Table II. Selected Thermodynamic Functions for Gold

T, ° K.	$-(G^\circ_T - H^\circ_{298.15})/T$, Cal./Mole/Deg.	$H^\circ_T - H^\circ_{298.15}$, Kcal./Mole	S°_T, Cal./Mole/Deg.	C°_p, Cal./Mole/Deg.
298.15	11.319 ± 0.059	0.0	11.319 ± 0.059	6.065
300	11.319	0.011	11.356	6.068
350	11.393	0.316	12.297	6.133
400	11.559	0.625	13.120	6.194
450	11.773	0.935	13.852	6.246
500	12.015	1.249	14.513	6.298
550	12.270	1.566	15.117	6.350
600	12.530	1.884	15.670	6.397
650	12.792	2.205	16.184	6.441
700	13.052	2.528	16.664	6.491
750	13.307	2.854	17.113	6.541
800	13.559	3.182	17.537	6.591
850	13.805	3.513	17.939	6.641
900	14.045	3.846	18.319	6.691
950	14.279	4.182	18.682	6.741
1000	14.509	4.521	19.030	6.791
1050	14.732	4.861	19.361	6.841
1100	14.949	5.205	19.681	6.891
1150	15.162	5.552	19.990	7.019
1200	15.369	5.908	20.292	7.222
1250	15.572	6.280	20.596	7.634
1300	15.772	6.670	20.903	8.007
1336(s)	15.913	6.964	21.125	8.300
1336(l)	15.913	9.925	23.342	7.953
1400	16.261	10.434	23.714	7.953
1500	16.776	11.230	24.263	7.953
1600	17.260	12.025	24.776	7.953
1800	18.148	13.616	25.713	7.953
2000	18.948	15.206	26.551	7.953
2200	19.674	16.800	27.309	7.953
2400	20.339	18.388	28.001	7.953
2600	20.953	19.978	28.637	7.953
2800	21.524	21.569	29.227	7.953
3000	22.056	23.159	29.775	7.953
3200	22.554	24.750	30.289	7.953
3400	23.024	26.340	30.771	7.953

$H^\circ_{298.15} - H^\circ_0 = 1434.8 \pm 6.6$ cal./mole.

THERMODYNAMIC FUNCTIONS

Thermodynamic function for Au (s,l) are tabulated in Table II. Functions for the solid are based on the sources listed by Hultgren *et al.* (*5*) plus the following additional sources: Martin (0.4° to 1.5° K., 3° to 30° K.) (*13*), du Chatenier and de Nobel (1° to 30° K.) (*1*), du Chatenier, de Nobel, and Boerstoel (1.3° to 30° K.) (*2*), Isaacs (1.5° to 4.2° K.) (*6*), Zimmerman and Crane (1.5° to 4.2° K.) (*19*), Will and Green (2° to 4° K.) (*17*), Franzosini and Clusius (12° to 273° K.) (*4*), and Plaza (404° to 1331° K.) (*14*). From the selected values of the thermodynamic functions of the solid and liquid the heat of fusion of gold is calculated to be 2961 cal. per mole at the defined melting point (IPTS) of gold, 1336° K. Hultgren *et al.* list 2955 cal. per mole for this quantity.

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Effect of Pressure and Temperature on Flammability Limits of Chlorinated Hydrocarbons in Oxygen-Nitrogen and Nitrogen Tetroxide–Nitrogen Atmospheres

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OF THE many halogenated hydrocarbons used as organic solvents, some are considered safer than others because they do not form flammable vapor-air mixtures at ordinary temperatures and pressure. For example, certain concentrations of methyl chloride and vinyl chloride vapors are flammable in air at atmospheric pressure and room temperature, whereas methylene chloride and trichloroethylene vapors are not flammable under the same conditions (*2*). However, many of the so-called "safe" halogenated solvents form flammable mixtures in air at elevated temperatures or reduced pressures where the fuel vapor pressure is not a limiting factor (*2, 7, 10, 13*). The flammability limits and burning velocities of such combustibles differ greatly from the values observed for their parent hydrocarbons (*1, 2, 6*); furthermore, the potential fire and explosion hazards are more serious in oxygen and nitrogen tetroxide atmospheres. However, flammability data in these atmospheres are meager for the halogenated hydrocarbons (*2, 9, 10*). Since this information is of interest in rocket and space flight applications, the current investigation was undertaken.

Lower and upper limits of flammability were determined

Limit-of-flammability data were obtained in oxygen and nitrogen tetroxide atmospheres for several chlorinated hydrocarbons that are currently of interest as solvents in rocket and space flight applications. Flammability diagrams that define the complete range of flammable mixtures that can occur with the combustibles are presented for various mixture temperatures (25° to 200° C.) and pressures (760 to 50 mm. of Hg). Generally, the range of flammable compositions does not vary greatly with temperature or pressure if the vapor pressure of the combustible is not a limiting factor. The range of flammable mixtures for the combustibles is usually greater in oxygen-nitrogen than in nitrogen tetroxide–nitrogen atmospheres. The minimum oxidant concentrations required for flame propagation are much less in atmospheres containing oxygen and tend to increase with the number of substituted chlorine atoms in the combustible.

in air, oxygen, and nitrogen tetroxide at various temperatures ($\leq 200°$ C.) and pressures (≥ 50 mm. of Hg) for the following solvents: methylene chloride, ethylene dichloride, methylchloroform, and *n*-butyl chloride. Also, the effect of nitrogen dilution on the flammability limits was determined to delineate the complete range of flammable mixtures that can occur with these combustibles and trichloroethylene in various oxygen-nitrogen and nitrogen tetroxide–nitrogen mixtures. The experiments were performed by observing the ability of the test mixtures to propagate flame traveling in the upward direction. Since the range of flammability can be greatly limited by wall quenching effects, particularly at reduced pressures where quenching distances are larger, the experiments were conducted in explosion vessels of sufficient diameter to minimize such effects.

