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NOTE TO USERS

THE FREE ENERGIES OF COMPLEX FORMATION AND OF ACTIVATION

FOR THE REACTION OF PERIODATE ION WITH GLYCOL

by

Vernon C. Bulgrin

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Head of Major Department

Dean of Graduate College

Iowa State College

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INTRODUCTION

The periodate cleavage of vicinal glycols has been used extensively in the field of organic chemistry as an analytical tool for the quantitative determination of compounds of this type, and in structure proof research. For these purposes, periodic acid has two important advantages over similar oxidants: it exhibits perhaps the highest degree of specificity for the cleavage reaction, and it may be used in aqueous solution.

Leon Malaprade (1,2), in 1928, was the first to demonstrate the usefulness of periodic acid as a reagent for the oxidation of 1,2- glycols. Subsequent work by Fleury and associates and Hudson and co-workers greatly extended the range of application of the reaction; their work is summarized in an excellent article by Jackson (3), who has critically reviewed the literature of periodate oxidations up to March, 1942. Later review articles by Smith (4) and by Waters (5) bring the subject up to date. Waters also compares the relative applicability of many specific oxidants, including lead tetraacetate, potassium permanganate, hydrogen peroxide, chromic acid and chromyl chloride and selenium dioxide.

The type of linkages which undergo cleavage by periodic acid are summarized in Table 1. The products are, in

Table 1. Linkages susceptible to cleavage by
periodic acid.

Group	Example	Remarks
- C - C - OH OH	ethylene glycol, pinacol, etc.	gives 2 moles aldehyde and/or ketone.
- C - C - C - OH OH OH	glycerol	inner R-C-OH group gives acid.

- C - C -
  O   OH
	dihydroxyacetone	- C - fragment
		   O gives acid.

- C - C - O O	diacetyl	gives 2 moles of acid.

- C - C -
  OH   NH-R
(R may be H)
	ethanolamine	gives aldehyde and/or ketone plus ammonia or amine.
		
		C - C
		         not attacked
		OH NR$_2$

Special cases	glyoxylic acid
	  HC - COOH
	     O
		slow

general, oxidized only very slowly, if at all, by periodic
and iodic acids, and the compounds themselves are not prone
to attack by iodic acid under the usual conditions.

Malaprade (1) pointed out that for each polyalcohol mole-
cule of the type $(CHOH)_n(CH_2OH)_2$ there are reduced (n+1)
molecules of periodic acid (to iodic acid) to give two
molecules of HCHO and n molecules of HCOOH. Compounds
containing

$$-\underset{\underset{OH}{|}}{C}-\underset{\underset{NH_2}{|}}{C}- \quad\text{or}\quad -\underset{\underset{OH}{|}}{C}-\underset{\underset{NH-R}{|}}{C}- \quad\text{groups oxidize}$$

readily, but $-\underset{\underset{OH}{|}}{C}-\underset{\underset{NH_2}{|}}{C}-$ is not attacked. β-hydroxy-α-

amino acids are oxidized quantitatively with liberation of
the stoichiometric amount of ammonia; other amino acids
are attacked very slowly, giving no ammonia, or else do
not react at all.

The mechanism of the oxidation has received but scant
attention, compared to its analytical applications.
Criegee and co-workers (6,7) concluded that periodate ion
coordinated two or more water molecules; a molecule of
glycol displaced two water molecules to form a cyclic
diester which decomposed rapidly to iodic acid, water and
a very reactive free radical which instantaneously split
to give two carbonyl groups.

Malaprade (1) had pointed out that the oxidation was
more rapid in acid than in basic solution. Price and

associates (8,9) studied the kinetics of the oxidation of
ethylene glycol, pinacol and cis- and trans- cyclohexene
glycols. For ethylene glycol, they found a nearly con-
stant rate of oxidation in the pH range three to seven.
The reaction appeared to be bimolecular, first order in
periodate and also first order in glycol; the authors
agreed with Criegee that the rate determining step of the
oxidation was the formation of a cyclic diester:

$$
\begin{array}{c}
- C - OH \\
\quad | \\
- C - OH
\end{array}
+ H_5IO_6
\ \overset{Slow}{\rightleftharpoons}\
\begin{array}{c}
- C - O \\
\quad | \\
- C - O
\end{array}
\!\!\searrow\!\! IO_4H_3
$$

$$\downarrow fast$$

$$HIO_3 + 2\ \ \rangle C = O + H_2O \ .$$
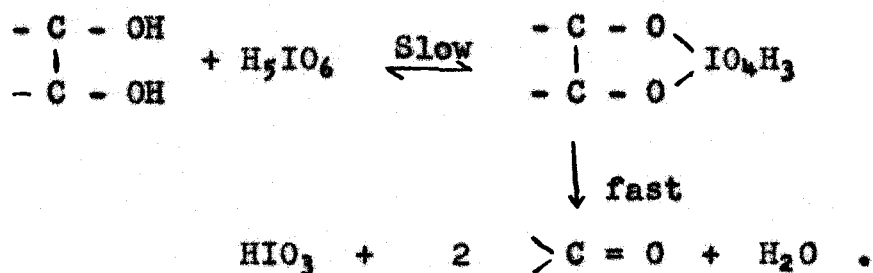
However, Price and his associates confined their measure-
ments to very dilute solutions, under which conditions a
limited amount of informative data could be obtained.
They also found that pinacol not only was oxidized at a
much slower rate but also exhibited a nearly first order
hydrogen ion catalysis over the pH range two to four; the
possibility of attack by undissociated H_5IO_6 was suggested
to explain the hydrogen ion dependence.

Heidt and co-workers (10) agreed with Criegee and
with Price regarding the formation of an intermediate
cyclic diester. Heidt also set forth a list of physical
properties that any oxidant able to cleave glycols must

have:

1. The central atom of the oxidant must have a diameter of 2.5×10^{-8} to 3.0×10^{-8} cm. (large enough to bridge the gap between OH groups).

2. The central atom must be able to coordinate at least two OH groups in addition to groups already on.

3. The valence of the central atom must exceed by two units that of the next lowest stable rate.

4. The oxidant should have an E° value of about -1.7 volts with respect to the next lowest stable valence state.

Duke (11,12) showed that ceric ion, which possesses none of the above properties, acts as a specific oxidant for the cleavage of glycols.

In 1948, Duke (13) studying the oxidation of ethylene glycol in acid solution, found that at higher glycol concentrations (0.2 M and above) the rate of reaction became virtually independent of glycol concentration. He further demonstrated that for glycol concentrations greater than three times the periodate concentration the reaction was first order overall, plots of the logarithm of the total periodate concentration versus time giving straight lines. The following scheme was proposed:

$$H_4IO_6^- + \text{Glycol} \underset{\text{rapid}}{\overset{K}{\longleftrightarrow}} \text{Complex} \overset{k}{\underset{\text{slow}}{\longrightarrow}} \text{products}$$
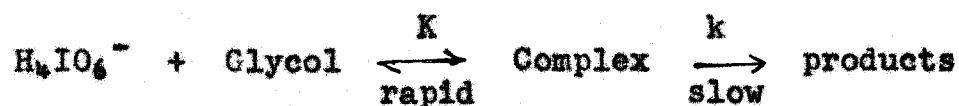
$$-\frac{dP_T}{dt} = k\,(\text{Complex}) = k'\,P_T$$

where $k' = \dfrac{kKG}{1+KG}$

P_T = total periodate concentration,
including all species.

G = concentration of uncomplexed glycol.

In a later paper, Duke and Bremer (14) showed that periodate coordinates not more than one glycole molecule.

PURPOSE AND SCOPE OF THE INVESTIGATION

A kinetic study of the oxidation of the homologous series ethylene glycol through pinacol was undertaken, with the following objectives:

1. To determine the free energies of activation and of complex formation for a series of glycols, with possible attempts to relate differences in reactivity to structure.

2. To ascertain whether or not a relationship might exist between the equilibrium constant for the formation of the complex and the rate constant for its disproportionation.

3. To observe the effect of methyl substitution on the rate of cleavage of ethylene glycol, and thereby gain some insight into the unusual pH dependence of the oxidation of pinacol.

4. To obtain more information about the nature of the reacting species; in particular, to attempt a quantitative correlation of the variation of rate with pH.

In connection with the last mentioned objective, Waters (5) attributed the constancy of the rate in the pH range three to seven to the fact that hydrogen ion catalysis is balanced by decreasing ionization of H_5IO_6 to the reactive $H_4IO_6^-$. Using the data of Crouthamel and

associates (15,16) for the equilibrium constants of periodic acid, it is possible to show that, in this pH range, the concentration of negative ion is nearly constant; the reaction (except in the case of pinacol) does not depend upon hydrogen ion concentration directly.

Previous investigators found the stoichiometry of the oxidation somewhat doubtful in many instances. For example, Jackson and Hudson (17) showed that, in the oxidation of starch, cotton and filter paper, considerable overoxidation occurred; the reaction slowed down considerably, however, after the consumption of an equivalent amount of periodic acid. Davidson (18) also reported overoxidation of cotton and filter paper, with formation of formic acid, formaldehyde and carbon dioxide. Head (19) found the oxidation of β-methyl glucoside and β-methyl cellobioside to be stoichiometric in solution of pH less than five, but that considerable overoxidation occurred in alkaline solution or in acid solutions exposed to bright sunlight. He further demonstrated that overoxidation of cellulose in acid solution did not occur in the absence of light, an equivalent amount of periodic acid being reduced and no formic acid, formaldehyde or carbon dioxide detected; when subjected to strong illumination, overoxidation occurred, the oxidized cellulose had an appreciable carboxyl content, and iodine and carbon

dioxide were formed.

Because of the possibility of non-specific oxidation in alkaline solution, the research of this thesis was concerned only with the acid cleavage. The stoichiometry of the reaction was checked in the cases of meso- and levo-butylene glycols and trimethylethylene glycol in acid solution (pH about one); the stoichiometry of the pinacol oxidation was checked in acid, neutral and alkaline solution. In all cases, a twenty per cent excess of periodic acid was allowed to react with a dilute solution of the glycol. The results are summarized in Table 2. It is apparent that periodate loses its specificity in alkaline solution in the case of pinacol.

Table 2. Check on the stoichiometry of the reaction

___

Meso- butylene glycol (1.04M). pH ca. 1

time of reaction	10 min.	1 1/2 hrs.	2 1/2 hrs.	21 hrs.
M_{glycol}[a]	1.05	1.05	1.05	1.08 1.08

Levo- butylene glycol (1.00). pH ca. 1

time of reaction	10 min.	30 min.	4 hrs.
M_{glycol}[a]	1.01	1.00^5	1.01

Trimethylethylene glycol (1.00M). pH ca. 1

time of reaction	2 hrs.	4 hrs.	13 hrs.	14 hrs.
M_{glycol}[a]	.99^5	.99^5	1.01^5	1.01

Pinacol (.207 M). pH ca. 1

time of reaction	5 1/4 hrs.	6 1/4 hrs.	23 hrs	25 hrs.
M_{glycol}[a]	.206	.207	.213	.214 .215

pH ca. 6

time of reaction	6 hrs.	12 1/4 hrs.	53 hrs.
M_{glycol}[a]	.196	.201	.204

pH ca. 8

time of reaction	5 3/4 hrs.	23 1/2 hrs.	31 hrs.
M_{glycol}[a]	.139	.248	.276

___

[a]Found by periodate oxidation.

EXPERIMENTAL

Inorganic Materials

Periodic acid, H_5IO_6, was obtained from the G. Frederick Smith Chemical Co. Analysis by reduction to iodate in neutral solution, and by titration with sodium hydroxide to the methyl red endpoint, revealed the purity to be not less than 99 per cent. Solutions of the acid were found to be quite stable over a period of several months, provided they were protected from light.

Arsenic trioxide used in the analyses was Mallinckrodt Co. primary standard grade. Solutions of 0.1 N sodium arsenite, with excess sodium bicarbonate, proved to be stable within three parts per thousand over a period of three months.

Sodium nitrate, sodium thiosulfate, sodium bicarbonate, iodine, potassium iodide and sodium hydroxide were Baker and Adamson Co. reagent grade.

The water used to make up all reactant solutions and for all dilutions had been redistilled from alkaline permanganate solution using a Barnstead conductivity water still with a silver pot and tin coils.

Glycols

Ethylene and propylene glycols of high purity were obtained from the Matheson Co., and were doubly vacuum distilled before use. Analysis by periodate oxidation showed a purity of 100 ± 1 per cent.

Meso-butylene glycol of about 90 per cent purity was obtained from the biochemical groups at Iowa State College. The glycol had been prepared (20) by the fermentation of corn meal using Aerobacter aerogenes; the main impurity was the dextro isomer. The glycol was subjected to a distillation through a 12 inch Vigreaux column, the first fourth and the last tenth being discarded. The distilled glycol was recrystallized at 0°C. three times from 300 ml. portions of Matheson Co. isopropyl ether (alcohol-free); the ether had been distilled, and the first portion, containing the water, discarded (21). The first crystallization required seeding, the seed being obtained by freezing a little of the impure glycol in an acetone-dry ice bath. After each crystallization, the porous glycol cake was washed with cold, dry isopropyl ether. The thrice crystallized glycol was filtered by suction, and most of the ether removed by attaching the flask to a water aspirator overnight. The glycol was then subjected to a distillation at atmospheric pressure, the last half being collected.

The freezing point of the distilled glycol was determined using a 0.1° thermometer immersed in the glycol in a test tube jacketed with a larger tube. Temperature versus time readings were made, starting about 5° above the freezing point. The freezing point was ascertained to be 33.6 ± .1°C., corresponding to a purity of about 99 per cent (21). This was regarded as the minimum purity, since water affects the freezing point in much the same way as do the d or l isomers. Analysis by periodate oxidation showed the purity to be 100 ± 1 per cent.

Levo-butylene glycol was prepared by the fermentation of Iowa yellow corn meal using an Aerobacillus polymyxa culture, which has been shown to produce nearly pure levo-isomer (20). Formula for the innocula was 5 per cent corn meal and 0.5 per cent calcium carbonate in distilled water; for the main fermentation batches, the corn meal was increased to 10 per cent. All media were sterilized at 18-20 pounds steam pressure for at least 30 minutes, then allowed to cool to room temperature before innoculation. One ml. samples of the stock culture (ISC B-34) were introduced into 10 ml. of medium in each of three test tubes; these were incubated for two days at 30°C. and used to innoculate three 200 ml. batches. The latter were incubated for 36 hours and used to innoculate the three main batches of 2500 ml. each. The main batches

were incubated for eight days at 30°C., after which time
the pH was adjusted to 9-10 by addition of sodium hydrox-
ide solution and the mixture filtered, first through
cheesecloth and then through diatomaceous earth. After
adjustment of the pH to about seven, the entire filtrate
was evaporated at 25-35°C. under the reduced pressure of
a water aspirator to approximately one liter. It was then
extracted for six days with ethyl ether, using a continu-
ous liquid-liquid extraction apparatus. The ether was
distilled off and the glycol distilled under the reduced
pressure of a water aspirator. There was collected a 47
gram sample which was water-white and had a refractive
index $n_D^{25°}$ equal to 1.4322, as compared to literature
values of 1.4318 at 26° (22) and 1.4324 (23) for the pure
compound. The freezing point of the glycol, obtained by
the same method as for the meso- isomer, was 16.8°C.;
this corresponded to a purity of at least 98 per cent,
based upon the freezing point diagram for mixtures of the
isomeric 2,3-butylene glycols (24). The optical rotation
$a_D^{20°}$ as determined by means of a Kern Full-Scale polari-
meter was -13.3 ± .1, compared to a literature value of
-13.34 (at 26°C) for the pure levo- compound (22).
Analysis by sodium hydroxide titration revealed an acid im-
purity of about 0.25 per cent; this was removed by distill-
ation from anhydrous potassium carbonate. Periodate

analysis gave a purity of 100.5 $\pm$ 1 per cent.

Trimethylethylene (2- methyl 2- butene) was prepared
(25) by distillation from a mixture of 1:1 sulfuric acid
and t- amyl alcohol. The distillate was dried over calci-
um chloride and Drierite and redistilled through a 12 inch
Vigreaux column, the fraction boiling from 36° to 39°
(uncorrected) being collected.

