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Equilibrium and Kinetic Study of the Substitution Reactions of Pentacarbonylaminetungsten (O) with Triphenylphosphine

William O. Bailey

Eastern Illinois University

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EQUILIBRIUM AND KINETIC STUDY OF THE SUBSTITUTION

REACTIONS OF PENTACARBONYLAMINETUNGSTEN (O)

WITH TRIPHENYLPHOSPHINE
(TITLE)

BY

William O. Bailey

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1972
YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
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EQUILIBRIUM AND KINETIC STUDY OF THE SUBSTITUTION

REACTIONS OF PENTACARBONYLAMINETUNGSTEN (0)

WITH TRIPHENYLPHOSPHINE

William O. Bailey

Bachelor of Science in Education

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August, 1968

Submitted in partial fulfillment

of the requirements for the degree of

Master of Science in Chemistry

at the

Graduate School

of

Eastern Illinois University

CHARLESTON, ILLINOIS

1972

EQUILIBRIUM AND KINETIC STUDY OF THE SUBSTITUTION

REACTIONS OF PENTACARBONYLAMINETUNGSTEN (O)

WITH TRIPHENYLPHOSPHINE

Thesis   Approved

DEDICATION

To my Father and Brothers
and Mother and Mike

The noblest ship
To sail this sea
Was wrought more of love
Than destiny.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Richard Keiter for suggesting the problem and for providing the guidance and the assistance needed in surmounting the more difficult obstacles encountered in the course of the investigation.

The author would like to give thanks to other members of the faculty for their interest and help.

Most special thanks are duly in order for the author's wife, Evelyn, who has provided immeasurable aid in typing the rough and final drafts of the thesis, and given sustaining encouragement and love--light, when little was evident at the farthest reaches of the tunnel.

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ABSTRACT

Title of Thesis: Equilibrium and Kinetic Study

of the Substitution Reaction of

Pentacarbonylaminetungsten (O)

with Triphenylphosphine

Name: William O. Bailey

Thesis directed by: Dr. Richard L. Keiter

A kinetic and equilibrium study of the reaction of triphenylphos-
phine (PPh_3) with pentacarbonylaminetungsten (O) [$(CO)_5WNH_2C_6H_5$] has
been reported previously.[1] Equilibrium constants for the reaction
$(CO)_5WNH_2C_6H_5 + PPh_3 = (CO)_5W[P(C_6H_5)_3] + C_6H_5NH_2$ in toluene were
reported to be 17.1, 49.2 and 65.7 respectively. In addition, the
entropy change (ΔS) for the reaction was found to be 86 ± 5 cal mol^{-1}
deg^{-1}.

In this study the above reaction was reinvestigated in order to
determine the cause of the abnormally large entropy change. The
reaction was investigated spectrophotometrically by monitoring the
absorption of the aniline complex at 406 nm. Other reactants and
products of the reaction do not absorb significantly at this wave-
length. The reaction was examined over a range of ligand concen-
trations and reaction temperatures.

When the conditions of the previous work were duplicated it was
found that the absorption due to the aniline complex disappeared
completely. Concentrations of starting reactants were adjusted in
order to shift the equilibrium position to the left. In no experiment

was there obtained any evidence for equilibrium. Therefore, if an equilibrium does exist, the equilibrium constant must be much larger than that previously reported. Furthermore, it was previously reported that equilibrium for the reaction is established in two days. In this study it was found that the aniline complex continues to react beyond two days in all experiments.

An attempt to determine the equilibrium constant for the reaction by approaching the equilibrium from the opposite direction was not successful. The intensity of the carbonyl absorption of $(CO)_5WPPh_3$ did not diminish with time upon treatment of this compound with a large excess of aniline nor was there any appearance of aniline complex. It is concluded that the position of equilibrium cannot be determined by the methods utilized in the previous study.

The previous workers reported that the aniline complex is stable in the presence of a large excess of aniline. In this study it has been found that this is not true for temperatures above 30° and that at temperatures above 40° rapid decomposition occurs.

It is the conclusion of this study that the thermodynamic data previously reported are unreliable.

[1]R. J. Angelici and C. M. Ingemanson, Inorg. Chem. **8**, 83 (1969).

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CHAPTER I

INTRODUCTION

The chemistry of metal carbonyls has enjoyed considerable prominence in recent years.[1] Complexes of the type $W(CO)_5L$, where L is an amine, phosphine, or phosphite are pseudo-octahedral complexes of C_{4v} symmetry.
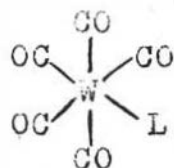
The bonding involved is perhaps best treated by employing molecular orbital theory, which treats the simultaneous interaction of the ligands with the central metal ion. Ligand orbitals will interact with metal orbitals of the same symmetry to a degree dependent upon the similarity of their respective energies. Sigma bonding may occur using the A_{1g}, E_g, and T_{1u} orbitals, while π-bonding is limited, through symmetry and energy restrictions, to the T_{2g} orbitals.

The type and degree of bonding in metal complexes is also dependent upon the nature of the ligand. When the ligand is an amine, the type of bonding available is

1

limited. In coordinating with the metal, the nitrogen atom of the amine donates its lone pair of electrons resulting in the formation of a dative σ-bond, $R_3N \rightarrow M$ (R = alkyl or aryl, M = metal). Nitrogen possesses no empty d orbitals of suitable energy to accept back donated electrons from filled metal d orbitals, thereby eliminating the possibility of d_π-d_π bonding.

In contrast, carbonyl groups are well known as good π-bonding ligands. The 2p antibonding orbitals of the carbon are well suited for accepting electron density from the metal, making π-bonding possible. However, it is with phosphorus ligands, R_3P, that considerable discussion, even argument, has arisen within recent years. Again, the dative σ-bond is formed through donation of the lone pair of phosphorus to the central metal. In addition, phosphorus possesses empty d orbitals of correct symmetry and energy for π-bonding to be a distinct possibility. It is over the relative merits of π-bonding in phosphorus ligands that the pendulum of discussion has swept, without any decisive elucidation of truth obvious.

Several approaches have been utilized in attempts to determine the absence or presence of π-bonding between metals and phosphorus ligands. Many attempts

have centered around studies of the carbonyl infrared
stretching frequencies of substituted metal carbonyls.
Figure 1 shows a typical infrared spectrum for a complex
of the type $LW(CO)_5$. The C_{4v} symmetry would predict
three infrared bands of weak, strong, and very strong
intensities--the ^2_1A, ^1_1A, and E vibrational modes,
respectively. The ^2_1A and E modes are assigned to the
four equivalent CO groups, while the CO group <u>trans</u> to
the ligand has been assigned to the ^1_1A vibrational mode.
There may also be a very weak absorption, a ^{13}CO satel-
lite of the E mode, in the range from 1900-1910 cm^{-1} as
well as the weak forbidden B_1 mode absorption from
1980-2000 cm^{-1}.[2]
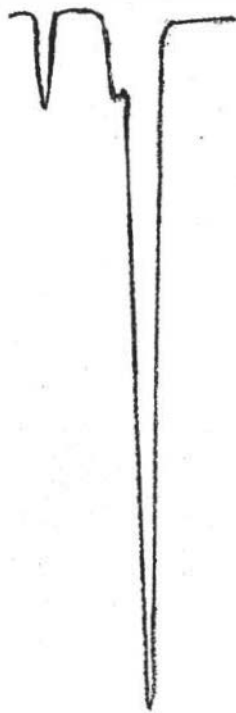
Figure 1   Carbonyl Stretching Region of the Infrared
            Spectrum of a $LW(CO)_5$ Complex.

Advocates of M-P π-bonding in metal-phosphorus complexes argue that a phosphine, for example, can accept electron density into its empty 3d orbitals thereby reducing the charge on the metal. This, in turn, decreases the M-CO π-bonding while increasing the C-O bond strength and thereby increasing the C-O stretching frequency. A study by Horrocks and Taylor[3] which uses substituted derivatives of cobalt tricarbonyl nitrosyl attributed increasing C-O and N-O stretching frequencies to increasing π-bonding ability of the incorporated ligands, i.e.: $PCl_3 > PCl_2C_6H_5 > PCl(C_6H_5)_2 > P(C_6H_5)_3$. The decreasing electron withdrawing ability of the substituents bound to phosphorus makes the ligands increasingly poorer π-electron acceptors, thereby increasing the charge on the metal which, in turn, is donated to antibonding orbitals of CO and NO, decreasing their stretching frequencies. Table I contains some of the data from which the aforementioned trend was noted.

Table I   Data for Phosphine Derivatives of $Co(CO)_3NO$[3]

	CO sym. cm^{-1}	CO antisym. cm^{-1}	NO cm^{-1}
$Co(CO)_3NO$	2100.3	2033.0	1806.2
One Ligand			
PCl_3	2073.1	2029.6	1805.7
$PCl_2C_6H_5$	2061.4	2014.4	1785.6
$PCl(C_6H_5)_2$	2048.5	1996.0	1772.5
$P(C_6H_5)_3$	2035.0	1981.2	1761.0
Two Ligands			
PCl_3	2044.5		1793.2
$PCl_2C_6H_5$	2023.6		1793.2
$PCl(C_6H_5)_2$	1987.3		1747.2
$P(C_6H_5)_3$	1956.7		1717.0

A study by Cotton[4] of substituted group VI carbonyls also indicated the presence of M-P π-bonding.   In fact, through examination of CO force constants (as calculated by the method of Cotton and Kraihanzel[5]), Cotton was led to the interesting, if not startling, conclusion that PF_3 is a stronger π-accepting ligand than CO.   For $Mo(PF_3)_3(CO)_3$ the force constant, k_1, was calculated to be 16.98 mdyne/Å, or almost 0.5 mdyne/Å higher than the value of 16.52 mdyne/Å for the similar CO force

constants for $Mo(CO)_6$ as reported earlier.[5] As a result it was reasoned that since the CO force constant in $Mo(PF_3)_3(CO)_3$ was 0.5 mdyne/$\overset{o}{A}$ higher than that in $Mo(CO)_6$, the CO bond orders are 0.07 higher, thus implying that each CO, in $Mo(PF_3)_3(CO)_3$, was receiving 0.14 electrons less than those in $Mo(CO)_6$. Thus, of the 6 $d\pi$-electrons available, the CO groups were receiving 3 - 3(0.14) = 2.58 electrons, while the PF_3 groups were left with 3.42. Thus, PF_3 is about 3.42/2.58 = 1.32 times stronger a π-electron acceptor than CO. Cotton estimated this figure to be reliable within the limits of 20%.

However, proponents of σ-bonding[6,7] allege that increases in C-O stretching frequencies are produced by the decreasing σ-bonding ability of the ligands subsequently reducing the charge on the metal. Inconclusiveness of evidence results, however, from the fact that the order of decreasing π-bonding potential is the order of increasing σ-bonding ability as indicated by the basicities of the ligands from pK_a and ΔHNP data.[8] ΔHNP is defined as the difference in half-neutralization potential between the ligand and N_1N'-diphenylguanidine in nitromethane. The smaller the ΔHNP, the more basic is the ligand.[9] Table II gives some typical ΔHNP and pK_a values for various phosphorus ligands.

Table II ΔHNP and pK_a Values for Phosphorus Ligands

L	ΔHNP[8]	p$\bar{K}_a$ [21]
$P(C_2H_5)_3$	111	---
$P(n-C_4H_9)_3$	131	8.4
$P(O-n-C_4H_9)_3$	520	3.3
P$(C_6H_5)_3$	573	2.7
$P(OCH_2)_3CCH_3$	665	1.5
$P(OC_6H_5)_3$	875	-1.2

Differentiation between π and σ inductive effects in the metal-ligand bond has proved difficult.

Angelici and Malone[2] studied the C-O stretching frequencies and force constants[5] of pentacarbonyltungsten complexes with known non-π-bonding amine ligands, along with those of potentially π-bonding pyridine and phosphine ligands. They found that the decrease in magnitude of the stretching frequencies and force constants with increasing basicity of L was virtually the same for all three groups of ligands. Table III presents some of their force constant data.

Table III Force Constants Obtained for $LW(CO)_5$ Molecules in Cyclohexane Solvent^2 (Mdynes/$\overset{o}{A}$)

L	pK_a	k_1	k_2	k_i
Amines				
$C_6H_5NH_2$	4.6	15.11	15.82	0.34
$4\text{-}CH_3OC_6H_4NH_2$	5.3	15.07	15.80	0.34
C_4H_9NC	8.3	15.12	15.77	0.34
$C_6H_{11}NH_2$	10.7	15.07	15.75	0.34
Pyridines				
$3\text{-}BrC_5H_4N$	2.8	15.16	15.85	0.34
C_5H_5N	5.2	15.11	15.80	0.34
$4\text{-}CH_3C_5H_4N$	6.0	15.07	15.77	0.34
Phosphines				
$(C_6H_5)_3P$	2.7	15.47	15.89	0.31
$(p\text{-}CH_3OC_6H_4)_3P$	4.5	15.43	15.85	0.31
$(n\text{-}C_4H_9)_3P$	8.4	15.47	15.78	0.32

The authors could detect little significant difference in frequency shifts and force constants as a function of basicity of the ligand for the non-π-bonding amines and the potentially π-bonding pyridine and phosphine ligands. Thus, they reasoned, postulation of M-L π-bonding was not required to explain the C-O stretching frequency shifts.

However, dissension over the results of Angelici
and Malone arose after completion of a study by Brown
and Dobson.[10] They reasoned that close examination of
the data of Angelici and Malone, as well as their own
independently obtained data for tungsten carbonyl com-
plexes containing pyridine and amine ligands, revealed
no trend in k_1, the axial carbonyl force constant, as a
function of pK_a of the ligand. This apparent lack of a
σ-bonding influence at the carbonyl <u>trans</u> to the ligand,
they asserted, made Angelici's attribution of changes
in carbonyl stretching force constants solely to σ-bond-
ing somewhat tenuous. The results were additionally
suspect, they reasoned, because of a probable misassign-
ment of band positions in the infrared spectrum. For
three of the five complexes studied, Angelici and Malone
were unable to resolve the ^1_1A and E bands of the spectra.
Thus, it proved necessary to estimate the position of the
^1_1A band. This position was highly critical in deter-
mination of the force constants. Their estimates were
based on the fact that in $LW(CO)_5$ complexes for which
the ^1_1A band is resolved, it is shifted by an amount
equal to the average of the shifts of the ^2_1A and E
bands. This was assumed to be the case for the other
complexes as well. Brown and Dobson argue that this

assumption is entirely without theoretical justification, and additionally, that any combination of σ- and π-bonding which would produce effects implied by their assumption would be highly improbable. Evidence of their claim is presented through a spectrum of $Ph_3PW(CO)_5$ which has a symmetrical E mode--this for a complex which, according to the Angelici assumption, should show a separation of the ^1_1A and E bands of 5.5 cm^{-1}, the former being observable as a shoulder on the E band. As a result, Brown and Dobson allege that the data of Angelici and Malone, and conclusions drawn from such, are questionable. They also noted that their results were consistent with a proposal, advanced by Fenske and DeKock[11] explaining similar variations of k_1 and k_2 in the series of complexes $Mn(CO)_5X$ (X = Cl, Br, I), which postulates direct overlap of the σ_z-bonding orbital of the halogen and the π orbitals of equatorial carbonyls.

Perhaps a more direct probe into M-P π-bonding is found through the examination of nuclear magnetic coupling constants, J_{M-P}, for those series of phosphorus complexes containing metals with a nuclear spin ½. A theoretical approach[12] proposed three possible contributions to the metal-phosphorus coupling constants: (1) a Fermi

contact term dependent upon electron densities between the two nuclei, i.e. s electron density, (2) coupling via spin-orbit motion (related to anistropy in screening), (3) dipole-dipole coupling of nucleus and electron spins (requiring low-lying electronic states and increasing with the effective nuclear charge.) By far the most significant contribution is made by the Fermi contact term as determined by the s character of the M-P σ-bond.

A study by Grim and co-workers[13] of the tungsten-phosphorus coupling constants $J_{183_W-31_P}$ of tertiary phosphine derivatives of tungsten hexacarbonyls showed J_{W-P} to decrease in the order $Ph_3P > Ph_2RP > PhR_2P > R_3P$. This is the order of increasing σ-donor ability. If, indeed, spin-spin coupling is transmitted mainly through σ-bonds, it might be expected that the worst σ-donor, Ph_3P, would have the smallest coupling constant. That exactly the opposite is true would seem to indicate the presence of M-P π-bonding. Back donation of tungsten 5d electrons to phosphorus would deshield the bonding 6s electrons of tungsten, thus increasing the Fermi contact term. Concurrently, phosphorus is accepting electron density into its 3d orbitals, thus shielding its 3s electrons. But the shielding is not as effective as the tungsten deshielding because the same principal

quantum number is involved for the phosphorus case. In addition, the synergic effect of the π-acceptor would increase the σ-bonding. An explanation for the observed trend would still be valid if the coupling constants were negative (thus reversing the trend), but this possibility is highly unlikely in light of studies on coupling constants of platinum-phosphorus compounds.[14,15] Thus, Grim's results would seem indicative of M-P π-bonding.

However, in a study of coupling constants for pentacarbonyltungsten by Keiter and Verkade[16], a different interpretation was used. They found that the magnitudes of the coupling constants increased linearly with an increase in electronegativity of the substituents on the phosphorus ligand. In fact, they obtained a correlation coefficient of 0.97 for the plot of the coupling constants against the Pauling electronegativity scale. Table IV contains some of their data for complexes exhibiting this trend.

Table IV Phosphorus-31 NMR Data[16,17]

Compound	$J_{183_W-31_P}$
$(C_4H_9)_3PW(CO)_5$	227
$(C_4H_9)_2C_6H_5PW(CO)_5$	235
$(C_4H_9)(C_6H_5)_2PW(CO)_5$	250
$(C_6H_5)_3PW(CO)_5$	280
$C_5H_{11}C\ CH_2N(CH_3)_3PW(CO)_5$	318
$C_5H_{11}C(CH_2O)_3PW(CO)_5$	393
$F_3PW(CO)_5$	485

They interpreted the trend as resulting from the
increasing s electron density of the W-P bond. This is
the result of the rise in positive charge on the phos-
phorus atom and the increase in R-P-R bond angle as more
electronegative substituents are bound to phosphorus.
Thus, they explained, because coupling is generally
agreed to occur through bonding orbitals of s character,
W-P π-bonding need not be invoked to account for the
correlation of coupling constants with electronegativity.

An additional tool with which to pry evidence for
or against M-P π-bonding is made available by obtaining
the crystal structures of the complexes in question.
Grim and co-workers[18] did this for triphenylphosphite
and triphenylphosphine complexes of pentacarbonylchromium.
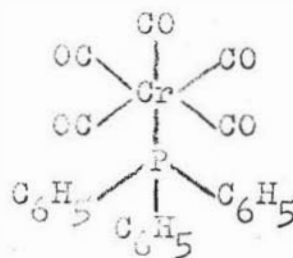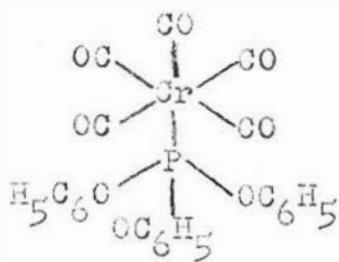
The bond lengths they obtained are presented in Table V.

Table V Phosphine vs. Phosphite Bond Lengths[16] ($\mathring{A}$)

Bond	Phosphite	Phosphine
Cr-P	2.309	2.422
Cr-C (trans)	1.861	1.844
C-O (trans)	1.136	1.154
Cr-C (cis, av)	1.896	1.880
C-O (cis, av)	1.131	1.147

As was predicted from π-bonding theory, the trans Cr-C
distance was significantly shorter than the cis Cr-C
distance, and the cis C-O distance was shorter than the
trans C-O distance. This evidence would seem to add
more fuel to the π-bonding fire, but, again, caution is
needed. Rudolph and Schultz[19] have shown, for example,
that the dative bond distance in $Me_3P \rightarrow BH_3$ is much
longer than that for $F_3P \rightarrow BH_3$, yet the shorter bond
appears to be the thermodynamically weaker bond. As a
result, bond length may be a less reliable criterion of

bond strength than previously thought.