EXPERIMENTAL

Physical Properties. The physical properties of the chlorinated hydrocarbons used in this investigation and the available flash point and minimum autoignition temperature data are listed in Table I; corresponding data for their parent hydrocarbons are also included. As noted, all the halogenated combustibles are liquids; two of them (ethylene dichloride and *n*-butyl chloride) have reported flash points less than 20° C.—that is, they are capable of forming flammable vapor-air mixtures at atmospheric pressure and room temperature. According to data obtained in the present work, methylchloroform also forms flammable mixtures in air at room temperature. The temperatures required for autoignition of the combustibles are less than 300° C. in nitrogen tetroxide and above 400° C. in air or oxygen, except for *n*-butyl chloride, whose autoignition temperature ($\sim 240°$ C.) does not vary noticeably in these oxidants. Also, except for methylene chloride, their autoignition temperatures are lower than the corresponding values listed for their parent hydrocarbons. All the combustibles were Fisher certified grade materials.

The nitrogen tetroxide (Matheson Co.) and oxygen were at least 99% pure. The nitrogen tetroxide concentrations specified in this report refer to the equilibrium compositions of nitrogen tetroxide and dioxide (the notation NO_2^* is used) which existed at the initial temperatures ($\leq 100°$ C.) and pressures (≤ 760 mm. of Hg) employed. According to the literature (*12*), the main constituent should be NO_2 (95%) at 100° C. and N_2O_4 (65%) at 25° C. and 1-atm. pressure. With decreasing pressure, the equilibrium shifts toward increasing NO_2 concentrations; little or no nitric oxide (NO) is expected in the equilibrium mixtures at the given test conditions.

PROCEDURE

The limit-of-flammability experiments were conducted with upward flame propagation in two different apparatus, depending on the test temperature. For determinations at ambient temperature (25° ± 5° C.), the apparatus shown in Figure 1 was designed with two steel explosion chambers and a common gas mixer; the explosion chambers were 1.5 meters long and 30 cm. in diameter. This design permitted the gases to be mixed in one chamber by a magnetically driven stirrer while the other chamber was being purged and evacuated. The explosion chambers were equipped with

Table I. Physical Properties of Combustibles

Combustible	Chemical Formula	Mol. Wt.	Spr.Gr.,[a] Air = 1	Boiling Point,[b] °C.	Flash Point,[a] °C.	Heat of Comb.,[c] Kcal./G.	Autoignition Temp., ° C.[d] Oxidant: Air	Oxygen	NO_2^*
Methane	CH_4	16.04	0.55	–161.5	–187	11.95	537	. . .	. . .
Methylene chloride (dichloromethane)	CH_2Cl_2	84.93	2.9	40.0	≥ 30	1.70	556	490	276
Ethane	C_2H_6	30.07	1.04	–88.3	–130	11.35	515	506	. . .
Ethylene dichloride (1,2-dichloroethane)	$C_2H_4Cl_2$	98.97	3.4	83.5	13	3.00	476	470	282
Methylchloroform (1,1,1-trichloroethane)	$C_2H_3Cl_3$	133.42	4.6 (calcd.)	74.1	≤ 25	1.64	458	418	270
Ethylene	C_2H_4	28.05	0.97	–103.9	. . .	11.25	490	485	. . .
Trichloroethylene	C_2HCl_3	131.40	4.5	87.0	32	1.75	416	402	200
n-Butane	C_4H_{10}	58.12	2.0	–0.3	–72	10.95	405	283	270
n-Butyl chloride (1-chlorobutane)	C_4H_9Cl	92.57	3.2	78.0	9	6.97	240	235	248

[a] Data from (*8, 13* and present work). [b] Data from (*4*). [c] Data from (*5, 11, 13*). [d] Data from (*3, 13*).

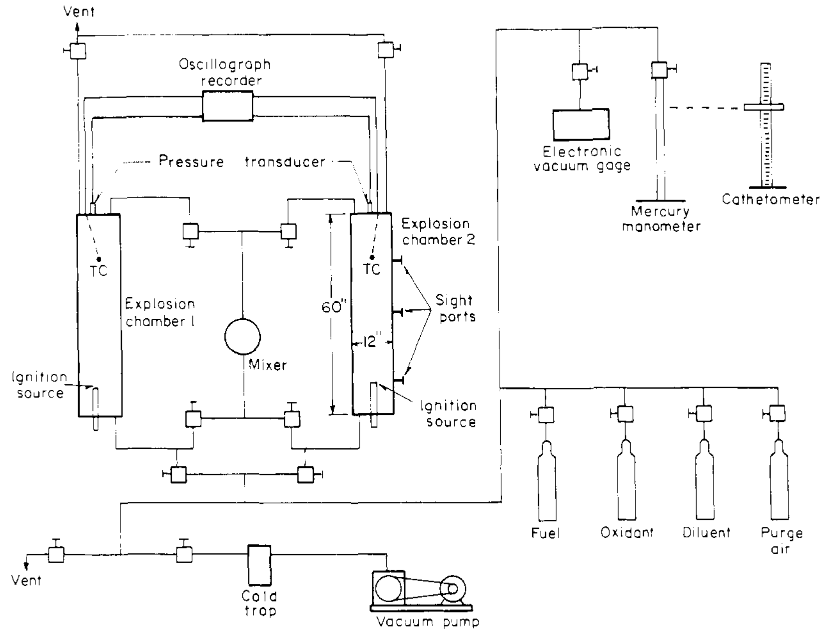

Figure 1. Limit-of-flammability apparatus

the hardware required for preparing the desired test mixtures and with strain gage pressure transducers for measuring the pressures developed following ignition; thermocouples were located near the top of the vessel to detect the presence of flame. The mixtures were ignited with an electric spark energy source located near the bottom of each vessel. When evidence of flame propagation appeared to be borderline, particularly at reduced pressures, the mixtures were also ignited with a short coil of 40-gage copper wire that was fused electrically; a few of the limits were widened slightly by the use of the fuse wire ignition source.

