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Conductivity of organic solutes in liquid sulfur dioxide. Part I. Anthracene, trinitrobenzene and their equimolecular complex. Part II. Triphenylcarbinol

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CONDUCTIVITY OF ORGANIC SOLUTES IN LIQUID SULFUR DIOXIDE

Part I: ANTHRACENE, TRINITROBENZENE AND THEIR EQUIMOLECULAR COMPLEX

Part II: TRIPHENYLCARBINOL

by

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PART I

ANTHRACENE, TRINITROBENZENE, AND THEIR 1:1 COMPLEX

Introduction

Complexes between aromatic nitro compounds and aromatic hydrocarbons or amines are known as stable compounds, usually highly colored and of a definite melting point. The nature of the forces holding the components together is not definitely established (c.f. the section on literature background). Various theories have been put forth including covalent bonding (1), dipole effects(2), and ionic bonding (21). It was the purpose of this research to measure the conductivity in liquid sulfur dioxide of trinitrobenzene, anthracene, and the 1:1 complex from these two to see whether there was any conductivity at all, and in the event of such conductivity whether the complex conducted more than the added conductivities of the two components. It was hoped that the results would give evidence directly bearing on the binding forces of the complex.

Literature background

Briegleb (2), in a study of molecular complexes, concluded that the binding mechanism was the result of a dipole-induced dipole interaction, the moment of the nitro group polarizing the electrons in the unsaturated bonds of the hydrocarbon. He thought that in complexes of this type in which a strong dipole could

interact with a strongly polarized system, the polarization effect was of considerable importance as compared with dipole-dipole interactions and dispersion forces, the two other types of van der Waals forces. The energy of binding depended on the number and position of the nitro groups and on the polarizability of the unsaturated hydrocarbon. Table I shows the binding energies of various complexes measured in carbon tetrachloride solution from the relative intensities of the absorption bands with temperature changes.

TABLE I

Complexes of naphthalene with:	Binding energy in kcal. observed	calculated
s-trinitrobenzene	3.6	4.6
m-dinitrobenzene	1.5	1.6
o-dinitrobenzene	2.9	3.0
nitrobenzene	.6	.6

Complexes of trinitrobenzene with:	Binding energy in kcal. observed	calculated	Polarizability of hydrocarbon $\times 10^{24}$
anthracene	4.4	4.6	30.8
phenanthrene	4.0	3.9	26.4
benzene	.6	1.0	10.4

It is seen that, with a given hydrocarbon, the binding energy increases with increasing nitro groups, and that, with a given nitro compound, the energy increases with the polarizability of the hydrocarbon. The calculated energies are derived on the basis of induced dipole

effects using the standard equation.* In the case of the anthracene-trinitrobenzene complex, the concentration of the anthracene was .028 moles/liter and the nitrobenzene was .01 normal (5).

Since the interaction energy was dependent on polarization effects Briegleb concluded the π electrons, since they are so easily polarized, were of special importance. The cloud of electrons of an aromatic system would be pulled toward the polar groups of the nitro compound and "the overlapping of the cloud systems constitutes a non-classical binding energy which is superposed on the classical polarization energy" (2).

That the binding energy of molecular complexes is dependent on the substituents of the hydrocarbon is shown in Table II (3).

TABLE II

One to one molecular complexes of trinitrobenzene:

Hydrocarbon	Binding energy in kcal.
benzene	.6
styrene	1.81±.11
stilbene	3.21±.04
phenylbutadiene	2.15±.17
diphenylhexatriene	2.45±.02

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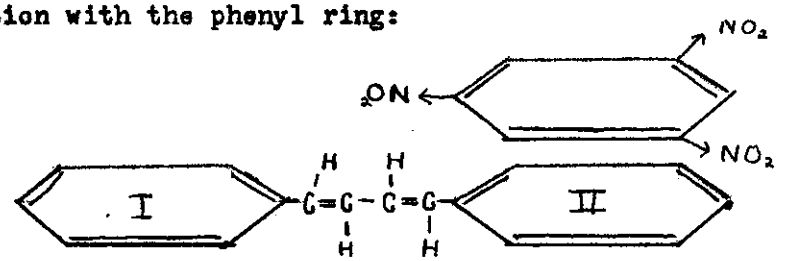
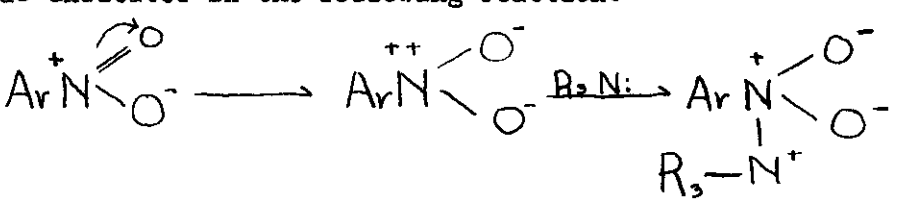
* In its simplest form $U = \frac{\alpha}{2} E^2$ where U = energy of binding due to induction effect, α = polarization of hydrocarbon, and E the field resulting from the moment of the polar group.

Briegleb visualized the trinitrobenzene molecule being in close association with the phenyl ring:



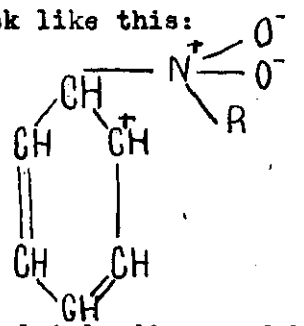
The increase in binding energy from benzene to stilbene shows the effect of the phenyl groups. Field interaction to ring I from the trinitrobenzene molecule directly is impossible since the distance is more than 5 Å. The disturbance of the electron cloud in one part of the molecule is carried through the conjugated system so that the whole molecule takes part in the binding. He calculated the interaction energies for all possible positions of the two molecules and concluded that the most probable one was with the planes of the hydrocarbon and nitro compound parallel. The binding energy decreases rapidly with distance, therefore the polar groups tend to be as near as possible to the polarizable bonds. Such a configuration is best achieved by a parallel orientation. This would explain why aromatic hydrocarbons form complexes more readily than aliphatic compounds, since aromatic compounds are planar.

Bennett and Willis (1) considered the components held together by a covalent bond, the union being through the basic nitrogen atom in the case of amines. They visualized the nitro groups as being activated as indicated in the following reactions:



The direct participation of the basic group was indicated by the formation of color with poly-nitro compounds and alcoholic ammonia, or piperidine and trinitro anisole because in these cases there was no point of attachment but the basic group.

The authors concluded that the complexes of polynitro compounds and aromatic hydrocarbons were quite similar, and the method of union was the same. The hydrocarbon, like the base, is a donor molecule. The complex would then look like this:



However, this was completely disproved by Powell and Huse in 1939 (15). These workers examined the crystal structure of a large number of complexes and found the molecules arranged in parallel planes. The particular example they described was the 1:1 molecular compound of picryl chloride and hexamethyl benzene. All the picryl chloride molecules lay in two sets of parallel planes, one above the other, separated by a distance of 7 Å. All the hexamethyl benzene molecules lay in two sets of planes parallel to and half-way between these; i.e., separated from them by 3.5 Å. In this case there was no possibility of covalent bonding between the components.

In 1943 Powell, Huse, and Cooke (16) examined the crystal structure of the complex of p-iodo-aniline and trinitrobenzene by means of x-ray diffraction. The atomic positions were determined by two and three dimensional Fourier analysis. Between the p-iodo-aniline

and trinitrobenzene molecules the interatomic distance was equal to or greater than 3.5 Å as would be expected for unlinked atoms. There was no distance of the order of magnitude of 1.5 Å which would be expected for a covalent link. Therefore, covalency between the components was excluded. There might be very weak hydrogen bonds between the amino groups and oxygen atoms of the nitro groups, but these are not essential for complex formation. However, the authors pointed out that what was true for one complex might not necessarily be true for another and they made no absolute claims as to the generality of their conclusions.

Weiss (21) considered the complex essentially ionic, there being an actual electron transfer from the donor hydrocarbon to the acceptor nitro compound. He felt that the complex was held together more firmly than by dipole interaction or dispersion forces since they existed in solution and their color could not be due to a saturation of residual valencies. The usual simple stoichiometrical ratio of 1:1 or 1:2 was strong evidence against ordinary polarization interactions.

The acceptor molecule must have a positive electron affinity so that an increase in electronegative groups favors formation of a molecular compound. This is borne out by the fact that complexes from di- and trinitro compounds are more stable than those from the mono compound.

From a consideration of energy curves, Weiss concluded an ionic bond was far more probable. In figure I (21), i and i' are the potential curves, i.e., the energy of interaction plotted against

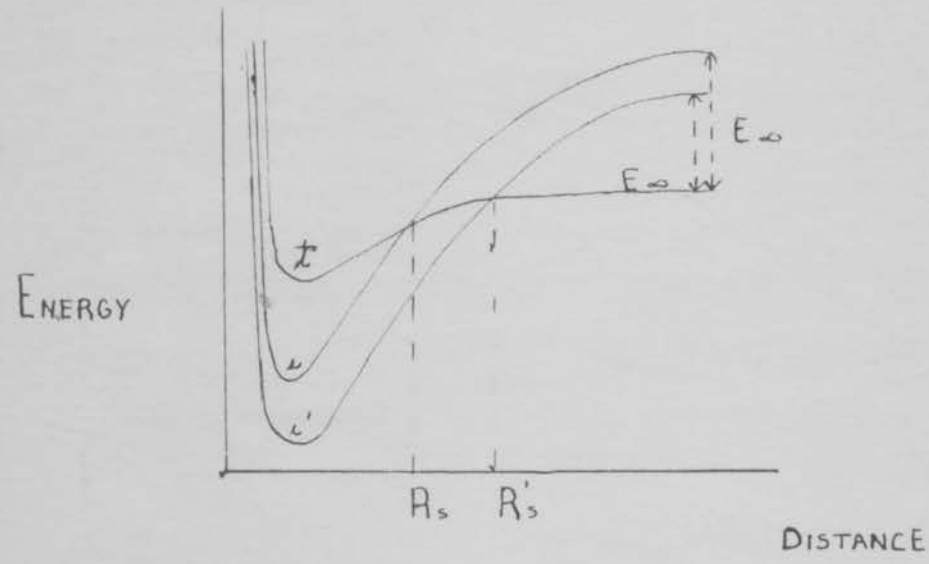


FIGURE I

intermolecular distance, if the complex is considered to be the result of an electron transfer. i and i' correspond to different values of E_∞ which is equal to $I_D - E_A$ where I_D is the ionization potential of the donor molecule and E_A the electron affinity of the acceptor molecule. t represents the potential curve if the complex is considered to be held together by van der Waals forces. The dispersion and dipole potentials fall off much more rapidly than the ionic potential and the lower energy values for the ionic state are obvious. Where the curves cross at R, both potentials have an appreciable value so that a linear combination of both is necessary, but at least these curves indicate the presence of ionic bonding in the complex. As further support he pointed out that the formation of the complex is fairly rapid and there is a low heat of activation which point to an ionic bond. According to Weiss, the donor molecule has a low ionization potential; the transition complex is first formed through dipole and dispersion interactions. This is then followed by an actual electron transfer, the whole procedure visualized as follows:

$$A + B \longrightarrow (AB)_t \longrightarrow (A)^+ + (B)^-$$

Weiss explained the formation of color as due to the fact that the ions each have an odd electron. This means a small excitation energy which leads to light absorption in the visible.

More corroborative evidence was obtained from crystal data; the interionic distance of 3 to 3.5 Å as measured by x-rays were of the same order of magnitude as other univalent.ionic crystals, like KCl(3.15Å). The NaCl structure was observed in the case of the complex between acenaphthene and 2:6 dinitro-m-xylene (9).

From this theory one would expect the molecular complex to have a measurable dipole moment due to the separate charges of the ions. It was found in many cases (4) (13) that compounds with zero dipole moment as trinitrobenzene, gave a measurable moment in solvents with which they formed complexes, as benzene, but not in solvents like carbon tetrachloride where there was no complex formed.

In discussing electrical properties of the complexes in solution, Weiss mentioned in particular the complex between trinitrobenzene and anthracene. This gave a yellow color in liquid sulfur dioxide and a small but measurable conductivity. At a concentration of 10^{-3} moles per liter the equivalent conductance was of the order of .1 at 0° C. He also mentioned data which he felt indicated the hydrocarbons as donor ions. Walden (16) had found that solutions of anthracene in liquid sulfur dioxide were deep yellow and showed a measurable conductance of approximately .1 at a concentration of 10^{-3} moles per liter at 0° C. Weiss considered this to demonstrate the positively charged anthracene ion; the conductance was due to the presence of $(C_{14}H_{14})^{+}$ and $(SO_2)^{-}$. According to Weiss (21) any system of conjugated double bonds is capable of forming ions; the π electrons were essential. He made several salts to prove this, among them anthracene perchlorate. The solution of this salt was a good conductor of electricity in acetone.

In 1943, Powell and Huse (17) reported some experimental data which they felt was evidence against the presence of ions in the crystal structure of such a complex. They maintained that an ionic crystal of the type envisaged by Weiss would have greater strength

than one held together by van der Waals forces. This greater strength would be evidenced by greater hardness and high melting point, which was not observed.

Moreover, according to Weiss (21), the carbon atoms of the component ions would be about 3.2 Å from each other which was not the case for the complex studied. The authors showed tables of melting points of complexes and their components. The melting point of the complex was usually lower than that of one of the components and in some cases the melting point of the complex was lower than that of either component. The x-ray photagraphs they obtained did not show any evidence of the increased hardness that would be expected for an ionic crystal.

It must be remembered, however, that a melting point is not in itself a diagnostic test of the type of bonding present in a system. According to Pauling (14) the melting point is rather a function of the number and distribution of bonds and this type of complex may be similar to SiF_4 which Pauling describes as having ionic bonds but a much lower melting point than, e.g., NaF. This is because whereas NaF is a giant crystal with every positive ion associated with six negative ions, SiF_4 has every positive ion associated with four fluoride ions with the different SiF_4 molecules held together by weak van der Waals forces. It is these weak fores which are destroyed when the compound melts, and not the ionic bonds.

