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A COMPARATIVE STUDY OF HCl AND HBr COMBUSTION INHIBITION

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ABSTRACT

A modelling study of combustion inhibition in an idealized well stirred reactor utilizing $H_2/O_2/Ar$ mixtures as the reactants is presented and discussed. The effect of two chemical inhibitors, HCl and HBr, on the combustion process has been investigated at pressures of 0.01 and 1.0 atmosphere over a range of equivalence ratios of 0.5 to 1.5 and inhibitor concentrations of 0 to 10 percent. Inhibitor effectiveness was determined by the competition between the radical scavenging ability of an inhibitor and the exothermicity of the scavenging reactions. For all cases considered HBr was more effective in scavenging active radicals than HCl. At 0.01 atmospheres, HCl was a more effective inhibitor in lean and stochiometric mixtures while HBr was more effective for rich mixtures at 0.01 atmosphere and for all atmospheric pressure mixtures.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098; and by the National Bureau of Standards, Center for Fire Research under Grant No. NBS-G7-9006.

1. INTRODUCTION

The present study was undertaken to acquire an improved understanding of the mechanisms involved in flame inhibition. In a previous paper by Brown and Schefer (1981) modelling calculations were presented describing the effects of inhibitor addition on the combustion characteristics of $H_2/O_2/Ar$ mixtures in an idealized perfectly stirred reaction. Two physical inhibitors, N_2 and Ar, and one chemical inhibitor, HBr, were considered in an attempt to differentiate betweeen physical and chemical influences. Molecular nitrogen and argon were relatively ineffective as flame inhibitors, since they acted primarily as thermal diluents, thus effecting the chemistry minimally and indirectly. Molecular nitrogen was somewhat more effective than argon due to its higher heat capacity. Hydrogen bromide was the most effective inhibitor, primarily due to its direct participation in the combustion reaction mechanism with a resultant reduction in hydrogen/oxygen radical pool concentrations. The reactions

$$HBr + H \rightarrow Br + H_2 \quad (18r)$$

and

$$H + Br + M \rightarrow HBr + M \quad (21r)$$

were the primary reactions responsible for radical removal, and HBr effectiveness was noted to result from a tradeoff between reaction exothermicity and radical scavenging ability.

An inhibition parameter, θ_t, was proposed in our earler study to provide a measure of inhibitor effectiveness. The parameter, θ_t, was found to be a reasonable choice for characterizing Ar and N_2 inhibition; however, large variations of θ_t with pressure, equivalence ratio and HBr

concentration were noted for HBr inhibition.

In the present paper these calculations were extended to include a second chemical inhibitor, HCl. The results presented emphasize the difference between HCl and HBr as flame inhibitors and discussion is provided on the importance of reaction exothermicity and radical scavenging ability in determining inhibitor effectiveness. In Section 2 of this paper the computational model is described and the chemical mechanism and kinetic data are presented. The results of the calculations for HCl inhibition and the effect of HCl addition on reactor performance are presented in Section 3. Comparisons are made with the results for HBr obtained in our previous study. In Section 4 these results are discussed in terms of the mechanistic details of the inhibition process.

2. THE MODEL

The idealized well stirred reactor is a constant volume steady flow reactor in which mixing is assumed to occur instantaneously between the incoming reactants and the reacting mixture in the reactor. This is an attractive feature for chemical kinetic studies since the composition within the reactor is homogeneous and the combustion process is kinetically controlled. Through variation of the mass flow rate through the reactor (or its inverse, residence time) it is possible to study inhibition characteristics over a range of combustion conditions from total equilibrium, at which point the reactor residence time is sufficiently long for the system to approach a state of total equilibrium, to shorter residence times at which, in the limit, the residence time is insufficient to maintain stable combustion in the reactor and blowout occurs. Reactor behavior under conditions approaching the blowout time are particularly sensitive to the combustion chemistry and the effect of inhibitor addition.

The governing equations for an idealized well stirred reactor and the solution procedure have been described in detail elsewhere in our earlier study. Briefly, the governing equations which must be solved are the energy and the species conservation equations. These were solved using a modification of a program developed by Pratt and Bowman (1972) based upon a Newton Raphson technique. With a series of residence times corresponding to stable combustion in the reactor as independent variables, the corresponding temperatures and compositions between the blowout condition and thermodynamic equilibrium were determined from solutions of the conservation equations. In the present investigation the hydrogen/oxygen combustion system was considered and the kinetic mechanism used is shown in Table I as reactions 1 through 13. The HCl and HBr kinetic mechanisms are also shown in Table I and consist of reactions 14 through 17 for HCl and reactions 18 through 21 for HBr. All forward and reverse reactions were considered in the calculations. Symbols (f) and (r) designate forward and reverse, respectively. The rate coefficient for reaction (17f): $H + Cl + M \rightarrow HCl + M$ was assumed to be $1.5 \times 10^{18}\ T^{-.7}$. Our rate coefficient is 1.5 times greater than the value reported by Dixon-Lewis and Simpson (1977) and was so adjusted to give better agreement with the data of Seery and Bowman (1968). All third body efficiencies were taken as values measured for argon.

A standard mixture of 50 percent combustibles and 50 percent argon was considered in the calculations with the inhibitor added to the mixture to give mole fractions of inhibitor ranging from 0.02 to 0.10. Equivalence ratios of 0.5, 1.0 and 1.5 were examined to determine the effect of stoichiometry, and mixtures reacting at pressures of 0.01 atmosphere and 1.0 atmosphere were compared to ascertain the effect of pressure.

3. RESULTS

3.1 HCl Inhibition

Blowout characteristics for HCl are summarized in Tables II-IV for the range of conditions considered. Results are tabulated in terms of residence time, t, temperature, T, and oxygen consumption at the blowout condition, O_2, and an inhibition parameter, θ_t which is given as

$$\theta_t = \frac{(t - t^{\circ})[O_2]}{t \quad [I]}$$

where t and t^{o} are respectively, the blowout residence time of the inhibited and uninhibited mixtures and [I] is the concentration of inhibitor added. The quantity θ_t was proposed as a parameter to characterize inhibitor effectiveness and is somewhat analogous to the parameter ϕ_v suggested by Fristrom and Sawyer (1971). Implicit in using the θ_t parameter to characterize inhibition is the assumption that molecular oxygen consumption is directly related to the branching process and is therefore related to combustion stability. The ratio $[O_2]/[I]$ does remove some of the composition dependence of the inhibition parameter. The analogy between this parameter and the θ_v of Fristrom and Sawyer is, however, imperfect since the relationship between blowout residence time and flame speeds is complex. Also shown for comparison are our previously determined results for HBr addition.

It is of interest to examine the effect of inhibitor concentration on the blowout characteristics of the reactor. The residence time at blowout increases with HCl concentration in agreement with results found for HBr. The temperature at blowout and the oxygen consumption also increase with HCl concentration due to the higher temperatures and longer residence times

necessary to sustain combustion. The inhibition parameter θ_t for HCl exhibits little variation over the range of conditions investigated, and assumes an average value of 0.26. This behavior is in contrast to the θ_t values associated with HBr which increased with HBr concentration, equivalence ratio and pressure. The values of θ_t for HCl were greater than those for HBr for low pressure lean and stoichiometric mixtures, and the converse was true for rich mixtures and for mixtures at atmospheric pressure.

The dependence of blowout residence time on HCl concentration is shown in Figures 1 and 2 for pressures of 0.01 and 1.0 atmosphere, respectively. At a given HCl concentration, blowout residence times are greatest at $\phi = 1.5$ and least for $\phi = 1.0$ at both pressures. Residence times at 0.01 atmosphere are approximately two orders of magnitude greater than comparable atmosphere pressure values. Lower residence times at atmospheric pressure reflect the increased relative importance of exothermic three body recombination reactions and the resulting increased temperature and faster chemistry.

