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Author

Brown, N.J.

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To be presented at the Western States Section/
The Combustion Institute Paper No. 78-43,
Spring Meeting, Boulder, CO, April 17-18, 1978

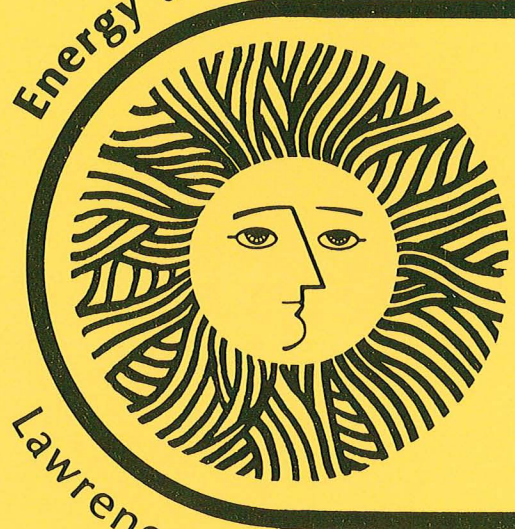
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A Computational Study of Physical
And Chemical Flame Inhibition

Nancy J. Brown and Robert W. Schefer

April 1978

Lawrence Berkeley Laboratory University of California/Berkeley

Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48
and supported by the National Bureau of Standards, Center for
Fire Research under Grant NBS-G7-9006

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A COMPUTATIONAL STUDY OF PHYSICAL
AND CHEMICAL FLAME INHIBITION

Nancy J. Brown
Robert W. Schefer

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

This paper reports a set of modelling studies that were undertaken to acquire a more detailed knowledge of combustion inhibition mechanisms. $H_2/O_2/Ar$ mixtures reacting in the idealized perfectly stirred reactor were investigated. Three H_2/O_2 kinetic mechanisms were considered, differing from one another by the number of HO_2 reactions included. Two physical inhibitors, Ar and N_2 and one chemical inhibitor, HBr, were investigated. Additional parameters considered were pressure, equivalence ratio, inhibitor concentration and rate coefficient variation. HBr was the most effective inhibitor and acted chemically in that it caused substantial reduction in radical concentrations in the mixtures considered. Ar and N_2 acted as physical diluents with N_2 the more effective of the two due to its larger heat capacity.

Research supported by the National Bureau of Standards, Center for Fire Research under Grant No. NBS-G7-9006. And supported by the U. S. Department of Energy.

1. INTRODUCTION

Flame inhibitors are broadly classified as being either of the physical or chemical type. The former type is believed to act simply as a physical diluent while the latter is thought to participate directly in the reaction mechanism important to flame propagation. Although no general consensus exists regarding the mechanism(s) of chemical inhibition (1), it is recognized that certain molecules have been observed to retard flame propagation out of proportion to their thermal influence. This leads to the supposition that this type of inhibition is directly linked to chemical reactivity. It must be recognized, however, that the classification of physical versus chemical is largely a matter of degree. Certainly any species added to a combustion mixture which acts as a thermal diluent and is "non-reactive" effects the chemistry indirectly by altering the temperature field. Likewise, some chemical inhibitors act as a diluent in that they also effect the temperature field.

There is a large body of literature associated with flame inhibition studies which are summarized in some excellent reviews. Friedman and Levy (2) presented an early survey of proposed extinguishment mechanisms. Recent reviews have been conducted by Creitz (3) and Hastie (4). The most recent collection of papers germane to the subject can be found in (1). A survey of the literature reveals that a wide variety of conditions have been employed in inhibition studies, and that it is not possible to formulate a generalized mechanism which can explain the various results.

This paper reports a set of modelling studies that were undertaken to acquire a more detailed knowledge of combustion inhibition mechanisms. $H_2/O_2/Ar$ mixtures, reacting in the idealized perfectly stirred reactor were investigated. Three H_2/O_2 kinetic mechanisms were considered,

differing from one another by the number of HO_2 reactions included. Two physical inhibitors, Ar and N_2 , and one chemical inhibitor, HBr, were studied. Inhibition by HCl was also investigated; however, the results are anomalous and require additional analysis, and will not be discussed here. Additional parameters considered were pressure, equivalence ratio, inhibitor concentration and rate coefficient variation.

Part two of the paper describes the formulation of the perfectly stirred reactor equations and discusses the chemical mechanisms and appropriate rate data used. Results are presented in part three of the paper. The blowout residence time which is the minimum residence time permissible for stable combustion in the reactor, was found to be especially sensitive to the set of parameters considered here. In addition, hydrogen/oxygen radical pool concentrations and temperature as a function of residence time in the reactor were examined. Heat release rates and reaction rates were also determined at the various residence times to obtain additional mechanistic information. A comparison of the various inhibitors is given in part four and the mechanistic details of inhibition of $\text{H}_2/\text{O}_2/\text{Ar}$ combustion in a perfectly stirred reactor are discussed.

2. THE MODEL

Combustion phenomena are often complicated by the strong coupling between chemistry and fluid mechanics. Moreover, the coupling creates inherent difficulties in analyzing and understanding the phenomena. Considerable simplification can result by working in combustion regimes that are strongly dominated either by chemistry or fluid mechanics. Since this work is directed toward improving the understanding of the chemical mechanism of inhibition, the configuration of the perfectly stirred reactor which is chemically dominated since mixing is assumed complete and instantaneous, is an especially attractive one and hence has been selected for study.

A brief description of the perfectly stirred reactor and the governing equations describing a combustion process in this system are given in this section. The section is concluded with a presentation and discussion of three H_2/O_2 mechanisms and the HBr mechanism used in this investigation.

2.2 The Perfectly Stirred Reactor

The idealized well stirred reactor is a constant volume steady flow reactor in which mixing is assumed to occur instantaneously between the cold incoming gas and the reacting mixture in the reactor. Thus, the composition within the reactor is homogeneous and the process is kinetically controlled. The governing equations, using the notation of Jones and Prothero(5) are given below.

The equation describing conservation of energy is

$$\sum_{i=1}^I \sigma_i^* h_i - \sum_{i=1}^I \sigma_i h_i = \frac{\dot{Q}}{\dot{m}} \quad (1)$$

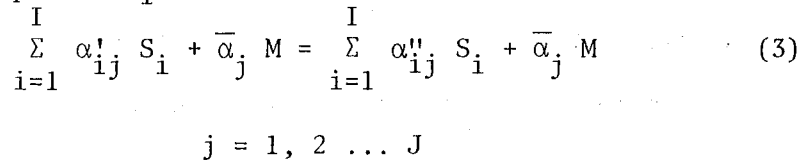
where σ_i^* and σ_i are the concentrations of the i th species (mole/gm) at the reactor inlet and exit, respectively. The species enthalpy is designated by h_i ; \dot{Q} is the rate of heat loss from the system which is zero for this study, and \dot{m} is the total mass flow rate through the reactor.

The chemistry enters into the reactor description through species conservation equations of which there are I in number.

$$\frac{\dot{m}}{V} (\sigma_i^* - \sigma_i) = \sum_{j=1}^J (\alpha'_{ij} - \alpha''_{ij}) (R_j - R_{-j}) \quad (2)$$

$$i = 1, 2 \dots I$$

where α'_{ij} and α''_{ij} are, respectively, the stoichiometric coefficients for the i th species in the j th forward and reverse reactions as defined by the general reaction for the species S_i .



Here $\bar{\alpha}_j$ denotes the stoichiometric coefficient of the third body M and J is the total number of reactions considered in the system. R_j and R_{-j} , the forward and reverse reaction rates of the j th reaction, are expressed as:

$$R_j = k_j (\rho \sigma_M)^{\bar{\alpha}_j} \prod_{i=1}^I (\rho \sigma_i)^{\alpha'_{ij}} \quad (4a)$$

$$j = 1, 2 \dots J$$

$$R_{-j} = k_j (\rho \sigma_M)^{\bar{\alpha}_j} \prod_{i=1}^I (\rho \sigma_i)^{\alpha''_{ij}} \quad (4b)$$

$$j = 1, 2 \dots J$$

where σ_m is the total concentration $\left(\frac{\text{total moles}}{\text{gm}}\right)$ in the reactor and k_j is the Arrhenius rate coefficient of the form

$$k_j = 10^{B_j} T^{N_j} \exp(-E_j/RT) . \quad (5)$$

Here, the reverse rate coefficient was obtained from the forward value and the equilibrium constant.

The equations were solved using a modification of the Pratt-Bowman program (6) which is based on an accelerated Newton/Raphson algorithm. The equations were solved for a series of residence times, and the corresponding compositions and temperatures between the blowout condition and thermodynamic equilibrium. All initial temperatures were 300 K.

2.3 The Chemical Mechanism

The hydrogen/oxygen flame system was selected for study since the kinetics of this system are the best established of any combustion system and are an important subset of the various kinetic schemes governing the combustion of hydrocarbons.

An update review (since Baulch, et al. (7)) was undertaken to determine a mechanism and appropriate rate data for the hydrogen/oxygen system. The results are shown in Table I which contains three hydrogen/oxygen mechanisms. Mechanism I consists of reactions (1) through (7), mechanism II contains reactions (1) through (9), and III is the full set of hydrogen/oxygen reactions. Much of the kinetic data associated with individual HO_2 reactions is estimated and is taken from the review article of Lloyd(12). The reactant HO_2 is difficult to generate without other radicals being present so that single elementary reactions of HO_2 cannot be isolated for study. It therefore appeared prudent to

segregate the hard kinetic data (Mechanism I) from those containing estimates (Mechanisms II and III). Since third body efficiencies appear better determined for argon as third body than other molecules; the rate coefficient with the argon efficiency was used throughout. This is likely to result in values that err on the low side. The HBr kinetic mechanism and rate data are also given in Table I. The halogen kinetics have been discussed in detail in a review article by Brown (14).

