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EXTRACTION OF $HReO_4$ BY TRIOCTYL PHOSPHINE OXIDE IN NITROBENZENE AND IN 1,2-DICHLOROETHANE

J. J. Bucher, T. J. Conocchioli and R. M. Diamond

March 1970

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

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DISCLAIMER

EXTRACTION OF $HReO_4$ BY TRIOCTYL PHOSPHINE OXIDE IN NITROBENZENE AND IN 1,2-DICHLOROETHANE[1]

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March 1970

Abstract

The extraction of $HReO_4$ or $HClO_4$ into dilute solutions of trioctyl-phosphine oxide (TOPO) in nitrobenzene and in 1,2-dichloroethane has been studied. In both diluent systems when the stoichiometric ratio $TOPO/H^+$ was > 2, the extracting species was a dissociated two-TOPO acid complex with which a negligible amount of water coextracted. That is, TOPO is sufficiently basic to extract a proton from the aqueous hydronium ion, somewhat similarly as do the more basic alkyl amine extractants. But two TOPO molecules are required to solvate and stabilize the cationic complex rather then one as with the amines. In this respect, as well as in regard to the magnitude of acid extraction, TOPO acts as a bridge, or is intermediate, between the alkyl amines and the more weakly basic alkyl phosphates, ethers, and ketones.

Introduction

Strong organic bases such as the alkyl amines dissolved in a relatively

inert diluent can react with solutions of strong aqueous acid by extracting

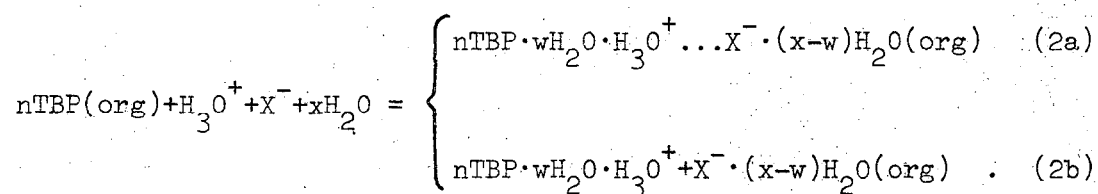the proton away from the water to form a one-to-one complex, the ammonium

ion,[2]

$$R_3N(org)+H_3O^++X^- \rightleftharpoons R_3NH^+...X^-(org)+H_2O \qquad (1)$$
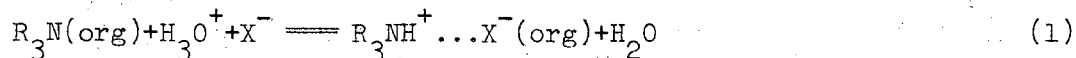
where the species $R_3NH^+...X^-$ may be dissociated, associated to ion pairs, or

aggregated to still higher associations depending upon its concentration and

the nature of the anion and of the diluent. With large anions, such as ClO_4^-

or ReO_4^-, and diluents of relatively high dielectric constant, such as nitro-

benzene, the ammonium salt is usually dissociated and essentially anhydrous.[3]

Weaker organic bases, such as tributyl phosphate (TBP), cannot take the

proton away from the water molecule, and so must extract the hydronium ion,

H_3O^+.[4,5] Depending upon the anion and diluent, three, or possibly two, TBP

molecules may be needed to satisfy the solvation requirements of the hydronium

ion, and additional water may be co-extracted.[6] Again, depending upon the

conditions, a dissociated or associated species may result,

$$nTBP(org)+H_3O^++X^-+xH_2O = \begin{cases} nTBP \cdot wH_2O \cdot H_3O^+...X^- \cdot (x-w)H_2O(org) & (2a) \\ \\ nTBP \cdot wH_2O \cdot H_3O^++X^- \cdot (x-w)H_2O(org) & (2b) \end{cases}$$

The alkyl phosphine oxides are intermediate in basicity[7-10] 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 proton or a hydronium

ion, and how many extractant molecules are necessary to provide solvation for

the cation. If a hydronium ion is involved, is it further hydrated? The use

of a large monovalent anion such as ClO_4^- or ReO_4^- (the latter is particularly

advantageous as it has a convenient tracer, ^{186}Re) minimizes the cation-anion

interactions and hopefully leads, in high dielectric constant media, such as

nitrobenzene (ε = 34.8 at 25°C)[11] and dichloroethane (ε = 10.4 at 25°C),[11]

to dissociated species.

Experimental

Reagents.—The $HClO_4$ solutions were prepared by dilution with distilled water of G. F. Smith reagent grade $HClO_4$, 70 to 72%. The stock 70 - 72% solution was standardized by titration with sodium hydroxide to the bromothymol blue endpoint. $HReO_4$ solutions were made by dilution from a stock solution, and standardized in the same way as the $HClO_4$. The stock solution was prepared by dissolving Re_2O_7 in water. The $^{186}ReO_4^-$ tracer solution was prepared by irradiating $KReO_4$ with neutrons for six days at a flux greater than 10^{14} neutrons/cm^2-sec in the Vallecitos Test Reactor and dissolving the product in distilled water. Eastman White Label nitrobenzene was used as obtained, as was the Matheson, Coleman and Bell "spectro" grade 1,2-dichloroethane.

