[1] Ref. (247)

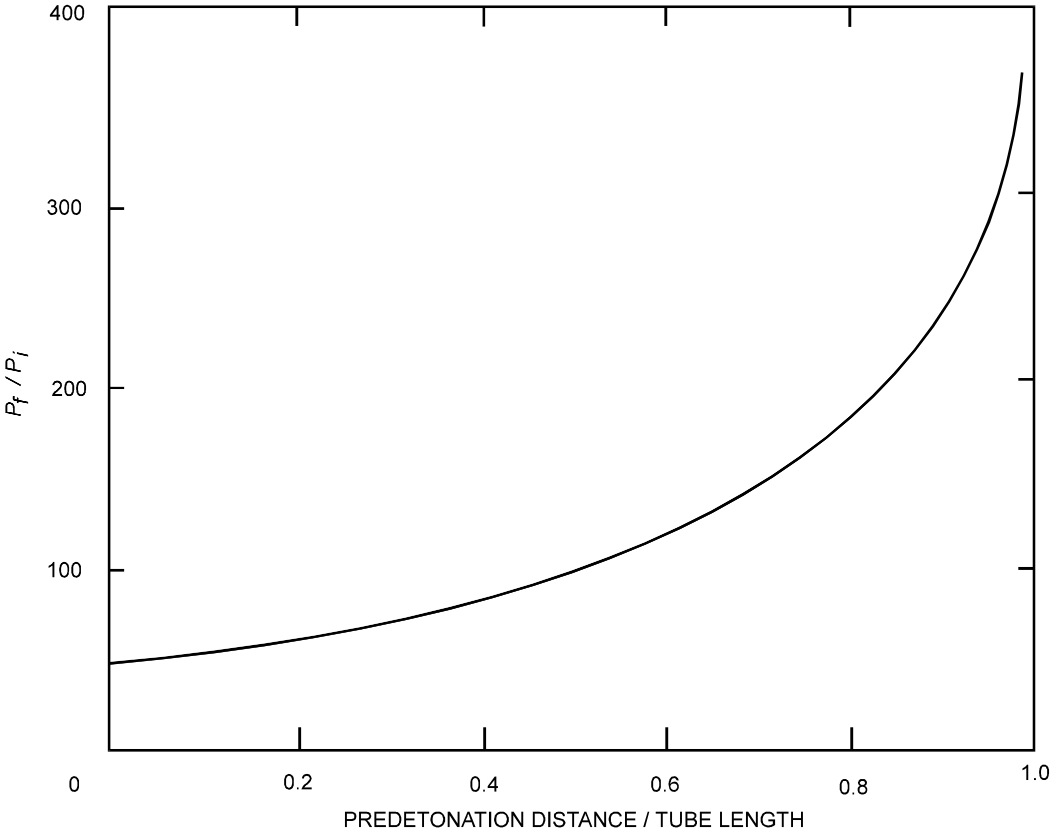

Figure 67—Final-to-Initial Pressure Ratios Developed by Acetylene With Detonation Initiation at Various Points Along a Tube.

The upper limits of the aromatics considered here at 100°C are included in table 11 (247). These were obtained at atmospheric pressure in a 2-inch-diameter tube, open at one end. Butler and Webb obtained upper limit data on a commercial grade cumene (93.3 pct cumene) in air at elevated temperatures and atmospheric and elevated pressures in a closed bomb (31). Their values range from 8.8 percent cumene (80°C and atmospheric pressure) to 10.8 percent cumene (146°C and 100 psig pressure).

Limits in Other Atmospheres

The limits of flammability obtained by Burgoyne (29) and by Jones (40) for benzene-carbon dioxide-air and benzene-nitrogen-air mixtures at atmospheric pressure and 25° C are given in figure 68; similar data are given for the last two mixtures at atmospheric pressure and 150°C. The inerting requirements at 25°C are approximately the same as those of *n*-hexane (fig. 33). Again, it should be noted that the methyl bromide data are not consistent with those obtained by Hill (compare figs. 28 and 33). These latter data (84) were used to construct the approximate (broken) flammability curves for the benzene-methyl bromide-air system.

