

# Flammability Studies of Isomeric Structures of Ethane Derivatives and Percolation Theory

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Published online: 1 September 2007  
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**Abstract** In order to analyze how isomeric structures will affect the combustion hazard, the lower flammability limits (LFL) of 1,1,1-trifluoromethane (R-143a) and 1,1,2-trifluoroethane (R-143) have been measured using a modified ASTM E681 method. The modification is a spark ignition source in which the current is set at 10 mA and the voltage is adjusted (7–12 kV) so that dielectric breakdown just begins to occur rather than 30 mA at 15 kV specified by the ASTM E681-04 method. An earlier study on the LFL of difluoromethane indicated that flammability limits by the modified ASTM E681 method are affected by vessel size. In order to investigate the vessel volume effect on the measured LFL, experimental measurements of the LFL of R-143 and R-143a are made at 21.5°C using 5-, 12-, and 20-L vessels. For vessel volumes of 5-L and larger, the LFL systematically shift to higher concentrations of R-143 and R-143a with increasing vessel size which is consistent with a percolation model. Extrapolation of the measured LFL data to infinite vessel size using a percolation model yielded 3.57 and 2.96 mol · m<sup>-3</sup> for R-143a and R-143, respectively.

**Keywords** ASTM E681 · Flammability · Percolation theory · R-143a · R-143 · 1,1,1-Trifluoroethane · 1,1,2-Trifluoroethane

## 1 Introduction

Environmental regulations require the complete phase-out of CFCs and HCFCs due to their stratospheric ozone depletion potentials. Although the leading class of alternative

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compounds, hydrofluorocarbons (HFCs), do not harm the stratospheric ozone, they may have an impact on global warming because of their long atmospheric lifetimes. The addition of hydrogen to these halogenated organics reduces the atmospheric lifetime of the compound while preserving the thermodynamic efficiencies that make them desirable in their roles as refrigerants. Unfortunately, the increased hydrogen content of these molecules also increases the probability that they become flammable, which is the case when the number of C–C and C–H bonds is greater than the number of C–F bonds [1]. These considerations have increased interest in studying refrigerant flammability in recent years and have resulted in several reviews and investigations of methods used for experimental investigations [2–4].

The application of flammable compounds, such as refrigerants, creates a potential hazard if a leak or some accidental release of the refrigerant were to occur in a refrigeration system. This liability necessitates the classification of the flammability characteristics for alternative refrigerants in order to be considered feasible for industrial use. So the problem is establishing a method to characterize the combustion hazards of these chemicals. The determination of flammability limits, most notably the lower flammability limit (LFL), is one methodology of combustion classification.

The manner of flame propagation is also of interest, especially in the determination of how molecular properties can affect flammability. Although the effect of molecular properties, in particular, intermolecular forces, on thermophysical properties of compounds such as boiling point, critical temperature, miscibility properties, etc. has been studied extensively, very little is known about their effect on flammability. In order to initiate a study of the effect of molecular properties on flammability, the flammability properties of two isomeric structures, CF<sub>2</sub>HCH<sub>2</sub>F (R-143) and CF<sub>3</sub>CH<sub>3</sub> (R-143a), are evaluated. The boiling points, dipole moments, and critical temperatures of these compounds differ significantly, but their enthalpy of formations are very similar (See Table 1).

Vapor flammability is defined as the ability to propagate a flame without limits upon initiating the flame by a spark, hot wire, or small match flame. The lower limit concentration of vapor in air where the onset of flammability begins to occur is called the LFL, and the upper limit concentration of vapor in air where the initiated flame just begins to be extinguished is referred to as the upper flammability limit (UFL). The ability to identify a concentration gap between LFL and UFL would mean that the vapor is flammable.

