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THE EFFECT OF BURNING VELOCITY INHIBITORS ON THE IGNITION OF  
HYDROCARBON-OXYGEN-NITROGEN MIXTURES

M. E. Morrison and K. Scheller

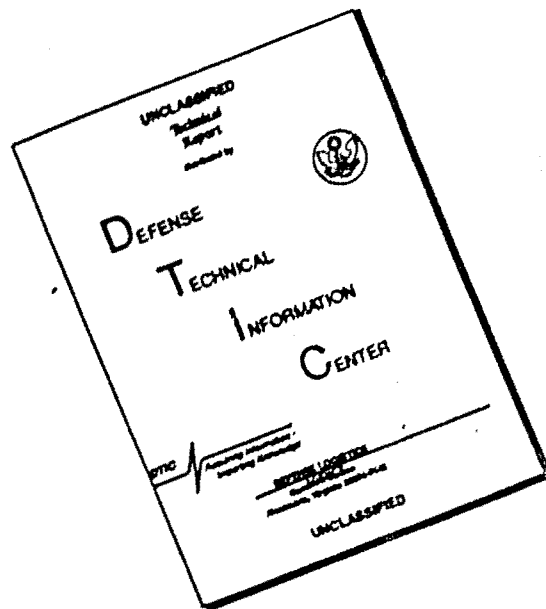
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Chemistry Research Laboratory  
Aerospace Research Laboratories  
Wright-Patterson AFB, Ohio 45433

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## ABSTRACT

It has been proposed that the mechanism of inhibition by halogens in hydrocarbon flames involves an increase in ignition temperature with a consequent prolongation of the preignition zone. An examination of this hypothesis was undertaken by a systematic investigation of the effect of a number of well-recognized burning velocity inhibitors on the ignition of hydrocarbon mixtures by hot wires in a 35 mm quartz tube. Data are reported for ignition temperature as a function of additive concentration for methane and/or propane mixtures with oxygen and nitrogen at ambient temperature and pressure.

Studies on the following twenty additives are described:  $\text{SnCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_3\text{H}$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{BBr}_3$ ,  $\text{CrO}_2\text{Cl}_2$ ,  $\text{POCl}_3$ ,  $\text{Fe}(\text{CO})_5$ . Although some of the experimental results are quite disparate, several groups of compounds do show similar behavior. The Group IVA chlorides show a trend somewhat similar to that reported in burning velocity experiments.  $\text{SnCl}_4$  and  $\text{GeCl}_4$  increased the ignition temperature of propane-air systems; while  $\text{SiCl}_4$  did not affect the ignition temperature and  $\text{CCl}_4$  lowered it.  $\text{SiCl}_3\text{H}$  and  $\text{PCl}_3$  decreased the ignition temperature of methane-air and/or propane-air mixtures;  $\text{AsCl}_3$  increased it slightly.  $\text{TiCl}_4$  did not affect the ignition temperature of propane-air mixtures for the concentration range studied. The methyl halides increased the ignition temperature of propane-air mixtures in the following order of effectiveness:  $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$ . A well-marked trend between ignition temperature increase for the propane-air system as a function of bromine atom concentration was found for  $\text{BBr}_3$ ,  $\text{Br}_2$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ , and  $\text{CHBr}_3$ . However, while the data for the latter additives could be correlated by a single experimental curve, both  $\text{BBr}_3$  and  $\text{Br}_2$  were more effective inhibitors

for the same bromine atom concentration. In relatively large concentrations of  $\text{Cl}_2$  ( $> 4\%$ ), the ignition temperature for mixtures of propane and air was decreased. The behavior of  $\text{BBr}_3$  and  $\text{CrO}_2\text{Cl}_2$  was completely unexpected. In propane-air mixtures, the ignition temperature increased linearly with  $\text{BBr}_3$  concentration up to the maximum investigated.  $\text{CrO}_2\text{Cl}_2$  did not affect the ignition temperature in this system. With enriched "air" (35%  $\text{O}_2$ ), however,  $\text{BBr}_3$  and  $\text{CrO}_2\text{Cl}_2$  reduced the ignition temperature with increasing concentration.  $\text{POCl}_3$  increased the ignition temperature slightly; while  $\text{Fe}(\text{CO})_5$  showed no effect in the propane-air systems studied. Possible mechanistic explanations of the experimental results are discussed.

## INTRODUCTION

Though reduction of the flame velocity in hydrocarbon-oxygen-nitrogen mixtures upon the addition of small quantities of various substances is a well-known phenomenon, the effect of these additives on the preignition zone is largely unknown. The inhibitors have generally been assumed to produce their effect by acting as chain breakers and reducing the concentration of free radicals in the flame important to the propagation reactions (i.e.  $\text{H}, \text{O}, \text{OH}$ ). Wilson<sup>1</sup> has recently examined the structure of a methane-oxygen flame inhibited by  $\text{CH}_3\text{Br}$  by measuring its temperature and composition profiles. His results showed a prolongation of the preignition zone and shift of the primary reaction zone to a higher temperature. Vanpee and Wolfhard<sup>2</sup> have studied the ignition of combustible hydrocarbon-air mixtures with hot gases. A limited amount of data was obtained on the effect of  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Cl}_2$ , and  $\text{CH}_3\text{Br}$  on the ignition temperature of these systems.  $\text{Pb}(\text{C}_2\text{H}_5)_4$  and  $\text{Fe}(\text{CO})_5$  had no effect on

the ignition temperature while  $\text{Cl}_2$  and  $\text{CH}_3\text{Br}$  increased it.

An understanding of the effect of the well-known inhibitors as well as other materials on the ignition of hydrocarbon-air systems is of considerable practical importance. Information of this type could lead to better techniques for fire suppression and possibly combustion promotion. Additives, which decrease the ignition temperature, might be of considerable value in increasing the effectiveness of supersonic combustion systems now under development.

Consideration was first given to shock tube studies to determine the effect of various additives on the ignition delay and build up of the concentration of important species in the reaction zone. Because such tests are relatively elaborate and lengthy, it was decided to use a simple approach to screen a large number of additives for their effect on the ignition of combustible mixtures. Vanpee and Wolfhard<sup>2</sup> have found that the ignition of combustible mixtures by hot gases was closely approximated by hot-wire ignition data. Therefore, the screening of a number of materials to select the most promising ones for future shock-tube studies was carried out by passing the combustible gases over a hot wire and noting the wire temperature required to bring about ignition. The data obtained in these tests are reported in this paper.

### EXPERIMENTAL

The C.P. grade gases were metered through appropriate rotameters into a quartz combustion tube with an inside diameter of 35 mm and overall length of 15 cm. The lower 7 1/2 cm of the tube was packed with a layer of glass wool topped with 2 mm pyrex beads. Combustible gases passing through the tube were ignited by an electrically heated bare nickel-chromium (80/20) wire. The wire traversed

the diameter of the tube 5 cm from the top and had a diameter of 0.86 mm. The temperature of the wire was measured with a pyrometer and reported as the black-body temperature at 6500 Å. Ignition was defined as that point where a visible flame or flashback was observed. The flow rate of gases through the combustion tube was maintained at 1000 cc/min. Addition of the liquid additives was affected by passage of nitrogen through a constant temperature saturator containing the substance to be investigated.

A typical test run was carried out by first passing pure nitrogen through the combustion tube to obtain a temperature-current curve for the nickel-chromium wire. Next the test hydrocarbon-air mixture was passed continuously through the combustion tube as the current through the wire was increased slowly until ignition was observed. The affect of a liquid additive on the ignition process was evaluated by diverting a portion of the nitrogen flow through the constant temperature saturator and again determining the wire temperature at the ignition point. Gaseous additives were passed through appropriate rotameters and mixed with the hydrocarbon-air system before entering the combustion tube. A new wire and temperature-current calibration curve were required for each test.

Several questions immediately arise in experiments involving ignition by hot surfaces. One concerns possible catalysis of preignition reactions by the surface. The work reported by Wolfhard<sup>3</sup> induced that little effect would be expected from the nickel-chromium wire. Hot-wire and hot-gas ignition temperatures agreed quite well in his experiments. A flow rate variation of as much as 100% in our apparatus were not anticipated to influence the measured ignition temperature in accordance with the findings of Kumagai and Kimura<sup>4</sup>. Since the wire diameter would undoubtedly affect the measured temperature, all tests were carried out using the same size wire. In view of the very good agreement between our ignition temperatures and those reported by Wolfhard<sup>3</sup> for methane or propane

and air mixtures, it appears that the combustion tube diameter did not affect the results in any way.

## RESULTS

Initial studies were directed toward an understanding of the influence of a number of well-known<sup>5-7</sup> burning velocity inhibitors on the ignition temperature of hydrocarbon-air mixtures. Wagner<sup>5</sup> has reported the effect of a large number of inhibitors on the burning velocity of n-hexane and air mixtures. His data is presented in Table I. Our first experiments were performed with those additives shown in Table I that have an appreciable vapor pressure at room temperature. Rather than using n-hexane, which required heating of the apparatus, methane and propane were employed as fuels.

The effect of  $\text{SnCl}_4$  on the ignition of propane and air is shown in Figure 1.\* Variation of the  $\text{O}_2/\text{C}_3\text{H}_8$  or  $\text{O}_2/(\text{O}_2+\text{N}_2)$  ratios did not change the ignition behavior. Addition of less than 2%  $\text{SnCl}_4$  increased the ignition temperature for this system by  $250^\circ\text{C}$ . A lowering of the burning velocity was qualitatively observed for all tests.

Ignition temperatures for  $\text{GeCl}_4$  in propane or methane and air mixtures are given in Table II. The data were not plotted since the ignition temperature was unaffected by additions of up to 2.9% with  $\text{CH}_4$  and 4.2% with  $\text{C}_3\text{H}_8$ . A further increase in the  $\text{GeCl}_4$  content produced very marked rises in the ignition temperature. The data for another member of the Group IVA halides,  $\text{SiCl}_4$ , are presented

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\*Each additional data point is denoted by a line attached to the symbol given on each figure. All data are reported as mole percent unless stated otherwise.

in Table III. It had no apparent effect on the ignition temperature of propane-air mixtures. A somewhat surprising reduction of the ignition temperature for this system was observed upon addition of  $\text{CCl}_4$ . Those data are plotted in Figure 2. The reduction in ignition temperature was even more pronounced for the enriched air (35%  $\text{O}_2$ ) system. One qualitative observation should be noted. The effectiveness of the Group IVa chlorides for inhibition of the burning velocity and ignition are similar, i.e.  $\text{SnCl}_4 > \text{GeCl}_4 > \text{SiCl}_4 > \text{CCl}_4$ .