In order to ascertain the sensitivity of HCl inhibition to the $H + Cl + M \rightarrow HCl + M$ reaction, the rate of this reaction was varied by 1/10 and 10 (over two orders of magnitude). Results of this variation for 0.01 atmosphere pressure stoichiometric mixtures are indicated in Figure 1. A reduction in the rate coefficient increases the residence time at blowout. Increasing the rate coefficient changes the behavior of residence time with HCl concentration markedly. The residence time initially declines, passes through a minimum, and then increases. This behavior is a manifestation of the complex tradeoff between reaction exothermicity and radical scavenging ability. We examined the total combustion heat release rate under these conditions and found that an increase in the HCl recombination rate results

in a substantial increase in the heat release rate which, in turn, raises the mixture temperature. The relatively large increase in temperature with HCl addition accelerates the chemistry. As further HCl is added, the fractional increase in heat release rate due to HCl reactions is relatively small; however, radical removal due to reactions (17f) and (14f) becomes more competitive with radical production via reactions (1) through (13). The net result is that at higher concentrations, HCl behaves more like an inhibitor with residence time at blowout increasing with inhibitor concentration. Similar behavior was noted for HBr addition under conditions of accelerating the H + Br + M → HBr + M rate.

3.2 Radical Concentrations

Our previous study revealed that inhibitor effectiveness is dependent on the radical scavenging ability of the inhibitor. The total number of active radicals in a mixture is reduced by various inhibitor reactions. The total hydrogen/oxygen radical pool concentration, normalized by the maximum possible pool concentration of the mixture, Z where

$$Z = \frac{N_H + N_O + N_{OH} + N_{HO_2}}{2N^i_{H_2} + 2N^i_{O_2} + N^i_{HBr}}$$

was computed for each residence time. The symbol N_j designates the concentration (moles j/grams mixture) of species j in the mixture, and the superscript i designates initial reactant concentrations. The normalization factor partially accounts for dilution by the inhibitor. Figures 3 and 4 are plots of Z as a function of residence time for stoichiometric mixtures of 2 and 10 percent HCl at 0.01 and 1.0 atmosphere, respectively. As residence time increases, Z increases to a maximum value and then decreases to the equilibrium value. Increasing the HCl

concentration from 2 to 10 percent reduces the radical pool function for all residence times. The effect of increasing the reactor pressure is to reduce the maximum radical pool function since three body recombination reactions become important at higher pressure. Similar behavior in Z was noted for HBr addition. The effect of equivalence ratio is illustrated in Figures 4-6 where Z profiles are presented for ϕ = 1.0, 0.5 and 1.5, respectively for mixtures at atmosphere pressure. The radical pool function achieves its maximum values under stoichiometric conditions. The decrease in Z with inhibitor concentration increases with equivalence ratio.

4. DISCUSSION

The inhibitors HCl and HBr show similar trends under the conditions considered in this study. They differ, from one another, in degree which reflects the subtleties of the complex tradeoffs between promotional effects of reaction exothermicity and the inhibitor effects of radical scavenging. Residence time at blowout provides a measure of inhibitor effectiveness, and is plotted as a function of inhibitor concentration for HCl and HBr at 0.01 and 1.0 atmosphere in Figures 7 and 8, respectively. Using increased residence time as a criterion for inhibitor effectiveness, HBr is more effective than HCl at atmospheric pressure and for rich mixtures at lower pressures. The same conclusion is reached when one considers θ_t as a measure of effectiveness. Rich mixtures are inhibited more than lean and stoichiometric mixtures for both inhibitors.

The effect of reactions involving HO_2 (reactions 8 through 13) was determined by performing calculations with and without HO_2 reactions for the case of HBr inhibition. This is discussed in our earlier paper Brown and Schefer (1981). Briefly, the effect of HO_2 reactions was more dramatic

at atmospheric pressure. The HO_2 reactions contribute substantially to the net heat release rates thus accounting for increased temperature and decreased residence times at blowout. At the blowout time, the radical pool function was slightly increased by the HO_2 reactions.

An examination of individual reaction rates shows that inhibition is due to a competition for hydrogen radicals between the primary chain branching reaction (3f) ($H + O_2 \rightarrow OH + O$) and the reaction $HX + H \rightarrow H_2 + X$ where X is a halogen atom. At atmospheric pressure, the reaction: $H + X + M \rightarrow HX + M$ also contributes to radical scavenging. This is illustrated in the last columns of Tables V and VI where the ratio of radical production to radical removal is given for stoichiometric mixtures for varying concentrations of the inhibitors HCl and HBr, respectively. The ratio declines with increasing inhibitor concentrations and declines more rapidly for mixtures at 1.0 atmosphere than for those at 0.01 atmospheres. Radical scavenging at atmospheric pressure is augmented by the reaction $H + X + M \rightarrow HX + M$. Under identical conditions, the ratio is less for mixtures inhibited by HBr since the reaction $H + HBr \rightarrow H_2 + Br$ is more effective at scavenging than the analogous HCl reaction.

Reaction exothermicity of the important inhibition reactions $H + HX \rightarrow H_2 + X$ and $H + X + M \rightarrow HX + M$ tends to cancel, in part, their inhibitory effect. The total heat release rate and the fraction of the heat release rate contributed by the H_2/O_2 reactions are given in Tables V and VI for low and high pressure stoichiometric mixtures inhibited with varying concentrations of HCl and HBr, respectively. The total heat release rate decreases with increasing inhibitor concentration but this is offset by the increase in residence time so that the heat release remains nearly constant for HCl addition and increases slightly for HBr addition. The fraction of

the total heat release rate contributed by the H_2/O_2 reactions declines with increased inhibitor concentration. This is attributable to two factors, the heat release contributed from reactions (1) through (13) decreases and that contributed from the halogen reactions increases. The decline is greater for HBr addition than for HCl. The decline for HCl is also greater at atmospheric pressure than the lower pressure since $H + Cl + M \rightarrow HCl + M$ is more important and it is very exothermic. An examination of the contributions of the individual reactions to heat release under the conditions of Tables V and VI for atmospheric pressure reveals approximately 80% of the total heat release due to reactions involving HBr is contributed by $H + HBr \rightarrow H_2 + Br$ while the remainder is contributed by the recombination reaction. In contrast heat release in the HCl system is dominated by the HCl recombination reaction (17f) with only 6% contributed by reaction (14f).

At lower pressures, under fuel lean and stoichiometric conditions, HBr is a less effective inhibitor than HCl, even though it is more effecive in removing radicals. The HBr reaction (18r) makes a substantial contribution to the heat release rate and this promotes combustion and tends to cancel the effect of radical scavenging. Under fuel rich conditions at low pressures, HBr is more effective than HCl since the HBr radical scavenging ability is enhanced and that of HCl is diminished. The HCl reactions (14f) and (14r) approach a partial equilibrium condition in the rich mixtures. At higher pressures HCl reactions (via HCl recombination) contributes more substantially to heat release than at lower pressures. In fact the contribution of HCl to heat release is comparable to that of HBr. The more effective inhibitor at atmospheric pressure is HBr due to its greater radical scavenging ability.

