A Study of the Vapour Phase of Iodine Trifluoride Dioxide by Mass Spectrometry and Electric Deflection

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The vapour phase of IF_3O_2 has been studied with the combined techniques of electric deflection and mass spectrometry of a modulated molecular beam. Flight-time distributions show that the molecule is essentially in the dimer form at room temperature. Decomposition of the dimer to monomers has been followed using flight-time distributions. Decomposition becomes significant above *ca.* 100 °C and is virtually complete by 185 °C. Electric-deflection measurements show that the monomeric form of IF_3O_2 has a polar structure, while the dimer is non-polar and therefore must be symmetric. No evidence for trimers has been found.

MEASUREMENTS on the recently prepared[1] compound IF_3O_2 have indicated that the molecule is polymeric, with a dynamic equilibrium existing between the oligomers and the monomer in the vapour.[2-4] Engelbrecht *et al.*[2] published a mass spectrum showing the presence of trimer ions; however, the details of the inlet and ion-source conditions were not given. Beattie *et al.*[4] and Engelbrecht *et al.*[2] proposed a double oxygen bridge for the dimer similar to those proposed by Seppelt[5] for TeF_4O and SeF_4O. Beattie's recent vapour-density measurements[4] indicate a predominance of dimers in the vapour for temperatures below *ca.* 100 °C. This appears to be inconsistent with the mass spectra given by Engelbrecht *et al.*[2] We have investigated the vapour phase of IF_3O_2 using the techniques of electric deflection, mass spectrometry, and flight-time (velocity) distribution measurement with our molecular-beam apparatus.[6-7] The objectives of this study were to determine whether significant quantities of oligomers existed in the vapour phase, to characterize the degree of association, to define the conditions under which oligomers decompose to monomers, and to examine both monomeric and associated species for the presence of asymmetric (polar) structures.

EXPERIMENTAL

Samples of IF_3O_2 were synthesized by the method of Engelbrecht *et al.*[1] and stored in borosilicate glass break-seal ampoules at -10 °C until needed. During the early experiments these ampoules were connected directly to the molecular-beam inlet of the mass spectrometer. More recently, the IF_3O_2 was vacuum-sublimed from the ampoule into an openable Monel reactor which had previously been prefluorinated and charged with P_4O_{10}. In either case, the sample temperature was maintained at 0 °C while generating the molecular beam, except when higher inlet pressures of *ca.* 2 Torr were desired.†

The basic characteristics of the modulated molecular-beam instrument have been described.[6] Figure 1 shows the details of the variable-temperature inlet arrangement used in this study. All the surfaces contacted by IF_3O_2 were constructed of Monel, with the exception of short sections of polyfluorocarbon (Teflon or Kel-F) tubing used on the inlet pipe to provide flexibility for ease of alignment. The capacitance manometer has a range of 0—1 000 Torr with a minimum detectable pressure of 0.01 Torr. The copper block heater has a 6-cm contact length with the Monel inlet pipe. Temperature uniformity was aided on the face of the Monel end cap by a threaded copper insert. The orifice used in this study was a 0.02-cm diameter hole in a 0.025-cm thick wall. The heater can produce temperatures in excess of 300 °C at the position of the thermocouple.

The mass spectrum was measured, and, in addition, the phase shift of the IF_3O_2 was measured as a function of inlet pressure at a constant inlet temperature of 25 °C, using the technique for measuring flight-time distributions of the neutral components in a molecular beam described in detail elsewhere.[7] The flight-time distributions, mass spectra, and electric-deflection behaviour were measured as a function of exit temperature at constant inlet pressure. The measured flight-time distributions were compared with calculated distributions[8] for a particular molecular weight, heat-capacity ratio, and Mach number for the expansion from the orifice. Electric-deflection measurements with this instrument have also been described elsewhere, and have been shown to be sensitive to permanent dipole moments as small as 0.02 D.[6] The inlet was conditioned by heating to 150 °C for several hours and subsequently fluorinating it while it cooled. Xenon hexafluoride was also used to condition the inlet at ambient temperature. These precautions minimize hydrolysis and decomposition of IF_3O_2 used in the measurements.