In hope of providing further insight into the discussion, Angelici and Ingemanson[20,21] conducted a study of the kinetics and determined some equilibrium parameters for the following reaction:

$$(Am)W(CO)_5 + L \rightleftarrows (L)W(CO)_5 + Am$$

where Am = amine
L = phosphine or phosphite

They discovered that the amine derivatives of $W(CO)_6$ react with a ligand L to form $W(CO)_5L$ as the only reaction product. Over a large range of ligand concentrations, the reaction was found to follow a two-term rate law:

$$\text{rate} = k_1\left[W(CO)_5(NR_3)\right] + k_2\left[W(CO)_5(NR_3)\right]\left[L\right]$$

They also determined pseudo-first-order rate constants, k_{obs}, whose dependence upon the ligand concentration is illustrated in the following expression:

$$k_{obs} = k_1 + k_2\left[L\right]$$

where k_1 can be associated with a dissociative mechanism involving a five-coordinated intermediate which then yields the product upon addition of ligand. It was found that as the basicity of the amine was increased, the first-order rate constant, k_1, decreased in value. Then, if bond strength is determined by the basicity of the amine, the negative dependence of k_1 upon pK_a would

be consistent with a reaction mechanism involving the
breaking of the tungsten-nitrogen bond. The authors
associated the second-order rate constant, k_2, with
S_N2 displacement involving nucleophilic attack by the
ligand upon the metal to form a seven-coordinated
intermediate which then yields the product.
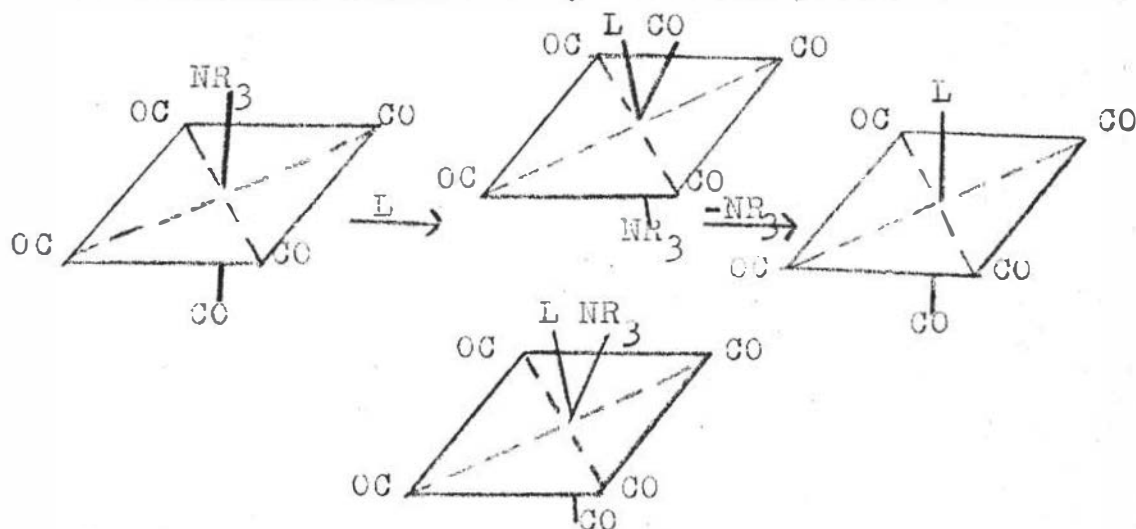
Angelici and Ingemanson found that, in general, k_2
increases with increasing basicity of the phosphorus
ligand. Their plot of $\log(k_2/k_1)$ versus pK_a of the
ligand shows a regular increase of $\log(k_2/k_1)$ with pK_a
except for sterically hindered $P(C_6H_5)_3$, which gives a
slower than expected rate, and the least sterically
hindered $C_2H_5C(CH_2O)_3P$, which reacts relatively faster
than other ligands. Since k_1 and k_2 are both sensitive
to amine basicity while, in addition, k_2 is affected by
steric factors and ligand basicity, the ratio k_2/k_1
would be expected to isolate the k_2 steric and ligand

basicity effects, eliminating the influence of amine
basicity. Table VI presents some of the kinetic data
from this study.

Table VI   Ratios of k_2/k_1 for Kinetics of the Reaction
of $W(CO)_5(NR_3)$ with L at $80.4^{\circ}C$ in Decalin[21]

Amine	$P(OC_6H_5)_3$	$P(C_6H_5)_3$	$P(n-OC_4H_9)_3$	$P(n-C_4H_9)_3$
ammonia	3.17	15.5	38.7	116
methylamine	23.1	47.9	140	340
dimethylamine	9.55	21.3	332	1300
piperidine	5.92	12.4	16.9	2020
morpholine	11.6	10.0	76.0	304
thimethylamine	1.64	0.0	37.9	304
average	9.20	21.6	107	731

The workers did not conduct kinetic studies of aromatic
amines because the rate expression for these was found
to be more complex than for the other amines.

From the equilibrium study several trends were
noted. The equilibrium constants for the reaction
decreased with increasing amine basicity. The K_{eq}
decreased in the order: p-anisidine > p-toluidine >
aniline > p-bromoanaline. On the other hand, K_{eq} was
found to generally increase with increasing basicity

of the phosphorus ligand. Table VII gives some
equilibrium constants for various ligands reacting with
$W(CO)_5$(aniline) at various temperatures in toluene.

Table VII Summary of K_{eq} for $W(CO)_5C_6H_5NH_2$ in Toluene[21]			
Ligand	35.4°C	40.5°C	45.4°C
$P(n-C_4H_9)_3$	225	345	359
$C_2H_5C(CH_2O)_3P$	263	418	613
$P(n-OC_4H_9)_3$	31.2	63.3	65.9
$P(C_6H_5)_3$	17.1	49.2	65.7
$P(OC_6H_5)_3$	6.6	12.4	25.4

Upon changing the ligand central atom the equilibrium
constants decreased in the order: $P(C_6H_5)_3 > As(C_6H_5)_3 >$
$Sb(C_6H_5) > Bi(C_6H_5)_3$. This order was also expected since
it follows the order of decreasing electronegativity of
the group V elements. Therefore, as the differences in
electronegativity decreased, the bonds became more co-
valent and weaker.

In addition to equilibrium constants, values for
the enthalpy changes for the displacement reactions were
also calculated. Table VIII presents a summary of these
parameters for several phosphorus ligands.

Table VIII Summary of Enthalpies and Entropies for the
Reaction of $(CO)_5WC_6H_5NH_2$ with Various Ligands
in Toluene[21]

Ligand	ΔH, kcal/mole	ΔS, eu
$P(n-C_4H_9)_3$	7.6 ± 2.6	36 ± 8
$P(n-OC_4H_9)_3$	14.2 ± 1.8	53 ± 6
$P(C_6H_5)_3$	24.8 ± 1.6	86 ± 5
$P(OC_6H_5)_3$	26.2 ± 0.5	89 ± 2

The authors noted the large positive ΔH's. Some
were, in fact, as large as the enthalpies of activation,
$\Delta H^{\pm}$, calculated in their kinetic study. They reasoned
that the closely similar values for ΔH and $\Delta H^{\pm}$ were
indicative that the large positive entropy change, ΔS,
was the controlling factor in the reaction. Indeed,
the ΔS values are quite positive and startlingly large.
A large and positive change in entropy would imply a
large increase in disorder of the system. For simple
displacement reactions, as these are, it is difficult
to conceive of any possible increase in disorder capable
of producing such large increases in entropy. Solvent
effects, as Angelici and Ingemanson noted, could not be
expected to account for such large ΔS's. Although they
were unable to account for these values they, nevertheless,

could offer no reason to doubt them. The variance of k_2 and K_{eq} with the basicity of the phosphorus ligand, Angelici and Ingemanson conclude, is evidence against W-P π-bonding and suggestive that the strength of the W-P bond is largely determined by the degree of W-P σ-bonding. However, some apparent anomalies in their results, particulary the exceedingly high entropy values, cast some shadow of doubt over their work. It was with the intention of perhaps elucidating these anomalies that this study was undertaken.

A. General Considerations

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Proton nmr spectra were measured with a Varian T-60 spectrometer which used saturated deuteriochloroform solutions with tetramethylsilane as an internal reference.

Infrared spectra were recorded with a Perkin-Elmer 237 grating infrared spectrometer.

Ultraviolet-visible spectra were recorded on a Beckman DB-G Spectrophotometer with an E. H. Sargent recorder.

Melting points were taken with an Arthur H. Thomas Unimelt apparatus.

B. Preparation of Complexes

1. Anilinepentacarbonyltungsten $(CO)_5WC_6H_5NH_2$

A solution of 5.0 g of $W(CO)_6$ and 10 ml of aniline in 200 ml of tetrahydrofuran was irradiated with ultraviolet light for five hours in a uv reaction vessel (diagrammed in reference 22). The resulting solution was evaporated to a thick yellow oil. The excess aniline was removed with dilute HCl and water, the resulting

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yellow crystals being filtered and dried. Excess $W(CO)_6$ was removed by sublimation. The complex was stored under vacuum.

Anal. Calcd. for C, 31.68; H, 1.69; N, 3.36.

Found: C, 31.42; H, 1.48; N, 3.21.

2. Pyridinepentacarbonyltungsten $(CO)_5WC_5H_5N$

A solution of 3.9 g $W(CO)_6$ and 6 ml of pyridine in 150 ml of THF was irradiated with uv light for 5 hours. The yellow solution was evaporated to a thick yellow oil, from which yellow crystals were precipitated through addition of dilute HCl and water. Excess $W(CO)_6$ was removed by sublimation.

3. Triphenylphosphinepentacarbonyltungsten $(CO)_5WP(C_6H_5)_3$

Anilinepentacarbonyltungsten (5.30 g, 12.7 mmoles) and triphenylphosphine (3.33 g, 12.7 mmoles) were dissolved in 100 ml of benzene and allowed to react for 20 hours. The solvent was then removed with a roto-evaporator. The resulting crystals were then dissolved in equal volumes of methylene chloride and methanol and refrigerated overnight. The resulting crystals were then filtered, then recrystallized from methylene chloride and methanol and dried. Excess $W(CO)_6$ was removed by sublimation at reduced pressure. (mp 145.5-146.0°C)

<u>Anal.</u> Calcd. for C, 47.13; H , 2.58; P, 5.28.
Found: C, 47.00; H, 2.65; P, 5.12.

C. Purification of Ligands and Solvents

1. Triphenylphosphine was recrystallized from ethanol. (obsd mp 79.9°C, literature 80.0°C)

2. Aniline was distilled on a Nester-Faust spinning band column. The distillation temperature was 60°C at 1.7 torr. Only the middle fraction was collected. Distilled aniline was stored under vacuum. (n obsd 1.5852, literature 1.5863)

3. Toluene was purified by distillation. (n obsd 1.4960, literature 1.4969)

D. Kinetic and Equilibrium Measurements

Angelici and Ingemanson maintain that under the appropriate conditions of ligand and amine concentrations, the reaction of $W(CO)_5(NR_3) + L = W(CO)_5L + NR_3$ exists in an equilibrium.[21] Then, knowing the initial concentration of $W(CO)_5NR_3$, the amine, the phosphorus ligand, and the fraction of $W(CO)_5NR_3$ reacted, the equilibrium concentrations of all participating species can be determined. Thus an equilibrium constant for the reaction can be calculated. The determination of the amount of $W(CO)_5NR_3$ reacted is facilitated by the fact that only the $W(CO)_5NR_3$ complexes, of all the reactant or product

species, is significantly colored. The visible spectrum of the yellow aniline complex, $W(CO)_5C_6H_5NH_2$, in toluene, shows an absorption at 406 mμ with a shoulder at around 445 mμ. The reaction product, $W(CO)_5P(C_6H_5)_3$, has a visible spectrum with very little absorption at 406 mμ. In fact, for the very low concentrations of ligand employed in our study, the absorption at 406 mμ is essentially insignificant. Sample spectra are shown in Figures 2 and 3. Consequently, the progress of the reaction can be effectively followed by observing the change in absorbance at 406 mμ.

As noted by Angelici and Ingemanson, the equilibrium constants can be calculated in the following manner:

$A_o X + A_\infty (1 - X) = A$ where: A_o = initial absorbance

$A_o X + A_\infty - A_\infty X = A$ A_∞ = absorbance of an equal concentration of product

$(A_o - A_\infty) X = A - A_\infty$ A = equilibrium absorbance

$X = \dfrac{A - A_\infty}{A_o - A_\infty}$ X = fraction of $W(CO)_5(NR_3)$ unreacted

Therefore, for the equilibrium $W(CO)_5(NR_3) + L = W(CO)_5L + NR_3$.

$$K_{eq} = \frac{(1 - X)[NR_3]}{X([L] - (1 - X)[W(CO)_5(NR_3)])}$$

where: $[NR_3]$ = original concentration of the amine

$[L]$ = original concentration of ligand

$[W(CO)_5(NR_3)]$ = original concentration of $W(CO)_5(NR_3)$

Figure 2 Ultraviolet-Visible Spectrum of $W(CO)_5C_6H_5NH_2$. 1.5×10^{-4} M
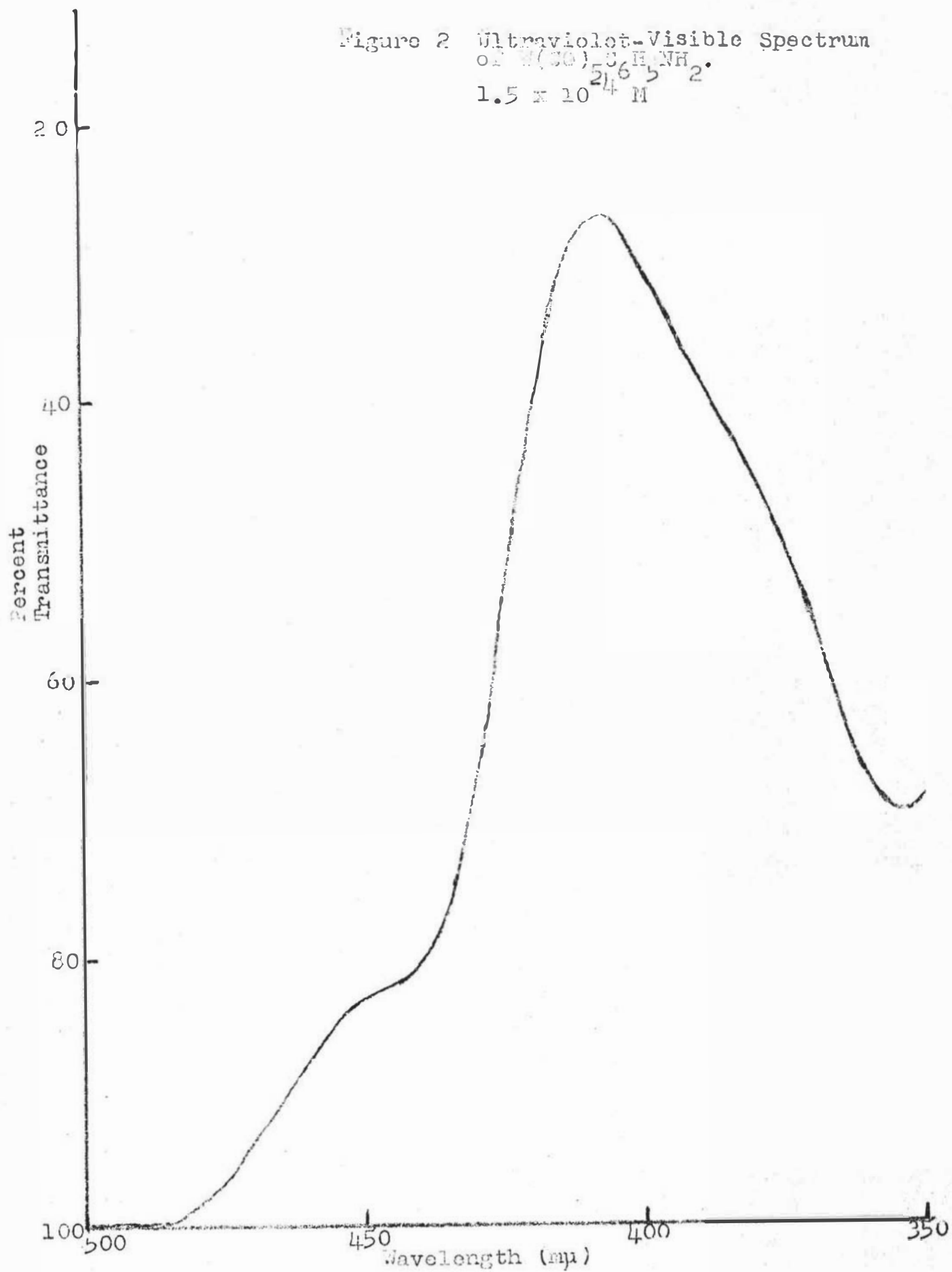
Figure 3 Ultraviolet-Visible Spectrum
of $H(SC)_2P(C_6H_5)_3$.
1.5×10^{-4} M
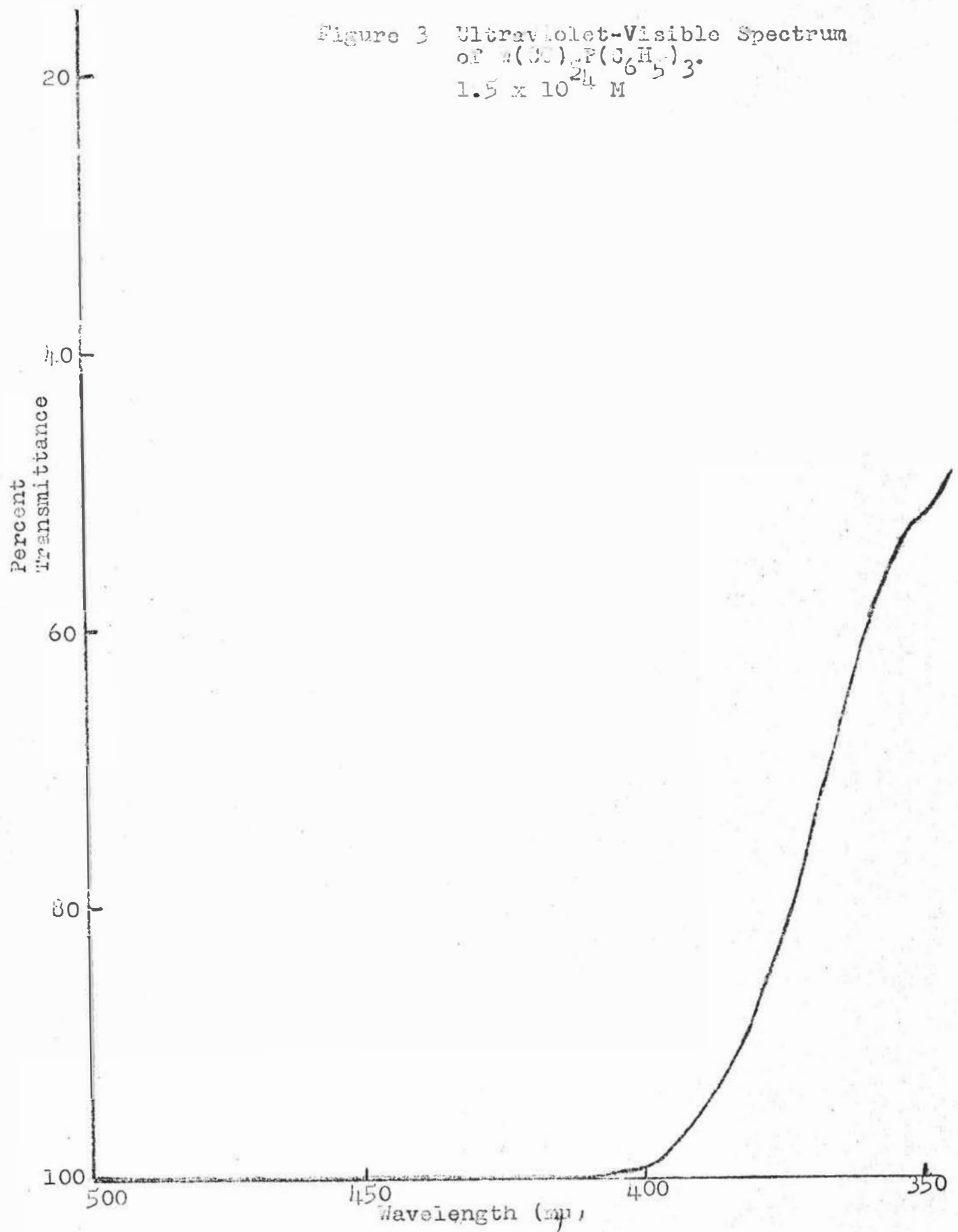
The concentration of amine can be considered constant because a large excess was originally added. The large excess was added to minimize decomposition of the amine complex, $W(CO)_5(NH_3)$. Solutions of the amine complexes are, by themselves, quite unstable. However Angelici and Ingemanson reported that in the presence of an excess of amine, the amine complex solutions remained stable.

In this study two approaches were used in attempts at obtaining equilibrium constants. One approach was an attempt to follow the reaction $(CO)_5W(NR_3) + PPh_3 \rightarrow (CO)_5WPPh_3 + NR_3$ (I) until equilibrium was attained The second approach was to follow the reverse reaction $NR_3 + (CO)_5WPPh_3 \rightarrow (CO)_5W(NR_3) + PPh_3$ (II) until equilibrium was reached. If the same constant were obtained by approaching the equilibrium from both directions, one could be reasonably confident that a true equilibrium had been established.

In these studies all solids were weighed with an analytical balance. The mass of aniline used was determined by weighing the aniline in a weighing vessel, then subtracting the weight of the weighing vessel. The amount of pyridine used was determined volumetrically. The reactants were dissolved in enough degassed toluene to make 250 ml of solution at the appropriate temperature

in a water bath. The volumetric flask was then wrapped
in aluminum foil to protect the solution from light. A
sample was then withdrawn and an absorbance determined
within 1--3 hours of mixing. Initially samples were
withdrawn daily. Thereafter samples were withdrawn
after longer intervals. The equilibrium determinations
attempted are indicated in Table IX. The Reaction I
equilibrium determination conducted at ambient temperature
was also conducted under a nitrogen atmosphere. A
positive nitrogen atmosphere was maintained when samples
were withdrawn to prevent contamination.

