# Lawrence Berkeley National Laboratory

**Title**
EXTRACTION OF HReO, HCIO, AND HAuCl, BY TRIOCTYL-PHOSPHINE OXIDE I1TBENZENE, 1, 3, 5-TRIETHYLBENZEWE AND CHLOROFORM

**Permalink**
https://escholarship.org/uc/item/0608j1s5

**Authors**
Bucher, J.J.
Zirin, Moshe H.
Laugen, Ronald C.
et al.

**Publication Date**
1970-09-01

# EXTRACTION OF $HReO_4$, $HClO_4$ AND $HAuCl_4$ BY TRIOCTYLPHOSPHINE OXIDE IN BENZENE, 1,3,5-TRIETHYLBENZENE AND CHLOROFORM

J. J. Bucher, M. Zirin, R. C. Laugen, and R. M. Diamond

September 1970

# LAWRENCE RADIATION LABORATORY
# UNIVERSITY of CALIFORNIA BERKELEY

## DISCLAIMER

EXTRACTION OF $HReO_4$, $HClO_4$ and $HAuCl_4$ BY TRIOCTYLPHOSPHINE OXIDE
IN BENZENE, 1,3,5-TRIETHYLBENZENE AND CHLOROFORM[1]

J. J. Bucher, M. Zirin,[2] R. C. Laugen[3] and R. M. Diamond

Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

September 1970

## Abstract

The extractions of $HReO_4$, $HClO_4$ and $HAuCl_4$ into dilute solutions of trioctylphosphine oxide (TOPO) in benzene, chloroform and 1,3,5-triethylbenzene have been studied. In both aromatic diluent systems, when the stoichiometric ratio TOPO/$H^+$ was > 2, the extracting species for $HReO_4$ and $HClO_4$ was an ion pair. This was also true for $HAuCl_4$ at concentrations < $10^{-3}$, but at higher organic-phase $HAuCl_4$ concentrations further aggregation occurred. In $CHCl_3$ both a one- and a two-TOPO acid complex were observed when TOPO/$H^+$ > 2. These $CHCl_3$ systems also indicated anion ($ReO_4^- > AuCl_4^-$) stabilization of the one-TOPO complex. Small amounts of water coextracted with the two TOPO acid-complex, but the amounts were always significantly less than would be needed for the formation of a hydronium ion in the organic phase: $[H_2O]_o/[H^+]_o < 1/2$. It is concluded that the extraction complex is a di-(mono-)TOPO solvate of a base proton. Extraction of acid was poorest into TOPO-$CHCl_3$, due to extensive complexing of TOPO by chloroform.

## Introduction

Strong organic bases such as alkylamines, dissolved in a relatively inert solvent can react with solutions of strong aqueous acids by extracting the proton from water to form a one-to-one complex: the ammonium ion.[4-6]

$$R_3N(org) + H_3O^+ + X^- = R_3NH^+ \ldots X^-(org) + H_2O \ . \qquad (1)$$
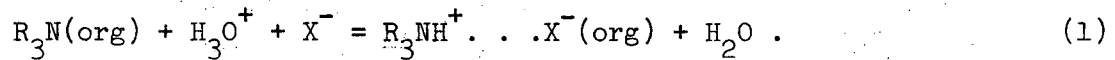
The species $R_3NH^+ \ldots X^-$ may be dissociated, associated to ion pairs, or aggregated to still higher associations depending upon its concentration, the nature of the anion $(X^-)$ and the "inert" diluent.

Weaker organic bases, such as trialkyl phosphates (tributyl phosphate (TBP) for example) cannot extract the proton away from a water molecule, and thus extracts at least the hydronium ion: $H_3O^+$.[7-9] Depending upon the accompanying anion and diluent, three, or sometimes only two TBP molecules are needed to satisfy the solvation requirements of the hydronium ion,[10] and additional water can also be co-extracted. Again, depending upon the conditions, a dissociated or associated species may result. The alkyl phosphine oxides are intermediate in bascity[11-15] between the two previously considered classes of extractants, and, therefore, might be expected to show an intermediate behavior. It is of interest to see, for example, if trioctyl phosphine oxide (TOPO) extracts a bare proton or a hydronium ion, and how many extractant molecules are necessary to provide solvation for the extracted cation. Also, if a hydronium ion is involved, is it further hydrated?

In this paper, benzene, 1,3,5-triethylbenzene and chloroform are used as diluents. The first two diluents represent low dielectric-constant solvents with a weak but discernable basic nature;[16] their basicity coming from the

mobile π-electron cloud.[17] Sym-triethylbenzene is considered less effectively

basic than benzene, as it is only partly aromatic; the aliphatic side chains

dilute the π-electron density, and sterically hinder their electron-donating

properties.[18] Chloroform was chosen to represent the behavior of an acidic

diluent.[19] Perrhenic ($HReO_4$) and chloroauric ($HAuCl_4$) acids were used to

minimize the possiblity of organic-phase cation-anion interactions, as these

are acids of very weakly-basic anions.


## Experimental

Reagents.—The TOPO used was obtained from the Carlisle Chemical Corp.,

Reading, Ohio. The technical grade TOPO was washed with mild base and distilled

water, and this material was then recrystallized four or five times from pentane.

The $HClO_4$ solutions were prepared by diluting a stock solution of reagent grade

$HClO_4$ (G. F. Smith) with distilled water. Standardization of the stock $HClO_4$

solution was by titration with sodium hydroxide, using bromothymol blue as an

endpoint indicator. $HReO_4$ solutions were made by dilution from a stock solution

and standardized as above. This stock solution was prepared by dissolving

$Re_2O_7$ (Varlacoid Chem. Co., 99.5% purity) in distilled water. A stock solution

of $HAuCl_4$ was made by dissolving Engelhard Industries gold chloride in water.

After filtering, determination of the stock solution was done by electrodeposition

onto platinum-iridium guaze electrodes from a basic gold cyanide-hydroxylamine

solution.[20] Dilutions from this gold stock were made with 0.010M HCl to prevent

hydrolysis and the concentration of these dilutions, in some instances, were

checked by means of x-ray fluorescence[21] using the L-lines of Au. Gold solutions

were stored in the dark.

Gold tracer, $^{198,199}$Au, was prepared by irradiating gold foil (>99.9% purity) with neutrons for six days at a flux greater than $10^{14}$ neutrons/cm$^2$-sec in the Vallecitos Test Reactor. After dissolving the gold foil in aqua-regia, the solution was taken to near dryness and then 6M HCl was added. This solution was also taken to near dryness and the gold tracer was finally prepared by adding 0.10M HCl. Rhenium tracer, $^{186}$Re, was also made by neutron irradiation under the same conditions as for gold. A few milligrams of KReO$_4$ was the material used, and after bombardment, was dissolved in distilled water to form a saturated ~ 0.04M solution.

Benzene and chloroform were both J. T. Baker Reagent grade and the benzene was used as received. Chloroform was stored in a brown bottle over Linde molecular sieves (type 5A) and was flushed with dry nitrogen gas, both to remove the alcohol added as a preservative and to prevent the decomposition of CHCl$_3$ to phosgene. Sym-triethylbenzene was obtained from the Dupont Organic Products division, and after washing with conc. sulfuric acid and water, was distilled and the middle fraction taken. Matheson, Coleman and Bell stabilized and premixed single-solution Karl Fischer reagent was used in the water determinations. Methanol used in the Karl Fischer analysis blank was Baker and Adamson, "Special anhydrous" reagent ($\leq$ 0.005% H$_2$O).

Procedures.—1) Standardized solutions of either HReO$_4$ or HAuCl$_4$ containing $^{186}$ReO$_4$$^-$ or $^{198,199}$AuCl$_4$$^-$ respectively, were shaken for not less than one hour (a sufficient time for attainment of equilibrium) with dilute solutions of TOPO in benzene, CHCl$_3$ or triethylbenzene. After centrifugation, aliquots of both the organic and aqueous phase were taken for gamma-counting in a well-type

Na(Tl)I scintillation counter. Knowing the original concentration of acid and

the total activity of the tracer, the measured counting rates yield the equi-

librium concentrations of $HReO_4$ and $HAuCl_4$ in each phase.

2) When sufficient $HClO_4$ acid extracted into the benzene and chloro-

form systems, acid-base titrations were used to determine the equilibrium acid

content of each phase.

3) TOPO solutions in both benzene and chloroform were partially con-

verted to the acid-complex form by contact with aqueous $HAuCl_4$ solutions.

After determination of the organic-phase acid concentration of these stock

solutions by means of tracer, a number of dilutions of these organic phases

were shaken with very small amounts of $H_2O$. After equilibrium was attained,

the organic phase was used for water determinations.

4) The concentration of water bound to TOPO in the organic phase and

the amount of water coextracted with $HClO_4$ and $HAuCl_4$ were determined in a

series of experiments by the Karl Fischer method using a dead-stop end-point.[22]

Correction of the Karl Fischer water data for the reduction of gold by iodide,

which generates more Karl Fischer Reagent, was done from the experimentally-

determined fact that one mole of $AuCl_4^-$ gave one mole equivalent of K. F.

