene – aniline	(34)	0.19	spectrophotometry in $CHCl_3$	18
sym-Trinitrobenzene – o-toluidine	(25)	3.40×10^{-3}	spectrophotometry in CCl_4	25
sym-Trinitrobenzene – m-toluidine	(25)	6.7×10^{-3}	"	"
sym-Trinitrobenzene – p-toluidine	(25)	1.4×10^{-2}	"	"
sym-Trinitrobenzene – m-chloroaniline	(25)	3.3×10^{-4}	"	"
sym-Trinitrobenzene – p-chloroaniline	(25)	1.1×10^{-3}	"	"

Complex (Molecular ratio 1:1 except as noted)	Reference	K_c	Method of Study	Temp., °C.
sym-Trinitrobenzene - o-chloroaniline	(25)	5.0×10^{-5}	spectrophotometry in CCl_4	25
2,4,6-Trinitrotoluene - aniline	(38)	1.79	partition between $CHCl_3 + H_2O$	18
2,4,6-Trinitrotoluene - naphthalene	(14)	0.464	cryoscopy in $C_6H_5NO_2$	3
Picric acid - benzene	(38)	11.11	partition between $CHCl_3 + H_2O$	18
Picric acid - benzene	(2)	2.32	"	"
Picric acid - toluene	(2)	7.84	"	"
Picric acid - toluene	(38)	8.33	"	"
Picric acid - ethylbenzene	(2)	2.22	"	"
Picric acid - n-propylbenzene	(2)	1.66	"	"
Picric acid - iso-propylbenzene	(2)	2.77	"	"
Picric acid - n-butylbenzene	(2)	2.85	"	"
Picric acid - sec.-butylbenzene	(2)	2.94	"	"
Picric acid - tert.-butylbenzene	(2)	3.22	"	"
Picric acid - n-amylbenzene	(2)	2.38	"	"
Picric acid - durene	(2)	0.99	"	"
Picric acid - hexamethylbenzene	(2)	0.57	"	"

Complex (Molecular ratio 1:1 except as noted)	Reference	K_c	Method of Study	Temp., °C.
Picric acid - o-xylene	(2)	1.58	partition between $CHCl_3 + H_2O$	18
Picric acid - o-xylene	(38)	6.25	"	"
Picric acid - m-xylene	(38)	1.66	"	"
Picric acid - m-xylene	(38)	7.14	"	"
Picric acid - p-xylene	(2)	1.63	"	"
Picric acid - p-xylene	(38)	6.25	"	"
Picric acid - mesitylene	(2)	1.47	"	"
Picric acid - mesitylene	(38)	5.55	"	"
Picric acid - bromobenzene	(38)	11.11	"	"
Picric acid - o-dichlorobenzene	(38)	10.0	"	"
Picric acid - p-dichlorobenzene	(38)	33.33	"	"
Picric acid - nitrobenzene	(38)	1.78	"	"
Picric acid - m-dinitrobenzene	(38)	.97	"	"
Picric acid - o-nitrotoluene	(38)	1.75	"	"
Picric acid - 2,4-dinitrotoluene	(38)	1.49	"	"

Complex (Molecular ratio 1:1 except as noted)	Reference	K_c	Method of Study	Temp., °C.
Picric acid - 2,4,6-trinitrotoluene	(38)	0.98	partition between $CHCl_3 + H_2O$	"
Picric acid - naphthalene	(14)	0.228	cryoscopy in $C_6H_5NO_2$	3
Picric acid - naphthalene	(38)	0.46	partition between $CHCl_3 + H_2O$	18
Picric acid - α-methylnaphthalene	(38)	0.36	"	"
Picric acid - β-methylnaphthalene	(38)	0.29	"	"
Picric acid - α-bromonaphthalene	(38)	4.34	"	"
Picric acid - α-nitronaphthalene	(38)	0.98	"	"
Picric acid - tetrahydronaphthalene	(38)	3.84	"	"
Picric acid - phenanthrene	(19)	2.27	dilatometry in xylene	24.9
Picric acid - stilbene	(1)	1.11	solubility in $CHCl_3$	18
Picric acid - stilbene	(1)	1.36	spectrophotometry in $CHCl_3$	18
Picric acid - α-methylstilbene	(1)	9.79	"	"
Picric acid - p-methylstilbene	(1)	1.31	"	"
Picric acid - p-methylstilbene	(1)	1.03	solubility in $CHCl_3$	"
Picric acid - p-chlorostilbene	(1)	0.91	spectrophotometry in $CHCl_3$	"
Picric acid - p-chlorostilbene	(1)	1.15	solubility in $CHCl_3$	"

Complex (Molecular ratio 1:1 except as noted)	Reference	K_c	Method of Study	Temp., °C.
Picric acid – ethyl cinnamate	(1)	3.14	solubility in $CHCl_3$	18
		K_p		
2,4-Dinitroiodobenzene – benzene (2:1)	(12)	0.067	dissociation pressure	30
2,4-Dinitrobromobenzene – benzene (2:1)	(12)	0.070	"	"
2,4-Dinitrochlorobenzene – benzene (2:1)	(12)	0.085	"	"
sym-Trinitrobenzene – benzene (1:2)	(40)	0.148	"	"
Picryl chloride – benzene (1:2)	(12)	0.118	"	"
Picric acid – benzene	(40)	0.128	"	"
Picric acid – benzene	(12)	0.133	"	"
2,4,6-Trinitro-m-cresol – benzene	(40)	0.141	"	"
		G^*		
Picric acid – benzene	(18)	0.934	solubility in water	?
Picric acid – fluorene	(18)	0.609	"	?
Picric acid – anthracene	(18)	0.512	"	?
Picric acid – indene	(18)	0.294	"	?
Picric acid – phenanthrene	(18)	0.155	"	?

Complex (Molecular ratio 1:1 except as noted)	Refer- ence	G^*	Method of Study	Temp., °C.
Picric acid - naththalene	(18)	0.126	solubility in water	?
Picric acid - acenaphthene	(18)	0.122	"	?
Picric acid - α-methylnaphthalene	(18)	0.120	"	?
Picric acid - β-methylnaphthalene	(18)	0.099	"	?

* Dimroth and Bamberger expressed stabilities in terms of the van't Hoff - Dimroth G, a value at least approximately independent of solvent.

The idea that there is an actual transfer of electrons from one molecule in the complex to another such molecule was originally proposed by Bennett and Willis (6) and Kremann (32). This idea was developed by Weiss (54) who believes that the bond must thus be ionic. He further states that electronegative groups are necessary in what he calls an acceptor molecule, such as picric acid, and that their presence in donor molecules hinders complex formation. He believes that the greater the number of these electronegative groups the greater will be the possibility of complex formation. This is true especially if they generate several resonating structures to accomodate the transferred electron which thereby becomes less available to the donor molecule. According to his theory the existence of complexes with a ratio of two acceptor molecules to one donor is sometimes to be expected since in a donor molecule there may be two more or less separate regions of influence. The donor molecule is much more apt to form a complex if it contains conjugated double bonds. The $C=O$, $C=S$ and $C\equiv N$ bonds exert about as much influence as the $C=C$ bond. Fieser (20) seems to agree with the idea of electron transfer.

Finally there are those who think that molecular compounds contain neither a covalent bond nor an ionic bond. According to Mulliken (39) opinions appear to be converging in this direction since the two previous ideas seem quantum-mechanically unsatisfactory. Pfeiffer's (42) idea that there is a saturation of residual valence, which was extended by Briegleb (11), is hard to visualize but presumably belongs in this group. Hammick, Yule and Sixsmith (26), (27) along with Gibson and Ioeffler (23), Ostromisslensky (41), and

Lextreit (35), suggested a polarization mechanism similar to oxidation-reduction, but one in which there was no transfer of electrons. Powell and Huse (43) in their X-ray study of several molecular compounds obtained results which do not fit the electron-transfer theory. Their work showed that the complexes were not ionic and suggested the possibility of a hydrogen bond. Many of the donor molecules used in their work were halogenated, one being sym-tribromoaniline. The presence of electronegative groups in the donor molecule, according to electron-transfer theories, should hinder complex formation since they would make the electron less available for transfer. Dewar (17) also points out that the presence of electro-negative groups, especially nitro groups, in molecules would certainly interfere with their acting as electron donors, as they must do according to the electron-transfer theory. He believes that as two molecules approach each other their electronic motions tend to synchronize with each other in such a way as to produce a net attraction and that the attractive forces vary with the polarizability of the molecules involved. He believes that these forces will account for almost all of van der Waals forces except those between the most polar molecules. Work by Lichen, Weston and White (36) gives evidence against ionic bond formation. The forces holding weak complexes together are presumably van der Waals forces or hydrogen bonds (9).