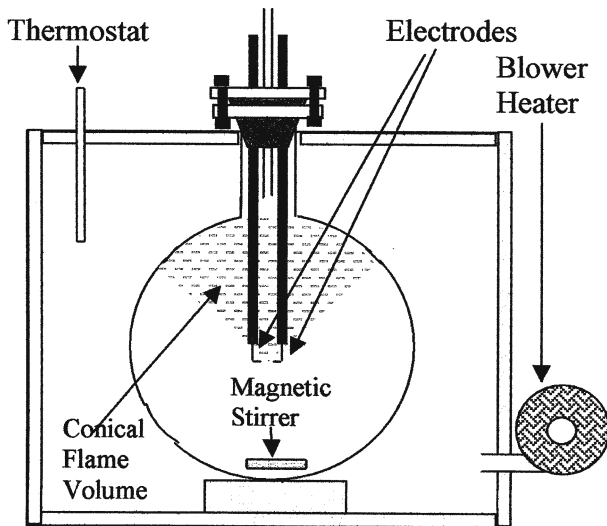
**Table 1** Boiling points, dipole moments, critical temperatures, and enthalpy of formation of R-143a and R-143

Refrigerant	Boiling point (°C)	Dipole moment (D)	Critical temperature (°C)	Enthalpy of formation (kJ · mol <sup>-1</sup> )
R-143a	-47.2 <sup>a</sup>	2.29 <sup>b</sup>	73.2 <sup>a</sup>	744.6 <sup>a</sup>
R-143	5.0 <sup>a</sup>	1.68 <sup>b</sup>	156.7 <sup>c</sup>	730.7 <sup>a</sup>

<sup>a</sup> Obtained from [5]

<sup>b</sup> Estimated with SPARTAN 5.1 Molecular Modeling Program.

<sup>c</sup> Obtained from [6]



**Fig. 1** Sketch of the flammability apparatus

The currently accepted and most widely used method for experimental studies of flammability is the ASTM E681-04 apparatus (see Fig. 1) [7]. This method involves a vapor–air mixture inside a round bottom flask, which may be either 5- or 12-L in volume. The 12-L flask is specified for halogenated hydrocarbons, and other difficult to ignite materials with large quenching distances. The flame is initiated at 1/3 of the diameter from the bottom of the flask by a spark. With this method the LFL is the lower limit concentration where the flame is propagated upward into a volume defined by a 45° conical angle measured from the vertical axis of a cone whose origin is the point of the flame initiator or spark. A similar criterion is used to determine the UFL. The earlier versions of the ASTM E681 method (ASTM E681-85 [8] and ASTM E681-94 [9]) also suggest other types of ignition sources (fused wire and match) for difficult-to-ignite vapors in 5-L flasks [9]. All three ignition sources (spark, fused wire, and match) have been used since the late 1980s. Earlier measurements of Coward and Jones [10] were performed by studying upward flame propagation in a tube rather than in a round bottom flask. Recent reviews have noted significant variations [4] in flammability measurements from different laboratories [2,3]. In view of the variations in flammability measurements by different laboratories, an ingenious counter-flow burner method has recently been proposed and developed by Womeldorf and Grosshandler [4], which is very reliable and provides for very accurate and reproducible results.

Nevertheless, the question of how experimental data obtained in a small-scale experiment (5- or 12-L flask) will carry over to the appraisal of a fire hazard in large-scale applications remains [2]. Our previous work [11] on trifluoromethane (R-32) showed that the LFL increased with vessel size. This is consistent with Richard [12], who found the LFL of R-134a/R-152a mixtures increased by 0.5 mass% (9.6–10.1 mass%) of the flammable component, R-152a, for measurements in a very large 200-L vessel as compared with the LFL in a 12-L vessel. Richard also studied R-125/R-152a mixtures

in a 200-L vessel and obtained similar results in which the LFL increased by 0.5 mass% (19–19.5 mass%) as compared with the LFL for a 12-L vessel. In our previous work [11], we used percolation theory [13] to explain the effect of vessel size on the LFL, and used the theory to obtain an LFL in the infinite volume limit. In our earlier work, we adhered to all ASTM E681-94 specifications [9], excepting for current and voltage settings. We used a 10 mA current and just sufficient voltage (7–12 kV) to generate a 0.2–0.4 s duration spark rather than 15 kV at 30 mA as specified by ASTM E681-94. The 15 kV at 30 mA would have placed a large perturbation on the system. Ideally, application of percolation theory would call for a negligible perturbation of the system by the flame initiator. Therefore, we selected minimal current voltage settings that are just sufficient to generate a spark. Although we did deviate from the current voltage settings specified by ASTM E681-94, results of our earlier work on difluoromethane using a 12-L vessel [ $6.02 \text{ mol}\cdot\text{m}^{-3}$  (14.7 vol%)] are in good agreement with the most recent results of Wilson and Richard [ $5.85 \text{ mol}\cdot\text{m}^{-3}$  (14.4 vol%)] [14], who used the ASTM E681-98 method [15]. It is probable that the slightly higher LFL obtained in our work reflects the minimal current voltage settings that we selected.