Two rather effective burning velocity inhibitors,  $\text{SiCl}_3\text{H}$  and  $\text{PCl}_3$ , produced no significant change in the ignition temperature of methane or propane-air mixtures at concentrations below ~ 2%. However, large quantities of either additive lowered the ignition temperature in the manner depicted in Figures 3 and 4. Wagner<sup>5</sup> reported that  $\text{AsCl}_3$  and  $\text{TiCl}_4$  were effective inhibitors for the burning velocity of n-hexane and air mixtures. However the data presented in Tables IV and V show very little effect, if any, on the ignition temperature of propane-air mixtures by these compounds.

An investigation of the effects of methyl halide addition on the ignition of propane-air mixtures was carried out. Data for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{F}$  are collected in Tables VI and VII respectively, and plotted for  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$  in Figures 5 and 6. Here the effectiveness of the methyl halides as inhibitors for the burning velocity and ignition temperature can be ranked in the order  $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$ . Both an increase in the percent oxygen in the system or an increase in the fuel content produced a marked decrease in the effectiveness of the additives as inhibitors.

Both methylene bromide and tribromomethane were evaluated as inhibitors for the propane-air system. The experimental results obtained for these mixtures is depicted in Figure 7 for  $\text{CH}_2\text{Br}_2$  and tabulated for  $\text{CHBr}_3$  in Table VIII. Both additives had a marked effect on the ignition temperature. As will be shown



later, the increase in ignition temperature can be directly correlated with bromine atom addition for  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ , and  $\text{CH}_3\text{Br}$ . Somewhat surprising affects were obtained with  $\text{Br}_2$  and  $\text{Cl}_2$  in the propane-air system. As may be seen in Figure 8,  $\text{Br}_2$  very effectively increased the ignition temperature; while  $\text{Cl}_2$  in concentrations above 4% decreased the ignition temperature.

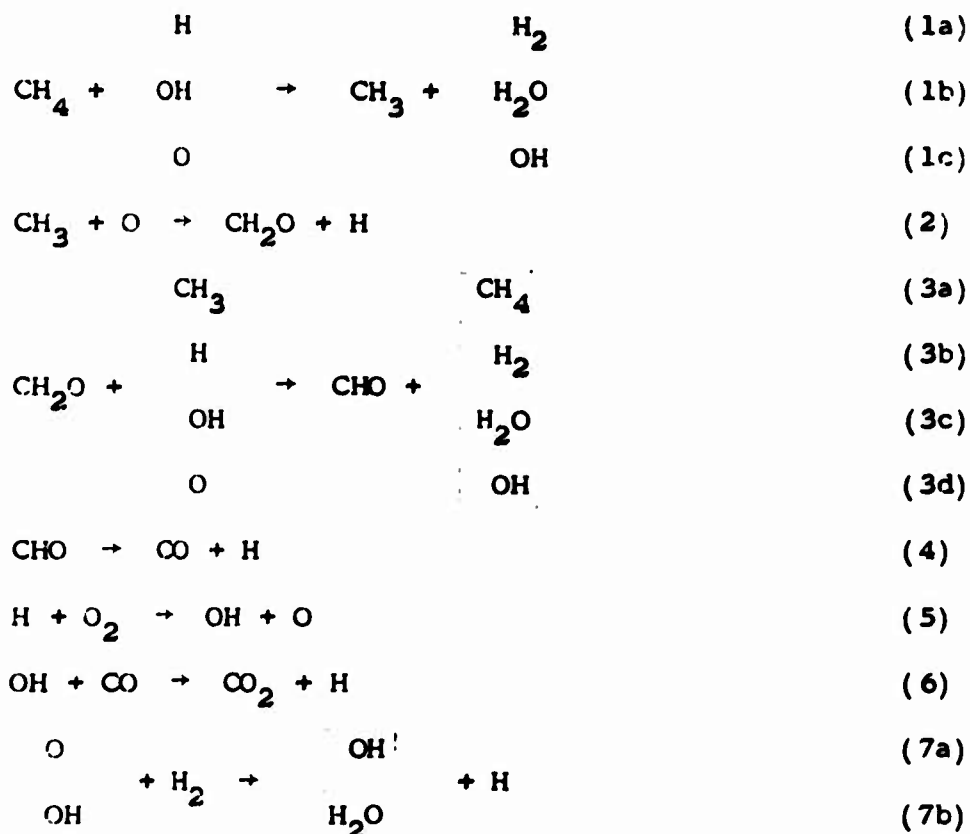
The influence of  $\text{BBr}_3$  and  $\text{CrO}_2\text{Cl}_2$  on the ignition of propane-oxygen-nitrogen mixtures, shown in Figures 9 and 10 respectively, proved to be quite interesting. For air (21%  $\text{O}_2$ )-propane mixtures there was a linear increase in ignition temperature, while  $\text{CrO}_2\text{Cl}_2$  did not influence the system in any way. Both additives decreased the enriched air (35%  $\text{O}_2$ )-propane ignition temperature,  $\text{BBr}_3$  more dramatically than  $\text{CrO}_2\text{Cl}_2$ . Qualitatively it appeared as if the burning velocity of the enriched propane-air system was decreased upon addition of  $\text{BBr}_3$  but increased with  $\text{CrO}_2\text{Cl}_2$ . All additives described in this study seemed to decrease the burning velocity with the exception of  $\text{CrO}_2\text{Cl}_2$  in the enriched air system. The increase in ignition temperature with  $\text{BBr}_3$  and  $\text{Br}_2$  in the propane-air (21%  $\text{O}_2$ ) mixture can be directly correlated with bromine atom addition.

Two very effective burning velocity inhibitors,  $\text{POCl}_3$  and  $\text{Fe}(\text{CO})_5$ , produced essentially no change in the ignition temperature for the propane-air systems in the concentration range studied. The data are reported in Tables IX and X respectively.

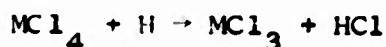
## DISCUSSION

One can divide a premixed flame into three zones<sup>8</sup>: (1) a preheat zone; (2) a reaction zone coinciding with the visible portion of the flame; and (3) a recombination zone for the various flame intermediates. Ignition of a

premixed hydrogen-air flame by a hot wire has many similarities. Initially, before the gases around the wire ignite, the process is very similar to that experienced in the preheat zone. As the wire temperature is increased further, the concentration of free radicals in a small volume of the gases about the wire reaches a concentration such that ignition occurs. Here the flame is clearly visible and corresponds to the reaction zone in a premixed flame. In order to understand the role of additives on the ignition of a premixed hydrocarbon-air flame, one must consider the reactions which occur in the preheat and reaction zone. At the onset of ignition the free radical concentration has reached a critical point, such that the reaction will continue to propagate. Quite naturally it would be supposed that the ignition temperature could be either raised or lowered by supplying or lowering the concentration of chain intermediates, i.e. H, O, OH. For discussion of this matter consider the reaction scheme proposed by Wise and Rosser<sup>8</sup> for methane oxidation in the reaction zone.



It is reasonable to suppose that the ignition process may be influenced by changes in the concentration of H, O or OH radicals. Let us consider this possibility in connection with the role of the Group IVa halides, the data for which are plotted in Figure 11. By way of preface, we may note that the bond energies for chlorine to the central atom are in the order  $\text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 \approx \text{CCl}_4$  being 91, 81, 76, and 78 kcal/mol respectively. Since their effectiveness as ignition inhibitors are, with the notable exception of  $\text{CCl}_4$ , in inverse order, i.e.  $\text{SnCl}_4 > \text{GeCl}_4 > \text{SiCl}_4$ , it might be postulated that the inhibiting action is related in some way to the ease with which the chlorine is removed from the compound. This supposition, however, does not seem capable of withstanding the light of more searching analysis. If the additive serves merely as a source of chlorine atoms which reacts with the hydrocarbon to form hydrogen chloride, which in turn reacts with hydrogen and hydroxyl radicals to form  $\text{H}_2$  and  $\text{H}_2\text{O}$  respectively and generate more chlorine atoms, then  $\text{CCl}_4$  should behave in the same manner as  $\text{SnCl}_4$  and  $\text{GeCl}_4$  and have an effect intermediate between the two. The same conclusion would apply to the case of stripping reactions:



where M = Sn, Ge, Si or C. In fact, of course,  $\text{CCl}_4$  is an ignition promoter. In this its behavior resembles that of the chlorine molecule itself, shown in Figure 8. The action of  $\text{CCl}_4$  on the ignition process appears to be quite definitely related to a role as a source of chlorine atoms and its promotion mechanism must be the same as that of the chlorine molecule. Furthermore, they seem to have about the same effectiveness, 9% of either additive reduces the ignition temperature by about  $150^\circ\text{K}$ . Thus one can suppose that the influence of the metal chlorides on the ignition process is completely different from that of  $\text{CCl}_4$  and that the correlation of their effectiveness with bond strengths is

fortuitous.

A somewhat more satisfying explanation may be proposed for the effect of methyl halides on the ignition of propane-air mixtures, illustrated in Figures 12 and 13. Their order of effectiveness as ignition suppressants is  $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$ , the latter acting virtually as an inert diluent. This is identical in manner to their action as burning velocity inhibitors<sup>5</sup>. Their influence correlates inversely in a well behaved fashion with their bond energies  $E(\text{CH}_3\text{I}) = 51 < E(\text{CH}_3\text{-Br}) = 67 < E(\text{CH}_3\text{-Cl}) = 78 < E(\text{CH}_3\text{-F}) = 107$  kcal/mole. If one supposes that the inhibition reactions of importance are:



followed by

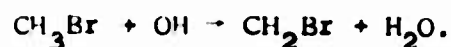


then one would expect the reaction rates for (8) and (9) to fall into the order  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ . Furthermore, since the bond strengths for HX also fall in the rank  $\text{I} < \text{Br} < \text{Cl} < \text{F}$ , the relative rates for reactions (10) and (11) would follow the same pattern. In the case of HF, moreover, reaction (10) would be endothermic by about 30 kcal and highly unlikely. For HCl, this reaction would be thermally neutral and not too significant. Thus it might be expected upon the basis of these considerations, that  $\text{CH}_3\text{F}$  is apt to act like an inert diluent and  $\text{CH}_3\text{Cl}$  to have a very small effect on the ignition process, exactly the behavior observed. The fact that  $\text{CH}_3\text{Cl}$  functions as a rather ineffectual inhibitor rather than promoter is somewhat perplexing in view of the role of  $\text{Cl}_2$  in reducing the ignition temperature, but further speculation regarding this point does not appear to be worthwhile considering that the small effect observed may well be within the experimental scatter of the data. Though a detailed mechanism for

the influence of methyl halides on the ignition of propane-air mixtures cannot be advanced upon the basis of the present experiments, it does appear that they inhibit the ignition process by removing H and OH atoms thus reducing the rate of the chain branching reaction (5) and the hydrogen abstraction reaction



Furthermore, since the additives were found to be more effective in fuel-rich mixtures than in stoichiometric mixtures and an increase in oxygen content reduced their inhibiting action markedly, it seems likely that their reaction with H atoms (8) is the predominant one. An increase in fuel content would increase the H atom concentration and reduce the effectiveness of the additive by exceeding its ability to react with the available supply. On the other hand, an increased oxygen content would lead to a reduction in H atom and increase in OH radical concentration. If reactions (8) and (9) were equally probable, no significant change would be expected in the effectiveness of the inhibitor. The fact that this is not observed, throws some doubt on the hypothesis of Wilson (1) that the primary reaction of methyl bromide is



It is interesting to relate the effectiveness of the bromine containing additives directly to their bromine atom content in the manner shown in Figure 13. For concentrations less than 2 atom percent, their influence on the ignition temperature varies directly with their bromine content. For greater concentrations, the data are correlated within the experimental scatter by a single curve for the methane derivatives, the results for Br<sub>2</sub> and BBr<sub>3</sub> falling significantly above this line well beyond the bounds of experimental error. The greater effect of the latter two additives is readily explained in terms of the affect of fuel addition on inhibition. The methane derivatives function as fuels as well as inhibitors, at the higher bromine concentrations the fuel-air

mixtures shift to the rich side with a concomitant reduction in the influence of the bromine atom concentration. No such factors are operative for the  $\text{BBr}_3$  and  $\text{Br}_2$  and their effect is directly proportional to the bromine concentration in the mixture. These data suggest, further, that the bromine content in each of these additives is equally available for reaction and not affected by the other moieties present in the molecule.

