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Thermal decomposition of $C_{60}Br_{24}$ and $C_{60}Br_8$: Absence of sequential elimination

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Abstract. *In-situ* infrared spectroscopic investigations of the thermal decomposition of $C_{60}Br_{24}$ and $C_{60}Br_8$ reveal that elimination reactions leading to C_{60} occur in a single-step process. No partially brominated structures are observed, although theoretical predictions exist about derivatives such as $C_{60}Br_n$ ($12 < n < 24$). The study suggests that the lack of such structures can be attributed to the unusual stability of the cage. Any activation of the spheroidal structure is evenly distributed resulting in the uniform excitation of all the vertices; a property attributed to the resilience, as evidenced by mass spectrometric experiments.

Keywords. Reactivity of buckministerfullerene; thermal decomposition of $C_{60}Br_n$; sequential elimination.

1. Introduction

The fairly large body of literature on the reactivity of buckministerfullerene C_{60}, can be rationalised in terms of the 5 (radialene) character of the pentagons and the cyclohexa-1,3,5-triene character of the hexagons (Taylor and Walton 1993; Diederich and Thilgen 1996). Since all the chemical properties cannot be appreciated on the basis of this localised alkene structure, considerations invoking the non-planarity of the ring system have been put forward. The chemistry of C_{60} can be best understood in terms of a non-planar, weakly-aromatic ring system, as suggested by Haddon (1993). The stability of a number of derivatives of C_{60} has long interested theoretical chemists, and a voluminous body of literature exists on this aspect (Cioslowski 1991; Cioslowski and Feischann 1991; Dunlap *et al* 1991; Saunders 1991; Thiel and Bakowies 1991; Bakowies and Thiel 1992; Dixon *et al* 1992; Guo and Scuseria 1992; Henderson and Cahill 1992; Matsuzawa *et al* 1992a, b; Raghavachari 1992; Scuseria 1992; Yoshida *et al* 1992; Rathna and Chandrasekhar 1993; Clare and Kepert 1995; Fowler and Sandall 1995; Morton *et al* 1995; Cahill 1996). This is necessary because a majority of the fullerene derivatives are not amenable to synthetic procedures for detailed understanding. The possibility of isomers (Balasubramanian 1991) and interconversion among the various forms involving facile sigmatropic rearrangements (Hirsch *et al* 1991), have hampered detailed understanding of a particular reaction. The simplest possible hydride of C_{60}, ($C_{60}H_2$) has been predicted to have 23 distinct isomers (Henderson and Cahill 1992; Matsuzawa *et al* 1992a) considering only exo-cage additions. Because of these complexities, many of the derivatives observed in mass spectrometry have not been isolated

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and characterised. For example, though derivatives such as $C_{60}H_{16}$, $C_{60}H_{18}$, $C_{60}H_{42}$ (Bruhwiler *et al* 1993; Gerst *et al* 1993), $C_{60}Ph_{12}$ (Taylor *et al* 1992) etc. have been observed as distinct species by a variety of spectroscopic tools, the pure compounds have still not been separated.

As earlier mentioned, an understanding of the reactivity of C_{60} has been of concern to theorists. Predictions on $C_{60}H_{12}$, $C_{60}H_{18}$, $C_{60}H_{36}$, $C_{60}H_{42}$ and $C_{60}H_{54}$ (Guo and Scuseria 1992; Bakowies and Thiel 1992; Yoshiba *et al* 1992) exist, and the stability beyond $C_{60}H_{36}$ is substantially reduced due to deformation of the cage (Matsuzawa *et al* 1992b). In $C_{60}X_n$ (derivatives where X is H, F, Cl, Br or I), for $12 < n < 24$, non-bonded interactions dominate resulting in the destabilisation of the structures. It has also been shown that such interactions affect the local structure of the fullerene. While the type of addition in $12 < n < 24$ is still debated, a number of studies (Guo and Scuseria 1992; Bakowies and Thiel 1992; Yoshiba *et al* 1992) suggest the existence of distinct derivatives with $n = 16$, 18, 38, 42 and 54. In experiments (Haufler *et al* 1990; Holloway *et al* 1991; Olah *et al* 1991; Selig *et al* 1991; Tebbe *et al* 1991), however, these addition products have been observed only in the case of hydrogen. In order to understand the evolution of reactivity in C_{60}, it is important to rationalise the addition pattern leading to higher derivatives. Although localised benzenoid structures tend to increase the stability of higher derivatives (considering 1,4-additions across the double bonds), the presence of the benzenoid system in derivatives is not experimentally proven. It can also be noted that apart from 1,4- and 1,2- additions, 1,3-additions (Peel and Rothwell 1994; Wang and Jansen 1995) are also seen in lower derivatives. While the former two are most commonly encountered in derivatives, for bulkier substituents, 1,3-addition is preferred as compared to 1,2-addition (Wang and Jansen 1995). The question as to why such intermediary derivatives are not observed in halogenated derivatives prompted us to investigate the decomposition pattern of $C_{60}Br_{24}$ and $C_{60}Br_8$. Birkett *et al* (1992) proposed a cascade process for the thermal elimination of $C_{60}Br_{24}$ because, at any given time, a mixture of C_{60} and $C_{60}Br_{24}$ was present in the infrared spectrum. Peel and Rothwell (1994) studied theoretically the energetics of $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$, and found them to be thermally stable. Kinetic data reported on the Diels-Alder adduct $C_{60}{\cdot}C_5H_5$, suggest a one-step decomposition (Giovane *et al* 1993), which when fitted to the Arrhenius form of the rate expression gives a pre-exponential factor of $A = 3{\cdot}89 \pm 2{\cdot}5 \times 10^{12}$ and an activation energy of $26{\cdot}7 \pm 2{\cdot}2$ kcal/mol. Kinetics of the reactions of C_{60} with numerous radicals such as alkyl (Guldi *et al* 1993), aryl (Krusic *et al* 1991) and methoxy (Dimitrijevic 1992) have also been studied. While the stability of the cage suggests a one-step decomposition pattern for the derivatives, the structural stability gained by releasing the strain by partial derivatisation would lead to stepwise elimination processes. Mass spectral evidence exists for the stepwise elimination of poly-substituted C_{60} (Olah *et al* 1991) but no such data are known for thermal elimination.