3. RESULTS

A perfectly stirred reactor can be viewed as a reactor in which stable combustion can occur when volumetric mass flow rates vary between the minimum value associated with full thermodynamic equilibrium in the reactor and that associated with the maximum throughput of the blowout condition. If the throughput exceeds that at blowout, chemical heat release rates are not great enough to sustain stable combustion. It is our contention that the blowout parameters are especially sensitive to inhibitor type and concentration.

The results of the various calculations will be presented in this section. For most of the mixtures considered, a standard mix of 50 percent combustibles and 50 percent argon was considered, with the inhibitor added to the mixture to give mole fractions of inhibitors ranging between 0.02 and 0.10. Since inhibition effectiveness appears to be pressure dependent, calculations were performed at pressures of 0.01 and 1.0 atmospheres using both mechanisms I and III of the $H_2/O_2/Ar$ scheme. The cases of Ar and N_2 inhibition were investigated using stoichiometric mixtures and the case of HBr inhibition was examined for mixtures of equivalence ratios, $\phi = 0.5, 1.0, \text{ and } 1.5$. Results are tabulated in terms of the temperature T , at the blowout condition, residence time, t° at blowout, oxygen consumption at the blowout residence time and a type of inhibition parameter θ_t which is defined as:

$$\theta_t = \left(\frac{t - t^\circ}{t} \right) \frac{(O_2)}{(I)} \quad (5)$$

where t° and t are respectively the blowout residence times of the uninhibited and inhibited mixtures. The residence time ratio is multiplied by the amount of molecular oxygen consumed at the blowout

residence time and divided by the concentration of inhibitor added. Implicit in using this 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. θ_t is somewhat analogous to the parameter ϕ_v suggested by Fristrom and Sawyer (17) to describe inhibition in premixed flames. The analogy is, however, imperfect since the relationship between blowout residence times and flame speeds is complex.

An additional way to characterize inhibition is to examine the effects of the inhibitor type and concentration on radical profiles. The total hydrogen/oxygen radical pool concentrations were plotted as a function of residence times in the reactor. To facilitate comparison and to partially account for dilution by the various inhibitors, the pool concentrations were normalized by the maximum possible pool function for a given mixture, that is the quantity

$$Z = \frac{(H) + (O) + (OH) + (HO_2)}{2n_{H_2} + 2n_{O_2} + n_{HBr}} \quad (6)$$

was computed at each residence time where n_i are the initial number of moles/g of the species i in the mixture, and the quantities in the parentheses are the number of moles per gram of the species indicated at a given residence time.

3.2 Comparison of the Various H_2/O_2 Mechanisms

It is important to understand the effects of the HO_2 reactions on the blowout characteristics of the $H_2/O_2/Ar$ mixture before discussing

inhibition effects. Figures 1 and 2 are, respectively, plots of blowout residence time versus equivalence ratio for mixtures reacting at 10^{-2} and 1.0 atmospheres pressure. The curves are parabolic in shape and thus typical. The residence times at the lower pressure are approximately 500 times less than at atmospheric pressure. Correspondingly, the temperatures at blowout are approximately 250 to 275 K less at the lower pressure. This behavior can be attributed to the relative increased importance of the three body reactions at the higher pressure. These reactions contribute substantially to the overall chemical heat release and thus account for the increased temperatures and decreased times of the one atmosphere cases.

Examination of the two figures reveals that the blowout characteristics are nearly identical for Mechanisms II and III. This is so since reactions (8) and (9) which are the only HO_2 reactions of Mechanism II are the dominant HO_2 reactions of Mechanism III. Since the differences were slight, it was decided to eliminate Mechanism II from any further consideration.

The low pressure mixture does not show as much variation with respect to mechanism as the mixtures reacting at one atmosphere since HO_2 formation rates are substantially reduced at the lower pressure and thus not nearly as competitive with the $\text{H} + \text{O}_2$ branching step. The differences with respect to mechanism decrease with increased equivalence ratio since HO_2 formation rates relative to $\text{H} + \text{O}_2$ branching rates are greatest for the lean flame and decrease with increased equivalence ratio. The higher temperatures and lower residence times associated with Mechanism III calculations relative to Mechanism I calculations are due to the contribution of the HO_2 formation reaction to the overall heat release in competition with the endothermic $\text{H} + \text{O}_2$ branching reaction.

The subsequent reaction of HO_2 via reaction (8) to generate OH which then reacts exothermically via (2) tends to further increase the heat release rates which in turn results in the increased temperature and decreased residence times at blowout.

3.3 Blowout Characteristics

The blowout characteristics of the argon inhibited stoichiometric mixtures are summarized in Table II. The residence time increases with increasing inhibitor concentration and the temperature decreases by approximately one degree per 0.02 mole fraction increase of argon. The molecular oxygen consumption exhibits a slight increase with inhibitor concentration and more oxygen is consumed for the atmospheric pressure mixtures. The inhibition parameter varies slightly over the range of variables considered and tends to increase with: 1) decreased inhibitor concentration, 2) mechanism I, and 3) increased pressure.

The characteristics of a mixture inhibited with molecular nitrogen behaves similarly to one inhibited with argon except that the effects are more exaggerated. These are summarized in Table III. Note for identical conditions θ_t is greater for N_2 than Ar.

Inhibition by HBr was investigated in mixtures of 0.5, 1.0 and 1.5 equivalence ratio and the behavior at the blowout condition is summarized in Tables IV, V, and VI, respectively. The residence time and molecular oxygen concentration increased with inhibitor concentration, behaving in a similar fashion to that noted for argon and nitrogen. The temperature, however, also increased with inhibitor concentration and this behavior is contrary to that noted for argon and nitrogen. Small variations were noted for θ_t at pressures of 10^{-2} atmosphere with

regard to changes in H_2/O_2 mechanism. At pressures of one atmosphere, θ_t increased with inhibitor concentration and was larger for Mechanism III than Mechanism I. This behavior is opposite to that noted for argon and nitrogen. For argon and nitrogen, very small changes in θ_t were observed for the variables considered, while for HBr much larger variations were noted.

The effect of mechanism on θ_t is most dramatic for the lean flame and decreases as the equivalence ratio is increased. Temperatures at blowout increased with equivalence ratio. With one exception (i.e. comparing Mechanism III, pressure of one atmosphere, $\phi = .5$ and 1.0) θ_t tends to increase with equivalence ratio.

3.4 The Radical Profiles

Rather than examine individual radical profiles, the quantity Z defined in Equation (6) was selected to ascertain the effects of the various parameters on radical concentration. Radicals are rapidly shuffled back and forth by a series of bimolecular reactions so that it appeared more reasonable to examine total radical concentrations than individual ones. This approach is also advantageous in that it simplifies the analysis. Z is the ratio of the actual hydrogen/oxygen pool radicals to the maximum number of radicals realizable if all the molecular hydrogen, molecular oxygen and hydrogen bromide dissociates to form radical species. Z was calculated for a series of residence times in the reactor which corresponded to stable combustion. The dependence of this function on inhibitor type and concentration, pressure, equivalence ratio, and mechanism is discussed in subsequent paragraphs.

The various Z profiles shown in Figures 3 through 7 have the same general shape. The value of Z at the blowout residence time increases and assumes a maximum value at times near but greater than blowout, then declines slowly (especially at 10^{-2} atmospheres) to the final thermodynamic equilibrium value.

A slight decrease in Z with argon and nitrogen addition occurred; however, a substantial decrease in Z was noted for hydrogen bromide addition. Figures 3 and 4 are plots of Z as a function of residence time in the reactor for 2 and 10 percent argon, and hydrogen bromide, respectively. The other variables are the same for both figures, so that comparison of them illustrates the effect of inhibitor type. It is reasonable to question the effect of the term n_{HBr} in the denominator of Equation (6). The effect of eliminating the term increases the 10 percent curve by 1.1 relative to the 2 percent curve; however, the difference between the two curves, though somewhat reduced, remains substantially greater than that observed for the physical inhibitors.

Figure 5 is analogous to Figure 4 except that the pressure associated with the profiles of Figure 5 is 1.0 atmosphere instead of 10^{-2} . A comparison of the two figures illustrates the dependence of Z on pressure and shows that Z was greater for the lower pressure cases. At the higher pressure, the three body reactions become competitive with the two body reactions and contribute to the heat release and affect reductions in radical concentrations. The decrease in Z with increased hydrogen bromide concentration is greater at the higher pressure.

Figure 6 is a plot analogous to Figure 5 except that the equivalence ratio is 1.5 rather than 1.0. Comparison of Figures 5 and 6 illustrates the effect of equivalence ratio on the Z profiles. Radical fractions are

largest for the stoichiometric flame; however, the decrease in Z with HBr addition increases with equivalence ratio.

The variation of θ_t with respect to mechanism was largest for the hydrogen bromide inhibited lean mixture. The effect of mechanism on Z is illustrated in Figure 7. The intersection of the curves at relatively short times was characteristic of the several cases considered. At the blowout condition associated with each of the four curves, Z was greater for mechanism I than III, while for short times between blowout which correspond to stable combustion for both mechanisms until the corresponding mechanism I and III curves intersect, Z is greater for II than I. At longer residence times, Z is greater for mechanism I. The decrease in Z with increased hydrogen bromide was greater for mechanism I than III.