In this work, the experimental methods and percolation theory developed in our earlier work [11] are used to study the flammability of the isomers 1,1,1-trifluoroethane (R-143a) and 1,1,2-trifluoroethane (R-143). (a) A primary motivation for this study is that we would like to examine isomeric effects because these could give information on how molecular properties may affect flammability of the two isomers, R-143a and R-143, one of which (R-143a) is an important refrigerant whose flammability has been recently studied [14]. The methods which we have developed should be ideal for studying isomeric effects because the volume effects and ignition source perturbations which might mask what may be small effects are either eliminated by application of percolation theory or minimized by employing a minimal current–voltage spark. (b) Secondly, we would like to confirm the predictions of percolation theory found in our earlier work [11]. These studies showed that the percentage difference between the LFL of R-32 obtained for the infinite volume limit using percolation theory and that for a 12-L vessel is 3.4%. (iii) A third goal is to determine if the 3.4% increase in the LFL for R-32 carries over to other systems, specifically R-143a and R-143. The practical implications of percolation theory predictions for intermediate volume containers, i.e., between 12-L and very large containers, are also examined. In the following sections, we present the results of this study.

## 2 Experimental Methods and Results

The reader is referred to the authors' previous publication [11] for a description of experimental methods. The chemicals, R-143 and R-143a, used in the experiments were purchased from SynQuest Labs and PCR, respectively, with 99% purity. The chemicals were used without further purification.

The apparatus used for the LFL measurements is constructed according to the design for the ASTM E681-04 method (see Fig. 1) [7]. The round bottom flask containing the vapor–air mixture was contained inside an insulated box with a Plexiglas door to observe flask contents as shown in Fig. 1. The temperature could be raised above

room temperature using a blower which contained a heating element for raising the temperature of the box. The temperature could be controlled via a trimmer heater and a thermostat. In general, flammability measurements are conducted at 23, 60, and 100°C [14]. However, for the purposes of this work, we only report results at room temperature, i.e., 21.5°C to within  $\pm 2^\circ\text{C}$ . Our average temperature is 1.5°C less than specified by ASTM E681-04 [7], but is within the uncertainty of the temperature that ASTM E681-04 specifies for temperature control at elevated temperatures ( $\pm 3^\circ\text{C}$ ). Although it is preferred to perform the experiments at the ASTM E681-04 specified temperature, we do not expect it to be a factor in comparing our results with other very recent work. The temperature was measured with a thermocouple to within  $\pm 0.1^\circ\text{C}$  and the exact temperature was used to convert the molar concentration of each gas to  $\text{mol}\cdot\text{m}^{-3}$  from the measured partial pressure.

The electrode assembly was held in place with a rubber stopper which also served to seal the round bottom flask. The stopper also provided entry into the flask for evacuation and introduction of gases at a desired pressure. The pressure was measured with a precision MKS Baratron capacitance pressure sensor (622A13TAD) with a sensitivity of  $\pm 0.015\text{ kPa}$  ( $\pm 0.1\text{ torr}$ ). The gases, R-143, R-143a, and air, could be metered into the flask to a desired pressure via a needle valve. Before introducing gases, the flask was evacuated to about  $1 \times 10^{-3}\text{ kPa}$ . After evacuation, there is a 15-min waiting period to be certain there are no leaks.

Before introduction of gases, water was first introduced into the flask via a septum, using a microsyringe, in order that the relative humidity within the flask is 50% at 21.5°C. The partially fluorinated hydrocarbon vapor, which is under investigation, is then introduced into the flask to its desired pressure (ranging from 8 to 9 kPa for R-143a, and 6 to 7 kPa for R-143). Lastly, dry air was then introduced into the flask until the pressure was 100 kPa (1 bar). The magnetic stirrer was turned on to mix the flask contents for about 5 min.

