Effect of Pressure and Oxidant Concentration on Autoignition Temperatures of Selected Combustibles in Various Oxygen and Nitrogen Tetroxide Atmospheres

ALDO L. FURNO, AGNES C. IMHOF, and JOSEPH M. KUCHTA
Explosives Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa. 15213

Minimum autoignition temperatures were determined at various pressures from 25 to 740 mm. of Hg for a number of combustibles in air, oxygen, and nitrogen tetroxide with either nitrogen or helium diluents. The combustibles included hydrogen, *n*-butane, *n*-hexane, *n*-heptane, 1-chlorobutane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, methylene chloride, hydrazine, mono-methylhydrazine, and unsymmetrical dimethylhydrazine. Lower autoignition temperatures were obtained in nitrogen tetroxide than in oxygen with all the combustibles except *n*-heptane and 1-chlorobutane. Generally, the AIT values for most of the combustibles increased slightly with decreased pressure and oxidant concentration to some critical value, and then they tended to increase noticeably. They also varied with the size of the reaction vessel.

MINIMUM autoignition temperature (AIT) data are insufficient or unavailable for many liquid rocket fuels in various oxidant-diluent atmospheres and over wide ranges of pressure. Similar data are also lacking in such atmospheres for other combustibles, including organic solvents, that are currently used in related space-flight applications. Data of this type are useful in defining hazardous situations that might occur when the combustibles are heated in various environments. Accordingly, the present work was conducted to obtain this information for 12 selected combustibles in atmospheres containing such oxidants as air, oxygen, and nitrogen tetroxide and a diluent like nitrogen or helium. The combustibles included rocket-type fuels—hydrogen (gas), hydrazine, mono-methylhydrazine, and unsymmetrical dimethylhydrazine—halogenated hydrocarbon-type solvents—1-chlorobutane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, and methylene chloride—and conventional hydrocarbon fuels (or solvents)—*n*-butane, *n*-hexane, and *n*-heptane.

Ordinarily, the autoignition temperatures of hydrocarbons and many other combustibles decrease with increasing initial pressure (*7, 14*); however, the pressure effect may vary for combustibles that behave like *n*-propyl nitrate and some hydrocarbon lubricants at elevated pressures (*14*). Similarly, as noted in the present study, autoignition temperatures do not always decrease when the oxidant concentration is increased. With such oxidants as nitrogen tetroxide, the results can depend greatly upon the vessel surface condition (*10*). The effects on vessel surface and size tend to be most pronounced at reduced oxidant concentrations or pressures (*6*) where the ignition quenching distances are ordinarily greater. In the present study, the effects displayed by such variables depended upon the fuel and oxidant employed. The data presented here were obtained under quiescent conditions using the heated vessel method.

EXPERIMENTAL

Table I lists some of the physical properties of the combustibles with flammability limit data. The table shows that several of the combustibles form flammable vapor-air mixtures over a wide range of fuel concentrations. They also can be expected to form flammable mixtures in nitrogen tetroxide atmospheres. The nitrogen tetroxide concentrations referred to in this report are the combined equilibrium compositions of nitrogen tetroxide–dioxide and-oxide (NO_2*)

Table I. Physical Properties of Selected Combustibles

						Flammability Limits in Air 25° C.[b]	
	Chemical Formula	Molecular Weight	Sp. Gr.[a,b] Air = 1	Boiling Point[c], ° C.	Flash Point[a], ° C.	Lower, Vol. %	Upper, Vol. %
Hydrogen	H_2	2.02	0.07	–252.8	...	4.0	75
n-Butane	C_4H_{10}	58.12	2.01	–0.6	...	1.8	8.4
n-Hexane	C_6H_{14}	86.17	2.98	69.0	–21.7	1.2	7.4
n-Heptane	C_7H_{16}	100.20	3.46	98.4	–3.9	1.05	6.7
1-Chlorobutane	C_4H_9Cl	92.57	3.2	78.0	–9.4	1.8	10 (100° C.)
1,2-Dichloroethane	$C_2H_4Cl_2$	98.97	3.4	83.5	13.3	...	...
1,1,1-Trichloroethane	$C_2H_3Cl_3$	133.42	4.6 (Calcd.)	74.1	...	...	...
Trichloroethylene	C_2HCl_3	131.40	4.5	87.0	32.2	12 (30° C.)	40 (70° C.)
Methylene chloride	CH_2Cl_2	84.93	2.9	40.0	...	...	...
Hydrazine	N_2H_4	32.05	1.11	113.5	52.2	4.7	100
Monomethylhydrazine	CH_3NHNH_2	46.08	1.59	87.5	21.1	4	...
Unsymmetrical dimethylhydrazine	$(CH_3)_2NNH_2$	60.08	2.08	63.0	1.1	2.0	95

[a] Data from reference (*8*). [b] Data from reference (*14*). [c] Data from reference (*4*).

that existed at the particular initial temperature and pressure. According to the literature (*13*), an equilibrium mixture of these gases at 1 atm. pressure contains 90 volume % of nitrogen dioxide at 100° C. and greater concentrations of the oxide than the dioxide above approximately 430° C. Most of the determinations described here required test temperatures above 100° C.