Rapson, Saunder, and Stewart (18) considered the Weiss electron transfer theory valid only in certain cases where deep color existed and the presence of ions was supported by other evidence. They thought

the interaction of dipoles, perhaps leading to an incipient oxidation-reduction was a more probable explanation of the observed phenomenon. As support of their contention they pointed to examples of complexes where the ratio of components was less simple than the 1:1 or 1:2 mentioned by Weiss. For example, the complex of trinitrobenzene and fluorene was in the ratio of 4:3. They themselves prepared complexes using 4:4' dinitrobiphenyl with 4:4' diacetoxybiphenyl, 4-acetoxybiphenyl, 4:4' dimethoxybiphenyl, and biphenyl and obtained ratios of 5:1, 4:1, 3.5:1, and 3:1 respectively; the colors ranged from cream to red. In a series of x-ray crystallographic studies they examined the crystal structure of various complexes and found that the acceptor dinitrobiphenyl molecules lie in planes one above the other separated by 3.7 $\mathring{A}$, while the donor molecules lie with their axes perpendicular to these planes. In Figure II an example of the complex between p-hydroxy biphenyl and 4:4 dinitrobiphenyl is presented. It was found that all the molecules were equally spaced from each other; there was no intermolecular distance shorter than that normally found in aromatic nitro compounds. There was one exception in that one OH...O bond distance was 3.0 $\mathring{A}$. Here, hydrogen bonding might be possible but it would not explain the observed ratio of 3:1. The approach of the nitro groups to the rings of the hydroxy compound was no closer than to the rings of the dinitribiphenyl molecules themselves which indicated no localized bonding between units in the crystal structure. This analysis was representative of other complexes examined. The authors finally concluded the molecular ratios were determined almost entirely by geometrical considerations;

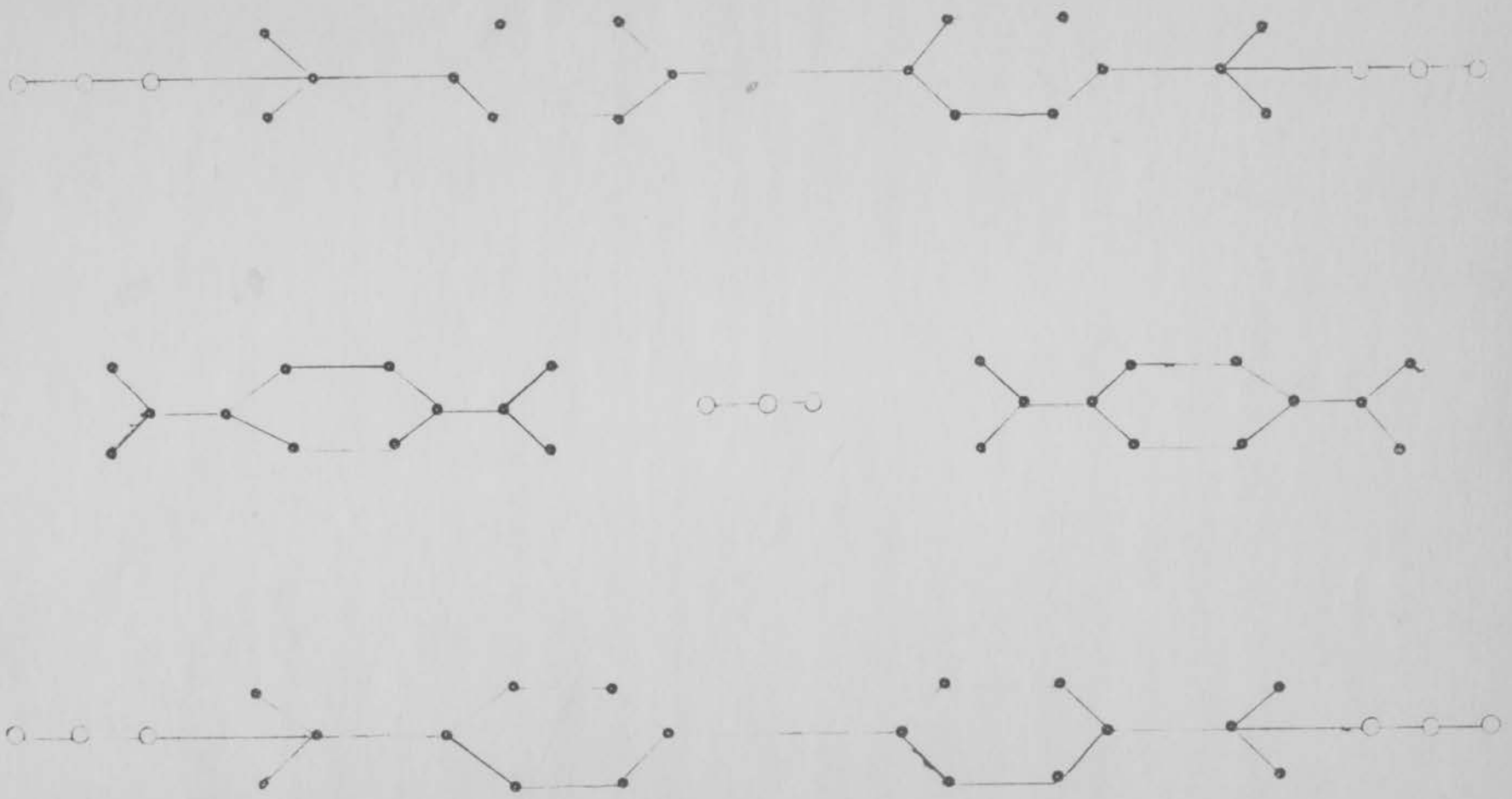


FIGURE II

DARK CIRCLES ARE DINITROBIPHENYL MOLECULES AND SHOULD BE VISUALIZED AS SEVERAL MOLECULES ONE ABOVE THE OTHER SEPARATED BY 3.7 A°

LIGHT CIRCLES ARE BIPHENYL NUCLEI OF DONOR COMPONENT SEEN ON END

the number of molecules of nitro compound that could be accomodated by each molecule of the donor component depended on the length of the latter. The comparison of observed ratios and those calculated on this basis were quite good; they calculated how many nitro compounds 3.7 Å apart could be accomodated at right angles to the donor molecules.

Hunter, Qureishy, and Samuel (10) were of the opinion that the complexes were associations produced by van der Waals forces rather than the results of an ionic bond and as support of their contention they reported data on the absorption spectra of various complexes in ethyl alcohol and hexane. They measured the spectra of naphthalene and picric acid, m-dinitrobenzene and β-naphthalamine, and their respective complexes. In each case they found that the spectra of the complex was a superposition of the curve of the first component on that of the second, with neither the position of the maxima nor log k indicating anything more than a small interaction between the components. They compared the log k of the complex with the sum of the values for the two components and found that deviations from the law of additivity were quite small, of the order of .2 which is of the same order as that observed for change of solvents.

Further work on absorption spectra was done by Jones and Neuworth (11) who measured the spectra of trinitrobenzene with such hydrocarbons as naphthalene, anthracene, phenanthrene, and chrysene, in methanol. They observed that at the concentration used (10^{-3} molar) the complexes were completely dissociated. They added the molar

extinction coefficients of the hydrocarbon and trinitrobenzene at a given wave length and compared the sum with the experimental molar extinction coefficient of the complex and found excellent agreement. The comparison between observed and calculated values in the anthracene trinitrobenzene complex is shown below:

TABLE III

mμ	calc.	obs.
252	5.29	5.30
298	3.07	3.08
311	3.23	3.23
325	3.49	3.49
340	3.92	3.90
358	3.90	3.87
378	3.76	3.74

Recent evidence that the complex does not exist as such in liquid sulfur dioxide has recently been obtained by Dr. Ralph Weston (23), who, while doing absorption studies in that solvent at Harvard University, was kind enough to measure the spectra of anthracene, trinitrobenzene, and their complex in a concentration range of 40 to 20,000 liters per mole. His data show that the complex does not exist in liquid sulfur dioxide; the spectrum of the complex is just the sum of the spectra of the two components within experimental error. The data are shown in Table IV; the figures refer to the extinction coefficients $\times 10^{-3}$.

TABLE IV

Wave length, mμ	Anthracene	Trinitrobenzene	Sum	Complex
340	6.55	.243	6.79	6.24
345	6.42	.230	6.65	6.15
355	5.77	.183	5.95	5.52
365	5.41	.131	5.54	5.09
375	5.14	.0835	5.22	4.81
385	4.73	.0485	4.78	4.40
395	4.12	.0248	4.14	3.81
410	3.00	.0078	3.00	2.80
430*	1.70	----	1.70	1.62

According to Weston, "Further evidence for complete dissociation lies in the fact that both the complex and anthracene obey Beer's Law at 430 mμ, and a_m** of the complex at this wave length is the same as that of anthracene alone."

* From absorbancies at four concentrations at this wave length,

$a_m = 1.45 \times 10^3$ for anthracene

$a_m = 1.35 \times 10^3$ for the molecular complex

** a_m molar absorbancy index $= \log \frac{I_o}{I} \Big/ cb$ where c is concentration in moles per liter, and b is the cell thickness in centimeters.

Results and discussion

The results of the first run on anthracene were in general agreement with those of Walden (20) who reported:

0° C.	Dilution, lit/mole	29	68	161
Λ	ohms^{-1} cm.^{2}/mole	.105	.110	.107

Attmepts to duplicate these results with more highly purified material led to lower results (cf. Table IV) which might conceivably have been due to elimination of impurities through vacuum sublimation.* # The recovered material had a slight yellow tinge and showed no obvious fluorescence; m.p. 215.2-216.8° C. The material had not been covered during evaporation of the solvent and possible resulting impurities may have caused a range in the melting point. There was not enough material to recrystallize.

The introduction of pumping in the measurements on anthracene led to still lower values of Λ (cf. Tables V-VI). There was no apparent sublimation along the walls of the cell and examination of the cold trap in the line revealed only water. It was felt, therefore, that the conductance of anthracene was so low that exact reproducibility was impossible with the apparatus used. The results

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* The temperature recordings for the last three readings are lacking because the Beckmann was broken, but the thermostat had maintained a fairly constant temperature, in general, not varying by more than .02.

Temperature of sublimation 120°

of the measurements on conductivity of trinitrobenzene are seen in Tables VII-XII. The conductivities seem to lie within a certain range as depicted on the curve (cf. end of section), the agreement being better at higher concentrations than in the more dilute regions. Purification, which consisted of vacuum sublimation,* resulted in slightly lower values, while pumping seemed to have no effect. There was no apparent reason for the lack of reproductivity, and again it was felt the conductivities were so low, no better precision was possible with this apparatus. Thus, the values of k for the solution run from about 93×10^{-8} ohms at a dilution of 145 liters per mole to 12×10^{-8} ohms at a dilution of 27,000 liters per mole while the values of k for the solvent run from 5 to 14×10^{-8} ohms. In run X-7, page 27, e.g., the specific conductance of the solvent at the first point (93.9 liters per mole) is 15% of that of the solution; at a concentration of 88,000 liters per mole k of the solvent is as much as 57% of that of the solution. The melting point of the recovered material averaged 123° C., and was fairly sharp.

The initial measurements on the complex, cf. Table XV, seemed promising in that the equivalent conductance was relatively much greater than that of either of the two components.**

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* Temperature of sublimation 100°

** The reason for the high resistance of the solvent (cf. page 30) is not understood since fair agreement was obtained with 50,000 ohms in parallel as well as 11,000. However, whether it was 17, 18, or 19 million ohms, the specific conductance was still 1×10^{-8} and the resulting values for Λ were unaffected.

The solution of the complex in liquid sulfur dioxide is deep yellow. The recovered material looked unchanged, but a sharp melting point could not be obtained. The crystals were in a semi-melt stage from 140-170 degrees; there was no homogeneous liquid. This could be due to dissociation of the complex with resultant formation of a mixture of complex, trinitrobenxene, and anthracene or perhaps a further complex formed between the solvent and the complex. Subsequently, evidence in favor of the former was obtained from spectroscopic measurements (cf. page 12.)

In connection with the indefinite melting point of the recovered material, a mixture of equimolecular amounts of anthracene and trinitrobenxene was prepared and its melting point determined. The mixture turned deep orange in part and melted from 160-162 degrees. In this range the sample presented the same semi-melt appearance as the recovered material; again there was no homogeneous liquid. A second melting point was taken on a mixture of about 10% complex and 90% of a mixture of equimolecular amounts of anthracene and trinitrobenzene. This mixture melted from 154-158 degrees, i.e. dark orange droplets formed throughout the mixture.

Further runs on the complex made from vacuum sublimed materials led to much lower results, cf. Tables XV-XVI. It seemed fairly evident that the conductivity of the complex is the sum of the equivalent conductances of the two components or of their impurities.

This means that there are no detectable ions in the solution which might be accounted for by either of two reasons. Either there was never an ionic bond holding the components together or the complex dissociates in liquid sulfur dioxide to such an extent that the conductivities of anthracene and trinitrobenzene, distinct in themselves are measured. The following table shows how the sum of the conductivities of the components compares with the conductivity of the complex.

TABLE V *

Dilution, lit./mole	Λ ohms^{-1} cm.^{2}/mole			
	Anthracene	Trinitrobenzene	Sum	Complex
100	.03	---	-	---
500	.075	.13	.205	.240
1000	.12	.27	.39	.340
2000	.18	.46	.64	.50

It is seen in Table XVI that the conductance of liquid sulfur dioxide is negligible; its maximum resistance lies in the range of seventeen million ohms. The first distillation lowered the value of k from 41 to 7.7×10^{-8} ohms^{-1} cm.$^{-1}$ Since the values of k for the solvent are taken only at the end of each run, one might account for the failure to obtain exactly reproducible results by considering this "solvent error". The values of k for the solvent are in many cases as much as 20 or 30% of the actual conductances of the measured compounds.