#### CONCLUSIONS AND RECOMMENDATIONS

The influence of twenty burning velocity inhibitors on the hot wire ignition temperature of propane or methane in ordinary and enriched air mixtures has been investigated. For the concentration range of less than 2% additive in air ( $\text{O}_2/(\text{O}_2+\text{N}_2) = 0.21$ ), the ignition temperature for these systems was unaffected or increased. This result is not in accord with the inhibition mechanism advanced by Wilson<sup>1</sup> upon the basis of his study with  $\text{CH}_3\text{Br}$ . Moreover, in the enriched air cases (35%  $\text{O}_2$ ) both  $\text{BBr}_3$  and  $\text{CrO}_2\text{Cl}_2$  lower the ignition temperature. Our qualitative observations indicate the burning velocity of the propane-air (35%  $\text{O}_2$ ) system to be decreased upon addition of  $\text{BBr}_3$ ; a finding in marked variance with the Wilson inhibition model. The seeming increase in burning velocity for the propane-air (35%  $\text{O}_2$ ) mixture upon addition of  $\text{CrO}_2\text{Cl}_2$  would be expected from the Wilson model. Burning velocity measurements for both of these systems should be carried out in the future to verify the qualitative results.

Our ignition data for propane or methane in air (21%  $\text{O}_2$ ) somewhat parallel the burning velocity results obtained by Wagner<sup>5</sup>. For known burning velocity inhibitors, the ignition temperature was either increased or remained invariant. In fact, the order of effectiveness of the Group IVa halides as burning

velocity inhibitors for the n-hexane-air (21% O<sub>2</sub>) mixtures was analogous to that found here with the hot-wire ignition tests, i.e. SnCl<sub>4</sub> > GeCl<sub>4</sub> > SiCl<sub>4</sub> > CCl<sub>4</sub>. Carbon tetrachloride actually reduced the ignition temperature in the propane-air (21%) system, corresponding in this respect to the behavior of relatively large concentrations of Cl<sub>2</sub> (> 4%).

The order of effectiveness for the methyl halides as ignition suppressants was identical to that reported by Wagner for the burning velocity CH<sub>3</sub>I > CH<sub>3</sub>Br > CH<sub>3</sub>Cl > CH<sub>3</sub>F, the latter acting virtually as an inert diluent. The activity of the halides decreased in fuel-rich mixtures and in enriched "air" (35% O<sub>2</sub>) compositions. These observations considered jointly suggest that the primary inhibition reactions might be that abstraction of the halogen by hydrogen atom to yield a hydrogen halide and alkyl radical followed by subsequent scavenging of H and OH radicals by the hydrogen halide to generate halogen atoms.

A direct correlation was found between total bromine content and ignition temperature elevation for the five additives: CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, Br<sub>2</sub> and BBr<sub>3</sub> tested. In the methane derivatives, the inhibiting effect of the bromine atom was moderated by the presence of the fuel moieties lowering their suppressant action markedly below that of the other additives at higher concentrations.

One of the most effective burning velocity inhibitors investigated by Wagner, Fe(CO)<sub>5</sub>, had no effect on the ignition temperatures of propane-air mixtures.

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TABLE I. Additional Amount of Inhibitors Required for 30% Reduction in the Burning Velocity of Stoichiometric n-Hexane/Air Mixtures (5).

<u>Inhibitor</u>	<u>Mol.Wt.</u>	<u>Burning Vel. of Inhibitor-Free Mixtures</u>	<u>Reduction in Burning Vel. in cm/sec</u>	<u>Vol.-% Inhibitor</u>	<u>Wt.-% Inhibitor</u>
n-C <sub>6</sub> H <sub>14</sub>	86.17	42.5	12.7	1.05	2.94
Cl <sub>2</sub>	70.914	41.5	12.5	3.3	7.41
Br <sub>2</sub>	159.84	41.5	12.5	0.7	3.59
N <sub>2</sub>	28.016	42.5	12.7	8	--
CO <sub>2</sub>	44.01	42.5	12.7	8	--
H <sub>2</sub> O	18.02	42.5	None	--	--
BBr <sub>3</sub>	250.57	41.8	12.5	0.18	1.47
PCl <sub>3</sub>	137.35	41.5	12.5	0.15	0.68
POCl <sub>3</sub>	153.35	41.5	12.5	0.19	0.96
PSCl <sub>3</sub>	169.41	41.5	12.5	0.13	0.72
PBr <sub>3</sub>	270.73	42.5	12.7	0.23	2.02
PSBr <sub>3</sub>	302.79	42.5	12.7	0.15	1.48
(CH <sub>3</sub> ) <sub>3</sub> PO <sub>4</sub>	140.12	46.0	13.8	0.26	1.19
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	182.20	45.7	13.7	0.27	1.61
AsCl <sub>3</sub>	181.36	42.5	12.7	0.39	2.27
SbCl <sub>3</sub>	228.13	45.3	13.6	0.22	1.64
CCl <sub>4</sub>	153.84	42.5	12.7	1.38	6.65
CHCl <sub>3</sub>	119.39	42.5	12.7	1.97	7.35
SiCl <sub>4</sub>	169.89	42.5	12.7	0.56	3.07
SiHCl <sub>3</sub>	135.44	42.5	12.7	2.9	11.80
GeCl <sub>4</sub>	214.43	42.5	12.7	0.50	3.44
SnCl <sub>4</sub>	260.53	42.5	12.7	0.19	1.61
TiCl <sub>4</sub>	189.73	42.5	12.7	0.19	1.18
SO <sub>2</sub>	64.06	42.5	12.7	4.9	9.85
SO <sub>2</sub> Cl <sub>2</sub>	134.97	42.5	12.7	1.36	5.8
SOCl <sub>2</sub>	118.97	42.5	12.7	1.80	6.73
S <sub>2</sub> Cl <sub>2</sub>	135.03	42.5	12.7	1.05	4.53
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>4</sub>	154.18	47.5	14.3	1.2	5.84
Si(CH <sub>3</sub> ) <sub>4</sub>	88.19	42.5	12.7	1.5	4.25
Fe(CO) <sub>5</sub>	195.50	42.5	12.7	0.0165	0.10
Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	323.45	41.5	12.5	0.014	0.15
CrO <sub>2</sub> Cl <sub>2</sub>	159.92	41.5	12.5	0.0235	0.18

TABLE II. Effect of  $\text{GeCl}_4$  on the Hot-Wire Ignition Temperature of Hydrocarbon-Air Mixtures.

$\frac{\text{O}_2}{\text{CH}_4}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{GeCl}_4$	Ignition Temperature, °C	Test
2	0.21	0	1240	1
2	0.21	7.35	>1370	1
2	0.21	0	1280	2
2	0.21	3.80	>1520	2
2	0.21	0	1240	3
2	0.21	1.96	1240	3
2	0.21	0	1240	4
2	0.21	2.90	~1310	4
2	0.21	0	1230	5
2	0.21	2.32	1230	5
2	0.21	0	1230	6
2	0.21	2.71	1230	6
2	0.21	0	1230	7
2	0.21	3.80	>1320	7
2	0.21	0	1230	8
2	0.21	3.23	>1370	8
2	0.21	0	1240	9
2	0.21	2.90	>1400	9
$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$				
5	0.21	0	1050	10
5	0.21	7.75	>1360	10
5	0.21	0	1070	11
5	0.21	4.03	1070	11
5	0.21	0	1070	12
5	0.21	2.06	1070	12
5	0.21	2.71	1070	12
5	0.21	3.23	1070	12
5	0.21	0	1080	13
5	0.21	3.23	1110	13
5	0.21	3.44	1120	13
5	0.21	3.63	1120	13
5	0.21	3.83	1120	13
5	0.21	4.05	1125	13
5	0.21	0	1070	14

TABLE II. (Continued)

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{GeCl}_4$	<u>Ignition Temperature, °C</u>	<u>Test</u>
5	0.21	4.03	1100	14
5	0.21	4.26	1100	14
5	0.21	4.46	1100	14
5	0.21	4.66	1110	14
5	0.21	0	1030	15
5	0.21	4.66	>1330	15
5	0.21	4.46	>1275	15
5	0.21	4.26	>1275	15
5	0.21	4.03	1110	15

TABLE III. Effect of  $\text{SiCl}_4$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{SnCl}_4$	Ignition Temperature, °C	Test
5	0.21	0	1070	1
5	0.21	3.61	1070	1
5	0.21	0	1070	2
5	0.21	22.1	1070	2
5	0.21	0	1070	3
5	0.21	12.5	1080	3
5	0.21	0	1050	4
5	0.21	10.3	1060	4
5	0.35	0	1040	5
5	0.35	9.0	1040	5
3	0.21	0	1070	6
3	0.21	10.0	1060	6

TABLE IV. Effect of  $\text{AsCl}_3$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{AsCl}_3$	Ignition Temperature, °C	Test
5	0.21	0	1060	1
5	0.21	0.94	1160	1
5	0.21	0	1060	2
5	0.21	0.47	1110	2
5	0.21	0	1060	3
5	0.21	0.71	1110	3
5	0.21	0	1050	4
5	0.21	0.71	1090	4
5	0.21	0	1060	5
5	0.21	0.47	1090	5
5	0.21	0	1060	5
5	0.21	0.94	1150	5
5	0.35	0	1020	6
5	0.35	0.76	1030	6
3	0.21	0	1020	7
3	0.21	0.92	1030	7
3	0.21	0	1030	8
3	0.21	0.92	1070	8