To initiate the flame with a spark, a DEL high voltage power supply is used that is capable of providing voltages up to 20 kV with currents as high as 50 mA. However, the flammability experiments were conducted by adjusting the voltage and current so that the electrodes just begin to generate a spark for 0.2–0.4 s across the electrode gap of 6.4 mm. The voltage ranged from 7 to 12 kV depending mostly on the flask size; the larger flask size requiring the greater voltage. We achieved great reproducibility and a precisely defined flammability limit [to within 0.015 kPa (0.1 torr)] by this procedure. This is somewhat different from what is prescribed by the ASTM E 681-04 method, which calls for 15 kV at 30 mA for the spark ignition source. Such a voltage and current would have produced a very strong spark in our experiments and would result in considerable energy dissipation in the mixture. This would place a strong perturbation on the system, and application of percolation theory would ideally call for a negligible perturbation on the system by the flame initiator. In stating this we are not advocating the modified currents and voltages for general applications. Rather these are being selected to achieve the goals of this research.

The flask and its contents were videotaped during the experiment with a Sony Handycam DVD R/RW camera, and the movie could be replayed in slow motion with a DVD player. We began with a mixture that was just below the LFL, and checked it for flammability by generating a spark. We would add a partially fluorinated hydrocarbon

**Table 2** LFL expressed as partial pressure of R-143a for various flask sizes (since the total pressure is 1 bar, the partial pressure in kPa is equal to vol% presented in the table)

Volume (L)	Radius (cm)	$T$ ( $^{\circ}\text{C}$ )	Flammability [ $\text{mol}\cdot\text{m}^{-3}$ (vol%)]
5.26	10.79	20.3	3.40 (8.26)
12.80	14.51	21.1	3.44 (8.38)
21.35	17.21	22.5	3.47 (8.50)

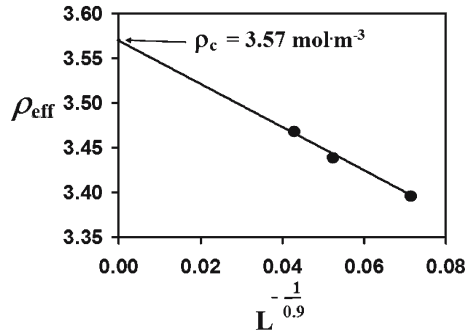
**Table 3** LFL expressed as partial pressure of R-143 for various flask sizes (since the total pressure is 1 bar, the partial pressure in kPa is equal to vol% presented in the table)

Volume (L)	Radius (cm)	$T$ ( $^{\circ}\text{C}$ )	Flammability [ $\text{mol}\cdot\text{m}^{-3}$ (vol%)]
5.26	10.79	21.5	2.82 (6.87)
12.80	14.51	18.0	2.86 (6.89)

(HFC) to the mixture until a flame just began to propagate into the conical volume generated by rotation of a  $45^{\circ}$  conical angle as illustrated in Fig. 1. This procedure would produce a final total pressure slightly above 100 kPa (1 bar) by about 0.25 or 0.4 kPa. We would then evacuate the flask and recharge it with the same partial pressure of the HFC and enough air to produce a total pressure of exactly 100 kPa (1 bar) and determine if the flame propagation is reproduced. We found that the pressure or concentration for the onset of flame propagation was reproducible to within  $\pm 0.4\%$ . The results for the LFL are presented in units of pressure, molar concentration in  $\text{mol}\cdot\text{m}^{-3}$ , and volume percent for three flask sizes; with nominal volumes of 5-, 12-, and 20-L in Tables 2 and 3.

