THE ACTION OF CHLOROSULFONIC ACID AND OF

FLUOSULFONIC ACIDS ON HYDROCARBONS

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ABSTRACT

When sulfuric acid and (+)3-methylhexane are agitated together at 60°, loss in rotation, isomerization and isotopic exchange (when D_2SO_4 is used) are observed. The rate constants of the three reactions are very nearly identical. We have proposed that the process occur by a chain reaction in which chain initiation occurs by oxidation of the alkane to a tertiary carbonium ion and chain propagation occurs by hydride ion transfer from the tertiary position of an alkane to a carbonium ion. The carbonium ion is assumed to come to equilibrium in regard to simple methyl shift and in regard to isotope exchange before the hydride ion transfer step occurs.

With chlorosulfonic or fluosulfonic acids at -33° or -78°, the rate constant of loss of rotation is much greater than that of isomerization. The rate constant of loss of rotation is also much greater than that of isotopic exchange. Also, unlike the case of sulfuric acid at 60°, the ratio of loss of rotation to isomerization depends upon the degree of stirring and increases with improved stirring. Similar though smaller excess of loss of rotation over isomerization occurs with mixtures of chlorosulfonic and sulfuric acids at 0° and with sulfuric acid at 0° and 30°.

The mechanism of the reaction with the halosulfonic acids at low temperatures seems to differ from that of sulfuric acid at 60° primarily in the relative rates of the hydride ion transfer reaction and the isomerization reaction. In contrast to the case with sulfuric acid, with halosulfonic acids, the rate constant of the hydride ion transfer reaction exceeds that of the isomerization reaction and increasingly as the temperature is lowered. At -78° it is fifty times as large. The relationship of the hydride ion transfer process and the isomerization reaction is paralleled by that of the hydride ion transfer reaction and the isotopic exchange reaction.

Commercial Practical Grade chlorosulfonic acid gives rates about ten times as large as pure synthetic material. A number of possible contaminants were examined as to their effect when added to the pure material. Hydrogen chloride leads to increased rates but not in degree adequate as the sole augmenting factor. Sulfuryl chloride is without effect, as are sulfur dioxide and sulfur trioxide. Chlorine inhibits the reaction completely.

The origin of the much greater rates observed with chlorosulfonic than with sulfuric acids may lie in one or more of the following factors: Greater solubility of alkane in the chlorosulfonic acid. Greater oxidizing potential of chlorosulfonic acid and consequently greater rate of chain initiation. More ready dissociation of alkyl esters of the acid. Greater chain length owing to lower rates of chain termination.

At -78°, (+)3-methylheptane is relatively rapidly racemized
by agitation with chlorosulfonic acid-d, but there is very little
accompanying isomerization or isotopic exchange;[1] whereas with 96%

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(1) G.S. Gordon, III, and R.L. Burwell, Jr., J.Am. Chem. Soc., 71
    2355(1949).

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sulfuric acid at 60°, the three reactions have rates of the same
order of magnitude. To accompany a more detailed study of the
sulfuric acid case,[2] further study of the behavior with chloro-

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(2) R.L. Burwell, Jr., R.B. Scott, L.G. Maury and A.S. Hussey,
    Technical Report No. 2 of this project.

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sulfonic acid was undertaken.

Experimental

Materials.-Preparation of the hydrocarbons has been
described.[2] The chlorosulfonic acid employed was of two sources,
a) freshly distilled commercial material, b) synthetic material
prepared as follows:[3] Phosphorus pentachloride (150 g.) was added

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(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical
    Chemistry," Longmans, Green and Company, New York, N.Y., 1930,
    Vol. X, p.686.

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slowly to fuming sulfuric acid (10.2% SO_3)(200 g.) at 15°. After
standing 12 hours at 25° the material was distilled in all glass
Vigreaux column of perhaps three theoretical plates. The fraction
boiling at 52° was accepted. The column must be clean and devoid
of greased joints since reduction products of the acid apparently
catalyse its decomposition.

Acid prepared by a) from Eastman Kodak Co. Practical Grade
was pale yellow. Exposure to air for a few minutes or standing

in a closed bottle for a few days caused it to become orange-yellow. The synthetic material was colorless but darkened on standing though more slowly.

The commercial acid contained an impurity which catalysed the reaction,

$$2HClSO_3 = H_2SO_4 + SO_2Cl_2$$

since upon attempting to fractionate the acid in a column packed with glass helices, we obtained an excellent yield of sulfuryl chloride.