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* Data from curves at end of section.

Experimental

Materials of research:

1. Anthracene: This was the commercial product of Reilly Tar and Chemical Corporation, Scintillation Grade. The crystals as supplied showed a pale blue fluorescence and had a melting point of 215.4-215.5° C. taken with a total immersion thermometer, allowing a sulfuric acid bath to heat up fairly rapidly until approximately fifteen degrees below the melting point at which time the rise in temperature was regulated to three to four minutes per degree until the material melted. Subsequent melting points given in this thesis were taken in the same bath and in the same manner. Literature values for anthracene are 217° (11), 214° (11), and 215-216° C. corr. (5).

2. Trinitrobenzene: This material was from the Eastman Kodak Co., while label, and had a melting point of 122.2-122.4° C.

3. The complex (5): Ethereal solutions containing .5 grams (.002 moles) of trinitrobenzene and .35 grams (.002 moles) of anthracene were mixed and warmed on a steam bath. An orange solution resulted which was filtered to remove any undissolved or unreacted material. The solution was allowed to evaporate to dryness in a vacuum desiccator containing sulfuric acid. Long orange needles resulted, mp. 163.8-164° C. A melting point of 164 has been reported (19).

4. Sulfur dioxide: This was the dry commercial product of the Matheson Co. (7).

The apparatus and experimental technique involved in the

measurements were the same as those employed by H. Glazer (7). The calibration data for the cell and thermometer are as follows:

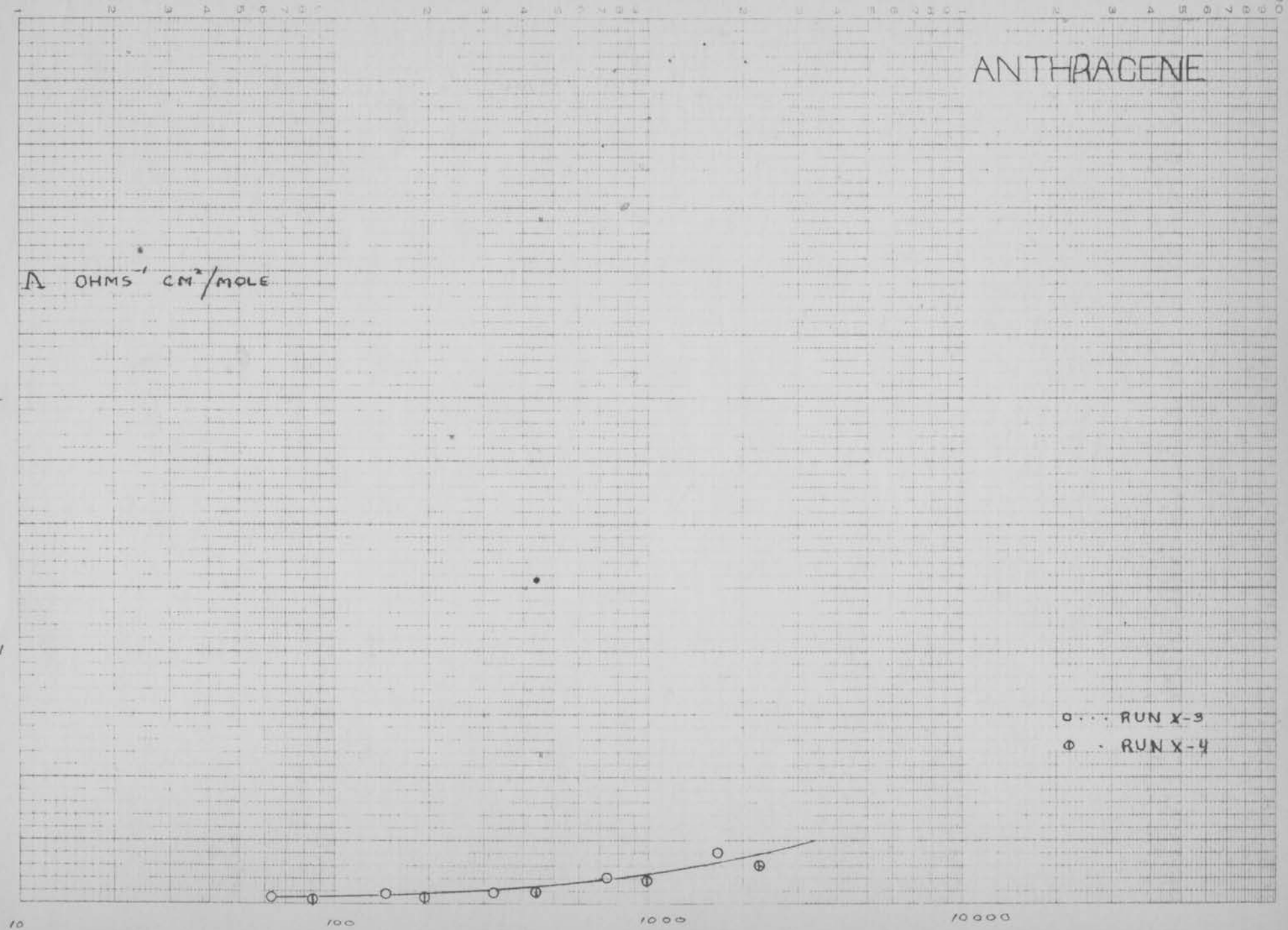
cell constant -- .2226

electrode bulb volume -- 43.000ml. at 1.185 ml. graduation

dilution bulb volume -- 18.730 ml.

Beckmann -- 4.780±0° C.

ANTHRACENE


Λ OHMS⁻¹ CM²/MOLE
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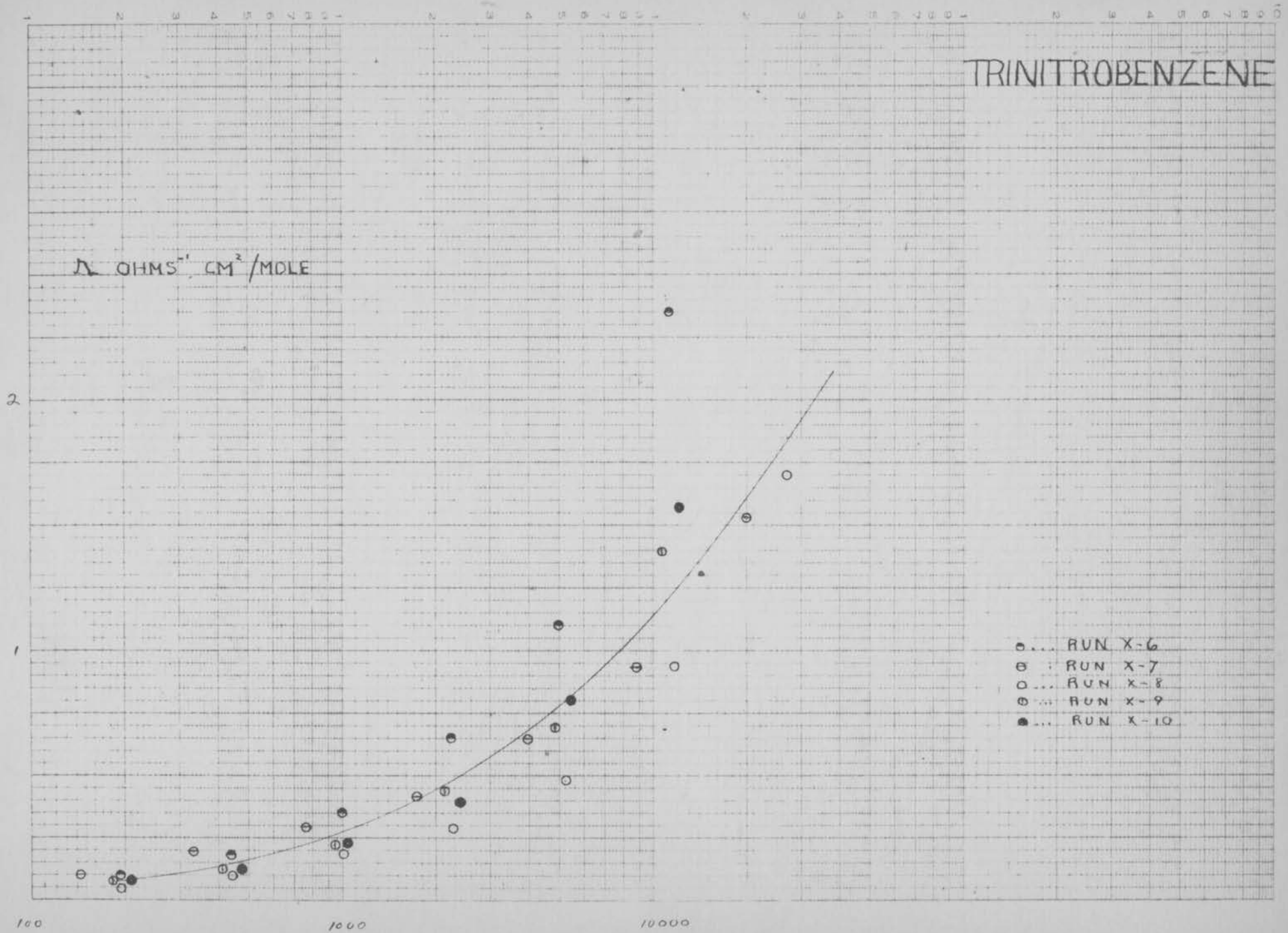
TRINITROBENZENE
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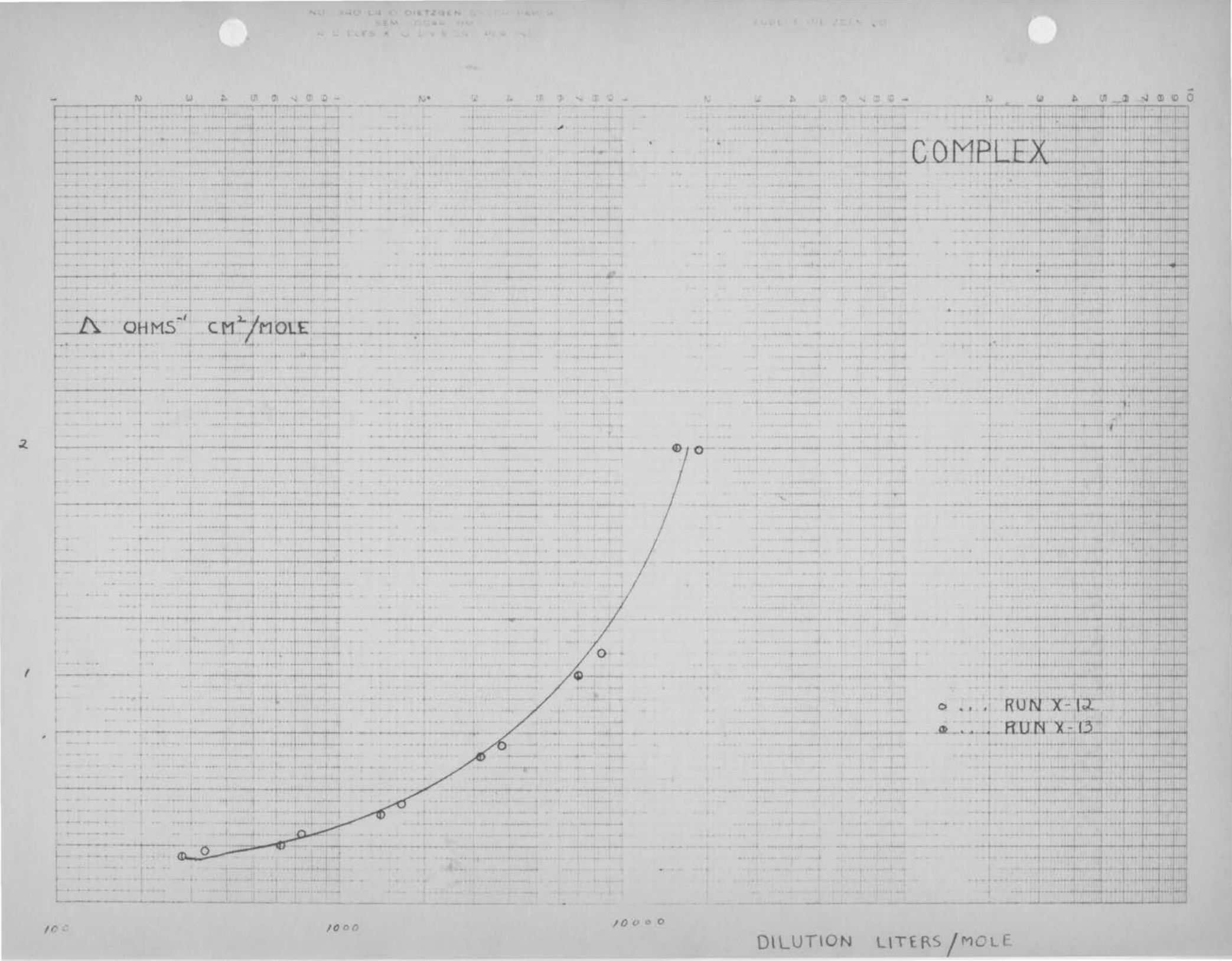
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10000
DILUTION LITERS/MOLE

Data

Anthracene

Run X-1, cf. Table VI.

In this run, the material was used as supplied without further purification. The sample was pumped for a total time of twenty-five minutes at the same time as the whole system to the sulfur dioxide tank was pumped. The material was not pumped for a longer period of time because it was thought the anthracene would sublime in part and cause errors in dilution values. The solution was bright yellow in agreement with Walden's observation (19). For these measurements a resistance of 10,000 ohms was put in parallel with the cell for the first reading; then 11,000 ohms were used. The cell was allowed to stay in the thermostat three to five minutes after dilution before each initial reading to allow for temperature equilibrium. After this initial reading, points were taken at five minute intervals until a constant reading was obtained.

Run X-2, cf. Table VII.

The material used in this run was that obtained by vacuum sublimation of the commercial product in a cold finger apparatus of standard type at a pressure of one millimeter, m.p. 215.4-C.