In most determinations, the explosion chamber was first evacuated to at least 500 microns of Hg, filled with the oxidant, and then evacuated again. The desired volumes of combustible vapor and oxidant were then introduced by the partial pressure method and the resulting mixture was circulated through the mixer and chamber for at least 15 minutes. Subsequently, the ignition source was energized and an abrupt temperature or pressure rise was taken as evidence of flame propagation. The flammability of the mixture compositions that defined a lower or upper limit was verified by observing the reaction through sight ports on one of the explosion chambers.

The determinations at elevated temperatures were made in a borosilicate glass tube, 10 cm. in diameter by 1.25 meters long, housed in a precision temperature-controlled oven (±1° C.). This apparatus (*14*) is equipped with gas and liquid feed assemblies for preparing the test mixtures. The mixtures were introduced into the flammability tube at near-stagnant flow conditions (≤ 2.5 liters per minute) and ignited as in the experiments at room temperature—that is, by an electric spark energy source or by fusing a short length of copper wire. Here, the mixtures were considered to be flammable if the flame propagated through more than half the length of the tube.

When nitrogen tetroxide was used as the oxidant in the elevated temperature experiments, the flow apparatus was modified to permit the gaseous mixtures to be prepared by the partial pressure method. This was done to minimize the possible effects of mixing time or premature reaction at elevated temperatures. For this purpose, the top of the flammability tube was fitted with a removable gas-tight glass plate. Also, a wire was passed through a hole (mercury seal) in the glass plate and connected to a perforated metal diaphragm for mixing the gases. Since the composition and volume of nitrogen tetroxide change with temperature, the oxidant was stored in a large glass vessel at the test temperature before use. Prior to firing a mixture, the glass plate was replaced with a piece of aluminum foil that would rupture and release the system pressure after an ignition.

Most of the limits were reproducible within approximately ±0.1% at low limiting concentrations (<10 volume % fuel) and ±0.5% at high limiting concentrations (>20 volume % fuel).

RESULTS AND DISCUSSION

Flammability Limits in Oxygen and Oxygen-Nitrogen Atmospheres. Table II compares the flammability limits of the chlorinated hydrocarbons examined in this work, together with those reported for other related hydrocarbon materials. All the halogenated paraffins examined form flammable fuel vapor-oxygen mixtures at 25° C. and atmospheric pressure. Their lower limits of flammability range from 1.8 volume % for *n*-butyl chloride to 13.6% for methylene chloride. The values for the highly halogenated materials—methylene chloride, ethylene dichloride, and methylchloroform—were all noticeably higher than the corresponding values cited for their parent hydrocarbons. This trend is partly attributed to the fact that the combustion enthalpy of a given hydrocarbon decreases with the number of substituted chlorine atoms and results in a corresponding decrease of flame temperature. Also, the chlorinated hydrocarbons can decompose to form chlorine atoms and hydrogen chloride which tend to inhibit flame propagation; furthermore, some of the highly chlorinated materials—e.g., methylene chloride—tend to form two flame fronts whose propagation is more sensitive to mixture strength than that observed for normal flames (*6*). Trichloroethylene should also form a lower limit mixture in oxygen at 25° C.; a value of approximately 8% is indicated by extrapolation of data reported at 100° C. (*10*).

With air as the oxidant, all the combustibles in Table II except trichloroethylene and methylene chloride form flammable mixtures at 25° C. and atmospheric pressure. Trichloroethylene requires a temperature of approximately 30° C. to provide sufficient fuel vapor to form flammable mixtures in air (*10*). Although methylene chloride also requires higher temperatures (>25° C.) to form flammable vapor-air mixtures, its vapor pressure is not a limiting factor. The lower limits obtained for ethylene dichloride,

Table II. Limits of Flammability for Chlorinated and Nonchlorinated Hydrocarbons in Oxygen (O_2), Air, and Nitrogen Tetroxide (NO_2^*) Atmospheres

			Lower Limit, Vol. %			Upper Limit, Vol. %		
			Oxidant					
Combustible	Temp., °C.	Press., mm. Hg	O_2	Air	NO_2^*	O_2	Air	NO_2^*
Methane[a]	25	760	5.0	5.0	...	61	15.0	...
Methyl chloride[a]	25	760	~8.0	10.7	...	~66	17.4	...
Methylene chloride	25	760	13.6	...	37.5	...	...	...
	100	760	11.7	15.9	26.5	68	19.1	75
	200	760	11.0	14.9	...	72	19.2	...
Ethane[a]	25	760	3.0	3.0	...	66	12.4	...
Ethyl chloride[a]	≥25	760	4.0	3.8	...	67	15.4	...
Ethylene dichloride	25	760	5.6	6.0	...	...	...	...
	25	100	...	...	13.5	...	...	50.5
	25	50	6.1	6.3	15.5	58.5	15.7	42.5
	100	760	4.0	4.5	13.7	67.5	17.3	48
	200	760	3.5	3.9	...	69	21.2	...
Methylchloroform	25	760	6.6	6.8[b]	...	...	10.5[c]	...
	100	760	5.5	6.3	14.9	57	13.0	52.5
	200	760	4.1	5.9	...	60	14.3	...
Ethylene[a]	25	760	2.9	2.7	...	80	36	...
Chloroethylene[a]	25	760	4.0	4.0	...	70	22	...
Trichloroethylene[d]	100	760	7.5	10.5	13.5	91	41	69
n-Butane[a]	25	760	1.8	1.8	...	49	8.4	...
n-Butyl chloride	25	760	1.8	1.9[b]	...	...	11.0	...
	25	100	2.2	2.3[b]	7.1	53.5	8.8	30.5
	25	50	2.3	2.5	7.3	51.5	8.8	26.5
	100	760	1.7	2.0	9.5	52	10.3	39.0
	200	760	1.6	1.8	...	56	12.0	...