Methods of Study. --- Many methods have been employed to study the stability and properties of polynitro aromatic compounds in complexes with aromatic hydrocarbons.

Phase-rule diagrams were put to good use in the previously mentioned work by Sinomiya; Mason, Rosen, and Swift (37) also used them to study naphthalene picrates. Naphthalene complexes with polynitro aromatic compounds have been studied by these other methods: Potentiometric (5,13), magnetic (3,8), spectrophotometric (10,28,38), cryoscopic (14), and calorimetric (53). Aromatic amine complexes have been studied spectrophotometrically (33,16,25) and by X-ray diffraction (43). Solubility methods were employed to study anthracene (4,18), and stilbene (17) complexes. Stilbenes were also studied photometrically while Drucker (19) used a dilatometric method to study phenanthrene complexes. Nease (40) and Broeg (12) used vapor pressure methods in their work with benzene complexes. The liquid-liquid partition method was employed by Moore, Shepherd and Goodall (38) and also by Anderson and Hammick (2) in their study of picrates.

THEORETICAL

Since the pressures of only the gaseous reactants and products of a heterogeneous reaction are necessary to determine the equilibrium constant, the application of vapor pressure methods is a theoretically sound approach to this problem.

If we let A represent the picric acid and B represent the olefin, the decomposition involved may be represented as follows:

$$A_x B_y \text{ (s)} \xrightarrow{\hspace{1cm}} xA \text{ (s)} + yB \text{ (g)}$$

and for this dissociation

$$\bar{K}_{diss.} = a_A^x \cdot a_B^y / a_{A_x B_y}$$

where a represents activity. If pure solid $A_{(s)}$ and $A_x B_{y(s)}$ are taken as the standard states then corresponding activities are unity and therefore

$$\bar{K}_{diss.} = a_B^y$$

but

$$a_B = f_B / f_B^o$$

where f_B^o is the fugacity of B in standard state. If the standard state of B is taken as one atmosphere then

$$\bar{K}_{diss.} = f_B^y$$

Since as $P_B \longrightarrow 0$, $f_B \longrightarrow P_B$ the approximate equation at low pressures is given by

$$\bar{K}_{diss.} \cong P_B^y$$

or in words, the dissociation constant is equal to the pressure of the olefin given off in the decomposition, raised to a power equal to the number of molecules of olefin produced by each molecule of the complex.

The van't Hoff equation,

$$d \ln K_p / dT = \Delta H / RT^2$$

which is a special development of the Gibbs-Helmholtz equation, enables us to determine ΔH from dissociation pressures if such ΔH is assumed constant over the temperature range involved. This is possible because the integrated form of this equation

$$\ln K_p = (-\Delta H / RT) + C \quad \text{or} \quad \log K_p = (-\Delta H / 2.303 \, RT) + C$$

is the equation of a straight line. By plotting $\log K_p$ against $1 / T$, ΔH can be found since ΔH is equal to the slope x -2.303 R.

An empirical equation relating the pressure to the temperature may also be obtained and has the general form

$$\log P_{atm.} = -A / T_K + B$$

where A is the slope of the line and B is the intercept on the log P axis.

The free energy of dissociation may be calculated from the equation

$$\Delta F_{(T)} = -RT \ln K_p.$$

EXPERIMENTAL

Apparatus. --- Two very well known and adequate methods for the static determination of vapor pressures are the isoteniscope method of Smith and Menzies (51) and the Bremer-Frowein tensimeter method (21).

The principal advantage of the isoteniscope method is the ease and assurance with which the system may be swept free of foreign gases by repeated evacuation of an excess of volatile component. This expulsion is continued until a constant pressure indicates that all foreign gases have been eliminated and the system is at equilibrium. This method has the disadvantage that pressures are measured against a variable atmosphere.

The tensimeter method is advantageous because the pressures are measured against a liquid whose vapor pressure is accurately known. Its disadvantage lies in the fact that one may not know when the system is free of foreign gases.

It was hoped that by combining and modifying these methods somewhat according to Gibson and Adams (22) the above mentioned advantages might be retained, the disadvantages eliminated, and a means of determining molecular ratios acquired. This hope was largely realized.

In order to clarify its operation and point out the modifications it will be necessary to describe fully the parts of the apparatus.

Figure 1 shows a diagram of the apparatus. The nonvolatile component to be studied, along with an excess of the volatile component, is placed in A which is a bulb of about 25 ml. capacity sealed to a ball-and-socket joint C. The upper part of this joint is sealed to stopcock 1 and thereafter to the three-way stopcock 2. The reference liquid is placed in bulb B which has about the same capacity as A and which is sealed to a ball-and-socket joint D. The upper part of this joint is sealed to the three-way stopcock 3. L and M lead to the vacuum reservoir, which may be operated by a water aspirator. Joints C and D facilitate the removal of flasks A and B for cleaning and weighing of A and refilling of B. Stopcock 1 allows the contents of A to be isolated and is necessary if molecular ratios are to be determined as will be explained later. Stopcocks 2 and 3 allow for the independent evacuation of the two halves of the system. H, I, J, and K are overflow bulbs which prevent the contents of the separate parts of the system from being sucked or forced to other parts of the system.

The bath is a battery jar 12 inches in diameter and 24 inches high. This bath is fitted with a mechanical stirrer and thermoregulator sensitive to at least .05° C. The thermometer used has previously been compared to one calibrated by the Bureau of Standards. The temperature of this bath can be maintained constant to 0.1°C.

Pressure differences exhibited in the U-tube are measured by means of a cathetometer graduated in 0.1 cm. and readable with a vernier scale to 0.01 cm.

The above system was proved to be free of leaks by putting a manometer in the system and allowing the whole to stand partially
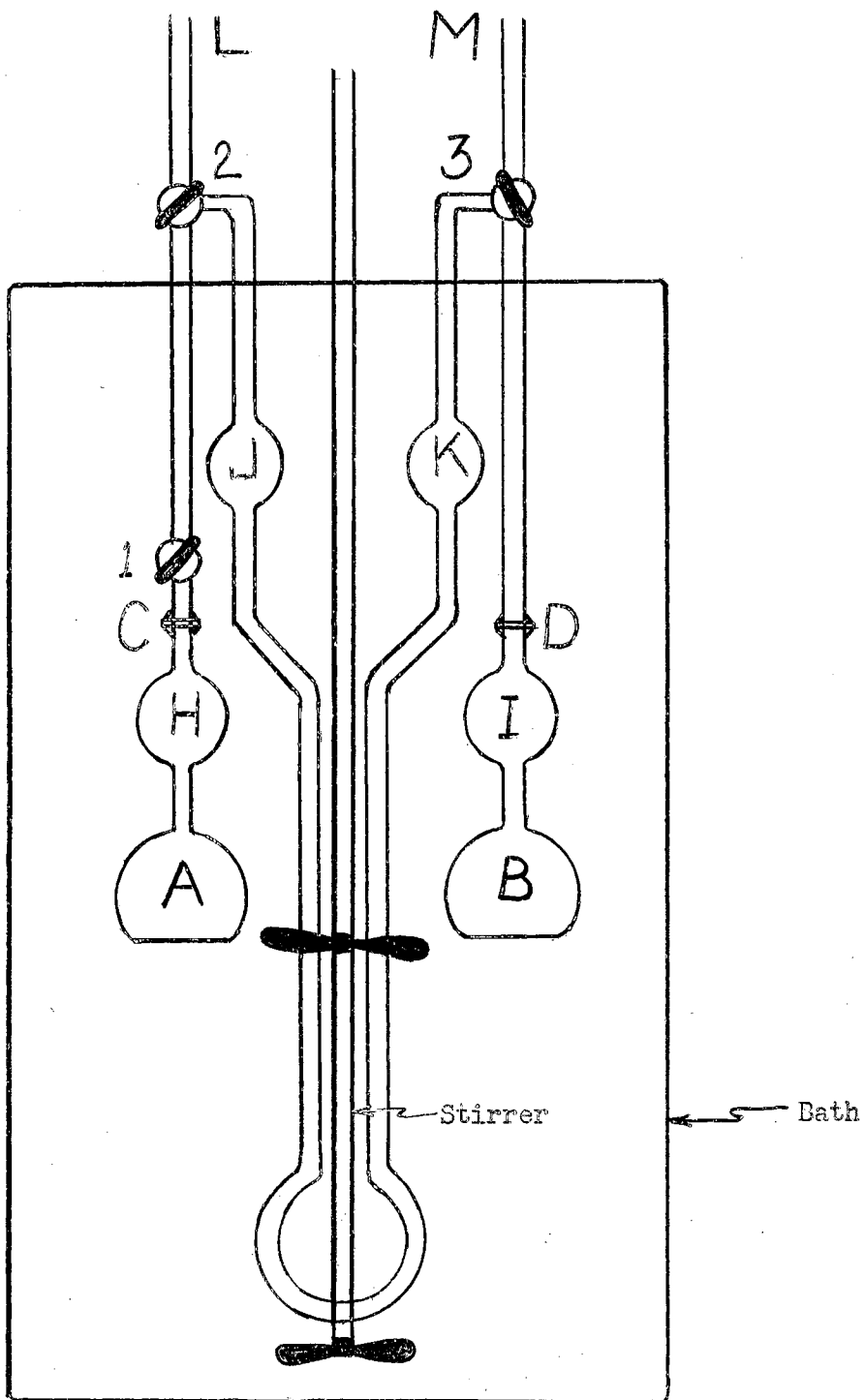
Fig. 1