The Bureau of Mines I-8 autoignition temperature apparatus, which is an ASTM type (*1*) equipped with a 200-cc. borosilicate flask, was used to obtain part of the data of this work. The determinations were made according to the ASTM procedure (*1*) with the reaction vessel essentially open (loose cover), except for those made at reduced pressures, and ignition was evidenced by the appearance of flame. However, a vessel of the above size is not always suitable for making such determinations at reduced pressures where wall effects can be great. Furthermore, AIT's for some combustibles may vary greatly with vessel size even at atmospheric pressure. Therefore, an apparatus having a larger reaction vessel was also used. Figure 1 shows a drawing of this apparatus, which was equipped with a 4900-cc. cylindrical stainless steel reaction vessel. Thermocouples (TC's) were positioned inside and outside the vessel for measuring the gas mixture and vessel temperatures, respectively. A pressure transducer, whose output was fed to a pen-oscillograph recorder, was used to measure the mixture pressure and the pressures developed during reaction. In all the determinations, the oxidant or oxidant-diluent mixture was introduced through the gas inlet port and allowed to heat to the vessel temperature. Subsequently, a measured volume of liquid or gaseous fuel at room temperature (25° ± 5° C.) was injected through a rubber septum into the vessel using a hypodermic syringe, and ignition was determined by the occurrence of the sudden pressure rise that was detected by the pressure transducer. The fuel volume and vessel temperature were varied to obtain the minimum AIT value at each pressure condition used. The mixture or total pressures referred to in this work are those after fuel injection and just prior to the ignition event. Since conditioning the vessel surface with a previous ignition ordinarily gives the lowest and most reproducible AIT values, this practice was used in all the determinations.

Generally, the AIT's were not very sensitive to fuel concentration except at near-limiting concentrations for ignition where they increased noticeably. This behavior is not unusual since the mixture compositions formed after fuel injection were not uniform, particularly in the case of the liquid fuels. In practical applications, nonuniform mixtures are encountered more often than uniform mixtures. The volume of liquid fuel used to obtain the minimum AIT value in air was several times greater than that required theoretically for complete combustion of the particular fuel; the optimum volumes for the gaseous fuels, hydrogen and *n*-butane, were near-stoichiometric quantities. With air at 1 atm. pressure, the optimum fuel volumes in the 200-cc. vessel were between about 0.05 and 0.15 cc. for the liquid fuels; the corresponding volumes in the 4900-cc. vessel were about 20 to 30 times greater. With oxygen or NO_2*, the optimum fuel volumes were generally equivalent to or less than the theoretical quantities required for complete combustion of the fuels in these oxidants.

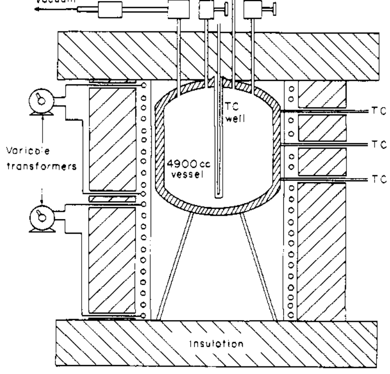

Figure 1. Autoignition temperature apparatus with 4900-cc. cylindrical steel reaction vessel

Minimum Autoignition Temperatures of Combustibles in Air, Oxygen, and NO_2* at Atmospheric Pressure. Table II lists the minimum autoignition temperatures (AIT's) obtained for the various combustibles in air, oxygen, and NO_2* at atmospheric pressure in the 200-cc. glass flask and the 4900-cc. steel vessel. Hydrogen was examined only in the small vented vessel because the pressure rises in hydrogen-oxygen explosions could be as high as about 20 times the initial pressure; the larger vessel was not designed to withstand such pressures at elevated temperatures. Generally, lower AIT's were found when the larger reaction vessel was used. One exception was 1,2-dichloroethane, whose values in air and oxygen were significantly higher in the larger vessel. However, results for this combustible were difficult to reproduce and appeared to depend greatly upon vessel material and vessel surface condition; conditioning the vessel surface with previous ignitions was particularly important in determinations with this material. The reproducibility of most of the AIT data of this work was ±2° C. at the lower temperatures (~200° C.) and ±10° C. at the higher temperatures (~500° C.).

As in most AIT determinations, the time required for autoignition increased with decreasing temperature. Thus, the minimum AIT data presented here are applicable to autoignitions with maximum ignition delays or fuel contact times. In oxygen at 1 atm. pressure, the ignition delays were at least about 10 seconds in the 4900-cc. vessel for each of the combustibles; the corresponding values were usually lower in the smaller vessel (200 cc.) or at reduced pressures, primarily because of the higher temperatures required for autoignition. At a given temperature, the ignition delays tended to be lower in oxygen than in air, but higher than those in NO_2*. The maximum explosion pressures that were measured for the ignitions in the larger vessel were generally at least about 1½ times the initial mixture pressure, depending upon the composition and concentration of the fuel and oxidant. They were noticeably higher in oxygen or NO_2* than in air atmospheres, since the optimum fuel volumes for obtaining the minimum AIT's in the former oxidants were larger and, at the same time, more near-stoichiometric. For stoichiometric fuel vapor-air mixtures, the ratio of the maximum explosion pressure to the initial pressure can be as high as about 8 to 1 under ideal conditions—e.g., homogeneous mixtures and large diameter vessels. Similarly, the maximum rates of pressure rise can be of the order of 1000 p.s.i. per second for such explosions in air and much higher for those in oxygen or NO_2*; here, however, they were much lower in all cases since the mixture compositions and other test conditions were not ideal for maximum heat release.