[a] Data from (*2, 13*). [b] Interpolated values from flammability diagrams. [c] Maximum fuel concentration examined because of vapor pressure limitation; represents upper limit in 14% oxygen and 75.5% nitrogen instead of limit in air. [d] Lower and upper limit data from (*10*).

methylchloroform, and *n*-butyl chloride were only slightly higher in air than in oxygen. However, except for *n*-butyl chloride, no upper limits were found for the above combustibles in air at 25° C. and atmospheric pressure, or for any of these materials in oxygen at ambient conditions, since the vapor pressure of each combustible was a limiting factor. At 100° C. and 1 atm., upper limit data were obtained for all the halogenated paraffins. The values were between 10 and 19% in air, compared with between 52 and 68% in oxygen; *n*-butyl chloride consistently gave the lowest values and methylene chloride the highest values. Except for methylchloroform, the upper limits were about equal to or slightly higher than those found for their parent hydrocarbons (*2*), but low compared to the values cited for trichloroethylene in air (41%) or oxygen (91%).

The results for methylene chloride in air at 25° C. are not totally unexpected, considering that a maximum burning velocity of only 11 cm. per second is reported for methyl chloride vapors in air (*6*) and the corresponding value for methylene chloride would be even lower, assuming that propagation is possible at this temperature. By extrapolating the data obtained by Kaesche-Krischer in various oxygen-nitrogen mixtures, a burning velocity of 4 cm. per second or less appears possible for methylene chloride–air mixtures at room temperature; this value is comparable to that (2 cm. per second) predicted for trichloroethylene-air mixtures at 40° C. (*7*). Therefore, like trichloroethylene, methylene chloride may form flammable vapor-air mixtures at temperatures only slightly above 25° C.

The ratio of the lower limit (*LL*) in air to the amount of combustible theoretically required for complete combustion (C_{st}) is approximately constant (~0.55) for many hydrocarbons (*13*). Generally, and as determined in this study, such ratios are not constant for halogenated hydrocarbons, since their ignitions involve various decomposition and oxidation products and the flame temperatures of their lower limit mixtures vary noticeably. Carbon dioxide, water, hydrogen chloride, and chlorine were assumed to be the reaction products in computing the stoichiometric mixtures. The LL/C_{st} ratios obtained in air were between 0.5 and 0.9 at 25° and 100° C. for the halogenated paraffins of this work, compared with approximately 1.1 for trichloroethylene; their LL/C_{st} ratios in oxygen varied between 0.1 and 0.25. The corresponding ratios obtained for the upper limit data of the halogenated paraffins varied more than their LL/C_{st} ratios, as observed for paraffinic hydrocarbons; the ratios were between 1.1 and 3.3 in air and only slightly higher in oxygen.

The flammability diagram in Figure 2 shows the complete range of flammable fuel vapor-oxygen-nitrogen compositions for methylene chloride at 25°, 100°, and 200° C. at 1 atm. As noted, the lower limits tend to decrease and the upper limits to increase slightly with increasing temperature. The flammability diagrams for the other chlorinated hydrocarbons displayed similar trends; the data obtained at 100° C. are included in Figures 5 through 8. Methylene chloride, which displayed a very narrow range of flammable mixtures in air, required the least dilution (≤68% of N_2) to prevent the formation of flammable mixtures at the given temperatures; *n*-butyl chloride required the greatest dilution (≥83% of N_2) at these conditions. Except where the fuel vapor pressure was a factor, the range of flammable compositions for *n*-butyl chloride is much the same as that reported for *n*-butane at the same temperature and pressure conditions (*2, 13*). For ethylene dichloride and methylchloroform, the flammability ranges are generally less than those observed for their parent hydrocarbons, primarily because the lower limits are noticeably higher for the halogenated materials.

The range of flammability decreased slightly for two of the combustibles, *n*-butyl chloride and ethylene dichloride, that were examined at reduced pressures. Figure 3

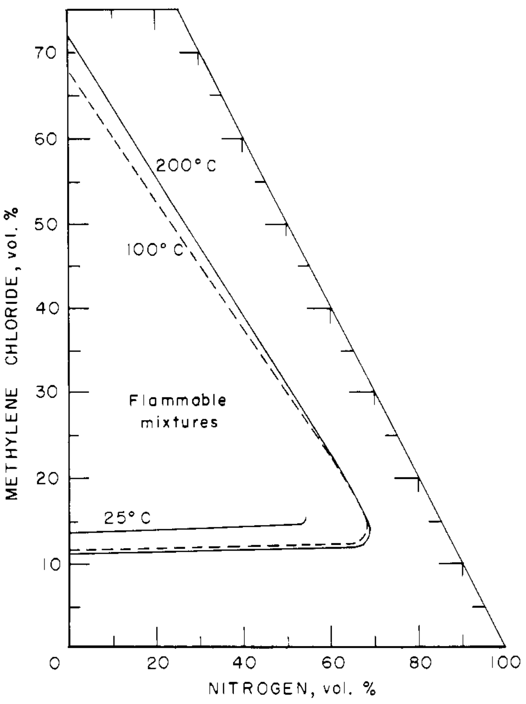

Figure 2. Limits of flammability of methylene chloride–oxygen-nitrogen mixtures
1-atm. pressure
25°, 100°, and 200° C.