Table IX Initial Concentrations of Reactants and Temperatures for Equilibrium Determinations

REACTION I

$[(CO)_5WC_6H_5NH_2]$ (M x 10^{-4})	$[P(C_6H_5)_3]$ (M x 10^{-4})	$[C_6H_5NH_2]$ (M)	Temperature (°C)	Table
1.572	1.508	0.1003	25.7	XII
1.620	1.052	0.0994	25.7	XIII
1.464	0.5642	0.0999	25.7	XIV
1.410	1.264	0.1000	35.0	XV
1.592	1.081	0.0988	35.0	XVI
1.458	0.4576	0.0992	35.0	XVII
1.602	1.264	0.1008	40.6	XVIII
1.410	1.066	0.0996	40.6	XIX
1.542	0.4576	0.0988	40.6	XX
1.648	1.480	0.1000	49.7	XXI
1.512	1.112	0.0996	49.7	XXII
1.448	0.4720	0.1009	49.7	XXIII

REACTION II

$[(CO)_5WP(C_6H_5)_3]$ (M)	$[C_5H_5N]$ (M)	$[C_6H_5NH_2]$ (M)	Temperature (°C)
2 x 10^{-4}	0.10	--	Ambient
0.91	0.99	--	Ambient
2 x 10^{-4}	--	0.10	41
2 x 10^{-4}	--	0.10	41

CHAPTER THREE

RESULTS AND DISCUSSION

To verify that Beer's Law was obeyed by the solution of $(CO)_5WC_6H_5NH_2$ in this study, a plot was made of absorbance versus concentration. This plot is shown in Figure 4. The data were fitted by the method of least squares, which yielded the equation

Absorbance 0.366 (conc x 10^4) 0.035.

The calculated extinction coefficient was 3.66×10^3 $cm^2/$ mole. The magnitude of the extinction coefficient suggests that the absorbance is due to a charge transfer transition. The above equation was used to determine the initial absorbance, A_o, of the aniline complex, $(CO)_5WC_6H_5NH_2$, in all of the runs.

From a kinetic study conducted with p-anisidine, Angelici and Ingemanson[20,21] concluded that the reaction $W(CO)_5(NR_3)$ PPh_3 $W(CO)_5PPh_3$ NR_3 reaches equilibrium in two days for all amines studied. Under this assumption they sealed a typical reaction mixture for two days, after which time a sample was withdrawn and an absorbance reading taken. At this time, the reaction was assumed to be at equilibrium. It was the finding of this study however, in contrast to theirs, that equilibrium is not reacted in two days.

Table X   Confirmation of Beer's Law
          Plot of Concentration of $(CO)_5WC_6H_5NH_2$
          versus Absorbance
          (Aniline concentration for each solution 0.10 M)

$[(CO)_5WC_6H_5NH_2]$	Absorbance
$(M \times 10^{-4})$	
1.765	0.624
1.563	0.524
1.189	0.395
1.026	0.335
0.767	0.257

Figure 4   Plot of Concentration of $(CO)_5WC_6H_5NH_2$ versus Absorbance. Confirmation of Beer's Law.
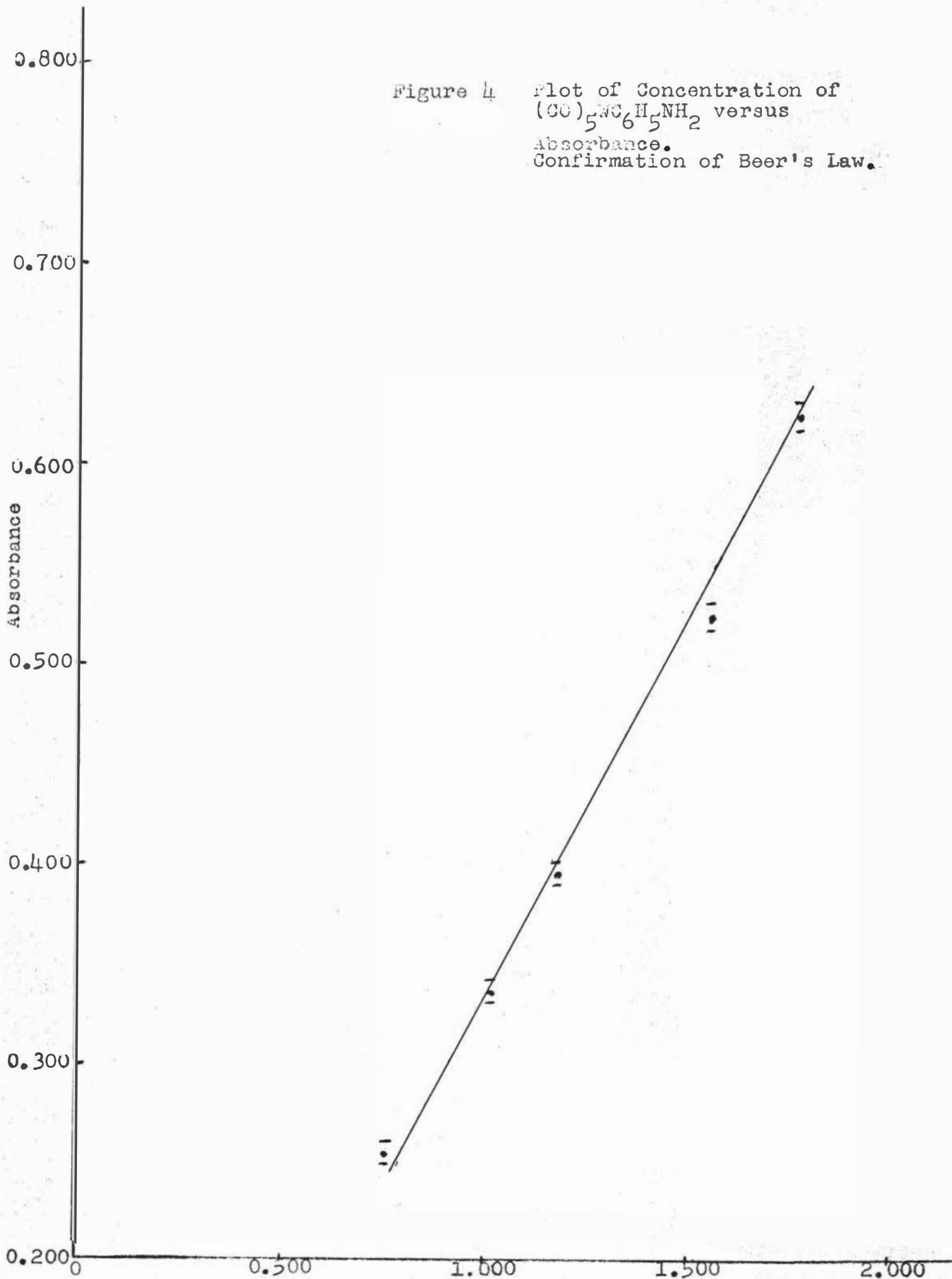
Angelici and Ingemanson, in their experiments, used 10-70-fold excesses of ligand $P(Ph)_3$ for the reaction $W(CO)_5C_6H_5NH_2$ $P(Ph)_3$ $W(CO)_5P(Ph)_3$. $C_6H_5NH_2$. In the preliminary reinvestigation of their work, these experiments were repeated. Table XI presents some data from one of these determinations and Figure 5 shows the corresponding slot of absorbance versus time. The absorbance shown were measured at 406 mu and are due to the absorption of $W(CO)_5C_6H_5NH_2$ at that wavelength. The disappearance of this absorbance shows that the reaction went essentially to completion in less than 20 days.

In an attempt to cause a shift in the position of equilibrium to the left, the concentration of ligand was decreased to equal to or slightly less than the concentration of $(CO)_5WC_6H_5NH_2$. Tables XII through XXIV present data and Figures 6 through 18 present the corresponding plots of absorbance versus time for these experiments. Approximately the same concentrations of aniline complex $(1.5 \times 10^{-4}$ M) and aniline (0.1 M) were used for each run, while three different concentrations of $P(C_6H_5)_3$ were used at each temperature.

As can be seen from the plots, the absorbance readings continue to decrease steadily after two days have elapsed. Thus the reaction continues beyond two

Table XI   Absorbance and Time for Equilibrium
Determination with 70-Fold Excess of $P(Ph)_3$
at Ambient Temperature

Initial Concentrations:

$$[(CO)_5 WC_6 H_5 NH_2] = 1.649 \times 10^{-4} M$$
$$[C_6 H_5 NH_2] = 0.0996 M$$
$$[P(C_6 H_5)_3] = 6.996 \times 10^{-3} M$$

Time (hrs)	Absorbance
0	0.568 (A_o)
68	0.420
94	0.358
169	0.222
213	0.176
263	0.128
333	0.086
385	0.048
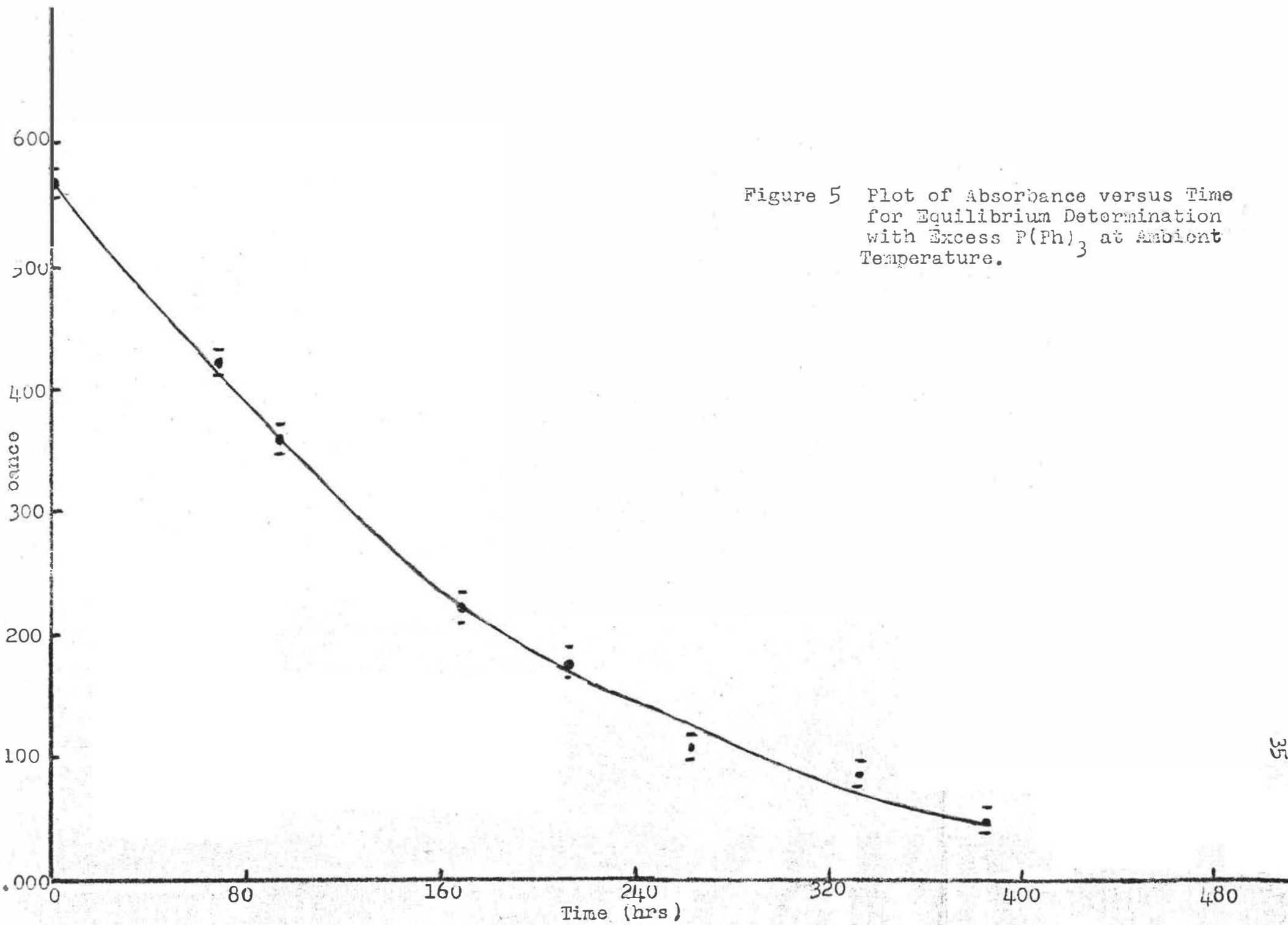
Figure 5   Plot of Absorbance versus Time for Equilibrium Determination with Excess P(Ph)$_3$ at Ambient Temperature.

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Table XII Equilibrium Determination at 25.7°C.
Solution 1

Initial Concentrations:

$[(CO)_5WC_5H_5NH_2] = 1.572 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.1003$ M

$[P(C_6H_5)_3] = 1.508 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.540 (A_o)
2	0.520
28	0.506
52	0.500
71	0.499
156	0.478
218	0.456
244	0.454
361	0.427
410	0.417
506	0.398
578	0.389
646	0.378
887	0.353
916	0.348
986	0.339
1007	0.339
1226	0.310

Figure 6   Plot of Absorbance versus Time
for Equilibrium Reaction I
at 25.7°C.
Solution 1.

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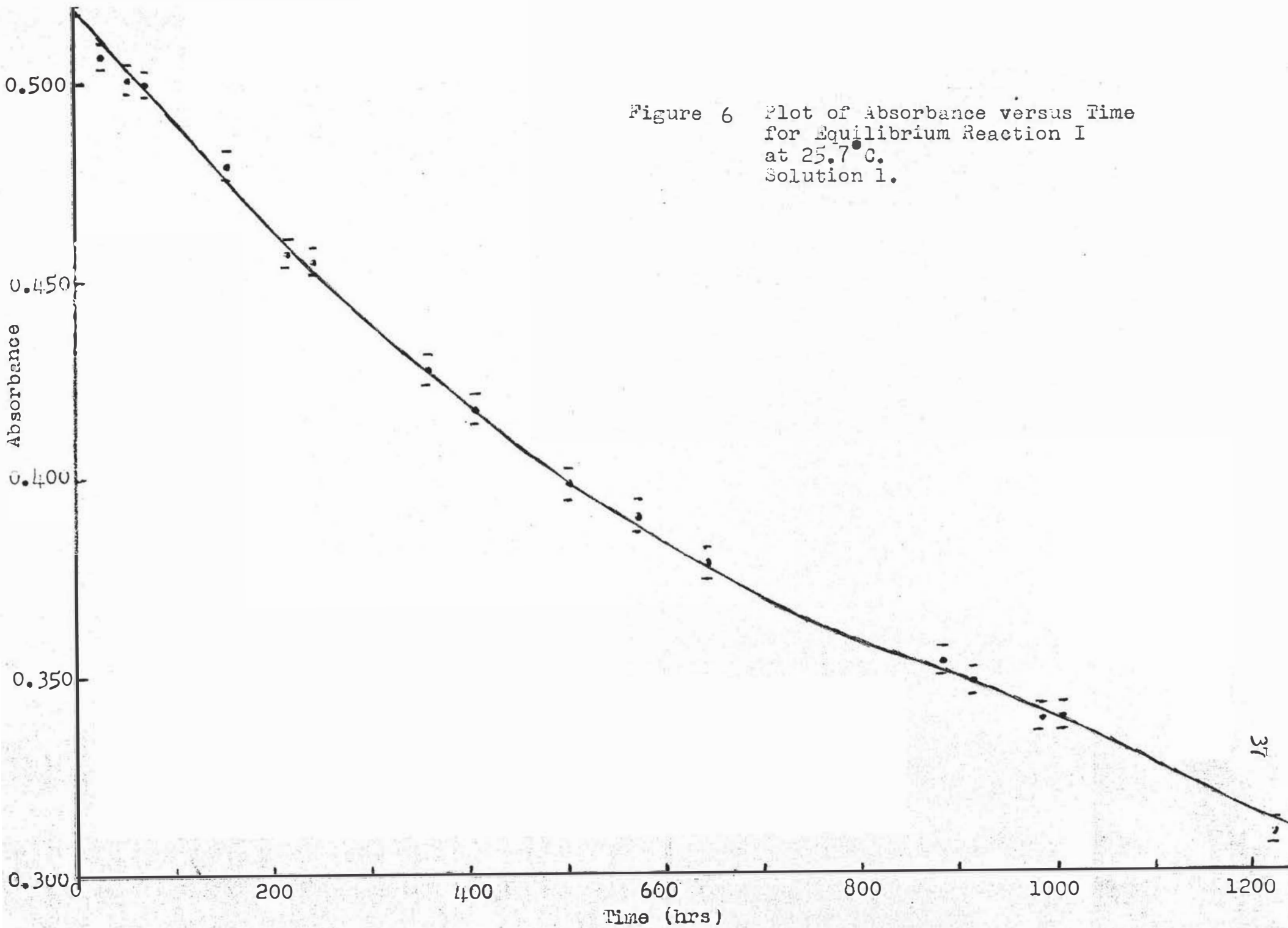
Table XIII Equilibrium Determination at 25.7°C.
        Solution 2

        Initial Concentrations:
            $[(CO)_5WC_6H_5NH_2]$ = 1.620 x 10^{-4} M
            $[C_6H_5NH_2]$ = 0.0994 M
            $[P(C_6H_5)_3]$ = 1.052 x 10^{-4} M

Time (hrs)	Absorbance
0	0.558 (A_o)
2	0.533
28	0.521
52	0.520
71	0.520
156	0.511
218	0.495
244	0.494
361	0.482
410	0.466
506	0.458
578	0.454
646	0.455
700	0.439
841	0.423
887	0.431
986	0.429
1007	0.426
1226	0.397

Figure 7 Plot of Absorbance versus Time
for Equilibrium Reaction I
at 25.7°C.
Solution 2.
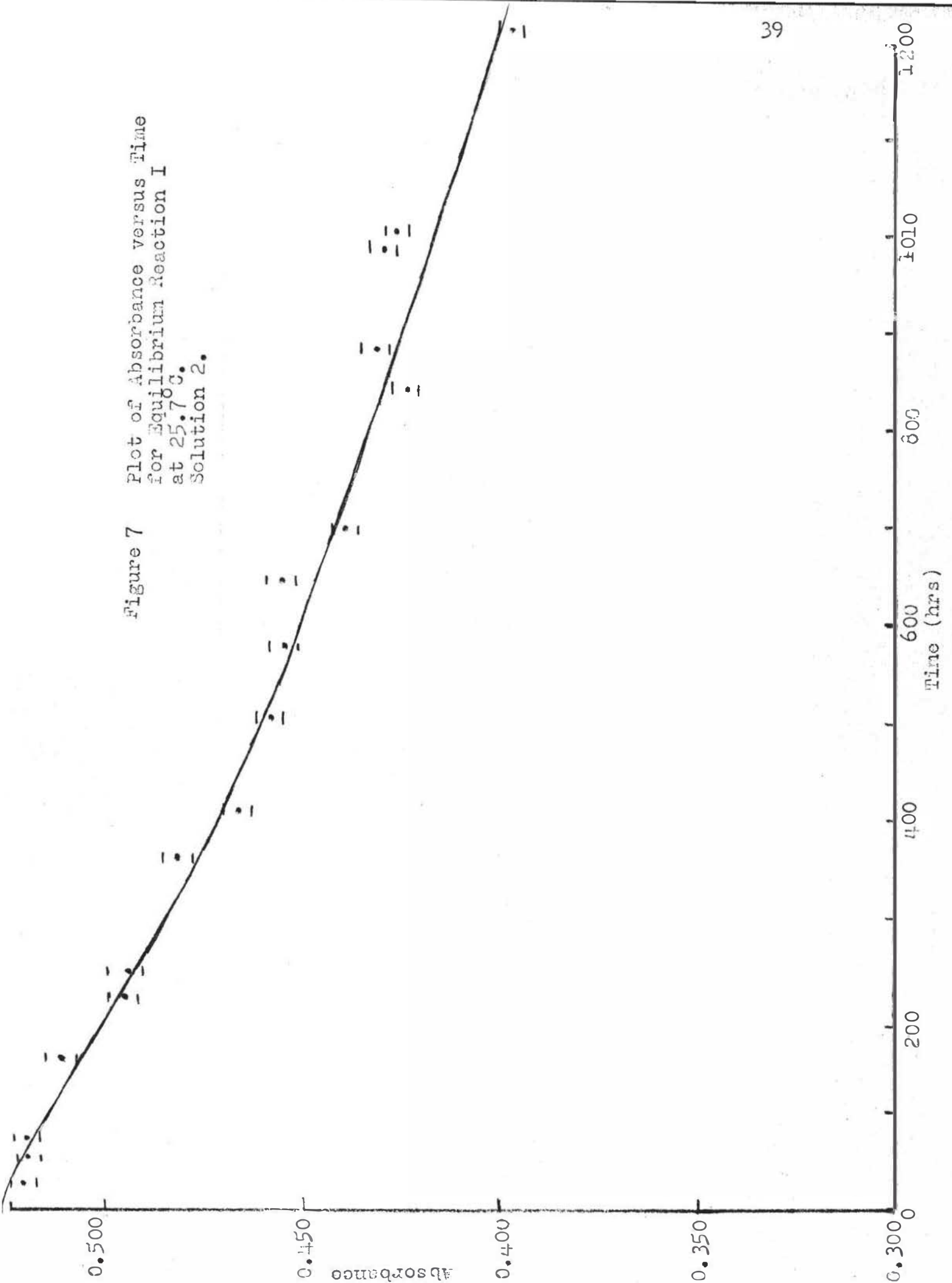
Table XIV Equilibrium Determination at $25.7^{\circ}C$.
Solution 3

