The Flammability Limits of Fluorobenzenes in Oxygen and Oxygen–Nitrogen Mixtures

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Fluorocarbons possess many chemical and physical properties of value in a variety of applications that depend on their low flammability. While it is known that the most highly fluorinated compounds are effectively "nonflammable" in air, there is little accurate information available concerning the flammability limits of such compounds in oxygen or oxygen-enriched air.

A systematic study has therefore been made of a considerable number of fluorobenzenes in both oxygen and oxygen–nitrogen mixtures, and this study shows clearly that the flammability of these compounds depends almost entirely on the degree of fluorination of the benzene ring and scarcely at all on the positions that the substituent fluorine atoms occupy.

Introduction

The development of practicable synthetic routes to an extensive range of highly fluorinated hydrocarbons at reasonable cost has resulted in the industrial use of such compounds becoming a viable proposition. The potential uses of fluorocarbons include functional fluids (such as lubricants, hydraulic fluids, evaporative coolants for electronic equipment, and liquid-coolants for power generators) and pharmaceuticals (e.g., inhalation anesthetics). It is evident, however, that if this potential is to be realized, then these compounds must be essentially nonflammable.

While it is known that the most highly fluorinated compounds are very much less flammable than their hydrocarbon analogues, there is little information regarding the precise flammability limits of organic fluorine compounds. It has been shown, for example, that mixtures of fluothane and oxygen containing between 0.1 % and 100 % fluothane are nonflammable. Indeed, fluothane acts as an inert diluent for flammable mixtures of diethyl ether and oxygen containing 3 % v/v diethyl ether, and it was

concluded, therefore, that fluothane is nonflammable under all ordinary conditions [1]. Similarly, tri-fluoro-di-chloroethane was found to be nonflammable for a wide range of concentrations in oxygen at temperatures from −16° to 30°C [2]. More recently, the lower limit of flammability of hexafluorobenzene in oxygen was found to lie in the range 4.0 %–4.2 % v/v [3]. However, no more systematic studies have been carried out, and the present paper describes the first attempt to obtain a quantitative correlation between flammability and the degree of fluorination.

Experimental

Oxygen and oxygen-free nitrogen from cylinders were dried by passage through columns of anhydrous magnesium perchlorate and then mixed in a large cylindrical Pyrex vessel packed with glass beads supported on a glass wool pad. The rate of flow of each gas was controlled and measured by needle valves and calibrated rotameters. Prior to the introduction of the mixed

gases into the combustion chamber, the percentage of oxygen in the mixture was measured to within 0.1% v/v by means of a Magnetic Oxygen Analyser.

The combustion chamber was a vertical glass tube (12 in. × 1 in.) open at the top end, into which two thin platinum electrodes were sealed with a spark gap of 0.125 in. The chamber and a 6-ft coil of glass tubing were mounted in a thermostatically controlled bath. The gases leaving the oxygen analyzer were passed through the coil and entered the explosion chamber through a small jet at its base, which was covered by the test compound to a depth of 1 in. The gaseous mixture flowing past the electrodes at a total flow rate of 45 ml min^{-1} thus consisted of oxygen (and nitrogen) and the test compound, the partial pressure of which was equal to its saturated vapor pressure at the temperature of the bath.

Flammability tests were carried out by passing a continuous discharge across the electrodes, which were connected across the secondary of an induction coil, the output voltage of which was 70 kV. Spark energies were, therefore, well above the respective threshold energies. Mixtures were considered flammable only if the flame propagated throughout the length of the combustion chamber. Since the combustion chamber was of somewhat smaller diameter than that recommended by Coward and Jones [4], control experiments were carried out to ensure compatibility with known hydrocarbon flammability data. The flammability limits for upward propagation for benzene and for n-heptane in air were therefore determined and found to agree within 0.02% v/v with those cited in the literature [4].