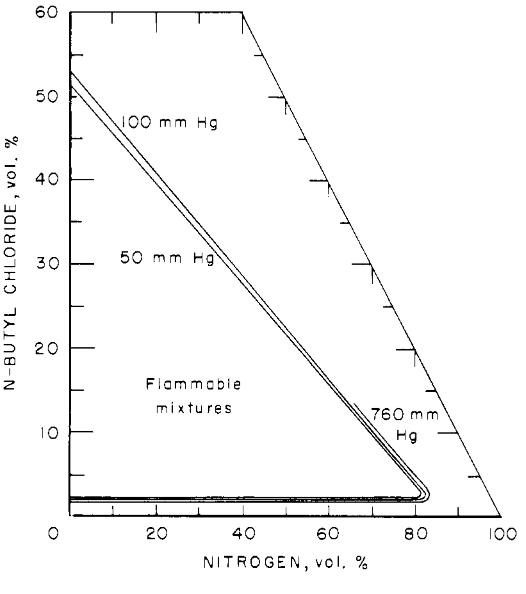

Figure 3. Limits of flammability of *n*-butyl chloride–oxygen-nitrogen mixtures
25° C.
760, 100, and 50 mm. of Hg

shows the flammability diagram obtained for *n*-butyl chloride at pressures as low as 50 mm. of Hg; the flammability limits are listed in Table II. Ordinarily, the flammability limits of most hydrocarbon combustibles do not vary greatly over such a range of reduced pressures when the reaction vessel is relatively large, as in the present case (30-cm. i.d.).

Flammability Limits in NO$_2^*$ and NO$_2^*$-Nitrogen Atmospheres. Of the five halogenated combustibles examined, only methylene chloride had sufficient vapor pressure to permit meaningful limit-of-flammability determinations in NO$_2^*$ at 25° C. and 1-atm. pressure. Its lower limit was 37.5 volume %, but its upper limit could not be determined because of the vapor pressure limitation. Flammable mixtures were obtained with all the combustibles at 100° C. (Table II). Their lower limits in this oxidant were much higher than those found in oxygen or air. Also, as in the determinations in oxygen, the highest values were obtained with methylene chloride and the lowest values with *n*-butyl chloride; at 100° C., the lower limits were 26.5 and 9.5%, respectively.

The corresponding upper limits of the combustibles at 100° C. were generally lower in NO$_2^*$ than in oxygen, except for methylene chloride, which had the highest upper limit value (75%). Accordingly, the UL/C_{st} ratios for most of the combustibles would be expected to be lower and the LL/C_{st} ratios greater with the NO$_2^*$ oxidant. The stoichiometric fuel concentrations (C_{st}) for complete combustion in nitrogen dioxide do not differ greatly from those in oxygen, assuming most of the reaction products are the same with both oxidants. Here, the NO$_2^*$ consisted largely of the dioxide.

Figures 4 to 8 show the complete range of flammable mixtures for the five chlorinated hydrocarbons in various NO$_2^*$-nitrogen mixtures at 100° C. and 1 atm.; the corresponding data for oxygen-nitrogen mixtures are included for comparison. From these figures, it is evident that the range of possible flammable mixtures for each combustible is smaller in the mixtures containing NO$_2^*$ than those containing oxygen. The lower limits of flammability of methylene chloride, ethylene dichloride, and methylchloroform in NO$_2^*$ decreased slightly with increasing dilution, contrary to the behavior ordinarily observed in oxygen-nitrogen mixtures. Although such anomalous behavior could result from varied degrees of mixing, the observed decrease of the lower limit was more pronounced for one combustible than for another. Perhaps more important was the extent of possible reaction of the different combustible mixtures prior to firing; flammability data were not obtained with the NO$_2^*$ oxidant at 200° C. because of excessive reaction. Of the combustibles, trichloroethylene tends to form the widest range of flammable compositions in NO$_2^*$-nitrogen and oxygen-nitrogen atmospheres, although not necessarily over the greatest range of nitrogen concentration.

All the combustibles should form flammable mixtures in NO$_2^*$ at 25° C., when the total pressure is reduced sufficiently to remove any vapor pressure limitation. The flammability diagrams obtained for ethylene dichloride (Figure 9) and *n*-butyl chloride (Figure 10) indicate that the limits in various NO$_2^*$-nitrogen mixtures are narrowed to some extent when the pressure is decreased from 100 to 50 mm. of Hg. Again it was observed that the lower limits decreased slightly with increasing nitrogen dilution, particularly at 100 mm. of Hg. In addition, the lower limit of *n*-butyl chloride in NO$_2^*$ at reduced pressure and 25° C. ($\leq 7.3\%$) was less than expected when compared with the value of 9.5% found at 1 atm. and 100° C. (Table II); here, the degree of any reaction before firing would be expected to be less at the lower temperature and may account for the observed differences.

Minimum Oxidant Concentration Requirements. A useful parameter in preventing gas explosions is the minimum oxidant concentration below which combustible mixtures will not propagate flame regardless of the combustible and diluent concentrations. Such values were determined from the flammability diagrams obtained for the halogenated materials with NO$_2^*$-nitrogen and oxygen-nitrogen mixtures. Table III lists the values found at 1-atm. pressure and 25° or 100° C.; the values for several hydrocarbons and other chlorinated hydrocarbons are included for comparison.