In related studies of inhibition by HX type compounds, Westbrook

(1980), Fristrom and Van Tiggelen (1979), and Dixon-Lewis and Simpson (1977) found that inhibition is kinetic in nature and linked to the competition for hydrogen radical between chain branching reactions and radical scavenging reactions whereby reactive radicals (e.g. H atom) are replaced by less active radicals (e.g. Br or Cl atoms). The results of our study concur with these findings. We also find that the relative effectiveness of inhibitors can only be assessed by considering both the radical scavenging ability of individual reactions and their contributions to overall heat release.

Westbrook found the effectiveness of HBr as an inhibitor in premixed CH_4/air flames was due primarily to reactions (18) and (19) that HBr recombination played a relatively minor role. Day et al. (1971) and Dixon-Lewis and Simpson found that recombination reactions contribute to controlling the size of the H_2/O_2 radical pool. Dixon-Lewis and Simpson found that, at temperatures comparable to the blowout temperatures of our own study, the reaction $H + HBr \rightarrow H_2 + Br$ was an efficient scavenger and that the analogous HCl reaction was not. They also found that HBr was a more effective inhibitor in rich mixtures than in lean, in agreement with our own results. Fristrom and Van Tiggelen found that inhibitor effectiveness at atmospheric pressure was dominated by the three body recombination $H + X + M \rightarrow HX + M$. It is important to note that they were concerned with systems of higher temperature than those of our study, and at higher temperatures the reactions $H + HX \rightarrow H_2 + X$ tend to become partially equilibrated and loses its radical scavenging ability.

The proposed inhibition parameter, θ_t, varies considerably with pressure and equivalence ratio for HBr and thus cannot be considered as a parameter which fully characterizes inhibitor effectiveness. As discussed

by Brown and Schefer the variation in θ_t is due to the complex trade-off between radical scavenging ability and exothermicity of the important inhibitor reactions. The analogous parameter ϕ_v proposed by Fristrom and Sawyer to describe inhibition in premixed flames is based on the competition between a rate limiting branching reaction, $H + O_2 \rightarrow OH + O$ and a bimolecular inhibition reaction $H + HX \rightarrow H_2 + X$ (where X denotes a halogen atom). Since no account has been taken of the dependence of θ_t on exothermicity of the inhibition reactions it is not surprising that considerable variation in θ_t is observed.

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LIST OF FIGURES

1. Residence time at blowout (sec) as a function of HCl concentration in mole fraction for mixtures at 0.01 atmospheres. Dotted line curves indicate the effect of varying the H+Cl+M recombination reaction rate coefficient for stoichiometric mixtures.

2. Residence time (sec) at blowout as a function of HCl concentration in mole fraction for mixtures at 1.0 atmospheres.

3. Normalized radical pool function Z, as a function of residence time in the reactor for stoichiometric mixtures at 0.01 atmosphere. ____ 2% HCl added to mixture, --- 10% HCl added to mixture.

4. Normalized radical pool function Z, as a function of residence time in the reactor for stoichiometric mixtures at 1.0 atmosphere. ____ 2% HCl added to mixture, --- 10% HCl added to mixture.

5. Normalized radical pool function Z, as a function of residence time in the reactor for lean mixtures (ϕ=0.5) at 1.0 atmosphere. ____ 2% HCl added to mixture, --- 10% HCl added to mixture.

6. Normalized radical pool function Z, as a function of residence time in the reactor for rich mixtures (ϕ=1.5) at 1.0 atmosphere. ____ 2% HCl added to mixture, --- 10% HCl added to mixture.

7. Residence time at blowout (sec) as a function of inhibitor concentration (mole fraction) for mixtures at 0.01 atmosphere. ____ indicates HCl, --- indicates HBr.

8. Residence time at blowout (sec) as a function of inhibitor concentration (mole fraction) for mixtures at 1.0 atmosphere. ____ indicates HCl, --- indicates HBr.

TABLE I

$H_2/O_2/Ar/HBr$ Kinetics

$k = AT^n \exp(-E_a/RT)(cm^3/mole)^{m-1} sec^{-1}$

	Reaction	log A	n	E_a(cal/mole)	H_R(cal/mole)	Ref.
1)	$O + H_2 \rightleftharpoons OH + H$	10.26	1.0	8900	+1970	Baulch et al (1973)
2)	$OH + H_2 \rightleftharpoons H + H_2O$	13.36	0.0	5200	-15300	Wilson (1972)
3)	$H + O_2 \rightleftharpoons OH + O$	14.34	0.0	16790	+16900	Baulch et al (1972)
4)	$OH + OH \rightleftharpoons O + H_2O$	12.80	0.0	1093	-17100	Baulch et al (1972)
5)	$H_2 + M \rightleftharpoons 2H + M$	12.35	0.5	92600	+104000	Meyerson and Watt (1968)
6)	$H + OH + M \rightleftharpoons H_2O + M$	21.92	-2.0	0	-119000	Baulch et al (1972)
7)	$O + O + M \rightleftharpoons O_2 + M$	17.11	-1.0	341	-119000	Johnston (1968)
8)	$H + O_2 + M \rightleftharpoons HO_2 + M$	15.18	0.0	-1000	-47100	Baulch et al (1972)
9)	$HO_2 + H \rightleftharpoons 2OH$	14.40	0.0	1900	-38200	Baulch et al (1972)
10)	$OH + HO_2 \rightleftharpoons H_2O + O_2$	13.70	0.0	1000	-72200	Lloyd (1974)
11)	$O + HO_2 \rightleftharpoons OH + O_2$	13.70	0.0	1000	-55100	Lloyd (1974)
12)	$H + HO_2 \rightleftharpoons H_2O + O$	13.70	0.0	1000	-55300	Lloyd (1974)
13)	$H + HO_2 \rightleftharpoons H_2 + O_2$	13.40	0.0	700	-57000	Lloyd (1974)
14)	$H + HCl \rightleftharpoons H_2 + Cl$	13.36	0.0	3500	-1150	Westenberg and deHaas (1968)
15)	$H + Cl_2 \rightleftharpoons HCl + Cl$	14.20	0.0	1800	-45200	Brown (1975)
16)	$Cl_2 + M \rightleftharpoons Cl + Cl + M$	13.94	0.0	48500	+57800	Jacobs and Giedt (1963)
17)	$H + Cl + M \rightleftharpoons HCl + M$	18.18	-0.7	0	-103000	Dixon-Lewis and Simpson (1977)
18)	$Br + H_2 \rightleftharpoons HBr + H$	14.13	0.0	18400	+16700	Seery and Bowman (1968) Vidal (1971)
19)	$H + Br_2 \rightleftharpoons HBr + Br$	14.53	0.0	903	-34100	Brown (1975)
20)	$Br + Br + M \rightleftharpoons Br_2 + M$	18.86	-1.42	0	-53500	McDonald and Burns (1977)
21)	$HBr + M \rightleftharpoons H + Br + M$	21.78	-2.0	88000	87600	Cohen et al (1973)

*all reverse rate coefficients are determined from forward values and equilibrium constants

m = order of the reaction

TABLE II $H_2/O_2/Ar/HCl$ or HBr

HCl, HBr Inhibition at a 0.5 Equivalence Ratio

Inhibitor Concentration (mole fraction)	P (atm)	t^a (sec)	T^a (K)	$O_2{}^a$ (moles)	$\Theta_t{}^a$	t^b (sec)	T^b (K)	$O_2{}^b$ (moles)	$\Theta_t{}^b$
0.00	10^{-2}	9.84×10^{-3}	839.	.260	--	9.84×10^{-3}	839	.260	--
.02		10.6	840.	.270	.24	10.3	851	.293	.16
.04		11.49	843.	.281	.24				
.06		12.44	847.	.293	.24	11.10	885	.349	.16
.08		13.49	851.	.304	.24				
.10		14.61	857.	.318	.23	11.90	913	.392	.15
0.00	1.0	1.41×10^{-5}	1102.	.288	--	1.41×10^{-5}	1102	.288	--
.02		1.53	1112.	.290	.28	1.58	1140	.323	.43
.04		1.67	1120.	.296	.28	1.79	1172	.356	.45
.06		1.82	1128.	.305	.27	2.01	1208	.389	.46
.08		1.99	1135	.312	.26	2.28	1248	.423	.46
.10		2.19	1140.	.319	.26				