Reagent. This was determined by titration of a series of quaternary ammonium

tetrachloraurate solutions whose concentrations were analyzed by an x-ray

fluorescence method in triethylbenzene that had been dried in a desicator over

$P_2O_5$. All experiments were performed at $23° \pm 2°$ C.

## Results and Discussion

The experimental results are shown mostly as log-log plots in

Figs. 1-9. The raw data are usually indicated by circles connected by solid

lines. Corrections made to the experimental points, as described below, are

usually indicated by square symbols connected by dashed lines.

TOPO-$H_2O$.—The equilibrium for the distribution of water into an organic-phase

solution of TOPO may be written:

$$nTOPO(org) + mH_2O = mH_2O \cdot nTOPO(org). \tag{2}$$
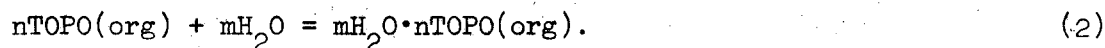
The corresponding equilibrium constant is:

$$K_{H_2O} = \frac{(mH_2O \cdot nTOPO)_o}{(H_2O)^m (TOPO)^n_o} = \frac{[mH_2O \cdot nTOPO] \, y_{H_2O}}{(H_2O)^m [TOPO]^n y^n_{TOPO}} = K_{H_2O} \frac{y_{H_2O}}{y^n_{TOPO}} \quad , \tag{3}$$

where parentheses signify activity, brackets denote molar concentrations, y is

a molar activity coefficient and K is a mixed concentration quotient. With

the assumption that $y_{H_2O}/y^n_{TOPO}$ is a constant in the dilute solutions used,

eq. 3 implies a log-log plot of organic-phase water concentration vs. equilibrium

TOPO concentration should generate a curve of slop n, where n is the number of

TOPO molecules coordinated in each extracted water complex. In Fig. 1, the

organic-phase water concentration, $[H_2O]_o$, is plotted against the initial (not

equilibrium) TOPO concentration. The amount of water extracted by the diluent

alone, calculated as the product of the molar solubility in the diluent and the

volume fraction of diluent in the organic medium has been subtracted to obtain

the points plotted. The water solubility found in this study for benzene is

0.032M, which can be compared with a literature value of 0.032±.001M at 25° C;[24]

and for $CHCl_3$ the value found is 0.086M, compared to a literature value of

0.083M at 25.0° C.[25]   A slope of one is obtained in Fig. 1 for TOPO-$CHCl_3$ up

to TOPO concentrations of 1.0M; for TOPO-benzene, a unit slope connects data

only for TOPO concentrations $\leq$ 0.1M.   This indicates only one TOPO molecule is

involved in each TOPO-water complex within the stated concentration limits.

Whether the increase of slope beyond 0.10M TOPO in benzene does indicate a

TOPO-water complex with n > 1, or only reflects a breakdown of the assumption

of a constant activity-coefficient ratio, or is due to a combination of these

possiblities, cannot be answered from the data in Fig. 1.   The data in Fig. 1

also do not allow any statement as to the number of water molecules involved

in the complex; this information can only be obtained from a study of water

extraction as a function of water activity.   In a later paper[26] dealing in more

detail with water extraction by TOPO in benzene and $CHCl_3$, as well as in nitro-

benzene and 1,2-dichloroethane, it will be shown that at least a mono- and a

dihydrate are extracted in TOPO-benzene, but only a monohydrate in TOPO-$CHCl_3$.

For the purposes of this study, however, it is not necessary to have a detailed

knowledge of the TOPO-diluent water extraction, but only to know how much water

is extracted by TOPO in benzene or $CHCl_3$ near a water activity of unity, in

order to correct the amounts of water coextracted with the various acid-complexes.

         The amount of free TOPO, uncomplexed by water, in TOPO-benzene is small,

and in this paper no distinction will be made between total and hydrated TOPO.

Thus, the symbol [TOPO] will denote the TOPO concentration not complexed by

acid.   Also, for TOPO-$CHCl_3$, although the amount of water-TOPO complex is less

than half the total TOPO concentration, the above lack of distinction will also

be observed, as that portion of TOPO not complexed by water is probably complexed by $CHCl_3$ (see later discussion).

$TOPO-H_2O - HReO_4$, $HAuCl_4$.—The extraction of HX by TOPO solutions to yield an ion-paired product may be expressed:

$$H^+ + X^- + xH_2O + nTOPO(org) = H^+ \cdot nTOPO \cdot wH_2O \dots X^- (x-w)H_2O(org) \quad (4)$$
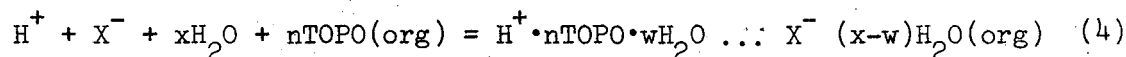
The corresponding equilibrium constant is:

$$K_n^a = \frac{[H^+ \cdot nTOPO \cdot wH_2O \dots X^- \cdot (x-w)H_2O]_o \, y_{HX}}{[TOPO]_o^n \cdot y_{TOPO}^n (H_2O)^x \, (HX)} = K_n^a \frac{y_{HX}}{y_{TOPO}^n} \quad (5)$$

with the same symbols as before and $K_n^a$ is a mixed concentration quotient. Since all three diluents used in this study have low dielectric constants (benzene[27] and 1,3,5-triethylbenzene[28] have E = 2.28 at 25° C and $CHCl_3$[27] has e = 4.80 at 20° C), the corresponding equations for dissociated species will not be considered.

Concentrations have been substituted for aqueous activities for $HAuCl_4$, as there should be little difference with the dilute solutions used. The product $[H^+][AuCl_4^-]$ is formed from the concentration of $AuCl_4^-$ and the concentration of hydrogen ion contributed by both $HAuCl_4$ and HCl. Activities of $HReO_4$ and $HClO_4$ were calculated from coefficients for aqueous $HClO_4$ solutions $\geq 0.10M$, and from HBr coefficients for solutions < 0.10M, as compiled by Gazith.[29] No values were listed for $HClO_4$ below 0.10M, but the values for both HBr and $HClO_4$ were quite similar just above 0.10M.

If eq. 5 is valid, log-log plot of the organic-phase acid concentra-

tion, $[H^+]_o$, vs. the aqueous-phase activity at a constant value of TOPO

concentration, should yield a straight line of unit slope. Such plots are

shown in Figs. 2 and 3. Fig. 2 contains data for 0.10M TOPO in benzene

(line 2), in triethylbenzene (line 3) and in $CHCl_3$ (line 4) and for 0.0020M

TOPO in benzene (line 5) and 0.010M TOPO in $CHCl_3$ (line 6). Curves with an

initial slope of unity are drawn through the data for each TOPO-diluent con-

centration, but most of these curves fall below a slope of unity at the

higher organic-phase acid concentrations. Correction of $[H^+]_o$ from the

equilibrium TOPO concentrations to a constant (initial) TOPO concentration is

by means of the expression:

$$[H^+]_o' = [H^+]_o \left( \frac{[TOPO]'}{[TOPO]} \right)^2 \qquad (6)$$

where the primed TOPO quantity denotes the initial concentration and the exponent

two is justified later. The square points in Fig. 2 connected by dashed lines

which are drawn with unit slope result from applying eq. 6. It should be

noted that the major portion of data on curve 2 needing correction, as shown

in line 1, is obtained from extraction of $HClO_4$ by TOPO in benzene, as measured

by acid-base titration. The corrected $HClO_4$ data joins quite satisfactorily

with data at lower $[H^+]_o$ (indicated by triangles) obtained from extraction of

$HReO_4$ by TOPO in benzene, as measured by $ReO_4^-$ tracer, and indicates there is

little difference between the extraction of $HReO_4$ and $HClO_4$ in this diluent and

under these conditions. The unit slopes for all five TOPO-diluent combinations,

after correction, indicate that $HReO_4$ or $HClO_4$ forms only ion-paired organic-

phase complexes, with no suggestion of dissociation or aggregation, in the range

of concentrations studied.

The extraction of $HAuCl_4$ in 0.01M HCl (a concentration of chloride sufficient to maintain the ratio of $AuCl_4^-/AuCl_3OH^- > 10^2$)[30] by 0.10M, 0.050M and 0.010M TOPO in benzene are shown in Fig. 3. As in Fig. 2, the initial slopes of the curves drawn through the data are unity for all three TOPO concentrations. (The dashed lines indicate extensions of the unit slope line.) Unlike the situation in Fig. 2, however, the curves deviate upward; the organic-phase chloroauric acid concentration increases more rapidly than should be possible if only ion-pairing were occuring. This deviation indicates, we believe, that aggregation of the organic-phase complex is starting at $[H^+]_o$ concentrations of $10^{-3} - 4 \times 10^{-3}$M $HAuCl_4$. It is also to be noted, particularly in lines 1 and 2 for 0.10 and 0.050M TOPO, respectively, that the stoichiometric limit of $[H^+]_o$ is tending to one-half the initial TOPO concentration. This stoichiometric limit of 2TOPO:$H^+$ suggests the same acid complex is involved at higher TOPO concentrations, as is shown later to be extracted in more dilute systems, although aggregation of the organic-phase gold complex is occurring.