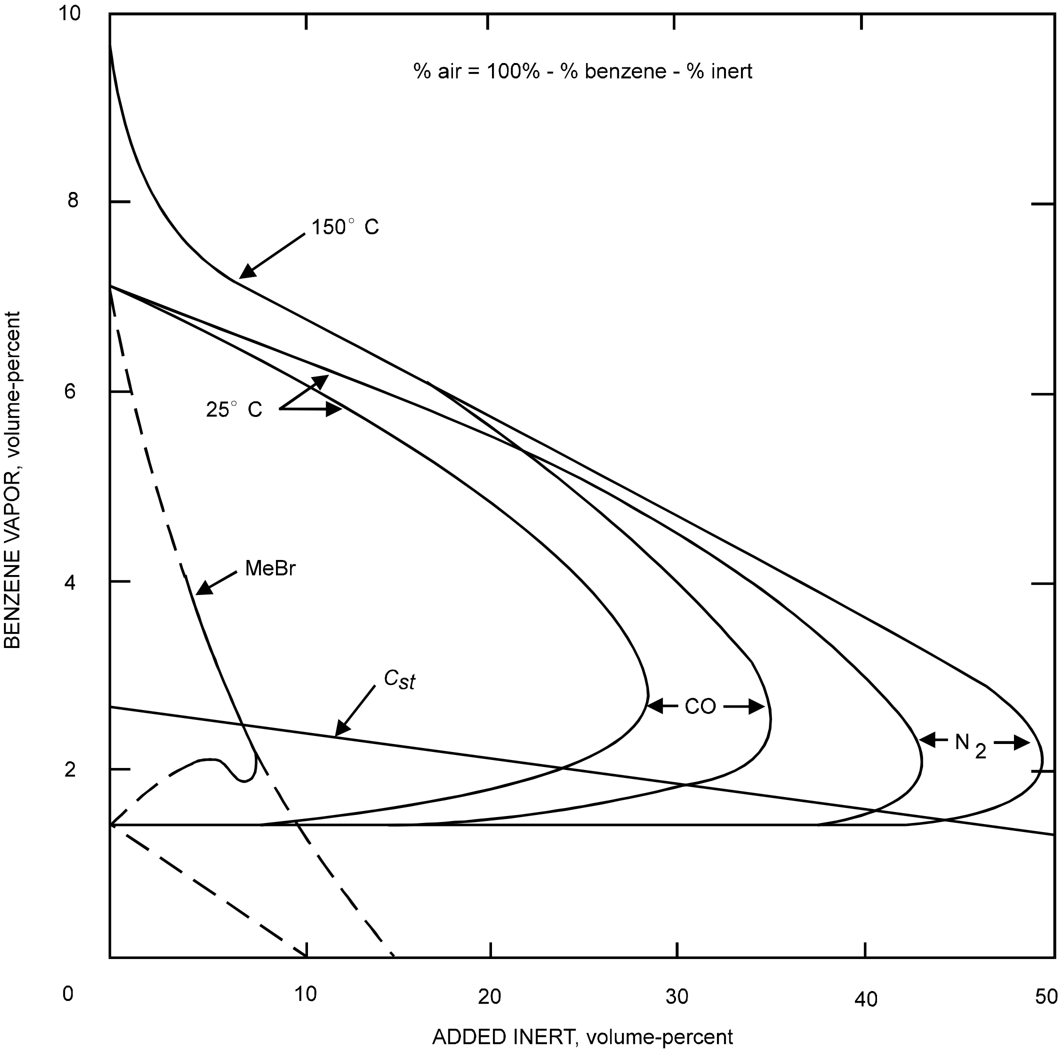

Figure 68—Limits of Flammability of Benzene-Methyl Bromide-Air Mixtures at 25°C and Benzene-Carbon Dioxide-Air and Benzene-Nitrogen-Air Mixtures at 25°and 150°C and Atmospheric Pressure.

The decrease in the minimum oxygen requirements for flame propagation (from 14.2±0.3 volume-percent at 25°C to 13.1±0.3 volume percent at 150° in a carbon dioxide-air atmosphere; from 11.4±0.3 volume-percent at 25°C to 10.1±0.3 volume-percent at 150° in a nitrogen-air atmosphere) is within the range predicted by the modified Burgess-Wheeler law (equation (35), fig. 23).