evacuated for several hours. Before use no pressure changes were noticed after eleven hours under reduced pressure.

Pressure determinations. --- Picric acid along with an excess of the volatile olefin is placed in bulb A. The reference liquid, which was benzene in every case, is placed in bulb B and the monometer fluid, mercury, is placed in the U-tube. Sulfuric acid proved much less satisfactory in the manometer. The bulbs are attached to the rest of the system and water is added to the bath.

Stopcock 1 is opened and stopcocks 2 and 3 are opened only to the U-tube. The U-tube is evacuated above the mercury while the bath is reaching the desired temperature. When the desired temperature is reached stopcocks 2 and 3 are opened slightly to bulbs A and B. The pressure above the benzene in B and the olefinic solution in A is reduced until both begin to boil. This boiling is continued until about one-third of the benzene has been eliminated. Stopcocks 2 and 3 are now placed in a position such that they connect the U-tube to the bulbs but not to the pump, and pressure differences are read with the cathetometer. This value always drifts, because at least one of the liquids is not in temperature equilibrium with the bath; therefore, a constant reading must be awaited. This procedure is repeated, A and B being periodically evacuated either independently or in unison, until the pressure difference is constant from evacuation to evacuation. Care must be taken not to deplete the system of benzene or olefin. This pressure difference, subtracted from or added to the vapor pressure of benzene at that temperature, gives the vapor pressure of a saturated solution of the complex in the olefin. Stopcock 3 is now closed and the excess olefin in A is boiled out until another constant

pressure level is attained which is lower than the previous one. The
new difference in levels, subtracted from or added to the vapor pressure
of benzene at that temperature, is the dissociation pressure of the com-
plex. If no complex exists no constancy can be obtained after the
excess liquid is eliminated from A.

Since a constant difference in pressure at this point indicates
that all air has been eliminated and that the dissociation pressure is
being measured it is unnecessary and undesirable to remove any more
vapor from A by further evacuation. It is undesirable because there
is danger of exhausting A of the volatile component.

The temperature is now raised to another desired point and after
equilibrium is established pressure differences are determined. This
procedure is repeated until determinations at all desired temperatures
are made.

At least three readings of constant pressure were taken at the
initial temperature, two at the second temperature, and only one
pressure reading thereafter.

Determinations of Molecular Ratio. --- As previously indicated
there is a drop in pressure when the system in A changes from a
saturated solution to a pure complex. It was reasoned that if the
contents of A could be isolated at or very near the time of that
pressure change, these contents would comprise the pure complex,
which could be weighed in situ and analyzed. Alternatively, if
the weight of nonvolatile component introduced originally were
known, the weight of the complex would permit calculation of the
composition.

Bulb A is weighed empty with a ground-glass stopper for C. Picric acid is added to A and it is again weighed with the stopper. The difference in weight is the weight of the picric acid. An excess of the volatile olefin is now placed in A and A is connected to the system. The procedure for determining equilibrium pressures is repeated until the previously noticed pressure change occurs. It is naturally desirable to pump down in small increments when the composition of the complex is approached, i.e., when the contents of the flask become dry, in order to overrun the "end point" as little as possible.

At this time stopcock 1 is closed, isolating bulb A and its contents from the rest of the system. The bulb is now removed from the system and immediately upon its removal the ground-glass stopper is placed in its top to prevent loss of olefin. The bulb and contents are again weighed; the weight of the contents is that of the olefin - picric acid complex. These weights and the molecular weights of the compounds involved are sufficient to establish the molecular ratio.

<u>Sample data for determination of molecular ratio</u>:

Weight of bottle + picric acid	27.7736 g.
Weight of empty bottle	25.4105 g.
Weight of picric acid	2.3631 g.
Weight of picric acid + bottle + allyl bromide	29.0683 g.
Weight of picric acid + bottle	27.7736 g.
Weight of allyl bromide	1.2947 g.
Gram-molecular weight of picric acid	229.11 g.
Gram-molecular weight of allyl bromide	120.99 g.

$2.3631 / 229.11 = 1.2947 / x$ $126.1 / 120.99 = 1.04$

$x = 126.1$ Ratio $= 1:1.04$ or $1:1$

Reagents. --- The chemicals used are listed below with an indication as to their purity.

Benzene	- C.P.
Picric Acid	- Reagent grade containing an added ten percent of water. The water was removed by azeotropic distillation with benzene. It was then dried in air. M.p. 121-121.5°C.
Cyclohexene	- The C.P. grade was distilled and the first fifteen percent of distillate rejected. It was then dried for several hours over calcium chloride.
Vinyl acetate	*
Acrylonitrile	*
Allyl chloride	*
Allyl bromide	*
Allyl alcohol	*, **
Cyclohexane	*
n-Heptane	*

* These reagents were all C.P. grade. Their purities were in-sured by treatment identical to that of cyclohexene.

**Was not dried over calcium chloride.

RESULTS

It is obviously necessary, since this method is a differential one, that the vapor pressure of benzene be known at the temperatures involved. The following table contains vapor pressures of benzene calculated from the equation (29):

$$\log_{10} K_{p(mm)} = - 0.05223 \ A \ / \ T + B$$

where   0 to 42° C.   A = 34,172   B = 7.9622

42 to 100° C.   A = 32,295   B = 7.6546

TABLE I

Variation of Vapor Pressure of Benzene with Temperature

Temp. (°K.)	Pressure (mm Hg)
303.2	118.2
303.3	119.3
306.2	135.9
306.6	138.6
308.2	146.6
308.6	150.9
310.9	165.1
313.2	181.1
313.3	185.4
318.3	226.8
322.9	270.0

TABLE I (continued)

Temp. (°K.)	Pressure (mm Hg)
328.2	325.3
333.2	391.4

Tables II-VIII present the data on dissociation pressures.

Dissociation pressures of benzene picrate were taken and compared to the values obtained by Nease and Broeg in order to test the apparatus. The dissociation pressures varied only slightly from those reported in the earlier theses.

An error of $0.1°$ in temperature measurement and one of 0.1 mm. in pressure measurement, if they reinforce each other, could produce the maximum error shown in the heats of dissociation. This indicates the same percentage of uncertainty in dissociation pressures.