Having established that the $HReO_4$ and $HClO_4$ acid-complexes are ion-paired, and that the $HAuCl_4$ complex is also ion-paired up to organic-phase concentrations of $10^{-3}$M (beyond which concentration it appears to aggregate further), it remains to determine the value of n, the number of TOPO molecules complexed per acid. From eq. 5, the slopes of log-log plots of extracted acid vs. TOPO concentration at a constant aqueous acid activity should yield directly the value of n for an ion-paired complex. Figs. 4-7 are such plots. Fig. 4 is for aqueous solutions of 0.437, 0.10, 0.040 and 0.010M $HReO_4$ and TOPO in benzene; Fig. 5 is for TOPO in $CHCl_3$ with aqueous concentrations of 0.10M $HAuCl_4$ in 0.010M HCl (line 1), 0.514M $HReO_4$ (line 2) and 0.040M $HReO_4$ (line 3).

Figs. 6 and 7 are log-log plots of the distribution ratio, D, for trace amounts

of HAuCl$_4$ and HReO$_4$ out of various aqueous HCl solutions vs. diluent TOPO

concentration.

In Fig. 4 the initial slope for each of the four sets of data is two.

The square symbols indicate correction of the data to an equilibrium

TOPO concentration; this correction for used-up TOPO was made assuming that

two TOPO molecules are coordinated per extracted acid, as suggested by the

initial slope of the curves, and it can be seen that the corrected points fall

on the same line of slope two, given by the data at lower concentrations where

the correction is negligible.  Thus, for HReO$_4$ extraction by TOPO in benzene,

n = 2, or two TOPO molecules are associated with the organic-phase acid complex

for TOPO concentrations from 3 × 10$^{-5}$M - 10$^{-1}$M.

In a similar fashion, slope analysis is applied to both HAuCl$_4$ and

HReO$_4$ extraction by TOPO in CHCl$_3$ in Fig. 5.  Here, however, $[H^+]_0$ does not

appear to have a single value for n over the range of TOPO concentrations

examined.  The initial slope that can be placed through the data for the

extraction of either HReO$_4$ or HAuCl$_4$ is unity.  Extension of that line of unit

slope (dashed line) and its subtraction from the raw data points gives a

resultant component of slope two.  There are a number of possible ways to

explain this multi-component extraction curve for TOPO-CHCl$_3$.  One is that a

2:1 complex is dissociating at low concentrations.  Another is that the TOPO

coordination number is changing.  The first possibility is, we believe, negated

by the data in Fig. 2 and in Fig. 5.  From Fig. 2 there is no evidence for

dissociation of the HReO$_4$ complex even at an organic-phase acid concentration

of 10$^{-7}$M, while curve 2 in Fig. 5 would require dissociation at 10$^{-4}$M to

explain the shape. Furthermore, a comparison of curves 2 and 3 show that the change in slope seems more related to the TOPO concentration than to the organic-phase acid concentration. If dissociation was occurring, it should occur at the same $[H^+]_o$. It is suggested that the second possibility, a change of TOPO coordination number, a process dependent upon organic-phase TOPO concentration, is occurring. This would be similar to results recently found in TBP-diluent-$HReO_4$[10] systems where step-wise complexing was observed in a number of diluents. The fairly strong hydrogen-bonding of $CHCl_3$ with alkyl phosphine oxides (estimated to have a bond strength of 5 Kcal/mole)[31] effectively lowers the activity of TOPO in $CHCl_3$ (in comparison to TOPO activity for the same molar concentration in benzene, for example),[32] and allows a 1:1 TOPO to $H^+$ complex to be observed at the same total TOPO concentration where the 2:1 complex is seen with benzene. In TOPO-benzene it should also be possible to see a 1:1 TOPO-acid complex, but only at somewhat lower TOPO concentrations than already used in this study. Our conditions, however, yield for TOPO-$CHCl_3$ both a two TOPO- and a one TOPO-acid complex in the extraction of $HReO_4$ and $HAuCl_4$.

A comparison of the TOPO concentrations in $CHCl_3$ at which equal amounts of 1:1 and 2:1 TOPO:$HAuCl_4$ and TOPO:$HReO_4$ complexes are present gives another interesting correlation. This crossover point for $HAuCl_4$ occurs at a TOPO concentration of $10^{-3}$M, while for $HReO_4$ this point occurs at $1.5 \times 10^{-2}$M. It is suggested that this difference reflects the different cation-anion interactions in the two 1:1 TOPO-acid species. That is, the 1:1 TOPO-acid complex can be stabilized somewhat by the presence of the anion, and the more so, the stronger the electrostatic interaction between the ions, e.g., the smaller the

anion. Another way of looking at this situation is to say that the anion
interaction helps replace the solvation (energy) lost by the lack of a second
coordinated TOPO molecule, and the more basic the anion, the better it can do
this. Both $AuCl_4^-$ and $ReO_4^-$ are usually considered to be very weakly basic
anions, but we consider $AuCl_4^-$ to be the larger and less basic of the two.
This assumption means $ReO_4^-$ should be better able to solvate the $TOPO \cdot H^+$/cation,
in effect replacing a TOPO molecule and extending by a factor of 15 over $AuCl_4^-$
the TOPO concentration to which 1:1 TOPO-acid complex predominates in $TOPO-CHCl_3$.
Extending this idea of anion solvation, it would be expected that a still
greater range of 1:1 complex would be observed in the extraction of acids
which have smaller and hence more basic anions such as HBr, HCl and $HNO_3$. A
later paper dealing with HBr extraction into $TOPO-CHCl_3$ will show that this
does indeed occur.[33]

Figs. 6 and 7 are log-log plots of D, the distribution ratio for
$HReO_4$ and $HAuCl_4$ extraction vs. TOPO concentration at a constant aqueous hydrogen
ion concentration. Since D is the ratio of $[H^+ \cdot nTOPO \cdot wH_2O \ldots X^- \cdot (x-w)H_2O]_o/[X^-]$,
substitution in eq. 4 results in

$$K_n^a = \frac{D}{[TOPO]_o^n [H^+] y_\pm^2} .$$                     (7)

Thus, Figs. 6 and 7 should yield another determination of n for extraction of
$HAuCl_4$ and $HReO_4$ by TOPO in benzene, $CHCl_3$ and sym-triethylbenzene. Fig. 6 is
for $TOPO-CHCl_3$ and $10^{-4}M$ $HAuCl_4$ in 1.00M HCl (line 1) and $4 \times 10^{-5}$ $HReO_4$ in
1.00M HCl (line 2) and can be resolved into the same one TOPO- and two TOPO-acid
complexes, with a crossing at approximately the same TOPO concentrations as

before (Fig. 5).  In Fig. 7, for TOPO-benzene and $10^{-4}$M $HAuCl_4$ in 0.027M HCl

(line 1) a line of slope two can be drawn through the data.  The same slope

(n=2) can be drawn through most of the data (line 2) for TOPO-triethylbenzene

and $10^{-7}$M $HReO_4$ in 0.10M HCl.  Thus, only a two TOPO-$HAuCl_4$ complex is found

in benzene for TOPO concentrations of $10^{-4}$ - $10^{-1}$M TOPO and a two TOPO-$HReO_4$

complex for triethylbenzene and TOPO concentrations of $10^{-3}$ - $10^{-1}$M.  The small

deviation of the curve in triethylbenzene probably does not reflect a new

species, but rather a change in the TOPO activity coefficient.  The actual

organic-phase $HReO_4$ concentration at 0.1M TOPO in line 2 is approximately $10^{-7}$M,

and it is not expected that the activity coefficient for this organic-phase

acid concentration is different in value from coefficients for even more dilute

organic-phase acid solutions obtained at lower TOPO concentrations.  Thus, it

is concluded that the activity coefficient, $y_{TOPO}^{n}$ , of TOPO in triethylbenzene

has probably changed.

     For 0.10M TOPO in benzene[17] and for 0.20M TOPO in $CHCl_3$ the amount of

water, less the diluent water, coextracted by the organic-phase $HAuCl_4$ complex

as the acid concentration increases is shown in Fig. 8.  In both diluent

systems the total amount of water decreases as $[H^+]_o$ increases.  But the amount

of water extracted by the non-acid-bound TOPO must be subtracted (Fig. 1); the

concentration of "free" TOPO is calculated as $[TOPO]_{total} - 2[H^+]_o$.  After this

correction, curves 1' and 2' result for $CHCl_3$ and benzene respectively.

Curve 1' indicates < 0.1 water molecule per extracted $HAuCl_4$, while curve 2'

gives a value of essentially zero.  At the TOPO concentrations in $CHCl_3$ used,

only the two TOPO complex is being extracted; and at the $[H^+]_o$ concentration

shown for $HAuCl_4$ extraction by TOPO in benzene, the two TOPO complex is probably

aggregated.