Procedure.—1) Standardized solutions of $HReO_4$ containing radioactive $^{186}ReO_4^-$ were shaken for not less than one hour with dilute solutions of TOPO in nitrobenzene and in dichloroethane. After centrifugation, aliquots of both the organic and aqueous phases were taken for gamma-counting in a well-type Na(Tl)I scintillation counter. Knowing the original concentration of acid and the specific activity of the tracer, the measured counting rates yield the equilibrium concentrations of $HReO_4$ in each phase. 2) When sufficient acid extracted, acid-base titrations were also used to determine the equilibrium acid content of each phase. 3) TOPO solutions in both nitrobenzene and 1,2-dichloroethane were partially converted to the acid-complex form by contact with an aqueous $HReO_4$ solution. After determination of the organic-phase acid content of these stock solutions by titration of small aliquots, a number of dilutions of these organic phases were shaken (back-extracted) with equal

volumes of distilled water to which a small amount of ReO_4^- tracer had been added. After equilibrium was attained, aliquots of both phases were gamma-counted and so the equilibrium acid concentrations in each phase were determined. 4) The concentration of water bound to TOPO in the organic phase and the amount of water coextracted with $HClO_4$ were determined in separate series of experiments by the Karl Fischer method using a dead-stop end-point, and, for 1,2-dichloroethane by means of tritiated water counted in a room-temperature liquid-scintillation counter. All experiments were performed at 23 $\pm$ 2°C.

Results and Discussion

The experimental results are shown mostly as log-log plots in Figs. 1-7. 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:
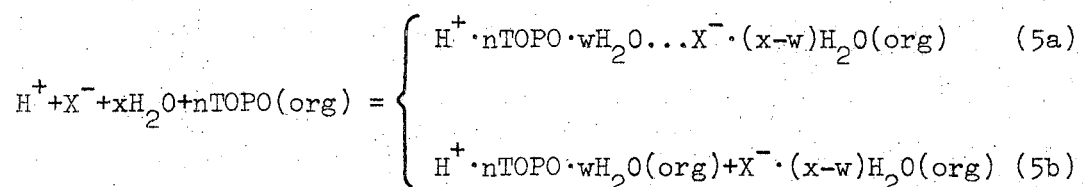
$$nTOPO(org)+mH_2O = mH_2O \cdot nTOPO(org) \quad . \tag{3}$$
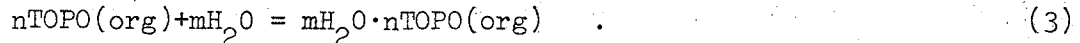
The corresponding equilibrium constant is

$$\mathcal{K}_{H_2O} = \frac{(mH_2O \cdot nTOPO)_0}{(H_2O)^m(TOPO)_0^n} = \frac{[mH_2O \cdot nTOPO]y_{H_2O}}{(H_2O)^m[TOPO]^n y_{TOPO}^n} = K_{H_2O}\frac{y_{H_2O}}{y_{TOPO}^n} \tag{4}$$

where parentheses signify activity, brackets denote molar concentrations, y is a molar activity coefficient, and K is the mixed concentration quotient. With the assumption that y_{H_2O}/y_{TOPO}^n is a constant in the dilute solutions used, Eq. (4) suggests that a log-log plot of organic-phase water concentration vs. equilibrium TOPO concentration should generate a line of slope n, where n is the number of TOPO molecules coordinated in each extracted water complex. In Fig. 1 the organic-phase water concentration, $[H_2O]_0$, 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 nitrobenzene was 0.17 $\underline{M}$, which can be compared with literature
values of 0.152 $\underline{M}$ (Ref. 12) and 0.187 $\underline{M}$ (Ref. 13). For 1,2-dichloroethane a
value of 0.125 $\underline{M}$ was determined, quite similar to a literature value of 0.129 $\underline{M}$
(Ref. 14). The slope of one found in Fig. 1 for each diluent-TOPO system
indicates that one TOPO molecule is involved in each TOPO-water complex. The
observed stoichiometry of one water per TOPO molecule in 1,2-dichloroethane
might suggest in addition that a monohydrate is formed, while in nitrobenzene
the ratio of water to TOPO of 1.3:1 indicates that an additional higher water
complex is also extracted. But in a later paper[15] dealing in more detail with
water extraction by TOPO in these two and other diluents, it will be shown that
at least a mono- and a dihydrate are extracted in both the nitrobenzene and
1,2-dichloroethane systems. The stoichiometric ratio of one water to one
TOPO in 1,2-dichloroethane is simply accidental and not an indication of the
TOPO-water complex structure. The amount of free TOPO, uncomplexed by water,
in each system is small, and in this paper no distinction will be made between
total and hydrated TOPO. Thus the symbol [TOPO] will denote the TOPO concentra-
tion not complexed by acid.