[a] Inhibition by HCl

[b] Inhibition by HBr

TABLE III

HCl, HBr Inhibition at a 1.0 Equivalence Ratio

Inhibitor Concentration (mole fraction)	P (atm)	t^a (sec)	T^a (K)	$O_2{}^a$ (moles)	$\Theta_t{}^a$	t^b (sec)	T^b (K)	$O_2{}^b$ (moles)	$\Theta_t{}^b$
0.00	10^{-2}	8.46×10^{-3}	871.	.23	--	8.46×10^{-3}	871	.231	--
.02		9.10	875.	.24	.27	8.93	888	.251	.22
.04		10.00	879.	.25	.31	9.39	904	.270	.21
.06		10.56	884.	.26	.27	9.88	945	.312	.23
.08		11.39	889.	.27	.26	10.30	954	.322	.22
.10		12.30	895.	.28	.26	10.80	964	.330	.21
0.00	1.0	1.37×10^{-5}	1138.	.24	--	1.37×10^{-5}	1138	.237	--
.02		1.45	1152.	.24	.22	1.51	1173	.261	.40
.04		1.57	1165	.25	.26	1.69	1208	.284	.43
.06		1.66	1178.	.26	.24	1.90	1244	.307	.45
.08		1.79	1188.	.27	.24	2.17	1286	.330	.47
.10		1.93	1198.	.27	.24				

[a] Inhibition by HCl

[b] Inhibition by HBr

TABLE IV

HCl, HBr Inbibition at a 1.5 Equivalence Ratio

Inhibitor Concentration (mole fraction)	P (atm)	t^a (sec)	T^a (K)	$O_2{}^a$ (moles)	$\Theta_t{}^a$	t^b (sec)	T^b (K)	$O_2{}^b$ (moles)	$\Theta_t{}^b$
0.00	10^{-2}	10.1×10^{-3}	888.	.21	--	10.10×10^{-3}	888	.209	--
.02		11.00	890.	.21	.32	11.11	904	.223	.37
.04		12.00	893.	.22	.31	12.34	919	.237	.39
.06		13.14	895.	.22	.30	13.93	935	.248	.40
.08		14.43	896.	.22	.29	16.11	954	.260	.42
.10		15.89	898	.23	.28	19.44	977	.271	.44
0.00	1.0	1.82×10^{-5}	1152	.21	--	1.82×10^{-5}	1152	.209	--
.02		1.96	1165.	.21	.28	2.13	1188	.226	.60
.04		2.11	1176.	.22	.27	2.55	1226	.241	.62
.06		2.30	1187.	.22	.27	3.22	1269	.257	.66
.08		2.52	1195.	.22	.27				
.10		2.78	1200	.23	.26	7.42	1394	.288	.73

[a] Inhibition by HCl

[b] Inhibition by HBr

TABLE V

HEAT RELEASE AND RADICAL PRODUCTION RATES

FOR STOICHIOMETRIC MIXTURE INHIBITED BY HCl

Percent HCl	Pressure (atm)	Q_{TOTAL} (cal/cm^3 sec)	Q_{1-13}/Q_{TOTAL}	RP/RR [a]
0	0.01	-5.72×10^{-5}	1.0	--
2		-5.29×10^{-5}	0.96	9.26
4		-4.76×10^{-5}	0.94	4.92
6		-4.44×10^{-5}	0.89	3.53
8		-4.09×10^{-5}	0.85	2.82
10		-3.72×10^{-5}	0.82	2.39
0	1.0	-4.07	1.0	--
2		-3.72	0.94	5.36
4		-3.42	0.86	3.11
6		-3.24	0.80	2.40
8		-3.05	0.71	2.03
10		-2.88	0.64	1.80

a) RP/RR is the ratio of the rates of radical production to radical removal

TABLE VI

HEAT RELEASE AND RADICAL PRODUCTION RATE

FOR STOICHIOMETRIC MIXTURE INHIBITED BY HBr

Percent HBr	Pressure (atm)	Q_{TOTAL} (cal/cm^3 sec)	Q_{1-13}/Q_{TOTAL}	RP/RR [a]
0	0.01	-5.72×10^{-5}	--	--
2		-5.49×10^{-5}	0.86	5.94
4		-5.26×10^{-5}	0.74	3.06
6		-5.13×10^{-5}	0.65	2.44
8		-4.96×10^{-5}	0.55	2.26
10		-4.74×10^{-5}	0.46	1.72
0	1.0	-4.07	1.0	--
2		-3.73	0.85	4.42
4		-3.40	0.72	2.35
6		-3.06	0.62	1.70
8		-2.70	0.52	1.40
10		-2.65	0.45	1.25

a) RP/RR is the ratio of the rates of radical production to radical removal.

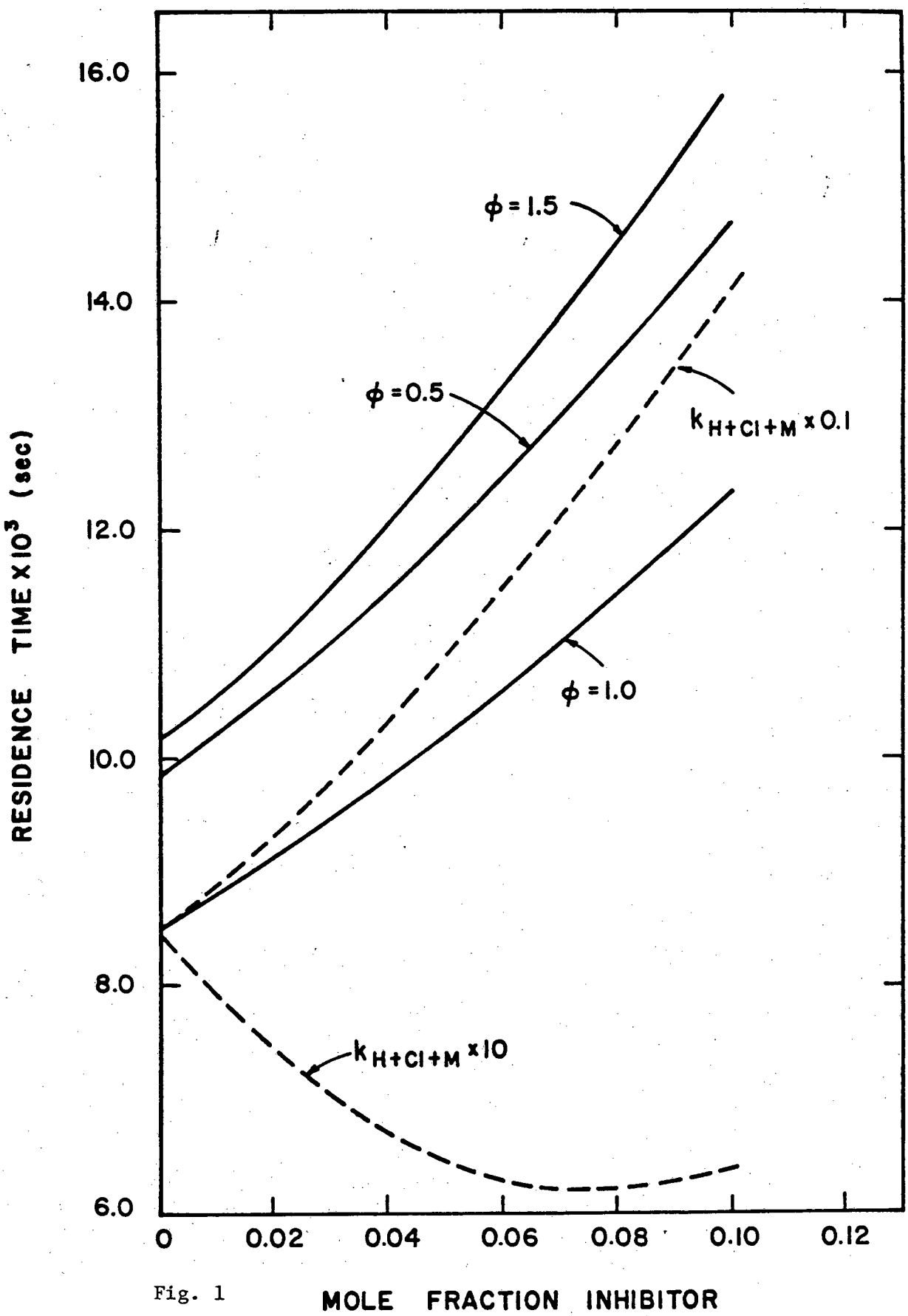
16.0
14.0
12.0
10.0
8.0
6.0
RESIDENCE TIME X 10³ (sec)
φ = 1.5
φ = 0.5
φ = 1.0
k H+Cl+M x 0.1
k H+Cl+M x 10
0
0.02
0.04
0.06
0.08
0.10
0.12
MOLE FRACTION INHIBITOR