4. DISCUSSION

Argon and nitrogen behaved similarly with regard to their inhibition characteristics. The addition of these inhibitors slightly lowered the temperature of the blowout condition; increased the residence times and slightly increased the oxygen consumption. Slight decreases in radical pool concentrations were also observed with increased inhibitor. These inhibitors act as thermal sinks since they use some of the chemical heat release to raise their temperature and, in so doing, effectively lower the temperature of the overall mixture. This, in turn, results in lowered reaction rates and consequent reduced heat release rates, and thus requires longer residence times (or conversely, reduced mass flow rates) in the reactor.

Whether the near constancy of θ_t reflects that it is a meaningful parameter to characterize physical inhibitors or whether the near constancy reflects the minor inhibitory effects of argon and nitrogen remains unresolved. If one does assume that the parameter is somewhat meaningful, it indicates that N_2 which has the greater heat capacity is a slightly better inhibitor than argon.

Larsen (18) has maintained that the primary role of halons in flame suppression is as heat sinks, and that they have a common mechanism with inert gases. Furthermore, he suggests that one should consider inhibitors on the basis of their weight percent in the total mixture. To check Larsen's ideas, a series of calculations nearly identical to the third group in Table V were performed. The rate coefficients of reactions (14) through (17) were set equal to zero for these calculations, and the results were nearly identical to the analogous case for nitrogen inhibition, and not to those given in Table V. Hydrogen

bromide only acts as an inert for the unrealistic case of zero reactivity. Furthermore, for this case, it behaves identically to nitrogen and on a molar, not weight, basis.

Hydrogen bromide is a different kind of inhibitor than argon and nitrogen. Clear evidence that it acts chemically is provided by the substantial decrease in the radical pool with increased hydrogen bromide concentration. The temperature increase at the blowout condition is another indication that hydrogen bromide acts chemically.

If one used residence time increases as the criteria for ranking inhibitors, hydrogen bromide would not be the most effective inhibitor for the entire range of variables considered. Figures 8 and 9 are plots of residence time versus inhibitor concentration for the three inhibitors at 10^{-2} and 1.0 atmospheres pressure, respectively. Based solely on residence time, nitrogen would be the best inhibitor at low pressure for mechanism I, while hydrogen bromide would be superior at higher pressure. Note for mechanism III, using the residence time criterion, hydrogen bromide is superior for the entire pressure range considered.

If one uses the parameter θ_t as a basis for comparing the three inhibitors, hydrogen bromide is the most effective inhibitor for the variables considered. If one compares the various hydrogen bromide cases, inhibition is most effective for mechanism III, for higher pressures than lower, and increases with equivalence ratio. Rosser et al. (19) found bromine inhibitors to be more effective in rich methane/air than in lean mixtures which concurs with the observed dependence of θ_t on equivalence ratio noted here. The large variation of θ_t with inhibitor concentration, however, leaves something to be desired. Nevertheless, it is reasonable to say that θ_t is sensitive to inhibitory effects, but the order of the sensitivity is unclear.

The variation of θ_t at atmospheric pressure is a reflection of the complex trade-off between the increased temperatures at blowout and decreased radical pools that result from hydrogen bromide addition. The increased temperatures at blowout affect individual reactions differently and can result in increased heat release rates and correspondingly shorter residence times.

Examination of reaction and heat release rates revealed that reactions (14r) and (17r), where r designates reverse, are responsible for the inhibitory action of hydrogen bromide. Reactions (15) and (16) are relatively unimportant in inhibition. Reactions (14r) and (17r) are both exothermic with the latter five times more so than the former. Both reactions scavenge hydrogen radical and thus interfere with radical generation. In low pressure mixtures (14r) is approximately twenty times faster than (17r), while at one atmosphere it is approximately six times faster, so that both reactions have nearly identical heat release rates.

The increase in blowout temperature which is, in part, associated with the contribution these reactions make to the overall heat release, would tend to increase the branching reactions requisite for stable combustion. This is in competition with the radical scavenging ability of these reactions which tends to reduce radical concentrations and hence reaction and heat release rates. In examining individual reaction rates at 10^{-2} and 1.0 atmospheres, the net rates of reactions (1) through (3) decreased with increasing hydrogen bromide, even though the temperature increased.

Rate coefficient variation provided additional information regarding the sensitivity of hydrogen bromide inhibition to reactions (14r) and (17r). Some of these results are summarized in Table VII. Case A is

the one which appears in Table V and thus has no rate coefficient variation. Case B is one where the forward and reverse rate coefficient of reaction (17) was set equal to zero, and in case C, the rate coefficients of reaction (17) were multiplied by one hundred. Neglect of reaction (17) results in lower temperatures at blowout for a given amount of hydrogen bromide than the corresponding case A results. θ_t is greater for case B than A, and nearly constant for B. Incrementing reaction (17), as illustrated by case C, results in a much larger temperature at blowout than is seen for the analogous case A results. A large decrease in residence time is noted for the addition of two mole percent hydrogen bromide; however, increases in residence time relative to the two percent case occur for subsequent additions of hydrogen bromide. The only concentration of hydrogen bromide that gives a positive θ_t is 10 mole percent. Cases B and C illustrate that reaction (14r) is the primary one responsible for hydrogen bromide inhibition since it has relatively greater radical scavenging ability for less exothermicity. Furthermore, the parameter θ_t would be a more reasonable parameter if the complex trade-off between exothermicity and radical scavenging especially manifest by reaction (17r) did not exist.

The increase in θ_t with equivalence ratio and with mechanism III over mechanism I is consistent with the preceding explanation. The rate of reaction (14r) increases relative to that of (17r) with equivalence ratio due to the higher temperature and greater hydrogen atom concentration at blowout. Enhancement of (14r) relative to (17r) also occurs with mechanism III relative to mechanism I.

4.2 Summary

Argon and nitrogen acted as physical inhibitors affecting lower

temperatures at blowout and increased residence times. Hydrogen bromine behaved like nitrogen for the artificial case of no hydrogen bromide kinetics. Hydrogen bromide addition resulted in increased oxygen consumption, increased blowout temperatures, increased residence times and reduced radical pool fractions. The parameter θ_t employed to provide some indication of inhibition effectiveness was a more reasonable choice to characterize argon and nitrogen inhibition but exhibited large variations with composition for hydrogen bromide inhibition. Using θ_t as an indicator of inhibitor effectiveness revealed that hydrogen bromide was the most effective and argon the least. Hydrogen bromide was found to be more effective at high pressures than low, for mechanism III relative to mechanism I, and for rich over stoichiometric and lean flames. The hydrogen bromide reactions important to inhibition are reactions (14r) and (17r), with the former the more important of the two. The effectiveness of hydrogen bromide resulted in a complex trade-off between reaction exothermicity and radical scavenging ability.

REFERENCES

1. Halogenated Fire Suppressants, ACS Symposium Series 16, (R.G. Gann, Editor), 1975.
2. Friedman, R. and Levy, J.B., Wright Air Development Center Technical Report 56-568, AD No. 110685, January 1957.
3. Creitz, E.C., J. Res. Nat. Bur. Stand. 74A, p. 521, 1970.
4. Hastie, J.W., J. Res. Nat. Bur. Stand. 77A, p. 733, 1973.
5. Jones, A. and Prothero, A., Comb. and Flame 12, 457, 1968.
6. Pratt, D.T. and Bowman, B.R., "A PSR-A Computer Program for Calculation of Combustion Reactions Kinetics in a Macromixed Perfectly Stirred Reactor," Circular 43, Engineering Extension Service, Washington State University, Pullman, Washington, 1972.
7. Baulch, D.L., Drysdale, D.D., Horne, D.G., and Lloyd, A.C., Evaluated Kinetic Data for High Temperature Reactions, Butterworths, London, 1972.
8. Baulch, D.L., Drysdale, D.D., and Horne, D.G., Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 107, 1973.
9. Wilson, W.E., Jr., J. Chem. Ref. Data 1, 535, 1972.
10. Myerson, A.L. and Watt, W.D., J. Chem. Phys. 49, 425, 1968.
11. Johnston, H.S., "Gas Phase Reaction Kinetics of Neutral Oxygen Species," NSRDS-NBS 20, 1968.
12. Lloyd, A.C., Int. J. Chem. Kinetics 6, 169, 1974.
13. Vidal, C., J. Chem. Phys. 68, 1360, 1971.
14. Brown, N.J., ACS Symposium Series 16, 341, 1975.
15. MacDonald, R.G., and Burns, G., J. Chem. Phys. 66, 3598, 1977.
16. Cohen, N., Giedt, R.R., and Jacobs, T.A., Int. J. Chem. Kinet. 5, 425, 1973.
17. Fristrom, R.M. and Sawyer, R.F., AGARD Conference Proceedings No. 84 on Aircraft Fuels and Lubricants, and Fire Safety, AGARD-CP-84-71, Section 12, North Atlantic Treaty Organization, 1971.
18. Larsen, E.R., ACS Symposium Series 16, 376, 1975.
19. Rossner, W.A., Wise, H., and Miller, J., Seventh Symposium (International) on Combustion, Butterworth Scientific Publications, London, 1959.