TOPO-H_2O-HReO$_4$.—The extraction of HReO$_4$ by TOPO solutions may be expressed:

$$H^+ + X^- + xH_2O + nTOPO(org) = \begin{cases} H^+ \cdot nTOPO \cdot wH_2O \ldots X^- \cdot (x-w)H_2O(org) & (5a) \\ \\ H^+ \cdot nTOPO \cdot wH_2O(org) + X^- \cdot (x-w)H_2O(org) & (5b) \end{cases}$$

where equation (5a) indicates the extracted species are ion paired and

equation (5b) indicates they are dissociated. The corresponding equilibrium

constants are:

$$\mathcal{K}_n^a = \frac{(H^+ \cdot nTOPO \cdot wH_2O \ldots X^- \cdot (x-w)H_2O)_0}{(TOPO)_0^n (H_2O)^x (H^+X^-)} = K_n^a \frac{y_{HX}}{y_{TOPO}^n} \qquad (6a)$$

$$\mathcal{K}_n^d = \frac{(H^+ \cdot nTOPO \cdot wH_2O)_0 (X^- \cdot (x-w)H_2O)_0}{(TOPO)_0^n (H_2O)^x (H^+X^-)} = K_n^d \frac{y_\pm^2}{y_{TOPO}^n} \qquad . \qquad (6b)$$

Since both 1,2-dichloroethane and nitrobenzene have relatively high

dielectric constants, it is likely that the extracted acid is dissociated in

these media. If so, Eq. (5b) should hold, and a log-log plot of the organic-

phase acid concentration, $[H^+]_0$, vs. the half-power of the aqueous-phase

activity should yield a straight line with a slope of unity, for a constant

value of the equilibrium TOPO concentration. Such plots are shown in Figs.

2 and 3 for 0.10 and 0.0010 M TOPO in 1,2-dichloroethane (Fig. 2) and for

0.50, 0.10, 0.0075 and 0.0010 M TOPO in nitrobenzene (Fig. 3). It can be

seen that the initial slope for each TOPO concentration is indeed one, but

departs from unity in some instances at higher concentrations. The square

points are corrected both for the TOPO used up in forming the extraction

complex and for the organic-phase activity coefficients. Correction of the

organic-phase acid concentrations from the equilibrium TOPO concentrations to

a constant (initial) TOPO concentration is by means of the expression,

$$(H^+)_{corrected} = (H^+) \frac{[TOPO]'}{[TOPO]} \qquad (7)$$

where the primed quantity refers to the initial concentration, and the first

power dependence on the TOPO concentration will be justified later. Activity

coefficients in the organic-phase were calculated from the Mayer-Poirier

expression.[16] For nitrobenzene, the best fit, especially for 0.10 $\underline{M}$ organic-

phase acid concentration or greater, was with a distance of closest approach,

a, of 8 Å, although values from 6 - 10 Å would give a satisfactory correction

for more dilute solutions. For 1,2-dichloroethane, the calculated activity

coefficients were satisfactorily used for concentrations up to $\sim 10^{-3}$ $\underline{M}$;

much beyond this concentration, the calculated coefficients seem to fall too

rapidly, leading to a downward deviation of the curve connecting the corrected

points. From the straight dashed lines of unit slope that can be drawn

through the corrected points (and are extensions of the lines of unit slope

given by the data at lower concentrations where corrections are negligible) it

can be concluded that the extracting species in both diluent systems is dis-

sociated.

It remains to determine the value of n, the number of TOPO molecules

complexed per acid. From Eq. (5b) the slopes of the log-log plots of extracted

acid vs. TOPO concentration at a constant a_{HReO_4} should yield directly the

value of n/2. Figure 4 is such a plot for aqueous solutions of 0.00030 $\underline{M}$

and 0.020 $\underline{M}$ HReO$_4$ with 1,2-dichloroethane as diluent and for 0.00033 $\underline{M}$ HReO$_4$

with solutions of TOPO in nitrobenzene. Again, corrections for organic-phase

activities and for equilibrium aqueous acid concentrations when different from

the initial values must be made and are indicated by the square symbols in the

plot. The slopes of the dashed lines through the corrected points are unity,

and indicate that two TOPO molecules are involved in the extracted species for

TOPO concentrations up to 0.50 $\underline{M}$ in nitrobenzene and $\sim$ 1.0 $\underline{M}$ in dichloroethane.

To evaluate K_n^d, a log-log plot (Fig. 5) of the square-root of the numerator in Eq. (6b) vs. the square-root of the denominator (the square-roots were taken so as to halve the number of decades necessary) is used. This plot combines some of the previous data from Figs. 2 - 4 as well as data obtained by the back-extraction technique (which are not conveniently presented in the previous types of plots) and covers organic-phase acid concentrations from 10^{-7} to 0.24 $\underline{M}$ and TOPO concentrations from 10^{-4} to 1 $\underline{M}$ for both diluent systems. The excellent fits to straight lines of unit slope indicate that over this range of conditions (up to 30 - 40% loading of the initial TOPO concentration), the two systems can be described by a single dissociated, two-TOPO organic-phase species. The values of K_2^d for $HReO_4$ in nitrobenzene and in 1,2-dichloroethane are $1._2 \times 10^3$ and $9._6$, respectively.

Figure 6 shows plots of the organic-phase acid concentration vs. the square-root of the $HClO_4$ activity for solutions of 0.30 $\underline{M}$ TOPO in nitrobenzene and in 1,2-dichloroethane. This figure suggests that the 2TOPO complex is the principal species extracted until the uncomplexed TOPO is nearly exhausted around 1.0 $\underline{M}$ $HClO_4$. Thereafter increasing amounts of acid are slowly extracted until a one-to-one ratio of acid to TOPO is reached. This behavior is similar to that already observed in other TOPO[17,18] and tributyl phosphate[4] diluent systems at very high acid concentrations, and suggests that a $TOPO \cdot HClO_4$ salt, perhaps resembling an ammonium salt, is formed under these conditions of high acid activity and low water activity.