Fluosulfonic acid (General Chemical Company) was fractionated in the small distilling column. It became colored much more slowly than the chlorosulfonic acid.

Procedure. - Halosulfonic acids and alkanes are not miscible. The reaction mixture was stirred by a magnetic stirrer in two ways, rapid and standard.[2] The former produced a better "emulsion" and is taken as giving better stirring. The reactants were used in the ratio of 3.25 cc. of hydrocarbon to 4.50 cc. of acid.

Thermostating at -78° was by a Dry Ice-chloroform-carbon tetrachloride mush and at -33° by refluxing ammonia.

To remove a sample, stirring was stopped for about a minute and enough hydrocarbon layer was removed with a pipette for infra-red analysis. Cessation of stirring apparently brought the reaction nearly to a dead stop. The hydrocarbon layer was run onto a 30% solution of potassium hydroxide. The considerable warming which occurred indicates, in contrast to the case with sulfuric acid, some solubility of the acid in hydrocarbon. To avoid possible side reactions, the hydrocarbon layer was run into the potassium hydroxide solution at -78°. This was then allowed to warm slowly.

Infrared analysis was by the procedures described for sulfuric acid.[2] It was assumed that the only isomerization product of 3-methylhexane was 2-methylhexane. The spread in the % isomerization computed at the five different wave lengths was small. For the purposes of this research, ignoring possible dimethylpentanes occasions no difficulty. The probable error in % 2-methylhexane is about 0.3 mole %.

Results

The data can be represented by the following first order equations:

$$- \ln (1 - \underline{X}_2/\underline{X}_2{}^{eq}) = \underline{k}_1 \underline{t} \tag{1}$$
$$- \ln (1 - \Delta\beta/\alpha_o) = \underline{k}_R \underline{t}$$

In these, $\underline{X}_2$ is the mole fraction of 2-methylhexane, β is the rotation and $\beta_o \equiv \alpha_o$ is the rotation of the initial 3-methylhexane. Rate constants are expressed in sec.$^{-1}$.

At -78° with halosulfonic acids and at 0° with chlorosulfonic acid-sulfuric acid mixtures, there seemed to be an induction period of the order of a few minutes and probably also at 30° with 100% sulfuric acid. The values of $\underline{X}_2{}^{eq}$ are:[4] -78°, 0.702 (extrapolated

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(4) I.G. Maury and R.L. Burwell, Jr. Technical Report No.5 of this project.
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from data at higher temperatures); -33°, 0.655; 0°, 0.628 and 30°, 0.612.

Since removal of alkane increases the proportion of acid, apparent values of the rate constants should increase after each removal of an alkane sample. This effect is small for the first two or three samples and has been ignored.

Table I

Isomerization and Racemization of (+)3-Methylhexane[a]

Run	Acid	Stirring	$k_R \times 10^5$	$k_1 \times 10^5$	k_R/k_1
		-78°			
A	$HClSO_3$	standard	33.4	1.0	33
A'	$HClSO_3$	standard	28.2	(0.4)	(70)
B	$HFSO_3$	standard	33.4	1.0	33
C	$HClSO_3$	rapid	51.1	1.0	51
D	$HFSO_3$	standard[c]	2.5	0.5	5
		-33°			
G	$HClSO_3$	slow[d]	6.7	4.3	1.6
H	$HClSO_3$	standard	370	23.4	16
I	$HClSO_3$[b]	standard	33.6	1.7	20
J	$HFSO_3$	standard	1050	210	5.0
K	$HFSO_3$	standard[c]	61	29	2.1
L	$HClSO_3$[b]	rapid	42	1.8	24
		0°			
M	$HClSO_3-H_2SO_4$[e]	standard	116	40	2.9
N	$HClSO_3-H_2SO_4$[e]	rapid	121	39	3.1
P[f]	96% H_2SO_4	standard	0.043	0.033	1.3
		30°			
Q	100% H_2SO_4	rapid	30.4	21.4	1.42
R	100% H_2SO_4	standard	25.3	18.3	1.38
S[f]	96% H_2SO_4	standard	0.54	0.53	1.02

[a] A different sample of commercial acid from the others. Precision in k_1 is low since X_2 was only 0.009.

[b] Synthetic $HClSO_3$.