Two attempts were made to prepare the glycol by the
method of Milas and Sussman (26), using a solution of hydro-
gen peroxide in dry t- butyl alcohol as hydroxylating
agent and osmium tetroxide as catalyst; yields were less
than 10 per cent. A method similar to that of Roebuck and
Adkins (27), using performic acid in aqueous solution,
proved to be much more satisfactory. A solution of 140
ml. of 30 per cent hydrogen peroxide and 600 ml. of 88
per cent formic acid (both Baker and Adamson Co. reagent
grade) was placed in a one-liter three-necked flask equip-
ped with a reflux condenser and stirrer; 130 ml. of tri-
methylethylene were added from a dropping funnel at such
a rate that the hydrocarbon refluxed gently after each
addition. The flask was cooled in an ice bath whenever
the refluxing became too vigorous. An hour after the re-
action appeared to be over, the mixture was evaporated,
under the reduced pressure of a water aspirator, to a
volume of about 300 ml. The formate ester was saponified

by adding, in small portions, an ice-cold solution of 80 grams of sodium hydroxide in 150 ml. of water. The glycol was extracted at a temperature of about 40° with 600 ml. of ethyl acetate in three portions; the solvent was distilled off. The glycol was distilled at atmospheric pressure to remove all traces of solvent, and was then subjected to a fractional distillation through a Todd Scientific Co. 40 plate column. A 60 ml. fraction boiling at 173.5 - 174.5°C (uncorrected) was collected, with an estimated 90 per cent coming over at 174.0°C. Analysis by periodate oxidation showed a purity of 100 ± 1 per cent.

Pinacol hydrate was prepared through the magnesium pinacolate by the condensation of acetone (28). The reaction proceeded very slowly when half of the acetone-mercuric chloride had been added; careful heating at this point caused the reaction to proceed vigorously, no further heating being necessary. The hydrate was purified by thorough washing with benzene and recrystallization from water. Dehydration was effected by a method similar to that of Ayers (29), using distillation under reduced pressure to remove most of the water. When the temperature reached 50°C, the remainder of the solution was distilled at atmospheric pressure, using an air condenser. The fraction boiling from 165° to 172°C was redistilled,

and the second half, boiling from 169° to 172° (uncor-
rected) collected as anhydrous pinacol.

Rate Determinations

Melting ice and melting benzene were used as constant
temperature baths to give temperatures of 0.00 ± .05° and
5.25 ± .05° respectively. The solid phase along with the
liquid, was placed into a two liter wide-mouth Dewar flask,
and the mixture was stirred with a mechanical stirrer.
The benzene used was Baker and Adamson Co. reagent grade;
excess water was added to saturate the benzene, giving
temperatures reproducible for different runs within 0.03°C.
The benzene was frozen in large test tubes in an ice bath.
A Beckman thermometer with 0.02° calibration marks and a
10° range was used to measure the temperature of the ben-
zene bath, after having previously determined the ice
point.

The addition and sampling pipettes were kept in glass
jackets in a bath similar to that of the reaction bath.

Runs at 25° for pinacol were made in a water bath
equipped with a mercury thermoregulator to give tempera-
ture control to ± 0.05°C.

The reactions were carried out in a 50 ml. glass
stoppered volumetric flask with an additional 48 ml. mark.

Five ml. of 2.0 M sodium nitrate (to maintain constant ionic strength) and the required amount of 1.0 M glycol and 0.20 M sodium hydroxide or 70 per cent perchloric acid to give the desired glycol concentration and pH were placed in the reaction flask and the contents diluted to the 48 ml. mark. After at least 30 minutes in the bath, 2.00 ml. of 0.200 M periodic acid solution at the bath temperature were added and the timer, an Air Force surplus stopwatch, started at the second shake of the reaction vessel. At various time intervals, 5.0 ml. samples were removed and discharged into the quenching mixture. Time was taken to be that for which the pipette had drained past a certain mark, approximately the half-way point in the discharge of the pipette.

For all reaction mixtures with pH higher than two, the quenching solution consisted of a measured excess, usually 0.500 to 1.000 ml., of 0.1000 N sodium arsenite, plus five ml. of 10 per cent potassium iodide solution saturated with sodium bicarbonate. Under these conditions, the periodate was reduced to iodate by the iodide, producing iodine which oxidized the arsenite. The excess arsenite was titrated with standard (.01 N) iodine solution.

For the reaction at higher acidities (pH less than two), the above technique proved to give erratic results,

local excesses of acid from the reaction aliquot causing
some periodate to be reduced to iodine. For these runs
the quenching mixture consisted of an acid solution of
potassium iodide. The periodate was reduced to iodine,
which was titrated with standard (.01 N) thiosulfate so-
lution. The periodate concentration was calculated from
the difference in thiosulfate titer for the reaction ali-
quot and that for an aliquot from a flask containing an
identical amount of periodic acid but no glycol. The
analytical error involved was considerably larger than
that for the arsenite procedure, an error of less than
one per cent in the blank being sufficient to give curves
instead of straight lines for the first order plots.
This difficulty was circumvented to a large degree by
comparing the slopes of the first order plots (log peri-
odate versus time) obtained by the arsenite and the thio-
sulfate procedures for runs at pH 2.20, and correcting the
blank for the thiosulfate determinations so as to give a
straight line with slope identical to that obtained by
the arsenite procedure. Once such a correction was ap-
plied to the blank, all first order plots by the thiosul-
fate technique gave good straight lines. Such a pro-
cedure was necessary only for the more rapid runs where
the periodate concentrations in the aliquots became very
small.

For the high acidity runs on pinacol, a different
procedure was used. The arsenite-bicarbonate-iodide
quenching technique was employed, but the reaction aliquot
was first discharged into a cold solution containing the
standard arsenite plus excess sodium bicarbonate; excess
potassium iodide was quickly added. Because the pinacol-
periodate reaction is five to ten times slower in solutions
of pH five to seven than in more acid media, such a procedure
introduced a negligible error in timing.

Levo- butylene glycol oxidized so rapidly at tempera-
tures above 0° that the reaction was substantially over
before the first sample could be withdrawn for analysis.
It was found possible to get data at a lower temperature,
using supercooled solutions. The bath consisted of an
ice-water-hydrochloric acid mixture; the temperature could
be controlled to within $\pm$ .02° by occasionally adding a
little concentrated acid to compensate for dilutions due
to melting ice. Although the reactants usually super-
cooled at the bath temperature of -4.12°C, a major diffi-
culty was encountered in that introduction of the sampling
pipette always caused freezing after the first or second
aliquot was taken. A survey of all previous data collected
in this research for glycol oxidations of comparable speed
showed that reproducibility of better than 5 per cent in
the rate constants could be expected if the initial

concentration of periodate and only one other point were used to determine the slope of the first order plot. The time of sampling for the one point was corrected by a constant number of seconds as determined from previous runs. It was felt that the accuracy of such a procedure for determining the rate constants was no worse than about five per cent.

All pH measurements were made at room temperature with a Beckmann Model G pH meter. Activity of hydrogen ion, A_{H+}, was calculated directly from each pH measurement. Some error, probably less than 0.1 to 0.2 pH unit was introduced by not correcting for the temperature or for the error in measuring extremely low pH values.

DISCUSSION

Variation of Rate with pH for Ethylene, Propylene, Meso- and Levo- Butylene and Trimethylethylene Glycols

Excellent first order plots were obtained for these glycols when the latter were present in two- to three-fold excess or more. The pseudo first order rate constants k' were obtained from the slopes of the plots of log P_T versus time, P_T being the total periodate concentration, including all species, complexed and uncomplexed. The observed variations of k' with pH are given in Tables 3-7 and illustrated by the points plotted in Figures 1-4. During a given run, the pH was found to change by less than 0.1 unit. All pH runs were made at initial periodate and glycol concentrations of .0080 M and .040 M, respectively. No deviation from first order kinetics was noted.

The falling off of rate in solutions with pH less than three suggested the reactive periodate species to be a negative ion, either IO_4^- or $H_4IO_6^-$. The kinetics data alone are not sufficient to demonstrate unequivocally which of these ions is doing the reacting, since they are in rapid equilibrium with one another and have a constant ratio of concentrations over the acid pH range. However, it is easy to picture coordination of IO_4^- ion with a

glycol molecule in much the same manner as with two water molecules, the tetrahedral IO_4^- ion assuming an octahedral configuration:

$$
\begin{array}{c}
\text{O} \diagdown \diagup \text{O}^- \\
\text{I} \\
\text{O} \diagup \diagdown \text{O}
\end{array}
\quad + 2H_2O
\qquad
\begin{array}{c}
\text{HO} \quad \text{OH}^- \\
\text{O} - \text{I} - \text{O} \\
\text{HO} \quad \text{OH}
\end{array}
$$

$$
\begin{array}{c}
\text{O} \quad \text{O}^- \\
\text{I} \\
\text{O} \quad \text{O}
\end{array}
\quad +
\begin{array}{c}
\text{CH}_2 - \text{CH}_2 \\
\text{OH} \quad \text{OH}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2 - \text{CH}_2^- \\
\text{O} \quad \text{O} \\
\text{O} - \text{I} - \text{O} \\
\text{HO} \quad \text{OH}
\end{array} \quad .
$$
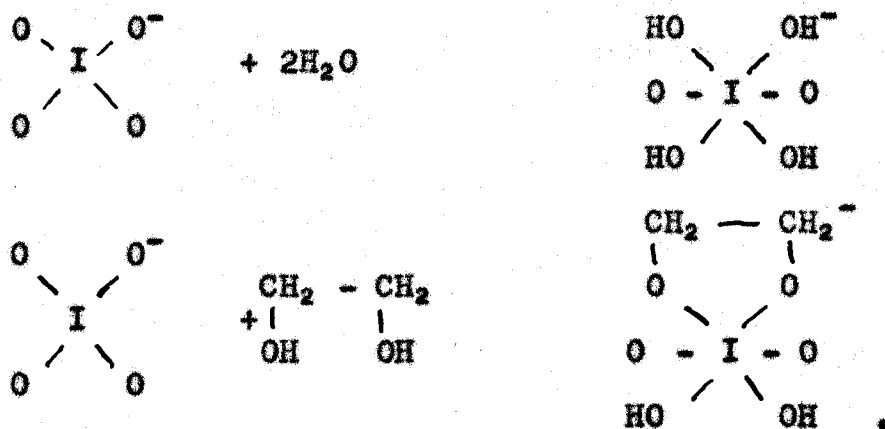
Assuming the reacting ion to be IO_4^-, the rate of the reaction

$$
IO_4^- + G \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} C \xrightarrow[\text{slow}]{k} \text{products}
$$
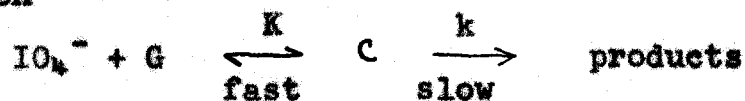
may be represented by

$$
- \frac{dP_T}{dt} = kC \tag{1}
$$

where P_T = sum of concentration of all periodate species

$\qquad = IO_4^- + H_4IO_6^- + H_5IO_6 + C^a$

$\quad C$ = concentration of complex.

Making use of the equilibrium constant K, the above expression for P_T and the dissociation constants of periodic acid (15),

---

[a] The ionization $H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^=$ is completely negligible in acid solution.

$$K_1 = \frac{A_{H^+} \, A_{H\,IO_6}^{-}}{A_{H_5IO_6}}$$

$$K_D = \frac{A_{IO_4}^{-}}{A_{H_4IO_6}^{-}} \quad ,$$

Equation 1 becomes

$$-\frac{dP_T}{dt} = k' P_T \quad , \text{ where} \tag{2}$$

$$\frac{1}{k'} = \frac{1}{k} + \frac{1}{kKG}\left(1 + \frac{1}{K_D}\,\frac{A_{H^+}}{K_1 K_D}\,\frac{\gamma_{IO_4}^{-}}{\gamma_{H_5IO_6}}\right) . \tag{3}$$

In Equation 3, G is the concentration of uncoordinated glycol[a], $\gamma_{IO_4}^{-}$ and $\gamma_{H_5IO_6}$ are the respective activity coefficients, and K is the (concentration) equilibrium constant for complex formation.

Using values of k and K determined as outlined in the next section, pseudo first order rate constants were calculated from Equation 3, and compared to the observed rate constants in Tables 3-7 and Figures 2-4. A value of 0.75 was estimated for the ration $\gamma_{IO_4}^{-}/\gamma_{H_5IO_6}$; K_1 and K_D were determined from the data of Crouthamel, Hayes and Martin

---

[a] The concentration of uncoordinated glycol remains nearly constant during a given first order run, as evidenced by the linearlity of all log P_T versus time plots. A simple calculation shows that such should be the case providing K is reasonably large (greater than about 10) and/or the glycol is present in sufficient excess.

Table 3. Ethylene glycol 0°C. Variation of pseudo
first order rate constants with pH.

(Glycol) total = .0400; (Periodate) = .0080

pH	A_{H^+}	$1/k'calc$*	$k'calc. \times 10^3$	$k'obs. \times 10^3$
2.23	5.9×10^{-3}	299	3.34	3.25
2.53	3.0	277	3.61	3.62
2.80	1.6	266	3.76	3.69
3.28	5.3×10^{-4}	258	3.88	3.89
3.68	2.1	256	3.91	3.94
3.93	1.2	255	3.92	3.94
5.07	8.6×10^{-6}	254	3.94	3.92
6.27	5.4×10^{-7}	254	3.94	3.92

*Calculated using Equation 3 and $k = 4.60 \times 10^{-3}$,
$K = 193$, (Glycol) uncoordinated = .034.

Table 4. Trimethylethylene glycol 0°C. Variations
of pseudo first order rate constants
with pH.

(Glycol) total = .0400; (Periodate) = .0080.

pH	A_{H^+}	1/k'calc.*	k'calc.	k'obs.
2.25	5.6×10^{-3}	76.6	13.1	15.5
2.60	2.5	62.8	15.9	18.5
3.10	9.5×10^{-4}	55.8	17.9	19.6
3.68	2.1	52.5	19.0	20.3
4.23	5.9×10^{-5}	51.9	19.3	20.5
4.63	2.4	51.7	19.4	20.4
5.30	5.0×10^{-6}	51.6	19.4	19.7
6.00	1.0	51.6	19.4	19.8

*Calculated using Equation 3 and k = 34×10^{-3},
K = 43, (Glycol) uncoordinated = .035.

Table 5. Propylene glycol 0°C. Variation of pseudo
first order rate constants with pH.

(Glycol) total = .0400; (Periodate)= .0080 .

pH	A_{H+}	$1/k'calc.$ [*]	$k'calc. \times 10^3$	$k'obs. \times 10^3$
0.70	.20	376.	2.7	2.4
1.07	.085	208.	4.8	4.1
1.33	.047	152.	6.6	5.9
1.57	.027	122.	8.2	7.2
2.15	.0071	92.7	10.8	10.6
2.49	.0032	86.9	11.5	11.5
2.82	.0015	84.4	11.8	12.3
3.14	7.2×10^{-4}	83.3	12.0	12.5
3.63	2.4×10^{-4}	82.6	12.1	12.3
4.16	5.3×10^{-5}	82.2	12.2	12.6
5.18	6.6×10^{-6}	82.2	12.2	12.1

[*]Calculated using Equation 3 and $k = 13.7 \times 10^{-3}$,
$K = 350$, (Glycol) uncoordinated = .033.

Table 6. Meso- butylene glycol 0°C. Variation of
pseudo first order rate constants with pH.

(Glycol) total = .0400; (Periodate) = .0080.

pH	A_{H^+}	1/k'calc.*	k'calc.x10^3	k'obs.x10^3
0.71	.19	915.	1.1	1.4
1.05	.089	466.	2.1	2.5
1.33	.049	279.	3.6	4.0
1.53	.030	204.	4.9	5.7
2.27	.0054	94.1	10.6	10.2
2.53	.0030	83.5	12.0	11.6
2.80	.0016	77.2	13.0	13.5
3.15	7.1×10^{-4}	73.3	13.6	14.2
3.55	2.8×10^{-4}	71.3	14.0	14.4
4.23	5.9×10^{-5}	70.3	14.2	14.4
4.80	1.6×10^{-5}	70.2	14.2	14.6
5.40	4.0×10^{-6}	70.1	14.3	14.5
5.70	2.0×10^{-6}	70.1	14.3	14.3
5.73	1.9×10^{-6}	70.1	14.3	14.4

*Calculated using Equation 3 and k = 20.8×10^{-3},
K = 73, (Glycol) uncoordinated = .034.

Table 7. Levo- butylene glycol 0°C. Variation of
pseudo first order rate constant with pH.