For 0.30 $\underline{M}$ TOPO in nitrobenzene and in 1,2-dichloroethane the amount

of water, less the diluent water, coextracted by the organic-phase acid

complex as the acid concentration increases is shown in Fig. 7. The range of

acid concentrations used are below the turnover in the curve in Fig. 6, that

is, below where the one-to-one acid-TOPO complex becomes significant. But

for 1,2-dichloroethane the organic-phase acid concentrations employed are

higher than the region shown to be dissociated in Fig. 2, so that it is

possible some ion pairing has occurred. In both diluent systems the total

amount of water decreases as $[H^+]_0$ increases. But the amount of water extracted

by the equilibrium uncomplexed TOPO must be subtracted; the concentration of

non-acid-bound TOPO is calculated as $[TOPO]_{total} - 2[H^+]_0$. After correction,

curves 3 and 4 result for 1,2-dichloroethane and nitrobenzene, respectively.

They suggest that essentially no water co-extracts with the acid complex

in either diluent; the complex is anhydrous.

Conclusions

At all organic-phase acid concentrations in nitrobenzene observed in this study (up to 10^{-1} $\underline{M}$) and at values of $[H^+]_0$ up to $\sim 10^{-3}$ $\underline{M}$ in 1,2-dichloroethane, the extracted acid species is dissociated. Combining the experimentally determined value of two for the coordination number of the complex toward TOPO with the result that essentially no water is coextracted, suggests that the dissociated extraction complex is

$$\begin{array}{c} R \\ R \end{array} \!\!\!\! P = O \cdots H^+ \cdots O = P \!\!\!\! \begin{array}{c} R \\ R \\ R \end{array} + X^-$$
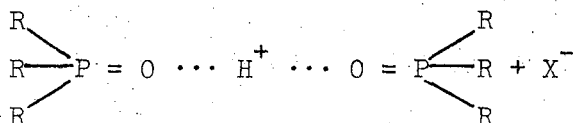
where X^- is ClO_4^- or ReO_4^-. We do not know if the TOPO molecules form symmetric hydrogen-bonds about the proton, or whether the bonds are asymmetric.

Such a structure seems reasonable considering the basicity of TOPO relative to the amines and to the phosphate extractants. The phosphine oxides are less basic than the amines, and so although they can destroy the hydronium ion and extract the proton away from water, as do the amines, two molecules of TOPO are necessary to provide adequate solvation for the proton whereas one amine molecule is sufficient. In addition, extraction is considerably lower. It can also be noticed that the TOPO-$HClO_4$ and TOPO-$HReO_4$ species are dissociated in both nitrobenzene and dichloroethane under the conditions of this work, while the corresponding salts of trilaurylamine are dissociated in nitrobenzene[3] but not in the 1,2-dichloroethane of lower dielectric constant.[3] This is a result of the better shielding afforded the proton by the two bound TOPO molecules relative to the single amine.

The still less basic phosphate extractants, such as TBP, cannot break into the hydronium ion, and so extract it as an entity. Two or three molecules of TBP (or of ethers or ketones) are required to solvate the H_3O^+, which may even be further hydrated depending upon the diluent, and extraction is still poorer than with TOPO. Thus the behavior of the $TOPO-HClO_4$ and $TOPO-HReO_4$ systems in nitrobenzene and in 1,2-dichloroethane is very nicely intermediate between that of the alkylamines and of TBP.

A few other studies of $HClO_4$,[18,19] or the similar strong acid $HTcO_4$ (Refs. 20 and 21) have been reported in the literature. Direct comparison with this work is not possible; however, from the distribution of TcO_4^- from aqueous solutions of HNO_3 and HCl into TOPO solutions of a hydrocarbon solvent and CCl_4, respectively, a complex of two TOPO molecules per TcO_4^- was found to be most consistent.[21] But the present results are in disagreement with an earlier study[17] of $HClO_4$ and $HReO_4$ extraction into CCl_4 where a 3:1 complex was proposed. Although the diluent is different in that case than in the present one, we believe that a dissociating medium like nitrobenzene should enhance the tendency toward the higher coordination number rather than reduce it,[6] so that the problem is real and we are re-investigating the previous system.

The present results, namely that the protonic cationic complex is both anhydrous and dissociated from the anion, leads to an interesting possibility. If a dissociated 2TOPO species is also found with other strong acids in these diluents, it seems reasonable to assume the same anhydrous cation. But then any coextracted water should be bound to the anion; values for the hydration of anions under these conditions can thus be determined. The extraction and anion hydration of HBr, HCl and HNO_3 will be discussed in a later paper.

Footnotes and References

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

(2) See the recent reviews by: Y. Marcus and A. S. Kertes, Ion Exchange
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Figure Captions

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

concentration in nitrobenzene and in 1,2-dichloroethane. $([H_2O]_0 = \text{total}$

H_2O minus H_2O dissolved by diluent.) Line 1, ● , is for TOPO-nitrobenzene

system. Line 2 is for TOPO-1,2-dichloroethane system; ○ denotes results

using Karl Fischer titrations, and ☐ denotes results using tritiated

water as a tracer. Lines are drawn with unit slope.