Initial Concentrations:
$$[(CO)_5WC_6H_5NH_2] = 1.464 \times 10^{-4} \text{ M}$$
$$[C_6H_5NH_2] = 0.0999 \text{ M}$$
$$[P(C_6H_5)_3] = 0.5642 \times 10^{-4} \text{ M}$$

Time (hrs)	Absorbance
0	0.501 (A_o)
2	0.476
28	0.465
52	0.467
71	0.469
156	0.460
218	0.452
244	0.451
361	0.439
506	0.427
578	0.423
646	0.418
749	0.415
887	0.412
916	0.410
1226	0.395

Figure 8   Plot of Absorbance versus Time
for Equilibrium Reaction I
at 25.7°C.
Solution 3.
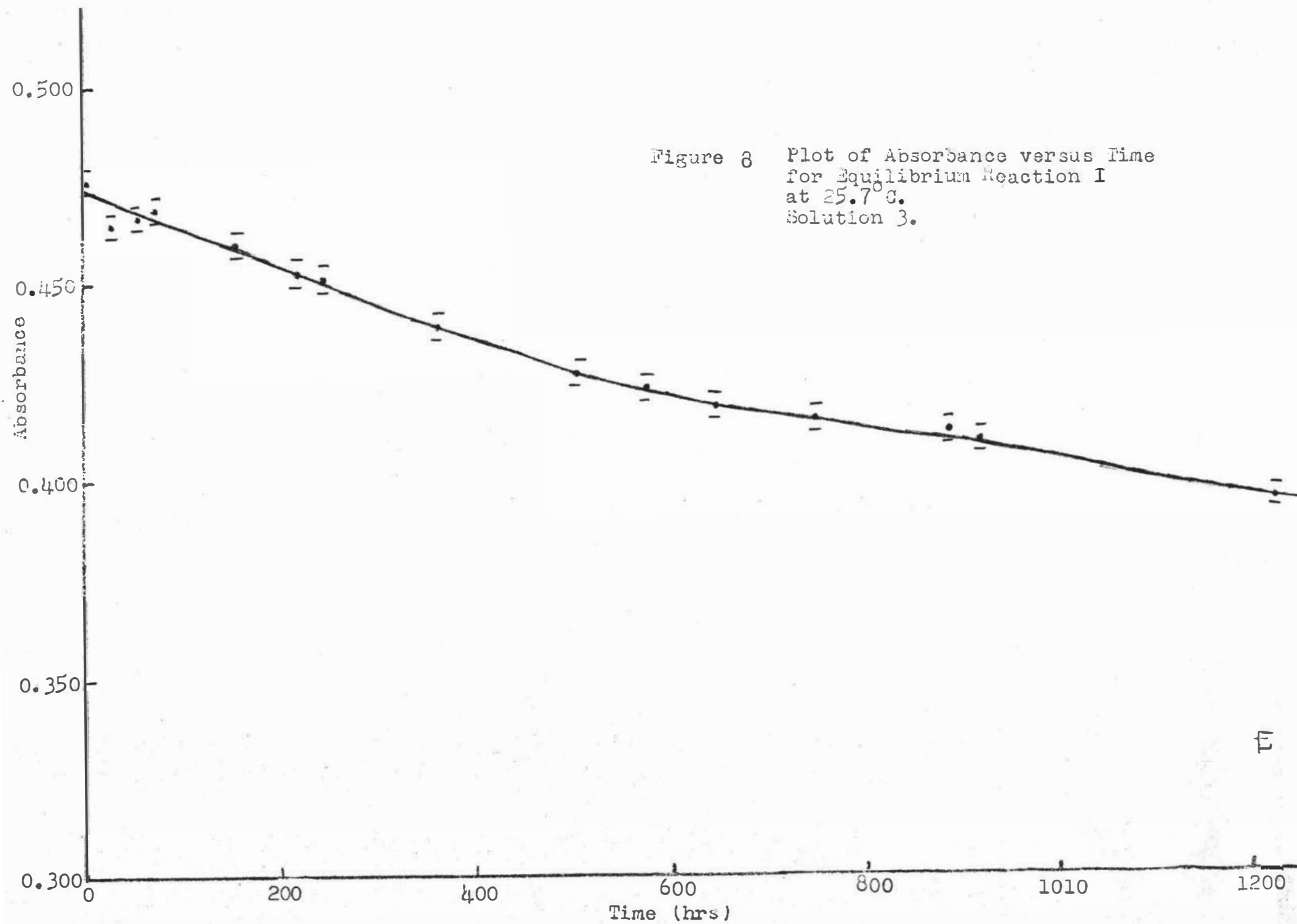
Table XV   Equilibrium Determination at 35.0°C.
        Solution 1

     Initial Concentrations:

$$[(CO)_5WC_6H_5NH_2] = 1.410 \times 10^{-4} \text{ M}$$
$$[C_6H_5NH_2] = 0.1000 \text{ M}$$
$$[P(C_6H_5)_3] = 1.264 \times 10^{-4} \text{ M}$$

Time (hrs)	Absorbance
0	0.481 (A_0)
3	0.471
74	0.453
98	0.445
124	0.436
147	0.432
171	0.427
266	0.417
338	0.402
461	0.387
626	0.362
845	0.346
914	0.338
1010	0.328
1178	0.304
1298	0.296

Figure 9   Plot of Absorbance versus Time
for Equilibrium Reaction I
at 35.0°C.
Solution 1.
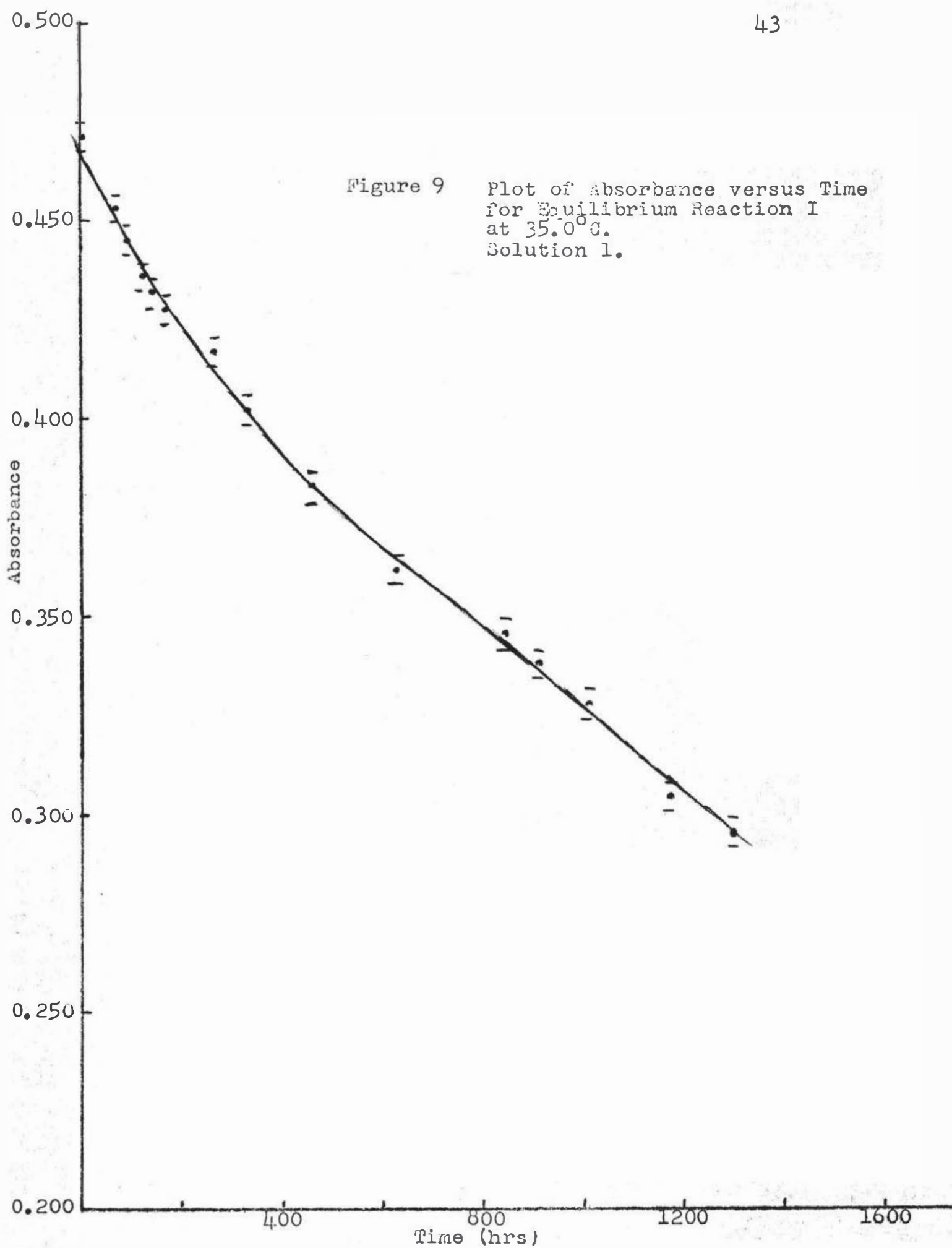
Table XVI Equilibrium Determination at 35.0°C.
Solution 2

Initial Concentrations:

$[(CO)_5 WC_6H_5NH_2] = 1.592 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.0988$ M

$[P(C_6H_5)_3] = 1.081 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.548 (A_o)
3	0.548
74	0.523
93	0.504
124	0.492
147	0.488
171	0.474
226	0.450
338	0.444
461	0.420
626	0.392
845	0.376
914	0.371
1010	0.370
1178	0.349
1298	0.349

Figure 10 Plot of Absorbance versus Time
for Equilibrium Reaction I
at 35.0°C.
Solution 2.
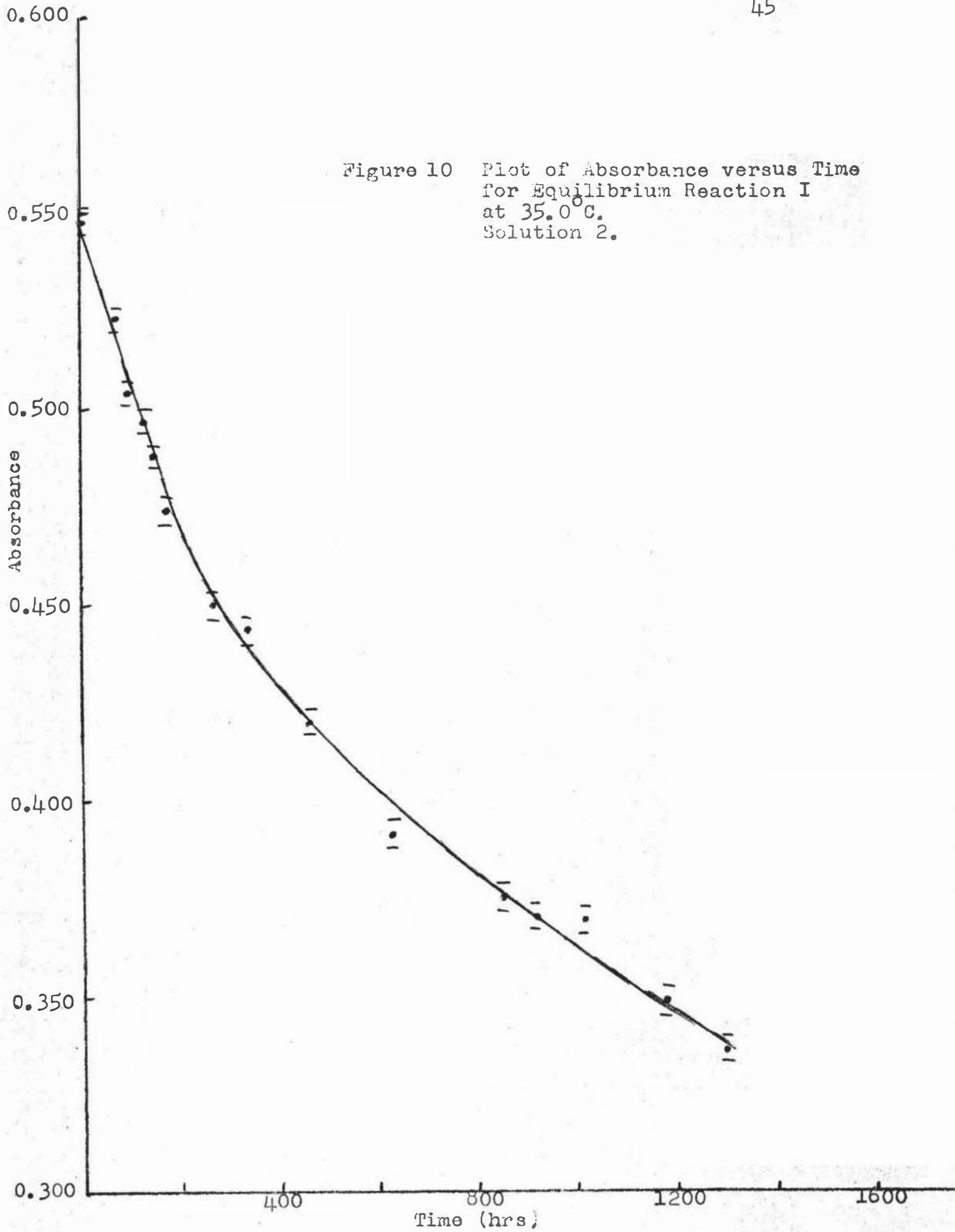
Table XVII Equilibrium Determination at 35.0°C.
Solution 3

Initial Concentrations:
$$[(CO)_5WC_6H_5NH_2] = 1.458 \times 10^{-4} M$$
$$[C_6H_5NH_2] = 0.0992 M$$
$$[P(C_6H_5)_3] = 0.4576 \times 10^{-4} M$$

Time (hrs)	Absorbance
0	0.498 (A_o)
3	0.483
74	0.475
98	0.470
124	0.463
147	0.461
171	0.452
266	0.438
338	0.428
461	0.407
626	0.381
845	0.364
914	0.363
1010	0.359
1178	0.352
1 298	0.351

Figure 11 Plot of Absorbance versus Time
for Equilibrium Reaction I
at 35.0 C.
Solution 3.
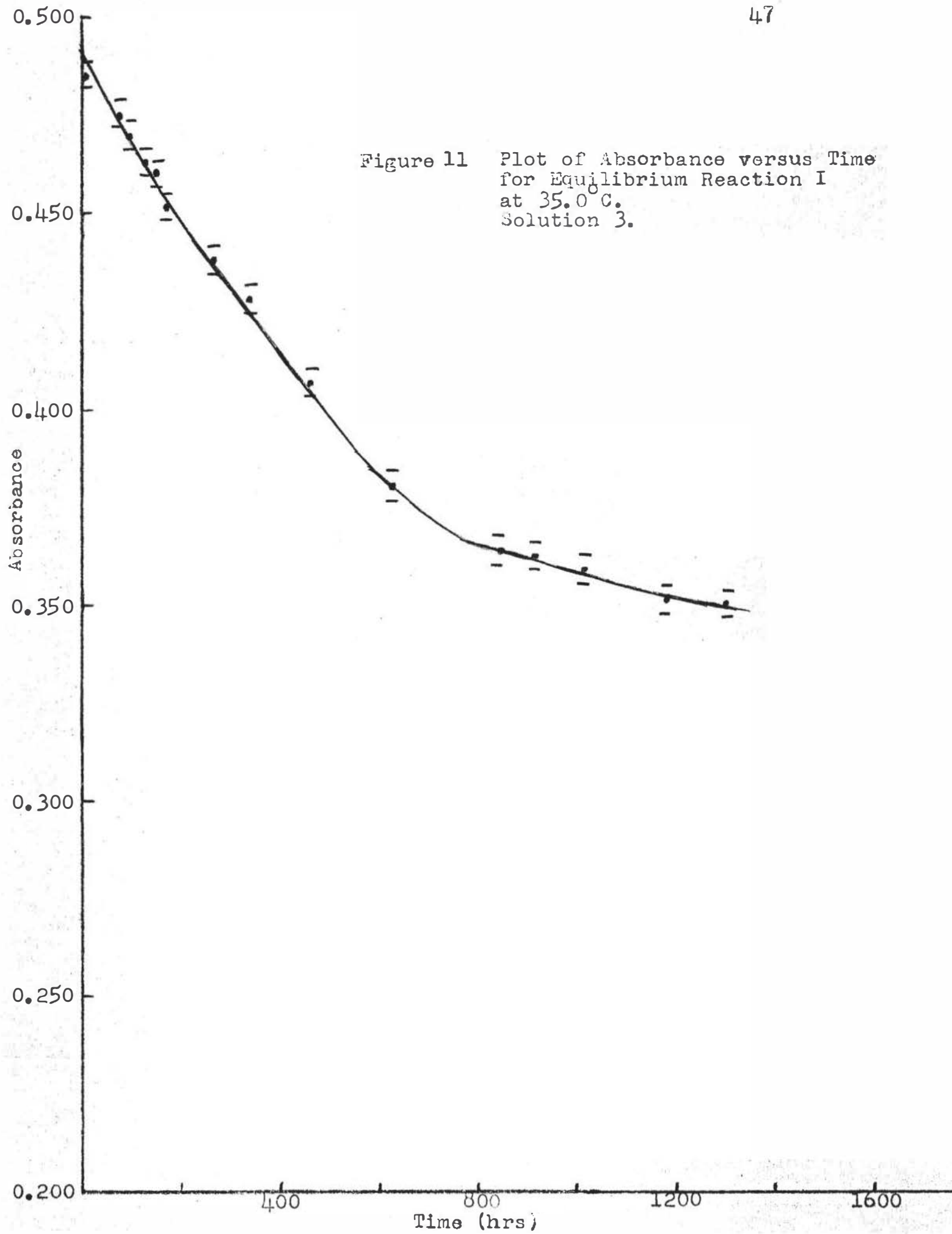
Table XVIII Equilibrium Determination at $40.6^{\circ}C$.
Solution 1

Initial Concentrations:

$[(CO)_5 WC_6H_5NH_2] = 1.602 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.1008$ M

$[P(C_6H_5)_3] = 1.264 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.551 (A_o)
1	0.542
73	0.495
169	0.462
265	0.428
337	0.399
434	0.382
554	0.349

Figure 12 Plot of Absorbance versus Time
for Equilibrium Reaction I
at 40.6°C.
Solution 1.