(Glycol)total = .0200; (Periodate) = .0080.

pH	A_{H+}	1/k'calc.*	k'calc.$\times 10^3$	k'obs.$\times 10^3$
0.68	.21	410.	2.4	6.2
1.08	.096	207.	4.8	10.6
1.57	.027	89.	11.2	18.9
2.17	.0066	45.0	22.2	26.4
2.18	.0066	45.0	23.2	26.0
2.35	.0045	42.9	23.3	25.8
2.73	.0019	36.9	27.1	29.4
3.54	2.9×10^{-4}	33.4	29.9	32.0
3.83	1.5×10^{-4}	33.0	30.3	31.1
3.93	1.2×10^{-4}	33.0	30.3	32.7
4.48	3.3×10^{-5}	32.7	30.6	31.1
6.2	6.3×10^{-7}	32.7	30.6	30.8
6.6	2.5×10^{-7}	32.7	30.6	29.0

*Calculated using Equation 3 and k = 47×10^{-3},
K = 180, (Glycol) uncoordinated = .012 for runs above pH2,
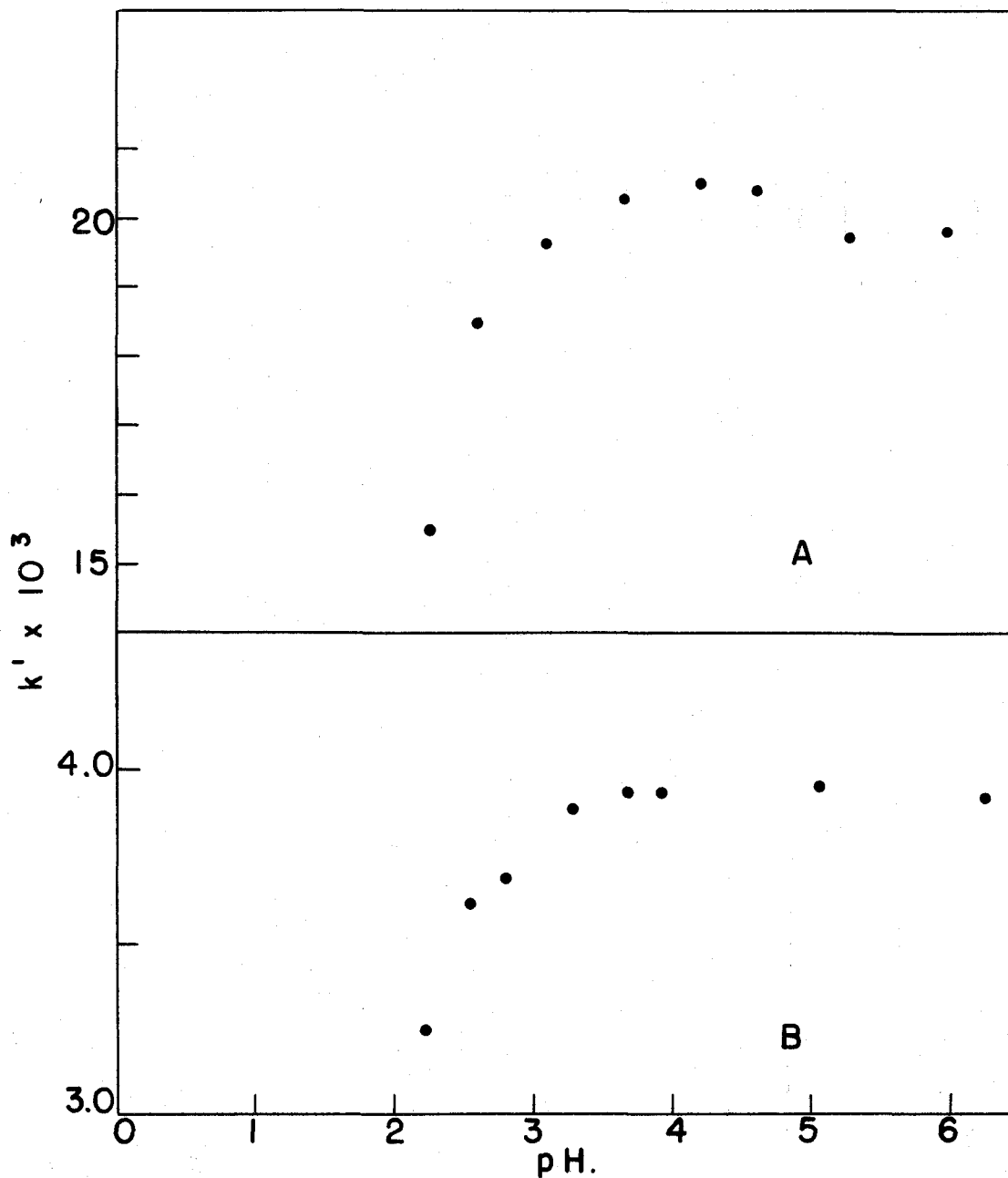.013 for pH 1.57 and 2.17, .0145 for pH 0.68 and 1.08.

FIG. 1. A. TRIMETHYLETHYLENE GLYCOL 0.00°C.
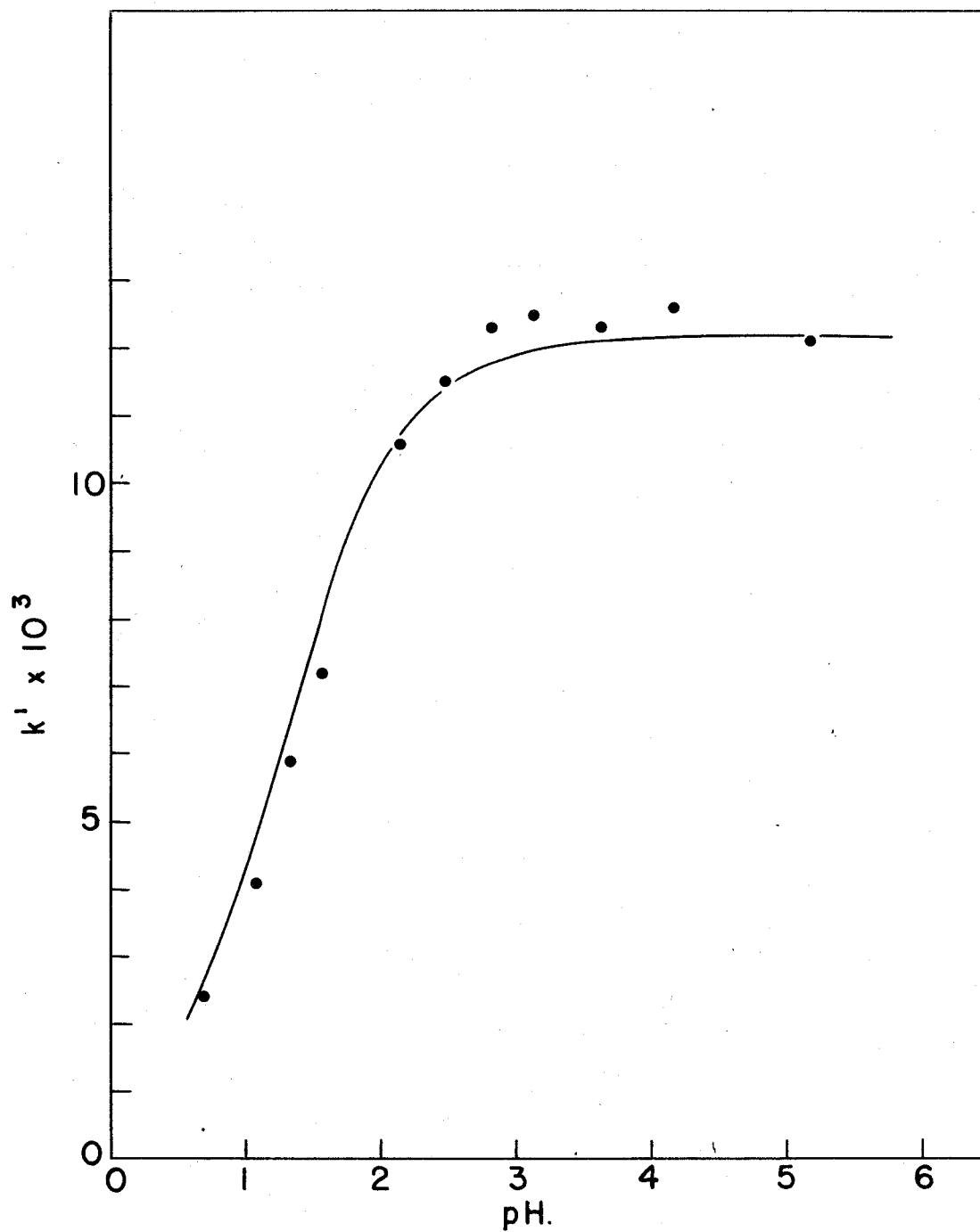B. ETHYLENE GLYCOL 0.00°C. FIRST
ORDER RATE CONSTANTS VERSUS pH.

FIG. 2. PROPYLENE GLYCOL 0.00°C. FIRST ORDER
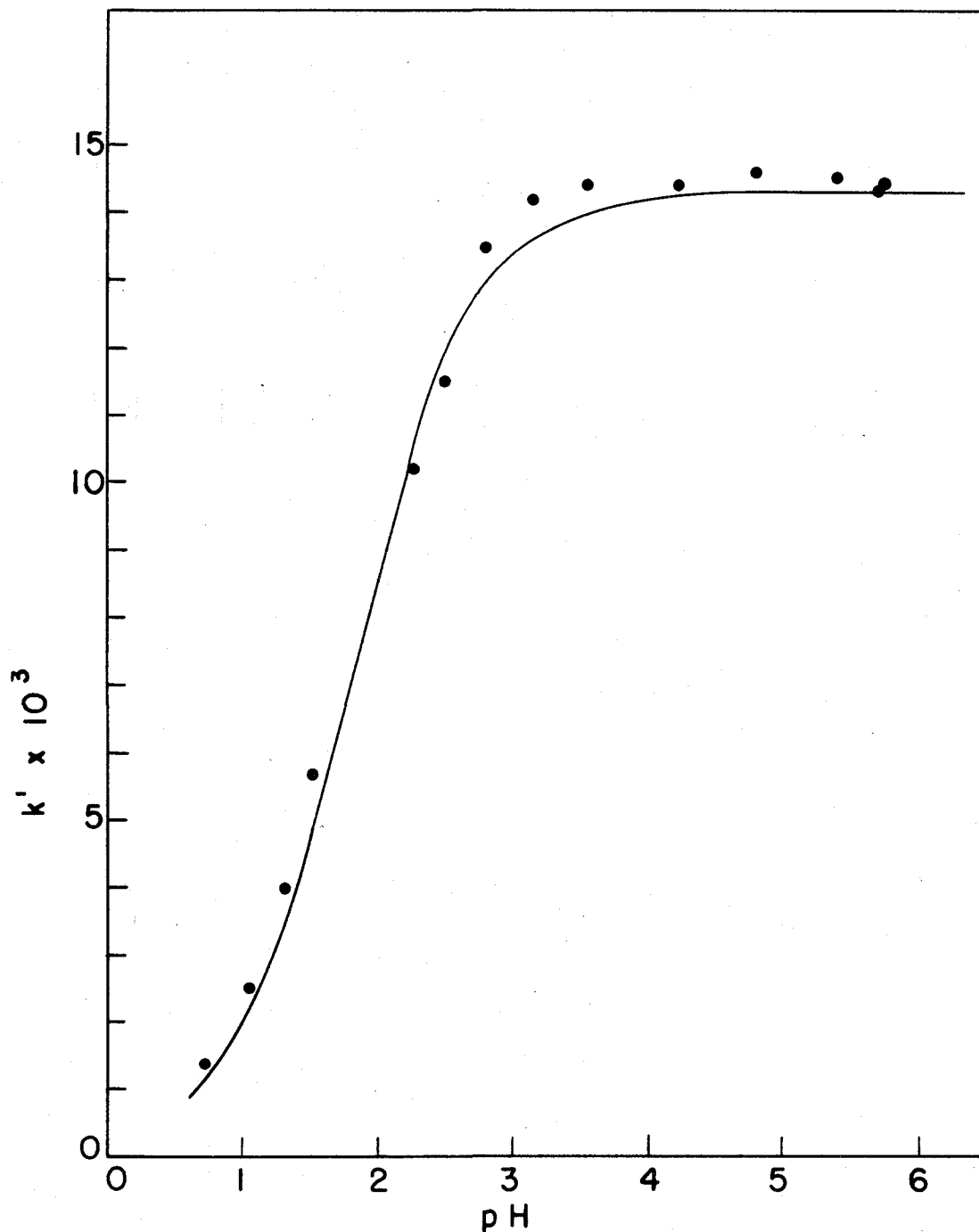RATE CONSTANTS VERSUS pH. CURVE
CALCULATED FROM Eq. 3

FIG. 3 MESO-BUTYLENE GLYCOL 0.00°C. FIRST
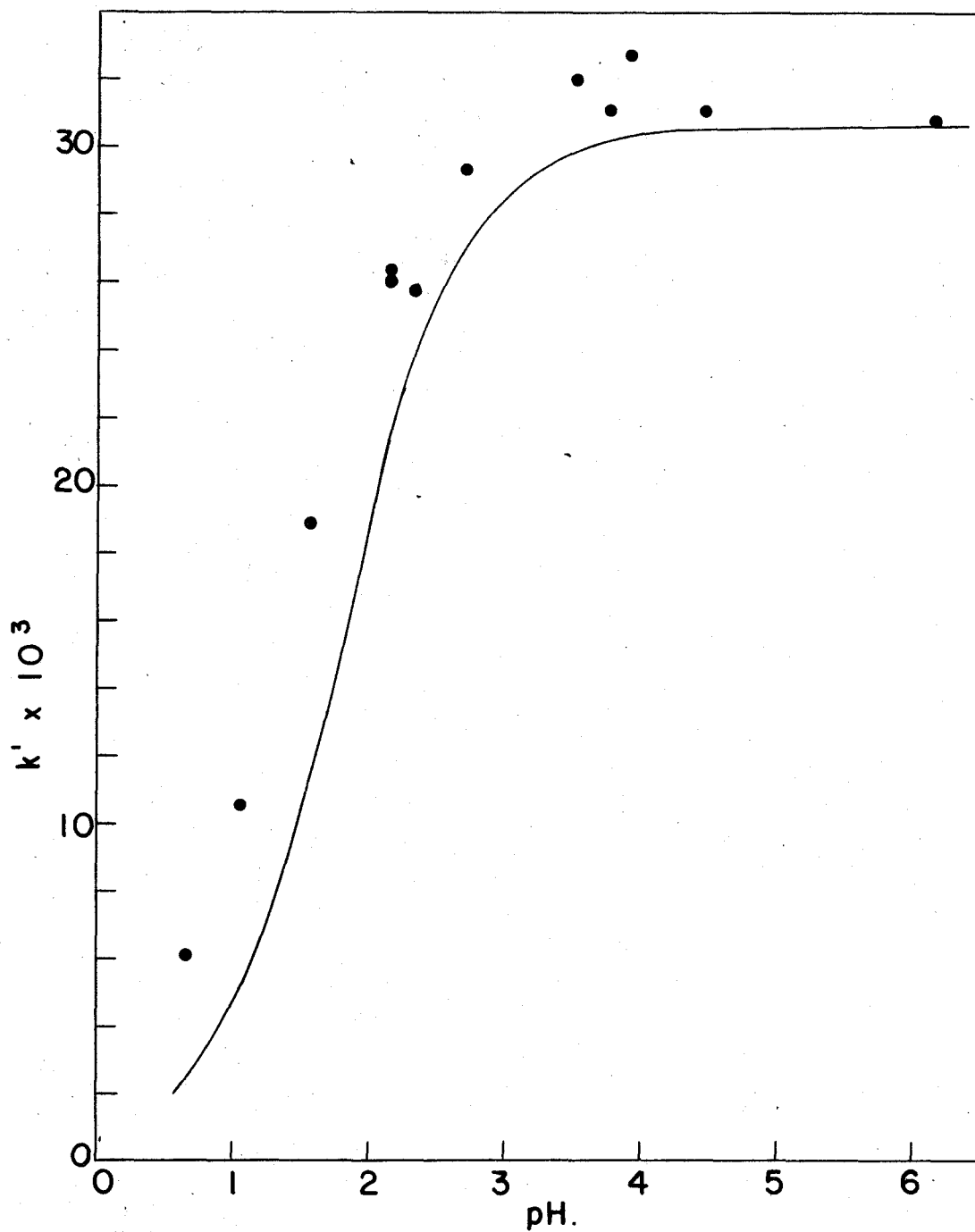ORDER RATE CONSTANTS VERSUS pH.
CURVE CALCULATED FROM Eq. 3

FIG. 4 LEVO-BUTYLENE GLYCOL 0.00°C. FIRST
ORDER RATE CONSTANTS VERSUS pH.
CURVE CALCULATED FROM Eq. 3

(16). A plot of the variation of K_D with temperature is given in Figure 5. Values of K_D used for the calculations were 7.1 at 0°, 12.0 at 5.2°, 40 at 25°, and 5.8 at -4.1°.

The agreement between the observed and calculated rates illustrated by Figures 2-4 substantiates the postulate that a monovalent negative ion, here assumed to be IO_4^-, is the reactive periodate species, that lowering of the rate in solution of pH less than three can be attributed quantitatively to diminishing concentration of negative ion with increasing acidity. Furthermore, undissociated H_5IO_6 plays a very small role, if any, in the oxidation.