As noted in Table III, the minimum oxygen values are highest for the fuel vapors of the halogenated hydrocarbons; they generally increase with an increase in the number

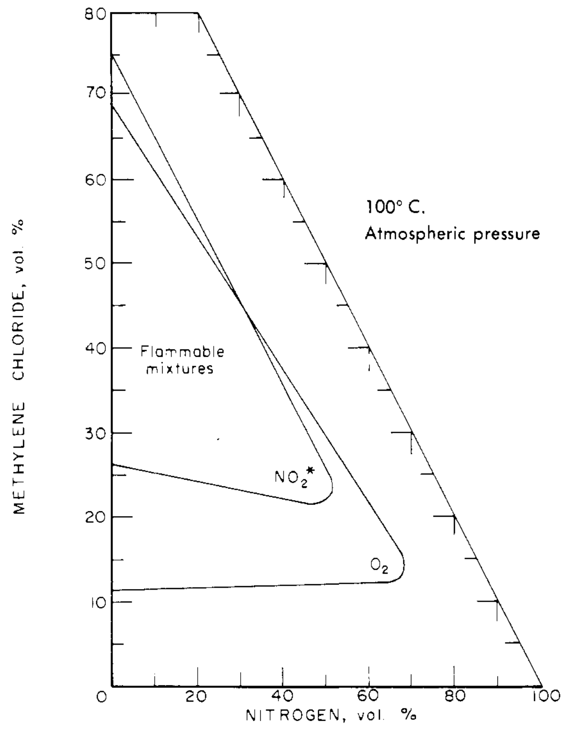

Figure 4. Limits of flammability of methylene chloride in oxygen-nitrogen and nitrogen tetroxide–nitrogen mixtures

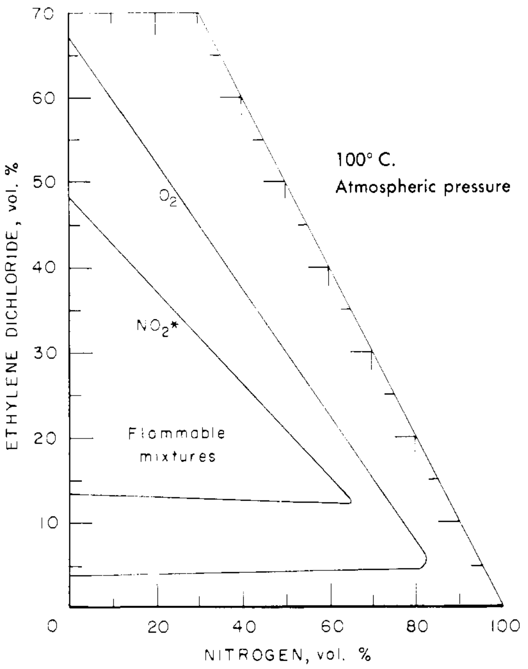

Figure 5. Limits of flammability of ethylene dichloride in oxygen-nitrogen and nitrogen tetroxide–nitrogen mixtures

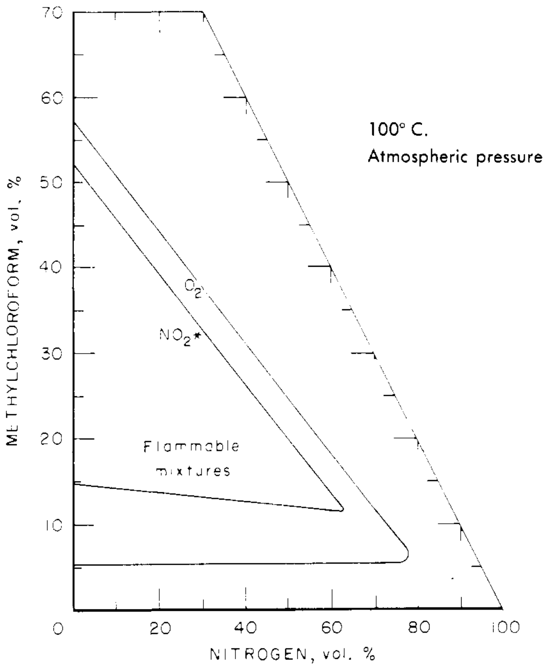

Figure 6. Limits of flammability of methylchloroform in oxygen-nitrogen and nitrogen tetroxide–nitrogen mixtures

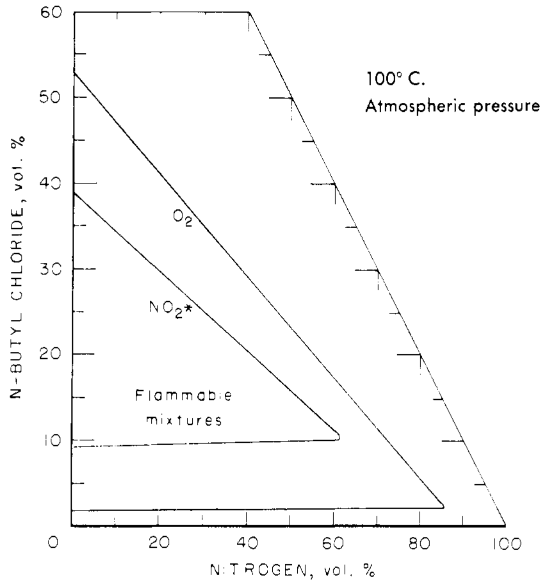

Figure 7. Limits of flammability of *n*-butyl chloride in oxygen-nitrogen and nitrogen tetroxide–nitrogen mixtures

of chlorine atoms substituted in the parent hydrocarbon. At 25° C., the minimum oxygen value for methane is only 12%, compared with 19% for methylene chloride at ~30° C. (*2*). The corresponding data for the other halogenated paraffins are between 13 and 14%, not much higher than those indicated for their parent hydrocarbons (11 to 12%). At 100° C., the values tend to be slightly lower. Of the halogenated materials examined, trichloroethylene has the lowest minimum oxygen value (9% at 100° C.). In comparison, the more fully halogenated materials like chloroform and tetrachloroethylene are reported to propagate flame only when the oxygen concentration of the oxygen-nitrogen atmosphere is about 100% (*6*, *7*).