Monofluorobenzene was obtained from British Drug Houses Limited and the difluorobenzenes from the Pierce Chemical Company. 1,2,4-Trifluorobenzene was prepared from 2,3,5,6-tetrafluorophenylhydrazine [5]; is was purified by repeated fractional distillation until gas chromatographic analysis and infrared spectroscopy showed the absence of impurities. The boiling point of the resulting sample was 88°C at 741.6 mm Hg (lit value = 89.9°C). Pure samples of the remaining fluorobenzenes were kindly given by Imperial Smelting Corporation Limited.

The vapor pressure of 1,2,4-trifluorobenzene and of the difluorobenzenes was determined over the temperature range used (Fig. 1), whereas that of the remaining fluorobenzenes was interpolated from the respective Antoine equations. The purity and vapor pressure data for each fluorobenzene are given in Table 1.

The lower limit of flammability for upward propagation for each fluorobenzene in pure oxygen was determined by cooling the bath to either −15°C or the melting point of the fluorobenzene under test (whichever was higher) and then allowing the bath temperature to rise slowly. Tests were made at intervals of 0.1°C. (For monofluorobenzene, 1,3-difluorobenzene, and 1,4-difluorobenzene it was necessary to cool the bath to −45°, −18°, and −20°C, respectively.) The remainder of each flammability diagram was constructed by finding the minimum percentage of oxygen in the oxygen-
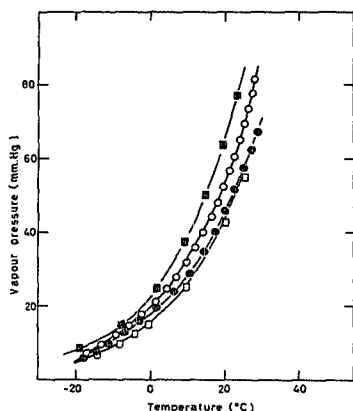

Figure 1. Vapor pressure curves for the difluorobenzenes and 1,2,4-trifluorobenzene. Open squares, 1,2-; solid squares, 1,3-; open circles, 1,4-; solid circles, 1,2,4-.

Table 1. Vapor Pressure Data and Purity of the Fluorobenzenes

Fluorobenzene	Vapor Pressure	Purity, %		
mono-	[6]	>98		
ortho-	Fig. 1	>98		
meta-	Fig. 1	>98		
para-	Fig. 1	>98		
1, 2, 4-	Fig. 1	>98		
1, 3, 5-	$\log P = 6.91873 - \dfrac{1196.385}{t + 219.019}$	>99		
1, 2, 3, 4-	$\log P = 7.19386 - \dfrac{1396.067}{t + 228.873}$	>97		
1, 2, 3, 5-	$\log P = 7.03481 - \dfrac{1258.429}{t + 281.476}$	>99		
1, 2, 4, 5-	$\log P = 7.04381 - \dfrac{1274.335}{t + 215.336}$	98.7	0.8 0.5	1, 2, 3, 5- 1, 2, 4-
penta-	$\log P = 7.03488 - \dfrac{1253.043}{t + 215.897}$	>99	0.5 0.1	C_6F_5Br unknown
hexa- [7]	$\log P = 7.01741 - \dfrac{1219.410}{t + 214.525}$	>99	0.2 0.1 0.1 0.2	penta- 1, 2, 3, 5- benzene unknown

nitrogen mixture required for flame propagation for a given concentration (% v/v) of fluorobenzene in the final mixture.

Results and Discussion

The flammability diagrams obtained are shown in Fig. 2–6. Table 2 shows the % v/v of fluorobenzene at the lower limit in pure oxygen and the lowest % v/v of oxygen that will sustain flame propagation together with the corresponding % v/v of fluorobenzene (see Fig. 2). The latter limit is referred to as the "lowest limit for all mixtures." It was not possible to obtain the lower limit for 1,3,5-trifluorobenzene by the present technique since this compound froze before the limit was reached.