TABLE II

Dissociation Pressures of Benzene Picrate

The molecular ratio of picric acid to benzene at both $30°$ and $10° = 1:1$

Temp. (°K.)	Press. (mm)	K_p(atm)	1/T	log K_p
303.2	97.1	.1277	.003298	-.8938
306.2	114.3	.1491	.003266	-.8265
310.9	130.0	.1711	.003213	-.7667
313.2	152.1	.2001	.003190	-.6988

Log K_p is plotted against 1/T in Fig. II and the best straight line drawn among the points. The following equation, with constants calculated by the method of least squares (15), relates the pressure to the temperature where the pressure is expressed in atmospheres
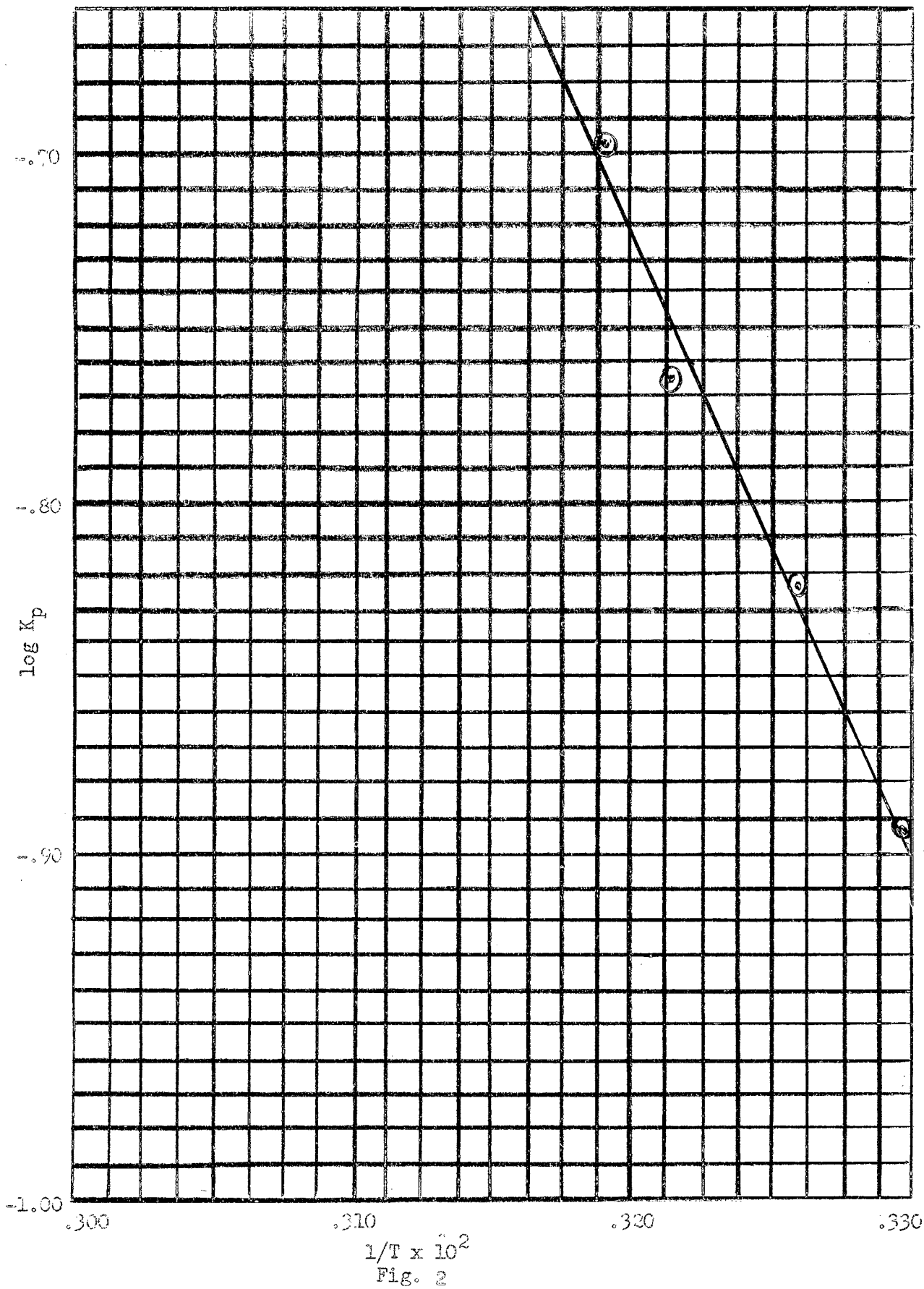
$1/T \times 10^2$

Fig. 2

and the temperature in degrees Kelvin:

$$\log P = -1890 / T + 5.78$$

The heat of dissociation was calculated from the slope of the line to be 8.65 $\pm$ 0.18 kcalories per mole. This value agrees with the value of 8.55 kcal. obtained by Nease.

TABLE III

Dissociation Pressures of Cyclohexene Picrate

The molecular ratio of picric acid to cyclohexene at 30° C. = 2:1

Temp. (^{O}K.)	Press. (mm)	K_p(atm)	1/T	$\log K_p$
303.2	67.7	.08908	.003298	-1.0502
307.5	74.4	.09789	.003243	-1.0092
313.2	86.9	.1130	.003192	-0.9469
318.2	94.7	.1246	.003141	-0.9044

Log K_p is plotted against 1/T in Figure III and the best straight line drawn among the points. The following equation relates the pressure to the temperature:

$$\log K_p = -960 / T + 2.22$$

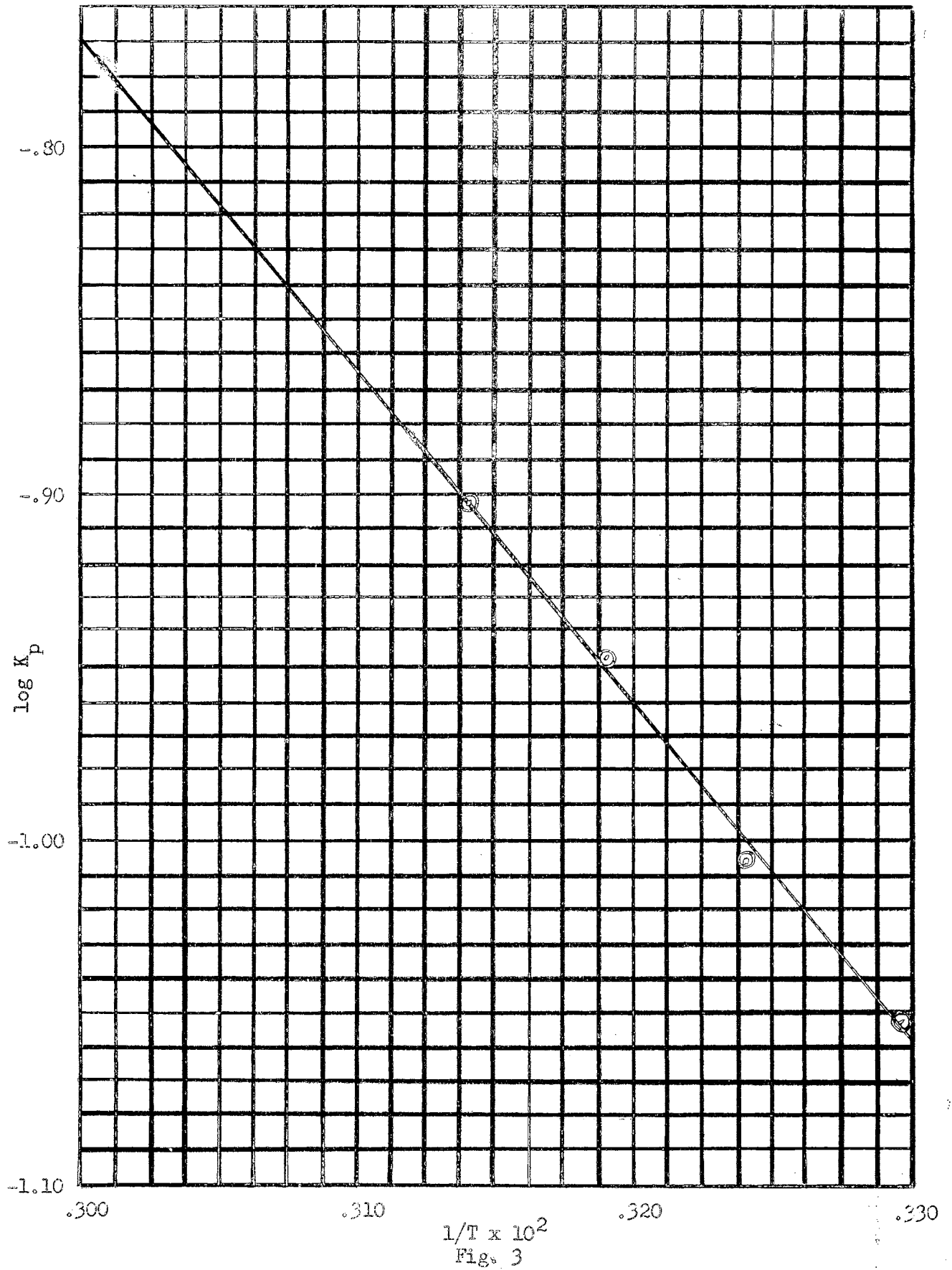The heat of dissociation was calculated from the slope of the line to be 4.39 $\pm$ 0.1 kcal. per mole.