RESULTS

Mass Spectra.—Mass spectra recorded for IF_3O_2 for 60-eV electrons are given in Tables 1 and 2 for a 25 °C inlet at a pressure of 0.3 Torr, and a sample-reservoir temperature of 0 °C. Table 1 contains mass spectra [including the species $IF_4O(OH)$] obtained in this study with and without correction for quadrupole discrimination against high-molecular-weight ions at an electron energy of 60 eV, and two spectra given by Engelbrecht and his co-

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† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 D ≈ 3.33×10^{-30} C m; 1 eV ≈ 1.60×10^{-19} J.

[1] A. Engelbrecht, P. Peterfy, and E. Schandara, *Z. anorg. Chem.*, 1971, **384**, 202.

[2] A. Engelbrecht, O. Mayr, G. Ziller, and E. Schandara, *Monatsh.*, 1974, **105**, 796.

[3] I. R. Beattie and J. Van Schalkwyk, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 343.

[4] I. R. Beattie, R. Crocombe, A. Germun, P. Jones, C. Marsden, G. Van Schalkwyk, and A. Bukovszky, *J.C.S. Dalton*, 1976, 1380.

[5] K. Seppelt, *Angew. Chem.*, 1974, **86**, 104; *Angew. Chem. Internat. Edn.*, 1974, **13**, 92.

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[7] M. J. Vasile and F. A. Stevie, *Internat. J. Mass Spectrom. Ion Phys.*, 1977, 24.

[8] J. B. Anderson and J. B. Fenn, *Phys. Fluids*, 1965, **8**, 780.

workers for 25-eV electron energy in ref. 2 and for 50-eV in ref. 1. Transmission corrections were made by measuring the resolution on each of the peaks and applying a known relation between transmission and resolution.[9] In all but one instance mass spectra were recorded at 60 eV in this study for purposes of increased signal level, which is a necessity with a 75-cm molecular-beam source.

Treatment with P_4O_{10} significantly reduced the amount of $[IF_4O(OH)]^+$ relative to our previous measurements without P_4O_{10} treatment, and correspondingly reduced the intensities of $[IF_4O_2]^+$, $[IF_4O]^+$, and $[IF_4]^+$. The compound $IF_4O(OH)$ is polar and also has ions at mass numbers corresponding to $[IF_2O]^+$ and $[IF_2O_2]^+$, so focusing of these peaks is not strictly a measure of the polarity of IF_3O_2. Table 2 shows that $IF_4O(OH)$ formed to some extent in the inlet pipe, and even the most careful and thorough pretreatments could not entirely remove its effect. Small differences in the 25 °C mass spectra obtained in this study (Tables 1 and 2) are not considered to be serious, and can be attributed to a difference in the conditioning of the inlet.