The minimum oxidant concentration requirements for flame propagation were much greater for the halogenated hydrocarbons in NO_2^* and nitrogen than in oxygen and

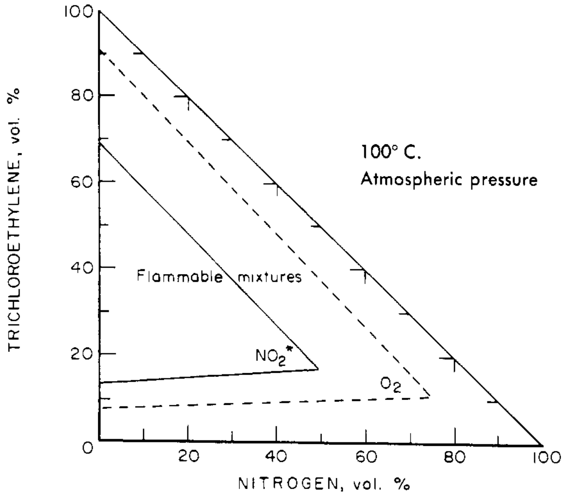

Figure 8. Limits of flammability of trichloroethylene in oxygen-nitrogen and nitrogen tetroxide-nitrogen mixtures

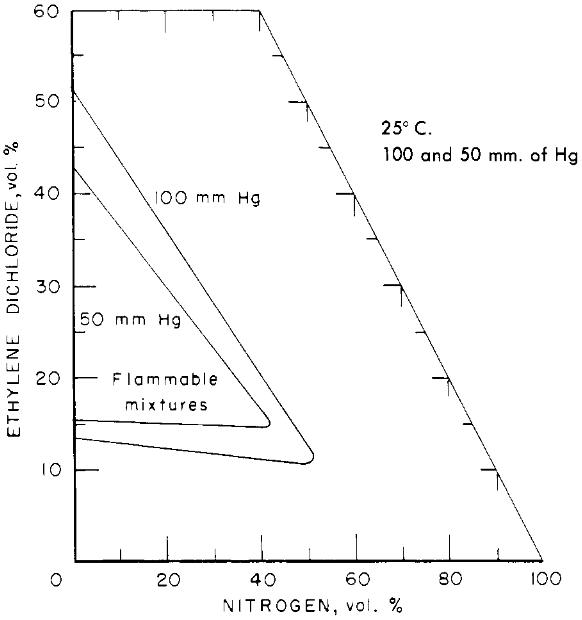

Figure 9. Limits of flammability of ethylene dichloride–nitrogen tetroxide–nitrogen mixtures

nitrogen. At 100° C. and 1 atm., the minimum NO_2^* values ranged from 22% for ethylene dichloride to 33% for trichloroethylene (Table III). The value for *n*-butyl chloride (29%) was noticeably higher than that for *n*-butane (23%). Although the data are meager, the minimum NO_2^* values also appear to increase with the number of chlorine atoms substituted in the combustible material. The trends noted in these flammability experiments cannot necessarily be predicted from those observed in autoignition temperature experiments (*3*) with the same combustibles and oxidants. These findings are not unusual, since the autoignitions were governed by low-temperature reactions and the flame propagations by high-temperature reactions.

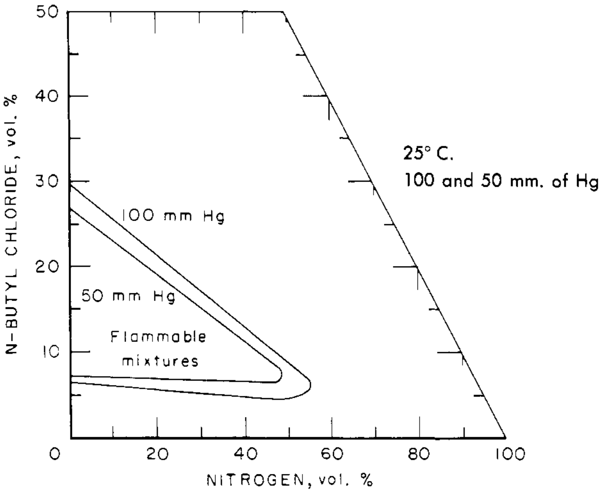

Figure 10. Limits of flammability of *n*-butyl chloride–nitrogen tetroxide–nitrogen mixtures

Table III. Minimum Oxidant Concentrations for Flame Propagation with Combustibles in Oxygen-Nitrogen and NO_2^*-Nitrogen Mixtures at 1-Atm. Pressure and 25° or 100° C.

	Minimum Oxygen, Vol. %		Minimum NO_2^*, Vol. %
Combustible	25° C.	100° C.	at 100° C.
Methane[a]	12	<12	...
Methylene chloride	19[a]	17	24
Chloroform[b]	Requires ~100% O_2	...	...
Ethane[a]	11	<11	...
Ethylene dichloride	13	11.5	22
Methylchloroform	14	14.5	25
n-Butane	12	10	23
n-Butyl chloride	14	12	29
Ethylene[a]	10	<10	...
Trichloroethylene	...	9	33
Tetrachloro-ethylene[c]	Requires ~100% O_2	...	...

[a] Data from (*2*) at 25° C. except for methylene chloride (~30° C.). [b] Data from (*6*). [c] Data from (*7*) at 80° C.