Fig. 2. Variation of acid content of the organic phase with the half-power

of the aqueous $HReO_4$ activity for 0.10 (line 1) and 0.0010 $\underline{M}$ (line 3)

TOPO in 1,2-dichloroethane; ○ denotes uncorrected data, and ☐ gives

data corrected for used-up TOPO and for activity coefficients of the

organic-phase acid. Dashed line 2 and line 3 are drawn with unit slope.

Fig. 3. Variation of acid content of the organic phase with the half-power

of the aqueous $HReO_4$ activity for 0.50, 0.10, 0.0075 and 0.0010 $\underline{M}$ TOPO

in nitrobenzene; ○ is uncorrected data, and ☐ indicates data corrected

both for used-up TOPO and for activity coefficients of the organic-phase

acid. The corrected (usually dashed) lines are drawn with unit slope.

Fig. 4. Variation of organic-phase acid content with TOPO concentration in

1,2-dichloroethane for aqueous $HReO_4$ concentrations of 0.020 $\underline{M}$ (line 1)

and 0.00030 $\underline{M}$ (line 4); and for 0.00033 $\underline{M}$ $HReO_4$ (line 3) and TOPO in

nitrobenzene. ○ gives uncorrected data, ☐ is data corrected for used-

up $HReO_4$ and for organic-phase activity coefficients (dashed lines 2

and 5). Lines 2, 3 and 5 are drawn with unit slope.

Fig. 5. Variation of square-root of the organic-phase acid activity vs. the product $\{[TOPO]_{(0)}^2 (HReO_4)\}^{1/2}$. Line 1 is for the TOPO-nitrobenzene system; line 2 is for the TOPO-1,2-dichloroethane system. Lines are drawn with unit slope.

Fig. 6. Variation of acid content of the organic phase with the half-power of the aqueous $HClO_4$ activity for 0.30 $\underline{M}$ TOPO in 1,2-dichloroethane ($\triangle$) and in nitrobenzene (∇).

Fig. 7. Water content vs. $HClO_4$ concentration in the organic phase (as the aqueous $HClO_4$ concentration increases) for a total TOPO concentration of 0.30 $\underline{M}$ in nitrobenzene and in 1,2-dichloroethane. Lines 1 and 2 are the total organic-phase water less diluent water for nitrobenzene and 1,2-dichloroethane, respectively. Lines 3 and 4 are the total organic-phase water less both the diluent water and the water bound to TOPO for 1,2-dichloroethane and nitrobenzene, respectively.
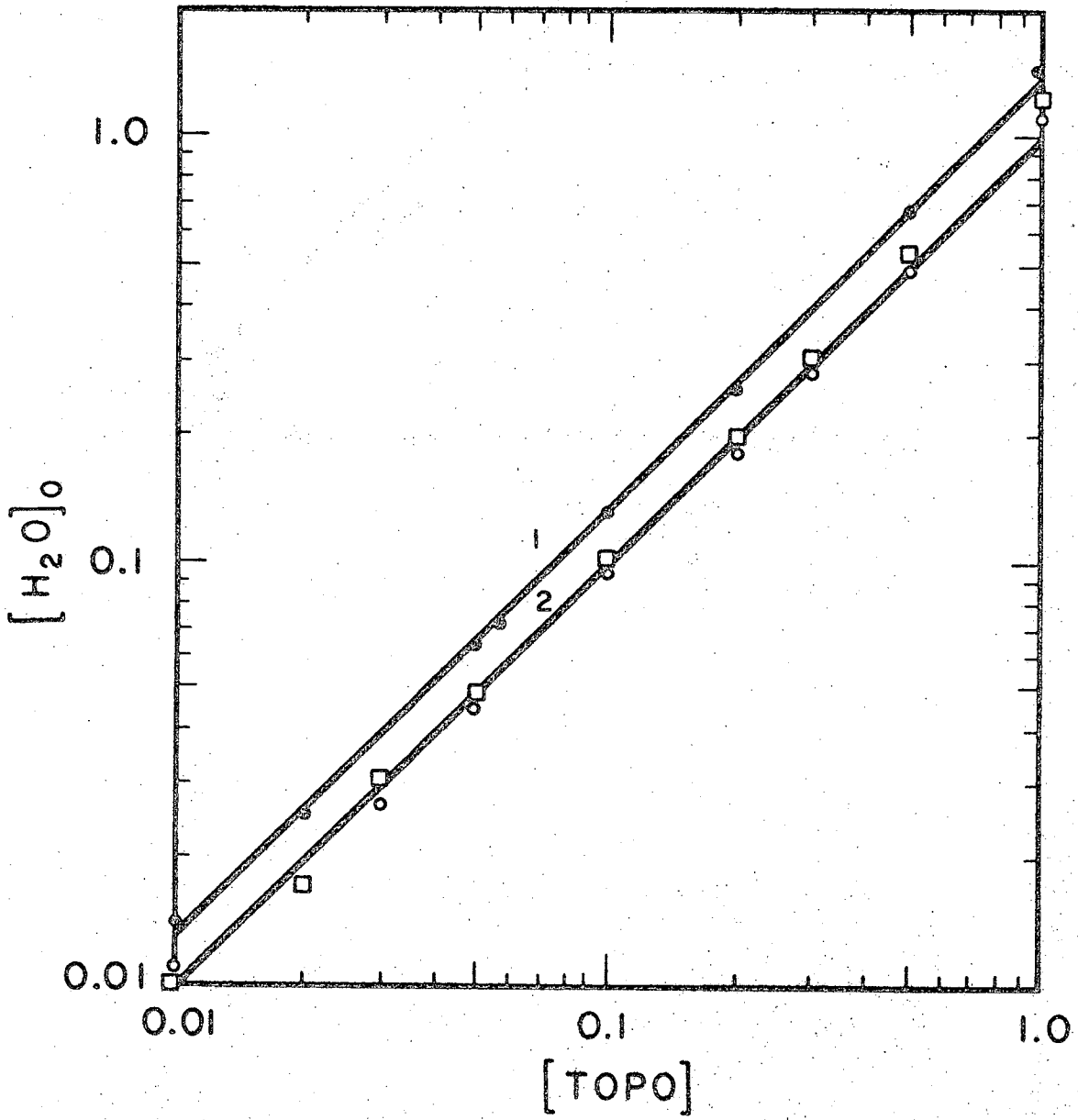
XBL 691-1898