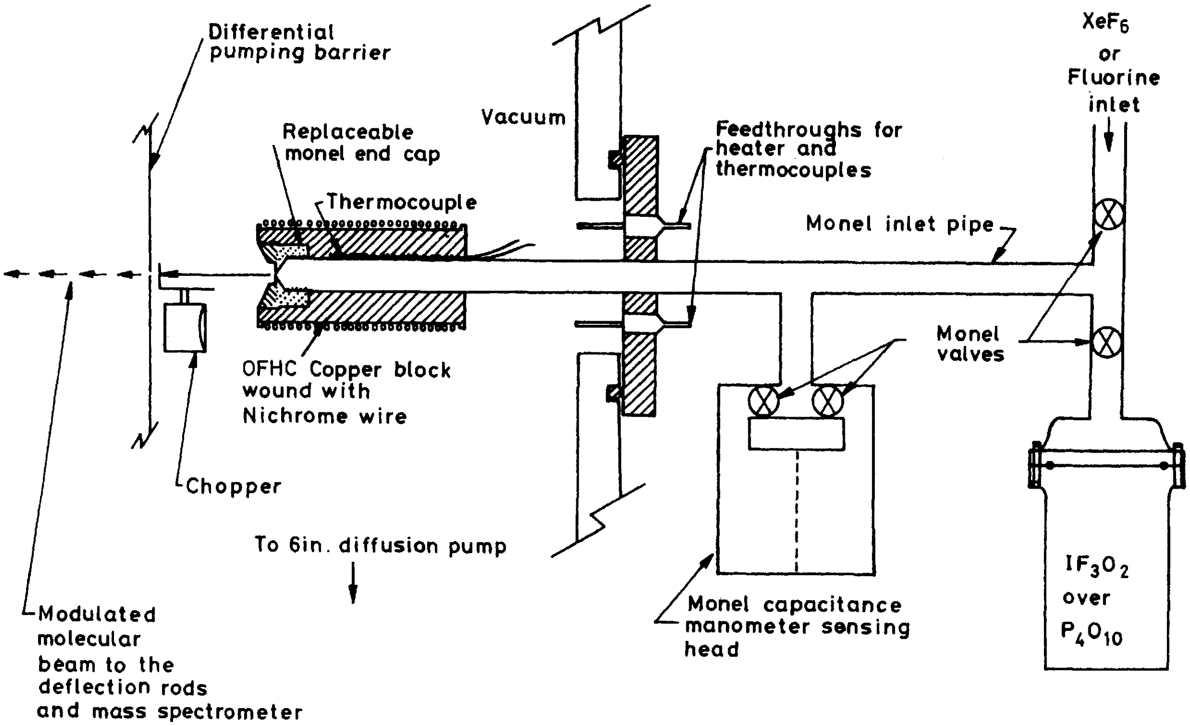

FIGURE 1 Variable-temperature inlet arrangement

The relative intensities of dimer ions observed in this study at 25 °C were consistently at the levels shown in Tables 1 and 2, and ions with three iodine atoms were not observed to one part in 10^4 when searching on either the 75- or 26-cm inlets. These are significant departures from the high-molecular-weight spectrum given by Engelbrecht *et al.*,[2] which has the dimer ions $[I_2F_6O_4]^+$ and $[I_2F_5O_2]^+$ as intense as $[IF_3O_2]^+$. The magnitudes of the discrepancies between these spectra are not entirely due to the election energies, since on reducing the electron energy to 30 eV the intensity quotients $[I_2F_5O_2]^+/[IF_2O]^+$ and $[I_2F_5O_2]^+/[IF_3O]^+$ increased only by a factor of five. If one includes the transmission correction for the quadrupole mass filter, this yields intensity quotients of $[I_2F_5O_2]^+/[IF_2O]^+$ and $[I_2F_5O_2]^+/[IF_3O]^+$ of 0.07 and 0.18. Such a correction still places the dimer intensities well below the values observed by Engelbrecht *et al.*[2] However, the appearance of four or five ions of relative intensity 100 in all the spectra reported in ref. 2 is very unusual, and suggests saturation of the detection electronics. This effect could be responsible for the major differences in the mass spectra.

The relative intensities of the monomer-region spectrum at 50 eV given in the earlier report by Engelbrecht *et al.*[1] [Table 1, spectrum (*d*)] agree much better with those obtained in this study, the only exception being the $[IF]^+$ peak intensity. Again, experience with mass spectra of a large variety of fluorides and fluoride oxides indicates that an $[MF]^+$ fragment ion arising from a five-co-ordinate precursor is unlikely to have such a high relative intensity.