[c] Standard stirring at half usual speed.

d
Stirring with a mechanical, propellor-like stirrer. It gave a much poorer "emulsion" than standard.

e
An equimolar mixture.

f
These values are computed from data at a single point assuming no induction period: $0°$, $\underline{X}_2 = 0.058$, $\Delta\beta/\alpha_0 = 0.118$ at 81 hours and $30°$, 0.067, 0.111 at 6 hours. Igncring any induction period should not affect $\underline{k}_R/\underline{k}_1$ but owing to the small value of $\underline{X}_2$ the ratio is of low precision.

Table II

Effect of Added Substances on $\underline{k}_R$ at $-33°$

| Added Material	$k_R \times 10^5$
none	42
4.5% SO_2Cl_2	46
1.5% Cl_2	0
2.0% Br_2	0
2.6% HCl	100
3.2% HBr	39
5.0% SO_3	55
3.0% SO_2	44

At -78°, extents of isomerization at very extensive losses
in rotation were only 5 to 10%. Thus, accuracy in k_1 is low.
The same is true for many runs at -33°. Data are presented in
Table I.

Since the redistilled commercial material was much more
active than the presumably pure synthetic material (run H vs. I),
an attempt was made to identify the source of the greater rates
of reaction. Results are presented in Table II. Rate constants
are computed from data at two time intervals, 10 and 25 min. and
have been divided by the mole fraction of the chlorosulfonic acid
in the mixture. All mixtures were prepared from freshly distilled
synthetic acid. The added materials, save for bromine and hydrogen
bromide, are substances which are formed in decomposition of
chlorosulfonic acid.[5]

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(5) O. Ruff, Ber., 34, 3509 (1901).

Discussion

A model has been proposed for the action of 96% sulfuric
acid on (+)3-methylhexane at 60° in which the carbonium ion,

$$\overset{+}{CCCCCC} \atop C$$
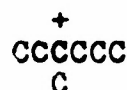
formed from 3-methylhexane by hydride ion transfer either to
sulfuric acid or to another carbonium ion, isomerizes rapidly
to an equilibrium mixture of this ion and the corresponding one
derived from 2-methylhexane. The carbonium ions then abstract
hydride ions from the tertiary positions of alkanes at such rates
as to form 2- and 3-methylhexane in their equilibrium ratio.[2]
Thus, the rate constants of loss of rotation and isomerization

expressed by equations (1) and (2) should be equal for the sul-
furic acid case. When values of X_2 are computed ignoring
dimethylpentanes, the ratio, k_R/k_1 is actually about 0.9 at 60°.

As may be seen from Table I, the rate of loss of rotation
upon using chlorosulfonic or fluosulfonic acids much exceeds that
of isomerization. With sufficiently good stirring, the ratio of
the rate constants reaches 51 at -78° and 24 at -33°. We propose,
under these conditions, that the rate of hydride ion transfer
considerably exceeds that of carbonium ion isomerization. Thus,
carbonium ions formed from (+)3-methylhexane largely revert to
(±)3-methylhexane and the overall reaction closely approaches a
pure racemization. This modification of the mechanism for sulfurio
acid at 60° seems necessary and sufficient to accomodate the
present data.

The representation of the chain carrying species is convenient
as a carbonium ion
but not essential to the general application of the mechanism.
The behavior of fluosulfonic acid resembles that of chlorosulfonic
acid. Roebuck and Evering[6] have reported the isomerizing activity

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(6) A.K. Roebuck and B.L. Evering, J. Am. Chem. Soc., 75, 1631 (1953).
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of fluosulfonic acid.

As with sulfuric acid,[2] it is not clear whether chain
initiation and hydride ion transfer occur at the hydrocarbon inter-
face or whether they involve alkane dissolved in the acid layer.[7]

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(7) An earlier suggestion[1] that these reactions occur in the hydro-
carbon phase is not now tenable.[8]

Isomerization of the carbonium ions and chain termination most
likely occur in the acid phase.

With sulfuric acid at 60°, the ratio k_R/k_1 is independent of stirring. As shown in Table I (compare runs A and C, B and D, G and H), k_R/k_1 increases markedly with improved stirring at -78 and -33°. A smaller effect is noticed at higher temperatures but in these cases variation in stirring was less extensive. In general, the lower the temperature, the larger the value of k_R/k_1.

If all reactions occur in the acid phase, improved stirring causes a more rapid interchange of alkane between the acid and the hydrocarbon phase and causes the concentration of alkane in the acid phase to approach the equilibrium solubility. If the true rate of the hydride transfer reaction in the acid phase is more rapid than that of isomerization, both consequences of improved stirring will lead to greater increase in the observed rate of loss of rotation than in the observed rate of isomerization.