The minimum AIT's of all combustibles were lower in oxygen than in air, although the variation was <20° C. for hydrogen and for *n*-butane, *n*-hexane, *n*-heptane, and some of the halogenated hydrocarbons (200- or 4900-cc. vessel). With the 200-cc. vessel, hydrogen and methylene chloride gave the highest autoignition temperatures in air and oxygen (>500° C.). With the 4900-cc. vessel, the AIT values in oxygen were between 200° and 280° C. for the three paraffins and 1-chlorobutane; the corresponding values

Table II. Minimum Autoignition Temperatures (AIT's) of Combustibles in Air, Oxygen, and Nitrogen Tetroxide (NO_2*)[a] Atmospheres at Atmospheric Pressure

Combustible	Minimum AIT, ° C. Air 200	Air 4900	Oxygen 200	Oxygen 4900	Nitrogen Tetroxide 200	Nitrogen Tetroxide 4900
	Vessel Volume, cc.					
Hydrogen	550	...	542	...	454	...
n-Butane	372	288	286	278	272	270
n-Hexane	234[b]	234	225[c]	218	...	216
n-Heptane	232	204	226	202	256	214
1-Chlorobutane	250	240	246	235	...	248
1,2-Dichloroethane	438	476	428	470	...	282
1,1,1-Trichloroethane	486	458	470	418	...	270
Trichloroethylene	420[c]	416	404	402	...	200
Methylene chloride	615[c]	556	534	490	...	276
Hydrazine	270	178	150	98	Hypergolic	
Monomethylhydrazine	184	150	...	72	Hypergolic	
Unsymmetrical dimethylhydrazine	252	226	224	184	Hypergolic	

[a] NO_2* = Equilibrium mixture of N_2O_4 and NO_2. [b] Data from reference (*15*). [c] Data from reference (*14*).

for the other halogenated hydrocarbons were between 400° and 500° C. On the basis of these and other data in the literature (*14*), the chlorinated hydrocarbons of ethane, butane, and ethylene tend to have lower autoignition temperatures than their parent hydrocarbons. The lowest AIT's in oxygen were obtained with the fuels hydrazine (98° C.) and monomethylhydrazine (72° C.) in the 4900-cc. vessel; the corresponding values in air were about 80° C. higher. Although the hydrazine fuel containing one methyl group gave lower AIT values than hydrazine, the opposite behavior occurred with the one containing two methyl groups (UDMH).

Lower autoignition temperatures were obtained in NO_2* than in oxygen with all the combustibles except *n*-heptane and 1-chlorobutane. The AIT values for the other four halogenated hydrocarbons and hydrogen were at least about 100° C. lower in NO_2* than in oxygen. The three hydrazine fuels were hypergolic with NO_2* at room temperature—that is, they reacted after being injected into this oxidant at room temperature and produced sufficient heat to effect ignition.

Variation of Autoignition Temperatures with Oxidant and Diluent Concentration at 1 Atm. The minimum autoignition temperatures of hydrogen, *n*-hexane, and *n*-heptane in oxygen were relatively unaffected by dilution with as much as 79 volume % nitrogen or helium (21% oxygen) at 1 atm. pressure (Figure 2). Also, the available data for *n*-hexane show only a slight increase of AIT as the oxygen content is decreased from 21 to 5 volume %. The autoignitions observed at such low oxygen concentrations may have been a "cool" flame phenomenon since at least 11.9% oxygen is reported to be required for flame propagation with homogeneous *n*-hexane vapor–air mixtures at 25° C. and atmospheric pressure (*3*); mixtures were not homogeneous in the present AIT work. In comparison, the AIT of *n*-butane increased when the oxygen concentration was less than approximately 50%; also, nitrogen caused a greater change than did helium, but vessel size or surface was a factor here. The effect of diluent and oxygen concentration was practically negligible when the 4900-cc. vessel was substituted for the 200-cc. vessel.

In NO_2*, the AIT's of hydrogen and *n*-butane varied little when diluted with nitrogen or air to about 25 volume % NO_2*. However, the values for *n*-heptane decreased initially and then increased with increased diluent. Figure 3 shows the data obtained using the smaller vessel. With further air dilution to zero % NO_2*, the AIT's of hydrogen and *n*-butane rose noticeably, whereas those for *n*-heptane displayed a maximum at 5% NO_2* and then decreased sharply.