$\log K_p$

$1/T \times 10^2$
Fig. 3

TABLE IV

Dissociation Pressures of Acrylonitrile Picrate

The molecular ratio of picric acid to acrylonitrile at 30° = 2:1

Temp. ($^{\circ}$K.)	Press. (mm)	K_p(atm)	1/T	log K_p
303.2	36.2	.04764	.003298	-1.3221
308.1	46.9	.06171	.003243	-1.2096
313.2	60.3	.07934	.003192	-1.1006
318.2	77.0	.10131	.003141	-0.9944

Log K_p is plotted against 1/T in Fig. IV and the best straight line drawn among the points. The following equation relates the pressure to the temperature:

$$\log P \; = \; - \; 2030 \; / \; T \; + \; 5.36$$

The heat of dissociation was calculated from the slope of the line to be 9.29 $\pm$ 0.19 kcal. per mole.

$1/T \times 10^2$
Fig. 4

TABLE V

Dissociation Pressures of Allyl Alcohol Picrate

The molecular ratio of picric acid to allyl alcohol at 30° = 1:1

Temp. ($^{\circ}$K.)	Press. (mm)	K_p (atm)	1/T	log K_p
303.2	36.6	.04816	.003298	-1.3164
306.6	44.4	.05842	.003261	-1.2334
308.1	45.7	.06001	.003243	-1.2218
313.2	58.5	.07697	.003192	-1.1142

Log K_p is plotted against 1/T in Fig. V and the best straight line drawn among the points. The following equation related the pressure to the temperature:

$$\log P = -1810 / T + 4.67$$

The heat of dissociation was calculated from the slope of the line to be 8.28 $\pm$ 0.17 kcal. per mole.
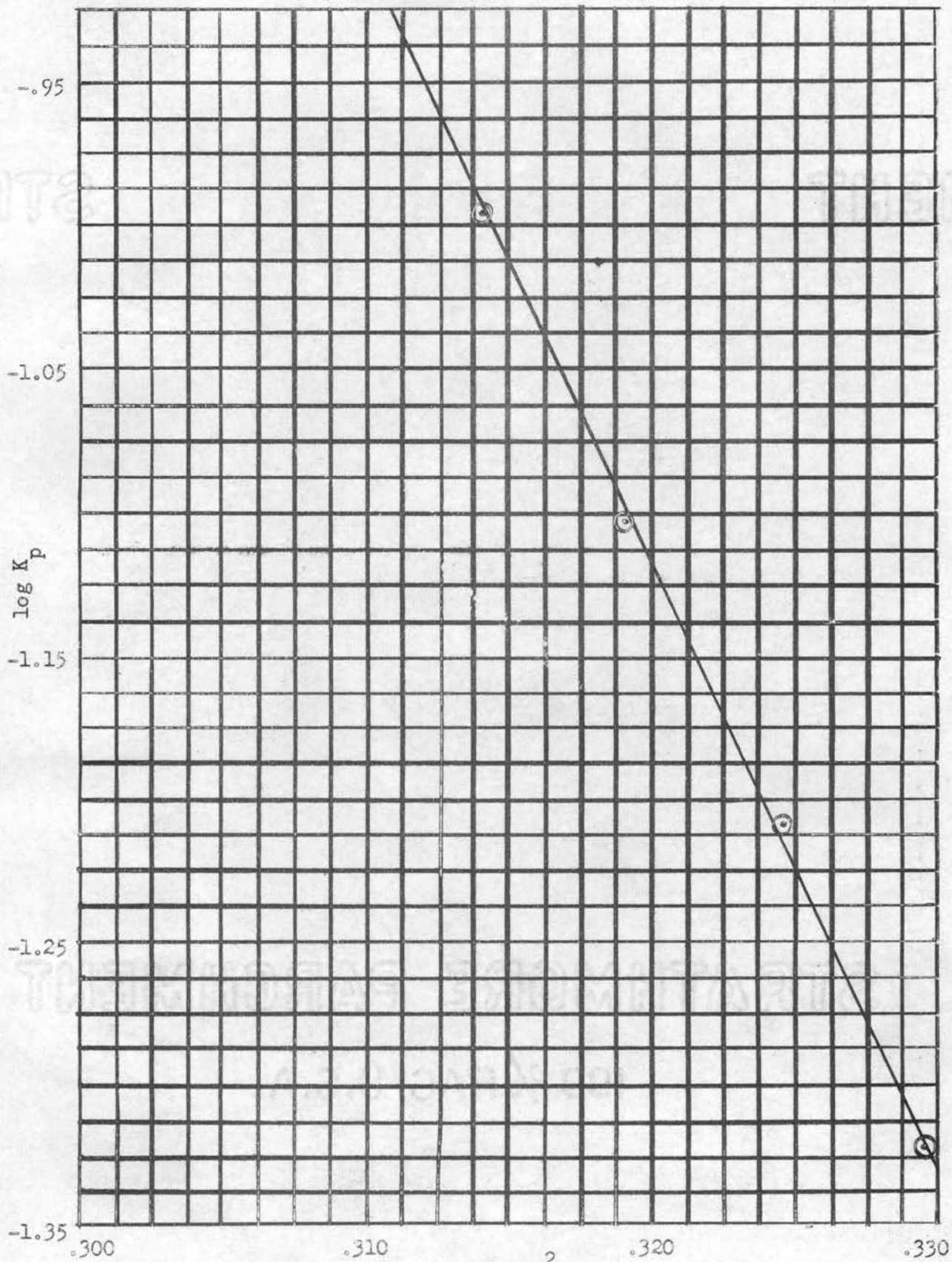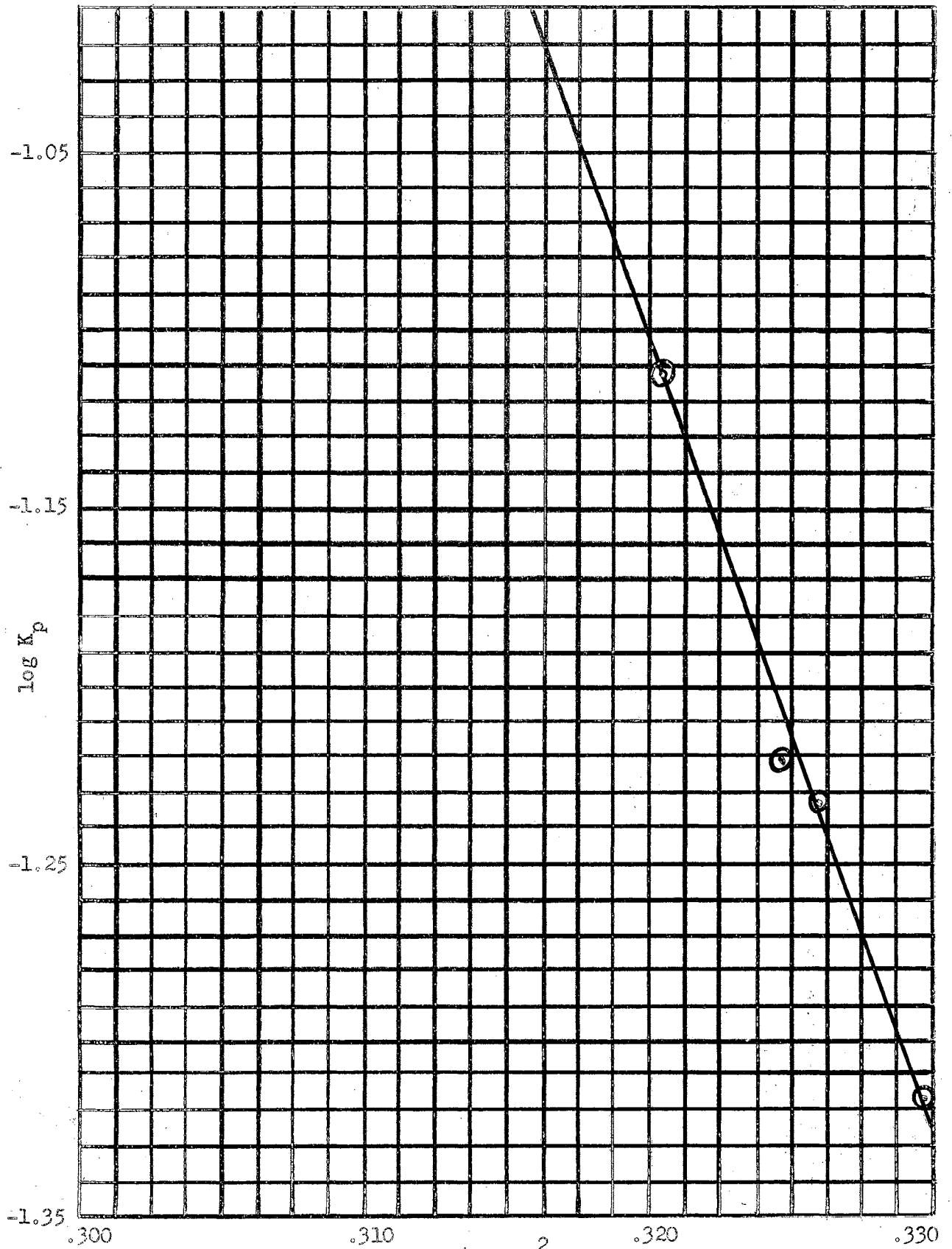
Fig. 5