If, however, the isomerization were to occur in the acid phase and hydride ion transfer at the hydrocarbon-acid interface, then the increased extent of interface consequent to improved stirring could lead to the same result. However, it is hard to see how the observed results could follow from a process in which both isomerization and hydride ion transfer occur at the interface.

From the decrease in the value of k_R/k_1 with temperature, the activation energy of the isomerization reaction appears to exceed that of hydride ion transfer by a few kcal. In our mechanism, we assume that isotopic exchange is confined to hydrogen atoms adjacent to the tertiary position. Thus, the relative extent of deuteration should decrease with decreasing isomerization but only to a lower limit corresponding to the

exchange of seven hydrogen atoms (the number adjacent to the tertiary position of 3-methylhexane) provided isotopic exchange is fast compared with hydride ion transfer as at 60° with sulfuric acid. Actually[1] the relative extent of isotopic exchange goes to very low values with chlorosulfonic acid at low temperatures paralleling the decline in relative rate of isomerization. This is shown in Fig. 1 where the ratios of the rate constants of loss of rotation and exchange[1] are plotted as a function of temperature. Thus, the actual rate of exchange of the chain propagating species (here treated as a carbonium ion) falls with decreasing temperature relative to hydride ion transfer. The isotopic exchange might occur consequent to the isomerization process itself but such an assumption is difficult to reconsile with the isotopic exchange patterns observed with D_2SO_4.[8]

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(8) D.P. Stevenson, C.D. Wagner, O. Beeck and J.W. Otvos, J. Am. Chem. Soc., 74, 3269 (1952).

In the discussion above, we have interpreted the changes in relative rates on the basis of temperature coefficients of the primary reactions and have ignored medium effects. This is an oversimplification as comparison of runs P and S in Table I with other runs at the same temperatures shows. The difference between 96 and 100% sulfuric acid accords with the isotopic exchange patterns reported by Stevenson et. al.[8]

By suitable choice of acid and temperature, one may secure any situation intermediate between that in which the carbonium ions come to equilibrium with respect to simple methyl shift (96% sulfuric acid at 60°) and that in which hydride ion transfer is so much more rapid than isomerization that one deals with a nearly pure racemization (chlorosulfonic acid at -78°).

The origin of the much greater activity of the halosulfonic acids may lie in one or more of these considerations:

1) Since the halosulfonic acids are much more soluble in hydrocarbons than is sulfuric acid, the solubility of hydrocarbon in acid is probably similarly increased. Thus, if the reactions actually occur in the acid phase, the rates of the reactions should be greater in the halosulfonic acids.

2) The oxidizing potential of the halosulfonic acids probably much exceeds that of sulfuric.

3) Although no definitive experimental data exist, one would expect replacement of HO- by F- or Cl- to lead to a stronger acid. Thus, if tertiary esters form a storage depot for carbonium ions, one would expect them to decompose to carbonium ions much more rapidly in the case of the halosulfonic ester than in the case of the bisulfate esters for the same reasons that the acids themselves deliver protons more readily.

4) The chain length may be greater with chlorosulfonic acid. A sample of redistilled commercial chlorosulfonic acid exhibited much greater activity than a synthetic material (runs H and I of Table I). As may be seen from Table II, no single product of the following decomposition reactions of chlorosulfonic acid seems to be involved in this increase save possibly for hydrogen chloride.

$$HClSO_3 = HCl + SO_3$$

$$2HClSO_3 = SO_2Cl_2 + H_2SO_4 = SO_2 + Cl_2 + H_2SO_4$$
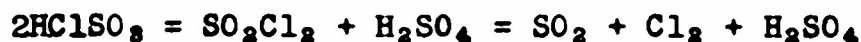
The observed effect of hydrogen chloride does not alone seem adequate to account for the increase.

The effect of chlorine and bromine in bringing the reaction to a dead stop is of interest. Presumably they eliminate tertiary

carbonium ions with the formation of tertiary halides and cut the chain length drastically. The chain length with pure chlorosulfonic acid must be long since the loss of rotation follows first order kinetics to large losses in rotation.

Below 30°, chlorosulfonic acid and chloroform are miscible. No reaction is observed in such a solution in several days at room temperature. A mixture of chlorosulfonic acid (1.4 parts), chloroform (3 parts) and (+)3-methylhexane (1 part) is also homogeneous at 0° and 25°. However, the mixture becomes orange and evolves sulfur dioxide. After a reaction period, such a solution was neutralized with alcoholic potassium hydroxide at -33° and washed several times with cold, concentrated sulfuric acid. Upon treatment of the acid washed material with alcoholic silver nitrate, a dense, white precipitate was formed. The filtered solution was washed with sulfuric acid to remove alcohol. With a reaction period of ten minutes at 0° negligible change in rotation occurred; in one hour, the rotation of the chloroform-hydrocarbon solution declined from 1.44° to 1.21°.