Most of the AIT data for the five halogenated hydrocarbons also displayed greater diluent effect at low oxidant concentrations. Figures 4 and 5 show the data for these combustibles in various oxygen-nitrogen and NO_2*-nitrogen mixtures, respectively, using the 4900-cc. vessel. With oxygen as the oxidant, the AIT's increased markedly when the oxygen concentration was decreased below approximately 20 volume % except for 1-chlorobutane; 1-chlorobutane displayed little diluent effect over oxygen concentrations ranging from 5 to 100%. The lowest values were obtained for 1-chlorobutane and the highest values for methylene chloride at all oxygen concentrations. Essentially the same

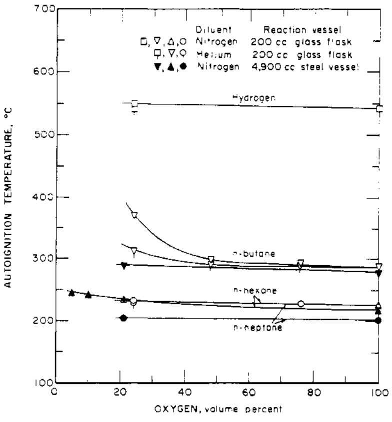

Figure 2. Minimum autoignition temperatures of hydrogen, *n*-butane, *n*-hexane, and *n*-heptane in various oxygen-nitrogen or oxygen-helium mixtures at 1 atm.

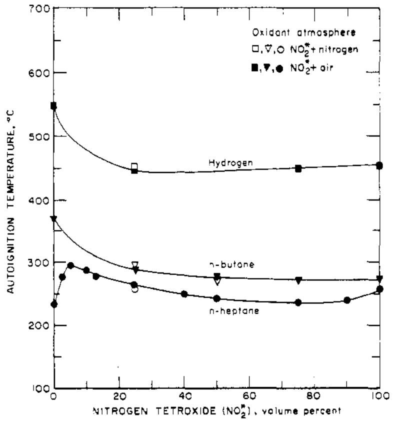

Figure 3. Minimum autoignition temperature of hydrogen, *n*-butane, and *n*-heptane in various nitrogen tetroxide–nitrogen or nitrogen tetroxide–air mixtures at 1 atm. (200-cc. borosilicate glass flask)

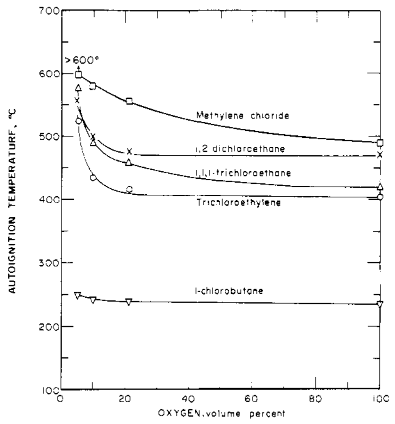

Figure 4. Minimum autoignition temperatures of five halogenated hydrocarbons in various oxygen-nitrogen mixtures at 1 atm. (4900-cc. steel vessel)

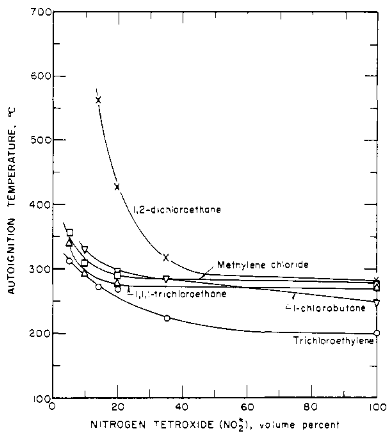

Figure 5. Minimum autoignition temperatures of five halogenated hydrocarbons in various nitrogen tetroxide (NO$_2$*)–nitrogen mixtures at 1 atm. (4900-cc. steel vessel)

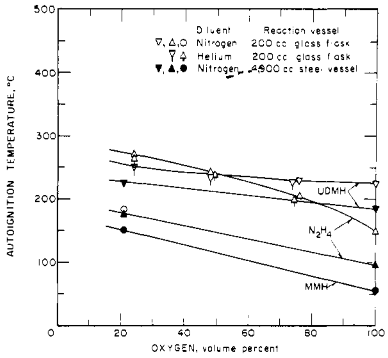

Figure 6. Minimum autoignition temperatures of hydrazine (N$_2$H$_4$), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH)in various oxygen-nitrogen mixtures at 1 atm.

results as shown in Figure 4 were obtained with helium as the diluent.

The diluent effect of nitrogen was pronounced for 1,2-dichloroethane and trichloroethylene at NO$_2$* concentrations less than about 35% (Figure 5). The critical NO$_2$* concentration for the other halogenated hydrocarbons was approximately 20%. With this oxidant, the lowest AIT values occurred with trichloroethylene and the highest values with 1,2-dichloroethane, whose ignitions were the most sensitive to diluent concentration.

Diluent effect data for the hydrazine fuels were limited to oxygen-nitrogen or helium mixtures containing 21 to 100% oxygen (Figure 6). The AIT's increased with the amount of dilution, particularly for hydrazine and monomethylhydrazine, but were not sensitive to the type of diluent. However, vessel size or surface was again a factor in that the samples tested in the larger vessel gave noticeably lower AIT's. UDMH in oxygen had the highest AIT values of the hydrazine fuels whereas, in air or comparable atmospheres, hydrazine had the highest value (200-cc. vessel). As the spontaneous decomposition temperature of hydrazine is about 160° C. (*2*) compared with about 400° C. (*9, 12*) for UDMH, it is not surprising that the greater variation of AIT occurs with the less thermally stable material.