The limits of flammability of orthoxylene ($C_6H_4{\bullet}(CH_3)_2$)-water-hydrogen peroxide mixtures were determined at 154°C and 1 atmosphere pressure by Martindill, Lang, and Zabetakis (140). The data are presented in a triangular plot in figure 69; compositions are expressed in mole-percent as in the original presentation. This system has no lower limit mixtures, as a flame can be initiated in hydrogen peroxide vapors (186). As a 90-weight-percent hydrogen peroxide was actually used to obtain these flammability data, all compositions were calculated to yield values based on a 100-percent hydrogen peroxide content. This could be done here because only three components are considered. Where four components are considered, the flammability data can be presented in a three-dimensional plot; if two of the components appear in fixed proportions, a triangular plot can be used with the two components (for example, 90-weight-percent hydrogen peroxide) considered as a single component. Such a plot is presented in figure 70 for 90-weight-percent hydrogen peroxide-orthoxylene-formic acid (HCOOH) at 154°C and 1 atmosphere. This was considered to be a plane in a regular tetrahedron in the original article and is therefore not a regular triangle. As before, only an upper limit curve is given because 90-weight-percent hydrogen peroxide is flammable. In addition, a calculated curve based on Le Chatelier's rule is given, as is the upper limit curve obtained with decomposed hydrogen peroxide. Decomposition of the peroxide lowers the upper limit appreciably and yields a system which has a lower limit of flammability (not determined in this study).

Autoignition

The minimum autoignition temperatures of a series of aromatic hydrocarbons in air at atmospheric pressure are given in figure 71 as a function of the correlation parameter L_{ave}. This parameter was determined by use of equation (49), treating the benzene ring as a $-CH_3$ group (241). When the benzene ring contains two side groups, L_{ave} is determined first for the side group that yields the largest average value and to this is added 1/2, 1/3, or 1/4 of the average chain length of the second side group; (1/2, 1/3, and 1/4 correspond to the ortho-, meta-, and para-positions, respectively). The data again fall into high- and low-temperature regions (fig. 43).

Burning Rate

Burning rates and detonation velocities of benzene in air and oxygen appear to be approximately the same as those of the higher paraffin hydrocarbons. For example, the results of Golovina and Fyodorov (211) show that the maximum burning velocities of benzene in nitrogen-oxygen mixtures range from about 295 cm/sec in oxygen to 45 cm/sec in air; the maximum burning velocities of hexane in various nitrogen-oxygen mixtures range from about 260 cm/sec in oxygen to 40 cm/sec in air. Similarly, Fraser (61) found the maximum detonation velocities of benzene and *n*-octane in oxygen to be 2,510 and 2,540 m/sec, respectively.