The effect of increasing the exit temperature to 184 °C on the mass spectrum can be seen in Table 2. The exit temperature was brought to a maximum of 253 °C, and only flight-time distributions and focusing were measured above 184 °C. The dimer region was not scanned as a function of exit temperature in order to conserve sample. However, the $[I_2F_6O_4]^+$ ion was monitored selectively at elevated temperatures for flight-time distribution measurements. The intensities of the dimer ions decreased below the noise level at *ca.* 150 °C. The impurity level indicated by the $[IF_4O(OH)]^+$ ion and its daughter ions $[IF_4O]^+$ and $[IF_4]^+$ did not increase significantly, while the parent monomer ion $[IF_3O_2]^+$ showed a four-fold increase in relative intensity at an exit temperature of 184 °C. This is undoubtedly a result of the breakdown of dimers into monomers, since increasing the internal energy of an IF_3O_2 monomer would produce additional cracking to daughter ions, not enhanced

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[9] M. J. Vasile, G. R. Jones, and W. E. Falconer, *Internat. J. Mass Spectrom. Ion Phys.*, 1972—1973, **10**, 457.

parent molecular ions. The appearance of an $[O_2]^+$ peak at high temperatures is evidence for the thermal decomposition of IF_3O_2 to IF_3O and O_2 according to equation (1).

$$I_2F_6O_4 \longrightarrow 2IF_3O + O_2 \qquad (1)$$

However, the superimposition of IF_3O_2 and IF_3O fragment ions in the mass spectrum does not allow this reaction to be unequivocally established. The amount of oxygen evolved was not large, and the increase in relative intensity of the $[IF_3O_2]^+$ ion to the $[IF_2O]^+$ shows that the preferred degradation path is (2).

$$I_2F_6O_4 \longrightarrow 2IF_3O_2 \qquad (2)$$

Phase Spectrometry.—Phase differences between $[I_2F_5O_2]^+$, $[I_2F_6O_4]^+$, and monomeric ions such as $[IF_2O]^+$ and $[IF_3O_2]^+$ were always in the range 0—5° with a 25 °C inlet. The phase shifts as a function of inlet pressure are shown in Figure 2 for IF_3O_2 (measured on the $[IF_3O_2]^+$ ion) and, in an independent measurement, for IF_5 with the same experimental conditions. Since IF_5 is known to be monomeric [10] and is only 6 a.m.u. heavier than an IF_3O_2 monomer, the phase shift of ions derived from neutral IF_3O_2 monomer should be very close to that of ions from IF_5, with IF_3O_2 preceding IF_5 slightly. Figure 2 clearly shows that IF_3O_2 *lags* IF_5 in phase by *ca.* 20° at any common inlet pressure. This must be the result of a dominant concentration of a high-molecular-weight species in the molecular beam. The changes in phase angle of the ions in the mass spectrum from the modulated beam as a function of pressure are due to changes in the velocity distribution that occur as the mean free path of the molecules becomes smaller than the orifice dimensions. The velocity distributions obtained from this apparatus are characterized by non-effusive flow from an orifice,[7,8] producing a supersonic molecular beam with low Mach numbers. Assignment of the molecular weight of the neutral precursor of a particular ion requires the knowledge of the flight-time distribution of that ion.