Fig. 9 shows similar water data as in Fig. 8 but for $HClO_4$ extracted

by 0.10M TOPO in benzene (line 1) and $CHCl_3$ (line 2). Again in both diluent

systems the total amount of water decreases as $[H^+]_o$ increases. Correction of

the data for water extracted by the non-acid-bound TOPO was done in the same

manner as for TOPO-HAuCl$_4$. The initial slope of curve 1' (benzene-TOPO) gives

a value of 0.5-0.6 molecules of water per extracted proton, but a higher $[H^+]_o$

concentrations this falls to a value < 0.5. Curve 2' ($CHCl_3$-TOPO) indicates

that the acid complex is nearly anhydrous at low concentrations and may have

~ 0.15-0.25 molecules of water per extracted proton at higher $[H^+]_o$ concentra-

tions. It is possible, however, that at higher $[H^+]_o$ concentrations, some 1:1

acid complex is being formed which would lead to an under correction for the

amounts of water complexed by TOPO, and also to smaller water:proton ratios.

In Table I the mixed equilibrium quotients are tabulated. The difference

between these values and the actual equilibrium constants arises from the neglect

of the organic-phase activity coefficient ratio $y_{HX}/y_{TOPO}^n$.

It is readily apparent when $K_2^a$ values for benzene and $CHCl_3$ are com-

pared, that the interaction of TOPO with $CHCl_3$ severely reduces the extraction

of either $HReO_4$ or $HAuCl_4$, at least when molar concentrations are used. It is

also to be noted that the $K_2^a$ values for $HReO_4$ extraction into benzene and

triethylbenzene only differ by a factor of three. This is in contrast to

results found for $HClO_4$ extraction by tertiary amines[34] in the same two diluents

where the ion-paired amine salt extracted a factor of 100 better into benzene

than into sym-triethylbenzene. The amine extraction data were interpreted to

mean the $\pi$-electron system of triethylbenzene. Because of the alkyl side

chains, triethylbenzene has a lower concentration of $\pi$-electrons, and interaction

with this $\pi$-electron system is probably somewhat hindered. With the coordination of two TOPO molecules about it, the proton is no doubt better protected from external influence that is the tertiary ammonium cation, and so it should matter less whether the diluent is benzene or sym-triethylbenzene. Thus the difference in extraction with TOPO in the two diluents drops to a factor of 3.

It is also obvious from the listed constants that chlorcauric acid extracts better than perrhenic acid. If the ratios of $K_2^a$, $HAuCl_4/HReO_4$, for these two acids in benzene and $CHCl_3$ are calculated, one obtains values of $2 \times 10^3$ and $3 \times 10^3$, respectively. We believe this indicates that even in these strong acid[35] extraction systems, the degree of extraction depends upon the hydration of the anion.[36] A small, strongly-basic anion will be more highly hydrated in the aqueous phase and so will be more difficult to transfer into the organic phase; where it may lose part of its hydration shell and will certainly receive poorer secondary solvation. Since $AuCl_4^-$ is larger than $ReO_4^-$ or $ClO_4^-$, it is less hydrated in water and the result observed is that $AuCl_4^-$ extracts better than $ReO_4^-$.

A comparison of the value for the ratio of $K_1^a$ for $HAuCl_4$ and $HReO_4$ in $CHCl_3$, $1.5 \times 10^2$, with the value of $3 \times 10^3$ for the ratio of $K_2^a$ in this same diluent, suggests again the previously discussed role the anion can play in the TOPO extraction process. This lower ratio for $K_1^a$ indicates to us that the solvation energy loss to the cationic complex upon losing one of the TOPO molecules is partially made up by the resulting stronger interaction (ion-pairing plus hydrogen bonding) of the cation with the anion. The smaller or more basic the anion, the stronger the ion pair formed and the greater the electrostatic solvation.[37] Thus $ReO_4^-$ interacts more strongly than $AuCl_4^-$ with

the 1:1 TOPO-acid complex, leading to better extraction of $HReO_4$ or $HClO_4$ than

might be expected from the ratio for the 2 TOPO complex, where the cationic

charge is better shielded from the anion.

## Conclusions

In no instance, for the four TOPO-acid-diluent combinations studied,

is sufficient water coextracted to support the idea of proton hydration; i.e.,

the formation of a hydronium ion, $H_3O^+$. Rather, the lack of coextracted water

and the TOPO coordination number of two suggests to us the cationic acid complex

in these three diluents can be written as

$$R \overset{R}{\underset{R}{>}} P = O \cdot \cdot \cdot H^+ \cdot \cdot \cdot O = P \overset{R}{\underset{R}{<}} R$$
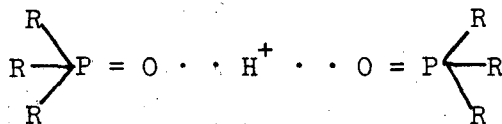
where it is not known if the TOPO molecules form symmetric or asymmetric

hydrogen bonds about the bare proton. Because of the low dielectric constants

of these diluents, the cation and anion form ion pairs, or even further

aggregates at higher $[H^+]_o$ concentrations. As a consequence of TOPO-$CHCl_3$

hydrogen bonding which lowers the TOPO activity, TOPO-acid complex was observed

with $CHCl_3$ as diluent.

The fractional amounts of water found to coextract in the TOPO-$HClO_4$-

benzene system, may reflect weak hydration of the "inert" $ClO_4^-$ anion in that

diluent. A similar interpretation of partial $ClO_4^-$ hydration would provide an

explanation for the water uptake for ion-paired tertiary alkylammonium perchlorate

salts in anisole and chlorobenzene where ratios of coextracted water to amine

salt of 0.3 and 0.25 were found,[34] respectively.

The present results are in disagreement with an earlier study of

$HClO_4$ and $HReO_4$ extraction by TOPO in $CCl_4$[38] where a 3:1 complex, based upon a

hydronium ion core was proposed. Although the diluent is different in that

case than in the present results, we believe from the present study that such

a change in diluent should not be able to make a marked change in the nature

of the extracted TOPO-acid complex. We are, therefore, reinvestigating the

$CCl_4$ system, as well as studying $HReO_4$ and $HAuCl_4$ extraction by TOPO in

aliphatic diluents, and this investigation will be the subject of a later

paper. Preliminary evidence indicates that the neglect of the possibility of

the $HClO_4$ acid-complex aggregating and the assumption of ideal behavior of

TOPO in $CCl_4$, in the TOPO concentration range previously examined, probably

were responsible for the different conclusion of the earlier work and the

present paper as to the nature of the extracted TOPO acid complex in $CCl_4$.

Footnotes and References

(1)  Work performed under the auspices of the U. S. Atomic Energy Commission.

(2)  Present address:  Ford Motor Company Scientific Research, Dearborn,

     Michigan.

(3)  Summer Visitor:  1965, National Science Foundation High School Teachers

     Research Participation Program.

(4)  Y. Marcus and A. S. Kertes, <u>Ion Exchange and Solvent Extraction of Metal</u>

     <u>Complexes</u> (Wiley-Interscience, New York, 1969), pp. 740-779.

(5)  R. M. Diamond, "Amine Extraction Systems", in <u>Solvent Extraction Chemistry</u>,

     D. Dyrssen, J. Liljenzin and J. Ryberg, eds. (North-Holland, Amsterdam,

     1967), pp. 349-362.

(6)  W. E. Keder and A. S. Wilson, Nucl. Sci. Eng. <u>17</u>, 287 (1963).

(7)  Y. Marcus and A. S. Kertes, <u>op. cit.</u>, pp. 650-694.

(8)  L. L. Burger, Nucl. Sci. Eng. <u>16</u>, 428 (1963).

(9)  R. M. Diamond and D. G. Tuck, in <u>Progress in Inorganic Chemistry</u>, Vol. II,

     F. A. Cotton, ed. (Interscience Pub., Inc., New York, 1960):  D. C. Whitney

     and R. M. Diamond, J. Phys. Chem. <u>67</u>, 209 (1963).

(10) J. J. Bucher and R. M. Diamond, J. Phys. Chem. <u>73</u>, 675 (1969);

     J. Phys. Chem. <u>73</u>, 1494 (1969).

(11) D. Hadži, C. Klofutar and S. Oblak, J. Chem. Soc. (A) <u>905</u> (1968).

(12) F. Krašovec and C. Klofutar, J. Inorg. Nucl. Chem. <u>30</u>, 1640 (1968).

(13) A. V. Nikolaev, Yu. A. Afanas'ev and A. D. Starostin, Doklady Akademic

     Nauk SSSR <u>168</u>, 1080 (1966).

(14) A. M. Rozen and N. A. Konstantinova, Doklady Akedemic Nauk SSSR <u>166</u>,

     132 (1966).

(15)  T. Gramstad, Acta. Chem. Scand. 15, 1337 (1961).

(16)  G. C. Pimentel and A. L. McClellan, The Hydrogen Bond (W. H. Freeman,

San Francisco, 1960), p. 202.

(17)  W. G. Schneider, J. Phys. Chem. 66, 2653 (1962).

(18)  N. Ogemachi, L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. 78,

2210 (1956).