Fig. 1

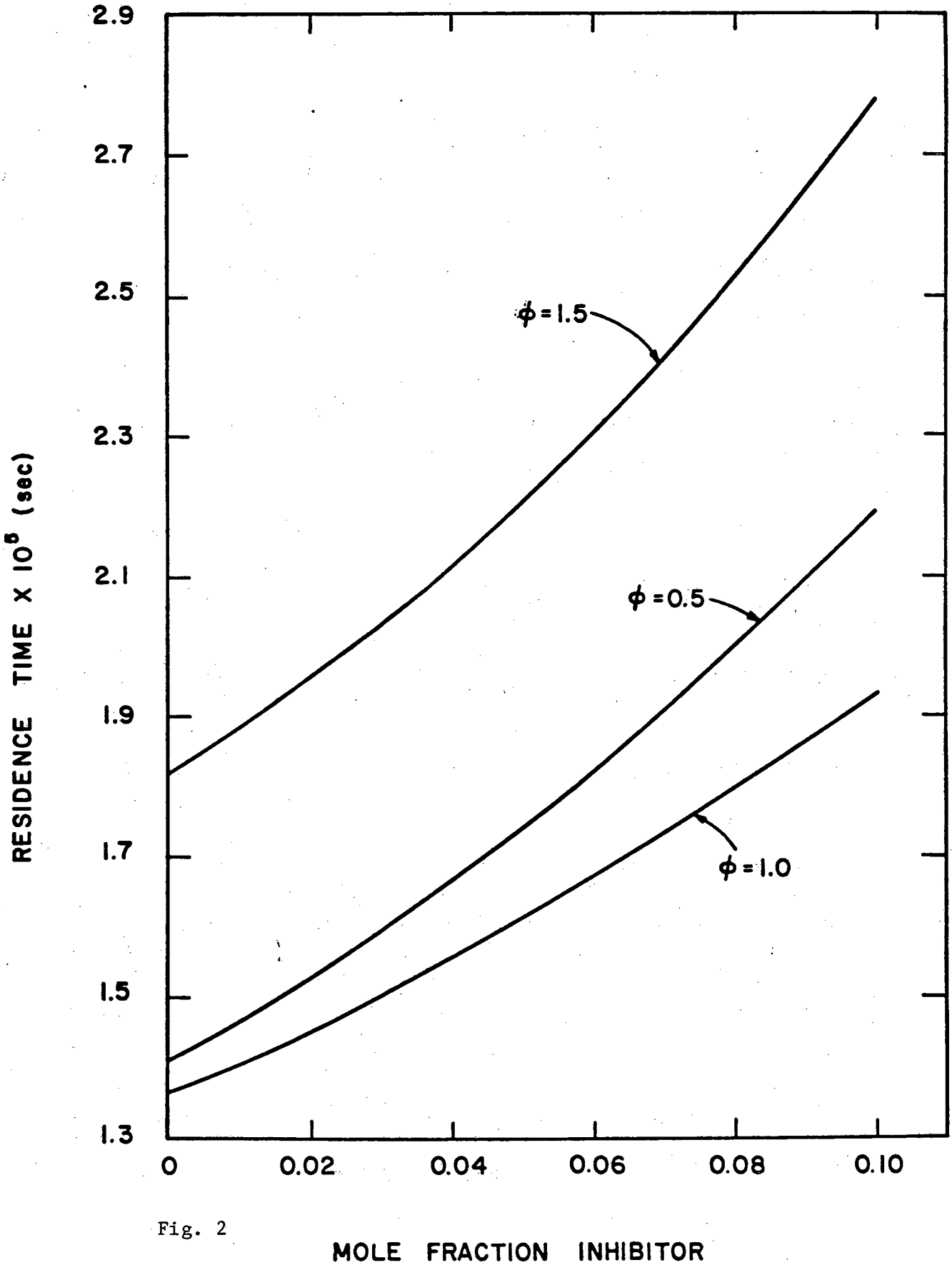
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
RESIDENCE TIME X 10^6 (sec)
ϕ = 1.5
ϕ = 0.5
ϕ = 1.0
0
0.02
0.04
0.06
0.08
0.10
MOLE FRACTION INHIBITOR