TABLE VI

Dissociation Pressures of Allyl Bromide Picrate

The molecular ratio of picric acid to allyl bromide at $30^{\circ} = 1:1$

Temp. ($^{\circ}$K.)	Press. (mm)	K_p (atm)	1/T	log K_p
303.3	88.4	.1018	.003298	-0.9921
306.6	98.9	.1301	.003261	-0.8857
308.2	105.0	.1381	.003243	-0.8597
313.3	128.5	.1704	.003192	-0.7685

Log K_p is plotted against 1/T in Fig. VI and the best straight line drawn among the points. The following equation relates the pressure to the temperature:

$$\log p = -2020 / T + 5.59$$

The heat of dissociation was calculated from the slope of the line to be 9.24 ± 0.19 kcal. per mole.
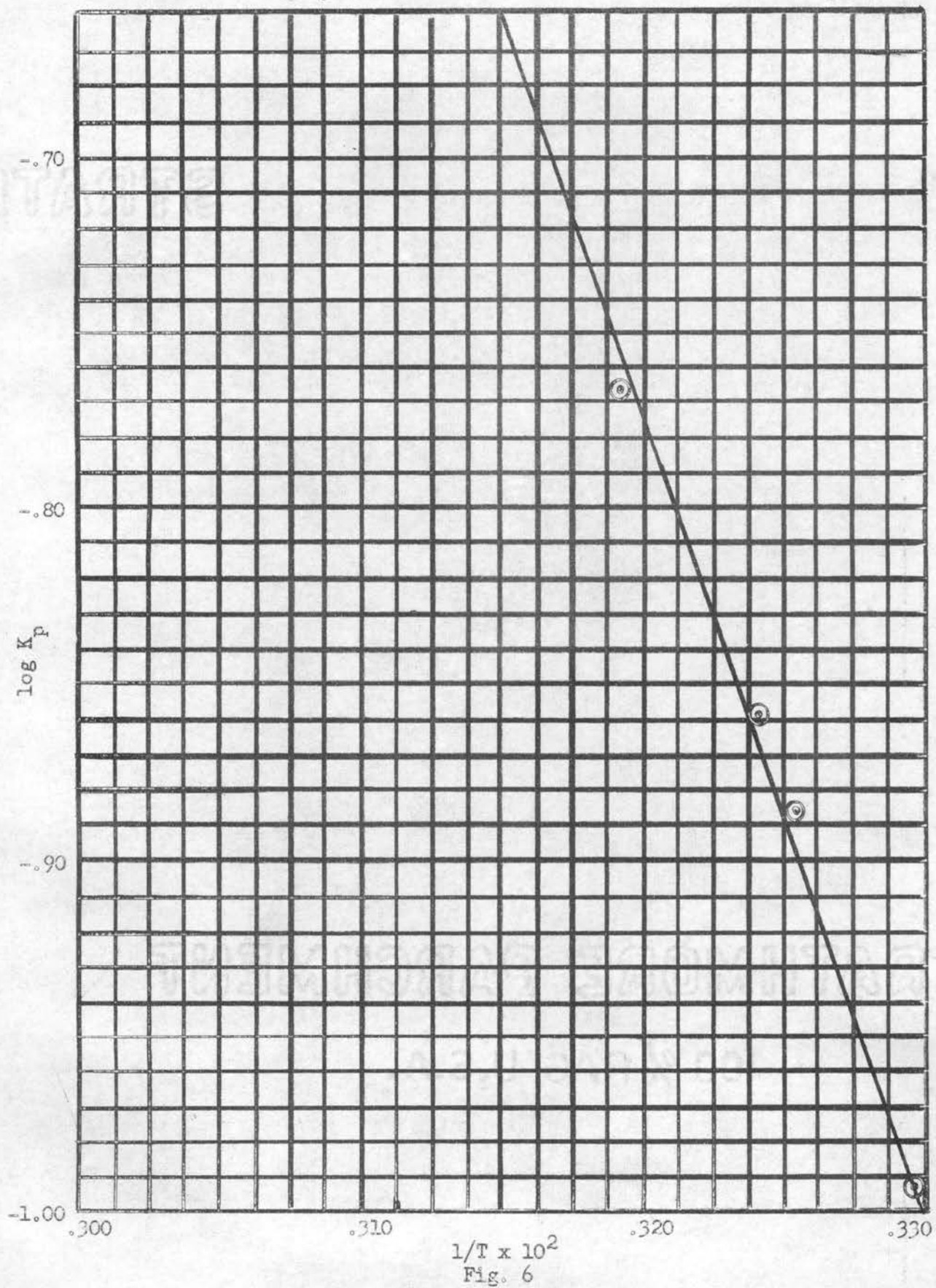
$1/T \times 10^2$

Fig. 6

TABLE VII

Dissociation Pressures of Allyl Chloride Picrate

The molecular ratio of picric acid to allyl chloride at 30° = 1:1

Temp. ($^{\circ}$K.)	Press. (mm)	K_p (atm)	1/T	log K_p
303.3	78.0	.1026	.003298	-0.9886
306.6	96.9	.1275	.003261	-0.8944
308.2	106.5	.1401	.003243	-0.8536
313.3	136.7	.1798	.003192	-0.7452

Log K_p is plotted against 1/T in Fig. VII and the best straight ling drawn among the points. The following equation relates the pressure to the temperature:

$$\log P = - 2120 / T + 5.92$$

The heat of dissociation was calculated from the slope of the line to be 9.70 $\pm$ 0.20 kcal. per mole.
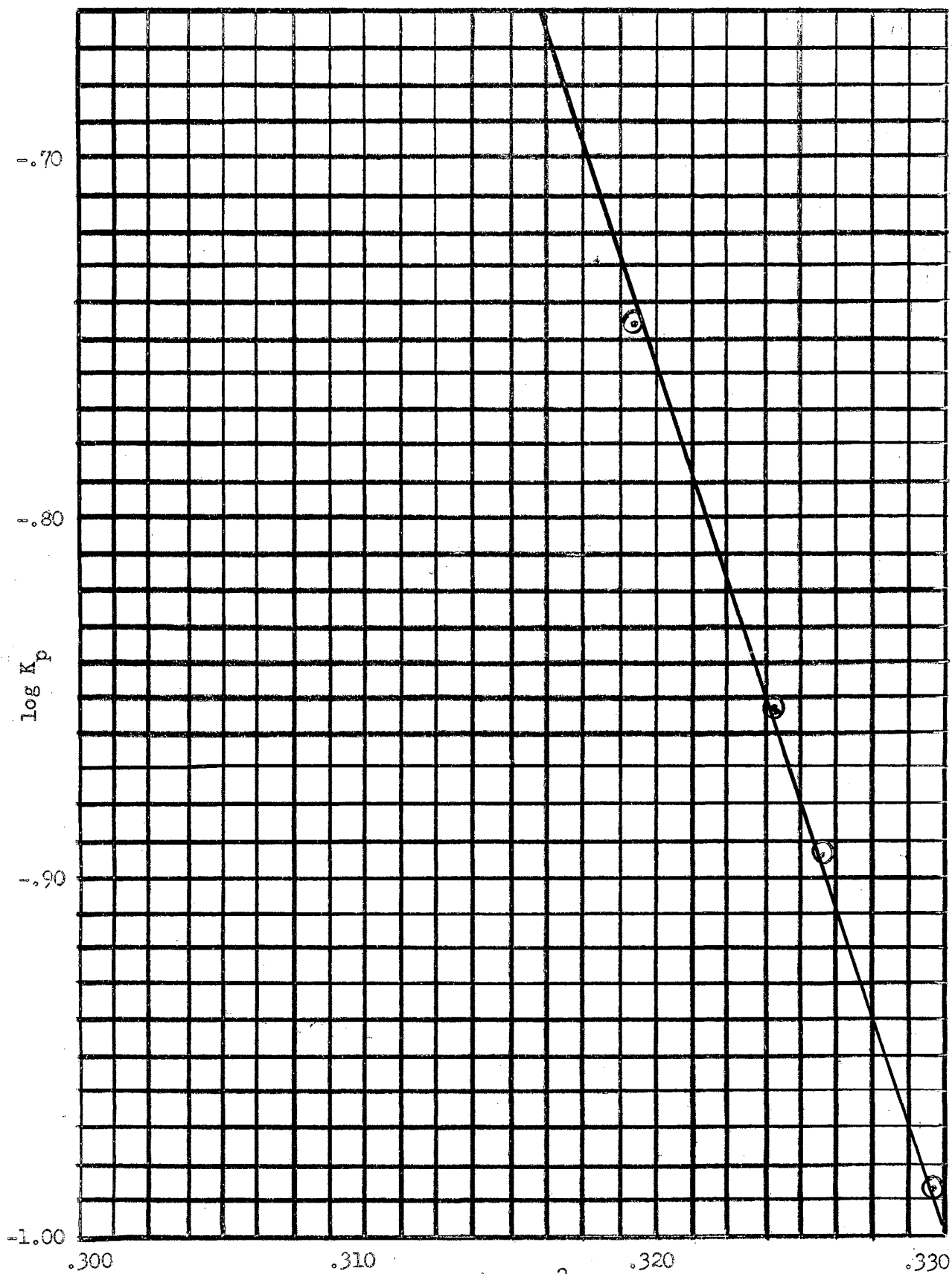
$1/T \times 10^2$