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TABLE I

H₂/O₂/Ar/HBr Kinetics

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

Reaction	log A	n	E _a (cal/mole)	Ref.
1) O + H ₂ → OH + H	10.26	1.0	8900	8
2) OH + H ₂ → H + H ₂ O	13.36	0.0	5200	9
3) H + O ₂ → OH + O	14.34	0.0	16790	7
4) OH + OH → O + H ₂ O	12.80	0.0	1093	7
5) H ₂ + Ar → 2H + Ar	12.35	0.5	92600	10
6) H + OH + Ar → H ₂ O + Ar	21.92	-2.0	0	7
7) O + O + Ar → O ₂ + Ar	17.11	-1.0	341	11
8) HO ₂ + H → 2OH	14.40	0.0	1900	7
9) H + O ₂ + M → HO ₂ + M	15.18	0.0	-1000	7
10) O + HO ₂ → OH + O ₂	13.70	0.0	1000	12
11) H + HO ₂ → H ₂ O + O	13.70	0.0	1000	12
12) H + HO ₂ → H ₂ + O ₂	13.40	0.0	700	12
13) OH + HO ₂ → H ₂ O + O ₂	13.70	0.0	1000	12
14) Br + H ₂ → HBr + H	14.13	0.0	18400	13
15) H + Br ₂ → HBr + Br	14.53	0.0	903	14
16) Br + Br + Ar → Br ₂ + Ar	18.86	-1.42	0	15
17) HBr + Ar → H + Br + Ar	21.78	-2.0	88000	16

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

m ≡ order of the reaction

TABLE II^a
Ar Inhibition

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O ₂ (moles) ^b	θ_t
Ar	0.0	1.0	10 ⁻²	I	9.11x10 ⁻³	870	.234	-
	0.02				9.47x10 ⁻³	869	.236	.15
	0.04				9.85x10 ⁻³	868	.236	.14
	0.06				10.25x10 ⁻³	868	.238	.13
	0.08				10.69x10 ⁻³	867	.238	.13
	0.10				11.15x10 ⁻³	866	.238	.13
Ar	0.0	1.0	10 ⁻²	III	8.46x10 ⁻³	871	.231	-
	0.02				8.79x10 ⁻³	872	.232	.14
	0.04				9.14x10 ⁻³	870	.232	.14
	0.06				9.52x10 ⁻³	869	.233	.14
	0.08				9.92x10 ⁻³	868	.234	.13
	0.10				10.35x10 ⁻³	868	.236	.13
Ar	0.00	1.0	1.0	I	1.80x10 ⁻⁵	1129	.252	-
	0.02				1.88x10 ⁻⁵	1128	.253	.18
	0.04				1.96x10 ⁻⁵	1126	.253	.17
	0.06				2.05x10 ⁻⁵	1125	.255	.16
	0.08				2.15x10 ⁻⁵	1124	.256	.16
	0.10				2.25x10 ⁻⁵	1123	.258	.16
Ar	0.00	1.0	1.0	III	1.37x10 ⁻⁵	1138	.237	-
	0.02				1.42x10 ⁻⁵	1137	.238	.14
	0.04				1.49x10 ⁻⁵	1135	.240	.15
	0.06				1.56x10 ⁻⁵	1134	.241	.15
	0.08				1.63x10 ⁻⁵	1132	.242	.15
	0.10				1.71x10 ⁻⁵	1131	.244	.15

a) Standard mix: 1.0 mole H₂, 0.5 mole O₂, 1.5 mole Ar. Additional Ar is added to dilute standard mix by initial mole fractions tabulated.

b) Moles of O₂ consumed out of a possible 0.5 moles.

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TABLE III
N₂ Inhibition

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O ₂ (moles) ^b	θ_t
N ₂	0.00	1.0	10 ⁻²	I	9.11x10 ⁻³	870	.234	-
	0.02				9.55x10 ⁻³	868	.234	.18
	0.04				10.00x10 ⁻³	867	.236	.17
	0.06				10.50x10 ⁻³	866	.239	.16
	0.08				11.00x10 ⁻³	865	.240	.16
	0.10				11.60x10 ⁻³	864	.240	.15
N ₂	0.00	1.0	10 ⁻²	III	8.46x10 ⁻³	871	.231	-
	0.02				8.86x10 ⁻³	871	.233	.17
	0.04				9.29x10 ⁻³	869	.233	.17
	0.06				9.75x10 ⁻³	868	.235	.16
	0.08				10.25x10 ⁻³	867	.236	.16
	0.10				10.78x10 ⁻³	866	.238	.15
N ₂	0.00	1.0	1.0	I	1.80x10 ⁻⁵	1129	.252	-
	0.02				1.90x10 ⁻⁵	1127	.253	.22
	0.04				2.00x10 ⁻⁵	1126	.255	.20
	0.06				2.11x10 ⁻⁵	1124	.257	.20
	0.08				2.24x10 ⁻⁵	1122	.259	.19
	0.10				2.38x10 ⁻⁵	1120	.261	.19
N ₂	0.00	1.0	1.0	III	1.37x10 ⁻⁵	1138	.237	-
	0.02				1.44x10 ⁻⁵	1136	.239	.19
	0.04				1.52x10 ⁻⁵	1134	.241	.19
	0.06				1.61x10 ⁻⁵	1132	.243	.19
	0.08				1.70x10 ⁻⁵	1130	.244	.18
	0.10				1.81x10 ⁻⁵	1128	.247	.18

a) Standard mix: 1.0 mole H₂, 0.5 mole O₂, 1.5 moles Ar. Additional N₂ is added to give indicated mole fraction.

b) Moles O₂ consumed out of a possible 0.5 moles.

TABLE IV^a

HBr Inhibition at a 0.5 Equivalence Ratio

Inhibitor	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O ₂ (moles) ^b	θ_t
HBr	0.00	0.5	10 ⁻²	I	11.50x10 ⁻³	828	.268	-
	0.02				12.00x10 ⁻³	842	.295	.14
	0.06				12.80x10 ⁻³	874	.350	.14
	0.10				13.00x10 ⁻³	913	.408	.11
HBr	0.00	0.5	10 ⁻²	III	9.84x10 ⁻³	862	.297	-
	0.02				10.30x10 ⁻³	851	.293	.16
	0.06				11.10x10 ⁻³	885	.349	.16
	0.10				11.90x10 ⁻³	913	.392	.15
HBr	0.00	0.5	1.0	I	2.33x10 ⁻⁵	1060	.299	-
	0.02				2.44x10 ⁻⁵	1089	.331	.18
	0.04				2.56x10 ⁻⁵	1120	.357	.19
	0.06				2.70x10 ⁻⁵	1155	.387	.21
	0.08				2.86x10 ⁻⁵	1198	.420	.22
HBr	0.00	0.5	1.0	III	1.41x10 ⁻⁵	1102	.288	-
	0.02				1.58x10 ⁻⁵	1140	.323	.43
	0.04				1.79x10 ⁻⁵	1172	.356	.45
	0.06				2.01x10 ⁻⁵	1208	.389	.46
	0.08				2.28x10 ⁻⁵	1248	.423	.46

a) Standard mix: 1.0 mole H₂, 1.0 mole O₂; 2.0 mole Ar. Inhibitor added to give indicated mole fraction.

b) O₂ moles consumed out of a possible 1.0 moles.

TABLE V^a

HBr Inhibition in a Stoichiometric Flame

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O ₂ (moles) ^b	θ_t
HBr	0.00	1.0	10 ⁻²	I	9.11x10 ⁻³	870	.234	-
	0.02				9.58x10 ⁻³	884	.254	.20
	0.04				10.00x10 ⁻³	900	.273	.19
	0.06				10.40x10 ⁻³	918	.293	.19
	0.08				10.90x10 ⁻³	937	.311	.20
	0.10				11.35x10 ⁻³	960	.332	.20
HBr	0.00	1.0	10 ⁻²	III	8.46x10 ⁻³	871	.231	-
	0.02				8.93x10 ⁻³	888	.251	.22
	0.04				9.39x10 ⁻³	904	.270	.21
	0.06				9.88x10 ⁻³	945	.312	.23
	0.08				10.30x10 ⁻³	954	.322	.22
	0.10				10.80x10 ⁻³	964	.330	.21
HBr	0.00	1.0	1.0	I	1.80x10 ⁻⁵	1129	.252	-
	0.02				1.91x10 ⁻⁵	1158	.271	.26
	0.04				2.04x10 ⁻⁵	1192	.292	.27
	0.06				2.22x10 ⁻⁵	1226	.312	.31
	0.08				2.45x10 ⁻⁵	1267	.333	.34
	0.10				2.80x10 ⁻⁵	1313	.356	.38
HBr	0.00	1.0	1.0	III	1.37x10 ⁻⁵	1138	.237	-
	0.02				1.51x10 ⁻⁵	1173	.261	.40
	0.04				1.69x10 ⁻⁵	1208	.284	.43
	0.06				1.90x10 ⁻⁵	1244	.307	.45
	0.08				2.17x10 ⁻⁵	1286	.330	.47

a) Standard mix: 1.0 mole H₂, 0.5 moles O₂, 1.5 moles Ar. Inhibitor added to give indicated mole fraction.

b) O₂ mole consumed out of a possible 0.5 moles.