Variation of Rate with Glycol Concentration;
Determination of Rate and Equilibrium Constants

Equation 3 predicted a linearity in rate for the pH range three to seven, the third term in parenthesis becoming negligibly small. This linearity was indeed observed for ethylene, propylene, meso- and levo- butylene and trimethylethylene glycols, and in the pH range three to seven Equation 3 reduced to:

$$\frac{1}{k'} = \frac{1}{k} + \frac{1}{kKG}\left(1 + \frac{1}{K_D}\right).$$

By varying the glycol concentration, a plot of $1/k'$ versus $1/G$ should give a straight line with intercept $1/k$ and
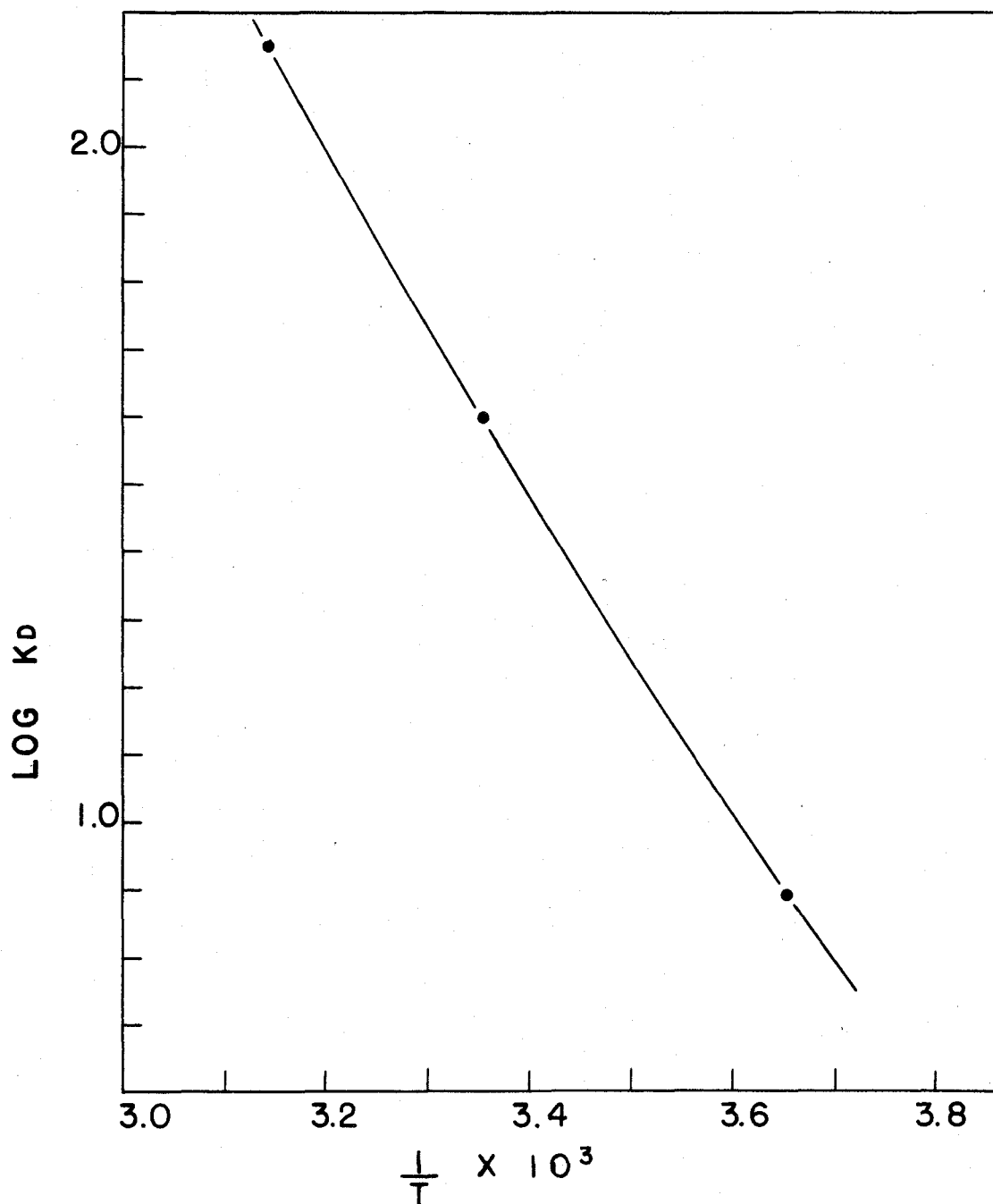
FIG. 5 PLOT OF LOG K_D FOR PERIODIC ACID
VERSUS RECIPROCAL TEMPERATURE.
FROM DATA OF CROUTHAMEL et al.(16)

slope $1/kK(1 + 1/K_D)$; the rate and equilibrium constants could both be determined from a single plot. The difficulty in such a procedure lies in the fact that the equilibrium constant K must be known in order to evaluate G, the uncoordinated glycol concentrations. One method would consist of calculating a rough value of K from the limiting slope of a plot of $1/k'$ versus the reciprocal of the total glycol concentration; the intercept is not very sensitive to changes in the slope. Using K determined in this manner, G would then be calculated and the data replotted as $1/k'$ versus $1/G$. This procedure would be repeated until self-consistency was attained, that is, until the slope of the line reproduced the same value of K used to calculate G.

For very dilute solutions of periodate and glycol, the reaction appears to be second order, (first order in periodate and first order in glycol), because of the relatively small amount of complex present. In the further case of equal concentrations[a] of total periodate and total glycol, the kinetics may be represented by

$$- \frac{dP_T}{dt} = kK(IO_4^-)(G) = kK \; f \; P_T^2 \tag{5}$$

where G = uncoordinated glycol concentration
P_T = total periodate concentration

---

[a] The initial concentration used was .00160 M.

and

$$f = \frac{G/P_T}{1+1/K_D+KG} \quad .$$

(6)

The factor f can be shown to vary by not more than about 10 per cent during a typical second order run, whereas P_T was determined over a five- to ten- fold change in concentration. Hence, it is possible to integrate Equation 5, a plot of $1/P_T$ versus time giving a straight line with slope equal to kKf.

In practice, a combination of the two foregoing methods was found to be quite satisfactory for determining K. Using the rate constant k determined from the intercept of the $1/k'$ versus $1/G_{total}$ plot, and the slope of the second order plot (equal to kKf), a first approximation to K was calculated. From this value of K, G, the average (nearly constant) value of uncoordinated glycol concentration for each first order reaction[a] was calculated, using the relations:

$$\frac{C*}{(IO_4^-)(G)} = K, \quad IO_4^- = \frac{P_T}{1 + \frac{1}{K_D} + KG} ,$$

and $C* = G_T - G$, which

---

[a]The concentration of uncoordinated glycol at the midpoint of each first order run was taken to be the average value for the run. The variation from this average value for a given run was not greater than 5 per cent for most of the runs, and in all no greater than 10 per cent.

combine to give

$$\frac{(G_T - G)\,(1 + \frac{1}{K_D} + KG)}{(P_T)(G)} = K \, , \qquad (7)$$

with G_T and P_T being the total glycol and periodate con-
centration, respectively, for the midpoint of each first
order run. A plot of $1/k'$ versus $1/G$ then gave a straight
line; from the intercept and slope of the plot, better
values of k and K were calculated. The entire process was
repeated to refine the constants; in every case the second
set of calculations gave values of K, determined from the
slopes of the $1/k'$ versus $1/G$ plot and the second order
plot, which agreed to within 10 per cent. The final sets
of calculations for the variation of rates with glycol
concnetration are given in Tables 8-12 and plotted in
Figures 6-10. The second order plots are shown in Figures
11-15.

Rate and equilibrium constants are given in Table 13.
The indicated errors are estimates based upon the repro-
ducibility of the rate constants and the agreement obtained
between the two methods for calculating K. There appears
to be no systematic correlation between the equilibrium
and rate constants for the reaction; the factors influ-
encing the formation of the complex cannot be identified
with those favoring its disproportionation.

Table 8. Ethylene glycol. Variations of pseudo first
order rate constants with glycol concen-
tration.

G_T initial	G_T*	G**	1/G	$k' \times 10^3$	1/k'
		0.00°C			
.0196	.0146	.0123	80.0	3.16	316
.0235	.0185	.0162	61.7	3.40	294
.0294	.0244	.0220	45.5	3.59	279
.0388	.0388	.0312	32.1	3.93	254
.098	.093	.090	11.1	4.32	231
.196	.191	.188	5.3	4.48	223
		5.25°C			
.0196	.0146	.0130	76.9	6.03	166
.0235	.0185	.0166	60.2	6.62	151
.0294	.0239	.0221	45.2	7.13	140
.0388	.0333	.0314	31.8	7.94	126
.098	.092	.090	11.1	9.25	108
.196	.190	.188	5.3	9.84	102

*The total glycol concentration at half-reaction.

**The average uncoordinated glycol concentration, calcu-
lated from Equation 7.

Table 9. Propylene glycol. Variation of pseudo
first order rate constants with glycol
concentration.

G_T initial	G_T*	G**	1/G	$k' \times 10^3$	1/k'
			0.00°C		
.0200	.0140	.0124	80.6	10.7	93.1
.0240	.0180	.0163	61.3	11.4	87.5
.0300	.0240	.0222	45.0	11.9	84.1
.100	.094	.092	10.9	13.1	76.4
.200	.194	.192	5.2	13.5	74.2
			5.25°C		
.0200	.0135	.0125	80.0	21.9	45.7
.0240	.0175	.0164	61.0	23.9	41.8
.0300	.0235	.0223	44.8	25.5 / 25.5	39.2 / 39.2
.0400	.0335	.0322	31.1	27.1	36.9
.100	.093	.092	10.9	28.3 / 29.0	35.3 / 34.5
.200	.193	.192	5.3	29.9	33.4

*The total glycol concentration at half-reaction.

**The average uncoordinated glycol concentration, calculated from Equation 7.

Table 10. Trimethylethylene glycol. Variation of pseudo first order rate constants with glycol concentration. pH 4.1-5.5.

G_T initial	G_T*	G**	1/G	$k' \times 10^3$	1/k'
		0.00°C			
.0200	.0145	.0136	73.5	12.7	78.7
.0240	.0180	.0172	58.1	15.0	66.7
.0300	.0240	.0233	42.9	17.1	58.5
				20.4	49.8
.0400	.0335	.0328	30.5	20.3	49.3
.0800	.0730	.072	13.9	26.0	38.5
		5.25 °C			
				18.1	55.2
.0200	.0140	.0137	73.0	17.9	55.9
.0240	.0175	.0172	58.1	21.8	45.9
.0300	.0230	.0227	44.1	27.8	36.0
				35.4	28.2
.0400	.0330	.0326	30.7	35.9	27.9
.0800	.0725	.072	13.9	54.7	18.3

*The total glycol concentration at half-reaction.

**The average uncoordinated glycol concentration, calculated from Equation 7.

Table 11. Meso- butylene glycol. Variation of pseudo
first order rate constants with glycol
concentration.

G_T initial	G_T*	G**	1/G	k'x10^3	1/k'
		0.00°C			
.0206	.0146	.0137	73.0	10.4	96.2
.0247	.0187	.0177	56.5	11.4	87.7
.0309	.0249	.0237	42.2	12.8	78.1
.0412	.0352	.0338	29.6	14.6	68.5
				17.7	56.5
.103	.097	.095	10.5	18.5	54.1
.206	.200	.198	5.1	19.6	51.0
		5.25°C			
				16.6	60.2
.0206	.0146	.0139	71.9	17.0	58.8
.0247	.0187	.0179	55.9	20.7	48.3
.0309	.0244	.0238	42.0	24.4	41.0
				27.4	36.5
.0412	.0347	.0338	29.6	27.8	36.0
				36.6	27.3
.103	.096	.095	10.5	37.0	27.0

*The total glycol concentration at half-reaction.

**The average uncoordinated glycol concentration,
calculated from Equation 7.

Table 12. Levo-butylene glycol. Variation of pseudo first order rate constants with glycol concentration.

C_T initial	C_T^*	C^{**}	1/C	$k' \times 10^3$	1/k'
			0.00°C		
.0100	.0045	.0036	278	18.4	54.3
.0120	.0065	.0054	185	22.3	44.8
.0140	.0080	.0070	143	27.4	36.5
.0160	.0100	.0088	114	28.5	35.1
.0180	.0115	.0105	95	30.8	32.3
.0200	.0130	.0120	83	33.6	29.9
.0240	.0170	.0163	61	34.2	29.2
.0300	.0230	.0227	45	33.8	29.8
			-4.15°C		
.0140	.0080	.0067	149	15.1	66.2
				14.5	69.0
.0160	.0100	.0085	118	15.6	64.1
.0200	.0135	.0123	81	17.8	56.2
				17.1	58.5
.0400	.0335	.0322	31	19.2	52.1
				19.9	50.2
.100	.0915	.090	11	20.9	47.8

*The total glycol concentration at half-reaction.