TABLE 1

Mass spectra * of IF_3O_2

		This study, 25 °C, 60 eV		Ref. 2, 25 eV	Ref. 1, 50 eV
m/e	Ion	(*a*)	(*b*)	(*c*)	(*d*)
127	I^+	1.5	0.84	n.r.	n.r.
143	$[IO]^+$	8.0	5.3	n.r.	3
146	$[IF]^+$	5.5	3.8	n.r.	100
159	$[IO_2]^+$	2.9	2.3	n.r.	4
162	$[IFO]^+$	17	13	n.r.	10
165	$[IF_2]^+$	8.6	7.3	n.r.	3
178	$[IFO_2]^+$	32	31	n.r.	65
181	$[IF_2O]^+$	100	100	n.r.	110
184	$[IF_3]^+$	8.2	8.3	n.r.	10
194	$[IFO_3]^+$			n.r.	n.r.
197	$[IF_2O_2]^+$	46	55	n.r.	51
200	$[IF_3O]^+$	31	39	100	63
203	$[IF_4]^+$	1.2	1.5	40	4
216	$[IF_3O_2]^+$	8.4	12	100	14
219	$[IF_4O]^+$	0.5	0.7	20	
222	$[IF_5]^+$			15	4
235	$[IF_4O_2]^+$			30	n.r.
236	$[IF_4O(OH)]^+$	0.3	0.56	15	
381	$[I_2F_5O_2]^+$	0.6	1.4	100	n.r.
397	$[I_2F_5O_3]^+$	0.04	0.1	30	n.r.
413	$[I_2F_5O_4]^+$			25	n.r.
432	$[I_2F_6O_4]^+$	0.6	1.8	100	n.r.
613	$[I_3F_8O_5]^+$			40	n.r.

* n.r. = Not reported; where values are not given, they could not be detected above the baseline noise. Intensities of peaks in this study are given relative to the most intense peak = 100. Column (*a*) was not corrected for quadrupole mass discrimination; (*b*) was corrected by the methods given in ref. 9.

TABLE 2

Mass spectra of IF_3O_2 as a function of exit temperature *

		Relative intensity electron energy 60-eV			
m/e	Ion	25 °C	75 °C	147 °C	184 °C
127	I^+	1.0	1.9	n.s.	n.s.
143	$[IO]^+$	6.0	3.8	n.s.	n.s.
146	$[IF]^+$	5.0	3.8	n.s.	n.s.
159	$[IO_2]^+$	2.0	1.9	n.s.	n.s.
162	$[IFO]^+$	15	13	n.s.	n.s.
165	$[IF_2]^+$	8.1	6.9	n.s.	n.s.
178	$[IFO_2]^+$	31	26	21	14
181	$[IF_2O]^+$	100	100	100	100
184	$[IF_3]^+$	8.2	8.1	13	23
194	$[IFO_3]^+$	0.5	0.6	2.2	4.4
197	$[IF_2O_2]^+$	51	56	45	24
200	$[IF_3O]^+$	37	41	46	56
203	$[IF_4]^+$	3.1	3.1	4.5	5.1
216	$[IF_3O_2]^+$	11	15	28	43
219	$[IF_4O]^+$	1.0	0.9	1.8	1.3
222	$[IF_5]^+$				
235	$[IF_4O_2]^+$				
236	$[IF_4O(OH)]^+$	1.0	1.9	1.8	2.6
381	$[I_2F_5O_2]^+$	0.5	n.s.	n.s.	n.s.
397	$[I_2F_5O_3]^+$	0.04	n.s.	n.s.	n.s.
413	$[I_2F_5O_4]^+$		n.s.	n.s.	n.s.
432	$[I_2F_6O_4]^+$	0.4	n.s.	n.s.	n.s.
613	$[I_3F_8O_5]^+$		n.s.	n.s.	n.s.

* n.s. = Not scanned; where values are not given, they could not be detected above the baseline noise.

In another series of experiments, flight-time distributions for the monomer and dimer ions were measured as a function of temperature. Figure 3 shows the flight-time distributions of the ions $[I_2F_6O_4]^+$ and $[IF_3O_2]^+$ at a 25 °C exit temperature and a source pressure of 0.7 Torr. The curve for ions with one iodine atom leads that for ions with two iodine atoms by only *ca.* 0.1 ms, when in fact the displacement between these two curves should be *ca.* 0.7—1 ms if the monomer ions were derived from monomeric