Table XIX   Equilibrium Determination at 40.6°C.
Solution 2

Initial Concentrations:
$[(CO)_5WC_6H_5NH_2] = 1.410 \times 10^{-4}$ M
$[C_6H_5NH_2] = 0.0996$ M
$[P(C_6H_5)_3] = 1.066 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.481 (A_o)
1	0.457
73	0.418
169	0.390
265	0.364
337	0.346
434	0.324
554	0.300

Figure 13   Plot of Absorbance versus Time
for Equilibrium Reaction I
at 40.6°C.
Solution 2.
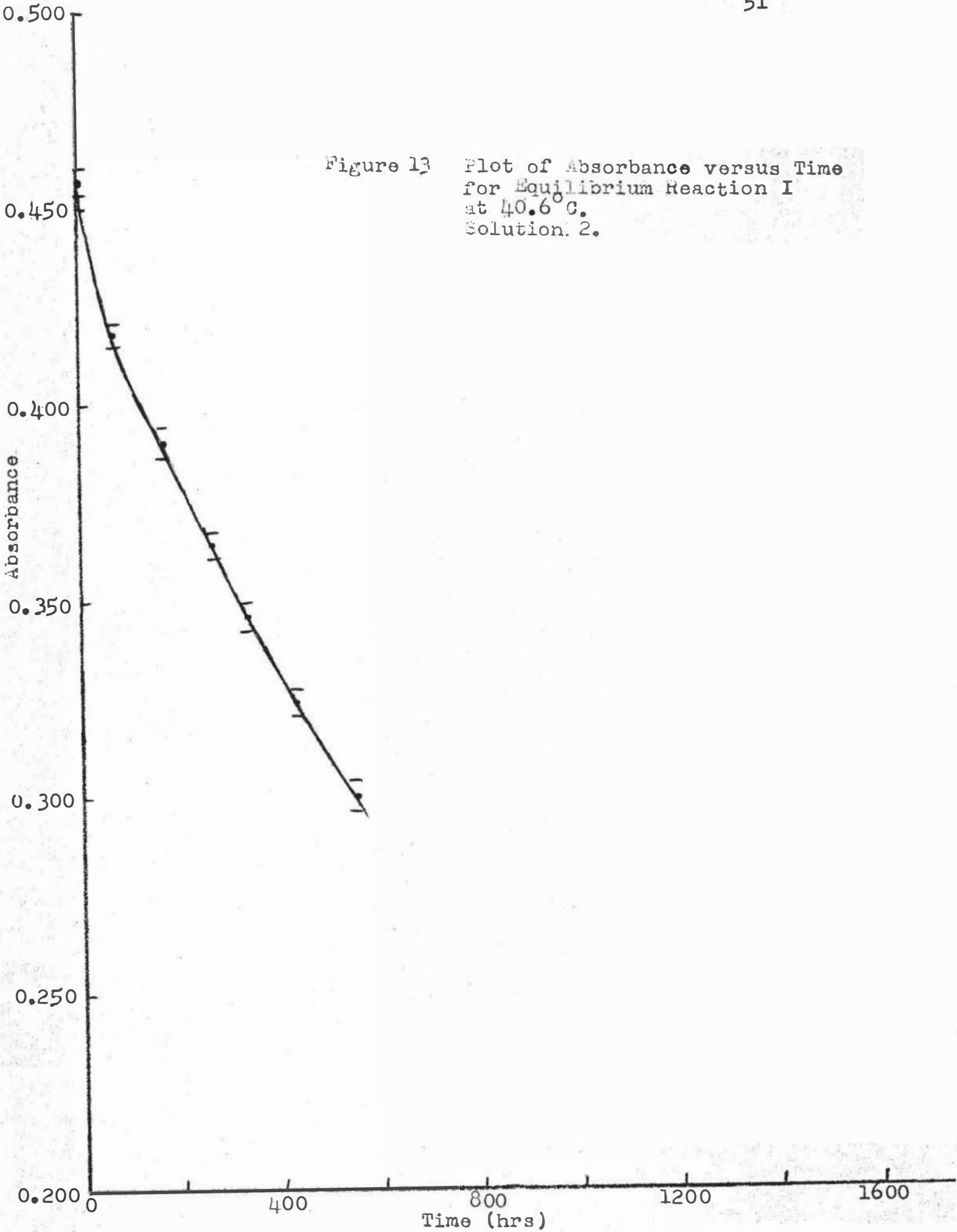
Table XX   Equilibrium Determination at $40.6^\circ C$.
           Solution 3

           Initial Concentrations:

$$[(CO)_5WC_6H_5NH_2] = 1.542 \times 10^{-4} M$$
$$[C_6H_5NH_2] = 0.0988 M$$
$$[P(C_6H_5)_3] = 0.4576 \times 10^{-4} M$$

Time (hrs)	Absorbance
0	0.529 (A_o)
1	0.511
73	0.478
169	0.453
265	0.432
337	0.414
434	0.388
554	0.380

Figure 14 Plot of Absorbance versus Time
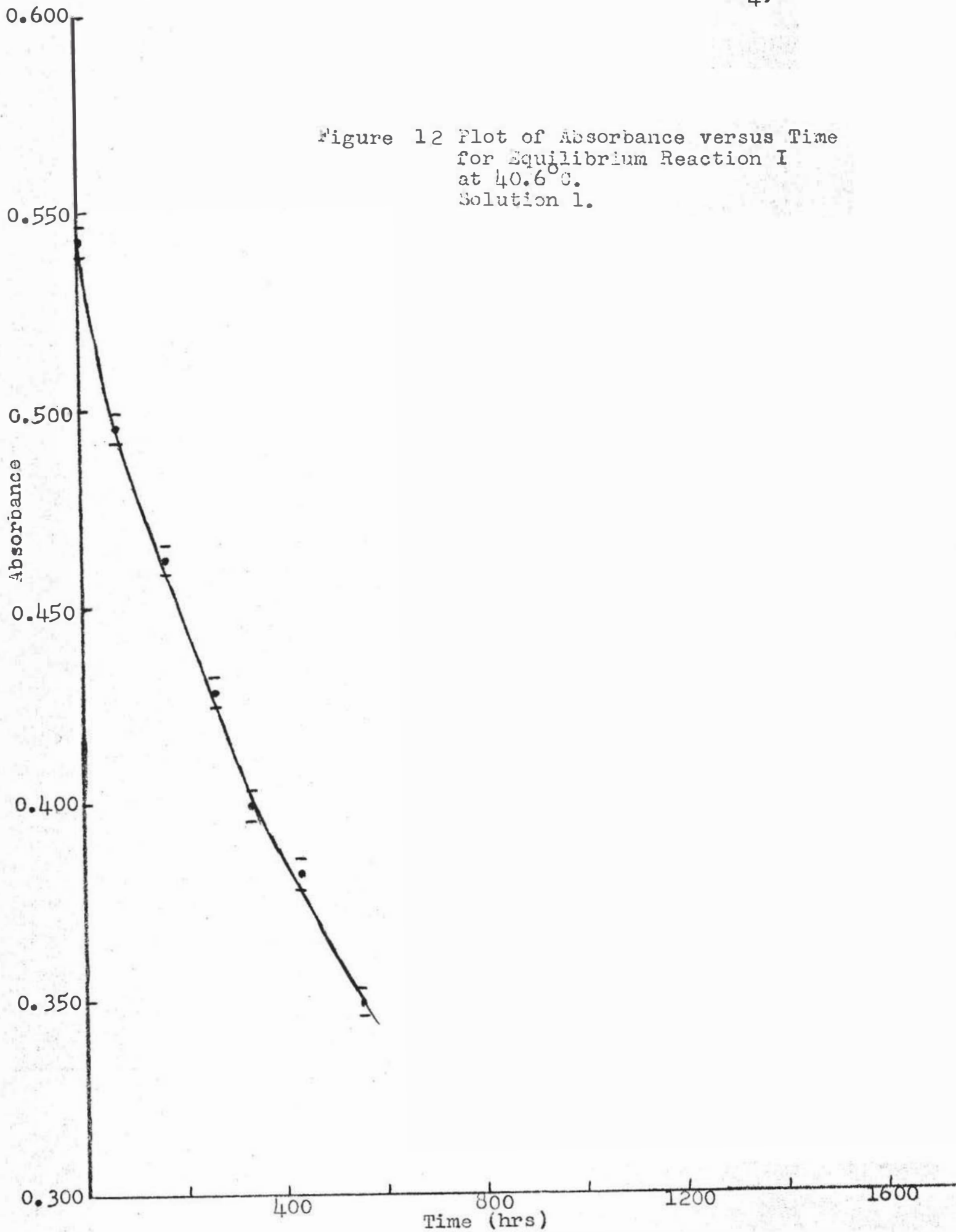for Equilibrium Reaction I
at 40.6° C.
Solution 3.
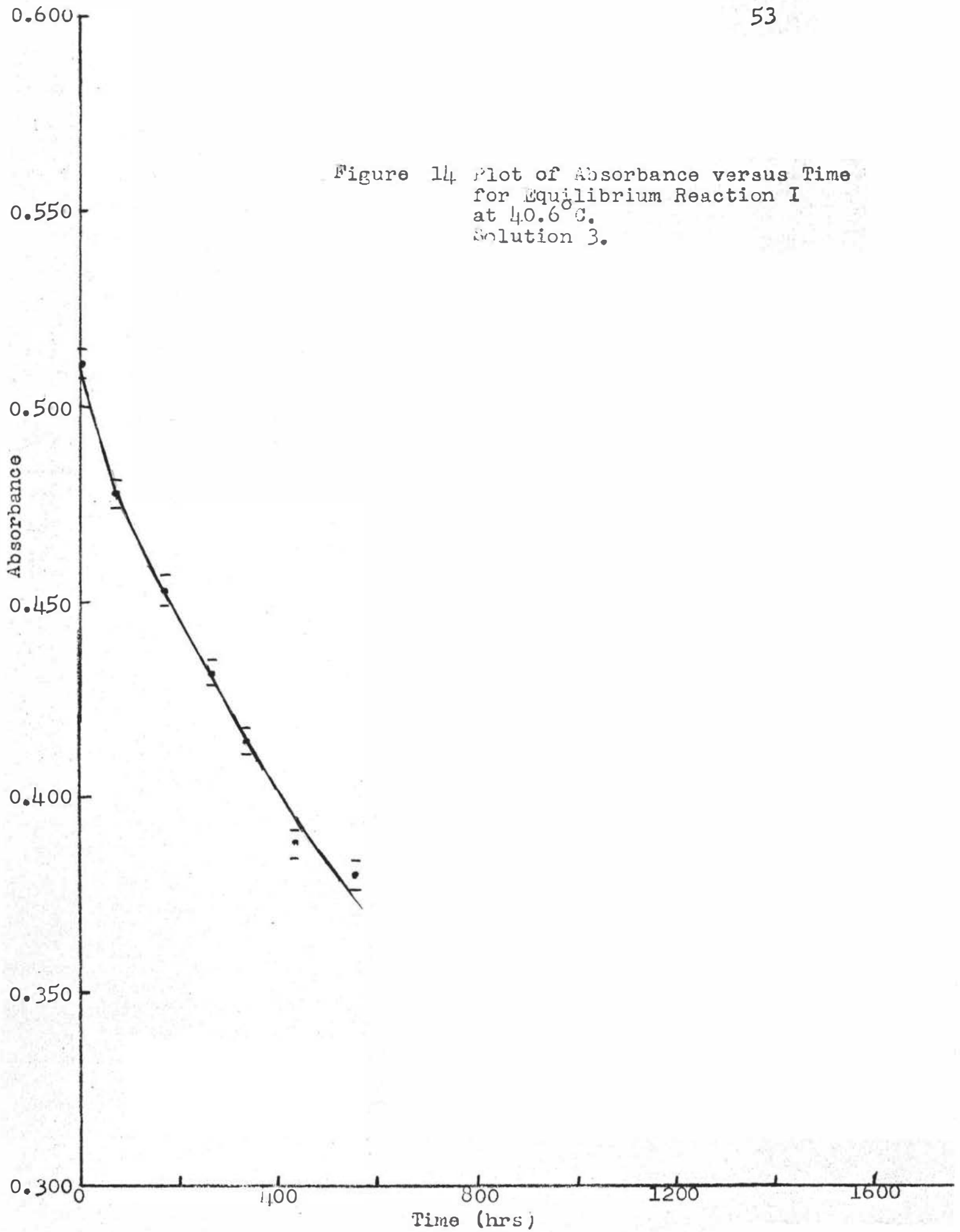
Table XXI Equilibrium Determination at 49.7° C.
Solution 1

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2] = 1.648 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.1000$ M

$[P(C_6H_5)_3] = 1.480 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.568 (A_o)
2	0.554
23	0.450
47	0.329
70	0.249
167	0.118
191	0.099
217	0.084

Figure 15   Plot of Absorbance versus Time
for Equilibrium Reaction I
at 49.7° C.
Solution 1.
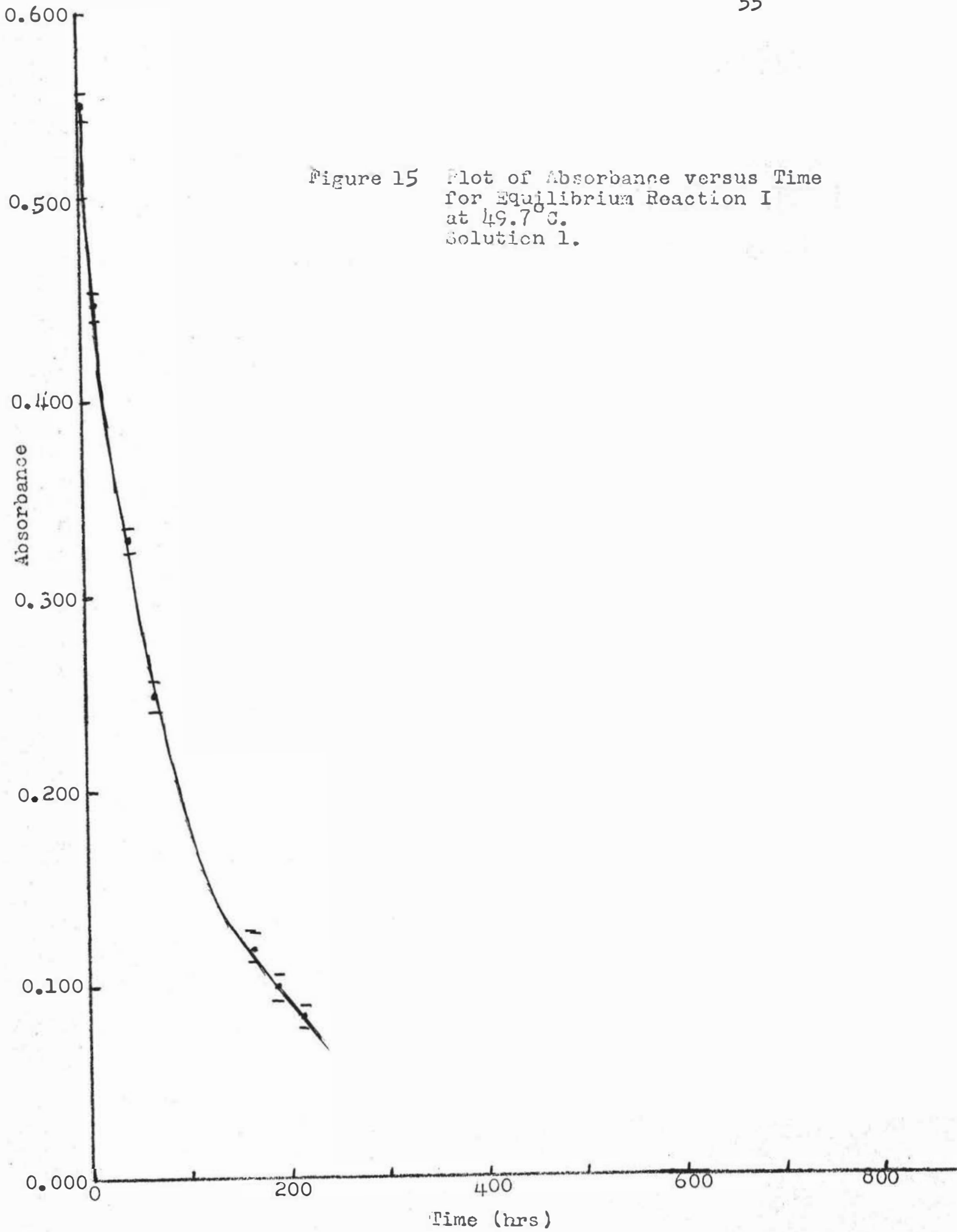
Table XXII Equilibrium Determination at 49.7°C.
Solution 2

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2] = 1.512 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.0996$ M

$[P(C_6H_5)_3] = 1.112 \times 10^{-4}$ M

Time (hrs)	Absorbance
0	0.518 (A_0)
2	0.502
23	0.445
47	0.377
70	0.328
167	0.221
191	0.203
217	0.188
239	0.181
307	0.148
361	0.139
406	0.116
480	0.099
549	0.093
577	0.086
647	0.077
668	0.071

Figure 16   Plot of Absorbance versus Time
            for Equilibrium Reaction I
            at 49.7°C.
            Solution 2.
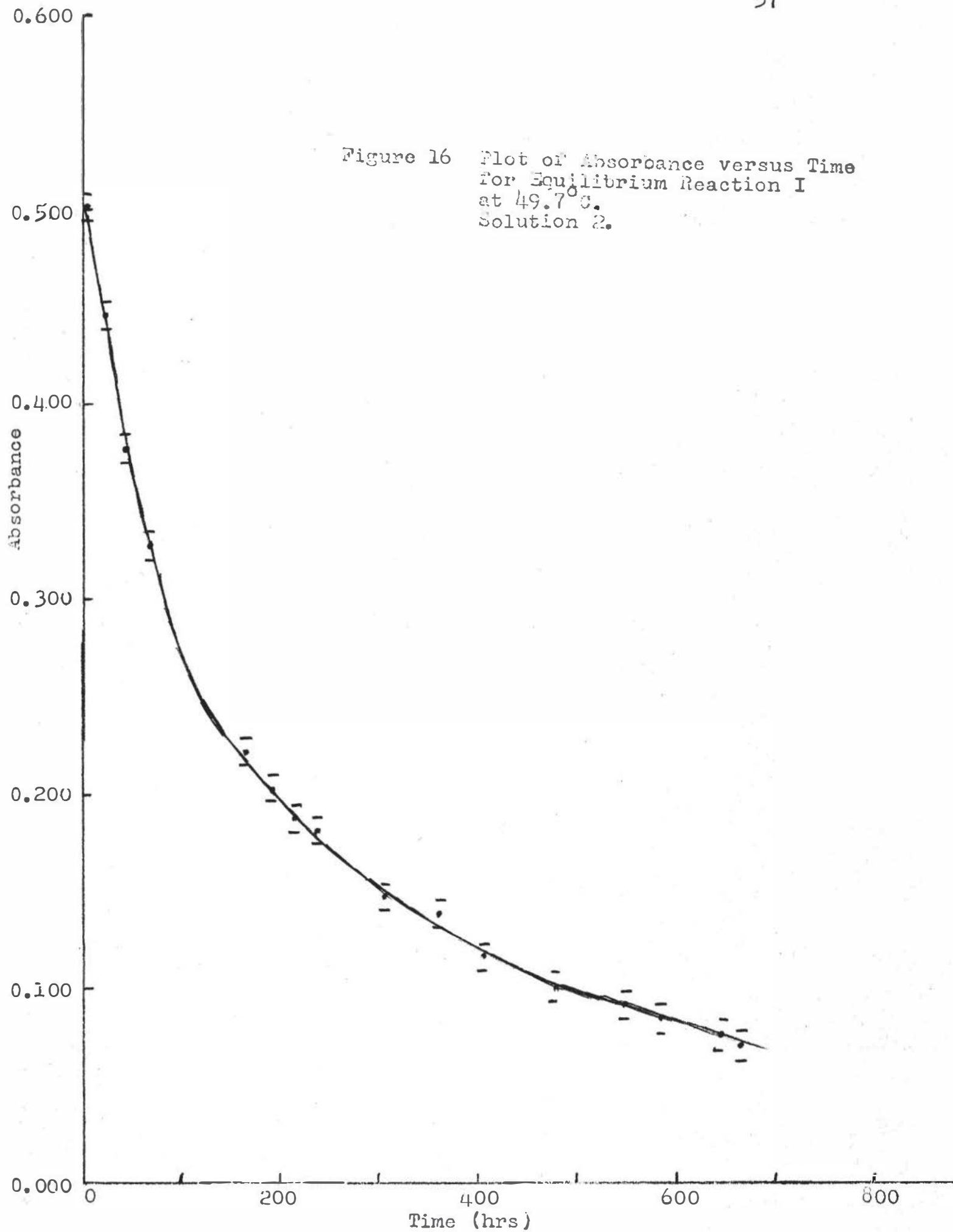
Table XXIII Equilibrium Determination at 49.7°C.
Solution 3

Initial Concentrations:

$$[(CO)_5WC_6H_5NH_2] = 1.448 \times 10^{-4} \text{ M}$$

$$[C_6H_5NH_2] = 0.1009 \text{ M}$$

$$[P(C_6H_5)_3] = 0.4720 \times 10^{-4} \text{ M}$$

Time (hrs)	Absorbance
0	0.495 (A_o)
2	0.498
23	0.461
47	0.420
70	0.393
167	0.335
191	0.322
217	0.308
307	0.266
406	0.234
460	0.222
503	0.213
549	0.199
577	0.188
647	0.171
668	0.171

Figure 17   Plot of Absorbance versus Time
            for Equilibrium Reaction I
            at 49.7°C.
            Solution 3.
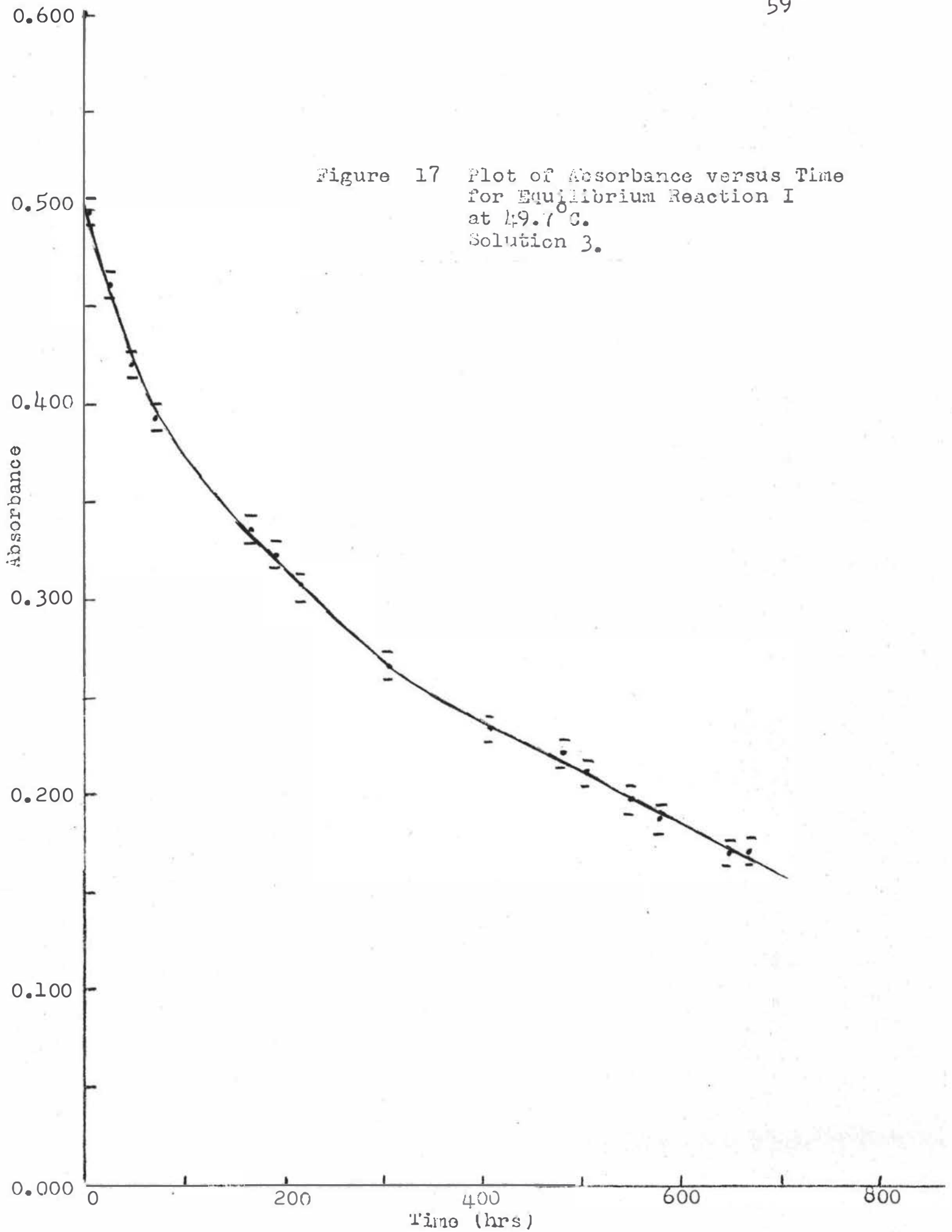
Table XXIV Equilibrium Determination at Ambient Temperature
(Conducted under nitrogen atmosphere)