(19)  N. M. Davis, Acid-base Behavior in Aprotic Organic Solvents,

N.B.S. Monograph 105, August 1968, p. 13.

(20)  C. L. Wilson, D. W. Wilson and C. R. N. Strouts, Comprehensive Analytical

Chemistry, Vol. II, Electric Methods (Elsevier, Amsterdam, 1964), p. 29.

(21)  H. R. Bowman, E. K. Hyde, S. G. Thompson and R. C. Jared, Science 151,

562 (1966).

(22)  J. Mitchell and D. M. Smith, Aquametry (Interscience, New York, 1948),

p. 79.

(23)  R. D. Giauque, Anal. Chem. 40, 2075 (1968).

(24)  E. Högfeldt and B. Bolander, Arkiv. För Kemi 21, 161 (1963).

(25)  E. Högfeldt, Trans. Roy. Inst. Technol., November 1963.

(26)  J. J. Bucher, A. Beck, R. M. Diamond, to be published.

(27)  A. A. Maryott and R. E. Smith, Table of Dielectric Constants of Pure

Liquids, N.B.S. Circular 514 (August 10, 1951).

(28)  A. Altshuler, J. Phys. Chem. 58, 393 (1954); F. H. Muller, Physik Z. 38,

283 (1937).

(29)  M. Gazith, Compiled and Calculated Molar and Molal Activity Coefficients

of Various Electrolytes, Israel Atomic Energy Commission Report,

IA-1004 (October 1964).

(30) L. G. Sillén and A. E. Martell, Stability Constants of Metal-Ion Complexes (Chemical Society, London, 1964), p. 288.

(31) S. Nishimura, C. H. Ke and N. C. Li, J. Phys. Chem. 72, 1297 (1968).

(32) M. F. Pushlenkov and O. N. Shuvalov, Radiohkimiyia 5, 551 (1963).

(33) J. J. Bucher, M. Zirin and R. M. Diamond, to be published.

(34) J. J. Bucher and R. M. Diamond, J. Phys. Chem. 69, 1565 (1965).

(35) N. Bailey, A. Carrington, K. A. K. Lott and M. C. R. Symons, J. Chem. Soc., 290 (1960); R. W. Duerst, J. Chem. Phys. 48, 2275 (1968).

(36) B. Chu, D. C. Whitney and R. M. Diamond, J. Inorg. Nucl. Chem. 24, 1405 (1962).

(37) W. E. Keder and L. L. Burger, J. Phys. Chem. 69, 3075 (1965).

(38) T. J. Conocchioli, M. I. Tocher and R. M. Diamond, J. Phys. Chem. 69, 1106 (1965).

## Table I

Mixed Equilibrium Quotients For Extraction of $HReO_4$ and $HAuCl_4$

| Diluent | Acid | $K_1^a$ | $K_2^a$ |
|---|---|---|---|
| Benzene | $HReO_4$ | -- | $1.3 \times 10^3$ |
| | $HAuCl_4$ | -- | $2.3 \times 10^6$ |
| Triethylbenzene | $HReO_4$ | -- | $4.2 \times 10^2$ |
| Chloroform | $HReO_4$ | $8 \times 10^{-2}$ | $6.9$ |
| | $HAuCl_4$ | $1.2 \times 10^1$ | $1.9 \times 10^4$ |

## Figure Captions

Figure 1.  Variation of water content of the organic phase with initial TOPO

concentration in benzene (line 1) and $CHCl_3$ (line 2). ($[H_2O]_0$ =

total $H_2O$ minus $H_2O$ dissolved by diluent.)  Lines are drawn with

unit slope except for the upper portion of 1; there, the dashed

line indicates an extension of unit slope.

Figure 2.  Variation of acid content of the organic phase with aqueous $HReO_4$

or $HClO_4$ activity for 0.10M TOPO in benzene (line 2), in sym-

triethylbenzene (line 3) and in $CHCl_3$ (line 4); and for 0.0020M TOPO

in benzene (line 5) and 0.01M TOPO in $CHCl_3$ (line 6). ●, denotes

uncorrected data, and ■ gives data corrected for used-up TOPO.

●, in line 2 denotes $HClO_4$ extraction as measured by titration,

while ▲ denotes $HReO_4$ extraction measured by tracer.  All straight

portions of the solid curves and the dashed lines are drawn with

unit slope.

Figure 3.  Variation of acid content of organic phase with aqueous $HAuCl_4$ in

0.01M HCl for 0.10 (line 1), 0.050 (line 2) and 0.010M TOPO (line 3)

in benzene. ●, uncorrected data. ■, corrected data for used-up

TOPO.  The dashed lines are extensions of the lines of unit slope.

Figure 4.  Variation of acid content of organic phase with TOPO in benzene for

aqueous $HReO_4$ concentrations of 0.437 (line 1), 0.10 (line 2),

0.040 (line 3) and 0.010M $HReO_4$ (line 4). ●, uncorrected data;

■, data corrected to equilibrium TOPO.  Straight portions of solid

curves or dashed lines are drawn with slope two.

Figure 5.  Variation of acid content of organic phase with TOPO in $CHCl_3$ for

aqueous 0.10M $HAuCl_4$ in 0.010M HCl (line 1) and for aqueous $HReO_4$

concentrations of 0.514 (line 2) and 0.040M (line 3). ●, uncor-

rected data; ■, data resulting from subtraction of component of

unit slope from uncorrected data. Dashed lines are drawn with either

unit slope or slope two.

Figure 6.    Variation of distribution ratio, D, with TOPO in $CHCl_3$ for $1 \times 10^{-4}$M

$HAuCl_4$ (line 1) and for $4 \times 10^{-5}$M $HReO_4$ (line 2) for an aqueous HCl

concentration of 1.0M. ●, uncorrected data; ■, data resulting

from subtraction of component of unit slope from uncorrected data.

Dashed lines are drawn with either slope two or one.

Figure 7.    Variation of distribution ratio, D, with TOPO in benzene for

$1 \times 10^{-4}$M $HAuCl_4$ and an aqueous HCl concentration of 0.027M (line 1);

and with TOPO in 1,3,5-triethylbenzene for $1 \times 10^{-7}$M $HReO_4$ and an

aqueous HCl concentration of 0.10M HCl. Straight portions of solid

curves and dashed lines are drawn with slope two.

Figure 8.    Water content vs. $HAuCl_4$ concentration in the organic phase (as the

aqueous $HAuCl_4$ concentration increases) for a total TOPO concentration

of 0.20M in $CHCl_3$ and 0.10M in benzene. Lines 1 and 2 are the total

organic-phase water less diluent water for $CHCl_3$ and benzene,

respectively. Lines 1' and 2' are the total organic-phase water

less both the diluent water and the water bound to TOPO for $CHCl_3$

and benzene, respectively.

Figure 9.    Water content vs. $HClO_4$ concentration in the organic phase (as the

aqueous $HClO_4$ concentration increases) for a total TOPO concentration

of 0.10M in benzene and $CHCl_3$. Lines 1 and 2 are the total organic-

phase water less diluent water for benzene and $CHCl_3$, respectively.