TABLE VI^a

HBr Inhibition in a 1.5 Equivalence Ratio Flame

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O ₂ (moles) ^b	θ_t
HBr	0.00	1.5	10 ⁻²	I	10.50x10 ⁻³	889	.213	-
	0.02				11.56x10 ⁻³	903	.226	.38
	0.04				12.79x10 ⁻³	919	.238	.38
	0.06				14.38x10 ⁻³	935	.250	.40
	0.08				16.56x10 ⁻³	954	.262	.41
	0.10				19.87x10 ⁻³	976	.272	.47
HBr	0.00	1.5	10 ⁻²	III	10.10x10 ⁻³	888	.209	-
	0.02				11.11x10 ⁻³	904	.223	.37
	0.04				12.34x10 ⁻³	919	.237	.39
	0.06				13.93x10 ⁻³	935	.248	.40
	0.08				16.11x10 ⁻³	954	.260	.42
	0.10				19.44x10 ⁻³	977	.271	.44
HBr	0.00	1.5	1.0	I	2.19x10 ⁻⁵	1150	.221	-
	0.02				2.47x10 ⁻⁵	1188	.234	.49
	0.04				2.87x10 ⁻⁵	1223	.247	.53
	0.06				3.51x10 ⁻⁵	1264	.261	.58
	0.08				4.71x10 ⁻⁵	1313	.274	.63
	0.10				7.64x10 ⁻⁵	1385	.288	.69
HBr	0.00	1.5	1.0	III	1.82x10 ⁻⁵	1152	.209	-
	0.02				2.13x10 ⁻⁵	1188	.226	.60
	0.04				2.55x10 ⁻⁵	1226	.241	.62
	0.06				3.22x10 ⁻⁵	1269	.257	.66
	0.10				7.42x10 ⁻⁵	1394	.288	.73

a) Standard mix: 1.0 mole H₂, .33 moles O₂, 1.33 moles Ar. Inhibitor added to give indicated mole fraction.

b) O₂ moles consumed out of a possible 0.33 moles.

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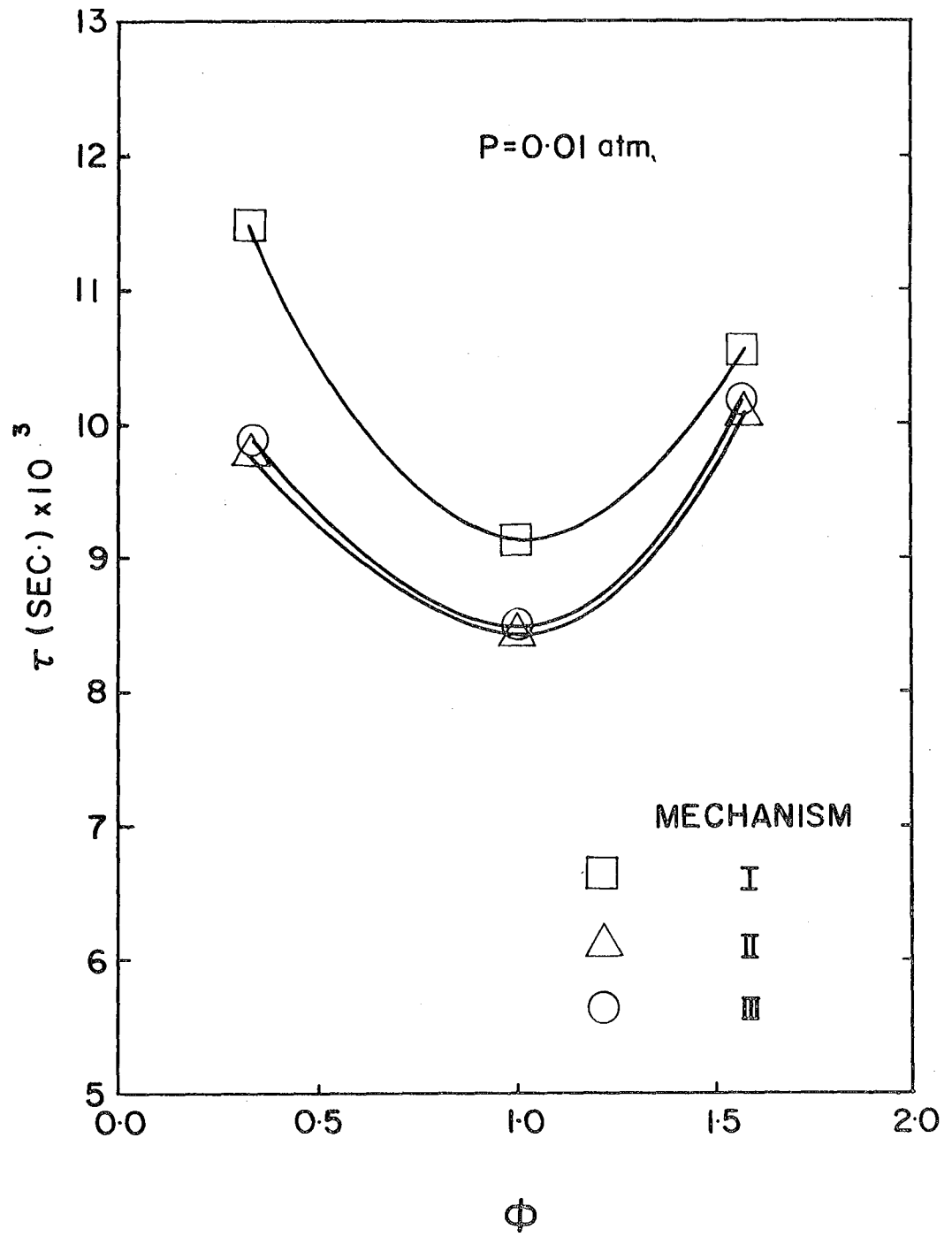
TABLE VII^a

Effect of Rate Coefficient Variation

Case	HBr Concentration (mole fraction)	t(sec)	T(K)	O ₂ (moles) ^b	θ _t
A	0.00	1.80x10 ⁻⁵	1129	.252	—
	0.02	1.91x10 ⁻⁵	1158	.271	.26
	0.04	2.04x10 ⁻⁵	1192	.292	.27
	0.06	2.22x10 ⁻⁵	1226	.312	.31
	0.08	2.45x10 ⁻⁵	1267	.333	.34
	0.10	2.80x10 ⁻⁵	1313	.356	.38
B	0.00	1.80x10 ⁻⁵	1129	.252	—
	0.02	2.04x10 ⁻⁵	1143	.271	.52
	0.04	2.33x10 ⁻⁵	1158	.290	.53
	0.06	2.69x10 ⁻⁵	1174	.312	.54
	0.08	3.15x10 ⁻⁵	1186	.331	.54
	0.10	3.76x10 ⁻⁵	1203	.352	.55
C	0.00	1.80x10 ⁻⁵	1129	.252	—
	0.02	.82x10 ⁻⁵	1516	.294	
	0.04	.93x10 ⁻⁵	1662	.323	
	0.06	1.19x10 ⁻⁵	1765	.347	
	0.08	1.68x10 ⁻⁵	1842	.368	
	0.10	2.51x10 ⁻⁵	1892	.383	.32

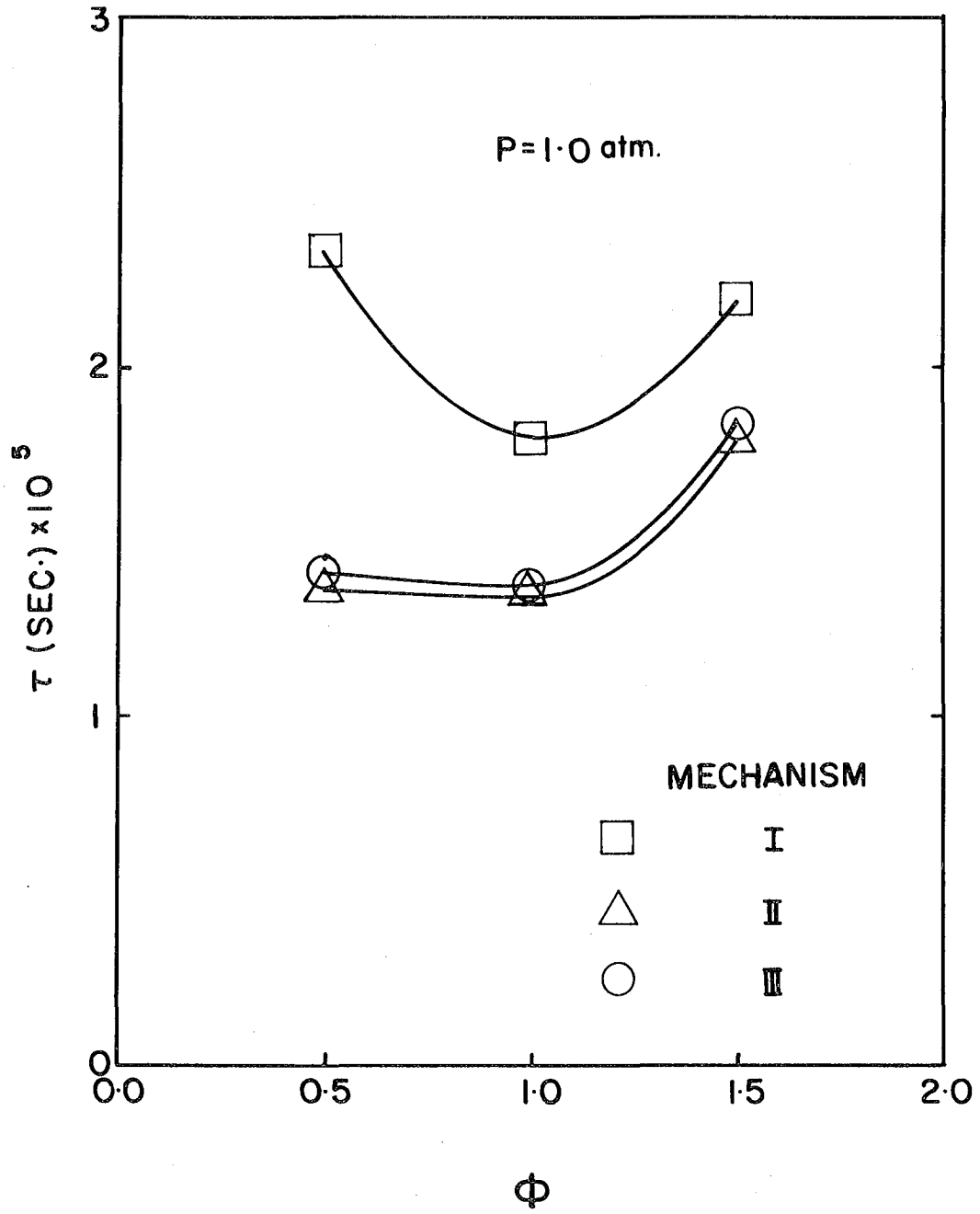
a) Stoichiometric, atmospheric pressure mixture with HBr inhibition, reacting via mechanism I.

b) O₂ moles consumed out of a possible 0.5 moles.