Run X-3, cf. Table VIII.

At this time it was felt that lack of pumping in the case of anthracene might be responsible for spurious results; i.e., the presence of varying amounts of water and other volatile impurities would lead to

non-reproducible results. Accordingly, the sample of vacuum sublimed material was pumped for twelve hours in an ice-water slush. The vacuum was .009 mm.; there was no evidence of sublimation.

Run X-4, cf. Table IX.

A sample from the same batch as that used in the preceding run was used; total pumping time was twelve hours at a pressure of .02 mm.* in an ice-water slush. As in the preceding run, there was no evidence of sublimation.

* At the close of the work reported in this thesis a new McCleod gage, of better construction than that used in these measurements, was put on the line. It was found that the line gave a pressure better than one micron. Since it was known that the old gage was of faulty construction, it was concluded that the pressures given in this thesis should read .001 mm. or less.

TABLE VI- Run X-1

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x10^{5}	Λ ohms^{-1} cm^{2}* /mole
.120	79.9	142	.098
.118	182.9	91	.152
.113	418.7	71	.266

Weight of sample-.0957 grams k solvent 10^{-5} x 7.6 ohms^{-1} cm.$^{-1}$

TABLE VII-Run X-2

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x10^{5}	Λ ohms^{-1} cm.^{2}/mole
.118	83.2	77	.058
.118	188.4	60	.099
.113	426.3	50	.183
.118	964.4	42	.337
.128	2180.8	33	.567
***#	4931.5	31	1.18
***	11159	27	2.23
***	25224	25	4.54

Weight of sample-.09095 grams k solvent 10^{-5} x 7.1 ohms^{-1} cm.$^{-1}$

*All values of Λ are corrected for the solvent conductance; values of k are uncorrected for the solvent conductance

Temperature recordings are lacking as the Beckmann was broken.

TABLE VIII-Run X-3

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x 10^{5}	Λ ohms^{-1} cm.^{2}/mole
.080	63.5	49	.028
.085	144.2	32	.040
.085	327.2	17	.043
.090	742.3	19	.112
.090	1683.8	16	.205

Weight of sample-.11962 grams k solvent 10^{-5}x3.8 ohms^{-1} cm.$^{-1}$

TABLE IX-Run X-4

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$x10^{5}	Λ ohms cm.^{2}/mole
.090	85.6	24	.016
.080	194.6	20	.027
.125	442.2	16	.048
.115	1004.4	13	.079
.105	2280.9	12	.157

Weight of sample-.08879 grams k solvent 10^{-5}x5.1 ohms^{-1} cm.$^{-1}$

Note: Data for these two runs does not extend to higher dilutions because the values of k were extremely low and the conductance of the solvent was 23% of that of the compound in table VIII and 42% in table IX at the last points.

Trinitrobenzene

Run X-5, cf. Table X.

The material was recrystallized from 95% ethyl alcohol; m.p. 122.2-122.4° C. The sample was pumped for a period of forty-eight hours at a pressure of .01 mm. The solution of this compound in liquid sulfur dioxide is colorless, except at very high concentrations, e.g., a faint yellow color was observed initially with the first few drops of solvent.

Run X-6, cf. Table XI.

At this time it was thought that trinitrobenzene might contain some alcoholate of recrystallization and accordingly a weighed sample was put in a drying pistol containing $CaCl_2$ and heated to 100° C.; the vacuum was supplied by an aspirator. At the end of eight hours a 2.2 mg. loss in weight was observed. At the end of seven more hours an additional 2.98 mg. was lost. A mechanical pump was than used as a source of vacuum and at the end of six hours most of the sample had gone over into the cold trap. Previous loss in weight could therefore be attributed to sublimation as well as loss of alcohol. This suggested a method of purifying trinitrobenzene and accordingly about a gram of recrystallized material was vacuum sublimed, the vacuum being supplied by the line (.02 mm.)* The material was a yellowish white powder m.p. 123.2-123.3° C. as compared with the light brown recrystallized product. This vacuum

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cf. footnote, page 21.

sublimed material was employed in this run. The sample was not pumped over an hour since it was discovered that the material sublimed under a vacuum. Of course, heat was applied during the sublimation but it is conceivable that under line vacuum some sample might sublime at room temperature. The sample was maintained at -20° C. during the one hour it was pumped.

Run X-7, cf. Table XII.

This sample was from the same batch as that of the preceding run; the conditions were duplicated as much as possible.

Run X-8, cf. Table XIII.

The sample used was from the same batch as those of the two preceding runs; conditions were the same.

Run X-9, cf. Table XIV.

The sample used was from the same batch as those of the three preceeding runs. Before doing this run the balance used in the weighings was checked against another balance and found to be not in error. The cell constant was redetermined and found to check with the previous value.

Run X-10. cf. Table XV.

A fresh sample of trinitrobenzene was vacuum sublimed on the line and used in this run. It was felt that in the case of trinitrobenzene as well as in that of anthracene lack of pumping might lead to erroneous results and this sample was pumped for thirteen hours in an ice-water slush.

TABLE X-Run X-5

Temp.° C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ $\times 10^{8}$	Λ ohms^{-1} cm.^{2}/mole
.127	197.5	46.8	.070
.112	451.9	52.6	.187
.112	1034.6	36.5	.261
.122	2367.2	30.3	.452
.102	5416.2	24.3	.709
.102	12380	23.2	1.48
.102	28345	17.7	1.84

Weight of sample--.04638 grams k solvent $10^{-8} \times 11.2$ ohms^{-1} cm.$^{-1}$

TABLE XI-Run X-6

Temp.° C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ $\times 10^{8}$	Λ ohms^{-1} cm.^{2}/mole
.152	194.9	58.9	.103
.102	442.2	47.4	.184
.212	1003	40.3	.347
.087	2256.3	34.4	.647
.142	5075.7	27.5	1.10
.122	11423	26.4	2.36
.122	25971	20.4	3.81

Weight of sample--.04646 grams k solvent $10^{-8} \times 5.7$ ohms^{-1} cm.$^{-1}$

TABLE XII-Run X-7

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm^{-1} x10^{8}	Λ ohms^{-1} cm.^{2}/mole
.132	146.6	93.9	.116
.132	353.3	72.3	.192
.137	757.2	53.5	.296
.142	1718.3	38.9	.420
.142	3902.1	31	.647
.147	8861.4	25	.939
.322	20147	22	1.53

Weight of sample-.06189 grams k solvent 10^{-8} x14.4 ohms^{-1} cm.$^{-1}$

TABLE XIII-Run X-8

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm^{-1}x10^{8}	Λ ohms^{-1} cm.^{2}/mole
.127	193.3	37	.060
.142	440.6	29	.101
.137	1004.2	25	.186
.142	2288.5	18	.286
.352	5209.3	15	.458
.352	11871	14	.937
.270	27021	12	1.70

Weight of sample-.04715 grams k solvent 10^{-8} x 6.4 ohms^{-1} cm.$^{-1}$

TABLE XIV-Run X-9

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm^{-1} x10^{6}	Λ ohms^{-1} cm^{2}/mole
.102	185.27	45	.071
.105	417.61	38	.129
.095	941.68	30	.220
.100	2123.4	28	.445
.095	4787	21	.694
.360	10786	20	1.39

Weight of sample-.04860 grams K solvent $10^{-6} \times 7.3$ ohms^{-1} cm.$^{-1}$

TABLE XV- Run X-10

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x 10^{6}	Λ ohms^{-1} cm^{2}/mole
.145	93.5	51	.043
.100	210.4	40	.073
.105	474.8	32	.128
.120	1067.6	27	.234
.080	2399.3	22	.407
.102	5394.9	20	.809
.110	12116	18	1.57

Weight of sample-,09615 grams k solvent 10×5^{-6} ohms^{-1} cm.$^{-1}$

Complex

Run X-II, cf. Table XVI.

The materials used to prepare the complex were those supplied and used without further purification. The sample was not pumped as it was felt some loss would be incurred through sublimation.

Run X-12, cf. Table XVII.

This sample and the one used in the following run were made from vacuum sublimed materials. Also it occurred to the author that, as in the case of the components, lack of pumping would lead to erroneous results, and accordingly this sample was pumped a period of twenty-two hours in an ice-water slush at a pressure of .02 mm.

Run X-13, cf. Table XVIII.

This was an effort to duplicate the results of the last run; the sample was pumped $14\frac{1}{2}$ hours in an ice-water slush at a pressure of .007 mm.

Solvent

At this time it was thought that determination of the values of k for the solvent alone might prove interesting and this was done. The dilutions were made pouring all the solvent over each time. The results are shown in Table XIX.

TABLE XVI-Run X-11

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm^{-1} x10^{5}	Λ ohms^{-1} cm^{2}/mole
.123	638.2	155	.98
.123	1451.7	108	1.55
.117	3300.7	92	3.00
.123	7502.7	99	7.35
.108	17034	71	12.09
.103	38674	53	20.11
.103	88014	41	36.08

Weight of sample-.02614 k solvent 10^{-5} x1 ohms^{-1} cm.$^{-1}$

TABLE XVII-Run X-12

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm^{-1} x10^{5}	Λ ohms^{-1} cm^{2}/mole
.105	330.4	76	.232
.080	741.5	47	.307
.095	1662.9	32	.440
.090	3731.9	24	.690
.090	8369.3	19	1..2
.092	18840	16	1.97

Weight of sample-.04977 grams k solvent 10^{-5} x 5.5 ohms^{-1} cm.$^{-1}$

TABLE XVIII-Run X-13

Temp.° C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x 10^6	Λ ohms^{-1} cm.^{2}/mole
.082	280.1	71	.198
.080	626.2	42	.263
.105	1400.4	27	.378
.085	3127.9	20	.656
.095	6986.4	15	1.04
.085	15623	13	2.03

Weight of sample-.05851 k solvent 10^6 x 2.9 ohms^{-1} cm.$^{-1}$

TABLE XIX

Temp. C.	# distillations	k, ohms^{-1} cm.$^{-1}$ x 10^6
.070	0	41
.050	1	7.7
.113	2	4.1
.090	3	4.7
.110	4	3.5
.045	5	2.3
.050	6	2.1
.090	7	1.3
.032	8	1.4

ABSTRACT

It has been proposed in the literature (18) that complexes between aromatic nitro compounds and aromatic hydrocarbons are the result of an electron transfer from the hydrocarbon to the nitro compound with the resultant formation of ions. The conductivity of such a complex, that between anthracene and trinitrobenzene, was measured in liquid sulfur dioxide to test this hypothesis. The conductivity of the complex was found to be the sum of the two components, which indicated no ions present in solution and pointed to the non-existence of the complex in solution. Spectral work done by R. W. Weston (20) supports the contention that the complex does not exist in solution. Ultraviolet absorption spectrum of the complex in liquid sulfur dioxide was the sum of the spectra of the two components.

BIBLIOGRAPHY

1. G. M. Bennett and G. H. Willis, J. Chem. Soc., 1929, 256.
2. G. Briegleb in "Zwischenmolekulare Krafte," G. Braun, Karlsruhe, pp. 12-15 (1949).
3. Ref. 2, pp. 54-57.
4. G. Briegleb and J. Kambeitz, Z. physik. Chem., B27, 11 (1934).
5. G. Briegleb and T. Schachowskoy, ibid., B19, 255 (1932).
6. L. Fieser, "experiments in Organic Chemistry", D. C. Heath and Co., Boston, 2nd edition, p. 344 (1941).
7. H. Glazer, A. M. Thesis, Boston University, p. 32 (1950).
8. ibid., pp. 22-27.
9. E. Hertel and H. Kleu, Z. physikal. Chem. B11, 59 (1930).
10. R. F. Hunter, A. M. Qureishy, and R. Samuel, J. Chem. Soc., 1936, 1576.
11. R. C. Jones and M. B. Neuworth, J. Am. Chem. Soc., 66, 1947 (1944).
12. Lange, "Handbook of Chemistry", Handbook Publishers Inc., Sandusky, 288 (1941).
13. Lefevre and Lefevre, J. Chem. Soc., 1935, 957.
14. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, 2nd edition, pp. 33-40 (1940).
15. H. M. Powell and G. Huse, Nature, 144, 77 (1939).
16. H. M. Powell, G. Huse, and P. W. Cooke, J. Chem. Soc., 1943, 153.

17. H. M. Powell and G. Huse, ibid., 435.

18. W. S. Rapson, D. H. Saunder, and E. T. Stewart, ibid., 1946, 1110.

19. Sudborough, J. Chem. Soc., 1916, 109, (1939).

20. P. Walden, Z. physikal. Chem., 43, 385 (1903).

21. J. Weiss, J. Chem. Soc., 1942, 245.

22. J. Weiss, Nature, 147, 512 (1941).

23. R. E. Weston, private communication.

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PART II

TRIPHENYLCARBINOL

Introduction

Walden (6), in 1902, measured the conductivity of triphenylcarbinol in liquid sulfur dioxide and obtained date indicating that the material showed a large drift at the first point; i. e., the resistance which was initially observed slowly decreased until it reached a limiting value after about twelve hours. On the other hand, Glazer (1), on the same compound, demonstrated the lack of a drift. Also, the values of the equivalent conductance obtained by Glazer seemed high in comparison with those of triphenylchloromethane, cf. Fig. 6. In general, there are two effects to be considered in comparing conductances of different colutes: the degree of dissociation, i. e., the number of ions; and the mobilities of the ions. Triphenylchloromethance would be expected to have a greater conductance than triphenylcarbinol inasmuch as the chlorine, being more electronegative than the hydroxyl group, would facilitate ionization, and the degree of dissociation would be correspondingly greater. At lower dilutions, this effect would be more important. The effect of the different ionic mobilities becomes more important as the dilution is increased, since at

infinite dilution the total charge of the ions is the same for equivalent solutions. At the present time, however, there is no data available in the literature for the mobilities of these ions in liquid sulfur dioxide so that a comparison of the curves from this point of view is not possible. However, referring to Figure 6, on the basis of the degree of dissociation it would appear that the differences between tri-phenylcarbinol and triphenylchloromethane at lower dilutions are not as striking as one might expect from general considerations.