TABLE V. Effect of  $\text{TiCl}_4$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{TiCl}_4$	Ignition Temperature, $^{\circ}\text{C}$	Test
5	0.21	0	1060	1
5	0.21	0.17	1070	1
5	0.21	0	1070	2
5	0.21	1.275	1075	2
5	0.35	0	1050	3
5	0.35	1.023	1050	3
3	0.21	0	1070	4
3	0.21	1.242	1070	4

TABLE VI. Effect of  $\text{CH}_3\text{Cl}$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{CH}_3\text{Cl}$	Ignition Temperature, $^{\circ}\text{C}$	Test
5	0.21	0	1040	1
5	0.21	4.76	1075	1
5	0.21	2.44	1050	1
5	0.21	6.98	1090	1
5	0.21	9.09	1115	1
5	0.35	0	1030	2
5	0.35	4.76	1040	2
5	0.35	6.98	1050	2
5	0.35	9.09	1060	2
5	0.35	2.44	1030	2
3	0.21	0	1040	2
3	0.21	6.98	1040	2
3	0.21	9.09	1100	2
3	0.21	4.76	1065	2
3	0.21	2.44	1060	2

TABLE VII. Effect of  $\text{CH}_3\text{F}$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{CH}_3\text{F}$	Ignition Temperature, $^\circ\text{C}$	Test
5	0.21	0	1060	1
5	0.21	4.76	1060	1
5	0.21	2.41	1060	1
5	0.21	6.98	1065	1
5	0.21	8.35	1065	1
5	0.35	6.98	1050	1
3	0.21	7.82	1065	1

TABLE VIII. Effect of  $\text{CHBr}_3$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{CHBr}_3$	Ignition Temperature, $^\circ\text{C}$	Test
5	0.21	0	1050	1
5	0.21	0.48	1100	1
5	0.21	0.32	1075	1
5	0.35	0.39	1020	1
3	0.21	0.47	1080	1

TABLE IX. Effect of  $\text{POCl}_3$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{POCl}_3$	Ignition Temperature, $^{\circ}\text{C}$	Test
5	0.21	0	1040	1
5	0.21	2.74	1080	1
5	0.21	1.37	1070	1
5	0.21	0	1070	1
5	0.21	0.685	1090	2
5	0.21	2.06	1120	2
5	0.35	1.23	1070	3
5	0.35	2.46	1070	3
3	0.21	0	1050	4
3	0.21	2.77	1080	4

TABLE X. Effect of  $\text{Fe}(\text{CO})_5$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

$\frac{\text{O}_2}{\text{C}_3\text{H}_8}$	$\frac{\text{O}_2}{\text{O}_2 + \text{N}_2}$	% $\text{Fe}(\text{CO})_5$	Ignition Temperature, $^{\circ}\text{C}$	Test
5	0.21	0	1065	1
5	0.21	2.39	1065	1
5	0.21	0	1075	2
5	0.21	1.21	1075	2
5	0.35	1.93	1075	2
3	0.21	0	1060	3
3	0.21	2.34	1060	3



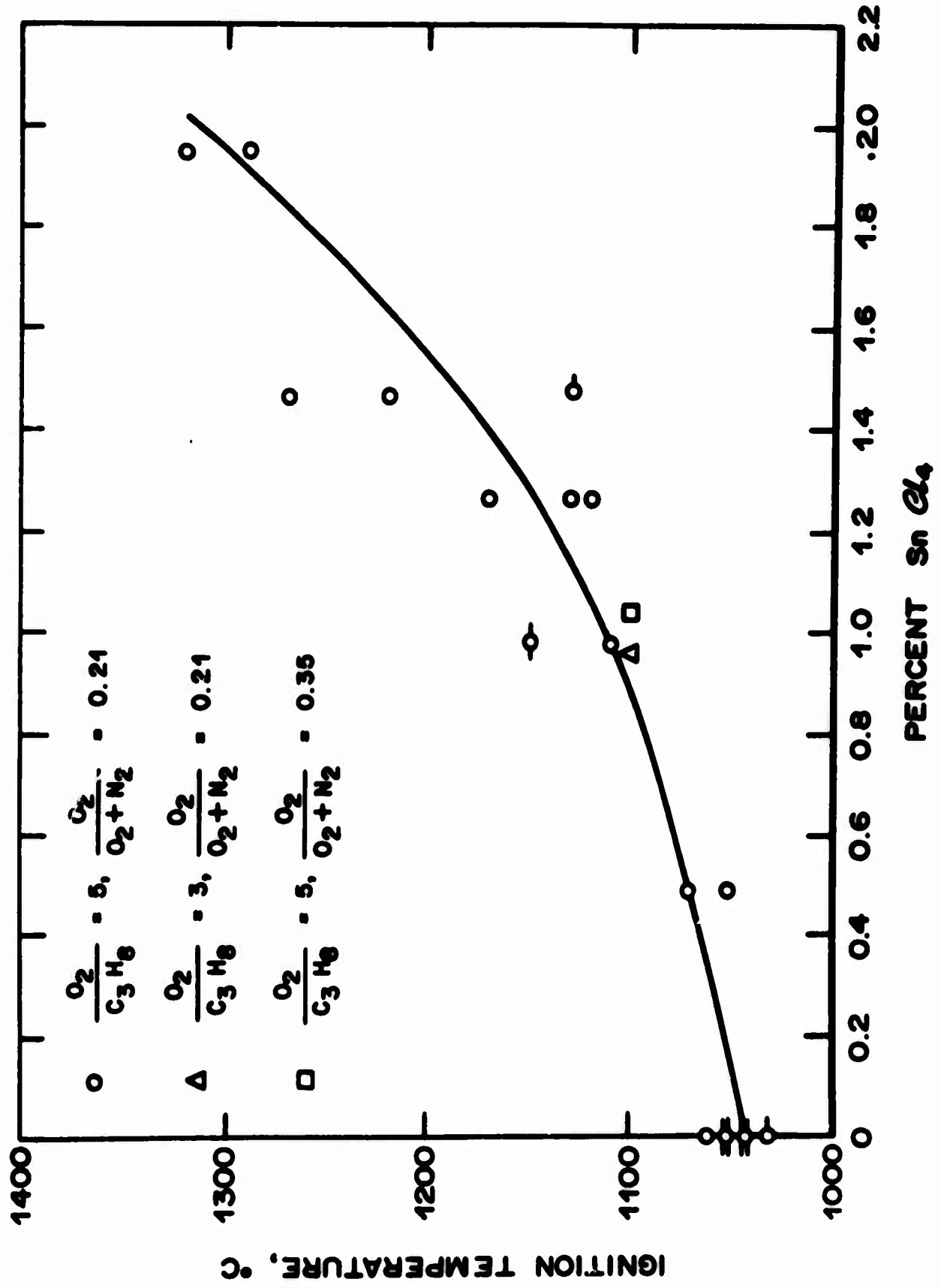


Figure 1. Effect of SnCl<sub>4</sub> on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

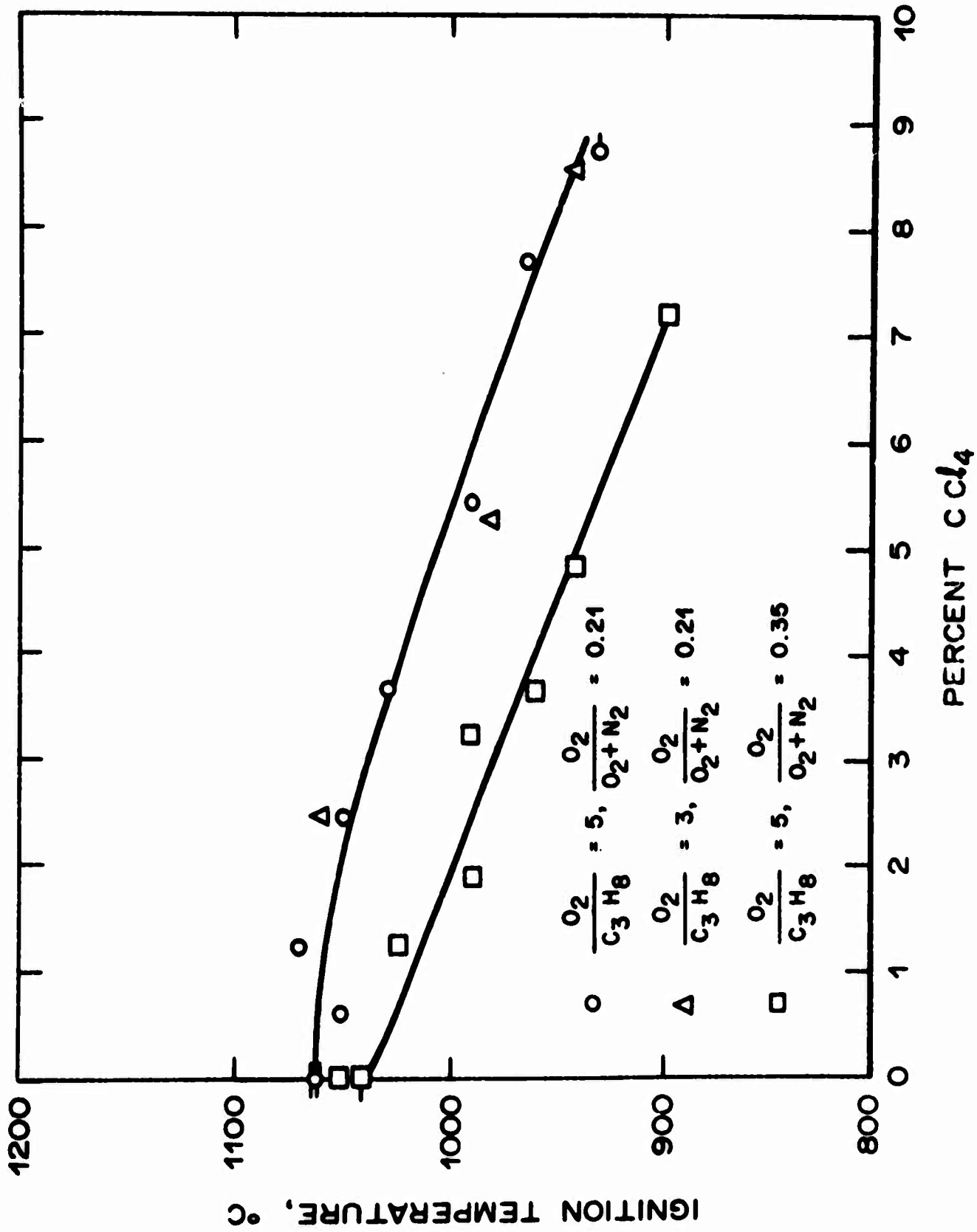


FIGURE 2. Effect of  $\text{CCl}_4$  on the Hot-Wire Ignition Temperature of Propene-Air Mixtures.