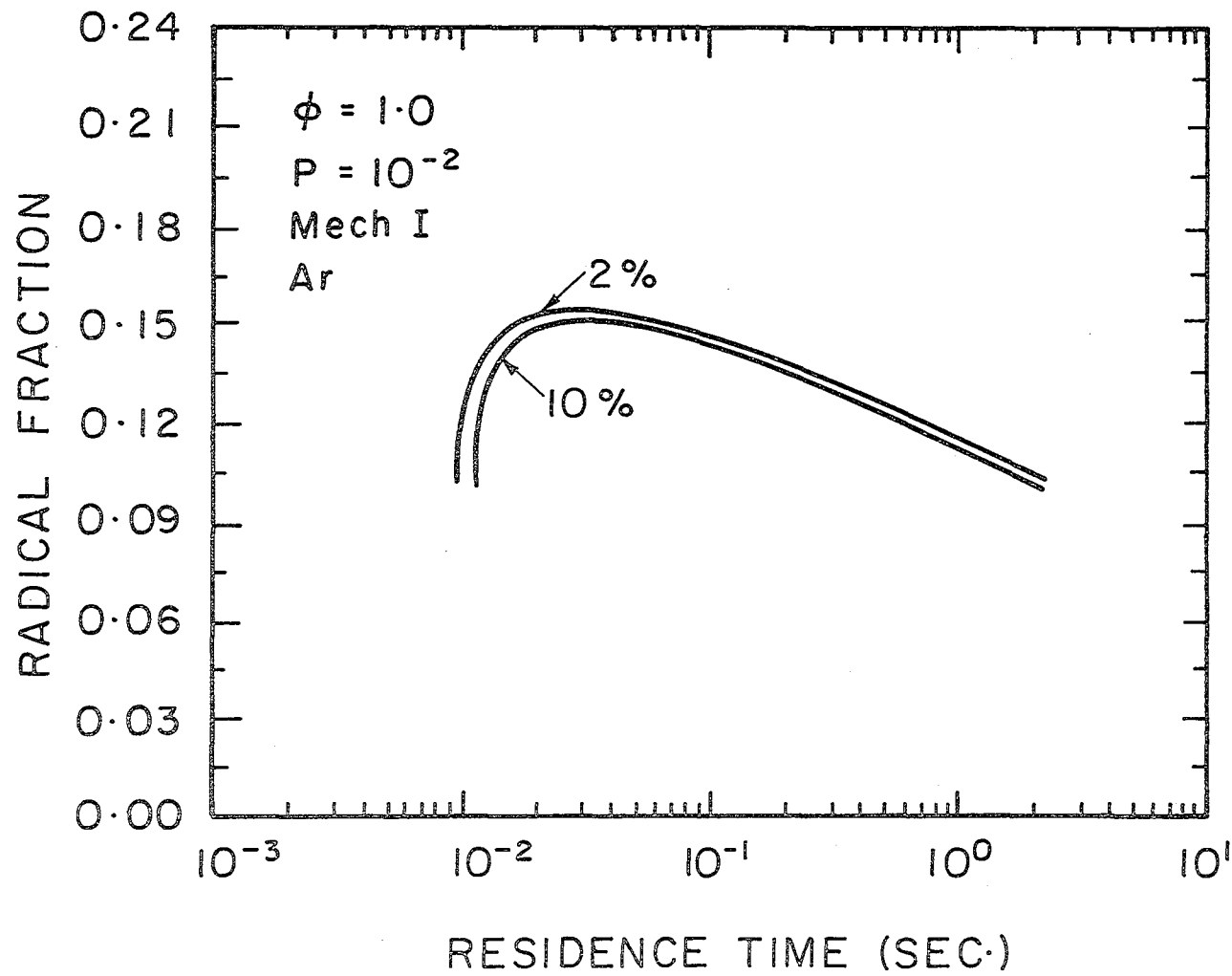
XBL 784-7958

Figure 1



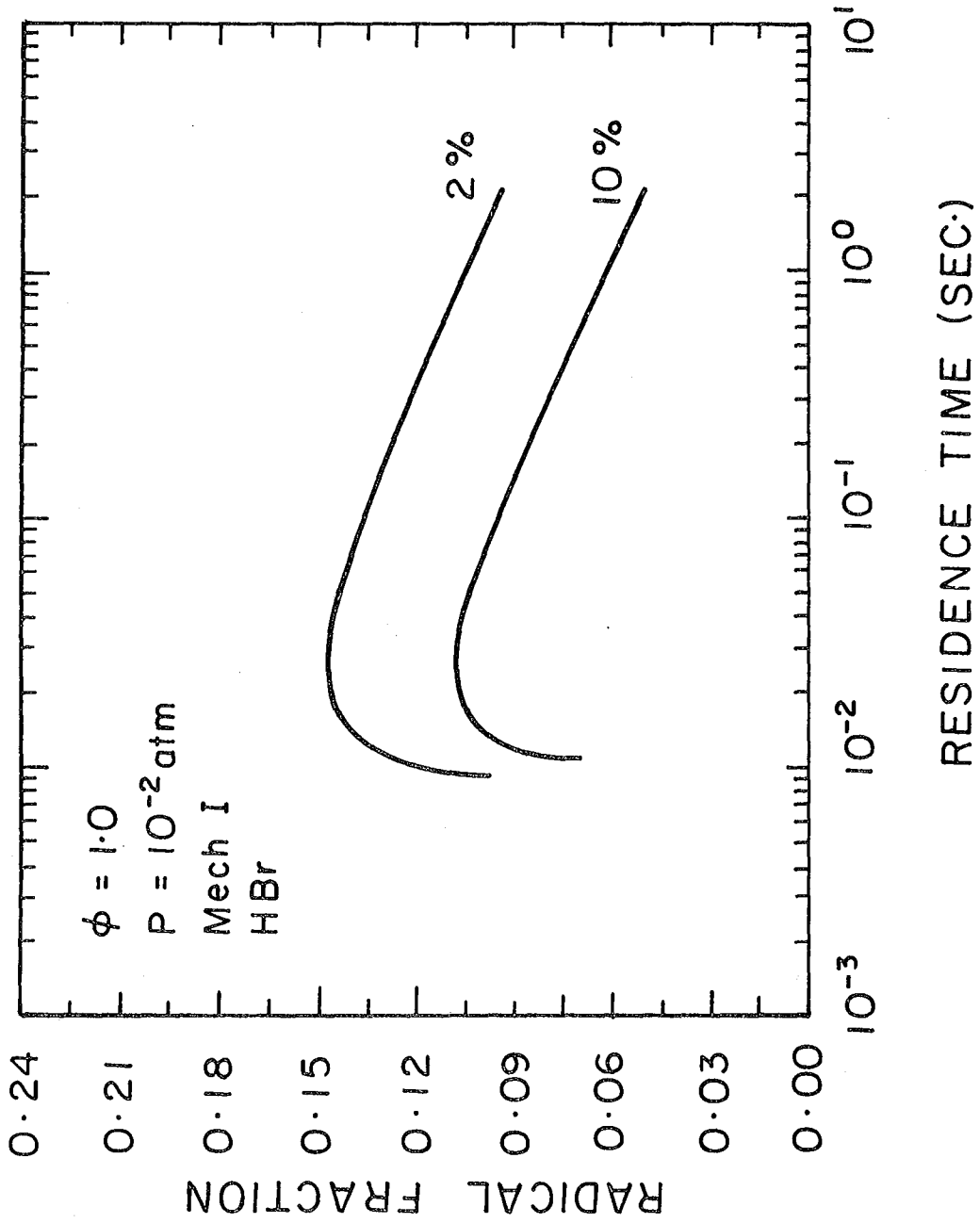
XBL 784-7959

Figure 2



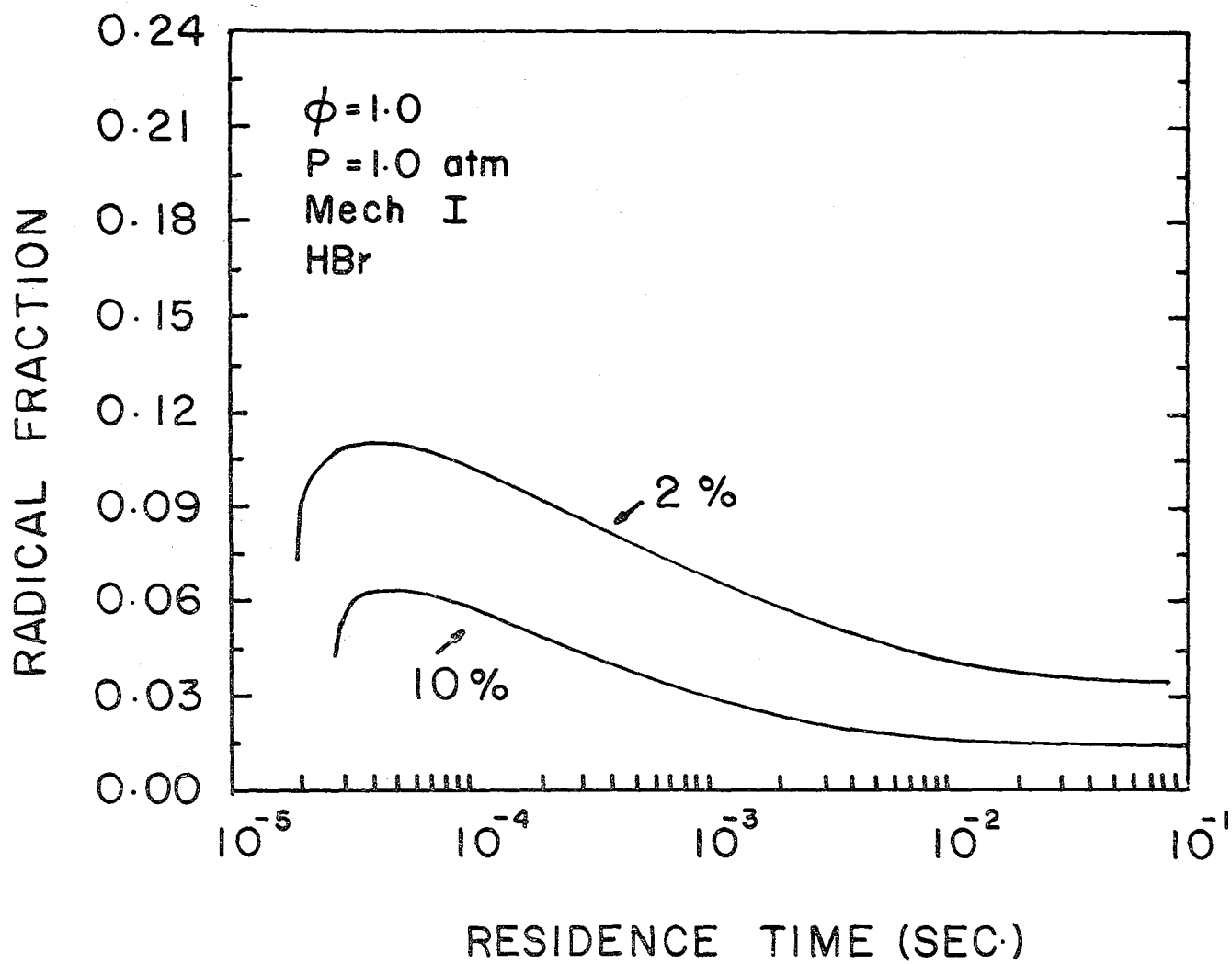
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Figure 