Glazer (1) also measured the conductivity of tris-p-tertiary butyl triphenylcarbinol and found that he could not obtain reproducible results. In a number of runs on this compound the values for the equivalent conductances were found to be lower each time the compound was investigated.

The purpose of this research, therefore, was twofold: to measure the conductivity of the substituted carbinol in order to obtain reproducible results: and to resolve the discrepancy existing between the work of Walden (6), on the one hand, and Glazer (1), on the other.

Experimental

The triphenylcarbinol (triply recrystallized) used for the first four runs, X-L, to X-4, was supplied by Dr. Lichtin and was drawn from the same sample as that used by Glazer (1), m.p. 163.4° corrected; material used for the last two runs,

X-5 and X-6, was the white label commercial product of Eastman Kodak Company, recrystallized from 95% ethyl alcohol. The recrystallized material was pumped overnight in a vacuum desiccator to remove any remaining traces of alcohol; m.p. 163.2 - 163.3° corrected.

The samples were pumped for from twelve to twenty hours before admission of SO_2. The solution of triphenylcarbinol in liquid sulfur dioxide is bright yellow; the color is observed immediately. The experimental technique was almost identical with that employed by Glazer (2). The data are presented in Tables I-XI; the drift for each run is recorded in a table preceding the conductivity data for that run.

Results and Discussion

The data for triphenylcarbinol contrast sharply with those obtained by Glazer (3), but agree with those of Walden (6), in that a sizable drift was observed at the initial concentration, cf. Table I, Run X-1. Moreover, the values of the equivalent conductances in Table II are, in general, about 50% lower than those obtained by Glazer. There was no apparent reason for the discrepancy between the work done by Glazer and that of this author; the measurements were performed with the same apparatus and technique, and with material from the same source.

Run X-2, cf. Tables III-IV was an attempt to reproduce the results of Run X-1. As can be seen in the tables, the conductance at the initial concentration still continued to drift in a regular fashion and at all dilutions was still at least 50% below that obtained by Glazer. The percent deviation between Runs X-1 and X-2 varied from 0 to 20%, the two curves crossing at about 7500 liters per mole. At higher dilutions the curve obtained by Glazer crossed these curves. These data, as well as those of Runs X-3 and X-4 are graphically presented in Figure 6.

Runs X-3 and X-4, cf. Tables V-VIII, were additional attempts to reproduce results and, as shown on the curve, the values were in the same range, with deviations up to 10%, all of these values being 50% lower than those of Glazer at lower

dilutions, and crossing over at more dilute points.

At this time a run was made on triphenylchloromethane in a concentration range of 246 to 169,000 liters per mole to establish with certainty that the anomalous results were due to the compound and not due to errors in technique or faulty equipment. The values obtained fell exactly on the smoothed data curve obtained by Lichtin (5). There was no drift observed, which agreed with the data of Lichtin (5), and Glazer (3).

The material used in run X-5 was taken from another source to test whether or not the difference was a function of the sample used, but as can be seen in Tables IX and X, the drift was still observed as well as the lower conductance.

The technique and apparatus employed by both workers was carefully re-examined and only one difference was noted: Glazer had used as drying agents for SO_2 in the vacuum line one column of $CaCl_2$ and one column of Drierite ($CaSO_4$). The present work on triphenylcarbinol was done with magnesium perchlorate and indicating Drierite in both columns.

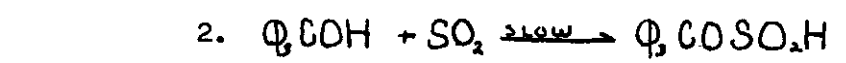
There are three phenomena to be accounted for: (1) the presence of the drift, (2) the lower conductivities at the higher concentrations, and (3) the lack of reproducibility.

Hammett (4) has interpreted Walden's results (6) as being due to a slow equilibrium ionization of triphenylcarbinol:

$$1.\quad \Phi_3COH + SO_2 \overset{\text{slow}}{\rightleftharpoons} \Phi_3C^+ + HSO_3^-$$

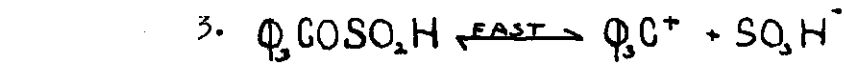
This would explain the drift at the first point but would not

explain the lack of drift at subsequent dilutions. This drift at the first point only may possibly be explained by means of a two-step mechanism. The first step may be a slow and complete formation of some intermediate compound such as the following:



2. $\phi_3COH + SO_2 \xrightarrow{\text{SLOW}} \phi_3COSO_2H$

The second step may be a fast equilibrium ionization:

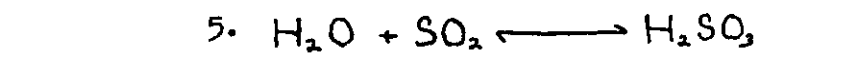


3. $\phi_3COSO_2H \xrightleftharpoons{\text{FAST}} \phi_3C^+ + SO_3H^-$

The SO_3H^- reacts further to produce H_2SO_3:

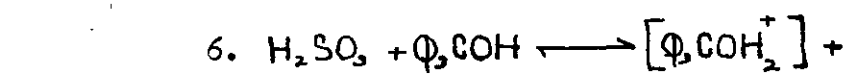
4. $2HSO_3^- \longrightarrow SO_3^= + 2H_2SO_3$

The presence of trace amounts of some impurities to account for the lack of reproducibility in the rate of ionization as well as in the equilibrated systems is assumed. The purity of the SO_2 supplied Part I, (7) is such that water seems the most logical imourity. Thus a set of reactions can be set up as follows:

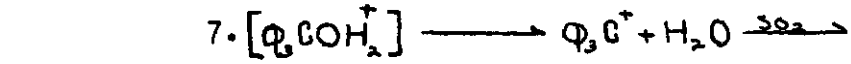


5. $H_2O + SO_2 \longrightarrow H_2SO_3$

The H_2SO_3 formed then reacts as an acid:



6. $H_2SO_3 + \phi_3COH \longrightarrow [\phi_3COH_2^+] + HSO_3^-$



7. $[\phi_3COH_2^+] \longrightarrow \phi_3C^+ + H_2O \xrightarrow{\text{SOL}} H_2SO_3$

This would explain the lack of reproducibility in the rate of ionization inasmuch as the rate in this set of reactions depends on the water concentration, so that varying amounts of water would

give rise to varying rates.

The presence of varying amounts of water can also explain the difference in conductance values at corresponding dilutions for each run, as well as the lower conductances obtained by this author relative to those of Glazer. In the presence of more H_2O the equilibrium of step 5 is driven to the right with the result that at equilibrium , the concentration of H_2SO_3 and thus the values of the conductivity (by steps 6 and 7) would be greater than in a drier medium. The difference in the equilibrium values of the conductivities may be due to the influence of H_2O on equation 4 since both the degree of dissociation and the mobility will depend on relative amounts of HSO_3^- and $SO_3^=$. This explanation of the higher values obtained by Glazer seems reasonable in view of the fact that $CaCl_2$ is a far less efficient drying agent than magnesium perchlorate.

The above reasoning could also be applied to explain the lack of a drift in Glazer's work since a comparatively high concentration of water would result in a concentration of H_2SO_3 high enough to effect the ionization of ϕ_3COH (by steps 6 and 7). The mechanism outlined in steps 1 and 2 would thus be nullified. An alternative explanation might be a reaction at the drying tube as follows:

$$8.\quad H_2O + CACL_2 + SO_2 \longrightarrow CASO_3 + 2HCL$$

According to Hammett (4) triphenylcarbonium ion may be produced

by the action of a strong acid on triphenylcarbinol; and the HCl produced in this reaction may be sufficient to account for the lack of a drift.

To test the validity of the assumption that the difference in values obtained by Glazer and the present author was a result of the change in drying agent, the magnesium perchlorate was removed from the line and calcium chloride substituted in its place; the measurements were carried out in the same manner as before. No drift was observed in this run, X-6, and, as seen in Table XI, the values for Λ are about 50% higher than those obtained by this author previously; i. e., they agree rather closely with those obtained by Glazer. There can be little doubt, therefore, that the behavior of triphenylcarbinol is a function of the drying agent used in these two cases.

It was felt that an interpretation of the kinetics of the reaction might prove instructive, and the conductivity data was adapted for this purpose in the following manner. If the reaction proceeds in the manner postulated, an examination of the kinetics should lead to a first order reaction since the solvent is present in such great excess in the rate determining step. To arrive at the concentrations of unreacted triphenylcarbinol the specific conductance of the first few points was plotted against dilution for each run (cf. Figures 1a, 2a, 3a, 4a, and 5a). Then to obtain the dilution of triphenylcarbonium ion (which is equivalent to the dilution of reacted triphenyl-

carbinol by steps 1 and 2) at any time during the drift period, it was necessary only to look up the specific conductance at any time in the drift tables and find its corresponding dilution on the curve. The dilution was that of the intermediate present and the concentration of intermediate was then obtained by evaluation of the reciprocals of the graphically determined dilutions. The concentration of unreacted triphenylcarbinol was then calculated by subtraction of the respective values of the concentration of intermediate from the initial concentration of unreacted triphenylcarbinol; the latter was independently determined from a knowledge of the weight of the sample and the volume of the solution employed. These concentration values were then used to plot rate curves, cf, Figures 1b, 2b, 3b, 4b, and 5b.

With the exception of Figure 1b, the reaction follows first order kinetics for the first three hundred minutes, at which time the points start to deviate from the line. This behavior is typical of complex systems in which there is more than one competing reaction. In this case, the rate determining step (2) is first order since the solvent is present in such great excess. After about three hundred minutes, the catalytic effect of step (6), using H_2SO_3 formed in (7), is enough to cause deviations from simple first order kinetics.

The suggested mechanism accounts for all the data available on this system at the present time; the drift (steps 1 and 2),

the lack of reproducibility (steps 5, 6, and 7), the deviation from first order kinetics (steps 5, 6, and 7, and the reverse of step 3), and the lower conductance values (steps 8 and 9). This mechanism attempts to analyze the data in a qualitative fashion only, and is meant to serve as a working hypothesis for future experimental work; it might prove to be only partly true, or it might be completely erroneous.

Further work on this problem might take several courses. Direct analysis of the solution for Cl^- is not feasible as it is probably present in amounts too small to be detected. A series of measurements might be undertaken with magnesium perchlorate as the drying agent and some controlled source of moisture to determine if the presence or absence of water is a factor. Or perhaps the sulfur dioxide could first be passed through a column of magnesium perchlorate with more or less assurance of the absence of moisture and then through a fresh column of calcium chloride since it is conceivable that the solvent is extracting something from the drying agent which might cause the observed discrepancy. (The drying agents employed were the standard commercial products and not highly purified.) It might be feasible to admit molecular HCl to the system (using magnesium perchlorate as the drying agent) and observe whether a drift was obtained or not.

TRIS-p-TERTIARY BUTYL TRIPHENYLCARBINOL

Experimental.

The material was supplied by Dr. Lichtin, m. p. 216.2-216.9° C. The experimental technique was identical with that employed by Glazer (2).

Results and Discussion.

As stated in the introduction, the purpose of this part of the research was to investigate the descending conductivity values of tris-p-tertiary butyl triphenylcarbinol. The results are presented in Tables XII and XIII, from which it is seen that this investigator found the same phenomenon of decreasing conductivity values for each run. At this point, work was begun on triphenyl carbinol, and it is felt that in view of the small amount of work done on this substituted carbinol, no conclusions can be drawn with any degree of certainty.*

* Magnesium perchlorate was used as the drying agent in the work done on this compound.

TABLE I - Run K-1

Time (minutes)	Resistance (ohms)	$kx10^6$ ohms^{-1}/cm.$^{-1}$	Dilution $\phi_3 C^+$ (dilution reacted $\phi_3 CrN$ liters/mole)	Concentration Reacted $\phi_3 Cr(x10^3)$ moles/liter	Concentration ($x10^3$)* Unreacted $\phi_3 CrN$ moles/liter
2	10679	20.8	820	1.22	0.28
7	10489	21.2	785	1.27	0.23
10	10445	21.5	780	1.28	0.22
13	10454	21.5	780	1.28	0.22
18	10418	21.5	780	1.28	0.22
21	10415	21.5	780	1.28	0.22
28	10396	21.4	775	1.29	0.21
45	10336	21.5	770	1.30	0.20
70	10290	21.6	765	1.31	0.19
190	10068	22.1	750	1.37	0.15
250	9985	22.2	725	1.38	0.12
481	9821	22.6	700	1.45	0.07
998	9659.5	23.1	670	1.49	0.01
1022	9643.5				
1040	9642.8				
1060	9637.0				
1085	9639.8				
1208	9638.2				
1577	9636.0				

The Time given in the Tables is the time elapsed since the cell was first put in the thermostat. The stoichiometric dilution at this first point was 667.9 liters/mole.

* The concentration given here are those calculated by means of the method described on pages 8 and 9.

Initial con'n ($x10^5$) 1.50 mole/liter.

TABLE II- Run X-1

Temp. C.	Dilution, lit./mole	k solution, $ohms^{-1}\ cm^{-1} \times 10^{6}$	$ohms^{-1}\ cm.^{2}/mole$
.100	667.9	23.08	15.34
.110	1504.4	14.44	21.57
.083	3385.9	8.98	30.06
.082	7616.9	5.92	44.33
.100	17134	4.58	76.76
.100	38544	3.75	140.68
.072	86708	2.07	170.81
	195058	1.06	187.25

Weight of sample .01646 grams k solvent $.098 \times 10^{-6}\ ohms^{-1}\ cm^{-1}$.