The results show clearly that fluorination of the benzene ring leads to a decrease in flammability. Indeed, the tetrafluorobenzenes, pentafluorobenzene, and hexafluorobenzene are not

flammable in air under any conditions. On the other hand, all the less highly halogenated fluorobenzenes are flammable in air, and their
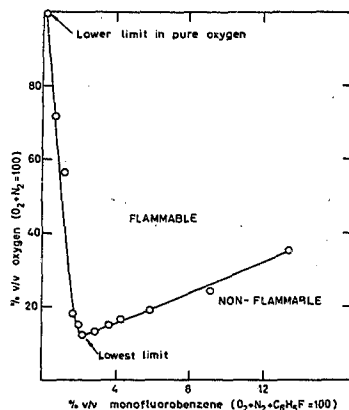

Figure 2. Flammability diagram for monofluorobenzene.

Figure 3. Flammability diagrams for the difluorobenzenes. Circles, 1,2-; squares, 1,3-; triangles, 1,4-.
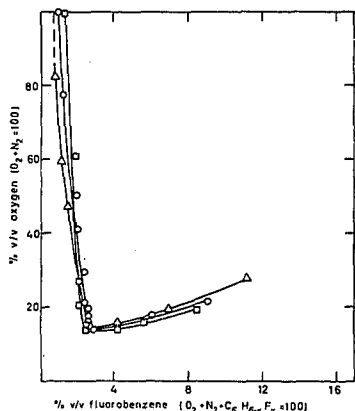

Figure 5. Flammability diagrams for the tetrafluorobenzenes. Circles, 1,2,3,5-; squares, 1,2,3,4-; triangles, 1,2,4,5-.

lower limits in air, which are compared with those of benzene in Table 3, increase with fluorine content.

The variation of % v/v of fluorobenzene at the lower limit in pure oxygen with the degree of fluorination of the benzene ring (i.e., molec-
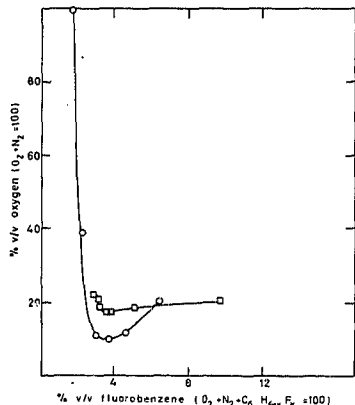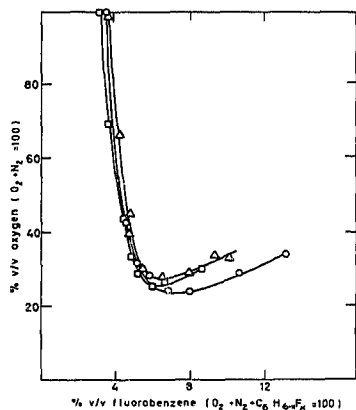
ular weight) is shown in Fig. 7 and may be expressed by the equation

$$L = 0.9M - 0.8$$

where L is the % v/v of fluorobenzene and M the number of substituent fluorine atoms. This

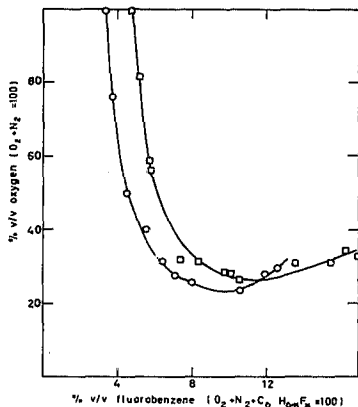Figure 4. Flammability diagrams for the trifluorobenzenes. Circles, 1,2,4-; squares, 1,3,5-.

Figure 6. Flammability diagrams for penta- (circles) and hexafluorobenzene (squares).