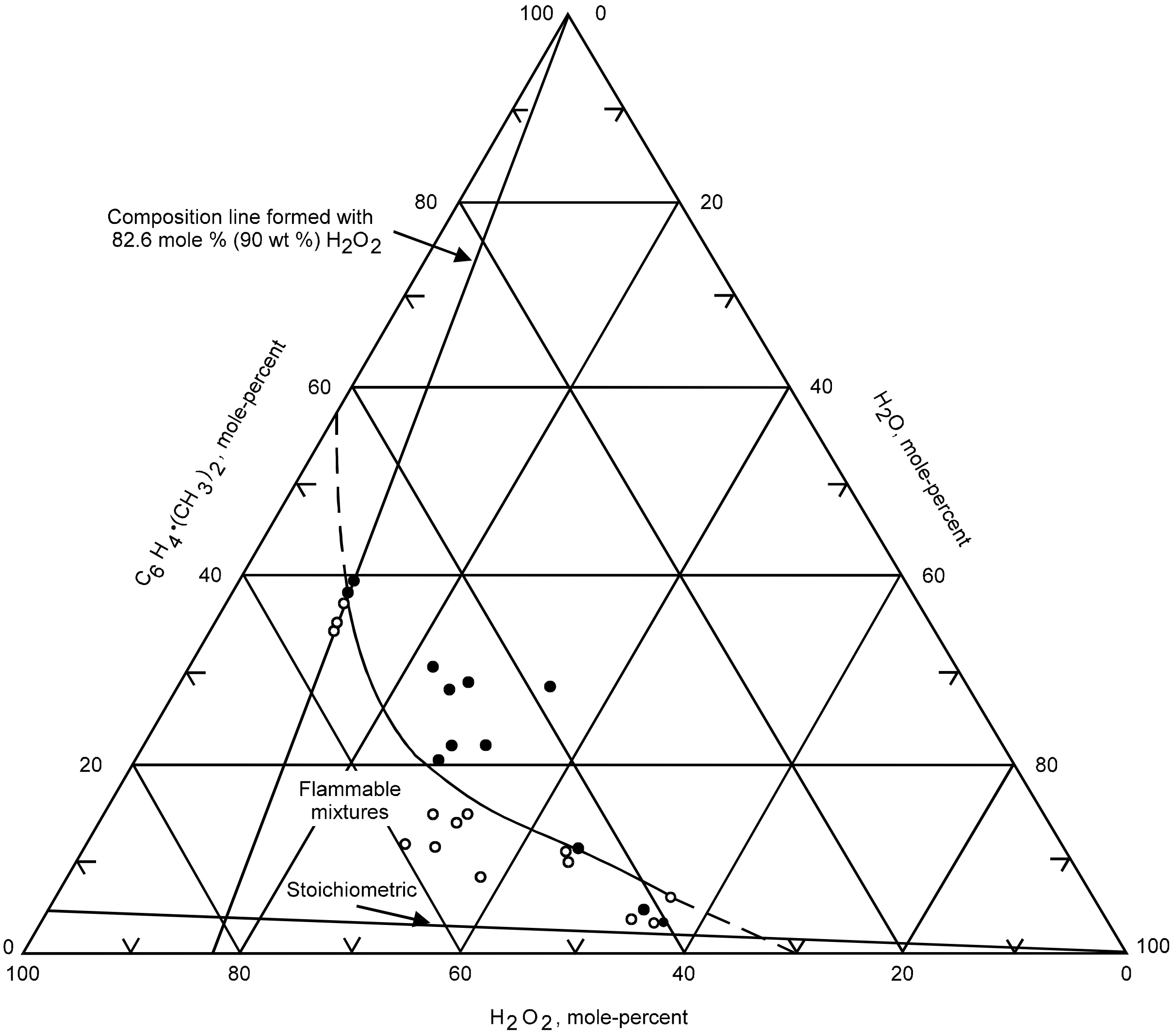

Figure 69—Limits of Flammability of H_2O_2-C_6H_4•$(CH_3)_2$-H_2O at 154°C and 1 Atmosphere Pressure.