Fig. 1.
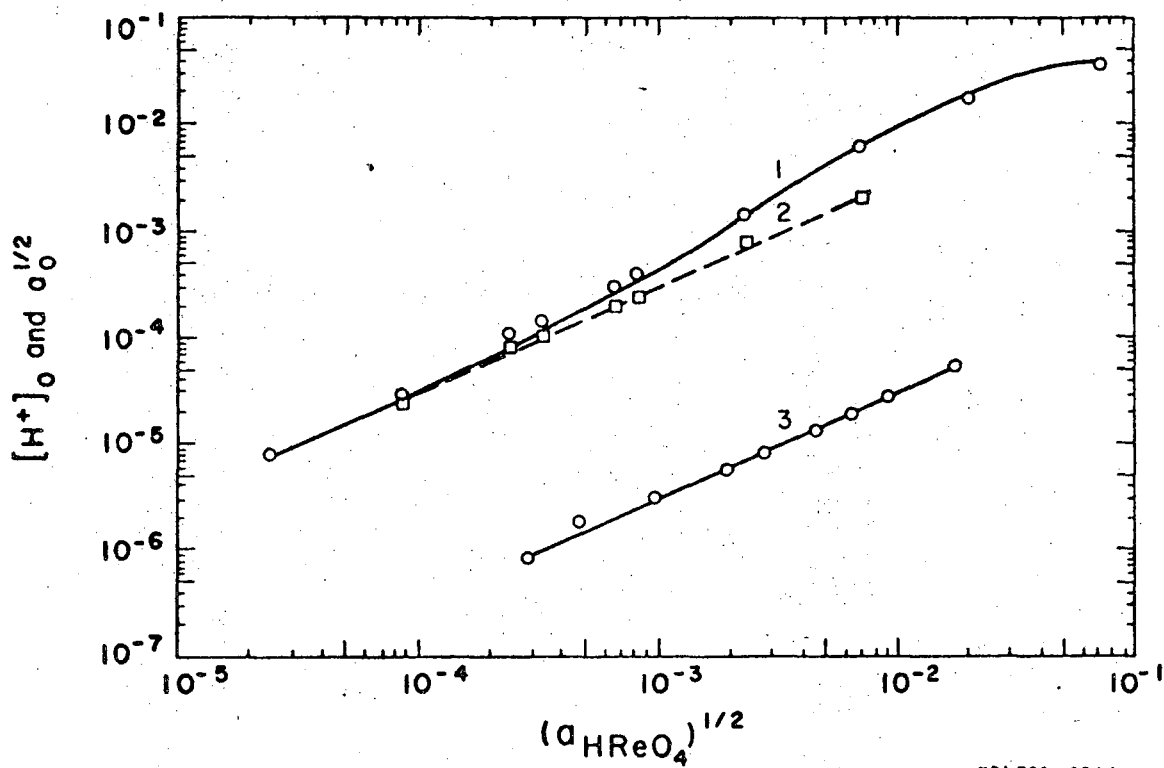
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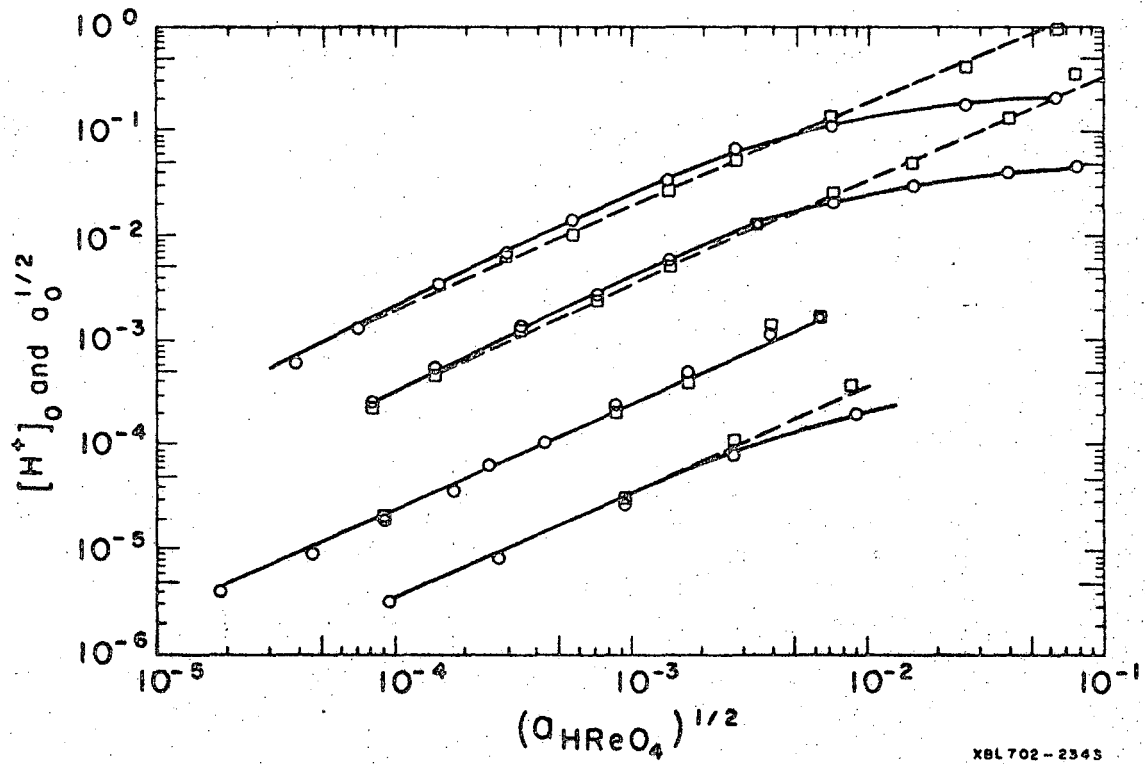
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Fig. 