In this work we have restricted our studies to flasks with volumes of 5-L or greater for the purposes of applying percolation theory to the extrapolation of the LFL to infinite vessel volume. The ASTM E681-04 method specifies a 12-L flask for halocarbons because this may have large quenching distances, which in some cases makes ignition with a spark difficult in a 5-L flask. This specification as a precautionary general constraint is needed for a standard method, i.e., the ASTM E681-04 method [7]. However, this does not imply that quenching is necessarily present or dominant for all halocarbons in vessel volumes less than 12-L. In our earlier work on R-32 [11], and in this work on R-143a and R-143, we found that quenching effects disappear with flask volumes of 5-L or greater and as such are very useful for establishing the volume dependence of LFL needed to apply percolation theory. This conclusion is based on two observations: (i) first, the measured LFL of the 5-L flask is less than that of the 12-L flask and (ii) second, the variation in the LFL increases linearly as predicted by percolation theory with  $L^{-1/0.9}$  (see Fig. 2 of this work and Fig. 2 of earlier work [11]), where  $L$  is the flask radius for 5-, 12-, and 20-L flasks. If quenching effects were dominant, one would expect the smaller flasks to have the larger LFL. To be certain that quenching effects manifest themselves in that manner, in our earlier work on R-32 we also performed experiments on 3-L vessels, where we expected quenching would certainly be present. As expected, these vessels yielded a substantially larger LFL [ $6.41 \text{ mol}\cdot\text{m}^{-3}$  (15.7 vol%)] than for the 5-L vessel [ $5.95 \text{ mol}\cdot\text{m}^{-3}$  (14.5 vol%)].

**Fig. 2** Plot of the LFL in  $\text{mol}\cdot\text{m}^{-3}$  for finite vessel volumes vs.  $L^{-\frac{1}{v}}$  for three-dimensional flame propagation. Experimental results are given as  $\bullet$  whereas the lines represent results of a linear least-squares fit



### 3 Percolation Theory and Flammability Measurements

We have described the application of percolation theory to the LFL in our previous publication [11]. However, for the benefit of the reader in this paper, we also include a brief description of using percolation theory to obtain an estimate of the LFL for the infinite volume limit from experimental measurements on finite vessels. Percolation theory is concerned with the propagation or growth of a process using a lattice model [13]. In the application of percolation theory, the type of point lattice one selects will depend on the nature of the problem, but for this description we consider two point lattices that are easily visualized, namely a two-dimensional square lattice and a three-dimensional simple cubic lattice. These lattices are assumed to extend to infinity in each dimension. The points of the lattice may be either occupied or vacant and the fraction of occupied points,  $p$ , is a parameter that the observer controls much like an experimentalist controls concentration of a chemical. The occupancy of points is purely random, which means that the probability of a point being occupied is  $p$ .

The next process we visualize is placing a bond between nearest-neighbor occupied points. This is referred to as a nearest-neighbor percolation model. One can then visualize sets of isolated occupied points in which all are connected to at least one other point in the set and there are no connections to occupied points outside of this set. Such a set of points is called a cluster. If one begins with no point occupied,  $p = 0$ , and gradually increases the number of occupied points, one will reach an occupation fraction where all occupied points are connected in one large cluster that spans the entire infinite lattice. The fraction of occupied points where this occurs is called the percolation limit,  $p_c$ . For a square lattice with nearest-neighbor bonding of occupied points,  $p_c = 0.59$ , and for a simple cubic lattice,  $p_c = 0.31$ . For intermediate  $p$ ,  $0 < p < p_c$ , we would find clusters of finite size (finite number of points) which would grow as we increase  $p$  toward  $p_c$ . The study of clusters and their growth is the subject of percolation theory.

In order to make a more direct connection with flammability, we next perform this same process on a lattice of finite length,  $L$ , in each dimension, where a unit length is set equal to the length of the side of a unit cell. One would again reach a point where a single cluster that spans the entire volume is obtained. However, the fraction of occupied sites, where this occurs, denoted as  $p_{\text{eff}}$  will be less than  $p_c$  for an infinite

lattice i.e.,  $p_{\text{eff}} < p_c$ . The distribution of  $p_{\text{eff}}$  with respect to volume dimension,  $L$ , is given by the proportionality,

$$p_c - p_{\text{eff}} \propto L^{-1/\nu}, \quad (1)$$

where  $L$  is the length of one dimension of the finite system which in flammability experiments may be the vessel radius. We could have also made the lattice finite by enclosing the lattice in a finite spherical volume, rather than a cubic volume in which case  $L$  would have been the radius of the spherical enclosure. The quantity,  $\nu$ , is an example of a power-law index, which, according to percolation theory, is postulated to obey universality principles [13], i.e., is independent of the lattice details, and is dependent at most on the dimension and symmetry of the system. The parameter,  $\nu$ , is the power-law index for the correlation length and its value has been calculated to be  $4/3$  for a two-dimensional system and  $0.9$  for a three-dimensional system [13]. Equation 1 is an asymptotic relation valid when  $p_{\text{eff}}$  is very near  $p_c$ . As  $p_{\text{eff}}$  first moves outside of the realm of validity of Eq. 1, one would expect its variation to level off with  $L$ , but would remain less than  $p_c$  in accordance with percolation theory [13].