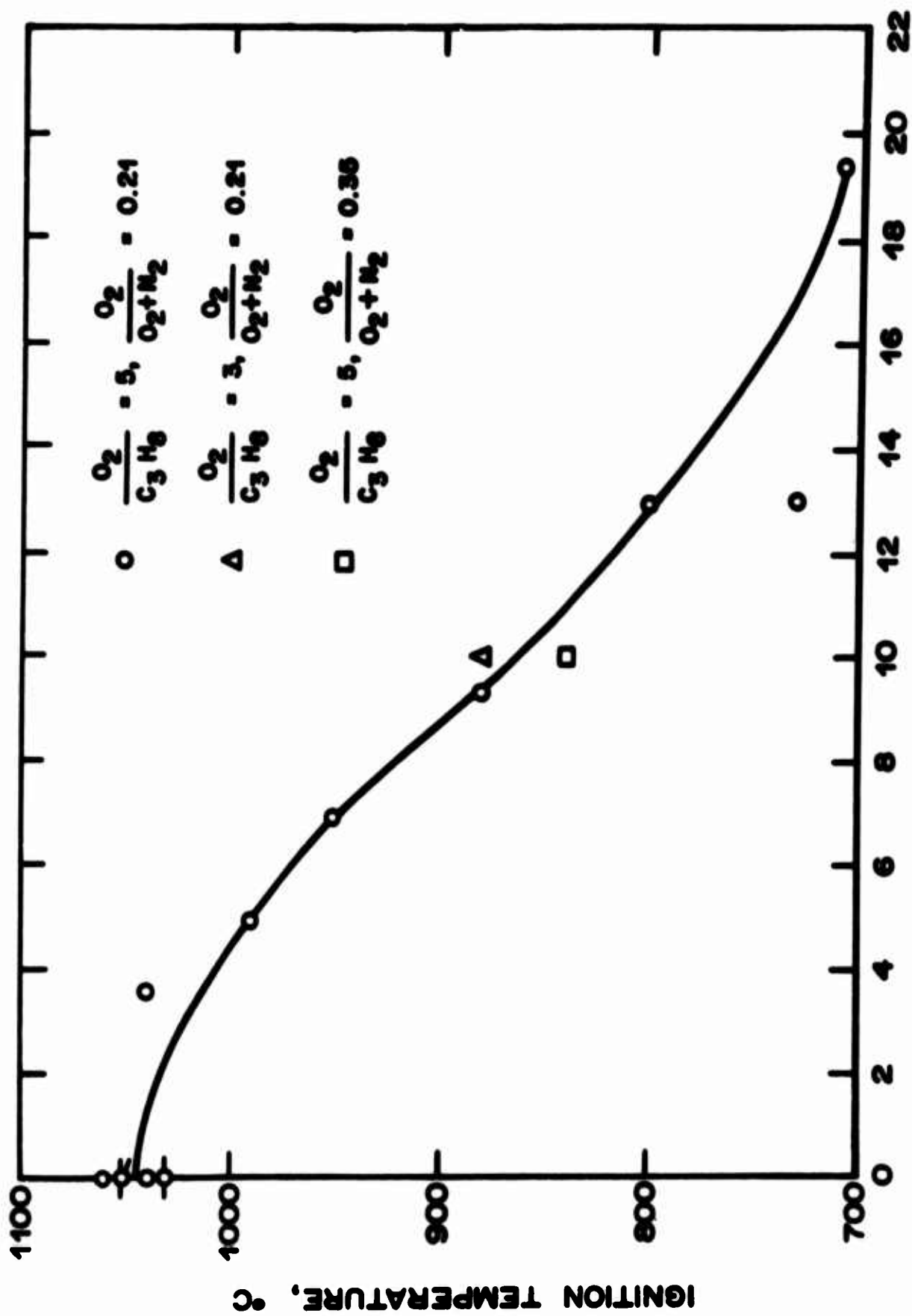


Figure 3. Effect of SiCl<sub>4</sub> on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

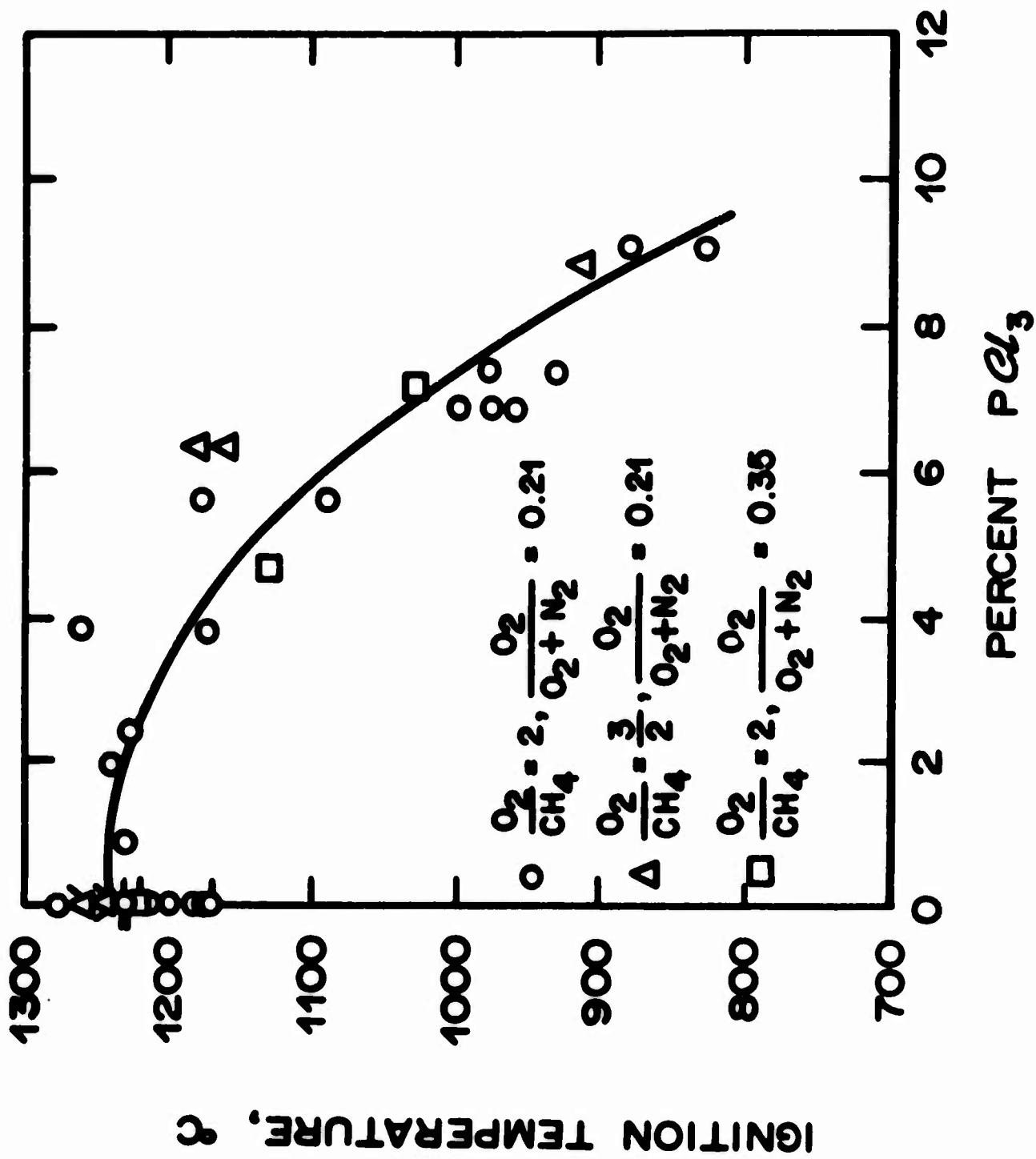


Figure 4. Effect of PCl<sub>3</sub> on the Hot-Wire Ignition Temperature of Methane-Air Mixtures.

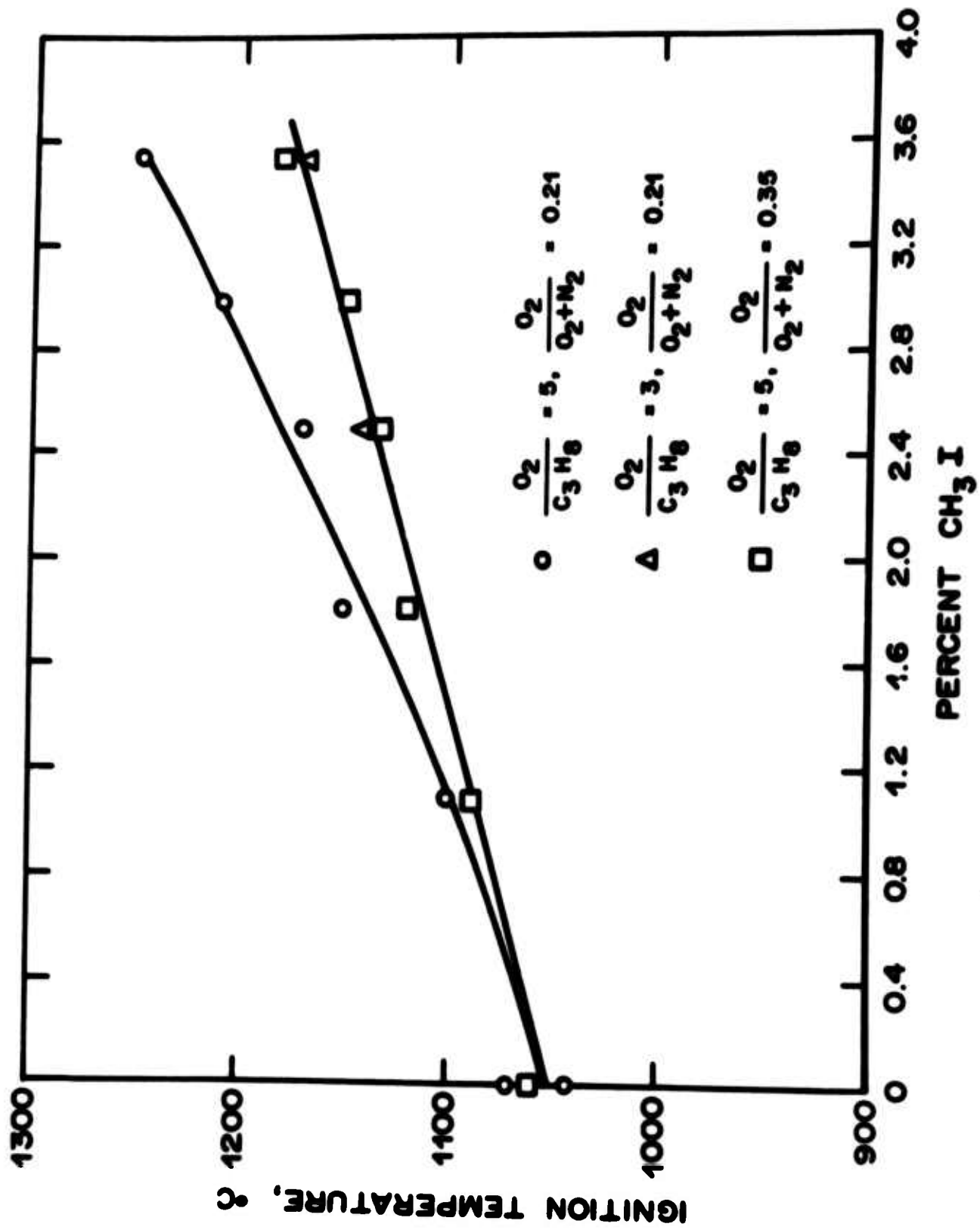


Figure 5. Effect of  $CH_3I$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