Variation of Autoignition Temperatures with Mixture Pressure. Table III lists the minimum autoignition temperatures obtained for the combustibles in air, oxygen, and NO$_2$* atmospheres at various mixture pressures ranging from 25 to 740 mm. of Hg and for both 200- and 4900-cc. vessels. The variation of AIT with pressure depended upon the fuel and oxidant, as well as the size of the reaction vessel. Generally the variation was similar to that observed in varying the oxidant percentage. The AIT's increased slightly with decreased pressure to some critical value, below which they tended to increase abruptly. For each fuel type, the critical pressures were usually higher in the smaller vessel (Table III). Figures 7, 8, 9, and 10 are based on data obtained from the determinations in the 4900-cc. vessel.

The AIT's increased noticeably below a critical pressure of approximately 100 mm. of Hg for *n*-hexane and *n*-heptane and below 400 mm. of Hg for *n*-butane in air and oxygen atmospheres (Figure 7). Normal butane displayed the greatest pressure dependence; this is probably attributed to a transition from "cool" flame ignition at the lower temperatures (higher pressures) to ordinary or "hot" flame ignition at the higher temperatures (lower pressures); Kane, Chamberlain, and Townend (*5*) reported the transition temperature to be 370° C. The AIT's were consistently higher in air and in the smaller vessel (Table III). The critical pressures for these fuels in NO$_2$* were about 300 mm. of Hg for *n*-butane and 400 mm. of Hg for the other two paraffins. Figure 8 shows that the AIT values for *n*-hexane and *n*-heptane are lower in oxygen than in NO$_2$*, but for *n*-butane they are lower in NO$_2$*.

Similar data are compared in Figure 9 for two of the halogenated hydrocarbons in oxidant atmospheres of air, oxygen, and NO$_2$*. The results for 1,2-dichloroethane in air and oxygen varied only slightly with decreased pressure to at least 50 mm. of Hg. Corresponding results for 1-chlorobutane, having lower AIT's, indicated a critical pressure of about 100 mm. of Hg in both air and oxygen. For both combustibles with NO$_2$*, the pressure dependence of the AIT's was similar to that noted above for the hydrocarbon fuels. The results for 1,2-dichloroethane in NO$_2$* and oxygen differ little at 25 mm. of Hg as compared with the great difference observed at 740 mm. of Hg. This behavior may be attributed partly to vessel surface effects, since the autoignition temperatures of this combustible were difficult to reproduce.

The AIT data for UDMH in air and oxygen indicated that this fuel had critical pressures between 100 and 200 mm. of Hg (Figure 10). In comparison, the data for the less thermally stable fuels, hydrazine and mono-

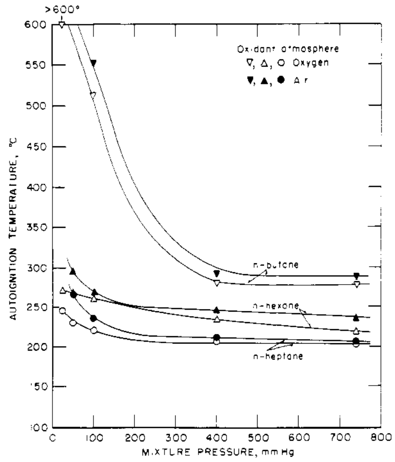

Figure 7. Autoignition temperature vs. mixture pressure for *n*-butane, *n*-hexane, and *n*-heptane in air and oxygen atmospheres (4900-cc. steel vessel)

Table III. Minimum Autoignition Temperatures (AIT's) of Combustibles in Air, Oxygen, and Nitrogen Tetroxide (NO_2*)[a] Atmospheres at Various Mixture Pressures

Combustible	Oxidant	Vessel Volume, Cc.	Minimum AIT, ° C. Mixture Pressure, Mm. of Hg 740	400	100	50	25
n-Butane	Air	200	372	442	...	...	>600
		4900	288	292	552	...	>600
	Oxygen	200	286	264	530	...	>600
		4900	278	280	512	...	>600
	NO_2*	200	272	275[b]	364	...	...
		4900	270	266	314	440	...
n-Hexane	Air	4900	234	244	268	296	...
	Oxygen	4900	218	234	260	268	270
	NO_2*	4900	216	238	316	364	426
n-Heptane	Air	200	232	470	...	...	>600
		4900	204	210	234	264	...
	Oxygen	200	226	220	490	...	>600
		4900	202	206	220	230	246
	NO_2*	200	256	265[b]	320	...	...
		4900	214	230	300[b]	342	...
1-Chlorobutane	Air	4900	240	246	264	302	...
	Oxygen	4900	235	238	246	252	260
	NO_2*	4900	248	272	318	362	426
1,2-Dichloroethane	Air	4900	476	484	500	494	...
	Oxygen	4900	470	478	476	476	500
	NO_2*	4900	282	290	348	414	470
Hydrazine	Air	200	270	292	...	...	...
		4900	178	245[b]	432	474	...
	Oxygen	200	150	216	302	350[b]	450
		4900	98	110	330	390[b]	424
	NO_2*	200	Hypergolic	...	Hypergolic	...	...
Monomethylhydrazine	Air	4900	150	190[b]	298	346	398
	Oxygen	4900	72	85[b]	168	268	344
	NO_2*	200	Hypergolic	...	...	...	...
UDMH	Air	200	252	254	...	...	...
		4900	226	245[b]	264	300	...
	Oxygen	200	224	230[b]	258	300[b]	354
		4900	184	205[b]	250	260[b]	270
	NO_2*	200	Hypergolic	...	Hypergolic	...	...

