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SHORT COMMUNICATION

IR Matrix Isolation Product Characterization from Low-Pressure Pyrolysis of $C_nF_{2n+1}I$ ($n = 1-4$) and C_6F_5I

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Studies directed at characterizing the IR matrix isolation spectra of the perfluoro-radicals-- CF_3 [1], CF_3O_2 [2], C_2F_5 [3], $n-C_3F_7$ [4], and $iso-C_3F_7$ [4] --have recently been described. Some observations are presented here on the pyrolysis behavior of the perfluoro-alkyl iodides CF_3I , C_2F_5I , $n-C_3F_7I$, and $iso-C_3F_7I$, which were successfully used to produce the corresponding perfluoro-alkyl radicals, and also on the pyrolysis behavior of $t-C_4F_9I$ and C_6F_5I , which did not produce the expected $t-C_4F_9$ and C_6F_5 radicals.

In the matrix isolation experiments, the perfluoro-alkyl iodides were decomposed in a very low-pressure (reactant pressure $\approx 10^2 Pa$) platinum pyrolysis reactor. Under the conditions used, reactor residence time was $\approx 3.4 \times 10^{-3}$ sec, with each molecule on average undergoing 10 wall collisions. Gas molecule-molecule collisions were about one hundredth of the wall rate. Under such conditions, the contribution of gas phase collisions to the overall reaction process may be ignored. The C_1 , C_2 , and C_3 perfluoro-alkyl iodides all showed substantial decomposition (30-80%) in the 900-700K temperature range, with somewhat lower average temperatures being required to obtain a given decomposition fraction in the order $C_1 > C_2 > C_3$. This finding is consistent with a recent determination of C-I bond energies [5] in CF_3I ($222.6 \text{ kJ mol}^{-1}$), C_2F_5I ($216.2 \text{ kJ mol}^{-1}$), and n - and $iso-C_3F_7I$ ($208.4 \text{ kJ mol}^{-1}$), assuming the primary process is simple C-I bond fission. In all these experiments there were moderate amounts of other products formed besides the respective radicals.

The pyrolysis of CF_3I always resulted in the formation of CF_3 , CF_4 , CF_2 , and C_2F_6 . Assuming that extinction coefficients for the C-F stretching modes of all four species are similar, their relative amounts may be estimated at 1:0.47:0.24:0.11 from data in a typical experiment. The presence of C_2F_6 could perhaps be justified in terms of incomplete isolation during the trapping

process, allowing the reaction $\text{CF}_3 + \text{CF}_3 \rightarrow \text{C}_2\text{F}_6$ to occur. The activation energy for this radical recombination is known to be close to zero. Indeed, the relative amount of $\text{CF}_3 : \text{C}_2\text{F}_6$ did show a marked sensitivity to matrix dilution, the ratio increasing noticeably as the dilution, and hence trapping efficiency, increased. This type of behavior was not shown by either CF_4 or CF_2 with respect to CF_3 . Furthermore, when CF_3 radicals were isolated in argon matrices containing 5-20% O_2 [2], no C_2F_6 was ever identified even though small amounts of unreacted CF_3 were always present. CF_4 and CF_2 were present to the degree normally associated with a pure argon matrix. These observations strongly suggest that the reaction $\text{CF}_3 + \text{CF}_3 \rightarrow \text{CF}_4 + \text{CF}_2$, which is exothermic by $\approx -182.4 \text{ kJ mol}^{-1}$ [7], does not occur in the matrix. Indeed, there does not appear to be any experimental evidence that at ambient or elevated temperatures [6] such a reaction channel exists. The conclusion seems inescapable that CF_4 and CF_2 must be formed heterogeneously on the walls of the platinum reactor. This conclusion is further reinforced by the observation that the amounts of CF_4 and CF_2 formed relative to CF_3 could be decreased by reducing the CF_3I pressure in the reactor during pyrolysis.