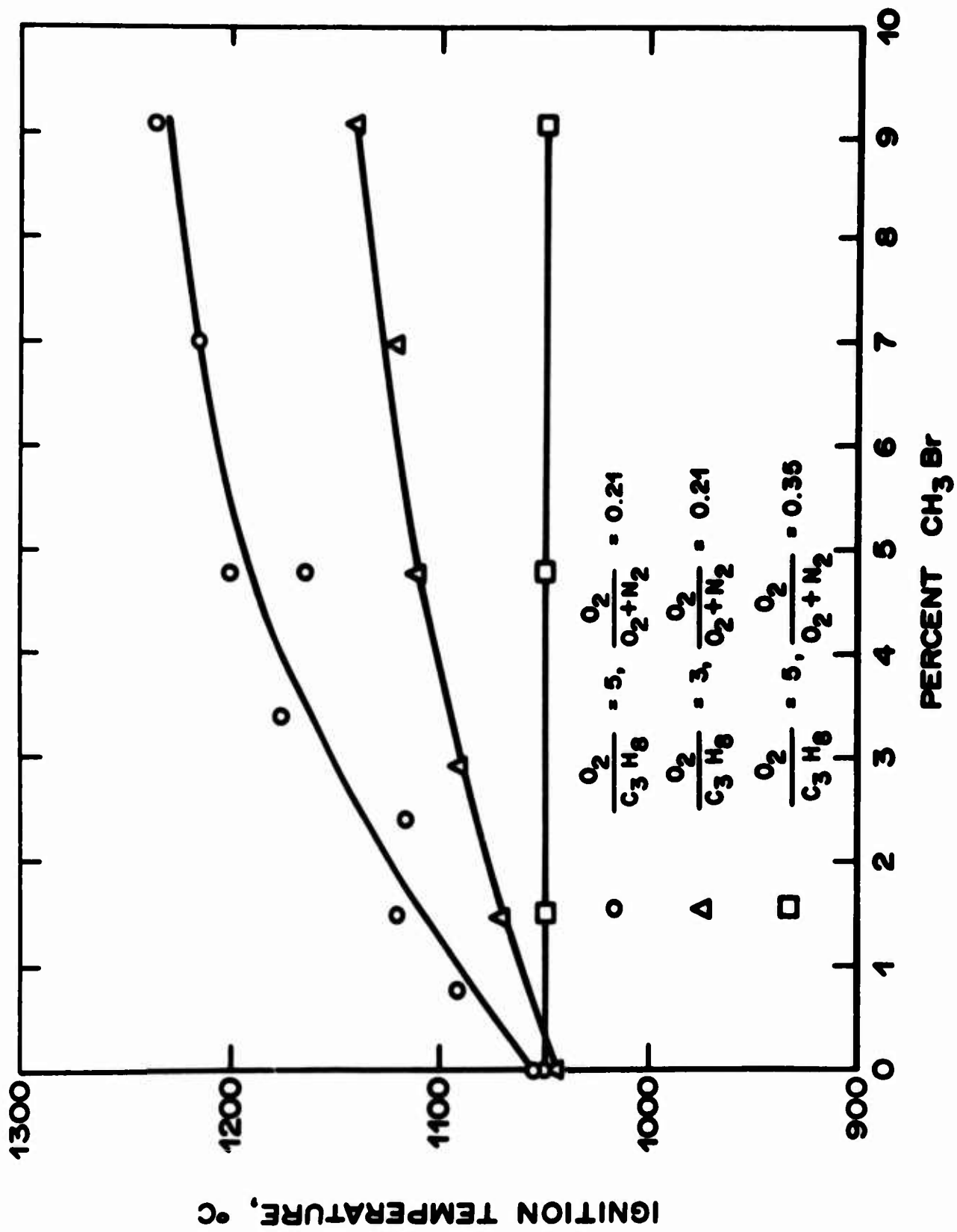


Figure 6. Effect of CH<sub>3</sub>Br on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

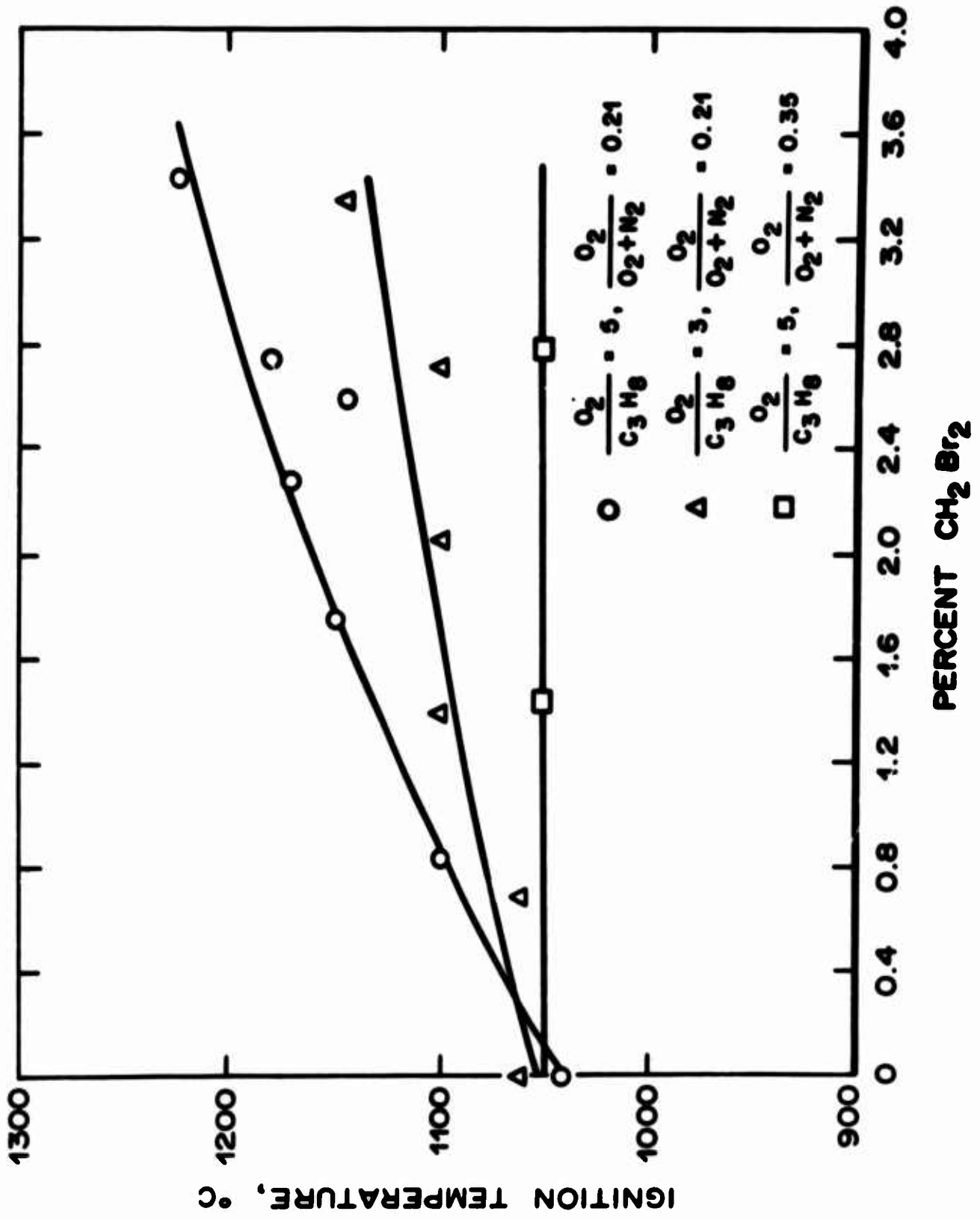


Figure 7. Effect of CH<sub>2</sub>Br<sub>2</sub> on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