[a] NO_2* = equilibrium mixture of N_2O_4, NO_2, and NO. [b] Interpolated values.

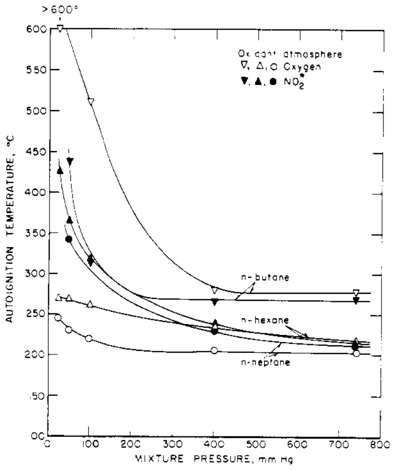

Figure 8. Autoignition temperature vs. mixture pressure for *n*-butane, *n*-hexane, and *n*-heptane in oxygen and nitrogen tetroxide (NO_2*) atmospheres (4900-cc. steel vessel)

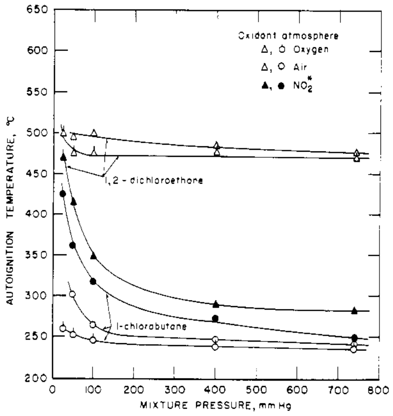

Figure 9. Autoignition temperature vs. mixture pressure for 1-chlorobutane and 1,2-dichloroethane in air, oxygen, and nitrogen tetroxide (NO_2*) atmospheres (4900-cc. steel vessel)

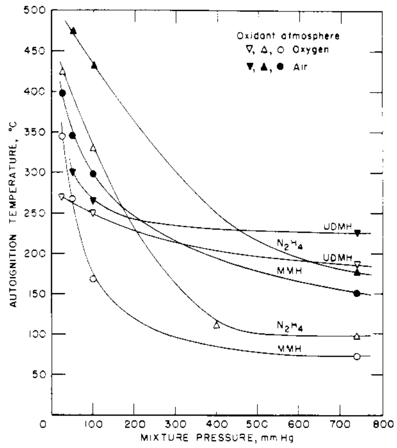

Figure 10. Autoignition temperature vs. mixture pressure for hydrazine (N_2H_4), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) in air and oxygen atmospheres (4900-cc. steel vessel)

methylhydrazine, were noticeably more pressure dependent; their critical pressure appeared to be about 400 mm. of Hg. Although the AIT's of these two fuels were much lower than those of UDMH at atmospheric pressure, at reduced pressure they were higher. This behavior is analogous to that observed for hydrazine and UDMH (Figure 6) where the oxygen concentration was varied at atmospheric pressure in the 200-cc. vessel. Thus, the order of their oxidative stability changes with decreasing pressure and oxidant concentration and cannot be predicted from their order of thermal stability in oxygen at 1 atm. pressure.

Since the observed pressure effect on the AIT's of the combustibles in NO_2^* may be attributed partly to the change in the NO_2^* equilibrium, the AIT data in Figures 8 and 9 were plotted as a function of the NO_2/NO mole ratio expected for equilibrium mixtures (*13*) at the various pressures and temperatures. Figure 11 shows that the AIT's did not vary greatly when the NO_2/NO ratio was greater than about 4; below this ratio and correspondingly lower total pressures, they increased greatly as the NO concentration increased. However, essentially the same behavior is reflected by the data in Figures 3 and 5 with various NO_2^*-nitrogen mixtures at 1 atm. Therefore, the AIT's of these combustibles appear to depend mostly on the partial pressure or percentage of the NO_2^* present in the oxidant atmosphere.

Dependence of Autoignition Temperature upon Total Mixture Pressure *vs.* Oxidant Partial Pressure. According to Semenov (*11*), the critical pressure for thermal ignition of a combustible mixture is an exponential function of temperature and dependent upon the order of the reaction. As a first approximation, a linear relationship should exist between the logarithm of the total pressure of the mixture (P_t) and the reciprocal of the autoignition temperature ($1/T$) over at least a limited temperature range. Except for monomethylhydrazine in oxygen, no such relationship was evident for the combustibles in air and oxygen. Only the data obtained for ignitions in the larger vessel were considered, since wall effects could have been predominant for the ignitions in the smaller vessel. In comparison, the results which were obtained for four of the combustibles in NO_2^* at various pressures (25 to 740 mm. of Hg) showed an exponential temperature dependence. Figure 12 shows that the plot of log P_t *vs.* $1/T$ is linear for monomethylhydrazine in oxygen and for *n*-hexane, *n*-heptane, 1-chlorobutane, and 1,2-dichloroethane in NO_2^*. The data for the latter four fuels in NO_2^* are grouped together and the slopes of their curves (5500 to 7500 mm. of Hg per $°K.^{-1}$) are more than twice as great as that for the hydrazine fuel in oxygen. Thus, the ignition process was less temperature dependent for the hydrazine fuel.