The fraction,  $p$ , of occupied sites may be regarded as proportional to the molar concentration in  $\text{mol}\cdot\text{m}^{-3}$ ,  $\rho$ , of a real system by a simple change of length scales. Thus, we rewrite the above relation in terms of  $\rho_{\text{eff}}$  and  $\rho_c$  as,

$$\rho_{\text{eff}} = \rho_c - AL^{-1/\nu}, \quad (2)$$

where the change in scale has been lumped into the proportionality factor  $A$ . This proportionality factor,  $A$ , also contains the effects of the chemical and physical properties involved in flame propagation. In modeling flame propagation,  $\rho_c$  would correspond to the flammability limit for an infinite vessel volume. The proportionality factor is dependent on the lattice and, therefore, would embody the detailed physical and chemical aspects of the percolation process, which in our case is flame propagation.

In modeling a real process, such as flammability, one would think of the bonds as steps in a process, and a set of bonds in a cluster as pathways to growth of the process. One can think of the points as molecules; however, in modeling a real process, one may have to take a more general view of a discrete model for the process. For applications to flammability, the theory has the advantage of focusing on flame propagation without explicitly considering the physical and chemical processes that are involved. The physical and chemical processes would impact the parameters of the lattice model such as distance between lattice points, number of nearest neighbors, and should next-nearest-neighbor as well as nearest-neighbor percolation be considered. The power of percolation theory lies in the fact that  $\nu$  is independent of the lattice, and is dependent at most on a dimension and the symmetry of the system. The chemical and physical processes are contained in the parameter  $A$ . In applications of percolation theory,  $A$  is obtained by fitting the data to  $A$ , and  $\rho_c$  using a value of  $\nu$  calculated from theory.

Since flame propagation is directed upward, the model for flammability is directed percolation rather than isotropic percolation. Consequently, the value of  $\nu$  may be intermediate between the value for three dimensions,  $0.9$ , and the value for two dimensions,  $1.3333$ . Lattice methods for the percolation process can be used to investigate if the 3D



**Table 4** Results of application of percolation theory and LFL for infinite vessel volume

Refrigerant	LFL relation ( $\text{mol}\cdot\text{m}^{-3}$ )	LFL for infinite vessel volume ( $\text{mol}\cdot\text{m}^{-3}$ )
R-143a	$\rho_{\text{eff}} = -2.417 L^{-1/\nu} + 3.57$	3.57
R-143	$\rho_{\text{eff}} = -2.004 L^{-1/\nu} + 2.96$	2.96

value is appropriate for the directed percolation process and may lead to an improved value of  $\nu$  [16]. However, power-law indexes such as  $\nu$  are not very sensitive to such changes in symmetry as long as the system remains three-dimensional. We also have found in our earlier work [11] that the extrapolation to the infinite volume flammability limit is not very sensitive to the value of  $\nu$  and its three-dimensional value is useful for obtaining the LFL for the infinite volume limit.

The application of percolation theory using the three-dimensional value of  $\nu$  ( $= 0.9$ ) to the data in Tables 2 and 3 yields the relations in Table 4 that express  $\rho$  (LFL in  $\text{mol}\cdot\text{m}^{-3}$ ) in terms of the vessel radius  $L$ . Figure 2 illustrates graphically the comparison of the equation in Table 4 to the experimental data for R-143a.