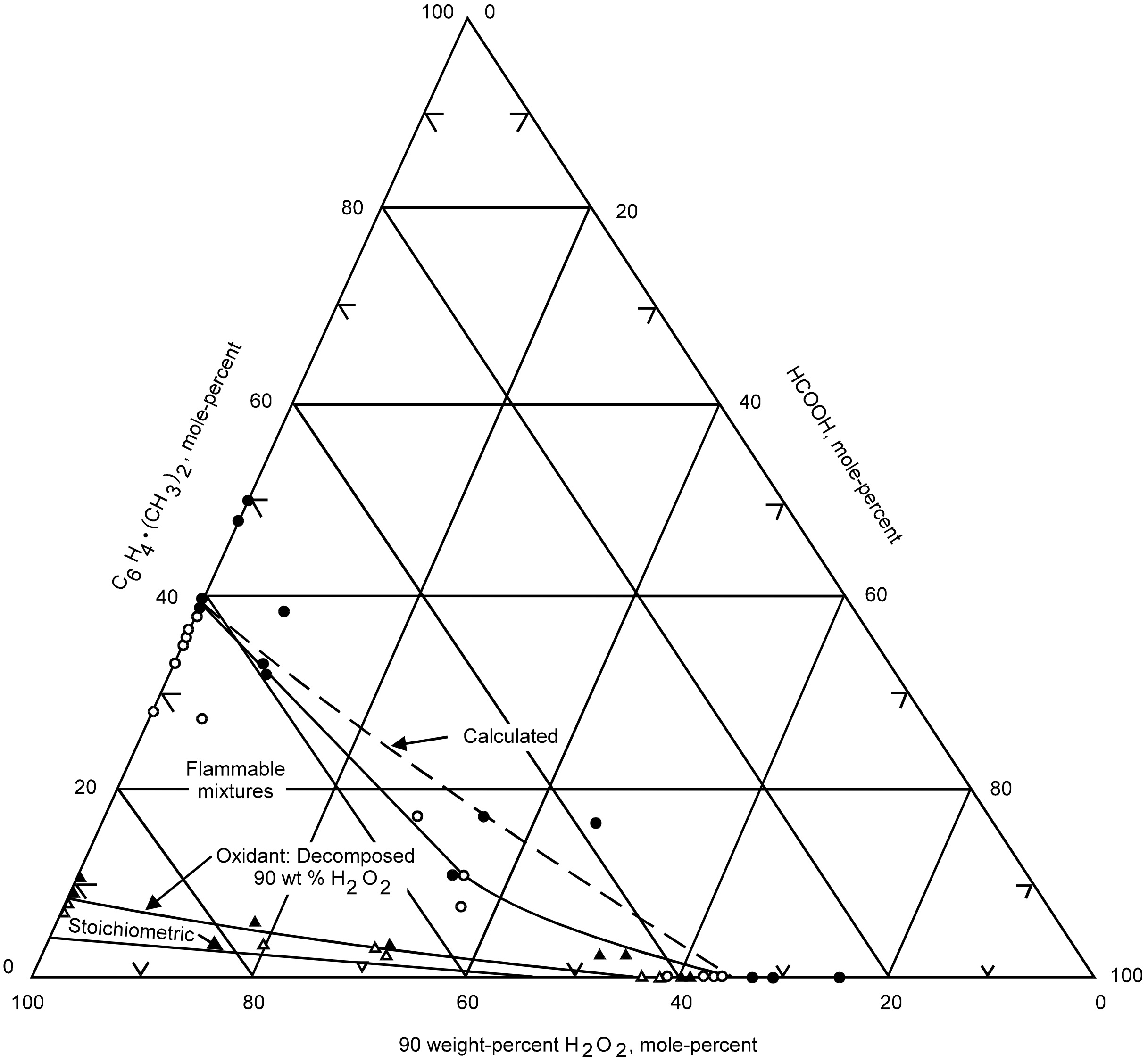

Figure 70—Limits of Flammability of 90-Weight-Percent H_2O_2-C_6H_4•$(CH_3)_2$-HCOOH at 154°C and 1 Atmosphere Pressure.

ALICYCLIC HYDROCARBONS (C_nH_{2n})

Limits in Air

A summary of the pertinent properties of some of the members of the series is given in table 12. The lower limits of flammability in air at atmospheric pressure and room temperature fall in the range from 48±3mg/l (.048±.003 oz combustible per cubic foot of air). By volume, this is equivalent to approximately 0.55 C_{st}, which is the same as for paraffin hydrocarbons. The ratio of the upper limit to C_{st} appears to increase with molecular weight.

According to Jones (40), the lower limit of cyclohexane in air at atmospheric pressure and 26°C determined in a 2.0-inch tube is 1.26 volume-percent. Under the same conditions, Burgoyne and Neale (26) found the lower limit to be 1.34 volume-percent, using a 2.5-inch tube. Matson and Dufour (141) found the lower limit to be 1.12 volume-percent at 21°C in a 12-inch diameter chamber about 15 inches long; however, there is evidence that they did not use the same criteria of flammability as did the other authors; only one observation window was provided at the top of a rather squatty chamber, whereas with the glass tubes used by Jones and by Burgoyne and Neale the flame could be observed along the entire tube. Accordingly, the data of Jones and of Burgoyne and Neale are used here.