Initial Concentrations:

$$[(CO)_5WC_6H_5NH_2] = 1.592 \times 10^{-4} \text{ M}$$
$$[C_6H_5NH_2] = 0.0992 \text{ M}$$
$$[P(C_6H_5)_3] = 0.975 \times 10^{-4} \text{ M}$$

Time (hrs)	Absorbance
0	0.548 (A_o)
3	0.542
23	0.539
47	0.529
96	0.510
120	0.506
147	0.496
171	0.493
195	0.483
266	0.479
315	0.470
339	0.466
363	0.462
458	0.436
531	0.439
648	0.427
696	0.422
818	0.407
937	0.399
1037	0.389
1106	0.391
1202	0.384
1274	0.374
1370	0.365
1490	0.363

Figure 18 Plot of Absorbance versus Time for Equilibrium Reaction I at Ambient Temperature. Conducted under Nitrogen.
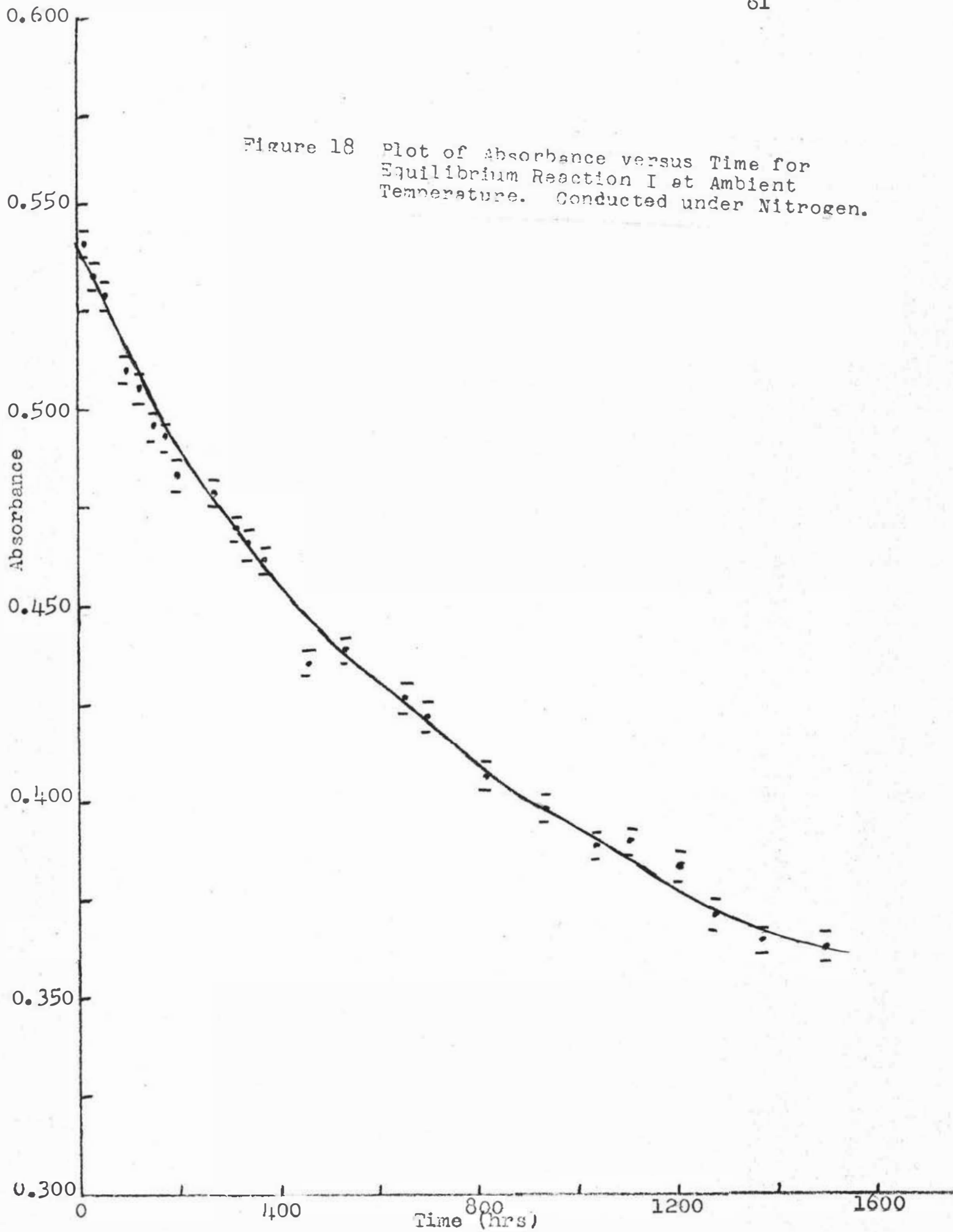
days. For the runs conducted at $25.7^{\circ}C$, the absorbance
continuos to decrease after 1200 hours. At $49.7^{\circ}C$,
the absorbances decrease more quickly until, for the sol-
ution of high ligand concentration, the absorbance is
approaching zero after 200 hours. The apparent rate of
reaction, as measured by the rate of decrease in absor-
bance, is seen to increase with increasing concentration
of ligand and with increasing temperature.

Another attempt to measure the equilibrium constant
for the reaction involved the use of proton nmr. It
was reasoned that the chemical shift of the protons of
the coordinated aniline would be different from the
chemical shift of the protons of the uncoordinated
aniline. From the nmr spectra of reaction mixtures,
therefore, concentrations of free and coordinated aniline
could be determined. However, this method proved im-
practical because the nmr signals for the free aniline
protons and the coordinated aniline protons were indis-
tinguishable, presumably due to chemical exchange.
Figure 19 shows the nmr spectrum of a solution of $C_6H_5NH_2$
and $(CO)_5WC_6H_5NH_2$. The aniline was added to retard
decomposition of the aniline complex.

The position of equilibrium for a reaction should
be approachable from either direction. For that reason
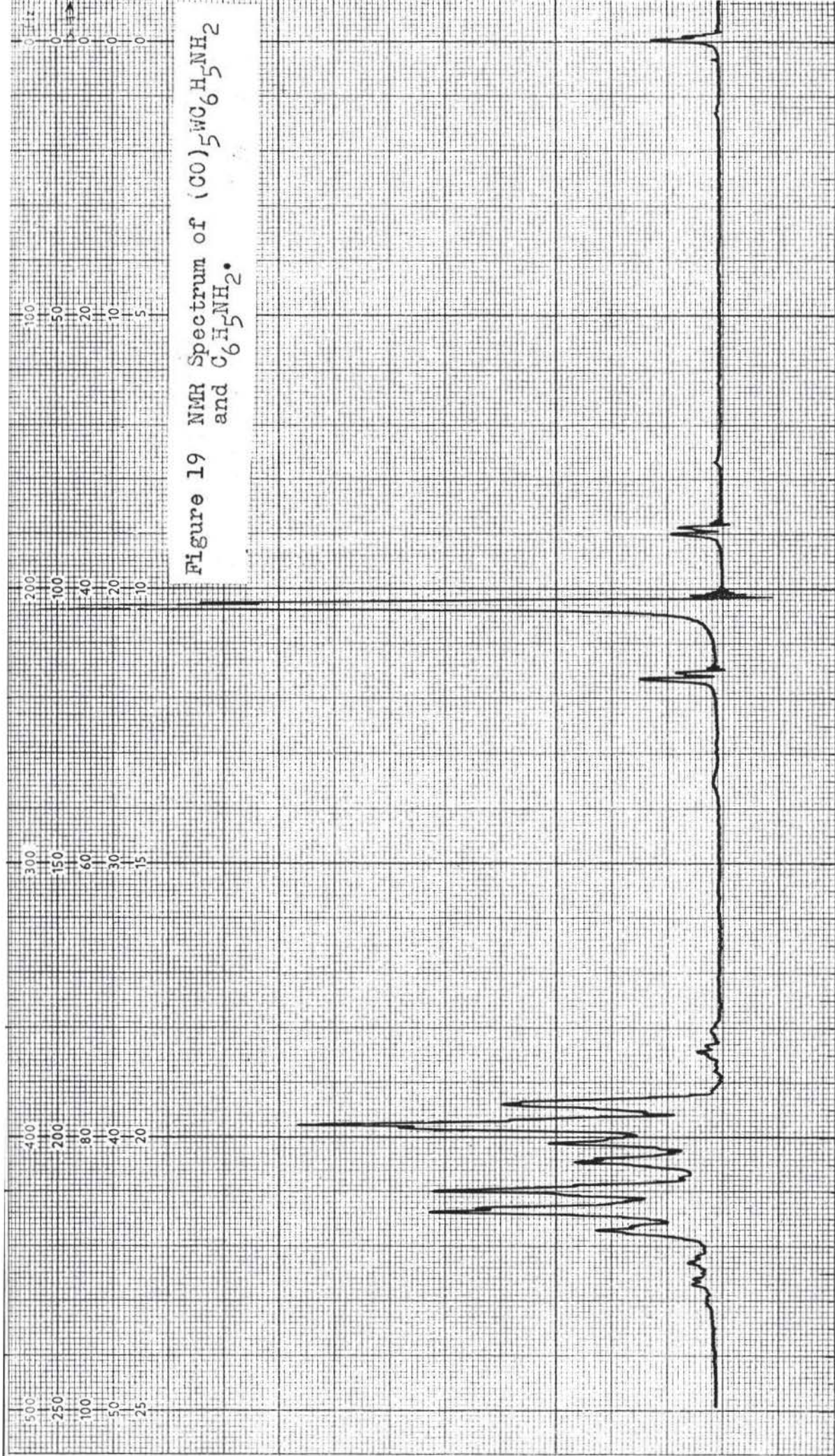
Figure 19 NMR Spectrum of $(CO)_5WC_6H_5NH_2$ and $C_6H_5NH_2$.

REMARKS: 0.0997 g $(CO)_5WC_6H_5NH_2$
and 0.0441 g $P(Ph)_3$ were
dissolved in $CDCl_3$ and
diluted to 3 inches in mm
60 MHz NMR

SAMPLE: $C_6H_5NH_2$ & $(CO)_5W$ $C_6H_5NH_2$

SOLVENT: $CDCl_3$

PPM (δ)
AUTO ☐   MANUAL
(250)   SWEEP TIME (SEC): 5.0
(500)   SWEEP WIDTH (Hz):
(2)   FILTER:
(.05)   RF POWER LEVEL:

SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 5.0
INTEGRAL AMPLITUDE:
SPINNING RATE (RPS):

CHART S-60T JB   DATE: OPERATOR:

CHART S-60T JB

an attempt was made to determine equilibrium constants for the reaction $(CO)_5WP(C_6H_5)_3 + Am \rightarrow (CO)_5W(Am) + P(C_6H_5)_3$ where the amine, Am, was aniline or pyridine. The reaction was attempted at both room temperature and at $40.9^{\circ}C$ with a 50-500 fold excess of amine. Evidence of reaction was sought in both the visible and infrared spectra of the reaction mixtures. However, no evidence of absorption in the visible or infrared spectra attributable to the amine complex, $(CO)_5WAm$, was ever detected. In addition no significant reduction in the infrared carbonyl stretching absorption of $(CO)_5WP(C_6H_5)_3$ was ever detected. Therefore, it must be assumed that the reaction is essentially irreversible, i. e., that K_{eq} for the reaction $(CO)_5WP(C_6H_5)_3 + Am = (CO)_5W(Am) + P(C_6H_5)_3$ (where Am = aniline or pyridine) is exceedingly small; or if the reaction does significantly proceed, it does so at an exceedingly slow rate.

In their study Angelici and Ingemanson[20,21] concluded that the amine complex, $(CO)_5WNR_3$, is stable in the presence of a large excess of the amines. The assumption of the stability of the amine complexes with the added amine is, of course, vital to their study if any validity is to be given to their results. However, it is the conclusion of this study that the aniline

complex, $(CO)_5WC_6H_5NH_2$, is not stable even in the presence
of added amine, especially at high temperatures. A
solution of 1.5 x 10^{-4} M $(CO)_5WC_6H_5NH_2$ and 0.1 M aniline
in toluene was placed in a water bath at 49.7°C. The
absorbance at 406 mμ, and therefore the concentration of
aniline complex, was found to decrease significantly
with time. Figure 20 shows the decrease in absorbance
with time. The concentrations used were approximately
the same as those used by Angelici and Ingemanson.
Another solution at 35.0°C led to the same conclusion.
The aniline complex did decompose even with the large
amount of aniline added. At 25.7°C the decomposition was
very slow and over a period of a month could be consid-
ered insignificant.

In addition to the equilibrium study of the reaction
$(CO)_5WC_6H_5NH_2 + P(C_6H_5)_3 = (CO)_5WP(C_6H_5)_3 + C_6H_5NH_2$,
the kinetics of the reaction were explored. In their
study Angelici and Ingemanson[20,21] reported that, for
aliphatic amines (NR_3), the reaction obeyed a two-term
rate law over a large range of concentrations of the
ligand.

$$rate = k_1 \left[W(CO)_5(NR_3) \right] + k_2 \left[W(CO)_5(NR_3) \right] \left[L \right]$$

They did not conduct kinetic studies of aromatic amines
because the rate expression was found to be even more

Figure 20   Plot of Absorbance versus Time Showing the Decomposition of $(CO)_5WC_6H_5NH_2$ with Free Aniline at 49.7°C.
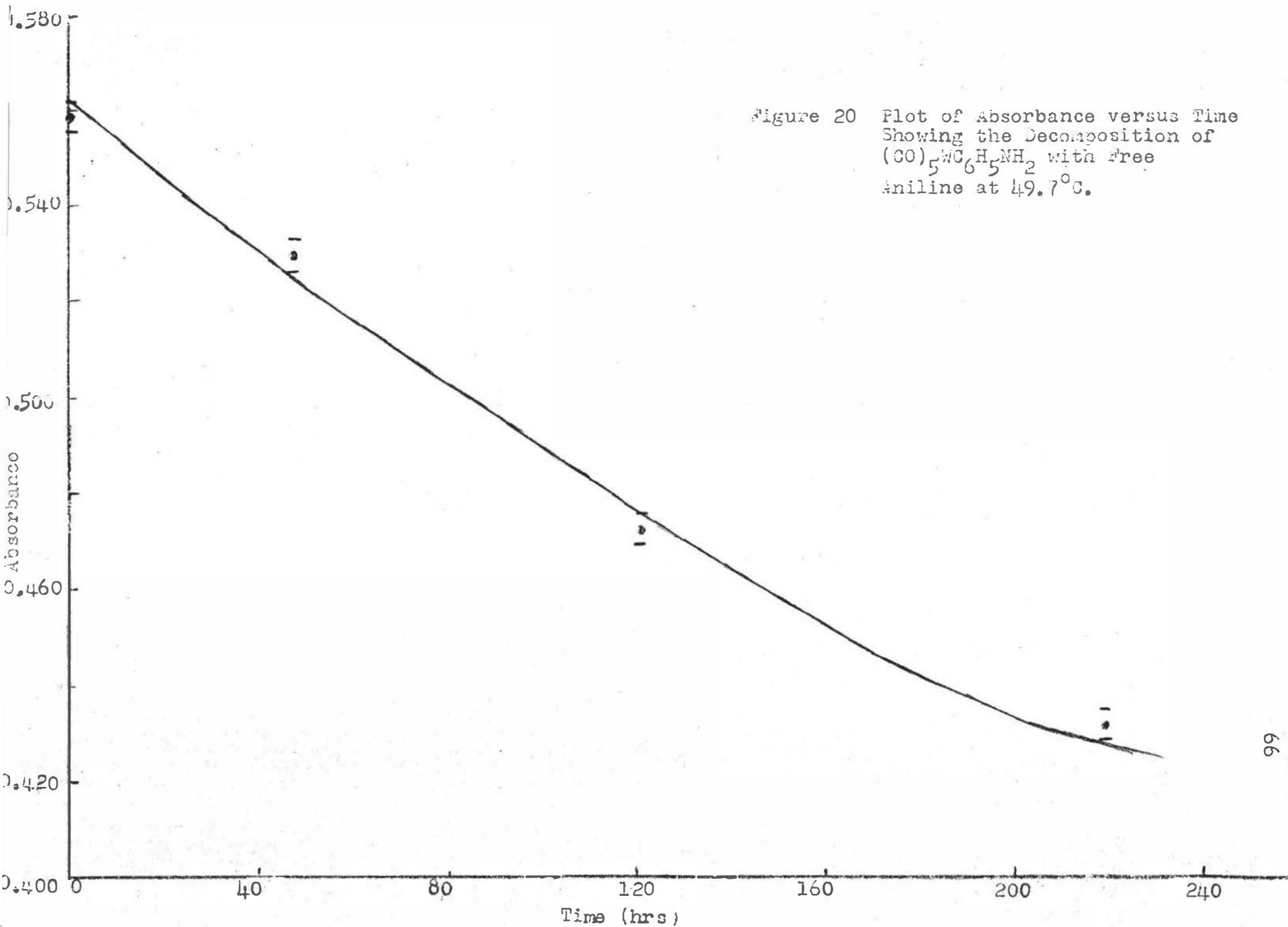
complex than for the other amines. From this study, as with theirs, it is apparent that a simple first or second order rate law is not followed by the reaction. A linear plot of log $[(CO)_5W(C_6H_5NH_2)]$ versus time would be indicative of a first order rate dependence for the reaction. Since absorbance $\propto [(CO)_5W(C_6H_5NH_2)]$, a plot of log A versus time should equally suffice. In the same way a plot of log $\frac{a - x}{b - x}$ versus time, where a and b are the initial concentrations of $(CO)_5W(C_6H_5NH_2)$ and $P(C_6H_5)_3$, should show any second order dependence. Tables XXV through XXIX and Figures 21 through 30 show some representative data and plots. As can be seen, none of the plots are linear. Therefore, the rate expression is more complex than first or second order.

Several conclusions can be drawn about the Angelici-Ingemanson study. Equilibrium is not established in two days as they believed. As a result, the equilibrium constants they determined are too small. Also although $(CO)_5W(C_6H_5NH_2)$ is reasonably stable in the presence of free aniline at $25.7^{o}C$, at $35.0^{o}C$ and $49.7^{o}C$ decomposition occurs at a significant rate. Therefore, all of the thermodynamic values they obtained for the aniline system are unreliable. The large ΔS values are the result of faulty experimental work. Any conclusions

they drew about the relative bond strength of metal-amine and metal-phosphine bonds are without foundation and therefore no contribution to the π-bonding controversy has been made.

Table XXV Data for Log A and Log $\frac{a - x}{b - x}$ versus Time for
Equilibrium Reaction I at 25.7°C.