One of the stated goals of this work is to apply the percolation theory equation to the experimental data in Tables 2 and 3, and to obtain the LFL for an infinite vessel volume, which is reported in Table 4. However, the equations in Table 4 could also be used to assess the LFL for intermediate vessel volumes. This would bring up the issue of the limits of validity of percolation theory with respect to vessel volume. Since percolation theory is a statistical model, it is valid for infinite volume by its very nature, and is also valid for very small volumes far below what we would realize experimentally. Even though percolation theory is valid for small volumes, Eq. 2 is an asymptotic relation, and by its mathematical nature is only valid for  $\rho_{\text{eff}}$  very near  $\rho_c$  [13]. It is important that even outside the realm of the validity of Eq. 2, other percolation theory predictions not dependent on Eq. 2, such as  $\rho_{\text{eff}} < \rho_c$ , would remain valid. Using computer simulations of cluster formation on simple cubic lattices [17], the range of validity of Eq. 2 expressed as a percentage,  $100(p_c - p_{\text{eff}})/p_c$ , is estimated to be about 5.0%. This indicates that the experimental LFL for a 5-L flask which is within 4.2% of the percolation limit (infinite volume limit) is just within the realm of validity of Eq. 2. Our experimental results in this work and previous work [11] confirm that Eq. 2 is valid for vessel sizes as small as 5-L.

The increase in the LFL with vessel volume implies that a mixture which may not be explosive in large (effectively infinite) vessel volumes may be explosive in smaller containers. Based on this result, one would recommend that the LFL measured using the ASTM E681-04 method would be preferred from a safety standpoint because it represents a lower limit value for all vessel volumes. However, another question arises what volumes can effectively be regarded as infinite, and are least likely to present an explosive hazard. This depends on the accuracy to which mixture compositions are known in practical applications. A composition uncertainty that is routinely achieved in the laboratory and is specified as the precision for mixture compositions by the ASTM E681-04 method is  $\pm 0.04 \text{ mol}\cdot\text{m}^{-3}$  ( $\pm 0.1 \text{ vol}\%$ ). The LFL for the smallest vessel volume,  $V$ , that is within the infinite vessel volume LFL by this uncertainty

may be estimated from the following sequence of equations:

$$L = (\Delta\rho/A)^{-\nu}, \quad (3)$$

$$V = 4\pi L^3/3, \quad (4)$$

where  $\Delta\rho = \rho_c - \rho_{\text{eff}} = 0.4 \text{ mol}\cdot\text{m}^{-3}$  is taken to be the uncertainty in LFL, the radius  $L$  is estimated from  $\Delta\rho$  and  $A$  using a rearrangement of Eq. 2, and  $V$  is the estimated vessel volume. Substituting 0.9 for  $\nu$ , and the values for  $A$  given in Table 4, one estimates vessel volumes of 163 and 270 L that are effectively at the infinite volume limit for R-143 and R-143a, respectively. The vessel volume of 163 L that is effectively at the infinite volume limit for R-143 is smaller than for R-143a (270 L) because R-143 has the smaller LFL and the differences between the infinite volume limit LFL and the finite volume LFLs are proportionately smaller, i.e., a smaller value for the parameter  $A$ . These estimates should be regarded as approximate magnitudes and flask volumes in the range 163 to 270-L, for example 200 L, are effectively at the infinite volume limit. Also using the above criteria, i.e., a fixed composition uncertainty, would mean that highly flammable hydrocarbons (low LFL) would effectively reach their infinite volume LFL at much smaller vessel volumes, which is consistent with experience.

The above analysis demonstrates that Richard [12] who studied R152a/R134a mixtures, which have a lower LFL than either R-143 or R-143a studied in this work, and R152a/R125 mixtures, which have an LFL comparable to R-143a, obtained results effectively near the infinite volume limit with the large volume 200-L vessel.

## 4 Conclusions

Our motivation for selecting the isomers, R-143a and R-143, for flammability studies is to isolate on molecular properties that may affect the flammability of an important alternative refrigerant, R143a. Isomeric effects are often revealing in this respect because most of their chemical properties that affect flammability are identical and observed differences can then be associated with isomeric structural differences. What is perhaps the most unexpected result of these studies is the relatively large difference (18%) between the LFL at the infinite volume limits for the two isomers. The enthalpies of combustion calculated from the enthalpies of formation in Table 1 assuming combustion products are hydrogen fluoride and carbon dioxide are  $-855.7 \text{ kJ}$  and  $-869.62 \text{ kJ}$  for R-143a and R-143, respectively. The larger negative enthalpy of combustion for R-143 is consistent with R-143 having the lower LFL, i.e., being the more flammable isomer. However, the differences between the enthalpies of combustion (1.6%) would never explain the full isomeric effect on LFL that is observed.