Fig. 2

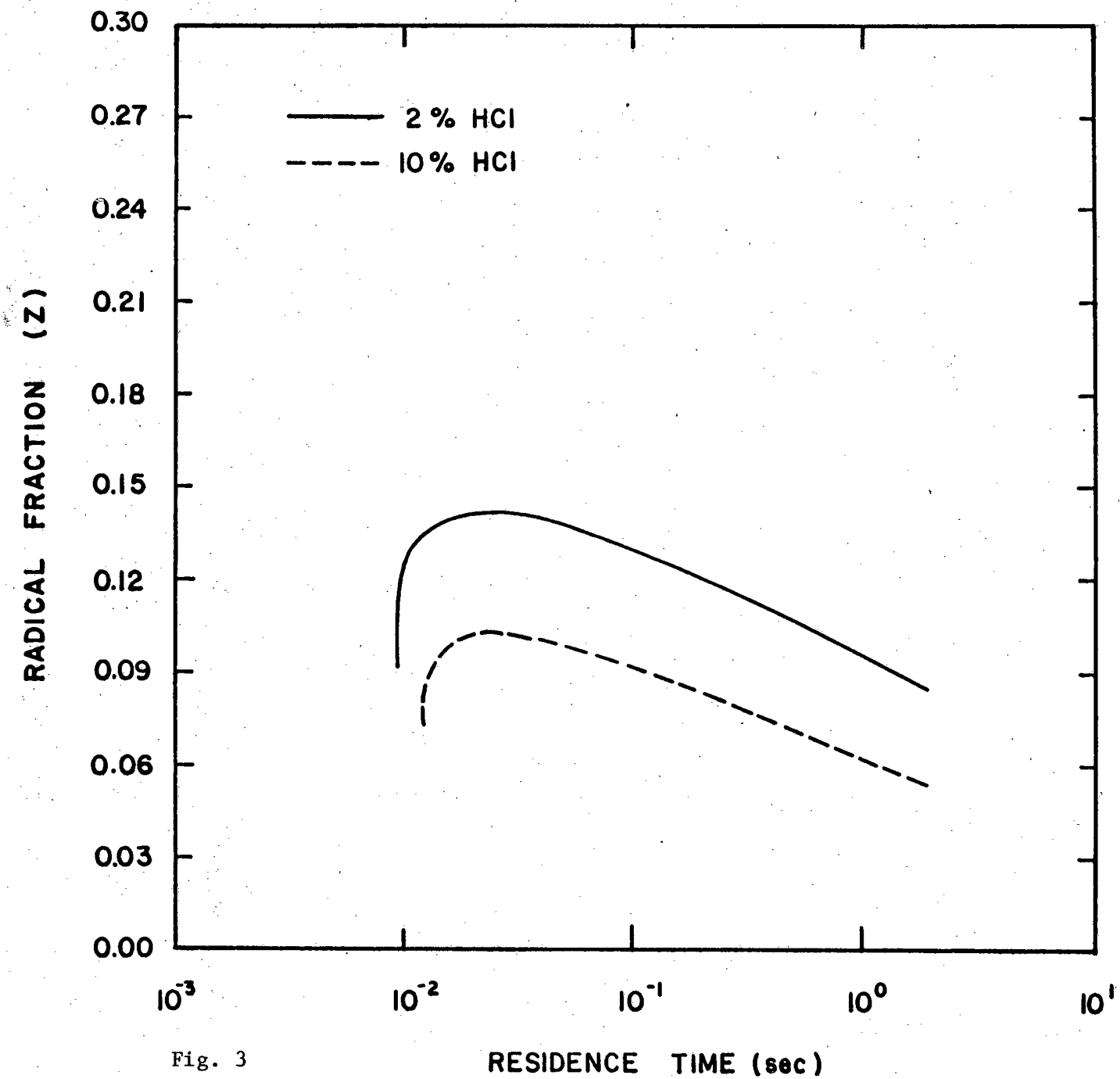
0.30
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0.00
RADICAL FRACTION (Z)
2 % HCl
10 % HCl
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
RESIDENCE TIME (sec)

Fig. 3

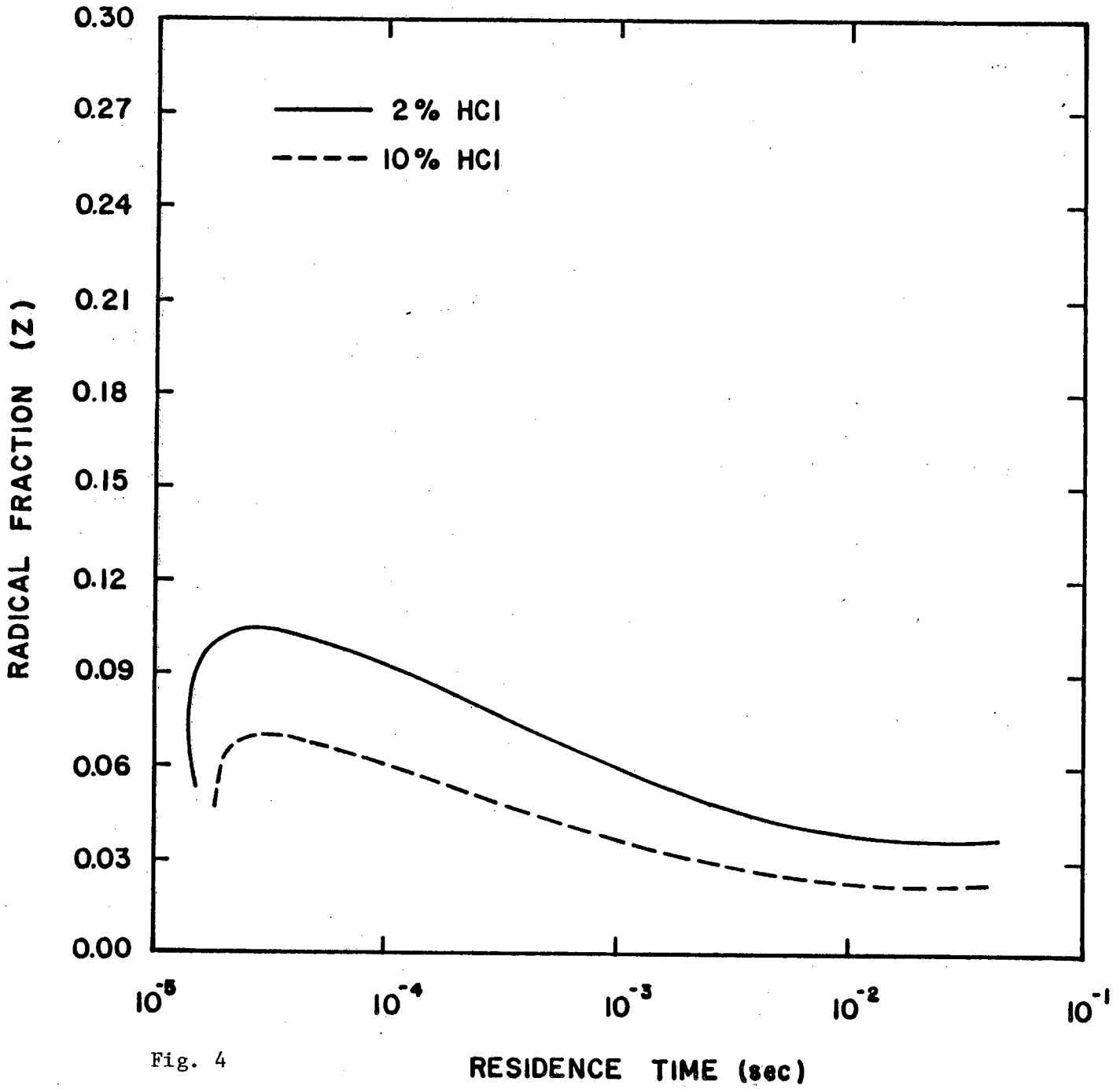
0.30
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0.00
RADICAL FRACTION (Z)
2% HCl
10% HCl
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
RESIDENCE TIME (sec)