In the pyrolysis of $\text{C}_2\text{F}_5\text{I}$ [3] to produce C_2F_5 , small amounts of CF_3 , CF_2 , and possibly C_2F_4 were formed, the amounts of CF_3 and CF_2 clearly increasing with respect to C_2F_5 at higher pyrolysis temperatures. Thermodynamic data [7] indicate a minimum activation energy for the homogeneous gas phase reaction $\text{C}_2\text{F}_5 \rightarrow \text{CF}_3 + \text{CF}_2$ at $326.4 \text{ kJ mol}^{-1}$, strongly suggesting this reaction is not important under our experimental conditions. Minimal activation energy for the gas phase reaction $\text{C}_2\text{F}_5 \rightarrow \text{C}_2\text{F}_4 + \text{F}$ [7,8], estimated at $316.3 \text{ kJ mol}^{-1}$, also eliminates this as a likely reaction. Again, the radical product distribution implies heterogeneous surface effects are important.

Pyrolysis of *n*- and iso- $\text{C}_3\text{F}_7\text{I}$ produced the desired radicals and fairly substantial amounts of C_2F_4 , CF_3 , CF_2 , and C_3F_6 , C_2F_4 , CF_3 , and CF_2 , respectively. Obviously C-C and C-F bond breaking occurred. Thermochemical data are not well defined for the perfluoro-propyl radicals and implication of surface effects cannot be invoked on this basis. The radical C_2F_5 was not detected in the pyrolysis of *n*- $\text{C}_3\text{F}_7\text{I}$ though some recent thermochemical-kinetic data [7] suggest that the reaction $\text{n-C}_3\text{F}_7 \rightarrow \text{C}_2\text{F}_5 + \text{CF}_2$ takes place at temperatures used in the study.

The pyrolysis of *t*- $\text{C}_4\text{F}_9\text{I}$ [9] was performed initially in the 900-700K temperature range with the other experimental conditions identical to that used with the lower homologues. Complete decomposition of *t*- $\text{C}_4\text{F}_9\text{I}$ to $(\text{CF}_3)_2\text{C}=\text{CF}_2$ occurred. The latter material was unequivocally identified by

comparison with the matrix spectrum of the pure compound [9]. At 575K, about 50% decomposition of the parent iodide occurred, with only one product, $(CF_3)_2C=CF_2$ identified at short deposition times (≈ 1 hr). At longer deposition times (4-5 hr), a very weak absorption band at 603 cm^{-1} also became apparent in addition to those expected for *t*- C_4F_9I and *iso*- C_4F_8 . Experimental identification of the feature at 603 cm^{-1} was not pursued, though an obvious possibility would be IF. The latter's gas phase vibration frequency has been reported [10] at 604 cm^{-1} . In this connection an effort was made to determine if the matrix did contain free fluorine atoms, possibly formed by elimination from *t*- C_4F_9I in the pyrolysis tube, which could lead to IF formation by matrix reactions between F and I atoms. To this end *t*- C_4F_9I was pyrolyzed into argon matrices containing 5% O_2 or 5% CO . If F-atoms were being injected into the matrix, previous work in this laboratory and elsewhere has shown that FO_2 or FCO would readily be formed [11,12]. In the present investigation, no FO_2 or FCO could be detected and the absorption band at 603 cm^{-1} remained. If indeed this feature were correctly assignable to FI, the latter must have originated in the pyrolysis tube and not from a matrix reaction between F and I atoms.