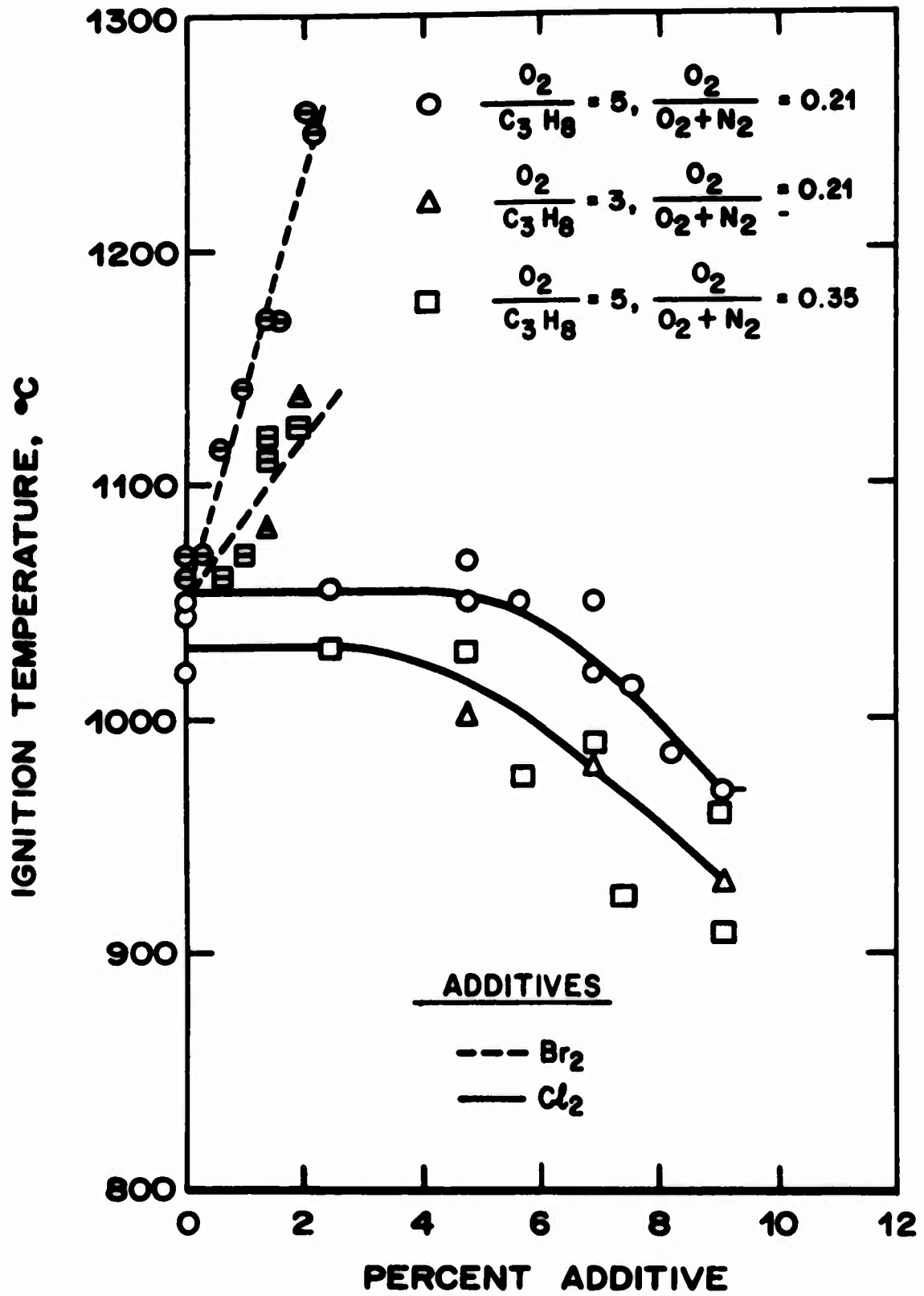


Figure 8. Effect of Br<sub>2</sub> and Cl<sub>2</sub> on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.



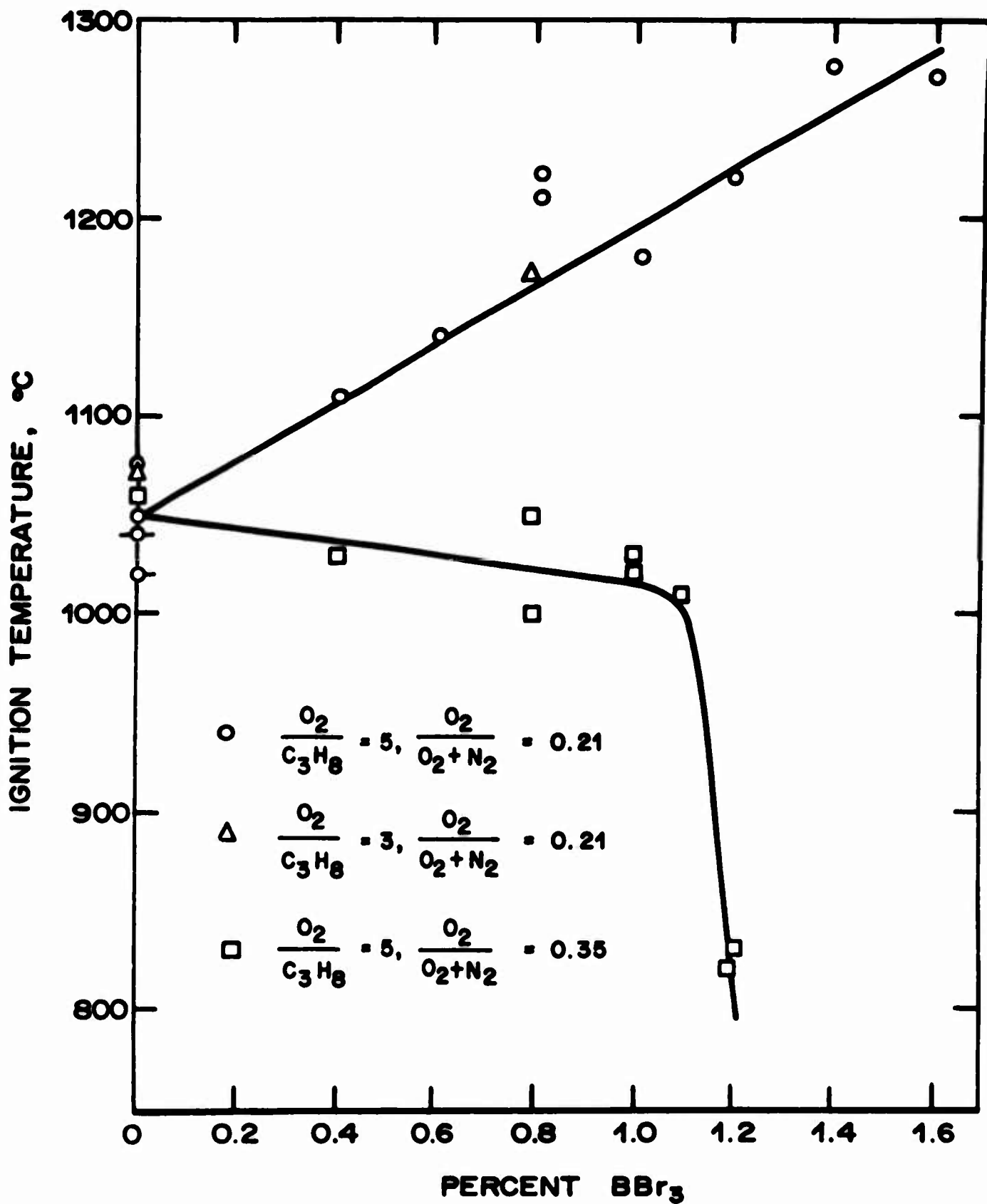


Figure 9. Effect of  $\text{BBr}_3$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

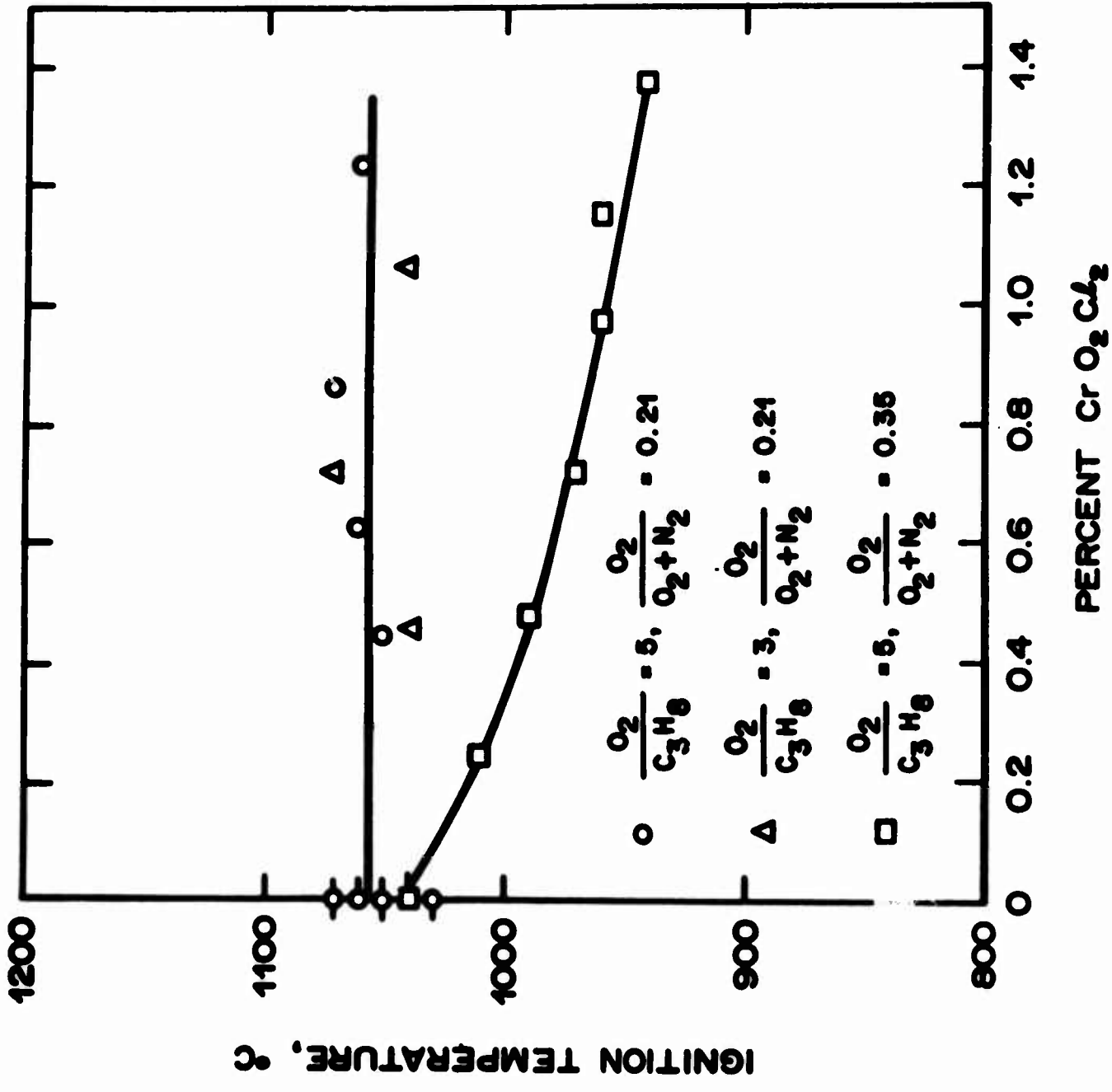


Figure 10. Effect of  $\text{CrO}_2\text{Cl}_2$  on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