TABLE III - Run K-8

Time (minutes)	Resistance (ohms)	$kx10^6$ ohms^{-1} cm^{-1}	dilution ϕ_3C^+ (dilution reacted ϕ_3CON, liters/mole)	Concentration Reacted ϕ_3CON ($x10^3$) moles/liter	Concentration ($x10^3$) Unreacted ϕ_3COH moles/liter
5	10980	20.5	495	2.02	1.67
19	10747	20.7	482	2.07	1.62
57	10428	21.5	460	2.17	1.52
124	9910	22.4	422	2.37	1.32
189	9438	23.5	392	2.55	1.14
251	9056	24.6	365	2.74	0.95
551	8529	26.1	330	3.05	0.66
1385	7569.0	30.2	271	3.69	0.00
1465	7565.0				
1519	7560.7				

initial conc'n ($x10^3$) 3.69

The time from when the sulfur dioxide was admitted to the cell to when the cell was put in the Thermostad was 95 minutes. The dilutions at this final point was 270.40 liters per mole.

TABLE IV - Run X-2

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x10^{6}	Λ ohms^{-1} cm.^{2}/mole
.082	270.8	30.20	8.14
.082	614.6	17.78	10.85
.115	1395.8	10.76	14.85
.070	3176.5	7.93	24.73
.058	7193.2	6.06	42.72
.070	16316	5.32	86.80
.050	37009	3.82	136.93
.095	83887	1.86	156.03

Weight of sample .04090 grams k solvent .121x10^{-6} ohms^{-1} cm.$^{-1}$

TABLE V - Run X-5

Time (minutes)	Resistance (ohms)	$k \times 10^{6}$ ohms^{-1} cm.$^{-1}$	dilution φ_{C^+} (dilution reacted $\varphi_{s,con}$) liters/mole	Concentration Reacted $\varphi_{s,con}$ ($\times 10^{3}$) moles/liter	Concentration Unreacted $\varphi_{s,con}$ ($\times 10^{3}$) moles/liter
3	10560	21.1	440	2.27	2.29
13	10144	21.9	408	2.45	2.11
28	10052	22.1	402	2.49	2.07
73	9780	22.7	382	2.62	1.94
136	9401	23.6	355	2.82	1.74
299	8463	26.3	295	3.39	1.17
539	7285.5	30.5	238	4.20	0.36
684	6976.9	31.9	228	4.39	0.17
1259	6672	33.3	220	4.55	0.01
1355	6662.6	33.5	220	4.55	0.01
1357	6662				
1372	6661.6				
1388	6660.4				

initial con'n ($\times 10^{3}$) $\frac{1}{219.40}$ 4.56 mole/liter.

The Time from when the sulfur dioxide was admitted to the cell to when the cell was put in the thermostat was 75 minutes. The dilutions at this final point was 219.40 liters per mole.

TABLE VI - Run X-3

Temp. °C.	Dilution, lit/mole	k solution, ohms^{-1} cm.$^{-1}$ x10^{6}	Λ ohms^{-1} cm.^{2}/mole
.088	219.4	33.41	7.31
.030	495.3	19.98	9.85
.063	1117.6	13.06	14.50
.090	2521.9	9.73	24.33
.032	5690.7	8.41	47.40
.062	12838	7.57	96.15
.030	28969	4.72	134.4
.050	65354	2.48	156.8
.032	147369	1.25	172.4

Weight of sample- .05023 grams

k solvent .08x10^{-6} ohms^{-1} cm.$^{-1}$

TABLE VII -Run K-4

Time (minutes)	Resistance (ohms)	$kx10^6$ ($ohms^{-1}$ cm^{-1})	Dilution ϕ_{SO_2} (dilution reacted ϕ_{SO_2} liters/mole	Concentration Reacted ϕ_{SO_2} ($x10^3$) moles/liter	Concentration Unreacted ϕ_{SO_2} ($x10^3$) mole/liter
5	11610	19.2	465	2.15	1.97
9	11318	19.8	418	2.39	1.75
58	11002	20.4	412	2.45	1.69
66	10988	20.7	408	2.45	1.67
144	10638	22.0	372	2.69	1.45
197	9988	25.0	360	2.78	1.34
256	9883	24.1	332	3.01	1.11
315	9880	25.0	318	3.14	0.98
498	9758	27.7	280	3.57	0.55
586	7688.0	28.5	272	3.68	0.44
1194	7608.0	30.0	260	3.85	0.27
1201	7608.8				
1209	7608.8				
1259	7608.8				
1278	7608.8				
1295	7405.4				

Initial con'n ($x10^3$) $= \frac{1}{242.7} = 4.12$ mole/liter

The Time from when the sulfur dioxide was admitted to the cell to when the cell was put in the thermostat was 55 minutes. The dilution at this first point was 242.7 mole/literϕ.

TABLE VIII- Run X-4

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x 10^{6}	Λ ohms^{-1} cm.^{2}/mole
.023	242.7	34.04	8.23
.030	552.5	17.16	9.42
.010	1257.8	10.16	12.64
.065	2863.1	6.92	19.49
.060	6517.2	5.91	37.79
.025	14824	5.76	83.75
.093	33720	4.19	137.57
.025	76702	2.23	162.60
.045	174473	1.11	174.47

Weight of sample-.04574 grams

k solvent .111x10^{-6} ohms^{-1} cm.$^{-1}$

TABLE IX - Run L-5

Time (minutes)	Resistance (ohms)	$kx10^6$ (ohm^{-1} cm^{-1})	Dilution ϕC^+ (dilution reacted $\phi_3 CON$) liters/mole	Concentration Reacted $\phi_3 Ca$ ($x10^3$) moles/liter	Concentration Unreacted $\phi_3 Co$ ($x10^3$) moles/liter
4	15180	16.9	540	1.65	1.41
14	15074	17.1	535	1.67	1.39
35	12953	17.2	530	1.69	1.57
46	12868	17.3	525	1.90	1.36
169	12067	18.4	480	2.06	1.18
171	12035	18.5	475	2.11	1.15
292	11256	19.8	420	2.38	0.88
514	9966	22.4	370	2.70	0.56
550	9917	22.4	370	2.70	0.56
1242	8599.0	22.8	370	2.70	0.56
1248	8598.0				
1294	8584.7				
1314	8579.0				
1418	8556.4				
1452	8554.3				
1460	8548.8				

initial con'n ($x10^3$) $\simeq \frac{1}{307.1}$ = 3.26 mole/liter

The Time from when the sulfur dioxide was admitted to the cell to when the cell was put in the thermostat was 61 minutes. The dilution at this first point was 307.1 liters/mole.

TABLE X -Run X-5

Temp. °C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x10^{6}	Λ, ohms^{-1} cm.^{2}/mole
-.040	307.1	25.88	7.90
-.037	696.6	14.32	9.86
-.032	1580.2	8.33	12.91
.012	3584.3	6.24	21.79
0	8125.4	5.86	46.31
.020	18409	5.46	97.56
.020	41707	3.65	145.55
.010	94436	1.93	167.15

Weight of sample-.03603 grams

k solvent .16x10^{-6} ohms^{-1} cm.$^{-1}$

TABLE XI- Run X-6

Temp. C.	Dilution, lit./mole	k solution, ohms^{-1} cm.$^{-1}$ x 10^6	Λ ohms cm.^{2}/mole
.025	282.1	59.13	16.64
.022	639.3	41.31	26.30
.032	1448.4	31.67	45.63
.010	3281.5	20.83	67.82
.032	7430.2	12.43	91.16
.030	16833	7.13	117.32
.012	38114	3.92	143.30
.012	86290	2.11	168.26

Weight of sample-.03917 grams k solvent .16x10^{-6} ohms^{-1} cm.$^{-1}$

Readings during equilibration of first point

Time*	Resistance, ohms
11:52	3910
11:57	3772
12:03	3764.9
12:12	3764.9
1:14	3761.0

* The cell was put in the thermostat at 11:50.

TABLE XII

Tris-p-tertiary butyl triphenylcarbinol

Temp.° C.	Dilution, lit./mole	k solution x10^{6} ohms^{-1} cm.$^{-1}$	Λ ohms^{-1} cm.^{2}/mole
.103	340.14	136.2	46.29
.100	772.44	65.76	50.71
.090	1753.7	31.21	54.55
.095	3981.6	14.61	57.77
.080	9035.6	6.96	61.98

Weight of sample-.05366 grams k solvent .116x10^{-6} ohms^{-1} cm.$^{-1}$

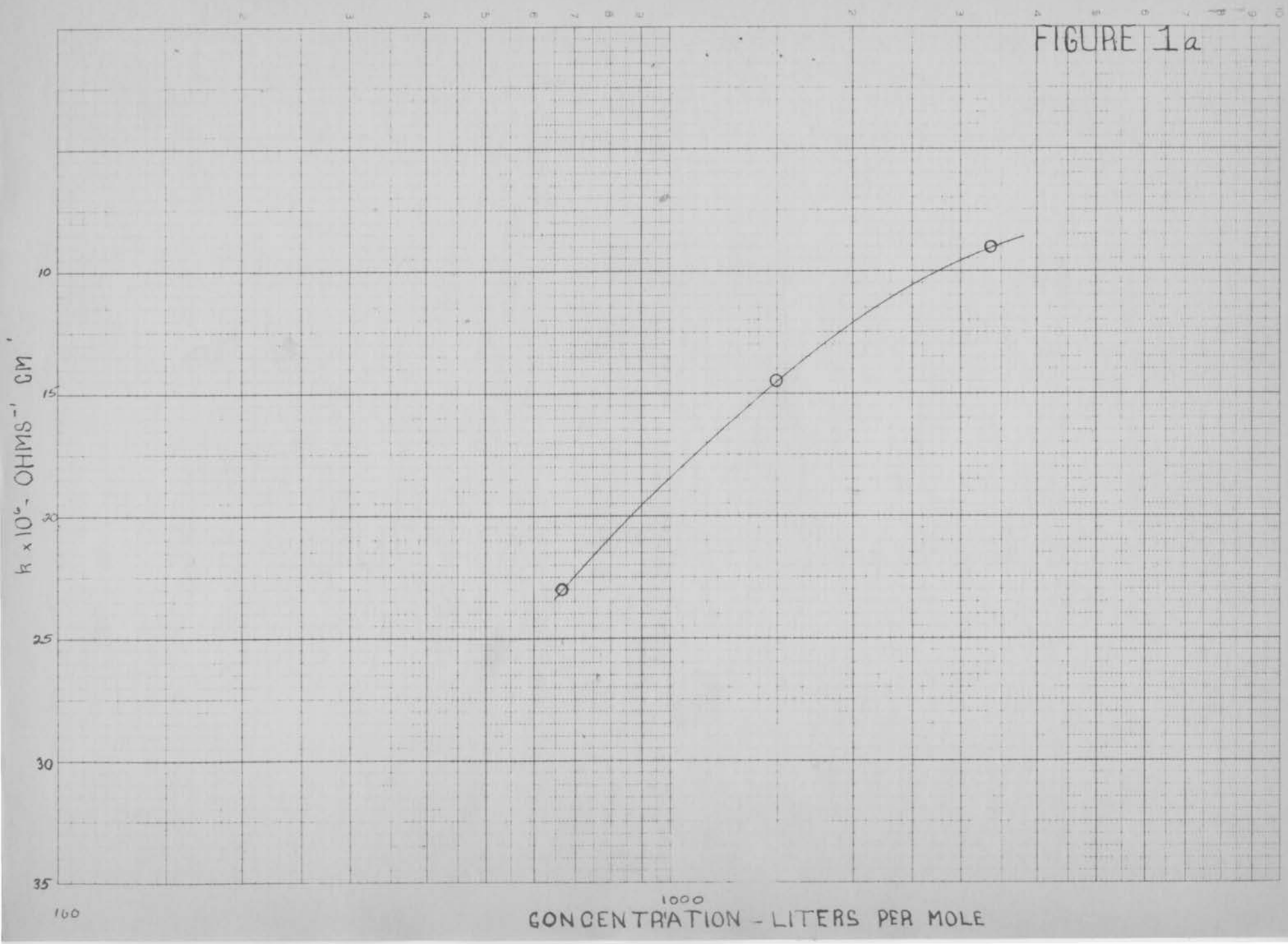
TABLE XIII

Tris-p-tertiary butyl-triphenylcarbinol

Temp.° C.	Dilution, lit/mole	k solutionx10^{6} ohms^{-1} cm.$^{-1}$	Λ ohms^{-1} cm.^{2}/mole
.102	342.83	122.8	42.03
.132	780.19	59.53	46.28
.082	1775.9	28.24	49.79
.111	4039.6	13.18	52.43
.092	9188.8	6.202	55.13
.085	20901	2.984	58.18
.090	47521	1.614	67.19
.120	108044	.941	80.06