Fig. 7

TABLE VIII

Dissociation Pressures of Vinyl Acetate Picrate

The molecular ratio of picric acid to vinyl acetate at 30° = 2:1

Temp. ($^{\circ}$K.)	Press. (mm)	K_p (atm)	1/T	log K_p
303.3	48.1	.06329	.003298	-1.1987
308.6	51.3	.06750	.003243	-1.1707
313.3	64.8	.08618	.003192	-1.0646
318.3	67.8	.08921	.003141	-1.0496
328.2	89.7	.11790	.003051	-0.9285
333.2	97.2	.12380	.003002	-0.9073

Log K is plotted against 1/T in Fig. VIII and the best straight line drawn among the points. The following equation relates the pressure to the temperature:

$$\log P = -1030 / T + 2.19$$

The heat of dissociation was calculated from the slope of the line to be 4.70 $\pm$ 0.11 kcal. per mole.
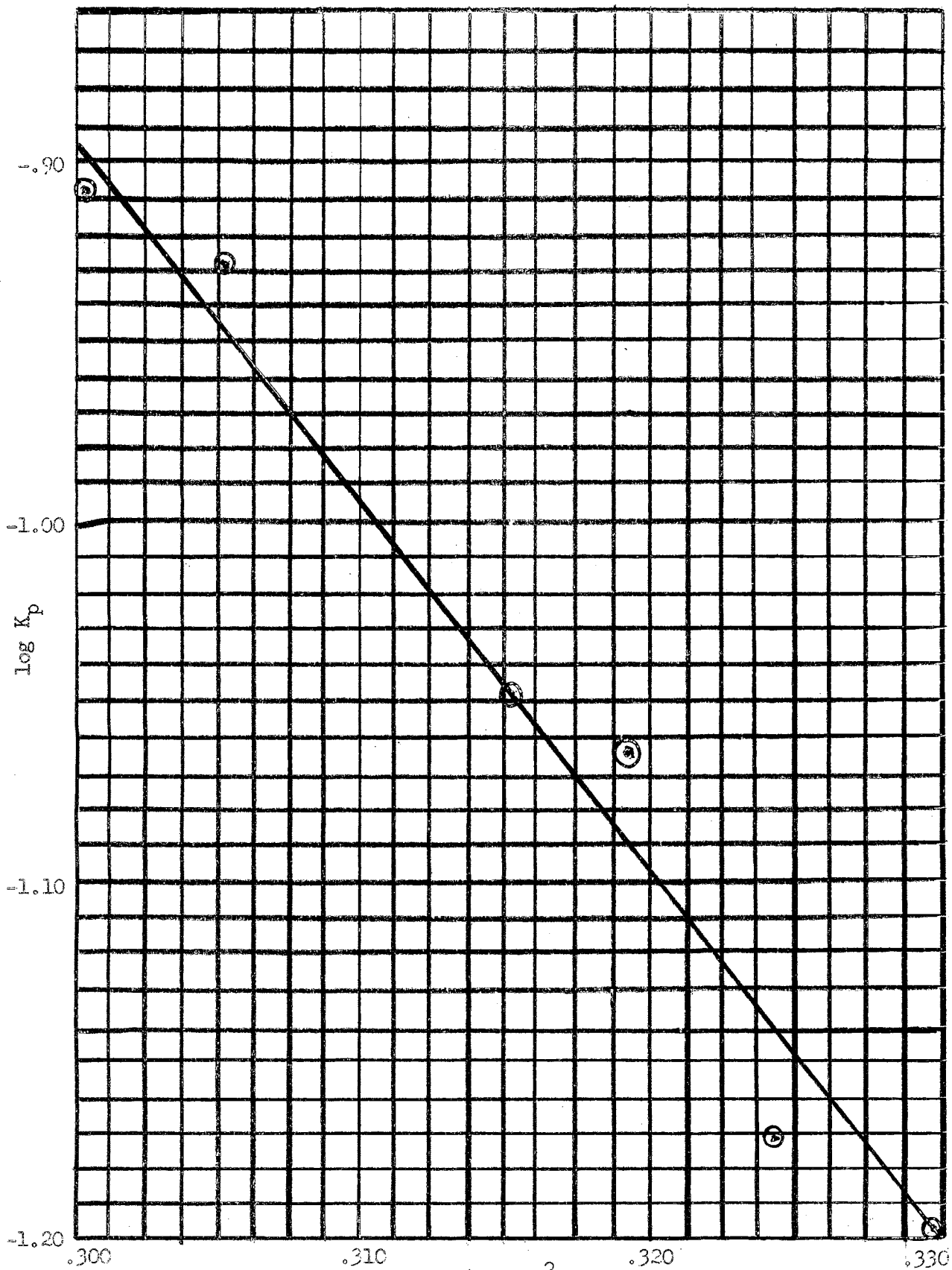
Fig. 8

Cyclohexane and n-heptane were found to give no addition compounds with picric acid since repeated evacuations gave only those constant pressure readings representing a saturated solution.

An attempt to study -pinene with picric acid was made. It is believed that a complex does form but the boiling point of -pinene was too high to permit its complete elimination from the connecting tubes outside the bath. The apparatus probably could be adapted for the study of complexes with higher-boiling liquids but time did not allow for it in this work.

DISCUSSION OF RESULTS

The results obtained from this study can be compared only to those found for complexes of aromatic hydrocarbons and their derivatives with polynitro compounds and to each other. Any conclusions are of little significance until further studies can be made.

The combined and modified isoteniscope-tensimeter has satisfied our hopes in that it has provided a rapid and apparently accurate method for determining molecular ratios and dissociation pressures.

In each determination the $\log_{10}K_p$ was found to be negative as can be seen in Tables II through VIII. From the equation

$$F = -RT \ 2.303 \ \log_{10}K_p$$

it is readily seen that each complex studied is thermodynamically stable within the temperature range involved since the free energy of dissociation in each case would be positive. The stabilities of all complexes decrease with increasing temperature.

Allyl alcohol, allyl bromide and allyl chloride each gave a 1:1 complex with picric acid. The stability of these complexes is indicated from the equilibrium constants to be Cl Br OH. This order of stability is the reverse to that to be expected from electron transfer theories since this is the order of decreasing electro negativity.

The molecular ratios of picric acid to cyclohexene, vinyl acetate and acrylonitrile were all 2:1. From the dissociation constants it is seen that the stability of cyclohexene picrate and vinyl acetate

pictrate is greater than that of acrylonitrile picrate at 30° C. and that the stabilities of both decrease more rapidly with temperature than the stability of acrylonitrile picrate.

Vinyl acetate and acrylonitrile both have two conjugated unsaturated regions. This, along with the fact that they both form 2:1 complexes with picric acid, gives support to the idea that a molecule may have two separate regions of influence. It does not follow, however, that $C=O$, $C=N$ and $C=C$ bonds exert the same influence. It would seem that the $C\equiv N$ bond exerts a greater influence than the $C=O$ bond (52).