3



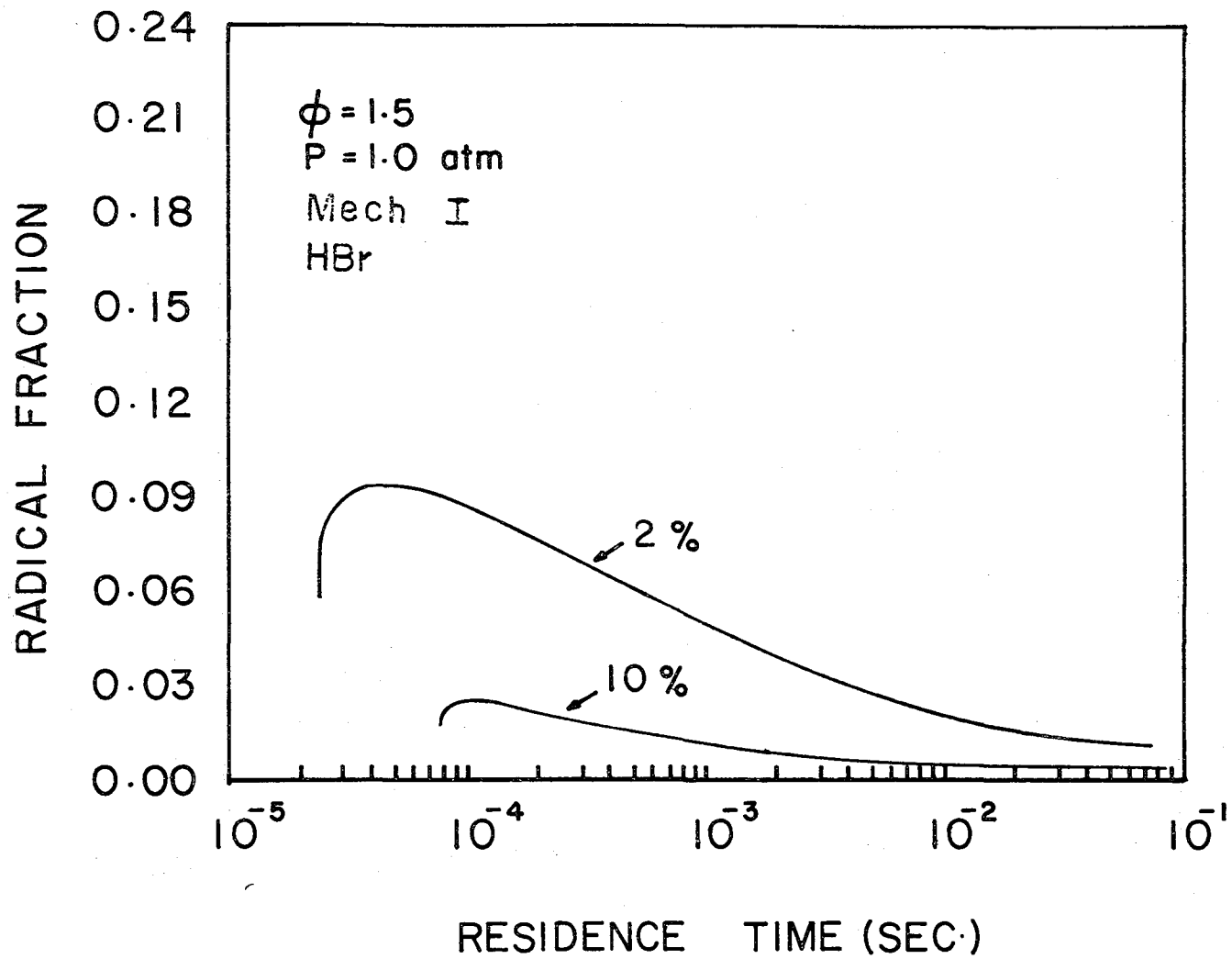
XBL 784-7963

Figure 4



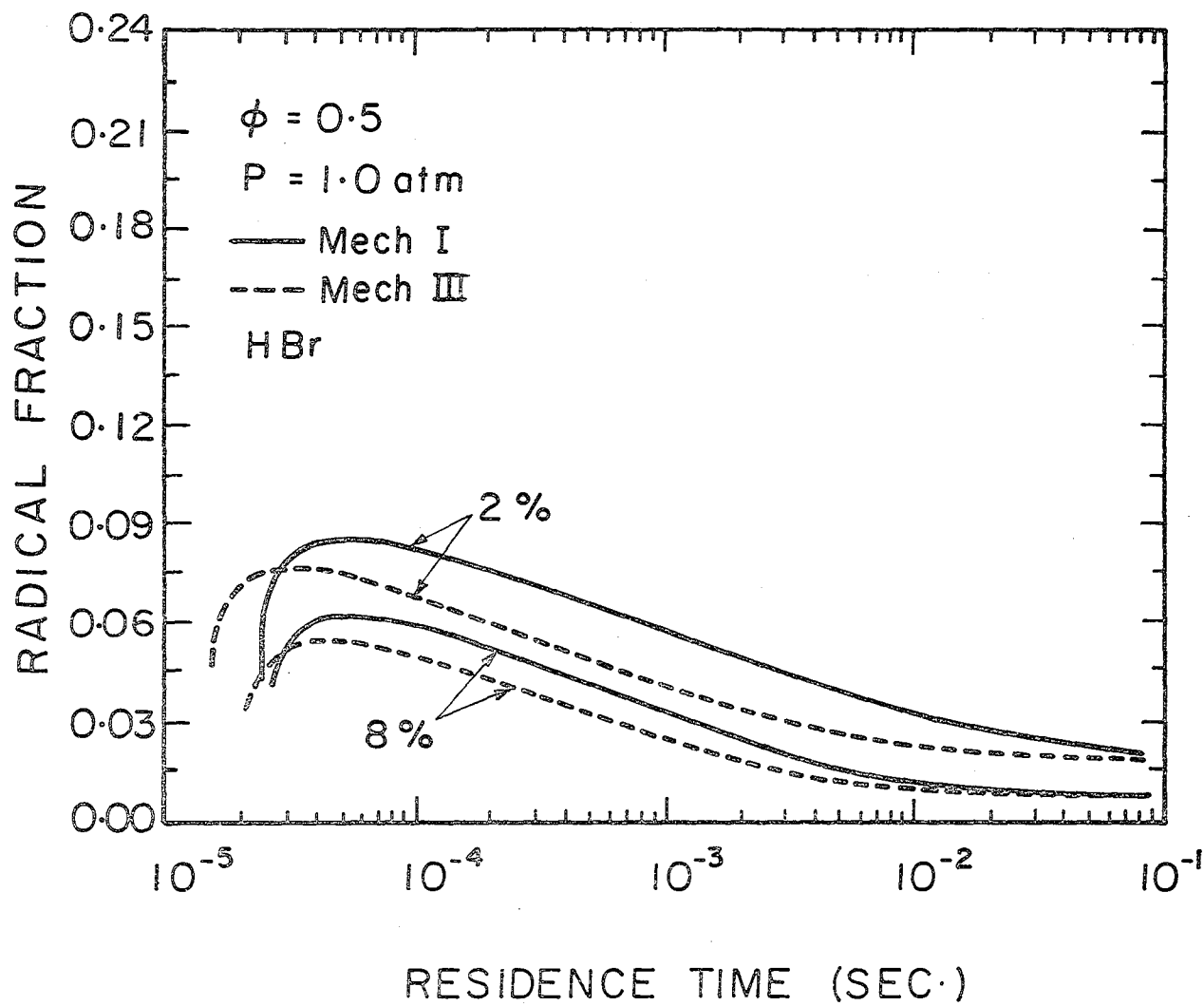
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Figure 5