Weight of sample-.05335 grams k solvent .188x10^{-6} ohms^{-1} cm.$^{-1}$

FIGURE 1a



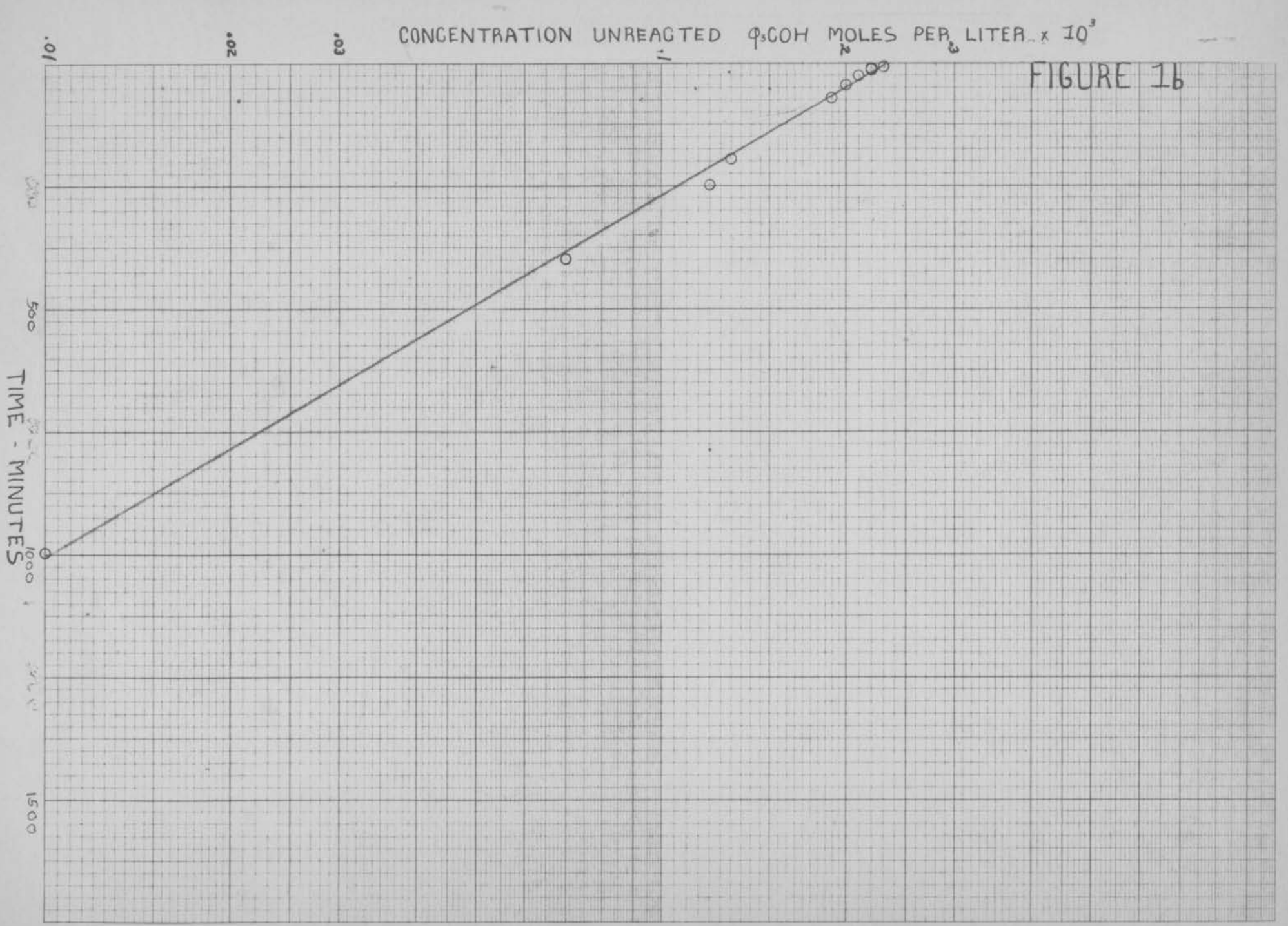

CONCENTRATION UNREACTED ϕ_3COH MOLES PER LITER x 10^3
.01
.02
.03
1
2
3
TIME - MINUTES
500
1000
1500

FIGURE 1b

FIGURE 2a

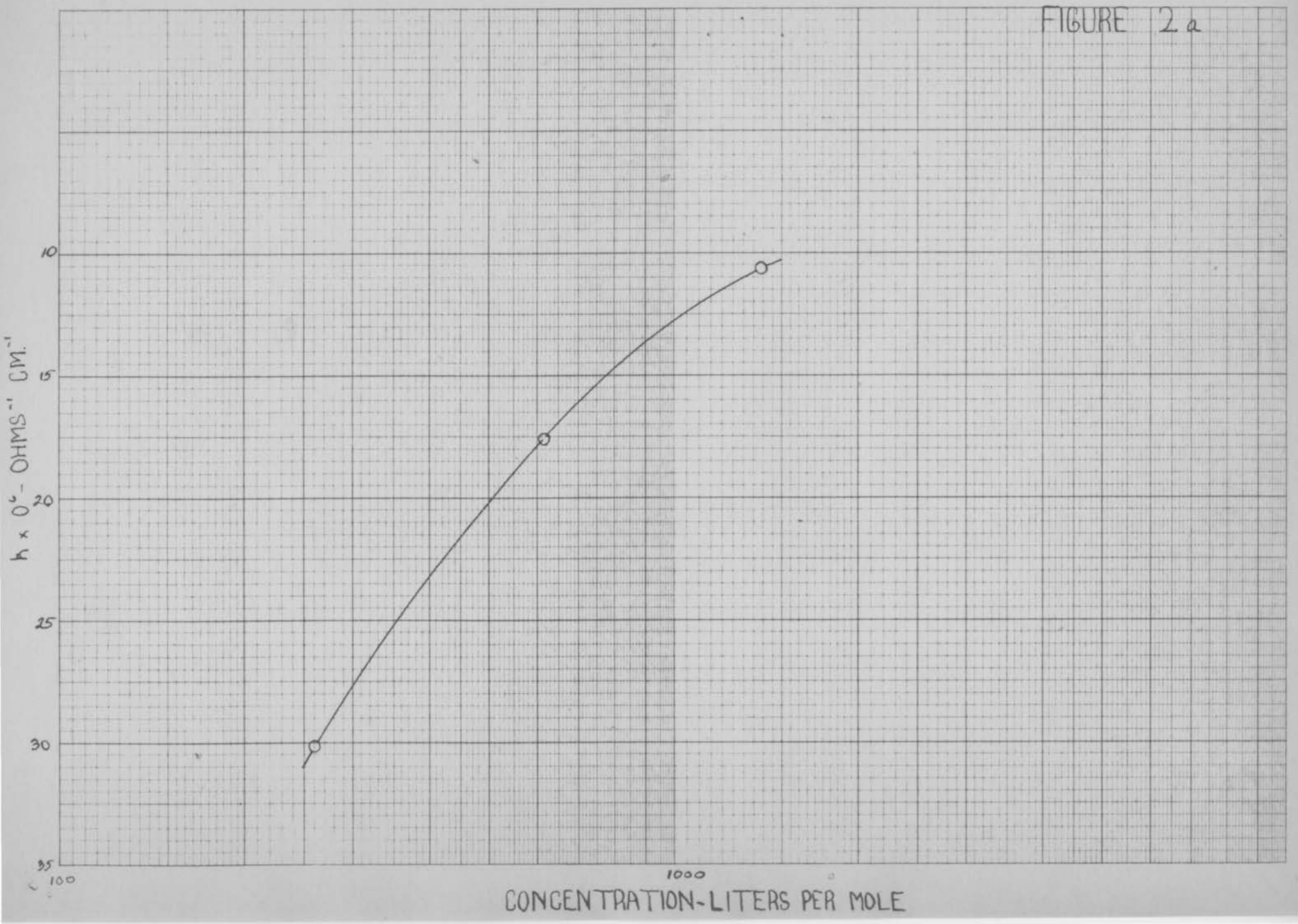

10
15
20
25
30
35
Λ x 10⁶ - OHMS⁻¹ CM.⁻¹
100
1000
CONCENTRATION - LITERS PER MOLE

FIGURE 2b

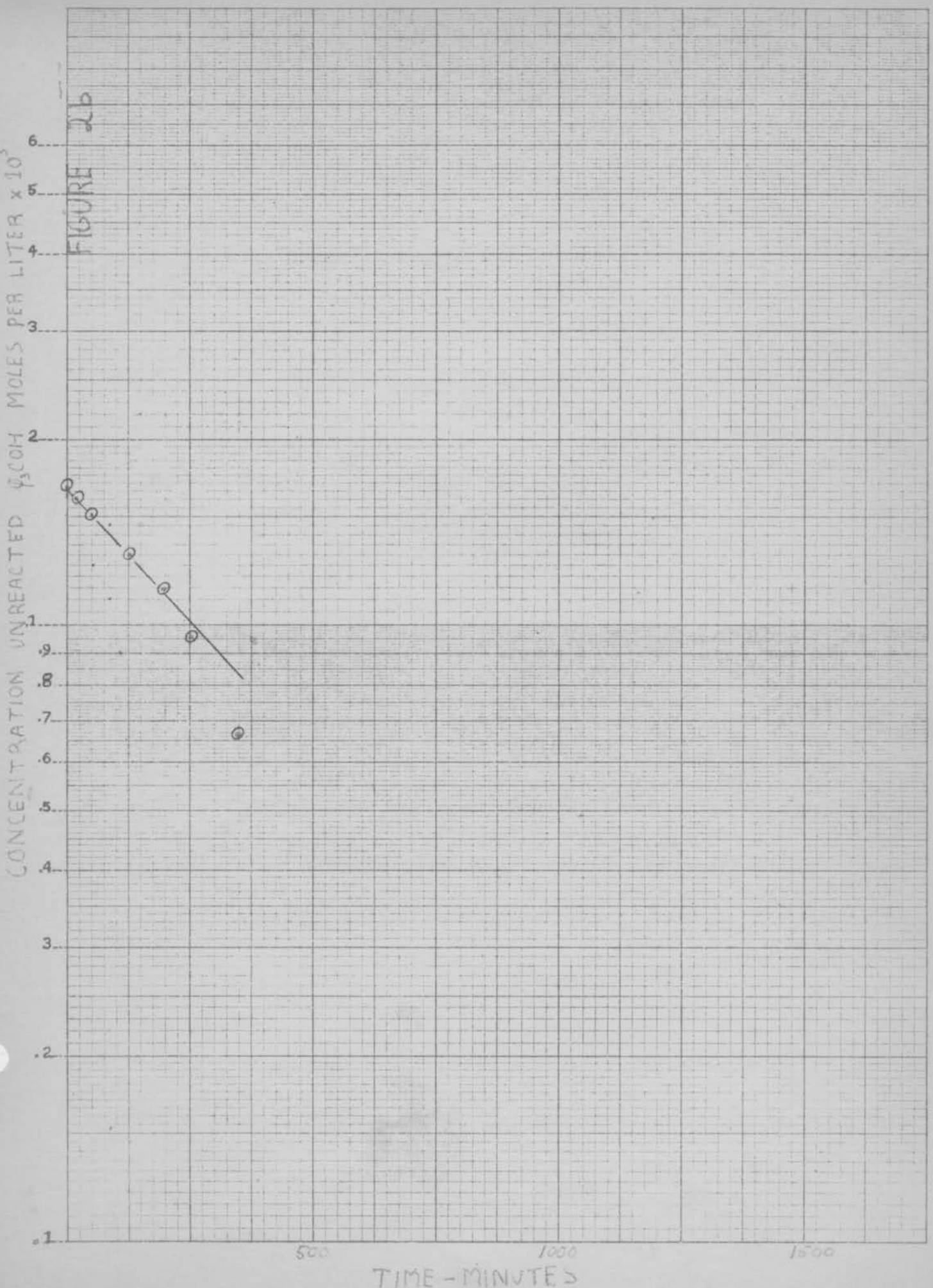
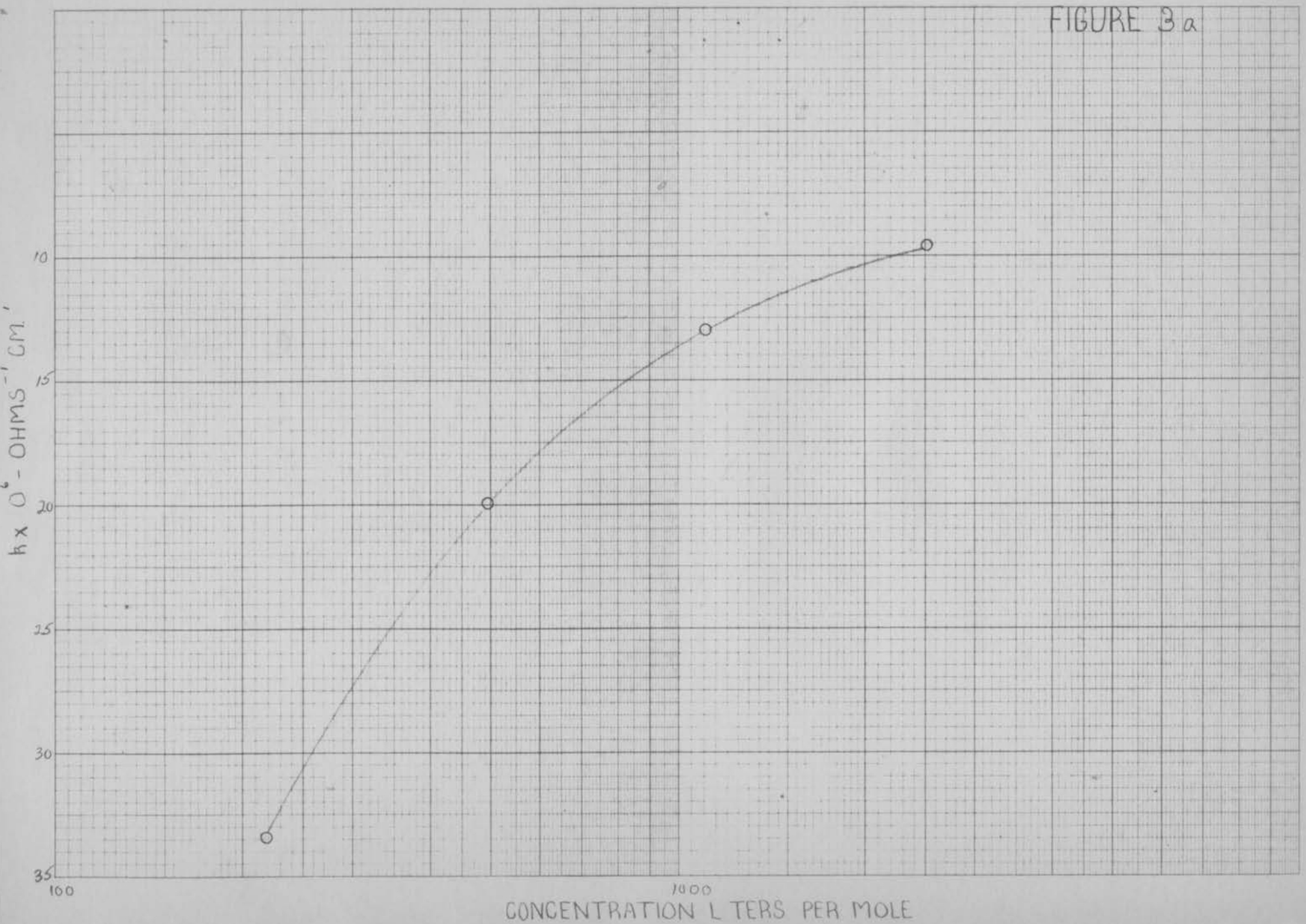