Lines 1' and 2' are the total organic-phase water less both the

diluent water and the water bound to TOPO for benzene and $CHCl_3$,

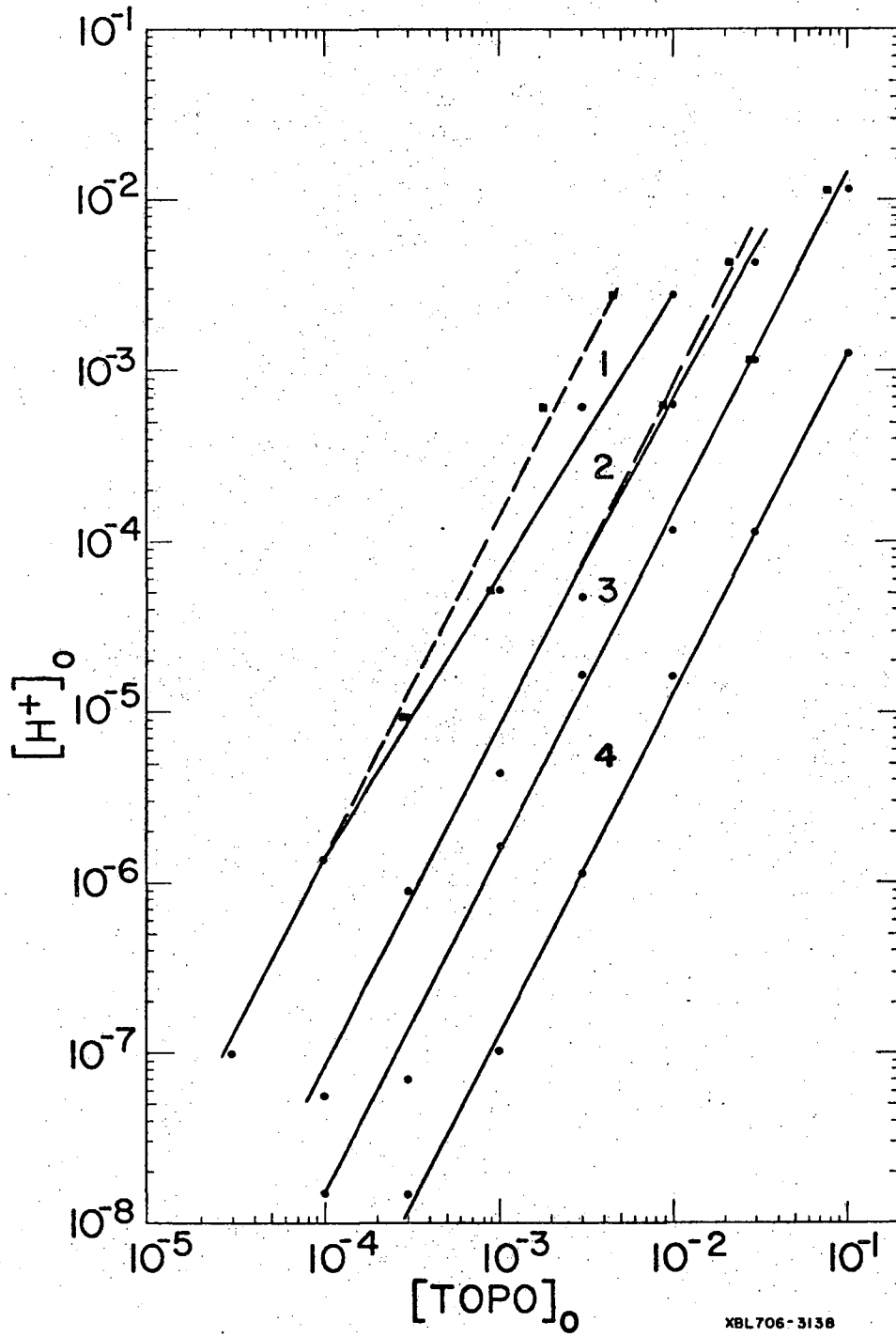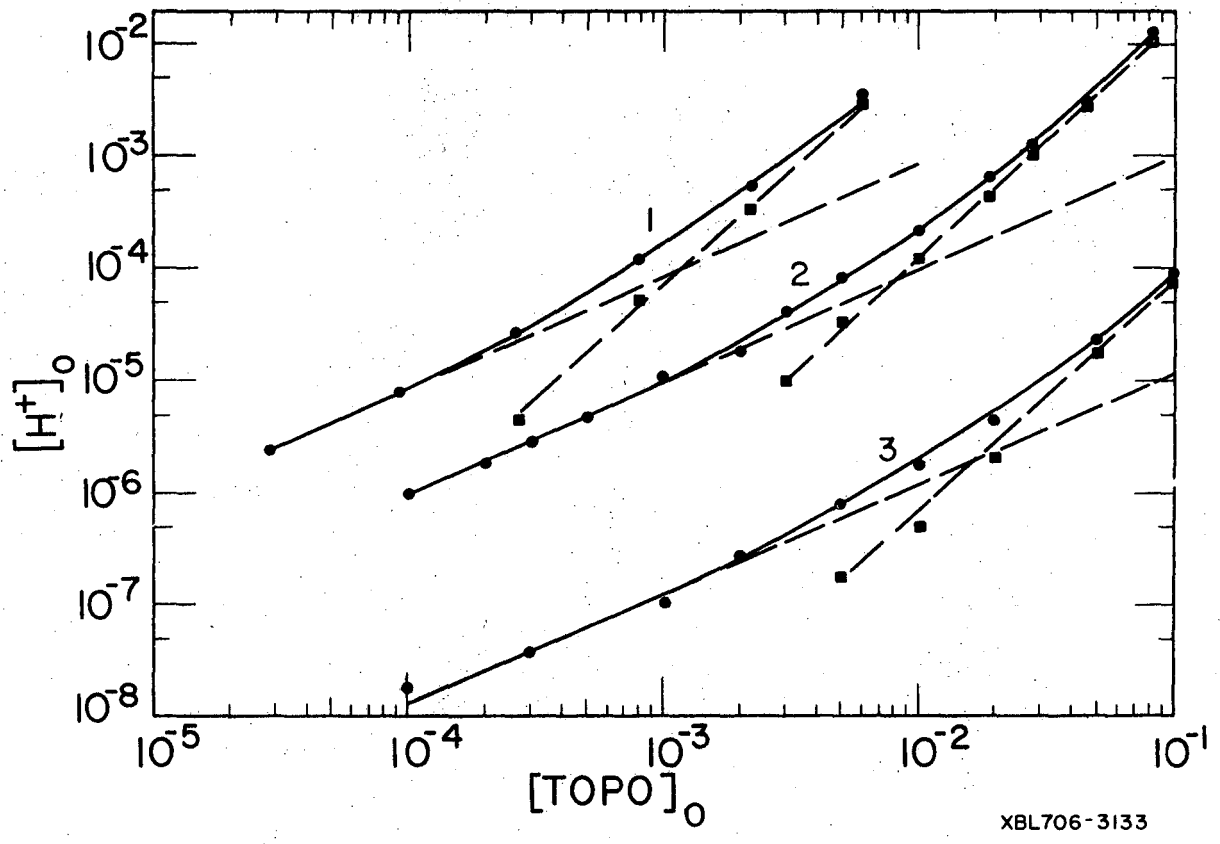respectively.
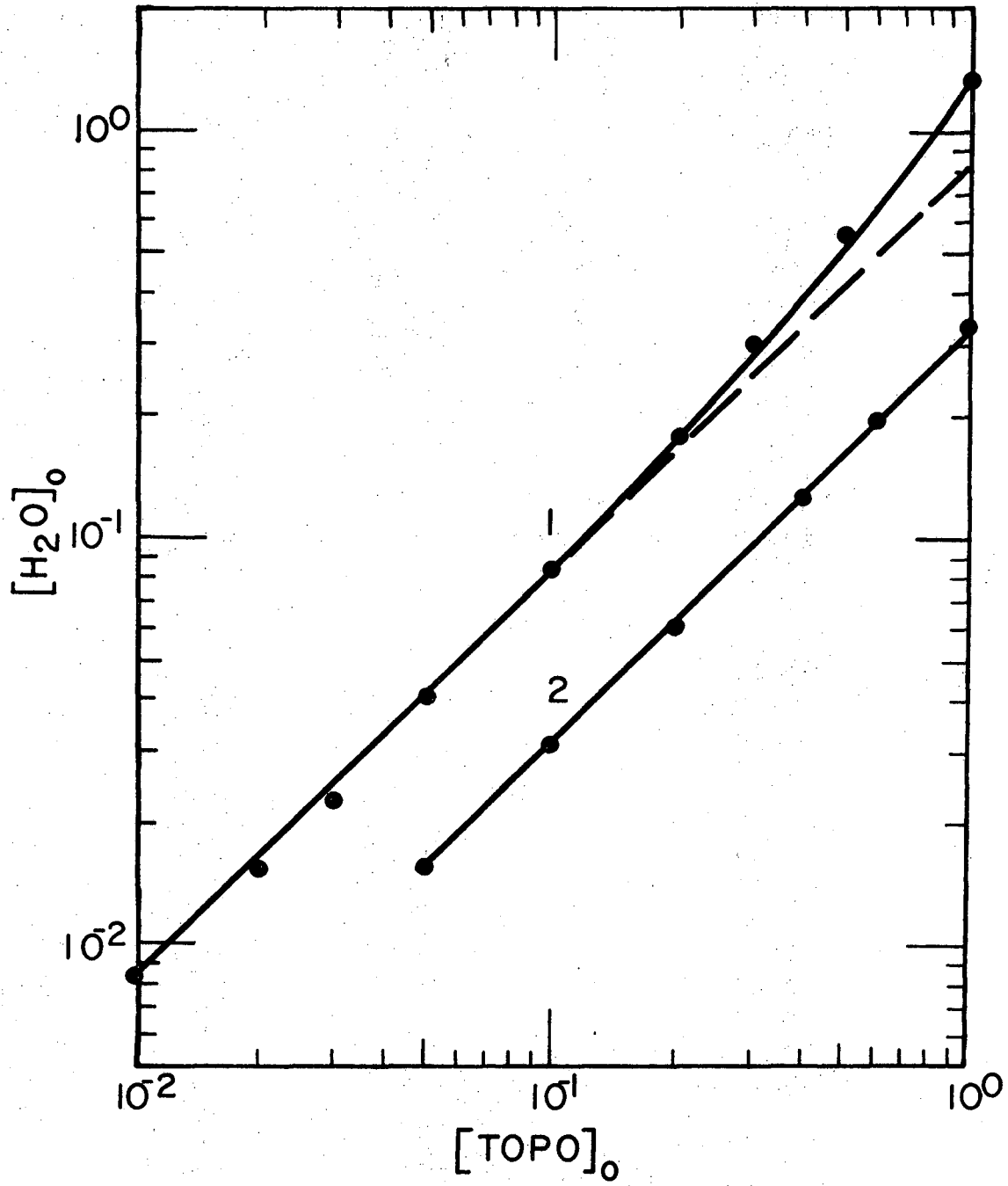
XBL706-3137