One must therefore turn to mechanistic arguments based on the chemical suppression of flames by free radicals formed in the combustion process to explain the isomeric effect on the LFL. Sheinson et al. [18] have shown that  $\text{CF}_3\cdot$  radical intermediates are highly effective suppressants in fire extinguishing agents of the type  $\text{CF}_3\text{Y}$  ( $\text{Y}=\text{F}, \text{Cl}, \text{Br}$ ). The  $\text{CF}_3\cdot$  radicals tend to react with oxygen radical intermediates (radical trap

mechanism) which are needed to sustain flammability. A very probable explanation for the lower LFL of R-143a ( $\text{CF}_3\text{CH}_3$ ) is that  $\text{CF}_3\cdot$  radical intermediates are formed in the combustion process, which tend to inhibit its flammability. Its isomer, R-143 ( $\text{CFH}_2\text{CF}_2\text{H}$ ), which does not contain the trifluoromethyl ( $\text{CF}_3-$ ) moiety, would not exhibit  $\text{CF}_3\cdot$  radical inhibition and hence has a higher LFL.

Our previous work on R-32 demonstrated that the LFL increases slightly with vessel volume, which is consistent with percolation theory. These predictions have been reconfirmed in this work on R-143a and R-143. This conclusion was also confirmed by Richard [15] who measured the LFL of the mixtures, R152a/R134a and R152a/R125, in a large volume 200-L vessel. More specifically, our earlier work and this work on R-143a (see Fig. 2) also demonstrates that the LFL expressed in  $\text{mol}\cdot\text{m}^{-3}$  varies linearly with  $L^{-1/\nu}$  ( $L$  = vessel radius and  $\nu = 0.9$ ), which is predicted by percolation theory.

The measurements were obtained using minimum current–voltage settings of 10 mA and 7–12 kV rather than 30 mA and 15 kV as specified by the ASTM E681 methods, because the ideal application of percolation theory requires negligible perturbation from the ignition source. Nevertheless our results for the LFL of R-32 [ $6.05 \text{ mol}\cdot\text{m}^{-3}$  (14.7%)] from our previous work at 21°C and the LFL of R-143a [ $3.44 \text{ mol}\cdot\text{m}^{-3}$  (8.4%)] of this work at 21.5°C are in good agreement with the most recent results [ $5.85 \text{ mol}\cdot\text{m}^{-3}$  (14.4%) and  $3.33 \text{ mol}\cdot\text{m}^{-3}$  (8.2%), respectively] obtained for these compounds at 23°C using the ASTM E681-98 method. Our results are about 3% higher than those obtained by the ASTM E681-98 method which is likely due to the fact we used a minimal current–voltage ignition spark in our measurements.

The difference between the LFL at the infinite volume limit and the LFL for a finite vessel volume such as 12-L varies proportionately with the LFL. This relative variation can be expressed as a percentage difference in terms of the percolation equation,

$$\text{Percent Difference} = 100 \frac{\rho_c - \rho_{\text{eff}}}{\rho_c} = 5.12 \frac{A}{\rho_c}, \quad (5)$$

where the radius for the 12-L vessel has been substituted into the above equation. Substituting the parameters for  $A$  and  $\rho_c$  into the above equation yields a percentage difference between the LFL for the infinite vessel volume limit and that of the 12-L flask. This percentage difference between the 12-L flask LFL and the infinite volume limit LFL shows remarkably little variation for R-32, R-143a, and R-143, being  $3.3 \pm 0.4\%$ . This result is also consistent with the results of Richard who compared the LFL measured for the 200-L vessel with that for the 12-L vessel and found a 5.0% difference for the R-152a/134a mixtures and 2.5% difference for R-152a/R125 mixtures [12]. This suggests that the relative constancy of this percentage difference between the LFL for infinite vessel volume and that for the 12-L vessel and equivalently  $A/\rho_c$  may be a useful concept that carries over to other systems.

**Acknowledgments** Grateful acknowledgments are made to a Provost Grant from Widener University and to Dr. N. Dean Smith of Air Pollution Prevention and Control Division, The U.S. Environmental Protection Agency in Research Triangle Park, North Carolina for providing us with his electrode assembly for our flammability apparatus.

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