3.
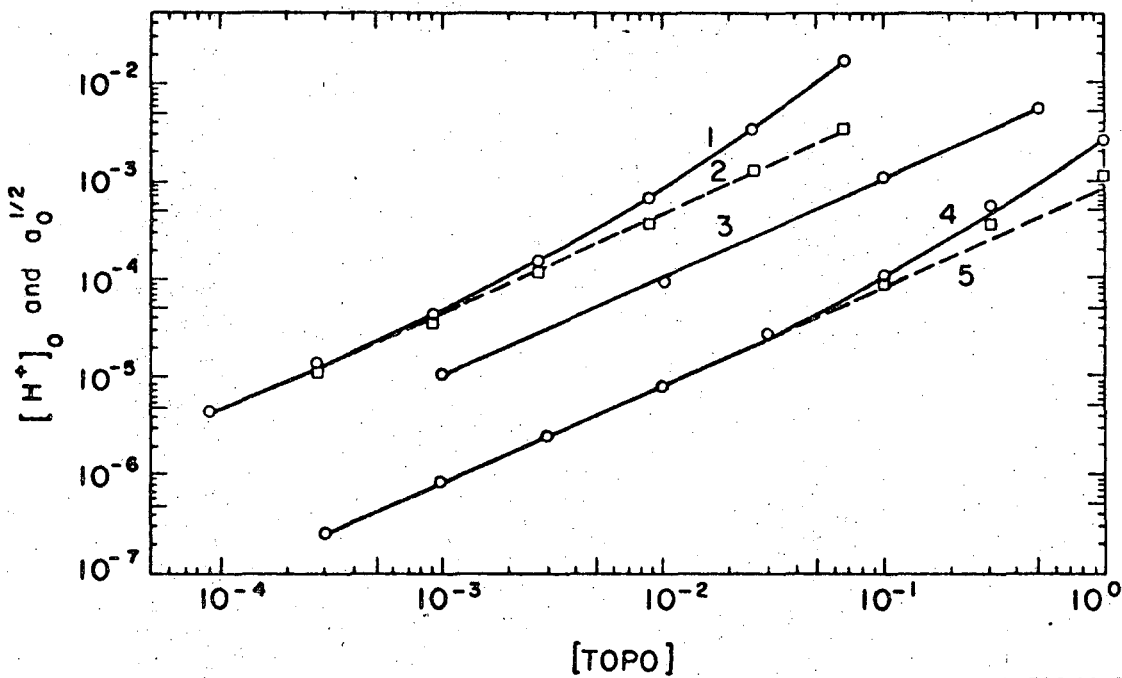
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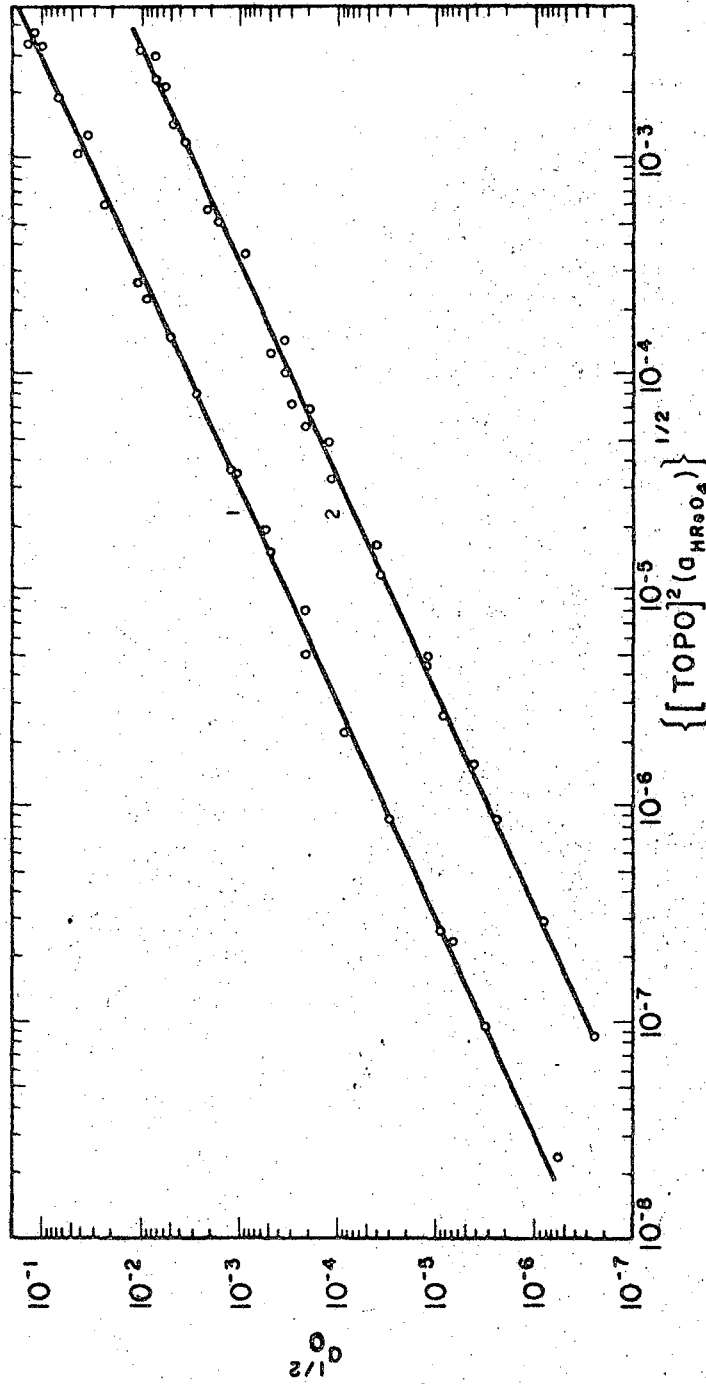
XBL 702-2345