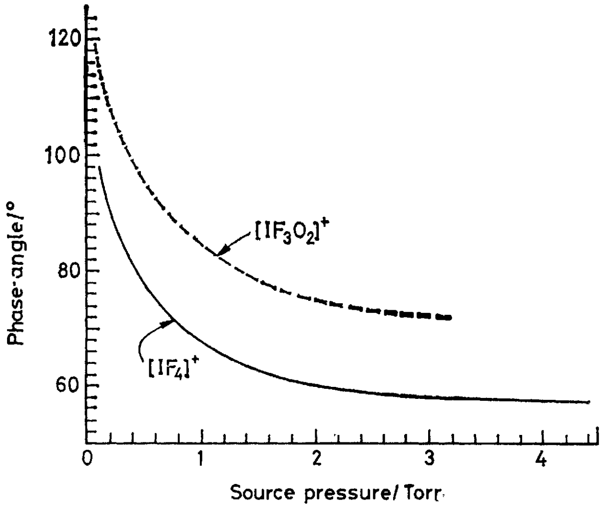

FIGURE 2 Phase angles due to time-of-flight of neutral IF_3O_2 and IF_5 from the molecular-beam source to the detector. The decrease in phase with increasing pressure results from the transition to supersonic flow. Modulation frequency, 70 Hz

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neutral species. Using identical inlet conditions, the experimentally obtained flight-time distribution of $[IF_4]^+$ from IF_5 (which is known to be monomeric in the gas phase) leads that of the $[IF_2O]^+$ ion from samples of IF_3O_2 by *ca.* 1 ms. If IF_3O_2 were a predominantly monomeric molecule in the gas phase, the $[IF_2O]^+$ flight-time distribution would *lead* that of $[IF_4]^+$ slightly.

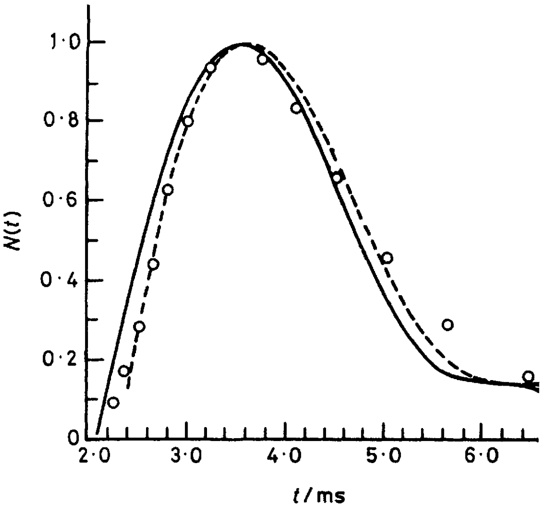

Figure 3 Flight-time distributions for the $[IF_3O_2]^+$ (——) and $[I_2F_6O_4]^+$ (- - -) ions at 25 °C and an inlet pressure of 0.7 Torr; (○), calculated for a dimeric species at 25 °C with Mach number 2

The dimer-ion flight-time distribution can be fitted very well by using a molecular weight of 432, a Mach number of 2, and a heat-capacity ratio of 1.25 in the theoretical expressions given by Anderson and Fenn.[8] These calculated points are shown as open circles in Figure 3. There is a departure from the theoretical expression for the low-velocity part of the flight-time distributions, which in part results from the measurement procedure, and is not considered to be serious.

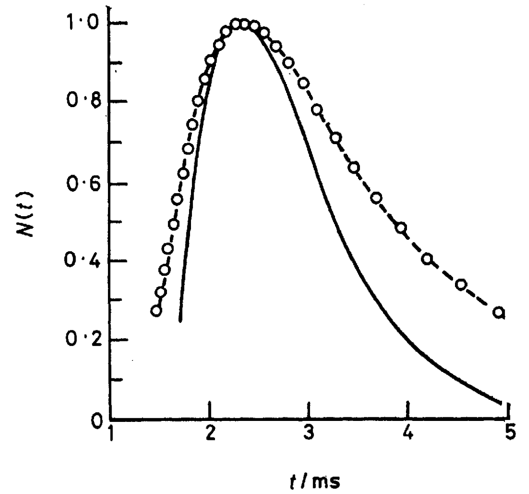

Figure 4 Flight-time distribution of $[IF_3O_2]^+$ (——) at an inlet temperature of 225 °C, under an inlet pressure of 0.7 Torr. The calculated distribution (○) is for a monomer molecular weight