The influence of mixture total pressure and oxygen percentage was compared by plotting the autoignition temperatures of the combustibles as a function of the oxidant partial pressure (P_{O_2}). Again, only the larger vessel data were used. Figure 13 shows a plot of log AIT *vs.* log P_{O_2} for the data obtained with *n*-hexane, *n*-heptane, 1,2-dichloroethane, and monomethylhydrazine in air and oxygen at various pressures and in various oxygen-nitrogen mixtures at 1 atm. The data for *n*-butane, hydrazine, and UDMH are not shown since they displayed noticeable inconsistencies in such a plot; also, those for 1-chlorobutane are not shown since they were comparable with those of *n*-hexane. In Figure 13, the dependence of the AIT's upon oxygen partial pressure between 10 and 740 mm. of Hg was approximately the same for the data at various mixture pressures and for those at various oxygen percentages. This behavior has also been observed in the autoignition of a hydrocarbon jet fuel at reduced and elevated pressures (*6*). Here however, only the autoignition temperatures of monomethylhydrazine varied noticeably with decreasing oxygen concentration. According to the slopes of the curves in

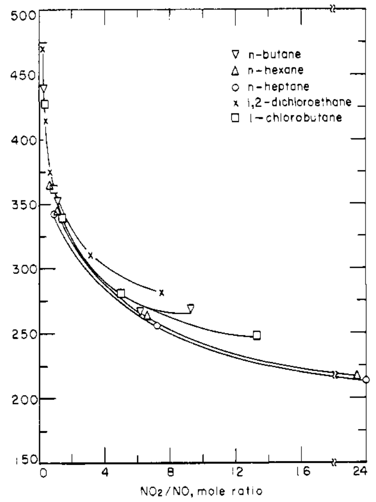

Figure 11. Autoignition temperatures *vs.* calculated ratio of NO_2/NO for autoignitions of combustibles in nitrogen tetroxide (NO_2^*) at various mixture pressures (AIT data from Figures 8 and 9)

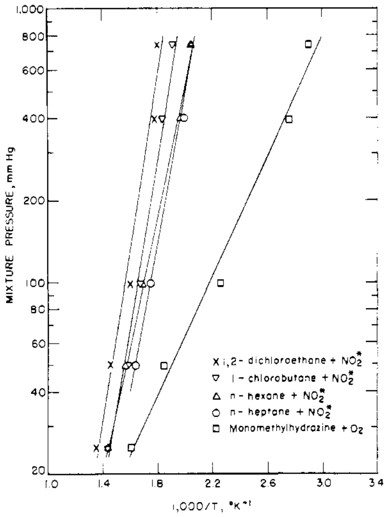

Figure 12. Logarithm mixture pressure *vs.* reciprocal autoignition temperature for various combustibles in nitrogen tetroxide (NO_2^*) or oxygen atmospheres (4900-cc. steel vessel)

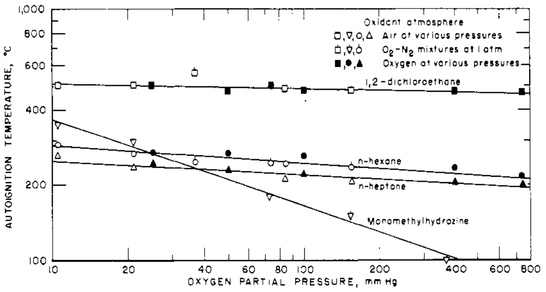

Figure 13. Logarithm autoignition temperature *vs.* logarithm oxygen partial pressure for four combustibles in oxygen and oxygen-nitrogen atmospheres at various mixture pressures (4900-cc. steel vessel)

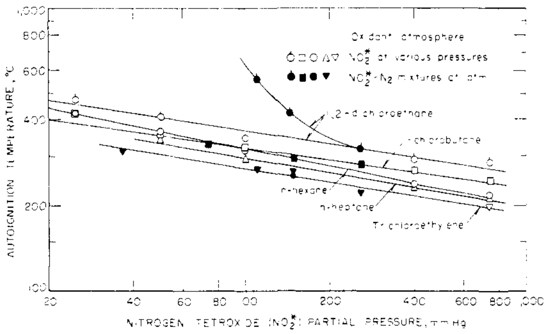

Figure 14. Logarithm autoignition temperature vs. logarithm nitrogen tetroxide (NO_2*) partial pressure for five combustibles in NO_2* and NO_2*–nitrogen atmospheres at various mixture pressures (4900-cc. steel vessel)

Figure 13, the autoignition temperatures (°C.) are inversely proportional to $P_{O_2}^{0.3}$ for monomethylhydrazine and to $P_{O_2}^{<0.1}$ for the other combustibles; P_{O_2} is the oxygen partial pressure in millimeters of Hg.