**The average uncoordinated glycol concentration, calculated from Equation 7.
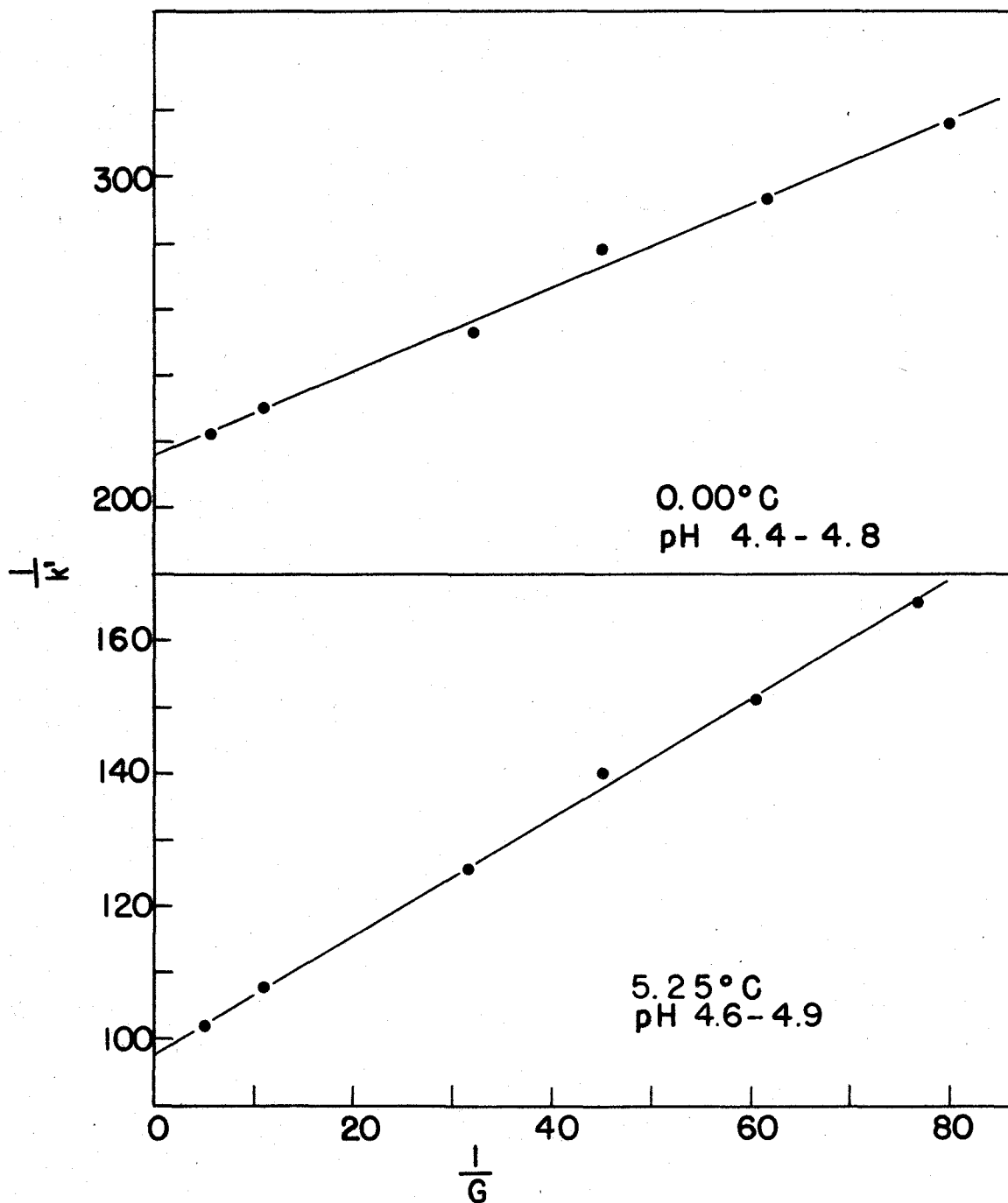
FIG. 6   ETHYLENE GLYCOL. RECIPROCAL PSEUDO
FIRST ORDER RATE CONSTANTS VERSUS
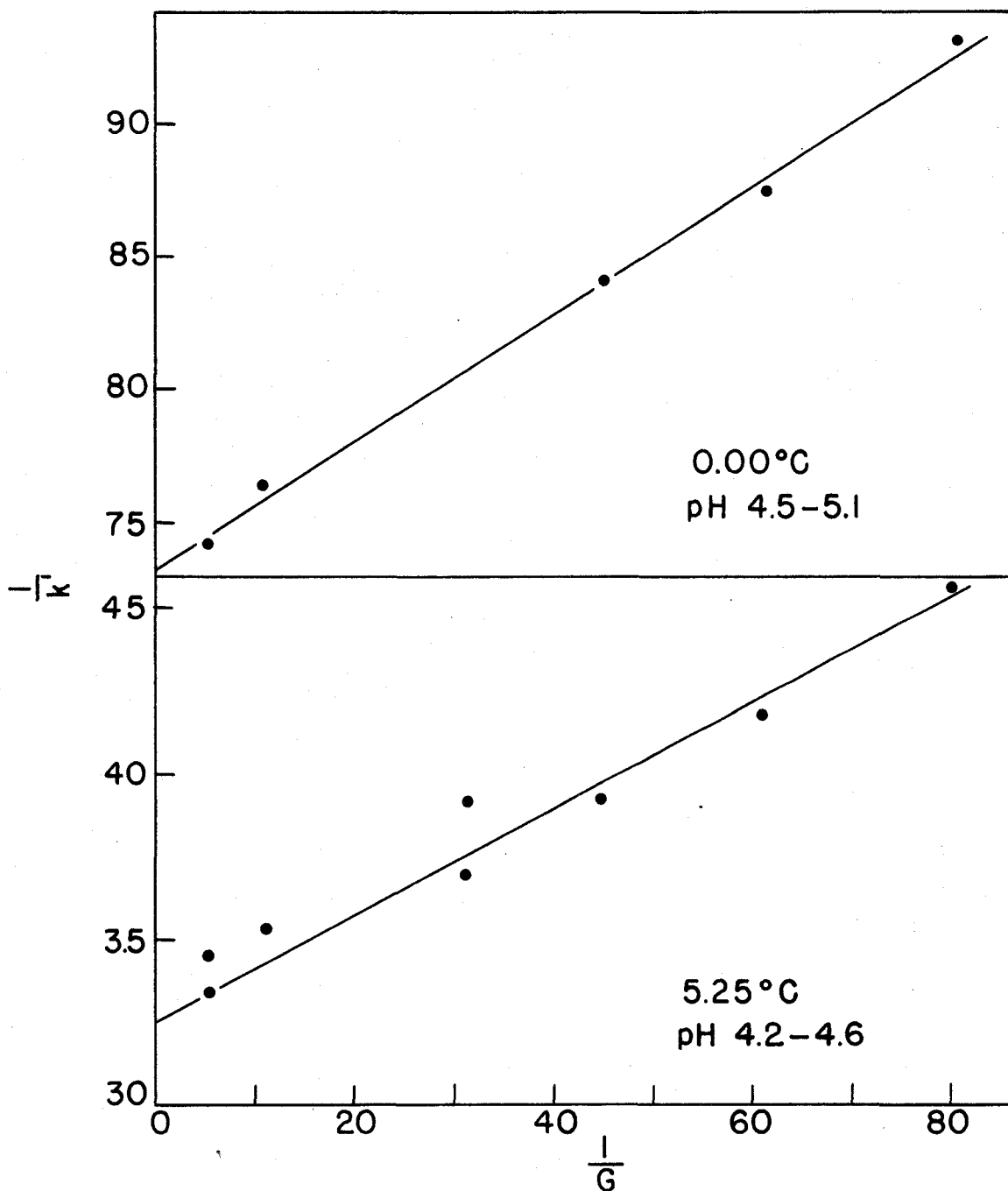RECIPROCAL GLYCOL CONCENTRATIONS.

FIG. 7 PROPYLENE GLYCOL. RECIPROCAL PSEUDO
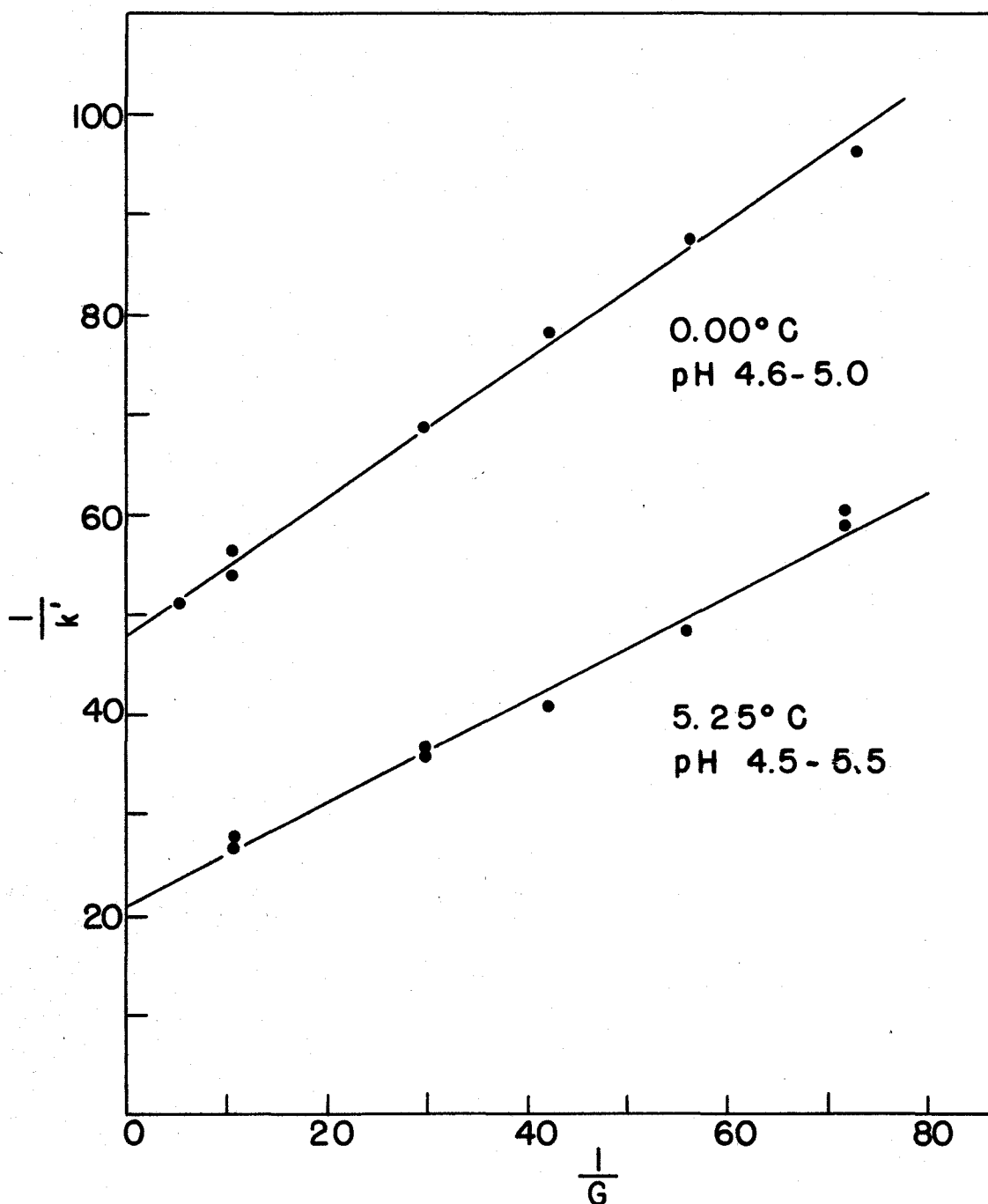FIRST ORDER RATE CONSTANTS VERSUS
RECIPROCAL GLYCOL CONCENTRATIONS.

FIG. 8 MESO-BUTYLENE GLYCOL. RECIPROCAL
PSEUDO FIRST ORDER RATE CONSTANTS
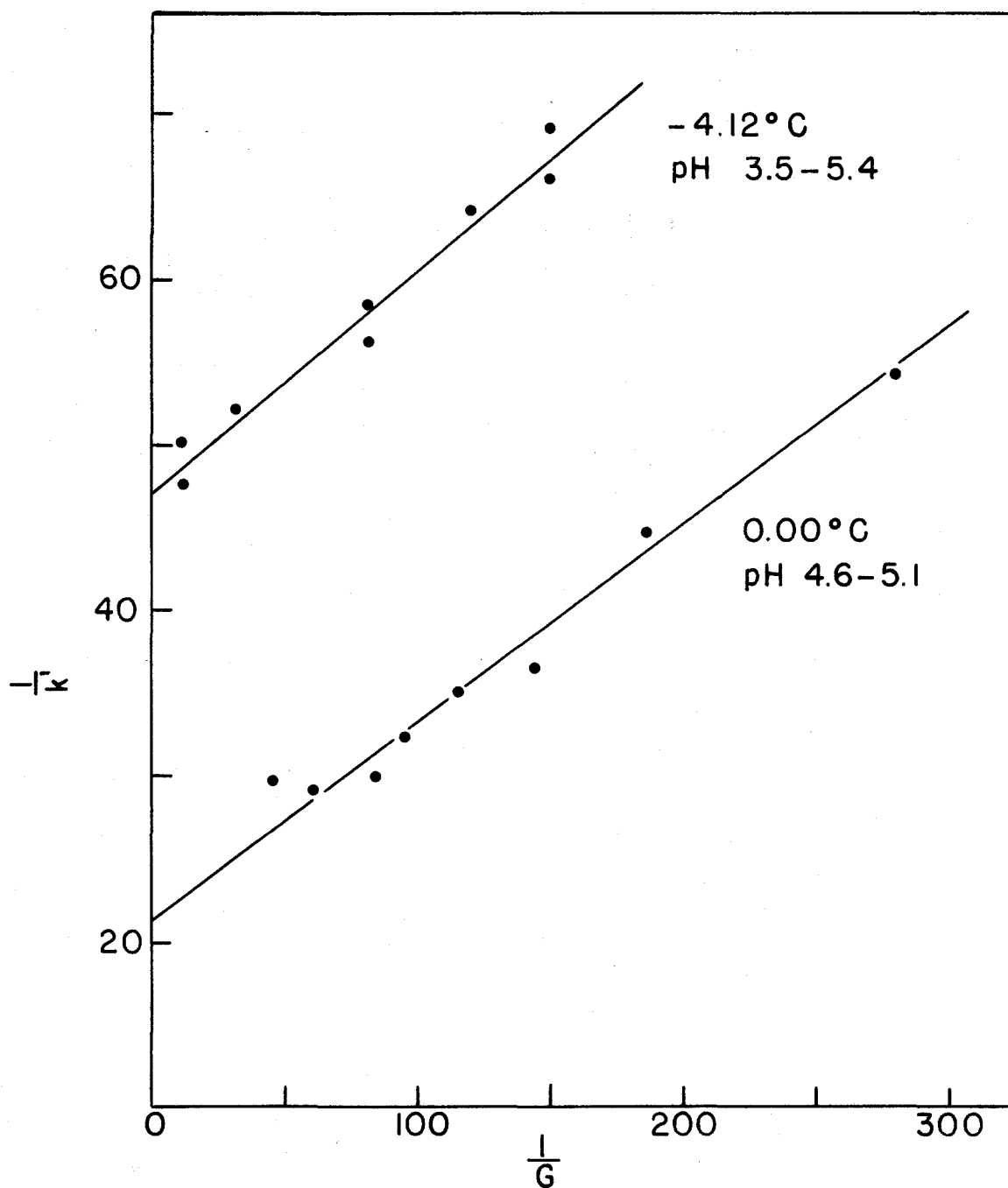VERSUS RECIPROCAL GLYCOL
CONCENTRATIONS.

FIG. 9 LEVO-BUTYLENE GLYCOL. RECIPROCAL
        PSEUDO FIRST ORDER RATE CONSTANTS
        VERSUS RECIPROCAL GLYCOL CONCEN-
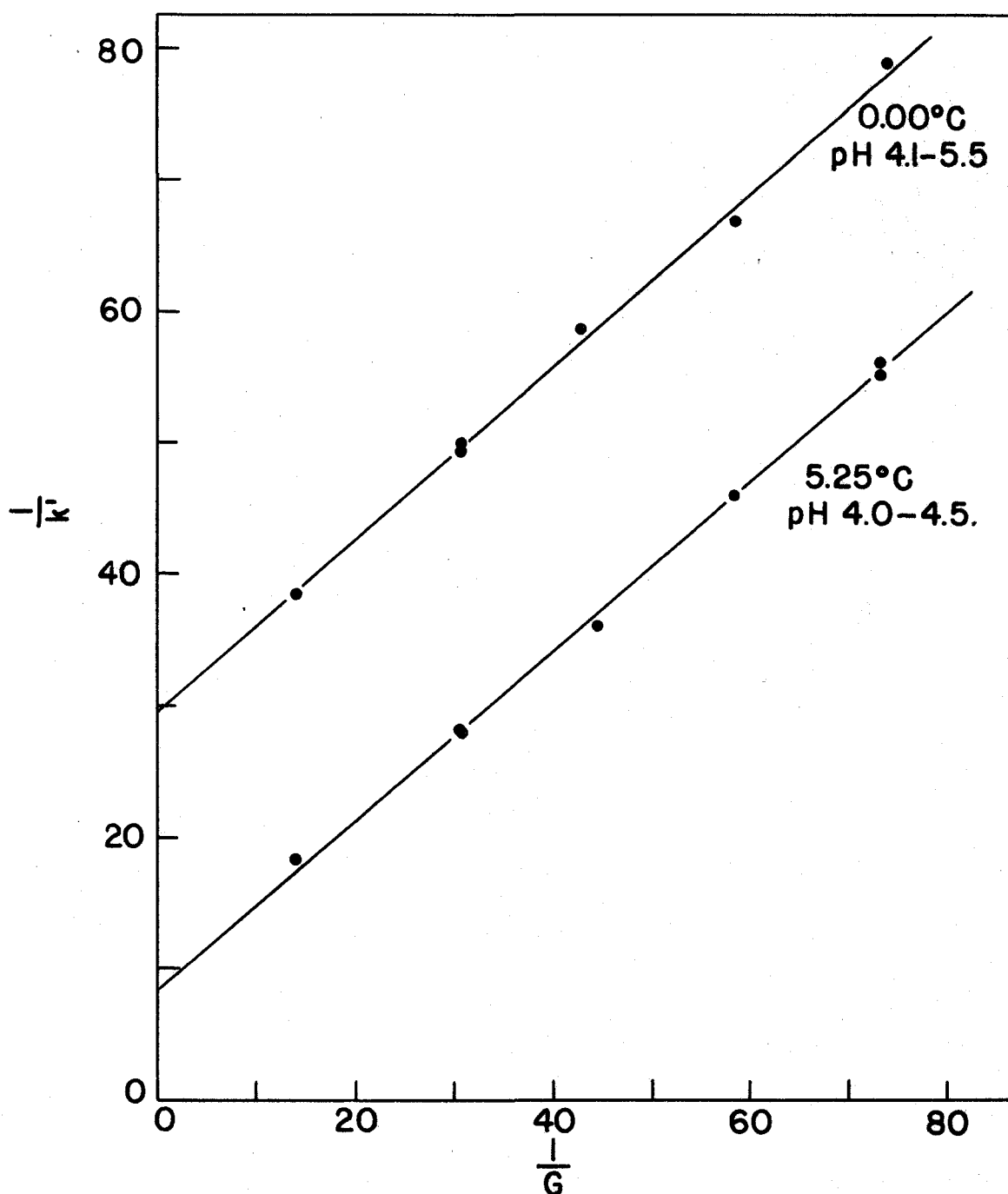   TRATIONS.