It is clear that dimeric neutral species which give rise to dimeric ions in the mass spectrum at the few tenths of a percentage level dominate the gas phase flowing in the inlet pipe and through the molecular-beam orifice. In other words, the neutral molecular beam at 25 °C is composed principally of dimeric species which crack on 60-eV electron-impact ionization to yield predominantly monomeric ions. Trimeric neutral species are not present to any measurable extent; attempts to fit the dimer flight-time distributions with a trimer molecular weight failed badly, even with Mach numbers up to 4.

The dispersion in the $[IF_3O_2]^+$–$[I_2F_6O_4]^+$ flight-time distributions was approximately the same at 75 as it was at 25 °C, indicating little additional decomposition. The experimental flight-time distributions of the monomer and dimer ions at an exit temperature of 114 °C showed that the high-velocity edges and maxima were separated by 0.3 and 0.2 ms, which is consistent with an increase in the concentration of monomer in the beam.

Dimer-ion intensities at 150 °C were too weak to obtain reliable flight-time distribution data, so only the monomer ions were used at ⩾150 °C. The flight-time distributions of the $[IF_3O_2]^+$ ion could be fitted reasonably well with the same values for the Mach number and heat-capacity ratio (0.8 and 1.25 respectively), and a monomer molecular weight at each temperature above 150 °C. Figure 4 shows the flight-time distribution of the $[IF_3O_2]^+$ ion at 225 °C and that calculated using the aforementioned parameters. The half-width of the theoretical expression could not be narrowed by introducing lower heat-capacity ratios, and the approximation to the experimental results could not be improved upon. However, the essential fact is that a monomer molecular weight is the principal factor in the expression, which represents a significant difference from the results at 25, 75, and 114 °C where the distributions could not be fitted by any reasonable set of parameters based on a molecular weight of 216 a.m.u.

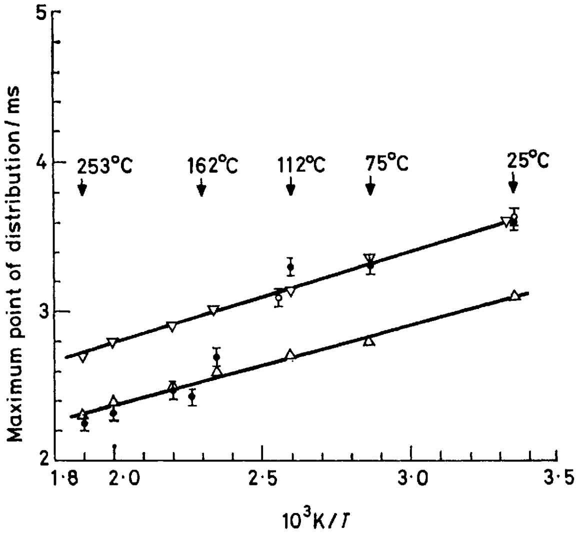

Figure 5 Plots of the maxima in the flight-time distributions as a function of temperature. Calculated values are based on the sets of parameters: Mach 2, $\gamma = 1.25$, and $M = 432$ (▽); Mach 0.8, $\gamma = 1.25$, and $M = 216$ (△). (○), Experimentally determined maxima for $[I_2F_6O_4]^+$; (●), experimentally determined maxima for $[IF_3O_2]^+$

The thermal decomposition from dimers to monomers is succinctly presented in Figure 5, which is a plot of the maximum point of the flight-time distributions for each of the species measured against the reciprocal of the absolute temperature. The calculated values for the dimer are for

Mach number 2 and a heat-capacity ratio of 1.25, and the calculated values for the monomer are for Mach number 0.8 and a heat-capacity ratio of 1.25. It is evident that from 25 to 114 °C the maxima in the experimental flight-time distributions for both monomer and dimer ions fall along the line predicted for the dimer molecular weight. At >160 °C, the experimentally obtained maxima fall on the line calculated for monomeric molecular weight.