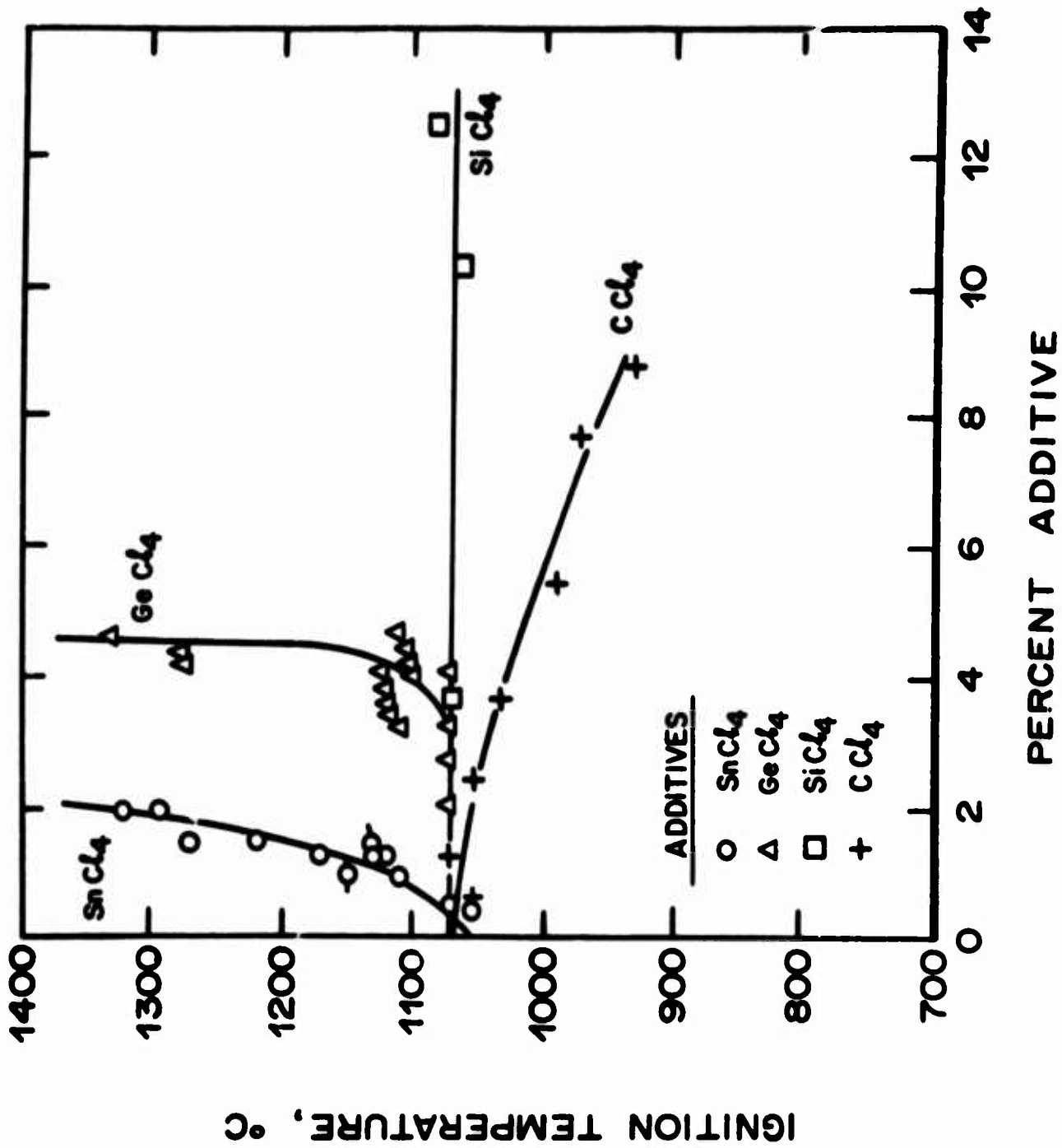


Figure 11. Effect of Group IVa Chlorides on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

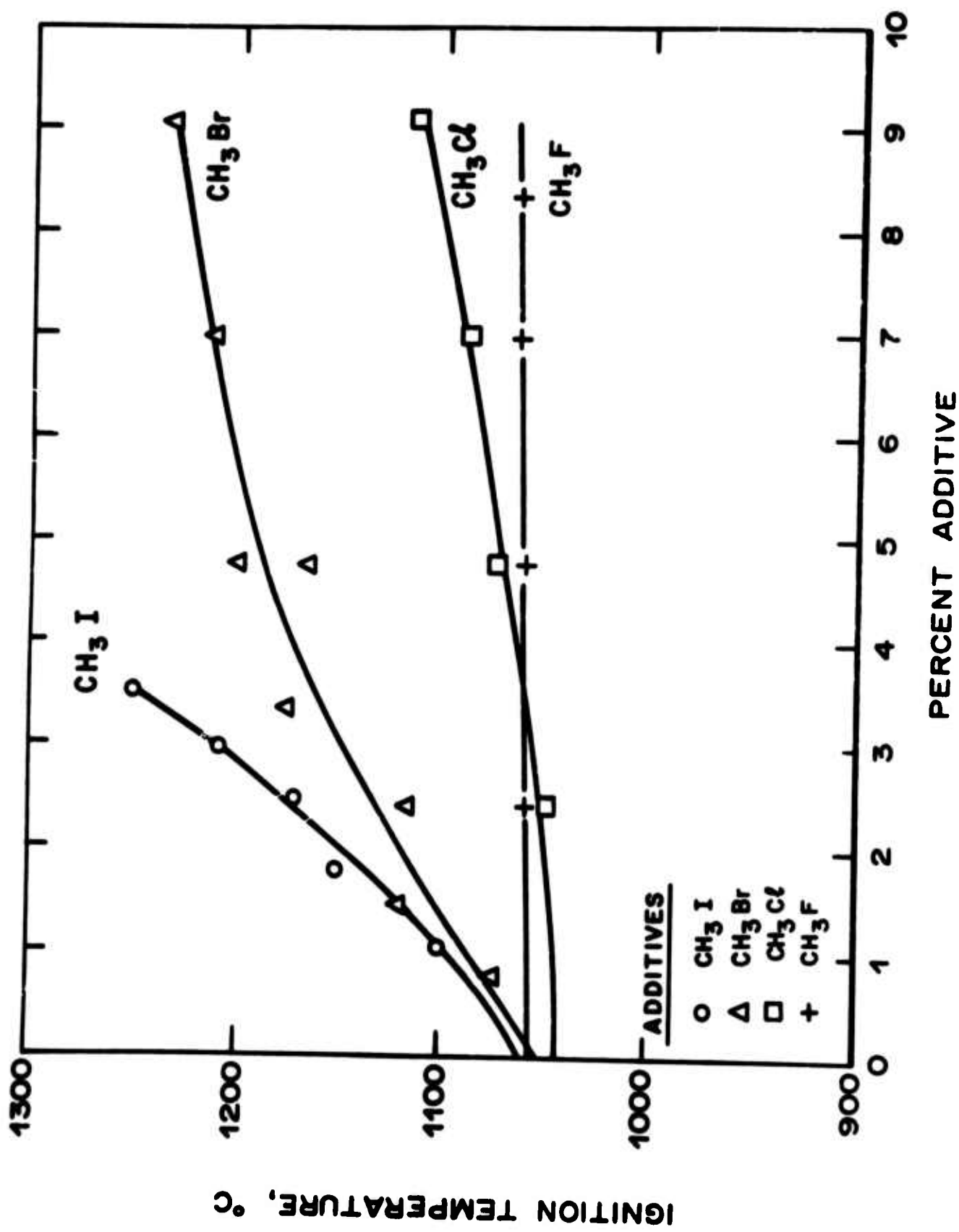


Figure 12. Effect of Methyl-Halides on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.

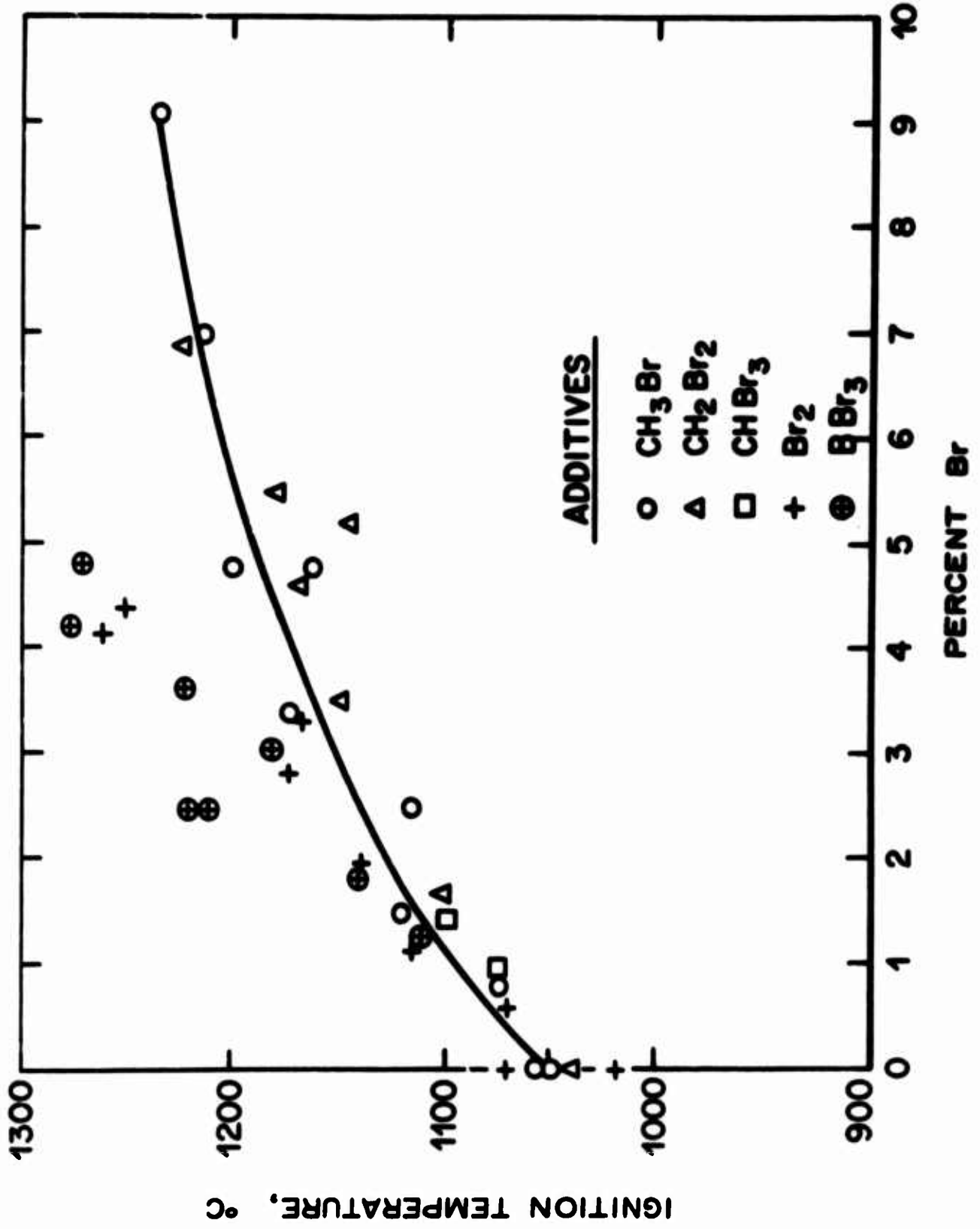


Figure 13. Effect of Bromine Atom Addition on the Hot-Wire Ignition Temperature of Propane-Air Mixtures.