FIG. 10 TRIMETHYLETHYLENE GLYCOL. RECIPROCAL
PSEUDO FIRST ORDER RATE CONSTANTS
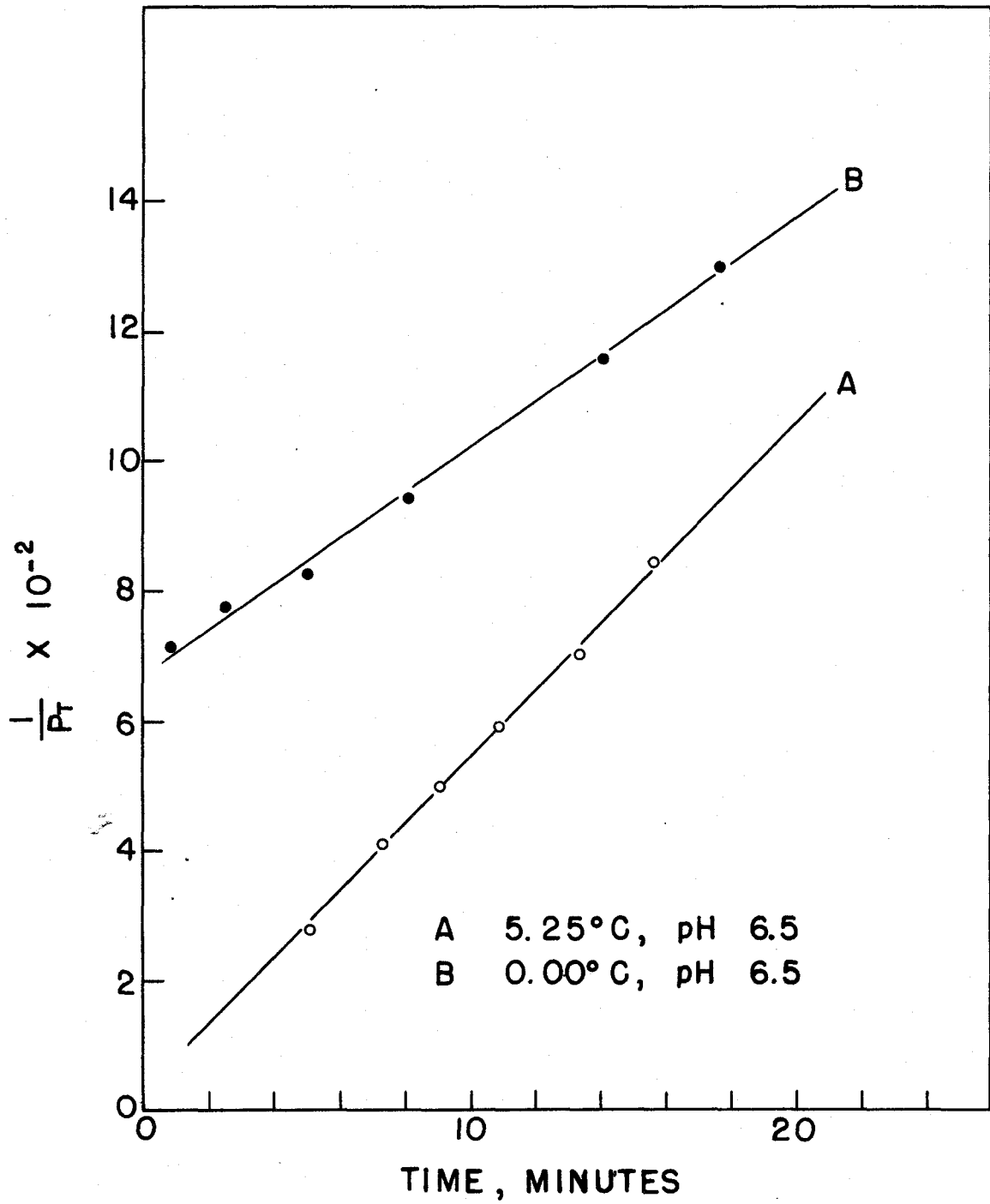VERSUS RECIPROCAL GLYCOL CONCEN-
TRATIONS.

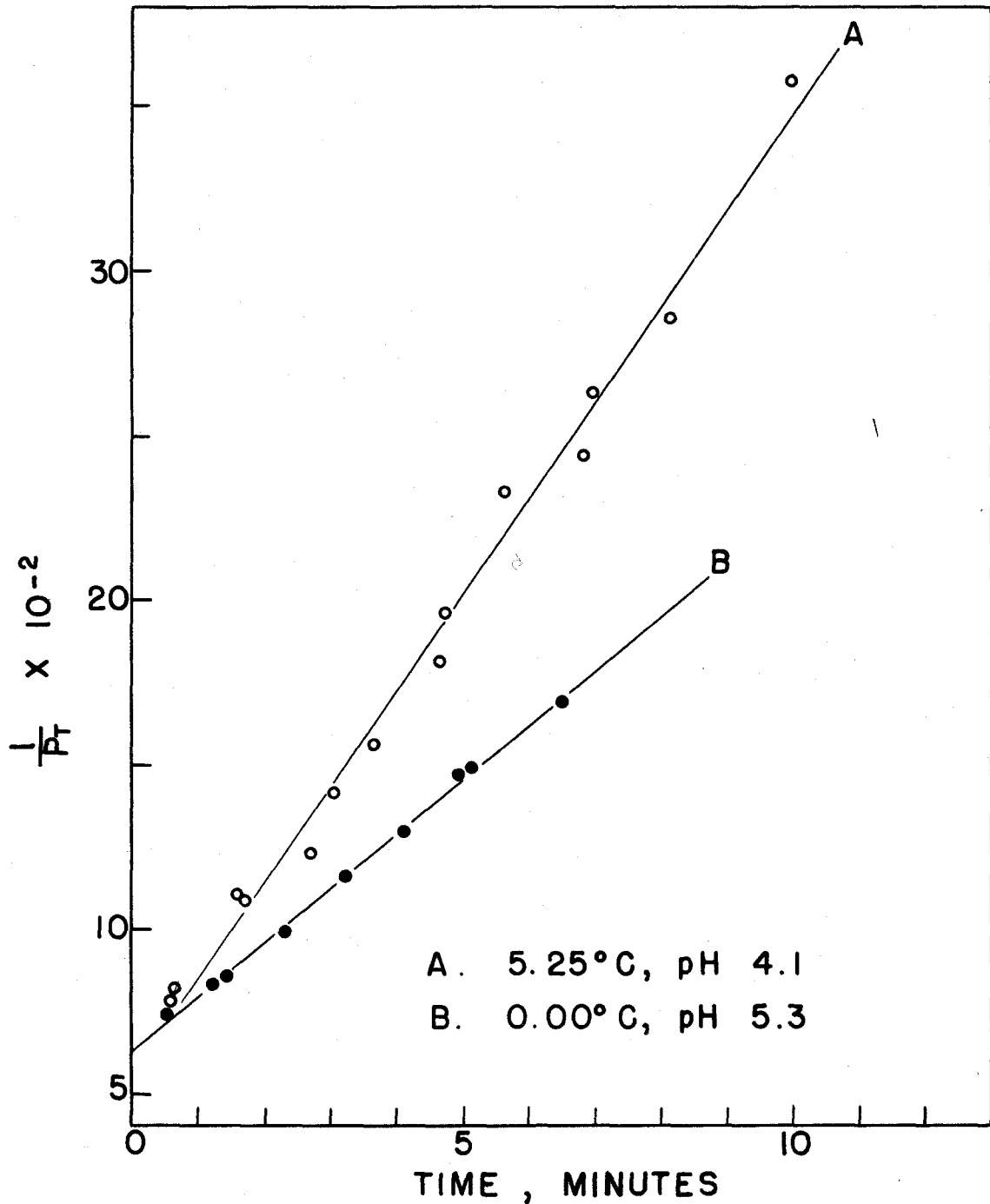FIG. 11 ETHYLENE GLYCOL. SECOND ORDER
RUNS.

FIG. 12 PROPYLENE GLYCOL. SECOND ORDER
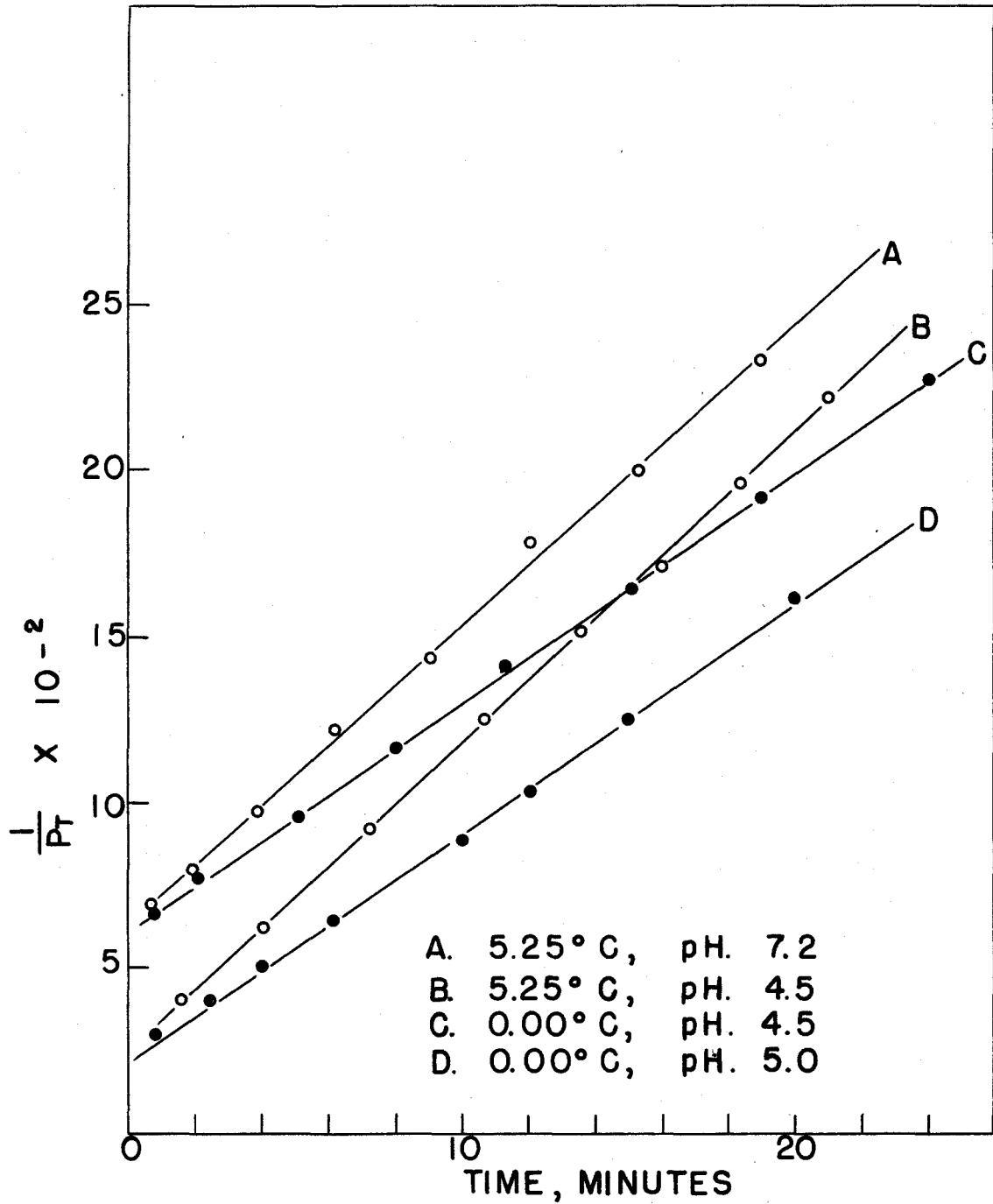RUNS. (5° DATA FROM TWO IDENTICAL RUNS,
PLOTTED TOGETHER).

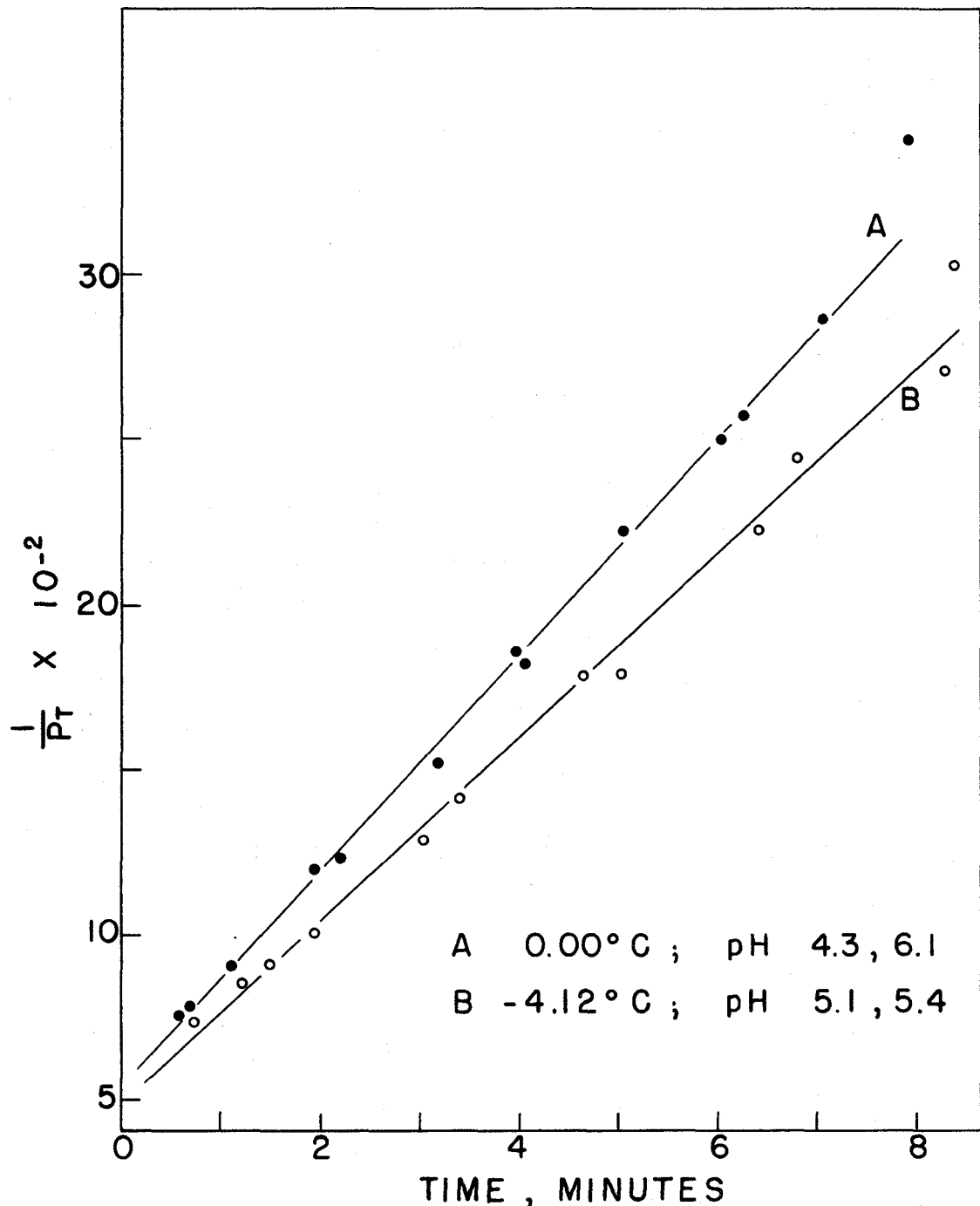FIG. 13 MESO-BUTYLENE GLYCOL. SECOND
ORDER RUNS.