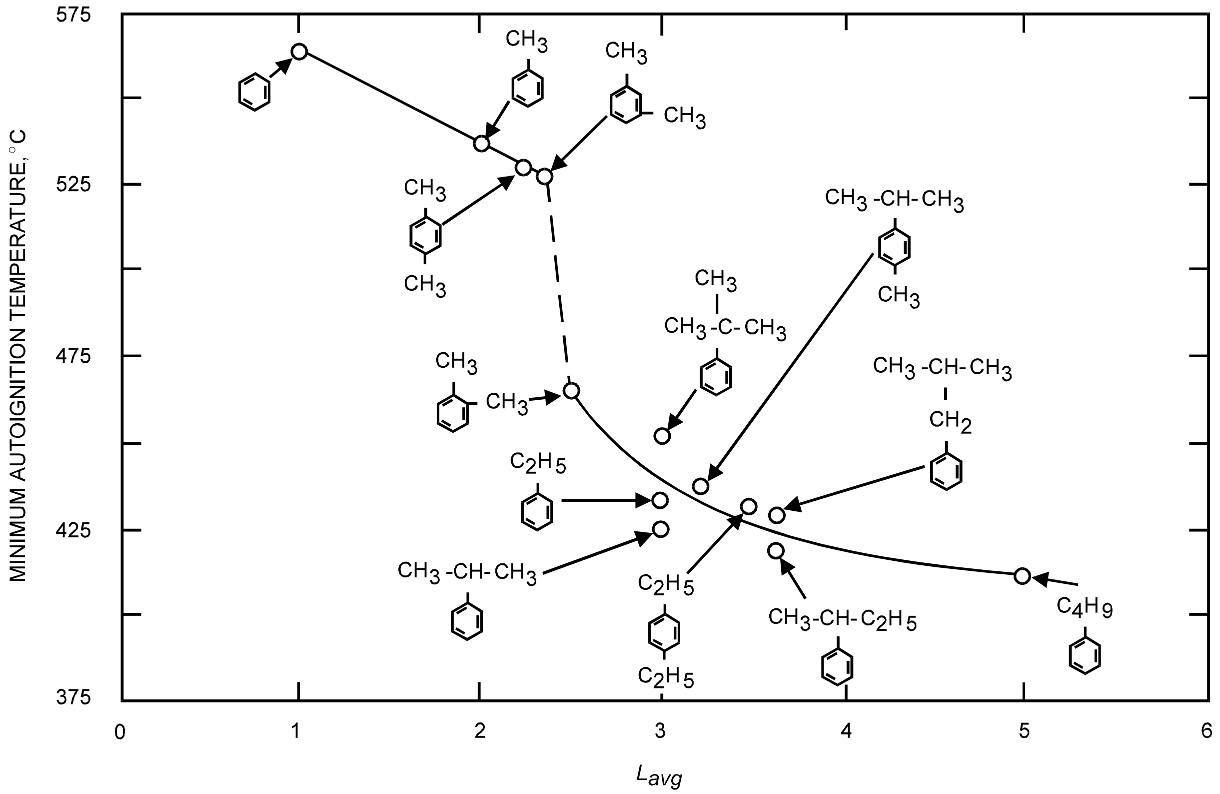

Figure 71—Minimum Autoignition Temperatures of Aromatic Hydrocarbons in Air as a Function of Correlation Parameter L_{ave}.

Table 12 — Properties of selected alicyclic hydrocarbons

Combustible	Formula	*M*	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	$L\left(\frac{mg}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	$U\left(\frac{mg}{1}\right)$	Ref.
Cyclopropane	C_3H_6	42.08	1.45	4.45	465	2.4	.54	46	(107)	10.4	2.3	220	(107)
Cyclobutane	C_4H_8	56.10	1.94	3.37	[1]600	1.8	.56	46	(1)	—	—	—	—
Cyclopentane	C_5H_{10}	70.13	2.42	2.72	740.8	1.5	.55	48	(1)	—	—	—	—
Cyclohexane	C_6H12	84.16	2.91	2.27	881.7	1.3	.57	49	(40)	7.8	3.4	320	(40)
Ethylcyclobutane	C_6H_{12}	84.16	2.91	2.27	[1]880	1.2	.53	46	(40)	7.7	3.4	310	(40)
Cycloheptane	C_7H_{14}	98.18	3.39	1.96	[1]1024	1.1	.56	49	(1)	6.7	3.4	310	(1)
Methylchcylhexane	C_7H_{14}	98.18	3.39	1.96	1026.0	1.1	.56	49	(40)	6.7	3.4	310	(1)
Ethylcyclopentane	C_7H_{14}	98.18	3.39	1.96	1032.6	1.1	.56	49	(40)	[2]6.7	3.4	310	(40)
Ethylcylcohexane	C_8H_{16}	112.21	1.71	1.71	1173.7	[3].95	.56	48	(40)	[3]6.6	3.9	350	(40)

[1] Calculated Value.
[2] P=0.5 atm.
[3] t=130° C.