CONCLUSIONS

The lower limits of flammability of four chlorinated paraffins examined in this study were noticeably lower in oxygen or air than in NO_2^*. Like trichloroethylene, methylene chloride does not form flammable mixtures in atmospheric air at 25° C. Although lower limits were obtained for all the combustibles in oxygen at 25° C. and 1-atm. pressure, higher temperatures or lower pressures were usually required to obtain corresponding data in NO_2^* or upper limit data in either oxidant. At 100° C. and 1 atm., the upper limits were lower in NO_2^* than in oxygen, except for methylene chloride which generally gave the highest values for both the lower and upper limits; *n*-butyl chloride always gave the lowest values. The upper limits of the combustibles in the above two oxidants were much higher than in air. Except where the fuel vapor pressure limitation was a factor, the flammability limits of *n*-butyl chloride in various oxygen-nitrogen mixtures did not differ greatly from those of *n*-butane at the same temperature and pressure; they varied only slightly with reduced pressures to 50 mm. of Hg. The ranges of flammability for the other chlorinated paraffins were somewhat less than those observed for their parent hydrocarbons, primarily because their lower limits were noticeably higher. In comparison, trichloroethylene has a wider range of flammable compositions in air, oxygen, or NO_2^*. The minimum oxidant concentrations for flame propagation were greater in NO_2^* and nitrogen than in oxygen and nitrogen; they tended to increase with the number of substituted chlorine atoms in the particular hydrocarbon-base material.

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Re-evaluation of the Dissociation Energy of CaF

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A disparity in the value for the dissociation energy of CaF is removed by an assessment of mass spectrometric thermodynamic observations of 14 vapor phase reactions involving CaF. D°_{298}(CaF) = 127.5 ± 2.5 kcal. mole^{-1} is indicated as the most reliable value. The data lead to the following values, D°_{298}(SiF) = 135 ± 3, $\Delta H^\circ_{298,\ \text{atoms}}$($SiF_2$) = 288 ± 3 and D°_{298}(GeF) = 120 ± 3 kcal. mole^{-1} which are between 2 and 5 kcal. mole^{-1} larger than previous measurements.

THE FREQUENT USE of CaF_2 as a fluorinating agent in exchange equilibria—e.g., $CaF_2 + Ge \rightleftarrows GeF + CaF$ (*3, 4*)—for obtaining bond dissociation energies [D°(GeF) in this case] requires the establishment of accurate dissociation energies for CaF_2 and CaF. Several values for D°_{298}(CaF) are given in the literature. Both Blue *et al.* (*1*) and Hildenbrand and Murad (*5*) support a value of 125 ± 2 kcal. mole^{-1}, whereas Ryabova and Gurvich (*13*) claim 135 ± 7. Recent re-evaluation (*6*) of the primary standard, D°_{298}(AlF), for the original work of Blue *et al.* (*1*), increases the lower value of D°_{298} CaF to 127.5 ± 1.4 kcal. mole^{-1}. This disparity of about 8 kcal. mole^{-1} between the data of Blue *et al.* and Ryabova and Gurvich also exists for the dissociation energies of SrF and BaF.

A review of reactions involving CaF supports the original data of Blue *et al.* (*1*). Table I lists a number of reactions and their enthalpies which either directly or indirectly involve CaF. These were obtained by the well established Knudsen effusion-mass spectrometric technique.

From Reactions 1 and 2 the original D°_{298}(CaF) value was obtained. The well-established (*6, 7*) value of D°_{298}(AlF) = 160.2 ± 1.2 kcal. mole^{-1}, the heat of formation of CaF_2(s), and free-energy functions for each species were used (*2, 7*) to calculate D°_{298}(CaF) = 127.5 ± 1.4 kcal. mole^{-1} (Reaction 1) and D°_{298}(CaF) = 127.3 ± 2.8 (Reaction 2). These third-law data probably have an extra uncertainty of not more than 1 kcal. mole^{-1}, owing to the approximations, such as estimation of cross sections and multiplier efficiencies for each species. Hence, on the basis of these

Table I. Reactions Relating to Formation of CaF

	Reaction	ΔH°_{298} (Reaction)[a], Kcal. Mole^{-1}	Ref.
(1)	$Ca + AlF = Al + CaF$	34.6 ± 2.7[b]	(*1*)
		32.7 ± 0.2	(*1*)
(2)	$Ca + CaF_2(s) = 2CaF$	120.7 ± 0.8	(*1*)
(3)	$Ca + BF_3 = BF + CaF_2$	12.2 ± 2.5	(5)
		15.6 ± 2.5[c]	
(4)	$2Ca + BF_3 = BF + 2CaF$	29.8 ± 2.0	(5)
		ΔH°_f(BeF)	
(5)	$Be + BeF_2 = 2BeF$	40.0 ± 1.5	(6)
(6)	$Be + CaF = BeF + Ca$	40.0 ± 3	(6)
(7)	$Be + AlF = BeF + Al$	40.0 ± 3	(6)
		ΔH°_{298}	
(8)	$2Ca + SiF_2 = Si + 2CaF$	34.7 ± 0.9	(4)
(9)	$Ca + SiF_2 = CaF_2 + Si$	20.1 ± 1.5	(*15*)
(10)	$Ge + SiF_2 = GeF + SiF$	31.8 ± 0.5	(*15*)
(11)	$Ge + CaF = Ca + GeF$	7.7 ± 0.3	(*15*)
(12)	$Ca + SiF_2 = CaF + SiF$	24.0 ± 0.5	(*15*)
(13)	$2SiF = SiF_2 + Si$	20.3 ± 2[d]	(4)
(14)	$ScF_3 + 3Ca = 3CaF + Sc$	63.0 ± 2	(*16*)

[a] All gas phase reactions unless otherwise indicated. [b] Second-law determination. All other data use third law. [c] Value obtained by use in third law calculation of more recently determined spectroscopic constants for CaF_2 (*11, 14*). [d] Recalculated from Ehlert's original equilibrium data, using recently established (*9*), more accurate SiF_2, free-energy functions.