Fig. 4

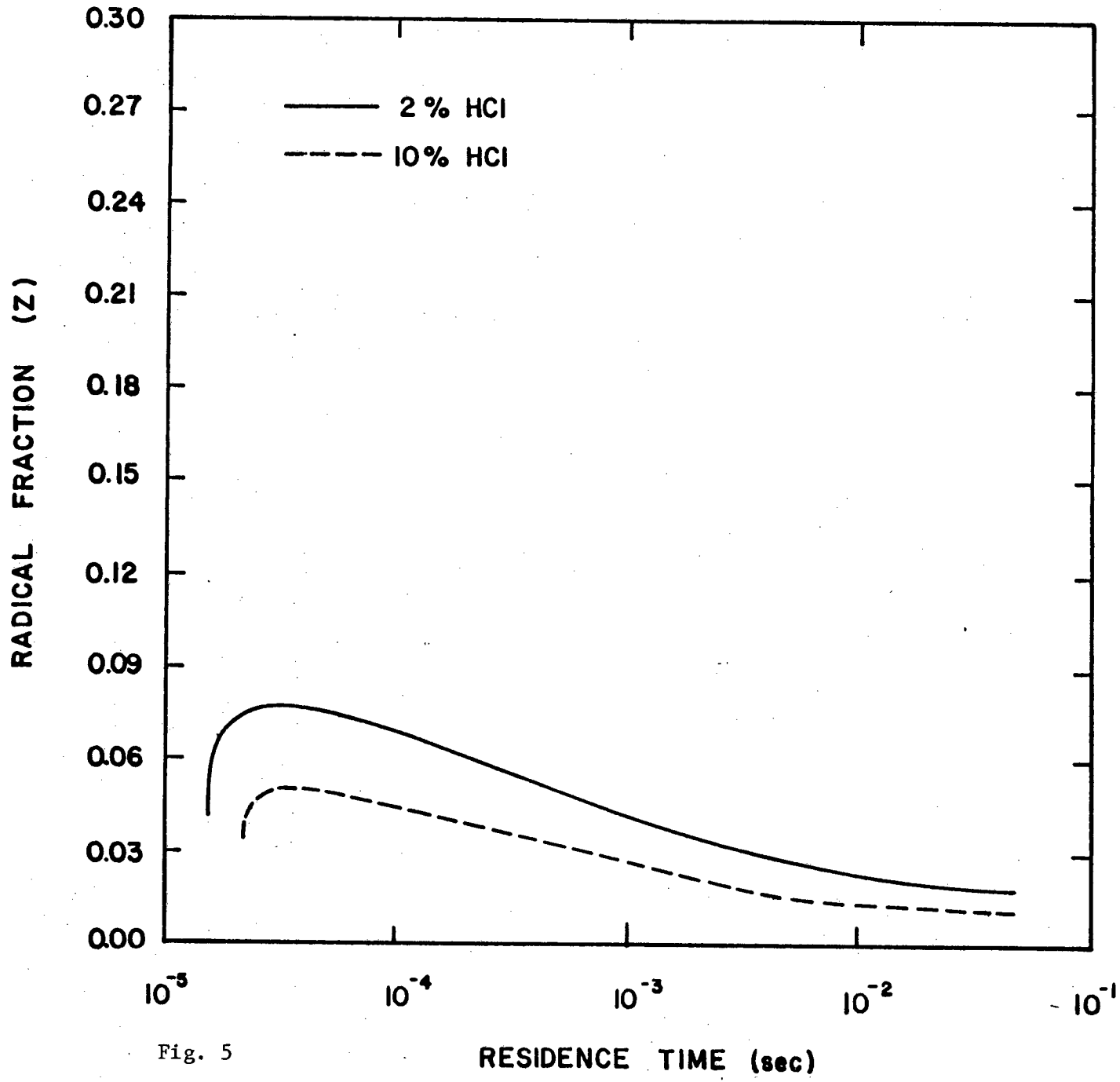
0.30
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0.00
RADICAL FRACTION (Z)
2 % HCl
10% HCl
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
RESIDENCE TIME (sec)

Fig. 5

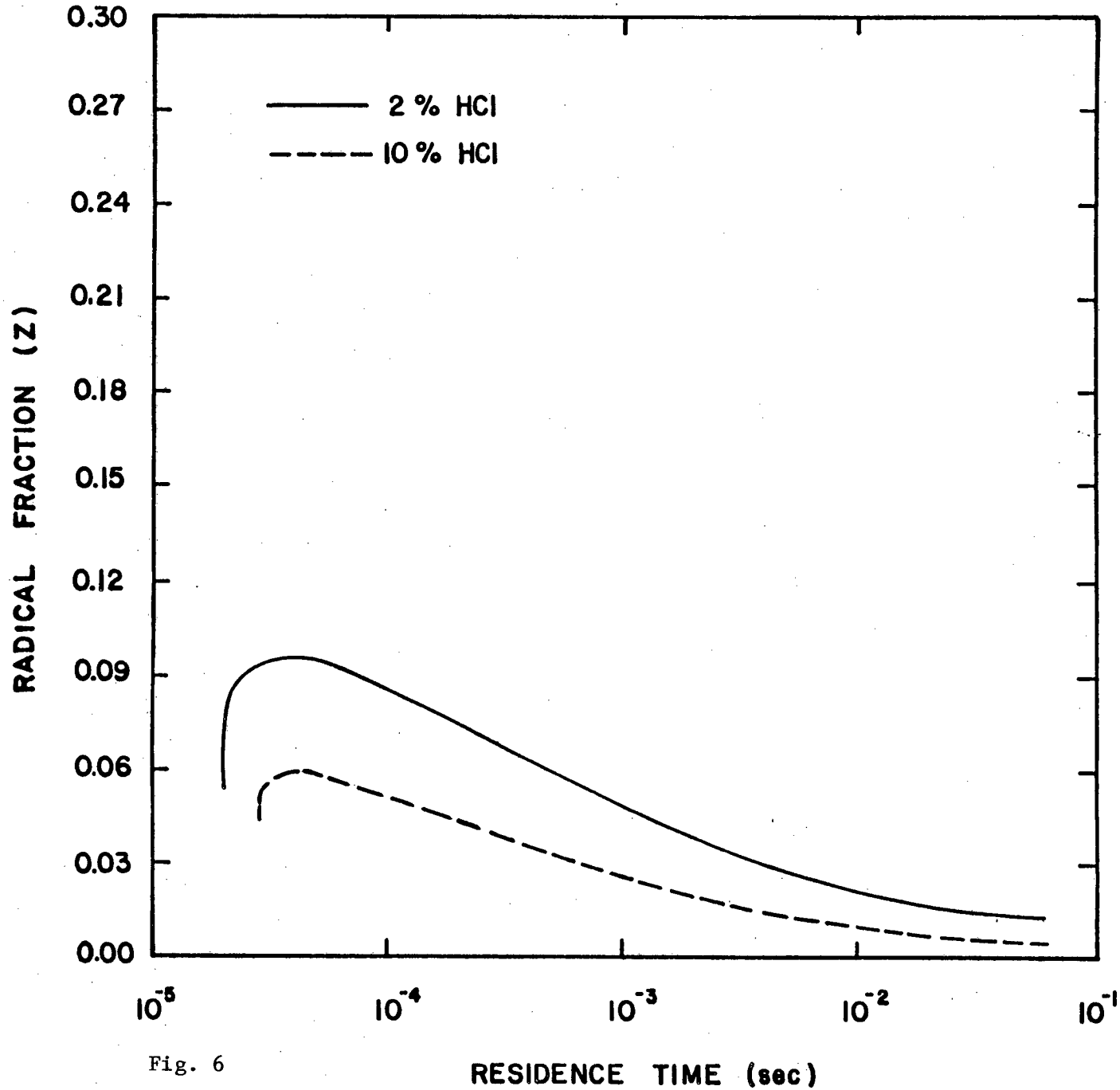
0.30
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0.00
RADICAL FRACTION (Z)
2 % HCl
10 % HCl
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
RESIDENCE TIME (sec)