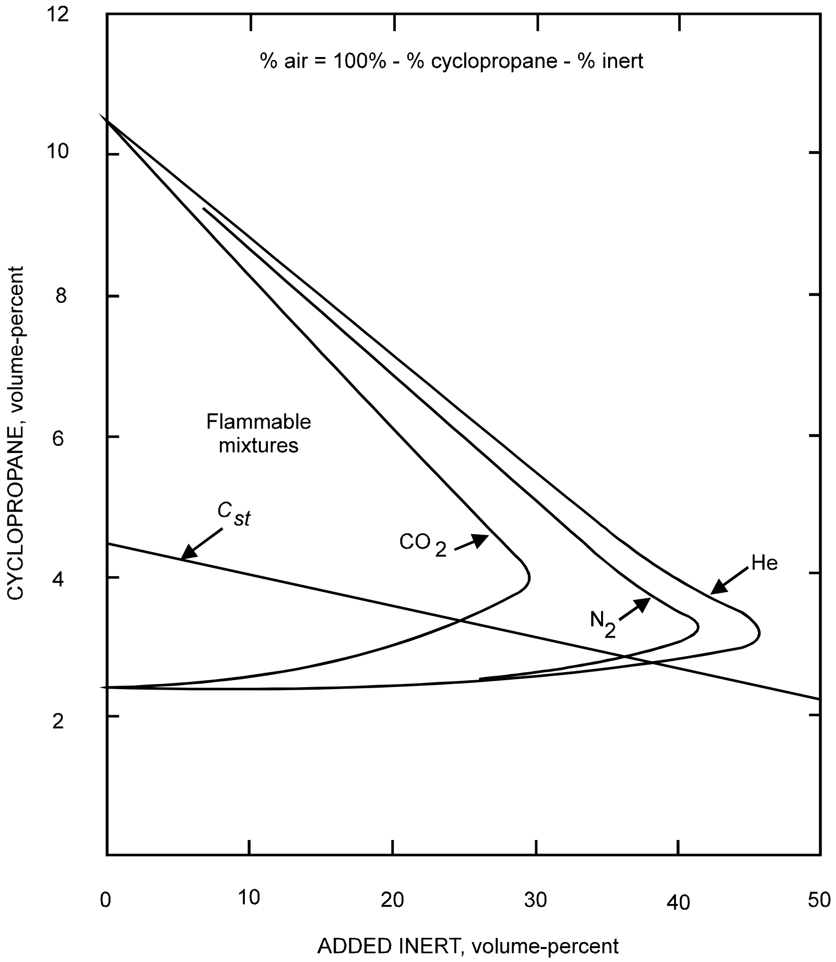

Figure 72—Limits of Flammability of Cyclopropane-Carbon Dioxide-Air, Cyclopropane-Nitrogen-Air, and Cyclopropane Helium-Air Mixtures at 25°C and Atmospheric Pressure.

Limits in Other Atmospheres

The limits of flammability of cyclopropane-carbon dioxide-air, cyclopropane-nitrogen-air, and cyclopropane-helium-air mixtures at 25°C and atmospheric pressure are given in figure 72 (106). The first two curves are similar to those obtained with paraffin hydrocarbons (fig. 35).

The limits of flammability of cyclopropane-helium-oxygen and cyclopropane-nitrous oxide-oxygen mixtures at 25°C and atmospheric pressure are given in figure 73 (106). The latter curve differs from the former, as both additives are oxidants (oxygen and nitrous oxide).

The limits of flammability of cyclopropane-helium-nitrous oxide mixtures at 25°C and atmospheric pressure are given in figure 74 (106). Here the minimum oxidant concentration (nitrous oxide) required for flame propagation is approximately twice the corresponding concentration of oxygen in the systems cyclopropane-helium-air (fig. 72) and cyclopropane-helium-oxygen (fig. 73).

ALCOHOLS ($C_nH_{2n+1}OH$)

Limits in Air

The alcohols considered here are listed in table 13 together with L_{25° and U_{25°. The ratios L_{25°/C_{st} are approximately 0.5. However, the L (mg/l) values decrease with increase in molecular weight. If L^* is taken to be the weight of combustible material (exclusive of the oxygen in the molecule) per liter of air, then for the simple alcohols:

$$L^* = L\frac{M-16}{M}. \qquad (54)$$

This equation gives the values listed in parentheses in the mg/l column; these are in fair agreement with the values obtained for the saturated hydrocarbons. Approximate L (mg/l) values can be obtained from the higher hydrocarbon values given in figure 22 by multiplying these by the ratio $M/(M–16)$. Further, figure 19 can be used to obtain L^* and L values in volume-percent.

For example, at 25°C, L^* is about 47 mg/l from figure 22; the corresponding L^*_{25} from figure19 for ethyl alcohol (M=46) is 2.2 volume-percent. Then, from equation (54), L is 3.4 volume-percent; the measured value is 3.3 volume-percent.

The lower limits of methyl alcohol have been determined by Scott and coworkers at 25°, 100°, and 200°C (192). The values at these three temperatures are 6.7, 6.5, and 5.9 volume-percent, respectively. The calculated values obtained from the modified Burgess-Wheeler law (fig. 23) at 100° and 200°C are 6.4 and 5.8 volume-percent, respectively.