Solution 3

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2]$ = 1.464 x 10^{-4} M

$[C_6H_5NH_2]$ = 0.0999 M

$[P(C_6H_5)_3]$ = 0.5642 x 10^{-4} M

Time (hrs)	Log A	Log $\frac{a - x}{b - x}$
2	-0.322	0.452
28	-0.333	0.471
52	-0.331	0.468
71	-0.329	0.465
156	-0.337	0.481
218	-0.345	0.497
244	-0.346	0.499
361	-0.358	0.525
506	-0.370	0.556
578	-0.374	0.566
646	-0.379	0.580
749	-0.382	0.589
887	-0.385	0.599
916	-0.387	0.604
1220	-0.403	0.657

Figure 21 Plot of Log A versus Time for Equilibrium Reaction I at $25.7^\circ C$. Solution 3.
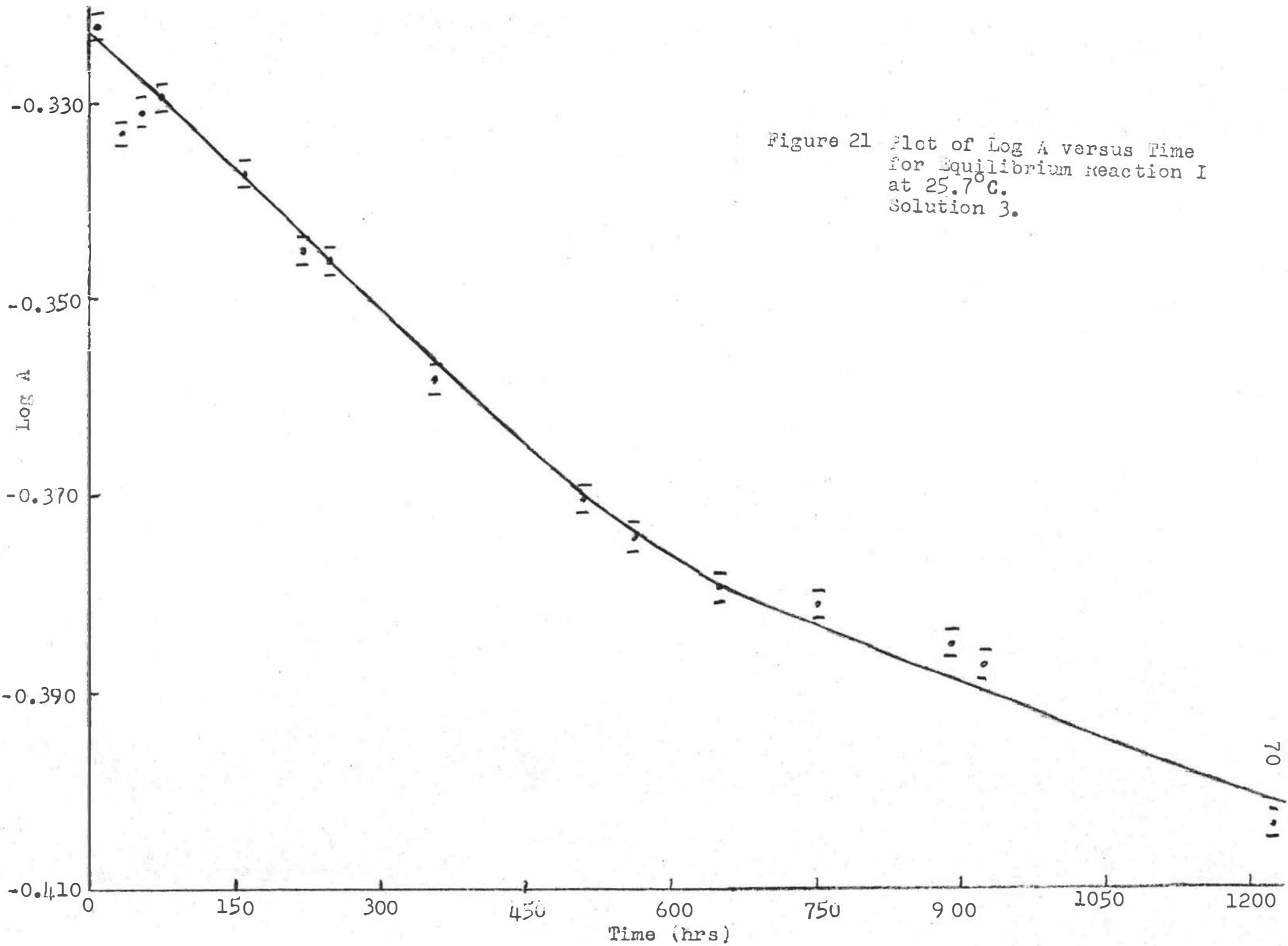
Figure 22   Plot of Log $\frac{a-x}{b-x}$ versus Time
            for Equilibrium Reaction I
            at 25.7°C.
            Solution 3.

Table XXVI Data for Log A and Log $\frac{a-x}{b-x}$ versus Time for Equilibrium Reaction I at 35.0°C.

Solution 2

Initial Concentrations:

$$[(CO)_5WC_6H_5NH_2] = 1.592 \times 10^{-4} \text{ M}$$
$$[C_6H_5NH_2] = 0.0988 \text{ M}$$
$$[P(C_6H_5)_3] = 1.081 \times 10^{-4} \text{ M}$$

Time (hrs)	Log A	Log $\frac{a-x}{b-x}$
3	-0.261	--
74	-0.282	0.178
98	-0.298	0.186
124	-0.308	0.192
147	-0.312	0.194
171	-0.324	0.201
266	-0.347	0.215
338	-0.353	0.218
461	-0.377	0.235
626	-0.407	0.256
845	-0.425	0.274
914	-0.431	0.279
1010	-0.432	0.280
1178	-0.457	0.303
1289	-0.472	0.318

Figure 23 Plot of Log A versus Time for Equilibrium Reaction I at 35.0°C. Solution 2.
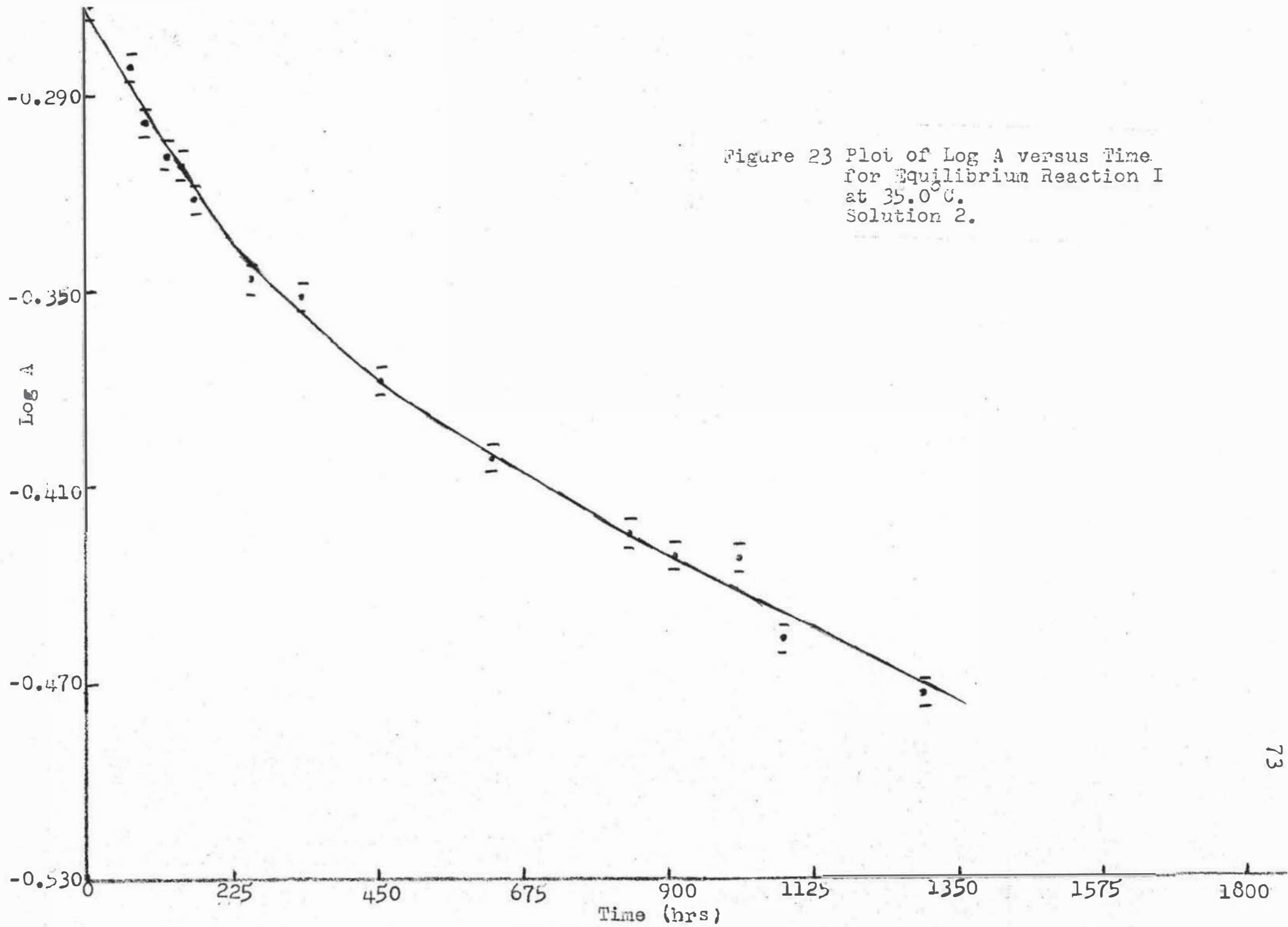
73

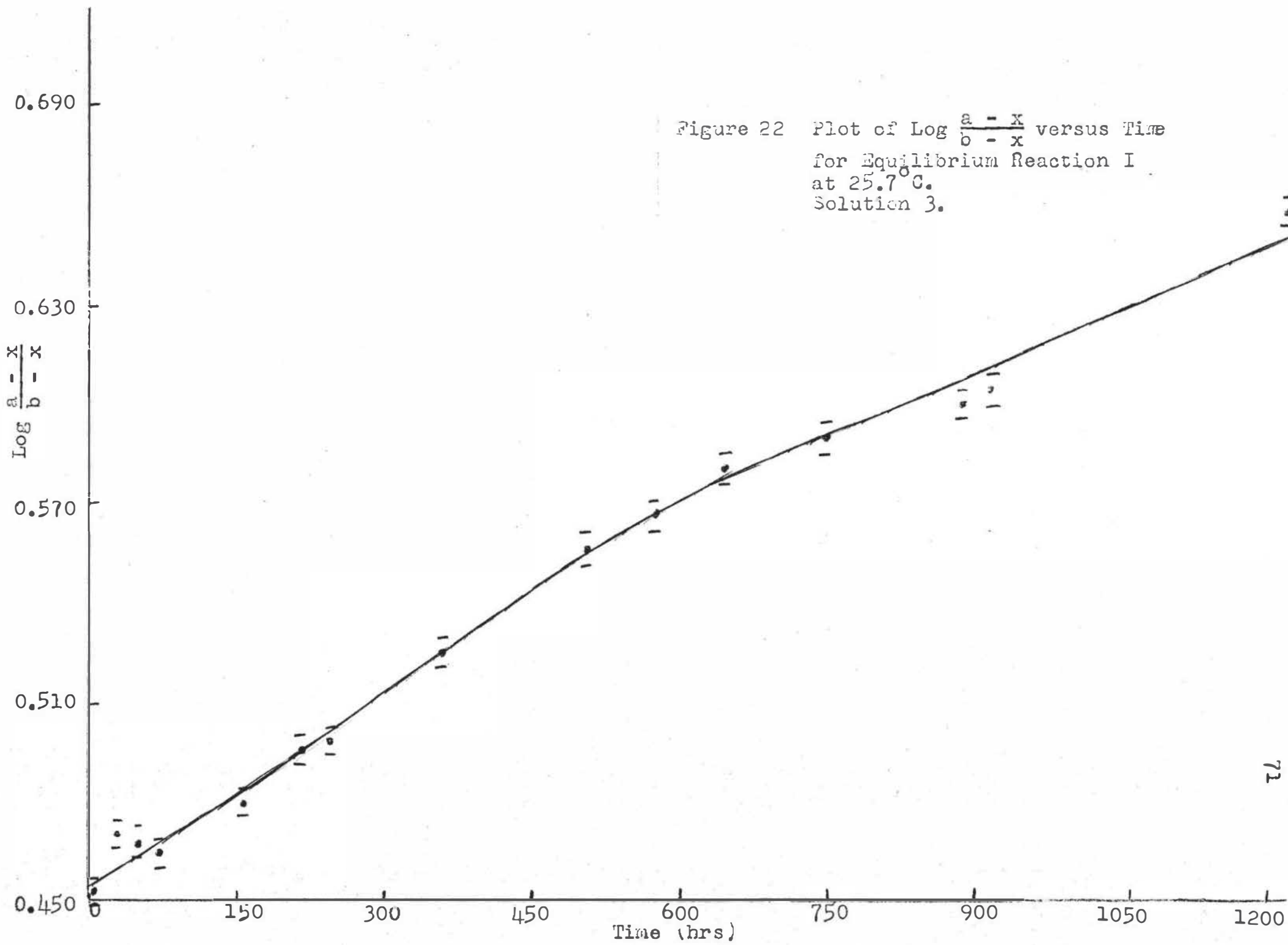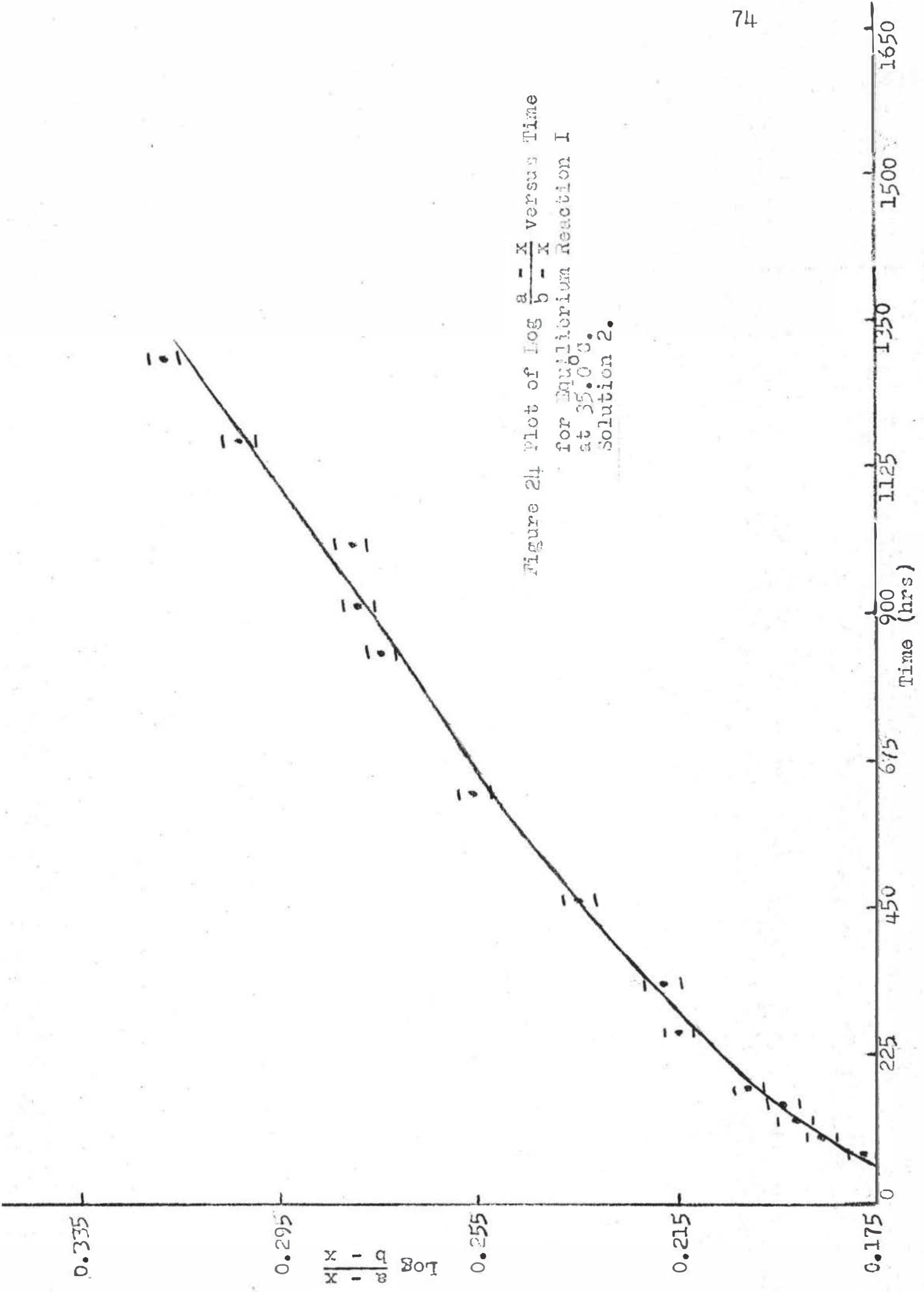Figure 24. Plot of Log $\frac{a-x}{b-x}$ versus Time for Equilibrium Reaction I at 35.0°C. Solution 2.

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Table XXVII Data for Log A and Log $\frac{a - x}{b - x}$ versus Time for
Equilibrium Reaction I at 40.6°C.
Solution 2

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2] = 1.410 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.0936$ M

$[P(C_6H_5)_3] = 1.066 \times 10^{-4}$ M

Time (hrs)	Log A	Log $\frac{a - x}{b - x}$
1	-0.340	0.129
73	-0.379	0.143
169	-0.409	0.155
265	-0.439	0.169
337	-0.461	0.180
434	-0.490	0.195
554	-0.523	0.215

Figure 25 Plot of Log A versus Time for Equilibrium Reaction I at 40.6°C. Solution 2.
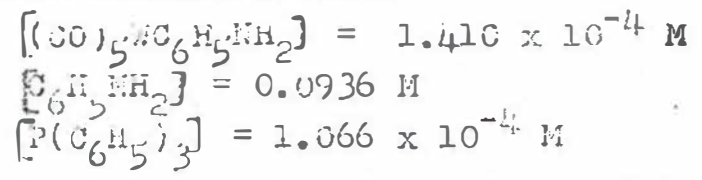
Figure 26   Plot of Log $\frac{a - x}{b - x}$ versus Time
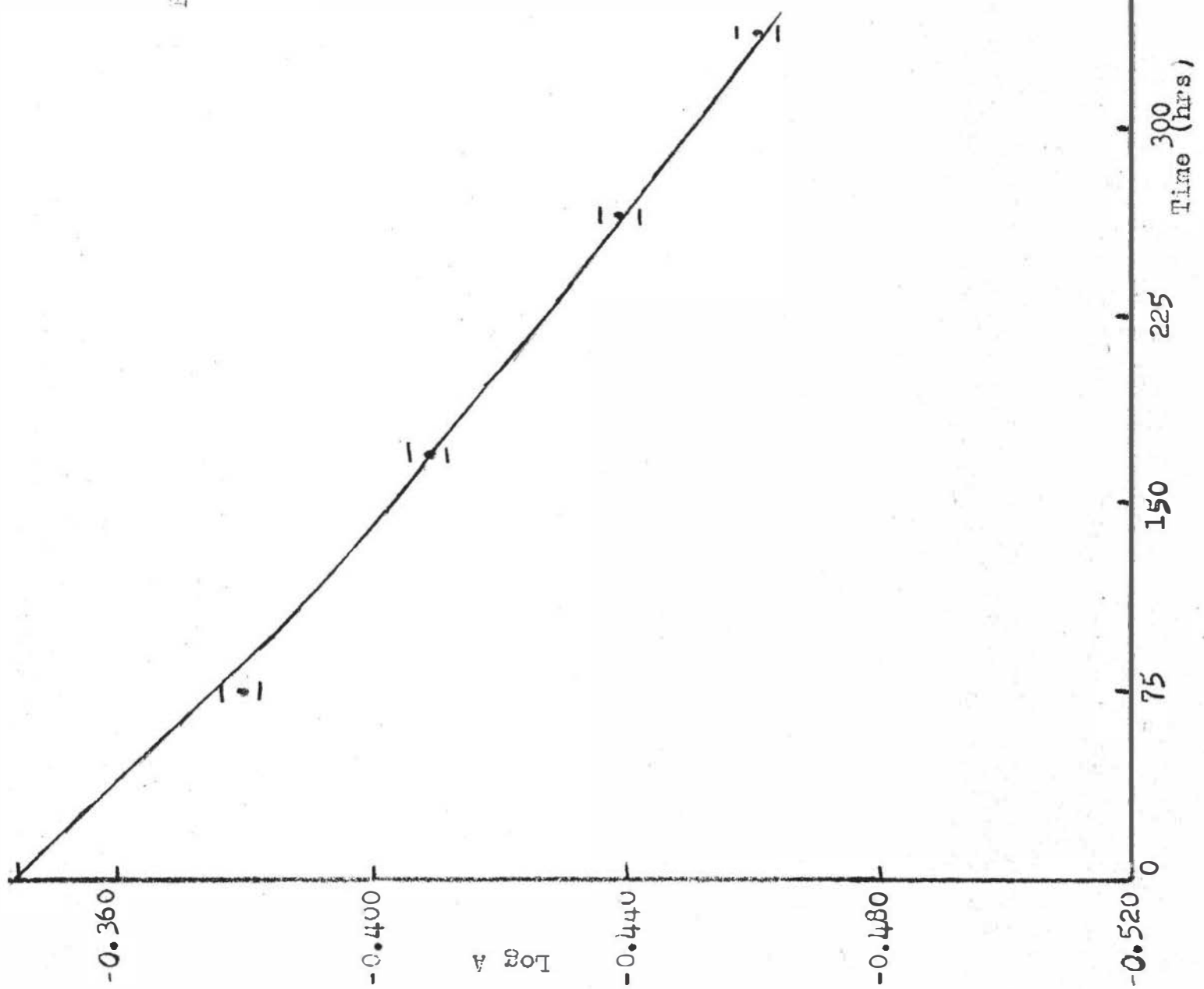for Equilibrium Reaction I
at 40.6°C.
Solution 2.