Fig. 1

Fig. 2

UCRL-19920
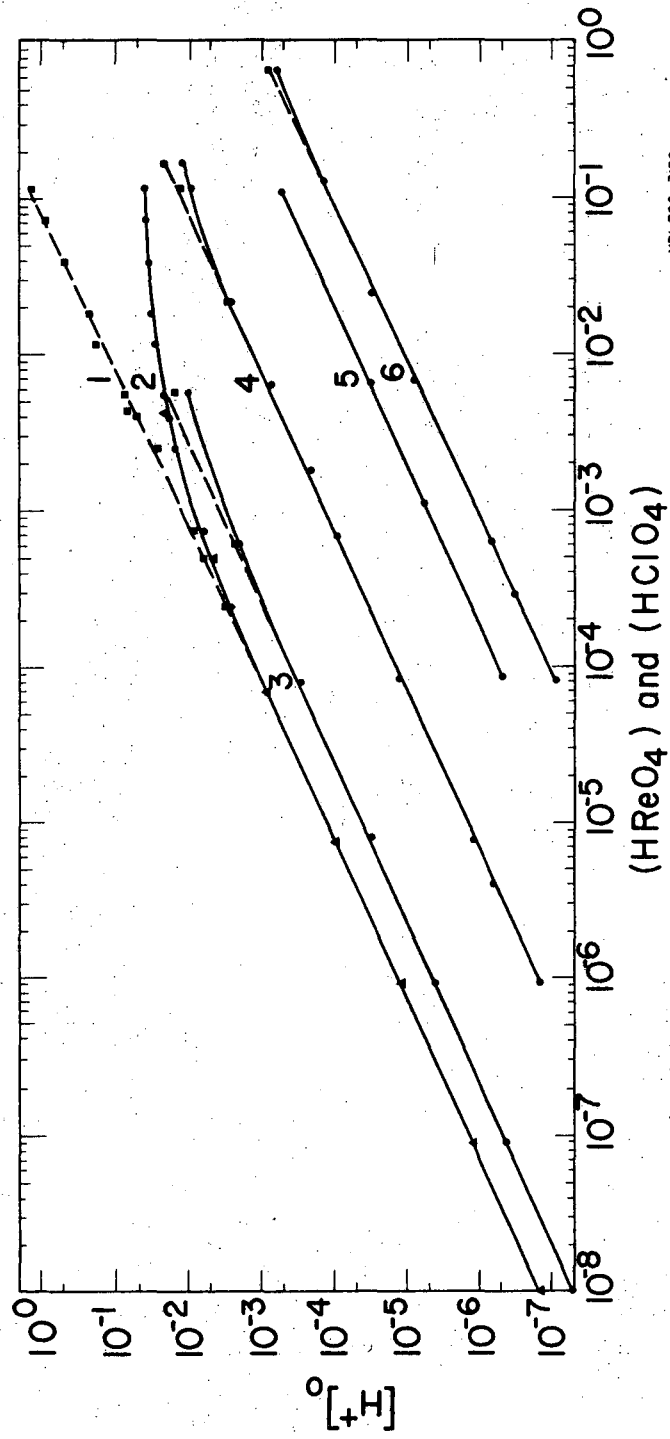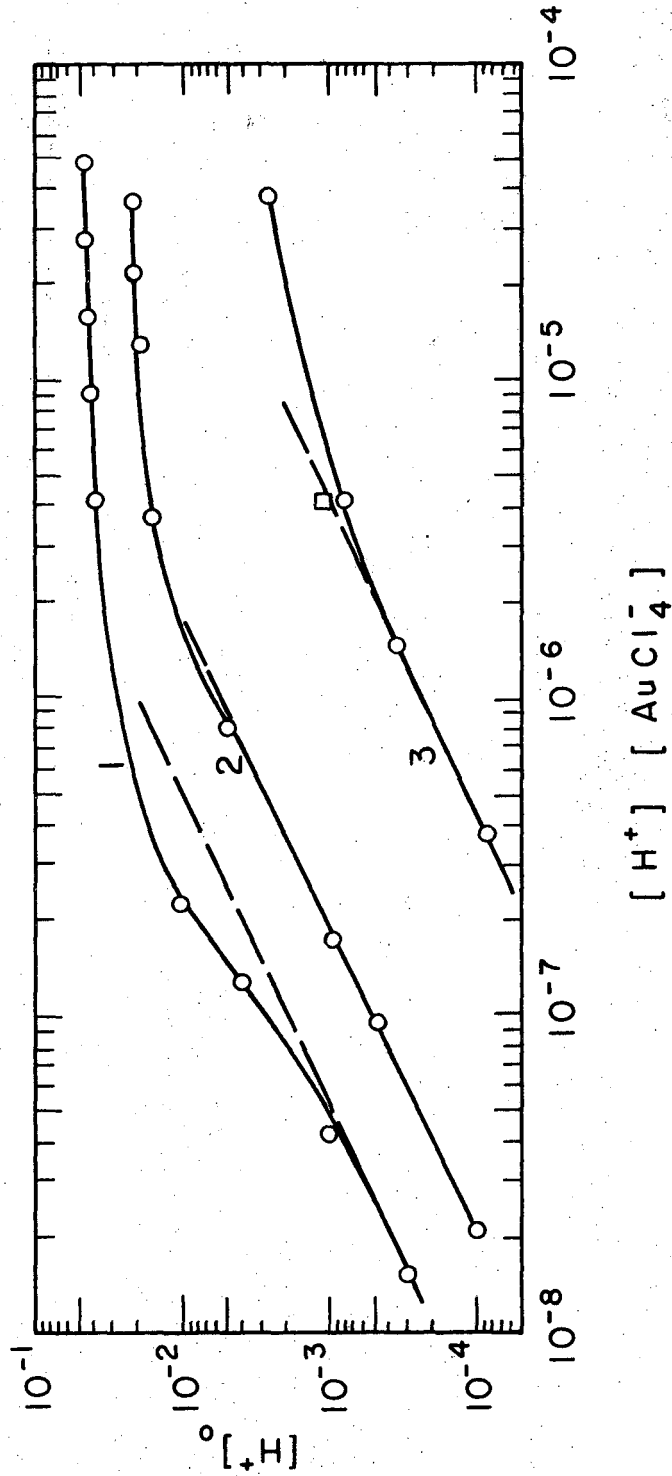
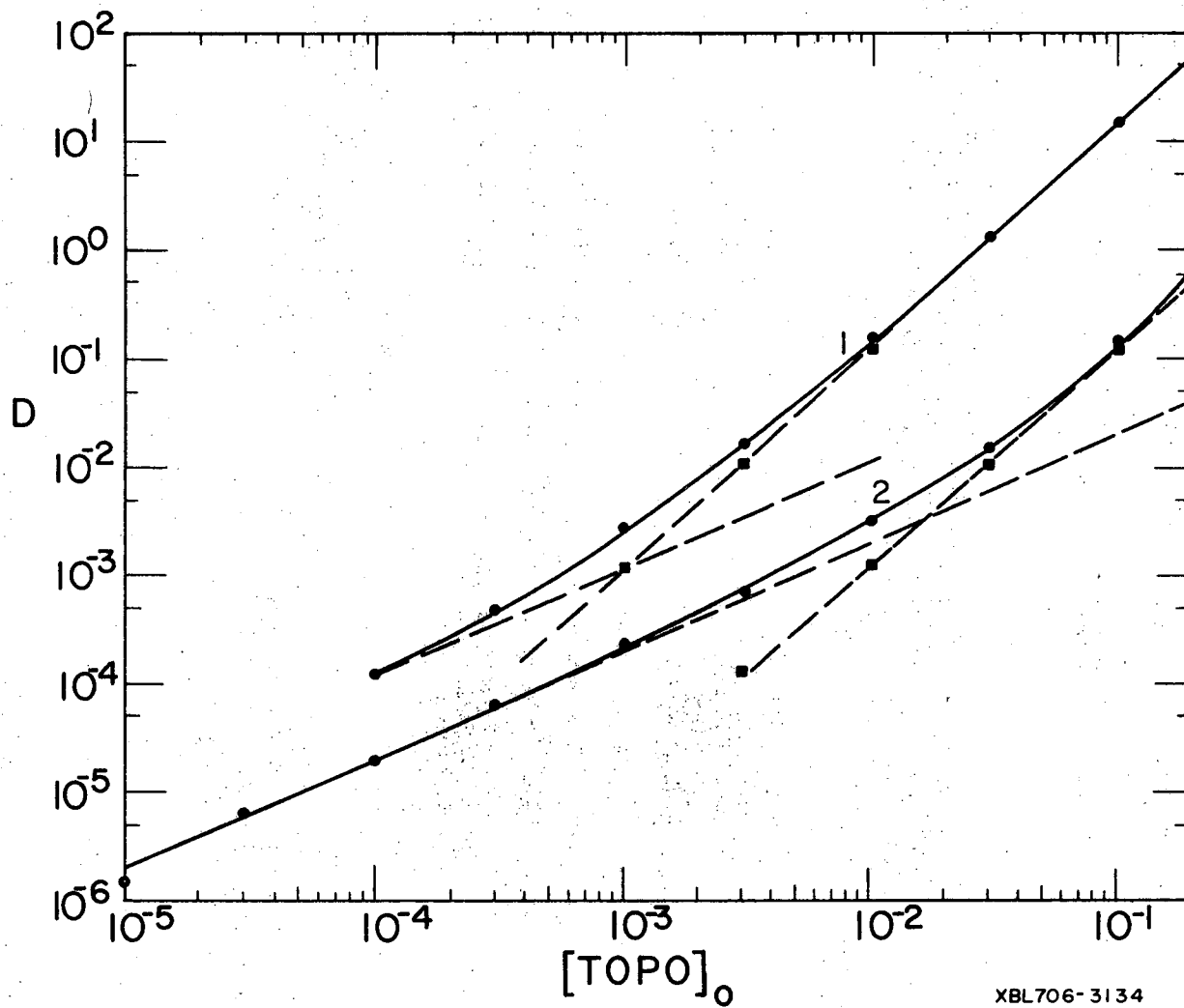