Table 2. Concentration of Fluorocarbon and Oxygen at the Limits

Compound	No. of F atoms	Lower Limit for Upward Propagation in Oxygen % v/v Fluorobenzene	Lowest Limit for Upward Propagation, % v/v	
			Oxygen $(O_2 + N_2 = 100)$	Fluorobenzene $(O_2 + N_2 + C_6H_{6-x}F_x = 100)$
C_6H_5F	1	0.13	12.5	2.4
$1,2\text{-}C_6H_4F_2$	2	0.86	14.0	3.0
$1,3\text{-}C_6H_4F_2$	2	1.25	13.5	3.0
$1,4\text{-}C_6H_4F_2$	2	0.75[a]	14.0	3.0
$1,2,4\text{-}C_6H_3F_3$	3	1.63	9.8	3.6
$1,3,5\text{-}C_6H_3F_3$	3	—	17.0	3.5
$1,2,3,4\text{-}C_6H_2F_4$	4	3.09	25.0	6.0
$1,2,3,5\text{-}C_6H_2F_4$	4	3.46	23.5	7.2
$1,2,4,5\text{-}C_6H_2F_4$	4	3.55	27.5	6.4
C_6HF_5	5	3.29	23.2	9.5
C_6F_6	6	4.66	26.0	11.5

[a] Obtained by extrapolation.

relationship is in direct contrast to the inverse relationship found for n-alkanes [8]:

$$\frac{1}{L} = 0.1347n + 0.0435$$

where n is the carbon number.

The % v/v of fluorobenzene at the lowest limit for all mixtures may also be correlated with the degree of fluorination (Fig. 8), but, in contrast, the relationship is not linear:

$$\frac{1}{L} = 0.455 - 0.061M$$

Correlation between the % v/v of oxygen and the degree of fluorination is, however, poor by comparison with that found for % v/v of

Table 3. Lower and Upper Limits for Upward Propagation in Air

	Limits, % v/v $(O_2 + N_2 + C_6H_{6-x}F_x = 100)$	
	Lower	Upper
Benzene	1.40	7.1
Monofluorobenzene	1.64	6.3
1,2-Difluorobenzene	2.42	8.0
1,3-Difluorobenzene	2.20	8.6
1,4-Difluorobenzene	2.52	7.3
1,2,4-Trifluorobenzene	2.45	6.4
1,3,5-Trifluorobenzene	3.16	8.0

fluorobenzene, as shown in Fig. 9. In particular, the value obtained for 1,2,4-trifluorobenzene appears to be anomalous. Even so, the decrease in flammability with increase in the degree of fluorination is again apparent and an inverse relationship is found:

$$\frac{1}{L} = 0.088 - 0.0085M$$

where L is the % v/v of oxygen in this case.

The flammability limits of the fluorobenzenes clearly depend almost entirely on the availa-
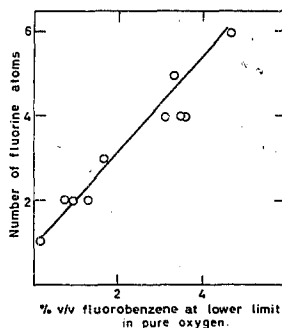

Figure 7. Influence of degree of fluorination on the limiting fluorobenzene concentration at the lower limit.
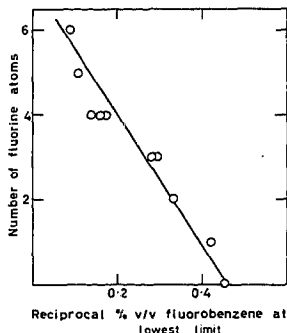
Figure 8. Influence of degree of fluorination on the limiting fluorobenzene concentration at the lowest limit for all mixtures.
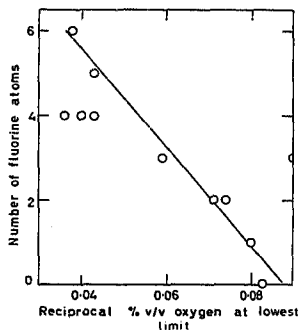

Figure 9. Influence of degree of fluorination on the limiting oxygen concentration at the lowest limit for all mixtures.

bility of the comparatively weak C—H bonds and little if at all on the position of substitution. This is in accord with spark ignition studies on hydrocarbons in general, where it is found that molecular structure, as opposed to molecular weight, has relatively little influence on the tendency of these compounds to spark ignition, particularly when compared with its effect on the tendency of these compounds to ignite spontaneously [8].

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