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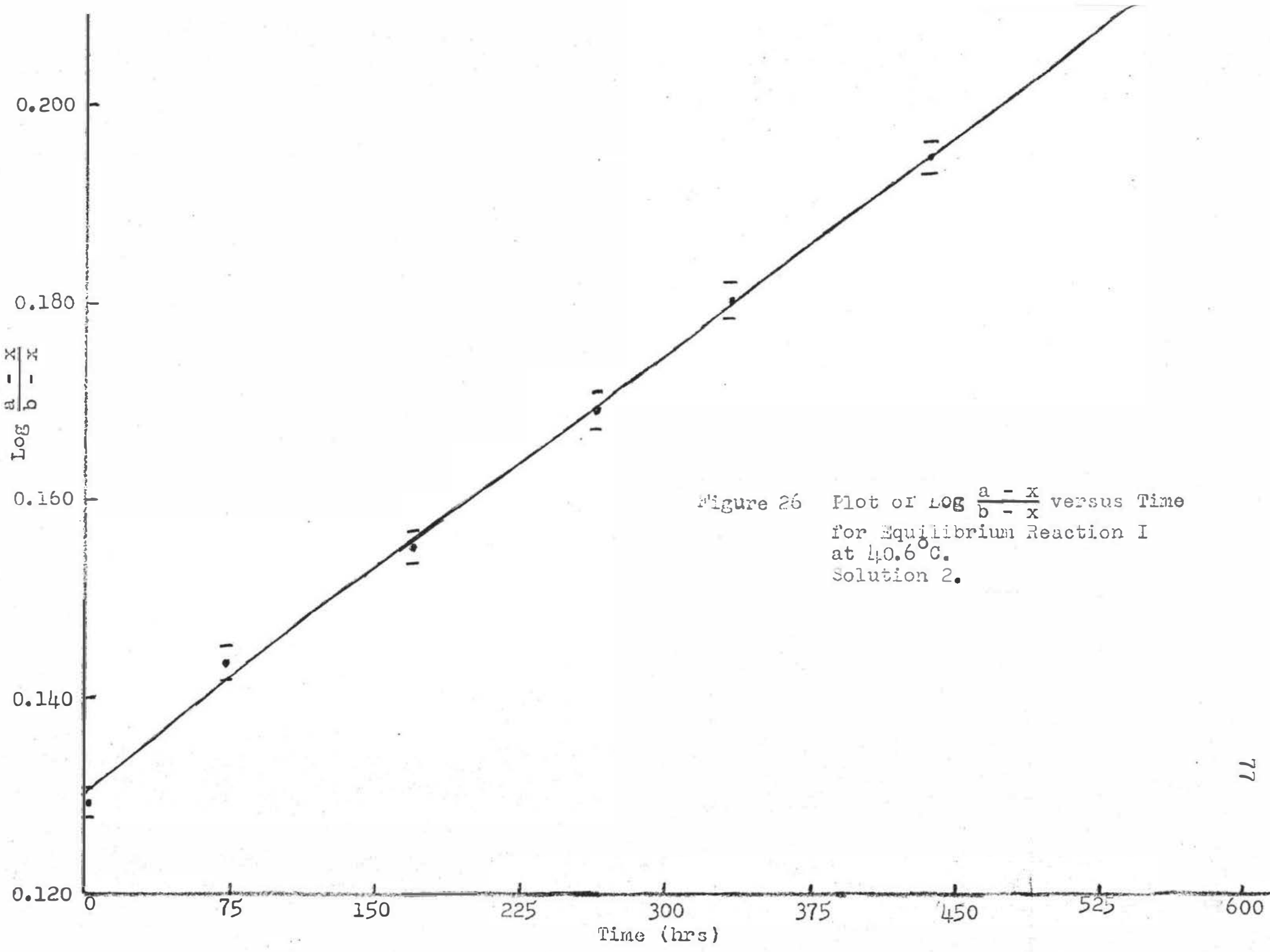
Table XXVIII Data for Log A and Log $\frac{a - x}{b - x}$ versus Time for
Equilibrium Reaction I at $49.7^{\circ}C$
Solution 1

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2] = 1.648 \times 10^{-4}$ M
$[C_6H_5NH_2] = 0.1000$ M
$[P(C_6H_5)_3] = 1.480 \times 10^{-4}$ M

Time (hrs)	Log A	Log $\frac{a - x}{b - x}$
2	-0.257	0.048
23	-0.347	0.060
47	-0.483	0.084
70	-0.604	0.115
167	-0.928	0.292
191	-1.076	0.507

Figure 27 Plot of Log A versus Time for Equilibrium Reaction I at 49.7°C. Solution 1.

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Figure 28 Plot of Log $\frac{a - x}{b - x}$ versus Time for Equilibrium Reaction I at 49.7°C. Solution 1.
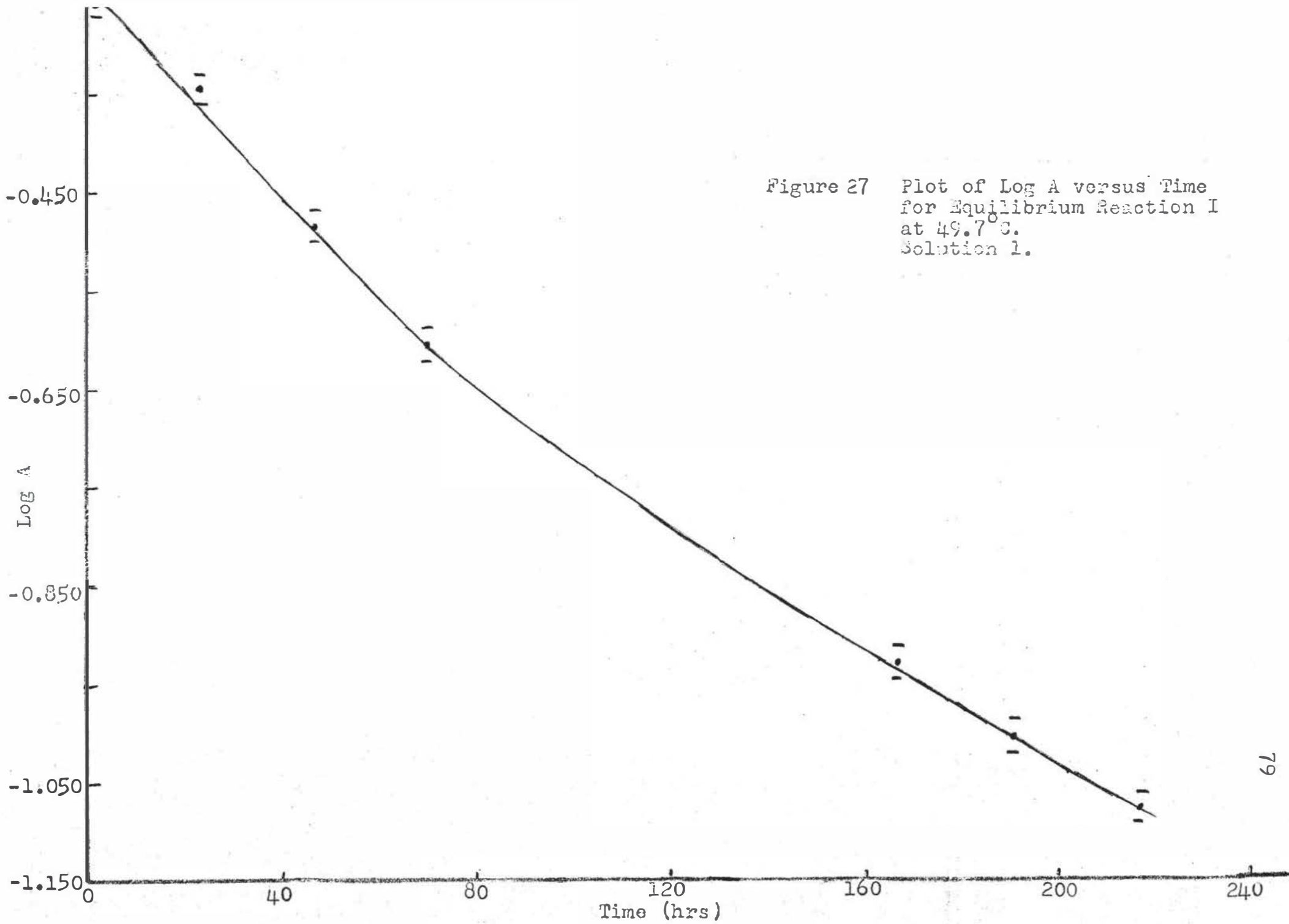
Table XXIX Data for Log A and Log $\frac{a - x}{b - x}$ versus Time for
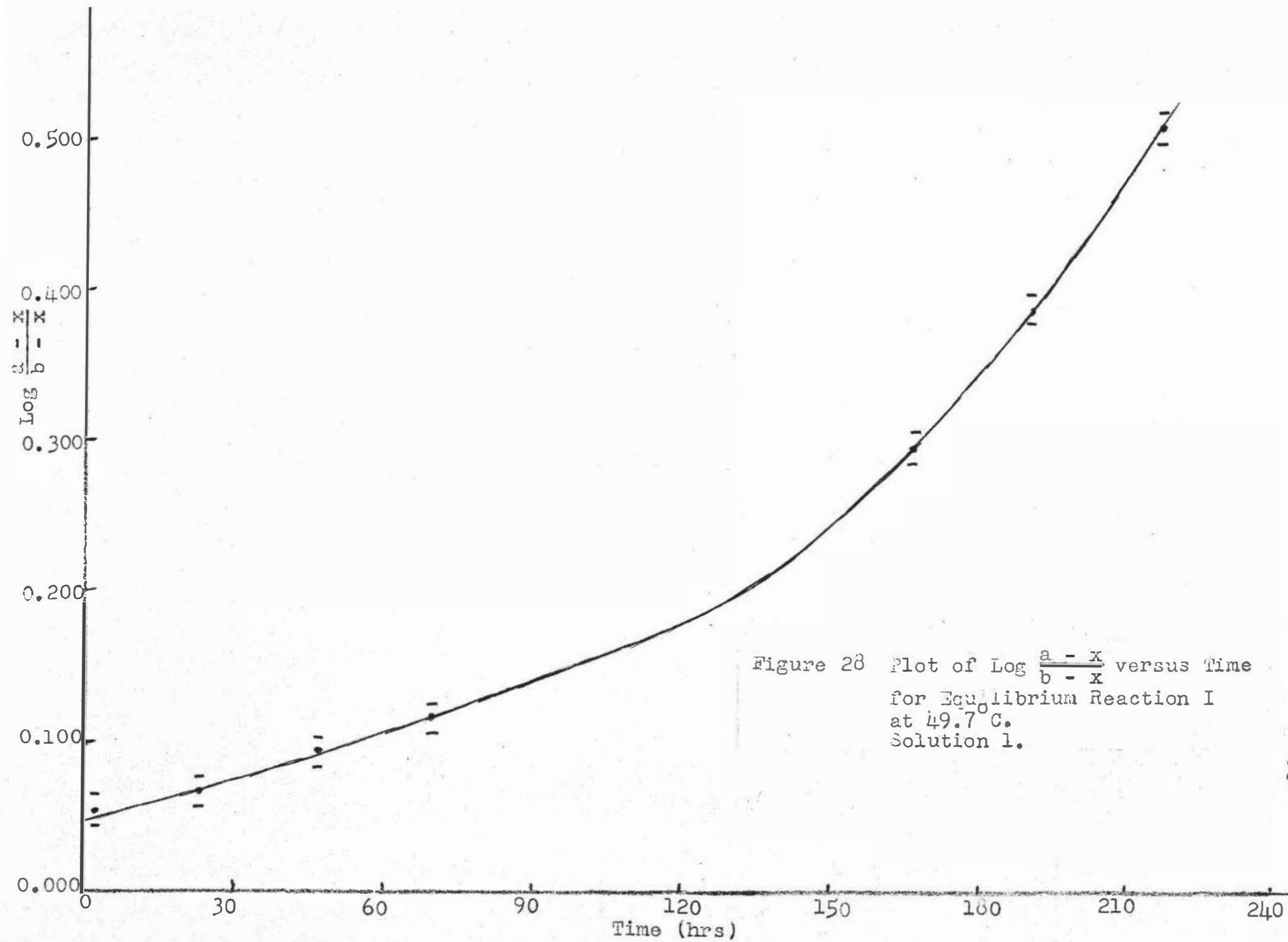Equilibrium Reaction I Conducted at Ambient
Temperature and under Nitrogen

Initial Concentrations:

$[(CO)_5WC_6H_5NH_2] = 1.592 \times 10^{-4}$ M

$[C_6H_5NH_2] = 0.0992$ M

$[P(C_6H_5)_3] = 0.9751 \times 10^{-4}$ M

Time (hrs)	Log A	Log $\frac{a - x}{b - x}$
3	-0.266	0.216
23	-0.268	0.217
47	-0.277	0.223
96	-0.292	0.234
120	-0.290	0.237
147	-0.305	0.243
171	-0.307	0.245
195	-0.316	0.252
266	-0.320	0.255
315	-0.328	0.261
339	-0.332	0.264
363	-0.335	0.267
458	-0.361	0.290
531	-0.358	0.287
648	-0.370	0.299
696	-0.375	0.304
818	-0.390	0.320
937	-0.399	0.330
1037	-0.410	0.343
1106	-0.408	0.340
1202	-0.416	0.349
1274	-0.427	0.365
1370	-0.438	0.379
1490	-0.440	0.382

Figure 29 Plot of Log A versus Time
for Equilibrium Reaction I
at Ambient Temperature.
Conducted under Nitrogen.

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Figure 30 Plot of Log $\frac{a-x}{b-x}$ versus Time for Equilibrium Reaction I at Ambient Temperature. Conducted under Nitrogen.

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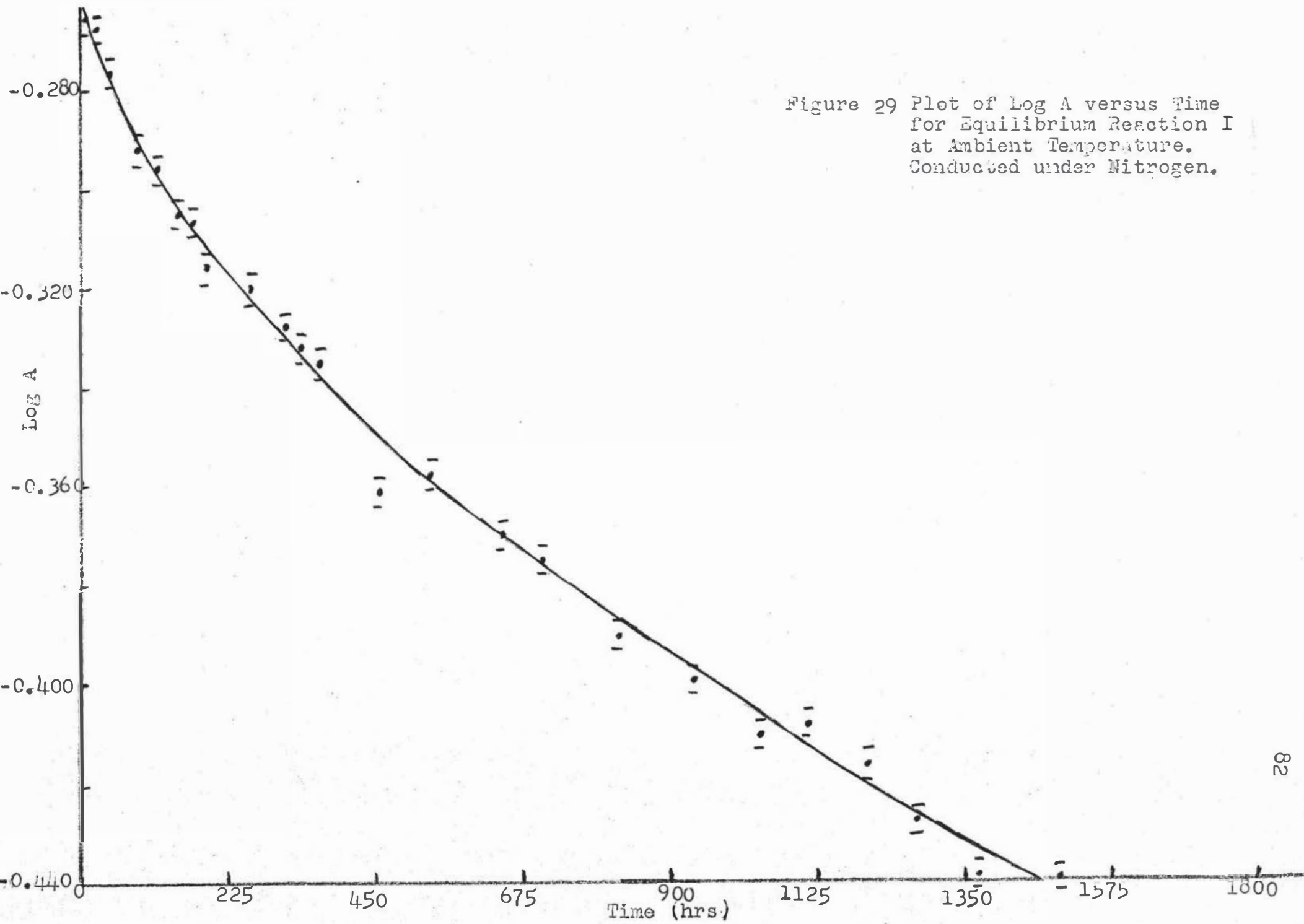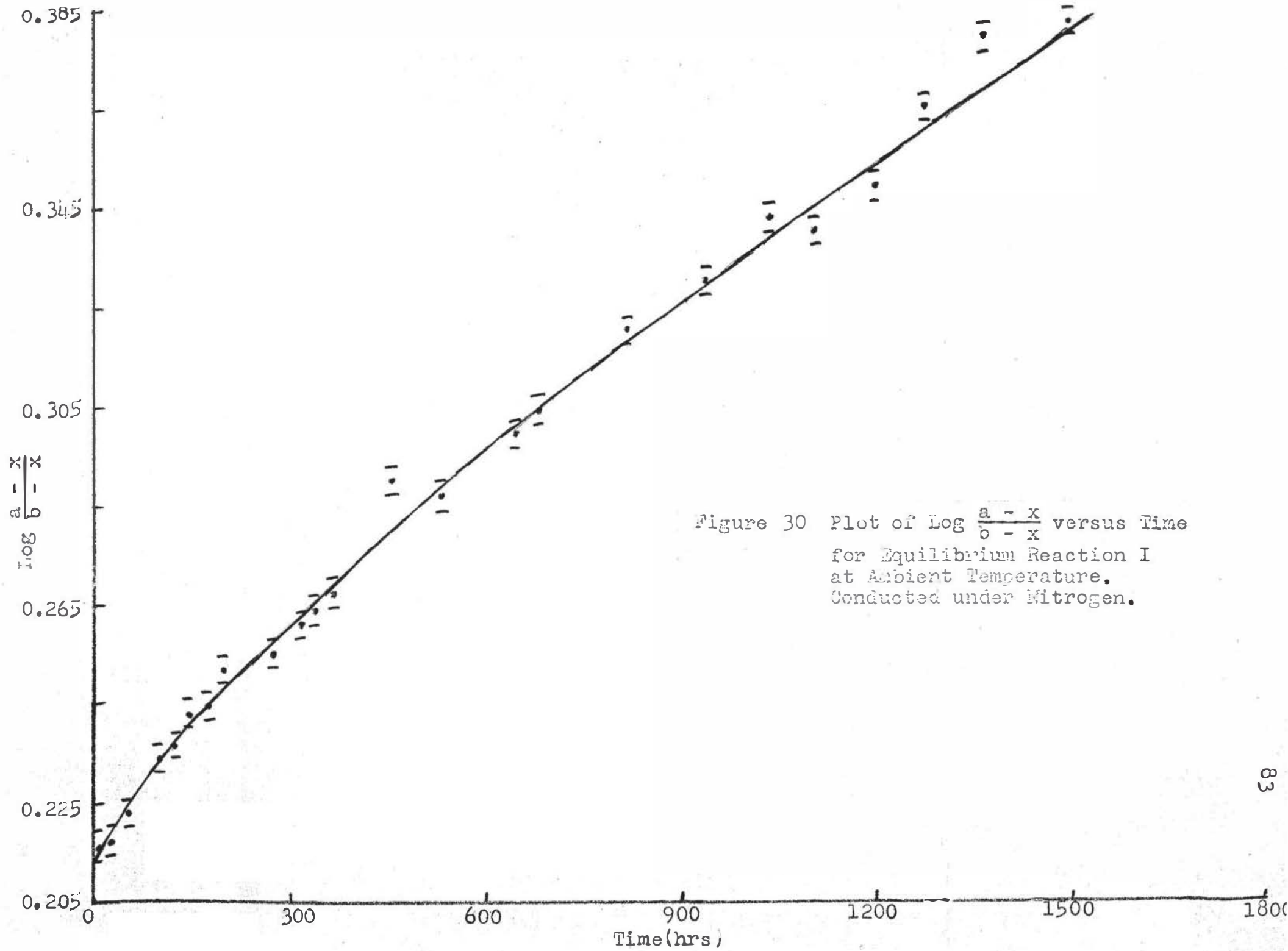
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