Fig. 6

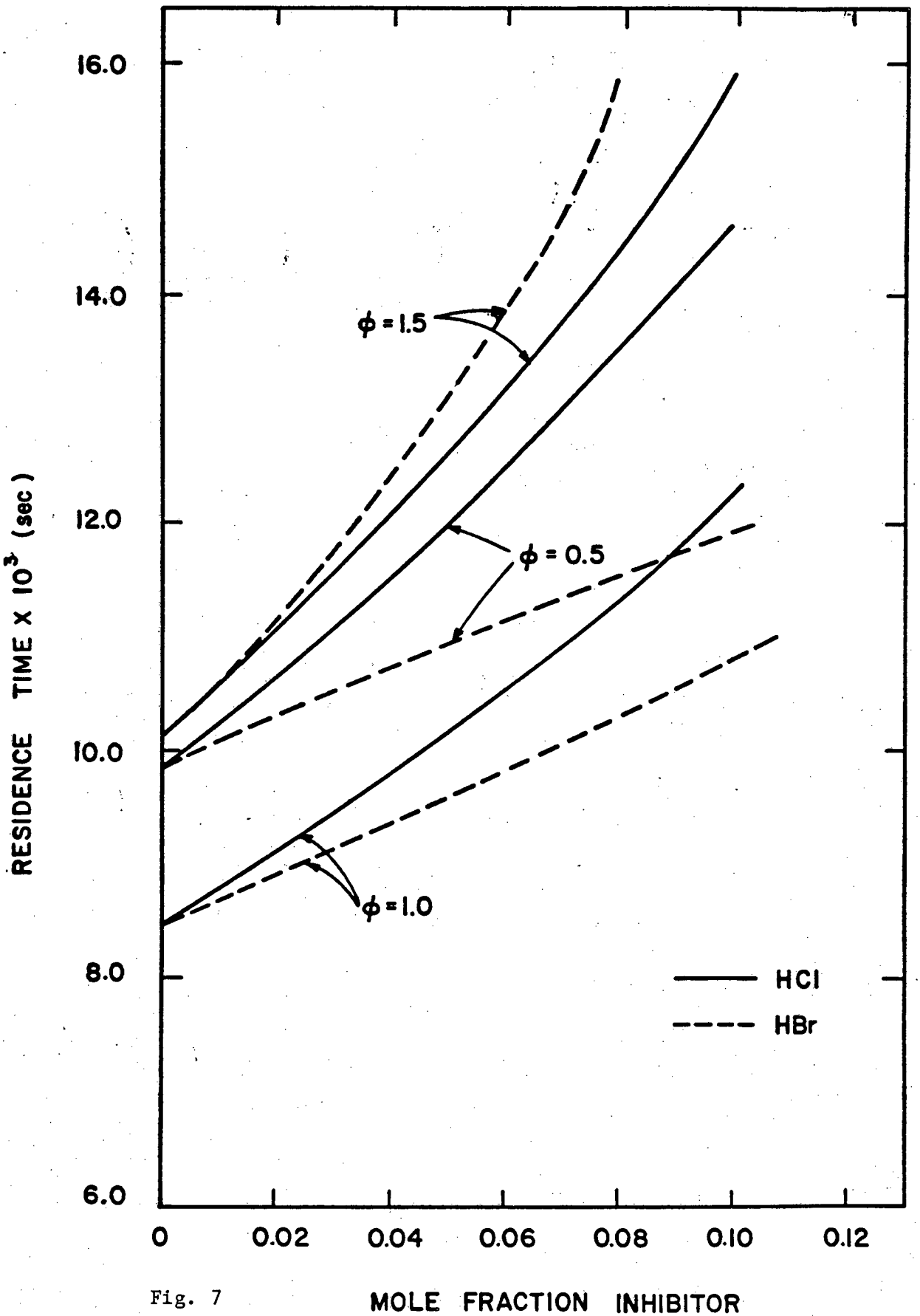
16.0
14.0
12.0
10.0
8.0
6.0
RESIDENCE TIME X 10³ (sec)
φ = 1.5
φ = 0.5
φ = 1.0
HCl
HBr
0
0.02
0.04
0.06
0.08
0.10
0.12
MOLE FRACTION INHIBITOR

Fig. 7

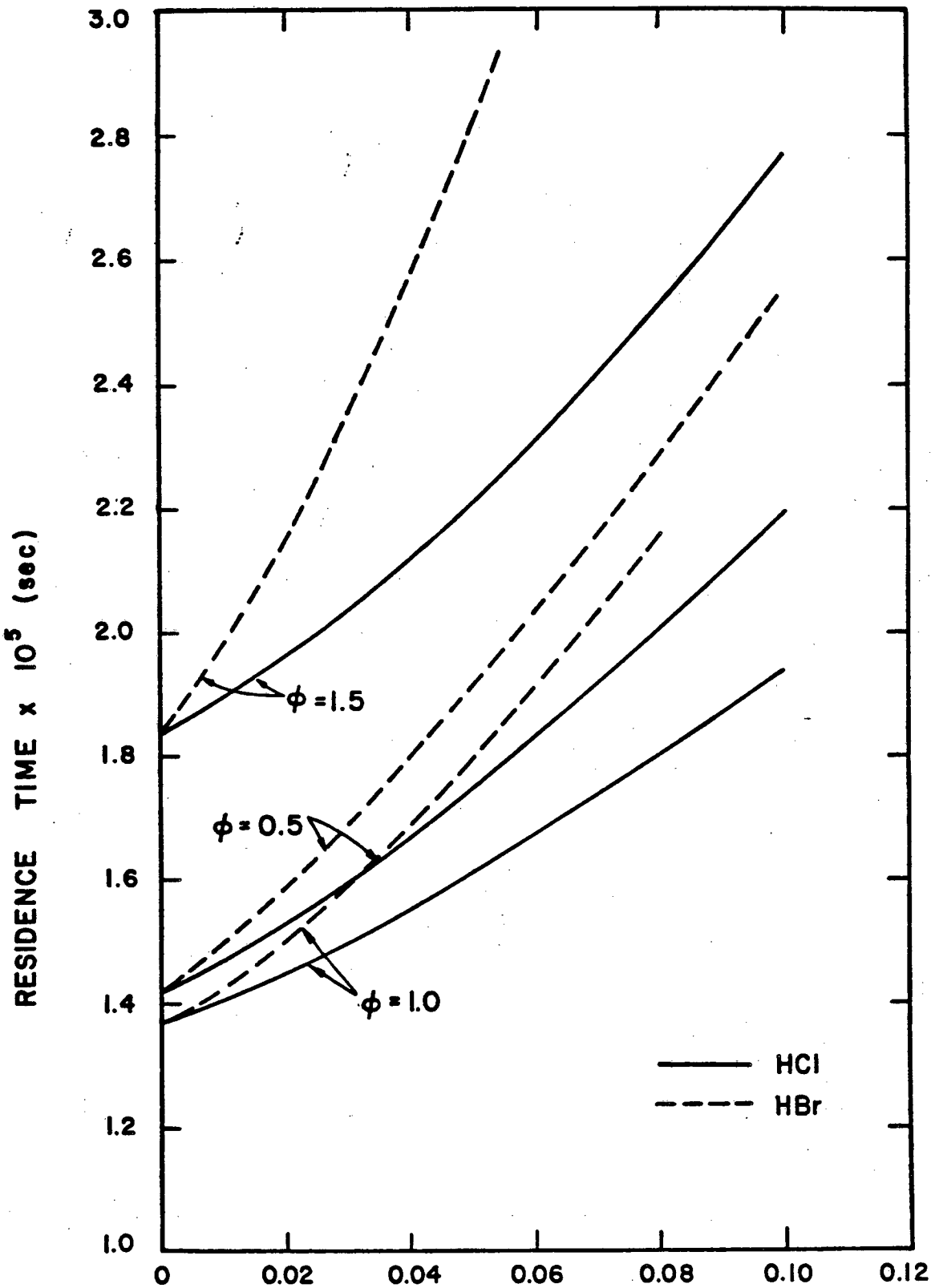
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
RESIDENCE TIME x 10^5 (sec)
0
0.02
0.04
0.06
0.08
0.10
0.12
MOLE FRACTION INHIBITOR
ϕ = 1.5
ϕ = 0.5
ϕ = 1.0
HCl
HBr

Fig. 8

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