Electric Deflection.—Focussing of *ca.* 1% was observed in the initial experiments, but it was not the same for each of the ions of the spectrum. A polar impurity is usually responsible for this behaviour, and it was quickly established that the focussing on the $[IF_2O]^+$, *etc.* ions was directly related to the relative intensity of the $[IF_4O(OH)]^+$ ion. When the relative intensity of $[IF_4O(OH)]^+$ was brought below 0.2, focusing could not be observed on any peak at an inlet temperature of 25 °C. When the relative intensity of $[IF_4O(OH)]^+$ was *ca.* 6, the focusing observed on $[IF_2O]^+$ was 1—1.5% of the straight-through-beam signal.

The most thorough pretreatment of the inlet (heating to 150 °C for 8 h, followed by XeF_6 treatment) resulted in an $[IF_4O(OH)]^+$ relative intensity below 0.2. A temperature-variation run was then made with the sample reservoir held at 0 °C and a constant inlet pressure of 0.3 Torr. By 133 °C, the $[IF_2O]^+$ and $[IF_3O_2]^+$ ions were focused by 1.5%. The observed focusing increased with temperature to 13% at 211 °C. The implication is that IF_3O_2 monomer molecules have a polar C_{2v} or C_s structure rather than the electrically centrosymmetric D_{3h} structure. Focusing was not observed under any conditions for the dimer ions. The absence of focusing from room temperature to *ca.* 100 °C indicates no dimer decomposition up to this temperature, and suggests a non-polar dimer structure.

DISCUSSION

The results presented in this paper support the contention of Beattie *et al.*[4] that IF_3O_2 vapour is composed principally of dimeric units at room temperature. These dimers start to decompose to monomers above *ca.* 100 °C with decomposition being essentially complete by *ca.* 180 °C. A symmetric, doubly oxygen-bridged, structure is most likely for the dimer, and the temperature required to decompose the dimers to monomers shows that this bridging is strong rather than weak.[11]

Monomers of IF_3O_2 are quite stable thermally, evidencing little decomposition up to 250 °C at pressures of a few Torr. The monomer is polar and therefore has an asymmetric structure, presumably C_{2v} as expected from considerations of electron-pair repulsions [12,13] and the tendency for the more electronegative ligand to occupy axial positions.[14]

Only a small number of five-co-ordinate molecules with either two or three oxygen atoms are known: XeF_2O_3, OsF_2O_3, OsF_3O_2, ReF_3O_2, ClF_3O_2, and the subject of this study, IF_3O_2. The three-oxygen–two-fluorine species XeF_2O_3 and OsF_2O_3 have both been reported as non-polar D_{3h} structures [15,16] from thorough spectroscopic studies. The low-temperature matrix structure (D_{3h}) of Beattie *et al.*[16] for OsF_2O_3 is quite convincing, although electric-deflection studies [17,18] on this molecule indicate polar species of lower symmetry at *ca.* 100 °C. Christe [19] assigned the structure of ClF_3O_2 as C_{2v}, and both ReF_3O_2 and OsF_3O_2 focus as expected for polar C_{2v} structures.[17,18] Matrix-isolation i.r. and Raman studies on ^{18}O–^{16}O isotopically substituted ReF_3O_2 show the presence of two equivalent oxygens.[20] On the basis of this observation, vibrational selection rules, and intensity considerations, this molecule has C_{2v} symmetry. Thus the observed behaviour of monomeric IF_3O_2 parallels the behaviour of other MF_3O_2 molecules, all of which are probably structurally similar.

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