A similar correlation of AIT with oxidant partial pressure was obtained for some of the present data in NO_2* at various pressures and in NO_2*-nitrogen mixtures at 1 atm. Figure 14 shows a plot of log AIT *vs.* log $P_{NO_2^*}$ for *n*-hexane, *n*-heptane, and three of the halogenated hydrocarbons. Here, most of the AIT data are inversely proportional to $P_{NO_2^*}^{0.15-0.2}$. However, those for 1,2-dichloroethane display a greater dependence upon NO_2* percentage than upon mixture total pressure (without diluent) below 250 mm. of Hg. Nevertheless, the autoignition temperatures of these combustibles appear to correlate in this manner over at least a limited range of mixture pressures and oxidant concentrations.

CONCLUSIONS

The minimum autoignition temperatures of the combustibles examined in this study are lower in oxygen than in air, although the variation is not great for most of the combustibles at atmospheric pressure. Of the combustibles, the highest AIT's in these oxidants are found with hydrogen and methylene chloride and the lowest values with hydrazine and monomethylhydrazine. Halogenated hydrocarbons such as 1-chlorobutane, 1,2-dichloroethane, 1,1,1-trichloroethane, and trichloroethylene tend to ignite at lower temperatures than their parent hydrocarbons. In comparison, NO_2* appears to be more effective than oxygen in promoting the ignition of all the combustibles except *n*-heptane and 1-chlorobutane; with this oxidant, the hydrazine fuels are hypergolic at room temperature.

The AIT's tend to increase abruptly when the pressure or oxidant concentration is decreased below some critical value, depending upon the fuel-oxidant system and the vessel size. Diluent type did not appear to be important. Some of the AIT data obtained at various test conditions correlate reasonably well with the oxidant partial pressure of the mixture.

LITERATURE CITED

(1) ASTM Standards on Petroleum Products, Part 17, ASTM Designation: D-2155-63T, Am. Soc. for Testing and Materials, Philadelphia, Pa., p. 863 (1965).
(2) Cloyd, D.R., Murphy, W.J., *Natl. Aeron. Space Admin.* **SP-5032**, Washington, D. C., p. 83, September 1965.
(3) Coward, H.F., Jones, G.W., *U.S. Bur. Mines Bull.* **503**, 155 pp. (1952).
(4) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 44th ed., 1963.
(5) Kane, G.P., Chamberlain, E.A.C., Townend, D.T.A., *J. Chem. Soc.* Part I, **1937**, p. 436.
(6) Kuchta, J.M., Bartkowiak, A., Zabetakis, M.G., *U.S. Bur. Mines Rept. Invest.* **6654**, 25 pp. (1965).
(7) Mullins, B.P., *AGARDograph* No. **4**, Butterworths, London, pp. 36, 78 (1955).
(8) *NFPA* No. **325M**, "Flammable Liquids, Gases, and Volatile Solids," National Fire Protection Association, Boston, Mass., 1965.
(9) Perlee, H.E., Imhof, A.C., Zabetakis, M.G., J. CHEM. ENG. DATA **7**, No. 3, 377 (1962).
(10) Perlee, H.E., Martindill, G.H., Zabetakis, M.G., *U. S. Bur. Mines Rept. Invest.* **6748**, 12 pp. (1966).
(11) Semenov, N.N., *Natl. Advisory Comm. Aeron. Tech. Note* **1024**, Washington, D. C., p. 39, August 1942.
(12) Spakowski, A.E., *Natl. Aeron. Space Admin. Memo* **12-13-58E**, December 1958.
(13) Svehla, R.A., Brokaw, R.S., *NASA Tech. Note* **D-3327**, March 1966.
(14) Zabetakis, M.G., *U.S. Bur. Mines Bull.* **627**, 121 pp. (1965).
(15) Zabetakis, M.G., Furno, A.L., Jones, G.W., *Ind. Eng. Chem.* **46**, 2173 (1954).

RECEIVED for review July 3, 1967. Accepted November 29, 1967. The work upon which this report is based was done by the Bureau of Mines, U. S. Department of the Interior, under George C. Marshall Space Flight Center Government Order H-76708.

Calorimetric Study of Iron(III) Chloride

W. H. MAPES and N. W. GREGORY
Department of Chemistry, University of Washington, Seattle, Wash. 98105

Enthalpies of sublimation and vaporization, 30.6 ± 1 (550° K.) and 12.4 ± 0.5 (583° K.) kcal. mole^{-1} Fe_2Cl_6, respectively, have been determined calorimetrically. Preliminary calorimetric results are also reported for the formation of Fe_2Cl_6(g) from the elements.

A VACUUM heat-leak calorimeter (*1*), suitable for measurement of heats of formation and vaporization of many substances volatile in the range between room temperature and 700° K., has been used for a thermochemical study of iron(III) chloride. A ca. 100-ml. round-bottomed borosilicate glass bulb was used as a reaction cell. After inserting a small capsule, containing either $FeCl_3$ or Fe, and a magnetically controlled drop weight system which served to break the capsule at the appropriate time, the flask was evacuated and baked out. Prior to final seal-off, it was filled with chlorine at a pressure sufficient either for the reaction of the iron and/or for the prevention of decomposition of the iron(III) chloride. The prepared cell was surrounded by a radiation shield and placed inside an isothermal iron cylinder, held within ± 0.01° C.; the whole assembly was covered with a steel bell jar and evacuated. The cell temperature was monitored with a calibrated Chromel-Alumel thermocouple, used in conjunction