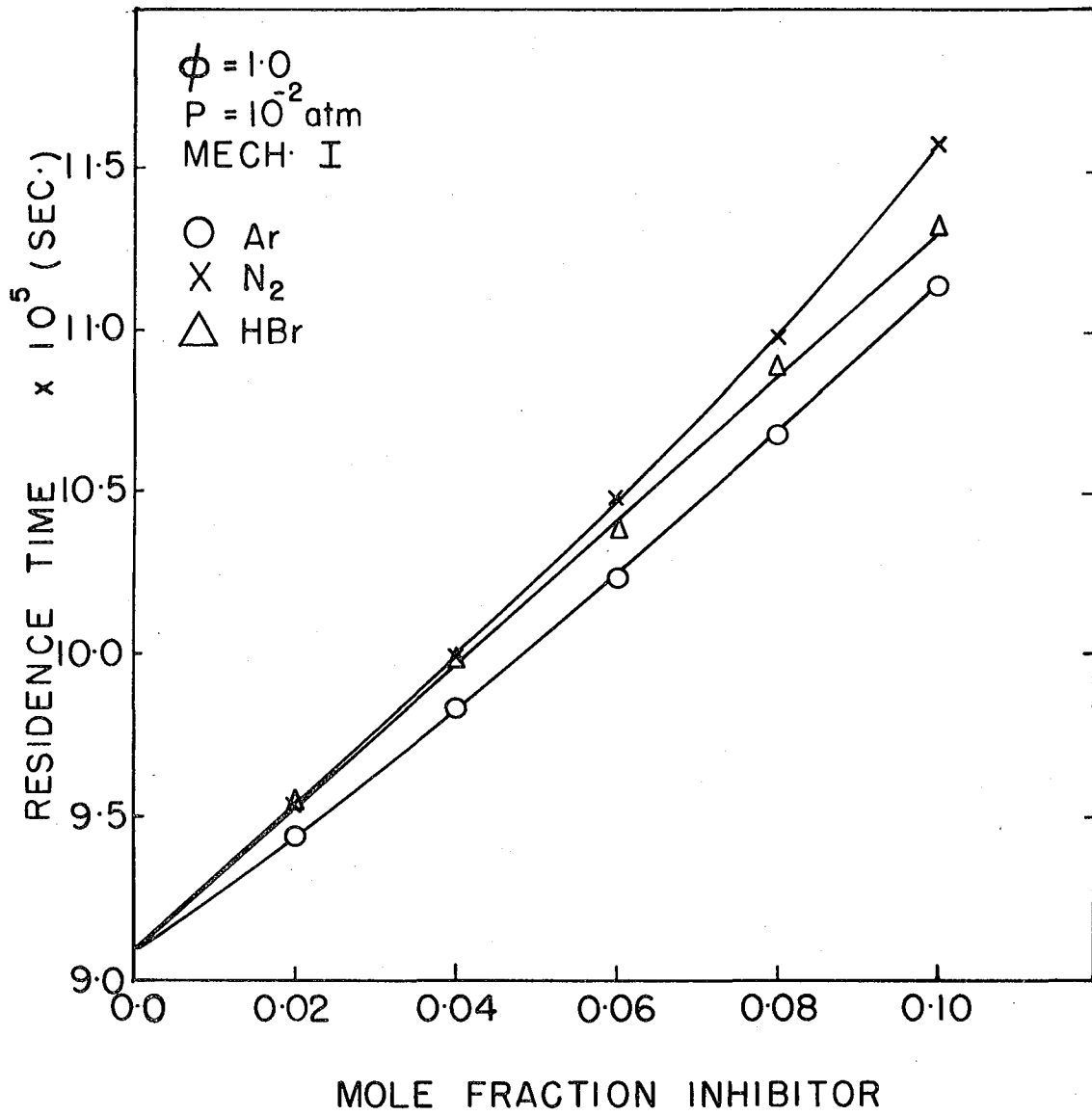
XBL 784-7965

Figure 6



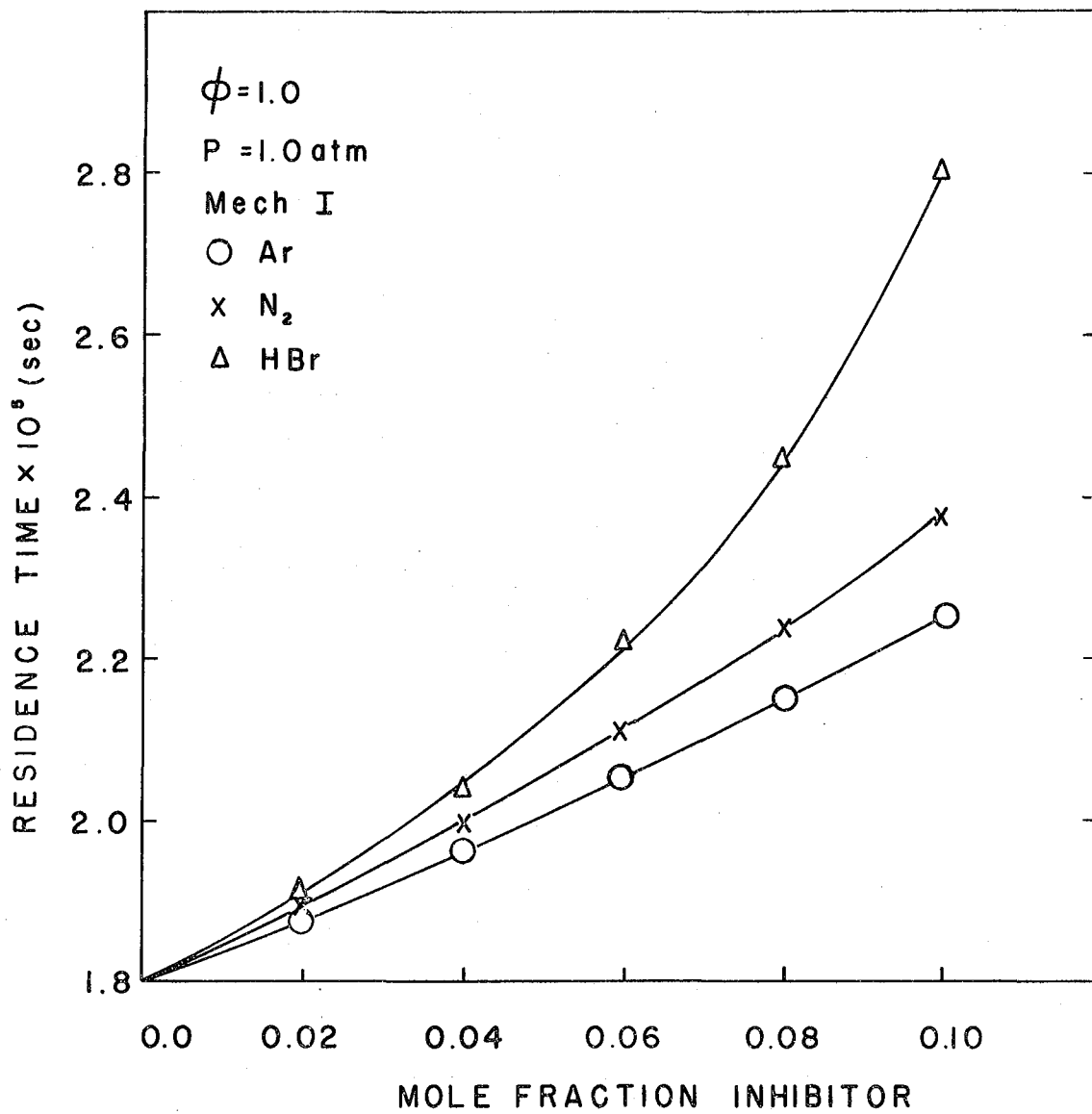
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Figure 7



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Figure 8



XBL 784-7960

Figure 9

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