That no *t*- C_4F_9 radical was found on pyrolysis of C_4F_9I may indicate that C-I bond fission is not the primary process in this system. The close similarity in C-I bond energies in the lower alkyl iodides (C_1 through C_3) with the analogous perfluoro-alkyl iodides [5] suggests that the C-I dissociation energy in *t*- C_4F_9I is probably a little less than in C_3F_7I , possibly by $\approx 8-12\text{ kJ mol}^{-1}$, which seems insufficient to account for the markedly lower pyrolysis temperature required for this compound. Again it appears necessary to invoke surface effects in the pyrolysis process with the possible formation of the perfluoro-butene, occurring via a concerted four center elimination reaction analogous to that occurring in the pyrolysis of some alkyl iodides [13]. A minimum activation energy for the latter process, ignoring surface effects, may be crudely estimated from C-F, C-I, and I-F bond dissociation energies of 456, 193, and 277 kJ mol^{-1} , and a π bond stabilization energy of 222 kJ mol^{-1} [14], at 150 kJ mol^{-1} a value which, with perhaps some surface assistance, is not inconsistent with the low pyrolysis temperature observed.

The pyrolysis of C_6F_5I required temperatures of 1000-1100K to obtain substantial decomposition, some 100-200K higher than in the C_1-C_3 perfluoro iodides, a finding consistent with C-I bond dissociation in C_6F_5I at 277 kJ mol^{-1} [15]. This latter value was determined using the toluene carrier gas technique. The presence of the C_6F_5 radical in the system was inferred from the formation of

C_6F_5H by H abstraction from the toluene carrier gas. In the matrix study the only products found on pyrolysis of C_6F_5I were unreacted C_6F_5I , CF_4 , CF_3 , and CF_2 in approximately equal amounts. No evidence of absorption features attributable to any other species was found. These results imply a complete breakdown of the benzenoid ring structure on pyrolysis. When the pyrolysis products were trapped in an argon matrix containing 5% O_2 , CF_3O_2 [2] was immediately recognizable in the product spectrum. No FO_2 was found, indicating the absence of free F-atoms in the pyrolysis reaction; nor was there any trace of COF_2 , invariably found when CF_3 , formed by the pyrolysis of CF_3I , was allowed to react with an oxygen-doped matrix in an earlier study [2]. Substantial amounts of CO and CO_2 were found; whether their formation occurred in the pyrolysis tube (by possible diffusion of O_2 into the pyrolysis zone) or by reaction of some carbon fragment in the matrix is not clear.

A few observations with respect to the overall pyrolysis behavior of these compounds will be noted. At the low pressures used in these studies, the activation energy for thermal decomposition is acquired solely by reactor-wall substrate interactions. The unimolecular reaction rate is expected to be well into the low-pressure fall-off region, yet the temperatures required to bring about substantial decomposition were about the same as would be required if the reaction were occurring at its high-pressure limit, assuming a normal Arrhenius factor [13] of $10^{16} \pm 1$ and a C-I bond dissociation energy at $\approx 210 \text{ kJ mol}^{-1}$. In contrast, experiments to dissociate CH_3I in the same reactor to produce CH_3 radicals required a temperature of about 1300-1400K to obtain a similar degree of decomposition, indicating the reaction was behaving "normally" and in its low-pressure fall-off region. The perfluoro-iodides must undergo relatively "sticky" collision with the platinum surface with very efficient energy transfer, though for what reason is not clear. The dipole moments of both compounds are similar [17], $CH_3I \approx 1.6D$ and $CF_3I \approx 1.0D$, with the difference in the wrong direction to invoke dipole-surface interactions as of importance. Possibly, the marked positive electron affinities of the perfluoro compounds [18,19] compared to their hydrogenated analogues may be connected with the strong surface interaction [20].

Another factor that may affect the overall product distribution after initial scission of the C-I bond is the possible formation of a weakly bound Pt-F species. It has been shown [18] that F-atoms at low pressure ($\approx 1Pa$) will attack platinum in the 800-1100K region, though the nature of the resulting species was not identified.

Finally, a possible advantage of the matrix isolation technique with respect to identifying the products of pyrolysis reactions influenced by surfaces is the unambiguous nature of the "IR fingerprint" of the product species. This is particularly valuable for identifying radicals in the presence of the parent molecule. The most widely used conventional approach to this analytical task is mass spectrometry, where radical detection is often conceded to be extremely difficult and sometimes impossible in the presence of the parent species.

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