The fact that the molecular ratio of benzene picrate is 1:1 whereas that for cyclohexene picrate is 2:1 would suggest that hydrogen bonding is holding these molecules together. This idea is invalidated by the results obtained with cyclohexane and n-heptane, since they formed no complexes with picric acid.

One source of error in this method of determining molecular ratios is that water from the bath which is held in the lip of the ball-and-socket joint C might be sucked into the flask when it is disconnected. This was noticed to happen during one of the early trial runs and thereafter a special effort was made to eliminate this water before the flask was disconnected.

Broeg in an earlier study of benzene picrate (among others) by vapor pressure methods (12) attempted to compare a literature K_c value to his K_p value by changing K_p to K_c using the equation $K_p = K_c RT^{n_g}$. It does not appear that this conversion is theoretically sound since these solid-vapor systems were not homogeneous, and recalculation even by his method does not give the agreement he claimed between the liquid partition method and the vapor pressure method.

SUMMARY

The isoteniscope and tensimeter were combined in hopes of providing a more accurate method for determining dissociation pressures, and modified so that molecular ratios might be found.

New molecular compounds of picric acid with cyclohexene, acrylonitrile, allyl bromide, allyl chloride, allyl alcohol and vinyl acetate were found. Picric acid does not form a complex with cyclohexane or n-heptane.

The dissociation pressures of these complexes were determined at several temperatures, from 30° to 60° C. From the results log K_p was plotted against 1/T and the heat of dissociation determined from the slope of the best straight line.

The free energies of dissociation indicate that these complexes are thermodynamically stable over the temperature range involved.

TABLE X

Calculated Results

Addition Complex of Picric Acid with	Molecular ratio Picric acid: olefin	K_p at 30° atm.	Constants for Equation*		H, at $30\text{--}60^\circ$ kcal/mole
			A	B	
Cyclohexene	2:1	.08908	−980	2.22	4.39±0.1
Acrylonitrile	2:1	.04764	−2030	5.36	9.29±0.19
Allyl alcohol	1:1	.04816	−1810	4.67	8.28±0.17
Allyl bromide	1:1	.1018	−2020	5.59	9.24±0.19
Allyl chloride	1:1	.1026	−2120	5.92	9.70±0.2
Vinyl acetate	2:1	.06329	−1030	2.19	4.70±0.11

* $\log_{10}P = A/T + B$

BIBLIOGRAPHY

(1)   Arends, Ber., 64, 1936-51 (1931)

(2)   Anderson and Hammick, J. Chem. Soc., 1950, 1089-94

(3)   Baddar and Mikhail, J. Chem. Soc., 1949, 2927-9

(4)   Behrend, Z. physik. Chem., 15, 183 (1894)

(5)   Bell and Fendley, Trans. Faraday Soc., 45, 121-2 (1949)

(6)   Bennett and Willis, J. Chem. Soc., 1929, 246

(7)   Bestougeff, Groupment Franc. develop. rechercher aeronaut No. 33, 89 (1946)

(8)   Bhalnagar, Neugi and Tuli, Indian J. Phys., 9, 311-17 (1935)

(9)   Brackman, Rec. trav. chim., 68, 147-59 (1949)

(10) Briegleb and Schachowski, Z. physik. Chem., B19, 255-77 (1932)

(11) Briegleb, "Zwischenmolekulare Krafte and Molekulstructur", Ferdinand Enke, Stuttgart, 1937

(12) Broeg, "Dissociation Constants of Aromatic Polynitro Compounds with Benzene" Master's thesis, Oklahoma A. and M. College, 1940

(13) Bronsted, Z. physik. Chem., 78, 284 (1911)

(14) Brown, J. Chem. Soc., 127, 345-8 (1925)

(15) Crumpler and Yoe, "Chemical Computations and Errors", J. Wiley and Sons, Inc., London, 1940, pp. 217-22

(16) Davis and McDonald, J. Research Natl. Bur. Standards, 42, 595-603 (1949)

(17) Dewar, Electronic Theory of Organic Chemistry, Oxford Press, London, 1949, p. 184-5

(18) Dimroth and Bamberger, Ann., 438, 67 (1924)

(19) Drucker, Trans. Faraday Soc., 34, 1214-18 (1938)

(20) Fieser and Fieser, "Organic Chemistry", D. C. Heath and Co., New York City, N. Y., 1950, p. 625

(21) Frowein, Z. physik. Chem., 1, 5 (1887)

(22) Gibson and Adams, J. Am. Chem. Soc., 55, 2681-95 (1933)

(23) Gibson and Loeffler, J. Am. Chem. Soc., 62, 1324 (1940)

(24) Halban and Zimpelmann, Z. physik. Chem., 117, 461-77 (1925)

(25) Hamilton and Hammick, J. Chem. Soc., 1938, 1350-2

(26) Hammick and Yule, J. Chem. Soc., 1940, 1539

(27) Hammick and Sixsmith, J. Chem. Soc., 1935, 580

(28) Hunter, Qureisky, and Samuel, J. Chem. Soc., 1936, 1576-80

(29) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology", McGraw-Hill Book Co., New York, 1926, 3, p. 221

(30) Kofler, Z. Elektrochem., 50, 200-7 (1944)

(31) Kremann, Monatsh., 29, 863-90 (1908)

(32) Kremann, Ahrens Vortrag, 27, 58 (1924)

(33) Kuriloff, Z. physik. Chem., 25, 419 (1898)

(34) Landuaer and McConnell, Anal. Chem., 23, 1044 (1951)

(35) Lextreit, Compt. rend., 102, 555 (1886)

(36) Lichten, Weston, and White, J. Am. Chem. Soc., 74, 4715 (1952)

(37) Mason, Rosen and Swift, J. Chem. Ed., 18, 473-4 (1941)

(38) Moore, Shepherd, and Goodall, J. Chem. Soc., 1931, 1447

(39) Mulliken, Abstracts, 118th meeting, A.C.S., September 3, 1950, p. 54Q

(40) Nease, "Dissociation Constants of Aromatic Polynitro Compounds with Benzene" Master's thesis, Oklahoma A. and M. College, 1939

(41) Ostromisslensky, J. prakt. Chem., 84, 489 (1911)

(42) Pfeiffer, "Organische Molekülverbindungen", Ferdinand Enke, Stuttgart, 1937

(43) Powell and Huse, J. Chem. Soc., 1943, 435-6

(44) Sinomiya and Asahina, J. Chem. Soc. Japan, 59, 341-51 (1938)

(45) Sinomiya, J. Chem. Soc. Japan, 59, 922-6 (1938)

(46) Sinomiya, J. Chem. Soc. Japan, 60, 170-82 (1939)

(47) Sinomiya, Bull. Chem. Soc. Japan, 15, 92-103 (1940)

(48) Sinomiya, Bull. Chem. Soc. Japan, 15, 137-47 (1940)

(49) Sinomiya, Bull. Chem. Soc. Japan, 15, 137-47 (1940)

(50) Sinomiya, Science Japan, 16, 215-16 (1946)

(51) Smith and Menzies, J. Am. Chem. Soc., 32, 1412-34 (1910)

(52) Sudborough, J. Chem. Soc., 79, 522 (1901)

(53) Vanzetti, Atti. accad. Lincei, 22, 103-9 (1935)

(54) Weiss, J. Chem. Soc., 1942, 245-9

VITA

Billy Gene Harper
candidate for the degree of
Master of Science

Thesis: COMPOSITIONS AND DISSOCIATED CONSTANTS OF MOLECULAR
COMPOUNDS OF OLEFINS WITH PICRIC ACID

Major: Chemistry

Biographical and Other Items:

Born: October 3, 1926 at Texarkana, Texas

Undergraduate Study: Parsons Junior College, 1947-48;
Northeastern State College, 1948-50

Graduate Study: O. A. M. C., 1952-53

Experiences: Projectionist, 1944-45; Army Air Force in
Germany, 1945-46; High School Teacher, 1950-51;
Graduate Assistant, 1951-53.

Member of Phi Lambda Upsilon, Kappa Mu Epsilon, Lambda Delta
Lambda, Alpha Chi, and Junior Member of The American
Chemical Society.

Date of Final Examination: May, 1953

THESIS TITLE: Compositions and Dissociation Constants
of Molecular Compounds of Olefins with
Picric Acid

AUTHOR: Billy G. Harper

THESIS ADVISER: Dr. O. C. Dermer

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