FIG. 14 LEVO-BUTYLENE GLYCOL. SECOND ORDER
RUNS. (EACH LINE FROM TWO IDENTICAL
RUNS, PLOTTED TOGETHER.)
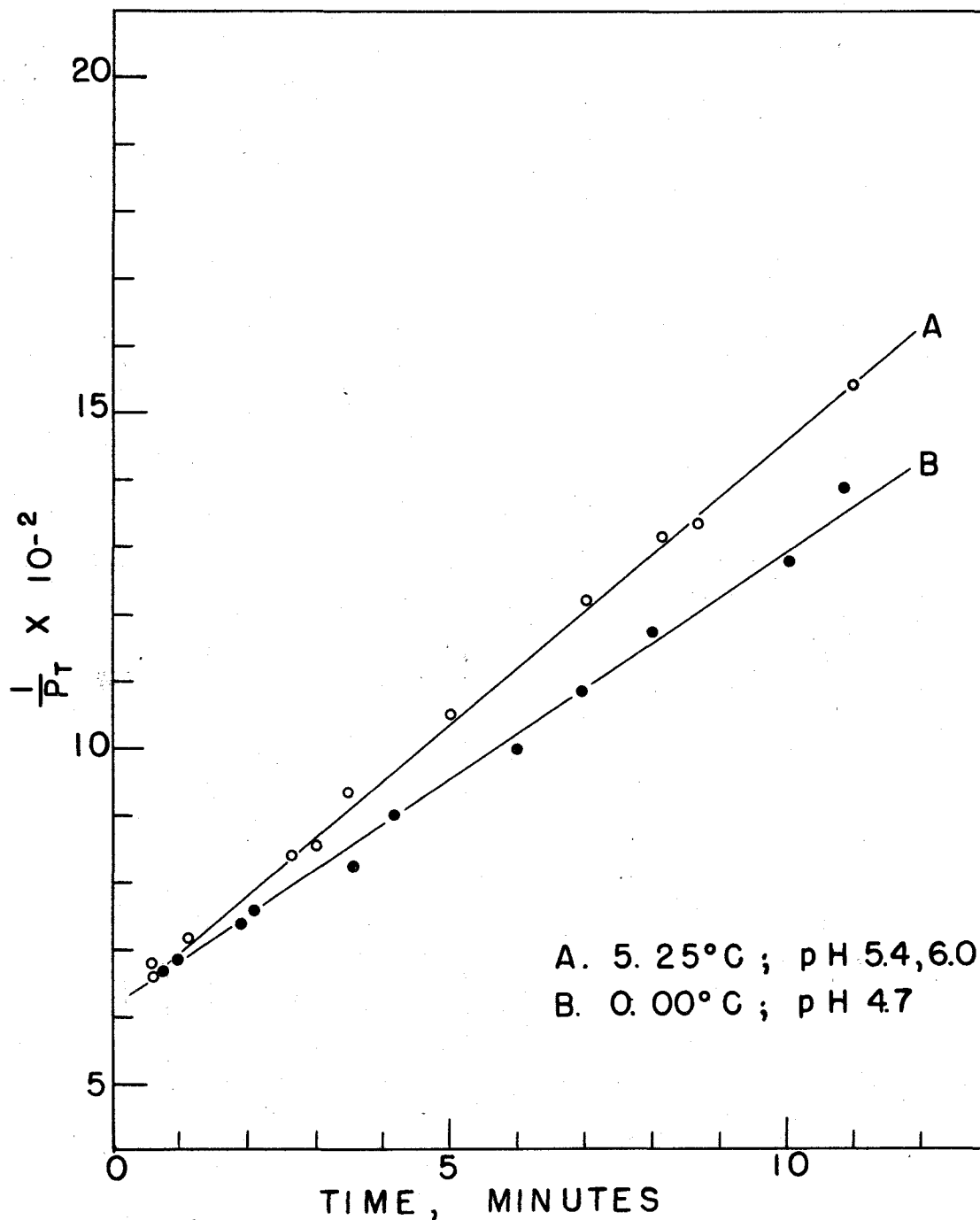
FIG 15 TRIMETHYLETHYLENE GLYCOL. SECOND ORDER RUNS. (EACH LINE FROM TWO IDENTICAL RUNS, PLOTTED TOGETHER).

Table 13. Equilibrium (K) and rate (k) constants:

$$G + IO_4^- \underset{K}{\overset{}{\rightleftarrows}} C \xrightarrow{k} \text{products.}$$

Glycol	K	$k \times 10^3$ sec.$^{-1}$
0.00 ± .05°C		
Ethylene	193 ± 10	4.60 ± .10
Propylene	350 ± 20	13.7 ± .5
Meso- butylene	73 ± 5	20.8 ± .5
Levo- butylene	180 ± 20	47. ± 2.
Trimethylethylene	43 ± 5	34. ± 1.5
5.25 ± .05°C		
Ethylene	124 ± 10	10.2 ± 0.2
Propylene	215 ± 15	30.8 ± 2.0
Meso- butylene	38 ± 4	48. ± 2.
Levo- butylene	395*± 20	21.3* ± 1.0
Trimethylethylene	13.7± 1.3	119. ±10.

*Levo- butylene at -4.12°C.

Table 14. Thermodynamic functions for complex
formations at 0°C.

$$G + IO_4^- \xrightleftharpoons{K} C$$

Glycol	ΔH kcal.	ΔF kcal.	ΔS e.u
Ethylene	-12.8+10%	-2.86±.02	-36±30%
Propylene	-14.0	-3.18	-40
Meso- butylene	-18.7	-2.33	-60
Levo- butylene	-27.8	-2.82	-92
Trimethylethylene	-32.8	-2.04	-113

Table 15. Activation energies and entropies for the
rate determining step for the range
0° to 5°C.

$$C \xrightarrow{k} \text{products.}$$
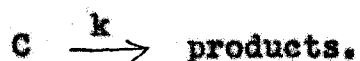
Glycol	$\Delta H^{\ddagger}$ kcal.	$\Delta F^{\ddagger}$ kcal.	$\Delta S^{\ddagger}$ e.u
Ethylene	+22.4±5%	+18.9±.0	+13±20%
Propylene	+23.5	+18.3	+19
Meso- butylene	+23.5	+18.1	+20
Levo- butylene*	+27.6	+17.6	+37
Trimethylethylene	+35.6	+17.8	+65

*Levo- butylene for the range -4° to 0°C. Errors
given are estimated maximum errors, based upon estimated
maximum errors in rate and equilibrium constants.

Steric effects when two or more methyl groups are present probably account for the observed decrease in equilibrium constants with increased methyl substitution. Steric considerations might also predict the observed difference in equilibrium constants for meso- and levo-butylene glycols, the hydroxyl groups of the meso- compound being forced somewhat further apart by interaction of the methyl groups. It has been found (30,31) that the levo-glycol forms a complex with boric acid much more easily than does the meso- compound, presumably for the same reason. Price and Knell (9) found that trans cyclohexene glycol was oxidized at a slower rate than the cis isomer; it remains to be shown, however, just how much of this difference can be attributed to a difference in equilibrium constants. In view of the uncertainty in the structure of trans cyclohexene glycol (32), which apparently consists of an equilibrium mixture of two isomers with very different O - O distances, it would be better to compare the rates of oxidation of cis and trans cyclopentene glycols.

The thermodynamic functions for complex formation and for the rate controlling step are given in Tables 14 and 15. For the equilibrium reaction, calculations were made from the following relationships:

$$\Delta F = -2.3 \; RT \; \log K$$

$$\Delta H = 2.3 \; R \; \frac{T_1 T_2}{T_2 - T_1} \; \log \; \frac{K_2}{K_1}$$

$$\Delta S = \frac{-\Delta F + \Delta H}{T} \; .$$

For the disproportionation reaction, the relations used were:

$$\Delta F = -2.3 \; RT \; \log \; \frac{k}{k_B T / h}$$

where k_B is Boltzmann's constant.

h is Planck's constant.

$$\Delta H = 2.3 \; R \; \frac{T_1 T_2}{T_2 - T_1} \; \log \; \frac{k_2}{k_1} \; - RT$$

$$\Delta S = \frac{-\Delta F + \Delta H}{T} \; .$$

Thus far, the reaction has been regarded as proceding through the sequence:

$$IO_4^- + G \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} C \overset{k}{\underset{\text{slow}}{\longrightarrow}} \text{products.}$$

It should be pointed out that kinetically one cannot distinguish between this mechanism and that represented by:

$$IO_4^- + G \overset{K}{\rightleftharpoons} C$$

$$IO_4^- + G \overset{k}{\underset{\text{slow}}{\longrightarrow}} \text{products.}$$
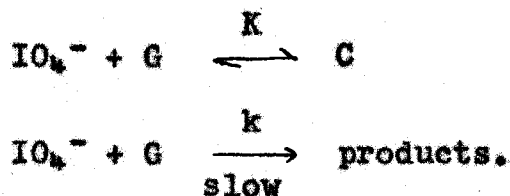
The equilibrium constants determined in the latter case are identical with those obtained in the former; the rate constants are larger by the factors K.

Assuming that two colliding reactant molecules IO_4^- and G must possess a total energy greater than a certain value E_1, in order to form a complex, and greater than E_2 $(E_2 > E_1)$[a] in order to react to give cleavage products, and further assuming a continuous distribution of energies, then a pair of colliding molecules having an energy greater than E_2 must also have possessed energy enough to form a complex. It is conceivable that one is not justified in regarding the two mechanisms as being distinct. In any case, little is sacrificed from the standpoint of theory by assuming the first representation to be the more correct; something is gained in that the specificity of the oxidation is made more readily apparent.

Pinacol

Trimethylethylene glycol had been shown (previous sections) to be oxidized in the same way as the other glycols studied. However, substitution of the fourth methyl

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[a]If E_1 were greater than E_2, it is doubtful that enough complex would be present to be detected by rate measurements.

group resulted in an abrupt change in reactivity. For pinacol, the reaction was found not only to be very much slower but also to follow the second order kinetics represented by

$$IO_4^- + G \xrightarrow{k''} \text{products}.$$

$$- \frac{dP_T}{dt} = k'' (IO_4^-)(G) = k' P_T G \quad . \tag{8}$$
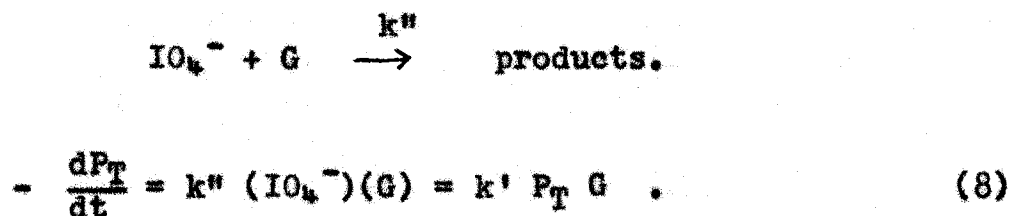
Plots of log $P_T/P_T + G_1 - P_1$ versus time, where G_1 and P_1 were the initial total glycol and periodate concentrations, gave excellent straight lines, with slopes equal to $k'(G_1 - P_1)/2.3$. Although the pH during a given run was found to vary by not more than 0.1 unit, there was a marked dependence of the rate upon the pH of the solution.

Table 16 gives values of the second order rate constants k' determined from different glycol and periodate concentrations at three selected pH values. Tables 17 and 18 and Figure 16 show the variation of the second order rate constants with pH. The flat portion of the curve in Figure 11 was taken to represent the reaction uncatalyzed by hydrogen ion; the value of k' in this region was taken to be k_0.

Assuming k' to be made up of k_0 plus a term involving hydrogen ion, and further assuming the dependence on hydrogen ion to be first order, Equation 8 takes the form:

Table 16. Pinacol 0°C. Second order rate constants determined from different glycol and periodate concentrations for three selected pH values.

pH	$G_{initial}$	$P_{initial}$	Slope	$k' \times 10^2$
1.6±.1	.0080	.0080	1.42×10^{-2}	1.43
	.0380	.0080	1.92×10^{-4}	1.46
	.0740	.0080	4.38×10^{-4}	1.53
	.093	.0080	5.67×10^{-2}	1.53
	.093	.093	1.69×10	1.69a
2.2±.1	.0080	.0080	1.02×10^{-2}	1.02
	.0380	.0080	1.39×10^{-4}	1.06
	.0740	.0080	3.02×10^{-2}	1.05
	.093	.0080	4.15×10^{-2}	1.12
	.093	.093	1.08×10	1.08b
6.2±.2	.0080	.0080	1.32×10^{-3}	.132
	.0380	.0080	1.65×10^{-5}	.127
	.0740	.0080	3.71×10^{-3}	.129
	.093	.093	1.70×10	.170c

a pH varied from 1.7 to 1.4 during run.

b pH varied from 2.3 to 1.7 during run.

c pH varied from 5.5 to 6.6 during run. For all other runs, pH varied less than .1 unit.

Table 17. Pinacol 0°C. Variation of second order rate constants with pH.

$G_{initial} = .0380;\ P_{initial} = .0080$

pH	A_{H+}	$k' \times 10^2$	f	fk'	$\log(fk'-k_0)$
0.40	.40	.72	95.	.68	.83 − 1
0.65	.22	1.01	54.	.54	.74
1.10	.080	1.24	19.9	.247	.39
1.33	.047	1.41	12.1	.171	.23
1.57	.027	1.46	7.47	.109	.03
1.77	.017	1.40	5.12	.072	.85 − 2
2.20	.0063	1.04	2.62	.0272	.41
2.57	.0027	.64	1.77	.0113	.00
3.00	.0010	.347	1.37	.0048	.53 − 3
3.56	2.8×10^{-4}	.194	1.20	.0023	.00
4.53	3.0×10^{-5}	.133	1.15	.0015	
5.81	1.6×10^{-6}	.126	1.14	.0014	
6.42	3.8×10^{-7}	.128	1.14	.0014	

Table 18. Pinacol 25.25°C. Variation of second
order rate constants with pH.

$G_{initial} = .0414;$ $P_{initial} = .0080$

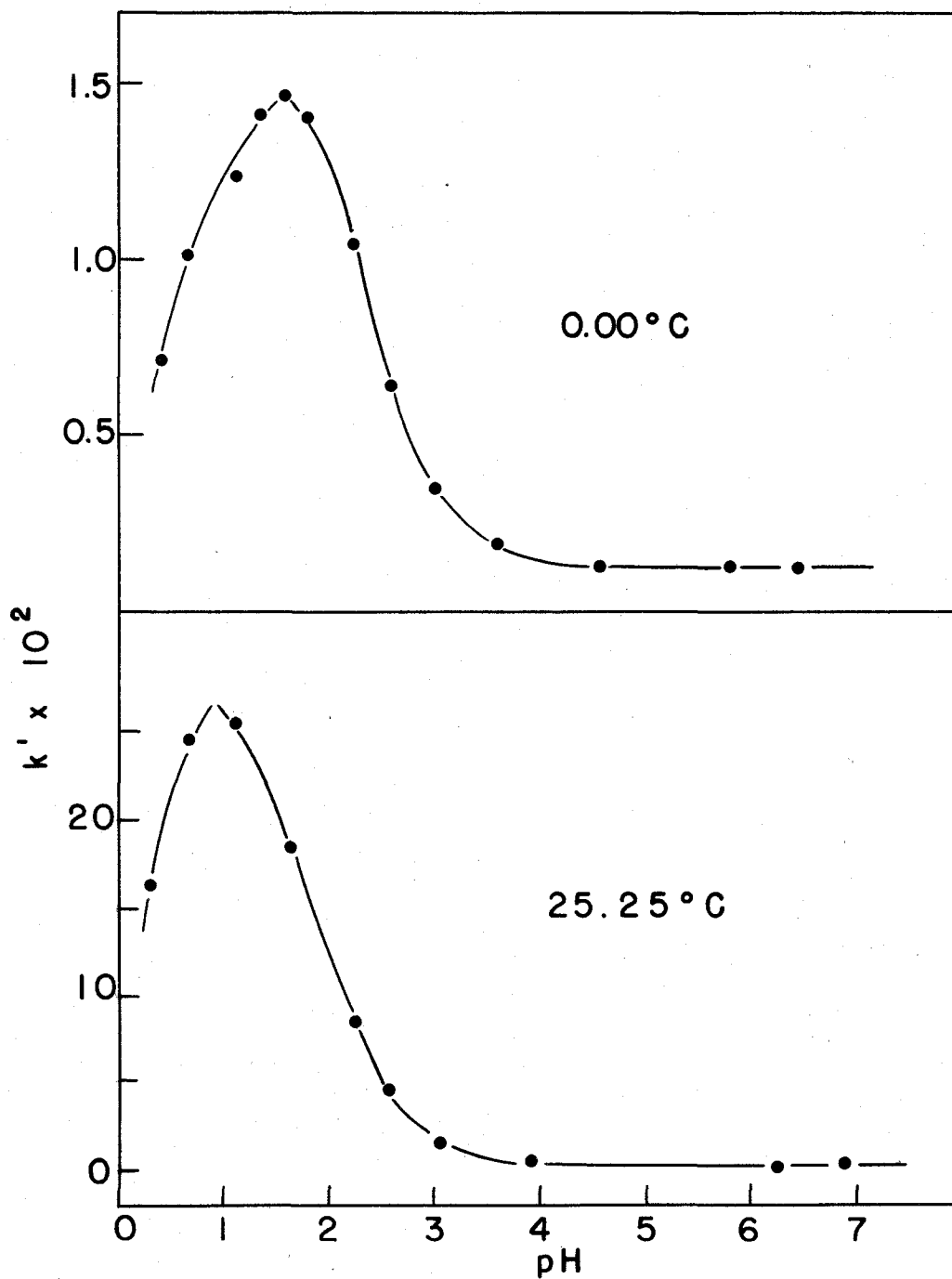| pH	A_{H+}	$k' \times 10^2$	f	fk'	$\log(fk'-k_0)$
0.30	.50	16.3	18.5	3.01	.48
0.67	.21	24.6	8.8	2.16	.33
1.10	.080	25.5	4.0	1.02	.01
1.63	.023	18.5	1.87	.346	.53 - 1
2.25	.0056	8.6	1.23	.106	.00
2.55	.0028	4.71	1.12	.053	.68 - 2
3.05	8.9×10^{-4}	1.74	1.05	.0183	.14
3.90	1.3×10^{-4}	.58	1.03	.0060	.20 - 3
6.24	$6. \times 10^{-7}$	.43	1.02	.0044	
6.84	$2. \times 10^{-7}$	.47	1.02	.0048	

FIG.16 PINACOL. VARIATION OF SECOND ORDER RATE CONSTANTS WITH pH.

$$-\frac{dP_T}{dt} = \frac{k_0 + k_H(H^+)}{f} \, P_T G_T \qquad (9)$$

where $f = (1 + \dfrac{1}{K_D} + \dfrac{A_{H^+} \, \gamma_{IO_4^-}}{K_1 K_D \, \gamma_{H_5IO_6}})$

P_T and G_T = total periodate and glycol glycol concentrations, respectively, at time t.

$$k' = \frac{k_0 + k_H(H^+)}{f}.$$

It is seen that a plot of $\log(k'f-k_0)$ versus $\log (H^+)$ should give a straight line with slope 1.0 and intercept $\log k_H$. If $\log (k'f-k_0)$ were plotted against pH, the slope should be -1.0 and the intercept $\log k_H/\gamma_{H^+}$, where γ_{H^+} is the activity coefficient of hydrogen ion. Such a plot is shown in Figure 17; the calculations are included in Tables 17 and 18. The straight lines in Figure 17 were drawn with slopes of -1.00 to illustrate agreement with first order hydrogen ion catalysis. It should be pointed out that pH measurements below one are subject to consider- able error; because A_{H^+} was evaluated directly from pH measurement, this error would be carried over in the calcu- lation of the factor f.