CONCENTRATION UNREACTED $(C_6H_5)_3COH$ MOLES PER LITER x 10^3
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
3
.2
.1
500
1000
1500
TIME - MINUTES

FIGURE 3a


10
15
20
25
30
35
$\Lambda \times 0^6$ - OHMS^{-1} CM.$^{-1}$
100
1000
CONCENTRATION LITERS PER MOLE

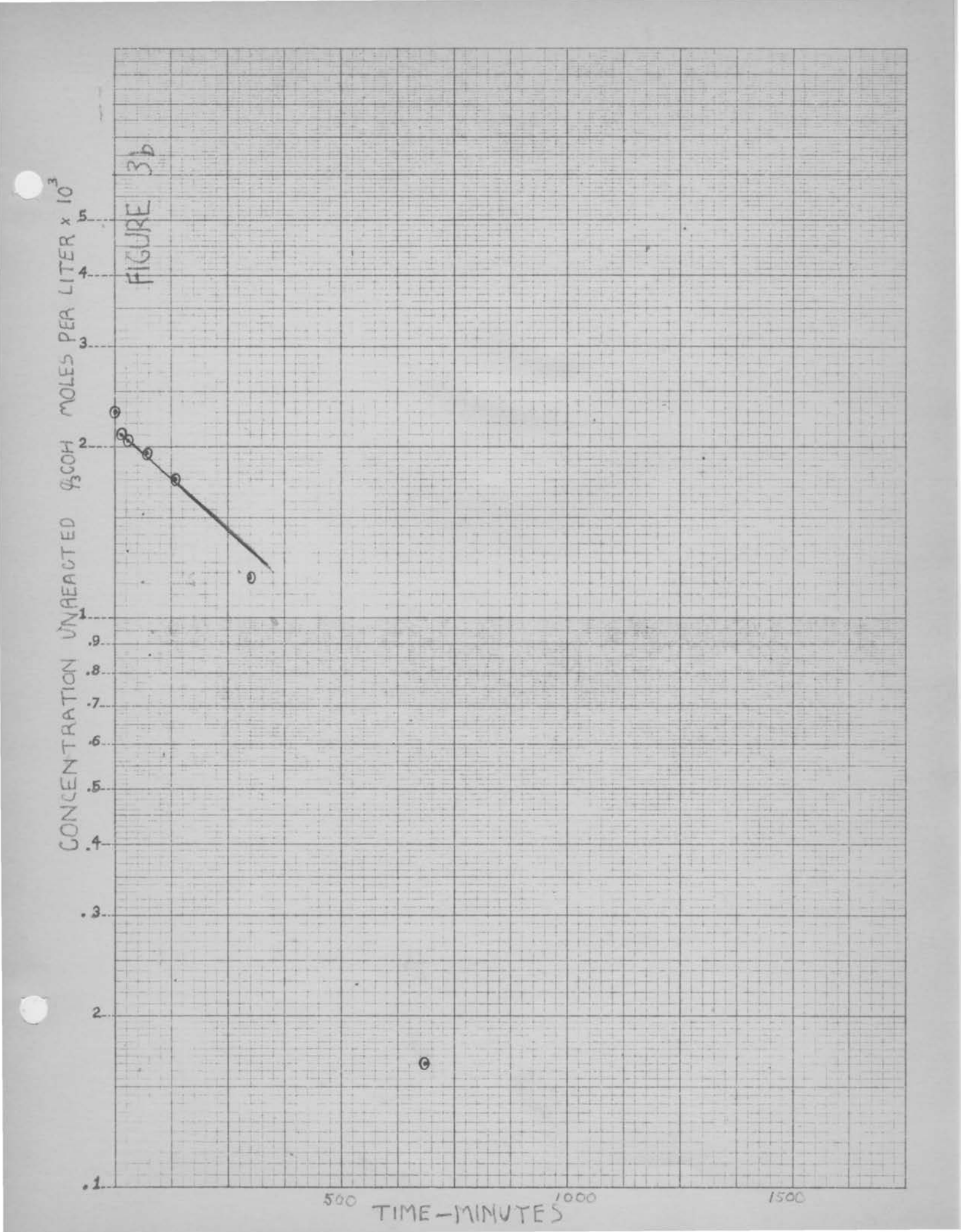


FIGURE 3b
CONCENTRATION UNREACTED ϕ_3COH MOLES PER LITER x 10^3
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
2
.1
500
1000
1500
TIME-MINUTES

FIGURE 4a

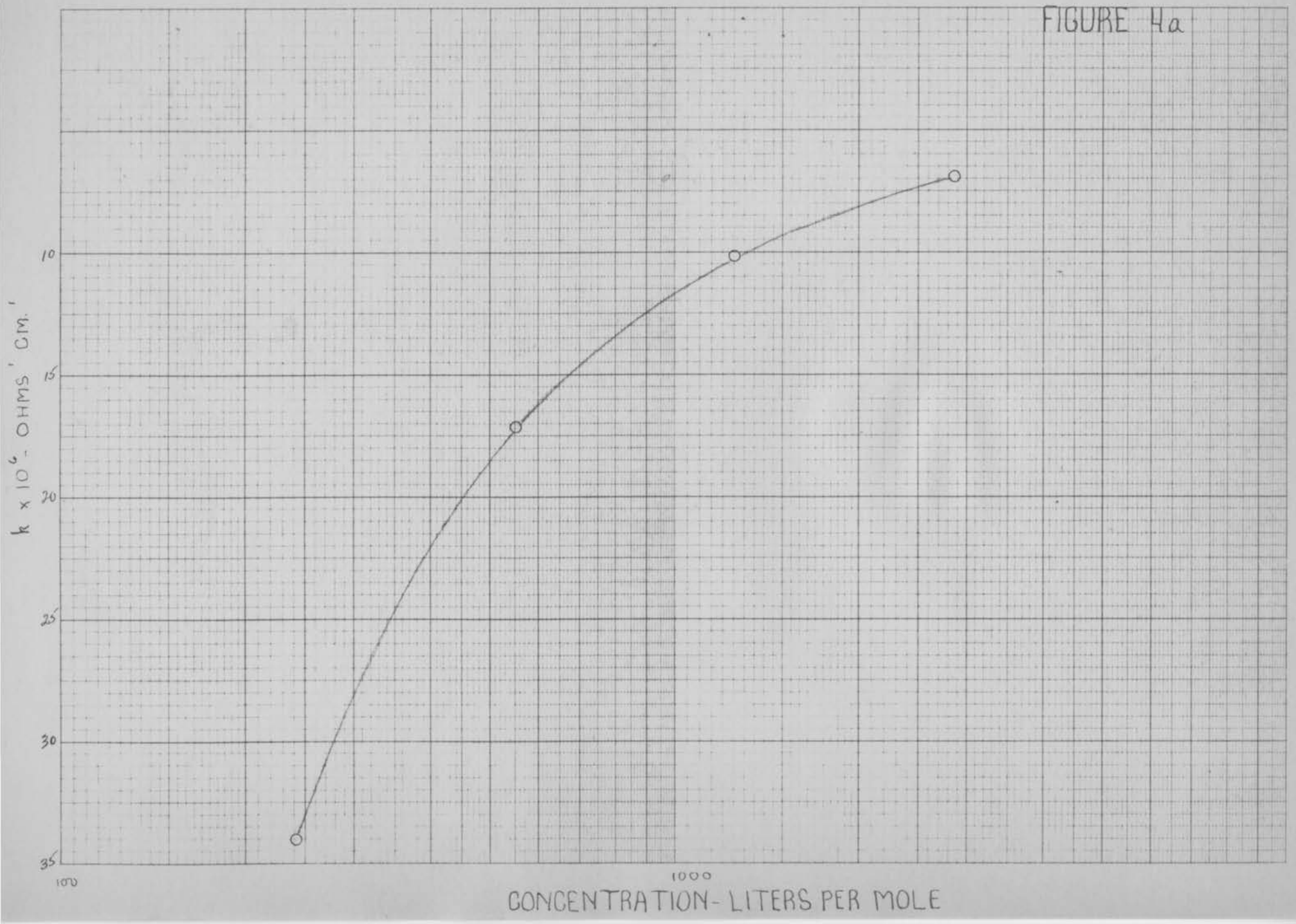
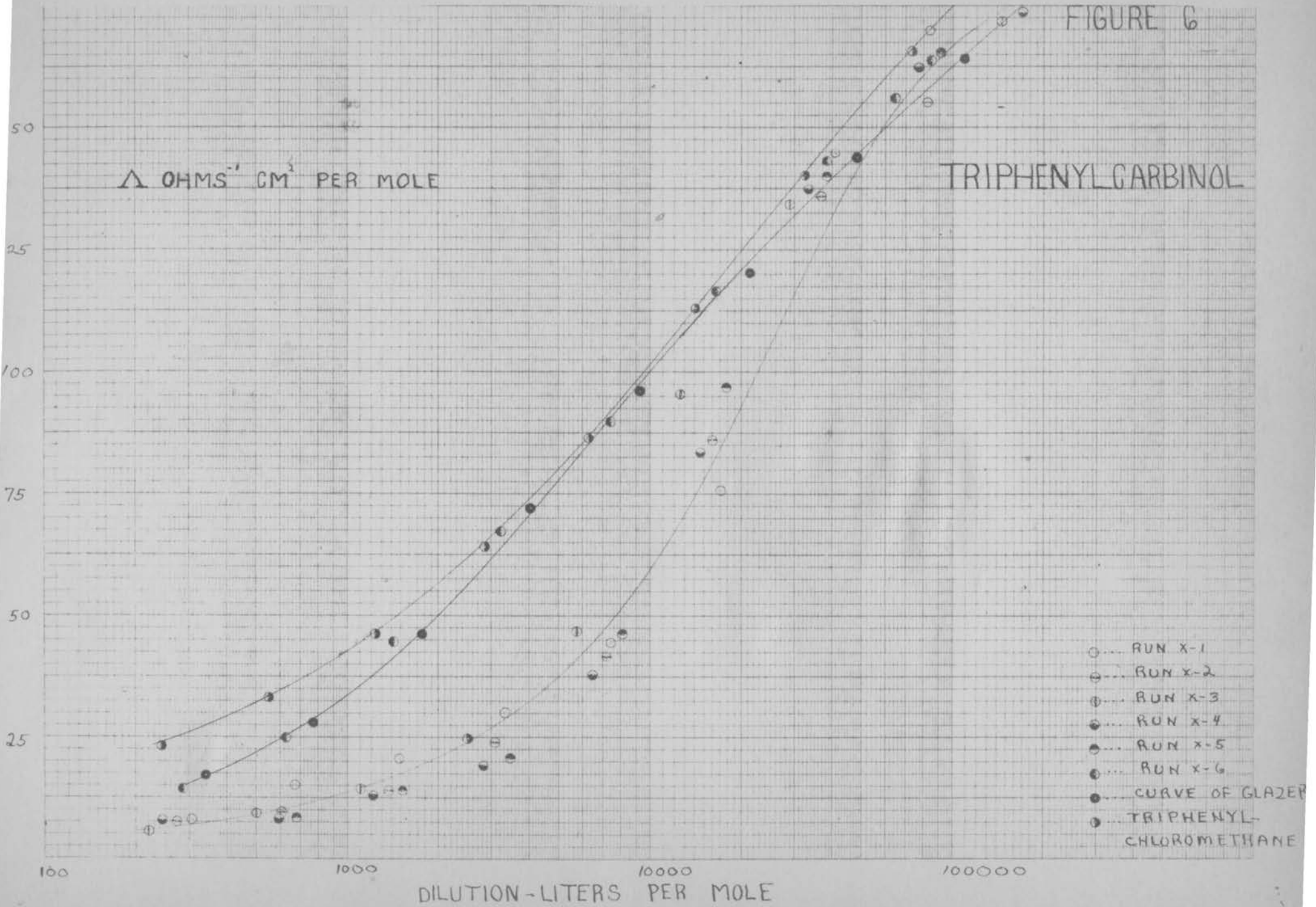

k x 10⁶ - OHMS⁻¹ CM.⁻¹
10
15
20
25
30
35
100
1000
CONCENTRATION - LITERS PER MOLE

FIGURE 5a


10
15
20
25
30
35
k x 10⁶ - OHMS⁻¹ CM⁻¹
100
1000
CONCENTRATION-LITERS PER MOLE

FIGURE 6


Λ OHMS⁻¹ CM² PER MOLE
TRIPHENYLCARBINOL
50
25
100
75
50
25
100
1000
10000
100000
DILUTION - LITERS PER MOLE
RUN X-1
RUN X-2
RUN X-3
RUN X-4
RUN X-5
RUN X-6
CURVE OF GLAZER
TRIPHENYL-CHLOROMETHANE

ABSTRACT

The conductivity of triphenylcarbinol was measured in liquid sulfur dioxide in a concentration range of 200-195,000 liters per mole. With magnesium perchlorate as the drying agent in the gas train a drift at the initial concentration, as well as lower conductivities at the higher concentrations was noted, in contrast to the work of Glazer (3). With $CaCl_2$ as the drying agent, no drift was observed, and conductivity values were in general agreement with those of Glazer. A possible mechanism for the observed results has been suggested.

BIBLIOGRAPHY

1. H. Glazer, A. M. thesis, Boston University, p. 42, (1950).

2. Ibid., pp. 23-28.

3. Ibid., pp. 42-43.

4. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, 1940, p. 55.

5. N. N. Lichtin, "The Conductivities in Liquid Sulfur Dioxide of Some Derivatives of Triphenylchloromethane", Doctor's thesis, Harvard University, Cambridge, 1948.

6. P. Walden, "Handbuch der Angewandten Physikalischen Chemie von Georg Bredig, Band XIII, Elektrochemie Nichtwassriger Losungen," Verlag von Johann Ambrosius Barth, Leipzig, 1924, p. 202.