XBL701-2201

Fig. 3

XBL706-3138

Fig. 4

XBL706-3133

Fig. 5

XBL706-3134

Fig. 6
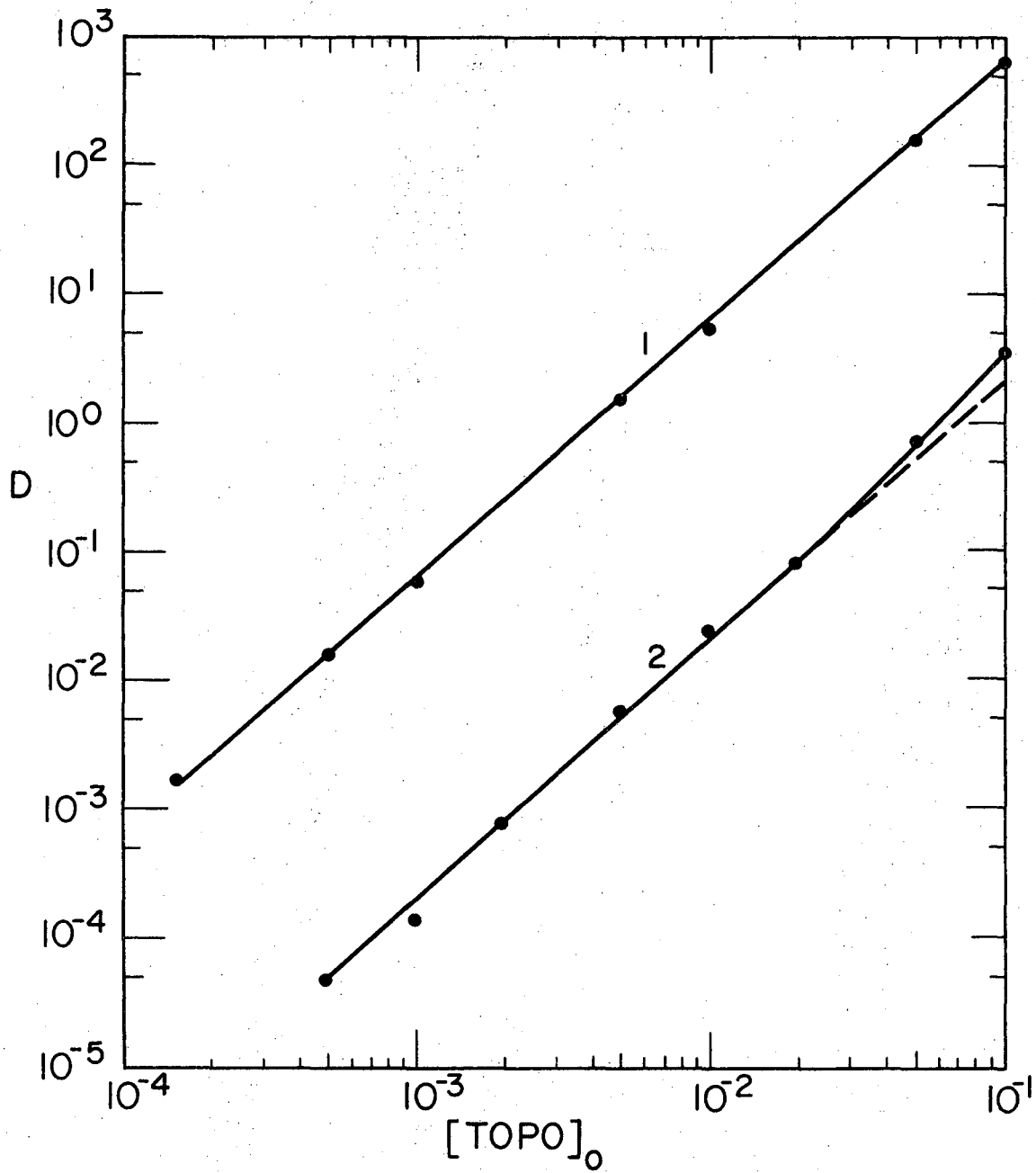
XBL706-3135

Fig. 7

XBL706-3139

Fig. 8

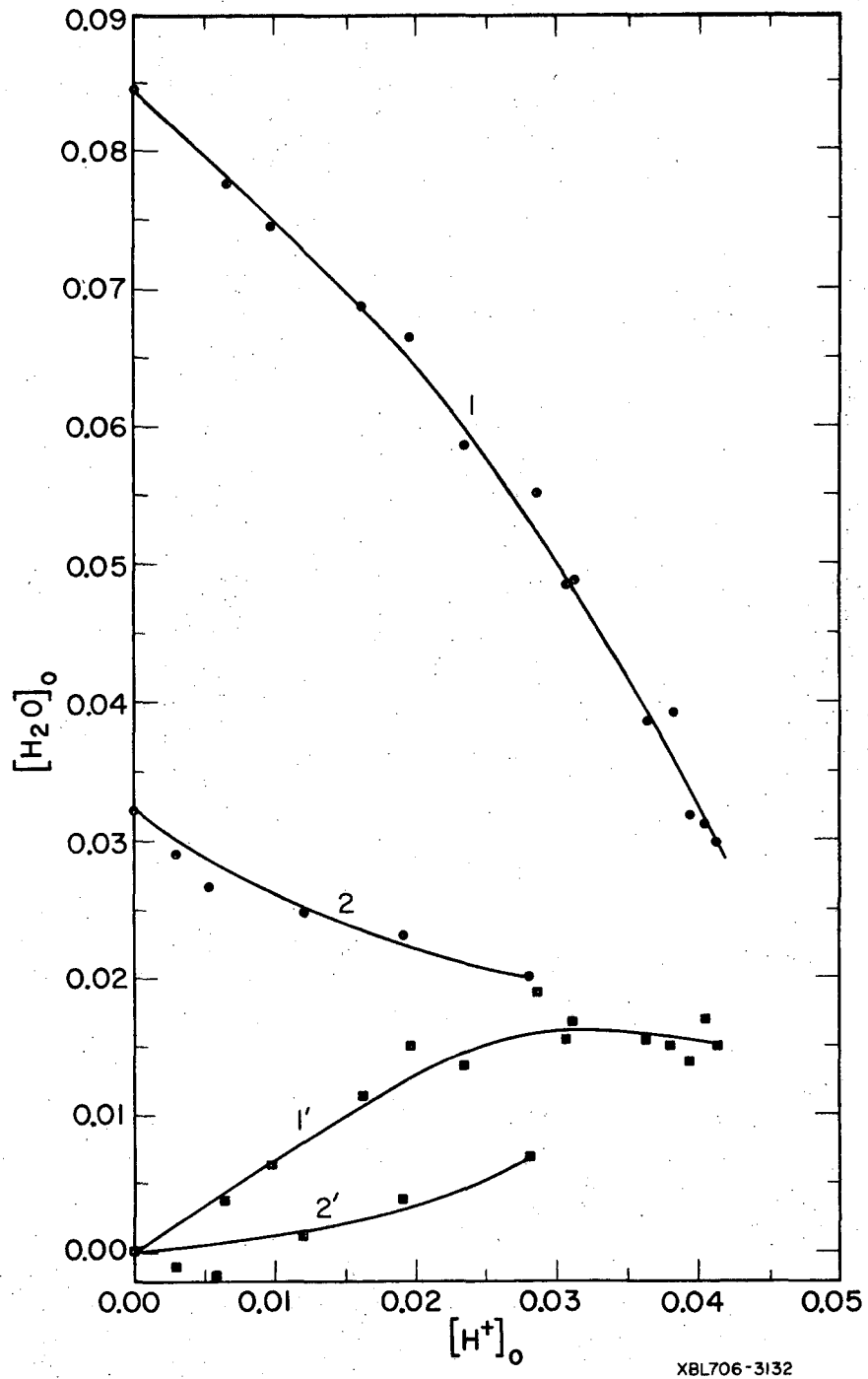Fig. 9

*TECHNICAL INFORMATION DIVISION*
*LAWRENCE RADIATION LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*