The rate constants k_H for the two temperatures were calculated from the intercepts of the plots in Figure 17, assuming a (constant) value of 0.80 for γ_{H^+}. The constants
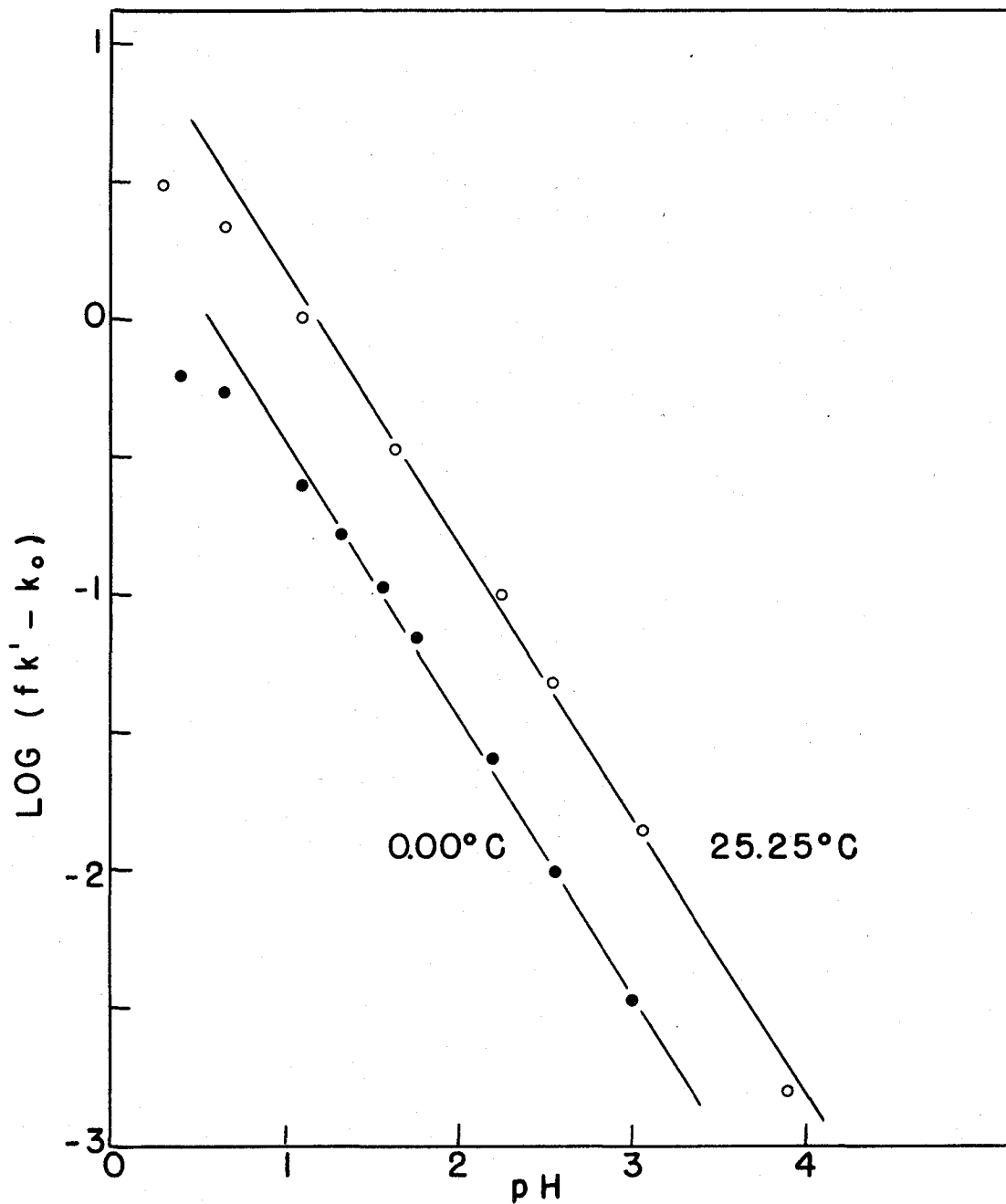
FIG.17 PINACOL. PLOT SHOWING FIRST ORDER HYDROGEN ION DEPENDENCY. SLOPE OF EACH LINE IS -1.0, INTERCEPT IS LOG $\frac{k_H}{\gamma_{H^+}}$.

k_0 and k_H are given in Table 19, along with the calculated thermodynamic functions.

Thus, the rate of the periodate oxidation of pinacol in acid solution may be represented by:

$$-\frac{dP_T}{dt} = \left[k_0 + k_H(H^+) \right] \ (IO_4^-)\ (G) \ .$$

It is possible that the uncatalyzed reaction is an unspecific oxidation which accounts for the slight overoxidation of pinacol in acid solution (see Table 2).

Any mechanism proposed for the pinacol oxidation in acid solution must take into account the apparent second order kinetics, the first order hydrogen ion catalysis and the constancy of the hydrogen ion concentration during a given reaction. The first of these could be accounted for by the following:

1. The oxidation is a bimolecular reaction involving a glycol species and periodate ion.

2. The reaction may proceed through an intermediate complex, with the rate determining step the formation of the complex.

3. The reaction may proceed through an intermediate complex, with the rate determining step the disproportionation of the complex, the equilibrium constant for its formation being so small that the complex would be very difficult to detect by means of rate data.

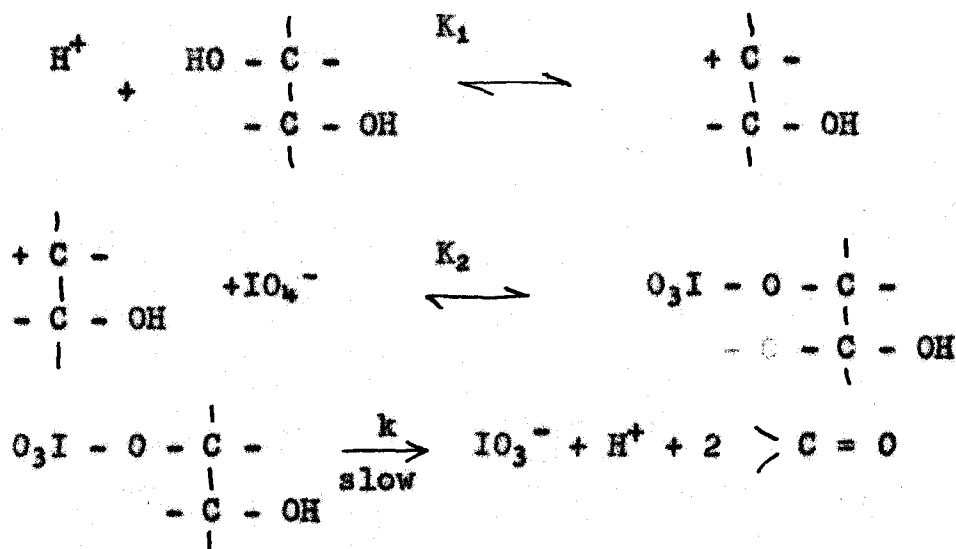Table 19. Rate constant and thermodynamic functions
for the pinacol oxidation.

$$-\frac{dP_T}{dt} = \left[k_0 + k_H(H^+) \right] (IO_4^-)(G)$$

Uncatalyzed reaction	0.00°C	25.25°C
k_0	.0014	.0044
$\Delta H_{kcal.}$	+7.2	
$\Delta F_{kcal.}$	+19.5	
$\Delta S_{e.u.}$	+45.	
H$^+$ catalyzed reaction		
k_H	4.0	13.2
$\Delta H_{kcal.}$	+7.6	
$\Delta F_{kcal.}$	+15.2	
$\Delta S_{e.u.}$	+28.	

(It is estimated that if the equilibrium constant were less than about one, rate determination could not detect the complex).

The observed hydrogen ion catalysis would be accounted for if the reactive glycol species were either the conjugate acid or a carbonium ion, the latter produced from the conjugate acid. It would also be explained if the conjugate acid of an intermediate complex were disproportionating at a rate much greater than that of the non-protonated complex.

The following reaction scheme is offered tentatively to explain the observed kinetics:

$$H^+ + \quad HO - \underset{|}{\overset{|}{C}} - \quad \underset{-C-OH}{} \quad \overset{K_1}{\rightleftharpoons} \quad + \underset{|}{\overset{\backslash}{C}} - \quad -\underset{|}{\overset{\backslash}{C}} - OH$$

$$+ \underset{|}{\overset{|}{C}} - \quad -C - OH \quad + IO_4^- \quad \overset{K_2}{\rightleftharpoons} \quad O_3I - O - \underset{|}{\overset{|}{C}} - \quad -\underset{|}{\overset{}{C}} - OH$$

$$O_3I - O - \underset{|}{\overset{|}{C}} - \quad -C - OH \quad \overset{k}{\underset{slow}{\longrightarrow}} \quad IO_3^- + H^+ + 2 \, \rangle C = O$$

The first two steps are in line with proposed mechanisms for the mineral acid esterification of secondary and tertiary alcohols (33). Tertiary alcohols react much more

rapidly in this manner than do secondary, while primary, with a few exceptions, do not react at all.

The above reaction scheme gives for the rate of the reaction:

$$- \frac{dP_T}{dt} = k \ K_1 \ K_2 \ (IO_4^-) \ (G) \ (H^+) \ .$$

K_2 might conceivably be fairly large but K_1 most certainly would be small. It seems highly reasonable that the product $K_1 K_2$ could be less than unity, leading to the observed second order kinetics. The scheme should be regarded as a possible mechanism, one which is consistent with the data; however, there is no real reason at the present time for discarding the several other possible mechanisms.

The low solubility of pinacol at 0°C prevents using high concentrations of the glycol to try to force as much of the periodate as possible to complex; alternatively, higher temperatures would probably decrease the equilibrium constant for complex formation. That pinacol does not form a detectable amount of an intermediate of the type formed by the other glycols studied might be expected from steric considerations, interaction of the methyl groups forcing the hydroxyls into a trans configuration.

Pinacol is known to form a fairly stable hexahydrate; it was thought conceivable that water tied up by the glycol might account for its slow rate of reaction. If such

were the case, the relative rates of oxidation of pinacol and ethylene glycol might be expected to reverse in solutions of low water concentration. Runs at 25°C in dry t- butanol indicated that this reversal does not occur.

SUMMARY

Ethylene, propylene, meso- and levo butylene and tri-methylethylene glycols have been shown to be oxidized by periodate in aqueous acid solution according to the following reaction scheme:

$$G + IO_4^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{Complex} \overset{k}{\underset{\text{slow}}{\longrightarrow}} \text{products.}$$

The variation of rate with acidity of the solution has been demonstrated to be explainable solely on the basis of the availability of negative periodate ion, probably IO_4^-.

Rate (k) and equilibrium (K) constants for the oxidation of the above glycols have been determined at two temperatures and the thermodynamic functions at 0°C calculated.

The rate of oxidation of pinacol in acid solution has been shown to be given by the expression

$$-\frac{dP_T}{dt} = \left[k_0 + k_H (H^+) \right] (IO_4^-)(G) \ .$$

The hydrogen ion catalysis has been demonstrated to be first order. Rate constants k_0 and k_H have been estimated at two temperatures, and the thermodynamic functions

estimated. Tentative explanations for the kinetic be-
havior have been offered; the possibility that the pina-
col reaction proceeds through an intermediate has not been
excluded, although it is doubtful that such an intermediate
would be of the same type as that for the other glycols
studied.

LITERATURE CITED

1. Malaprade, L., Compt. rend. 186, 382 (1928).

2. Malaprade, L., Bull. soc. chim. 43, 683 (1928).

3. Jackson, E. L., in Adams, R., "Organic Reactions",
       Vol. II, chapter 8, John Wiley and Sons, Inc.,
       New York, N. Y., 1944.

4. Smith, G. F., "Analytical Applications of Periodic
       Acid and Iodic Acid and Their Salts", G. Freder-
       ick Smith Chemical Co., Columbus, Ohio, 1950.

5. Waters, W. A., in Gilman, H., 'Organic Chemistry",
       Vol. IV, Chapter 12, John Wiley and Sons, Inc.,
       New York, N. Y., 1953.

6. Criegee, R., Kraft, L. and Rank, B., Ann. 507, 159
       (1933).

7. Criegee, R., Sitzber. Ges. Beforder ges. Naturw.
       Marburg 69, 25 (1935).

8. Price, C. C. and Kroll, T. J., J. Am. Chem. Soc. 60,
       2726 (1938).

9. Price, C. C. and Knell, M. J., J. Am. Chem. Soc. 64,
       552 (1942).

10. Heidt, L. J., Gladding, R. R. and Purves, C. B.,
       Paper Trade J. 121, No. 2, 35 (1945).

11. Duke, F. R. and Forist, A. A., J. Am. Chem. Soc. 71,
       2790 (1949).

12. Duke, F. R. and Bremer, R. F., J. Am. Chem. Soc. 73,
       5179 (1951).

13. Duke, F. R., J. Am. Chem. Soc. 69, 3054 (1947).

14. Duke, F. R., and Bremer, R. F., Iowa State Coll. J.
       Science 25, 327 (1951).

15. Crouthamel, C. E., Meek, H. V., Martin, D. S. and
       Banks, C. V., J. Am. Chem. Soc. 71, 3031 (1949).

16. Crouthamel, C. E., Hayes, A. M., and Martin, D. S., J. Am. Chem. Soc. 73, 82 (1951).

17. Jackson, E. L. and Hudson, C. S., J. Am. Chem. Soc. 59, 2049 (1937).

18. Davidson, G. F., J. Text. Inst. 32, T109 (1941).

19. Head, F. S. H., Nature 165, 236 (1950).

20. Kooi, E. R., "Production of the 2,3- Butanediols by the Fermentation of Starch", Unpublished Ph.D. Thesis, Ames, Iowa, Iowa State College Library, 1946.

21. Wilson, C. E. and Lucas, H. J., J. Am. Chem. Soc. 58, 2396 (1936).

22. Curme, G. O. and Johnston, F., "Glycols", p. 289, Rheinhold Publishing Corp., New York, N. Y. 1952.

23. Lees, T. M., "Quantitative Determination of Mixtures of the Isomeric 2,3- Butanediols", Unpublished M. S. Thesis, Ames, Iowa, Iowa State College Library, 1942.

24. Knowlton, J. W., Schieltz, N. C. and MacMillan, D., J. Am. Chem. Soc. 68, 208 (1946).

25. Underkofler, L. A., "Laboratory Experiments in Organic Chemistry", W. C. Brown Co., Dubuque, Iowa, 1942.

26. Milas, N. A. and Sussman, S. J., J. Am. Chem. Soc. 58, 1302 (1936).

27. Roebuck, A. and Adkins, A., "Organic Synthesis", Vol. 28, p. 35, John Wiley and Sons, Inc., New York, N. Y., 1948.

28. Adams, R. and Adams, E. W., "Organic Syntheses", Coll. Vol. I, 2nd Ed., p. 459, John Wiley and Sons, Inc., New York, N. Y., 1941.

29. Ayers, G. W., J. Am. Chem. Soc. 60, 2959 (1938).

30. Boesken, J. and Cohen, R., _Rec. trav. chim._ 47, 839 (1928).

31. Lees, T. M., Fulmer, E. I. and Underkofler, L. A., _Iowa State Coll. J. Science_ 18, 359 (1944).

32. Ottar, B., _Acta Chemica Scandinavia_ I, 521 (1947).

33. Cowdrey, W. A., Hughes, E. D., Ingold, C. K. and Scott, A. D., _J. Chem. Soc._ 1937, 1266.

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