Fig. 5.
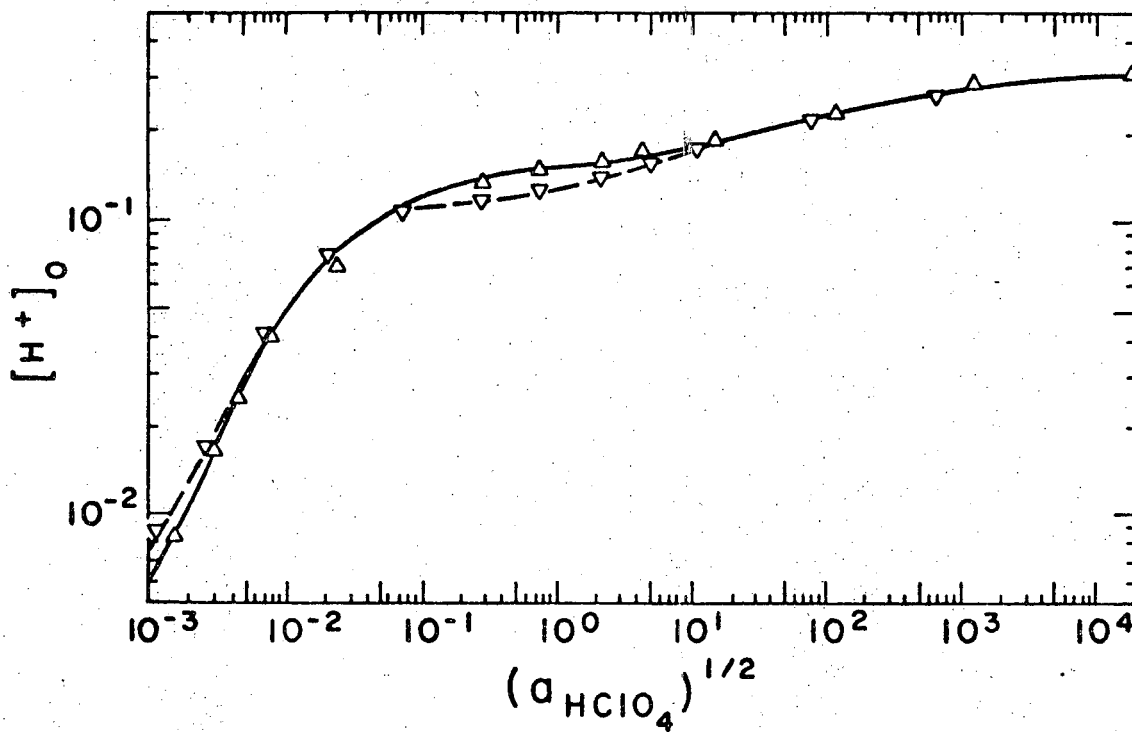
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Fig. 6.

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Fig. 7.