The failure of a reaction of long chain length to occur may be associated with the decreased dielectric constant of the medium and with reaction of any carbonium ions with either chlorosulfonic acid or chloroform to form the tertiary chlorides which appear to be present.
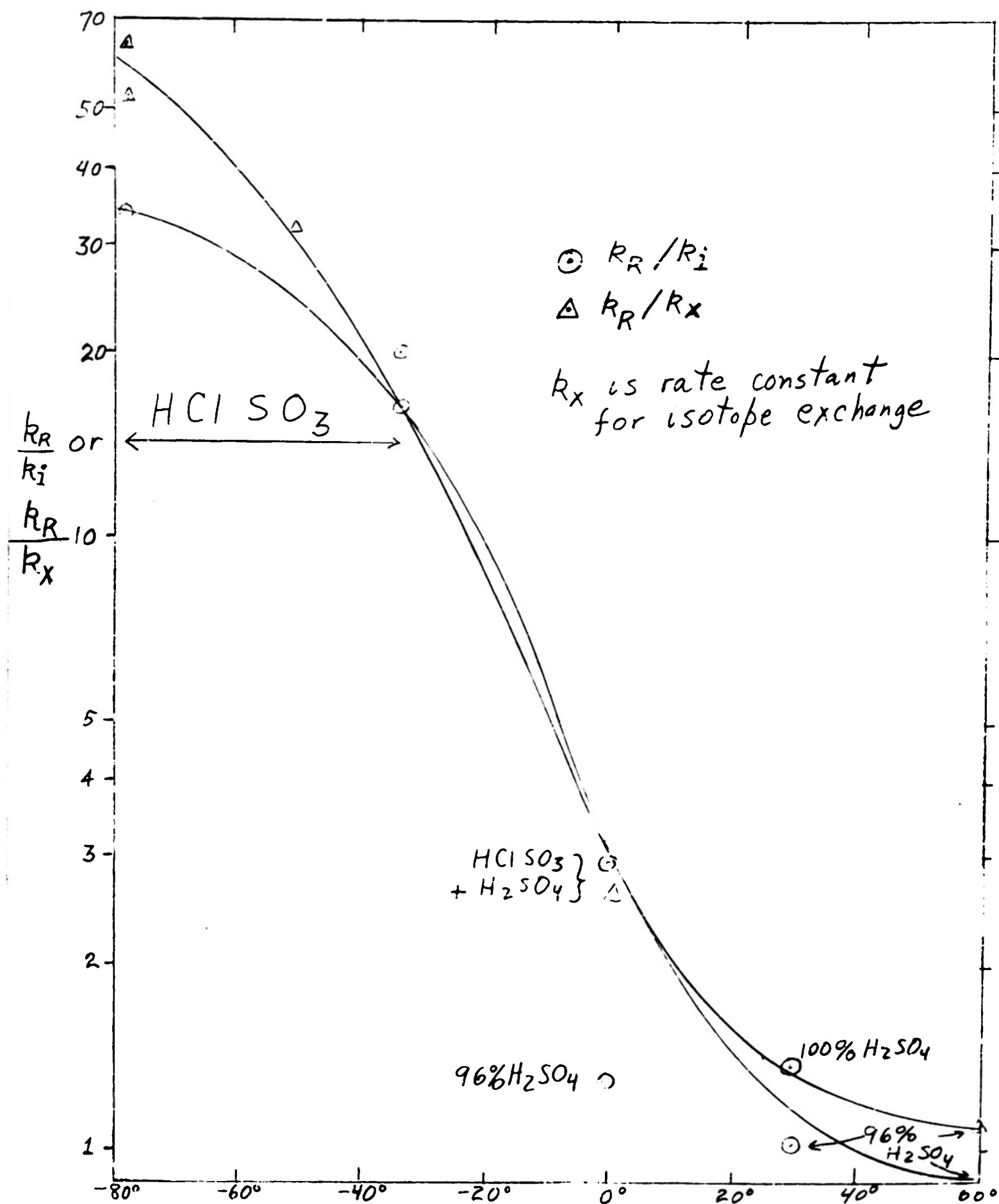
Fig. 1

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