In this paper, we present an infrared spectroscopic investigation of the thermal decomposition of $C_{60}Br_{24}$ and $C_{60}Br_8$. Our results are also supported by thermogravimetric measurements. These studies confirm that the elimination processes in these systems are unimolecular; in $C_{60}Br_{24}$ the reaction sets in at 363 K and becomes prominent at 395 K. Analysis of the $C_{60}Br_{24}$ data gives an activation energy of $6{\cdot}2 \pm 0{\cdot}8$ kcal/mol and a pre-exponential factor of $A = 3{\cdot}4 \pm 0{\cdot}6 \times 10^3$. The activation energy value for $C_{60}Br_8$ is lower, suggesting the higher stability of $C_{60}Br_{24}$. The most important observation from this study is that it is impossible to stabilise partially brominated structures during decomposition. The formation of C_{60} always occurs in a one-step manner. The only reason that can be attributed to this is the electronic and structural stability of the cage. As noted by earlier workers, it could be due to the resilience of the cage, which has been eminently demonstrated by ion/surface collision experiments (Beck *et al* 1991; McElvany *et al* 1991; Busmann *et al* 1993; Kane *et al* 1993)

2. Experimental

$C_{60}Br_{24}$ was prepared by adding excess bromine (neat) to about 5 mg of C_{60} (Texas Fullerene Corporation, USA) and the reaction allowed to proceed overnight (Tebbe *et al* 1992). After pumping away the excess bromine, the product was separated as a yellow powder. For the temperature-dependence studies, a 10% (by weight) pellet of the sample was made by mixing with pure KBr powder. A glass apparatus fitted with a heater and a Perkin–Elmer 983 dispersive infrared spectrometer were used for the measurements. The spectra were recorded in the scan range 500–1600 cm^{-1}. The experiment was carried out under an inert argon atmosphere. For $C_{60}Br_{24}$ the temperature range scanned was from 299 to 412 K. At each of these temperatures, the sample was left to stabilise for 15 minutes and then the time-dependent data were recorded in order to study the kinetics of the reaction. Three to four such measurements were made at each temperature, which was initially increased in steps of 25 K and was later reduced to 10 K, once the decomposition reaction commenced. On enhancement of the kinetics at 393 K, the increment was further reduced. The reaction was monitored until complete decomposition of $C_{60}Br_{24}$, which was manifested by the disappearance of the most prominent band at 851 cm^{-1}.

$C_{60}Br_8$ was prepared by treating solutions of C_{60} and Br_2 in CS_2 (Birkett *et al* 1992). The crystals were separated, dried and recrystallised from CS_2. Similar experimental conditions as for $C_{60}Br_{24}$ were used to follow the decomposition kinetics of $C_{60}Br_8$ also. The temperature range scanned was from 299 to 402 K. The disappearance of the most prominent band at 849 cm^{-1} was used as a parameter to monitor the progress of reaction.

Thermogravimetric measurements were made on a Delta Series 7 TGA apparatus using 1·632 mg of the sample in nitrogen atmosphere.

3. Results and discussion

It can be inferred, from the thermogravimetric data of $C_{60}Br_{24}$, that decomposition commences at 363 K as reported earlier. The maximum weight loss occurs between 423 and 468 K and is about 72·39%. This is in good agreement with the results of TGA measurements (Dinnebier *et al* 1995), reported to be 73·5–74% between 375 and 475 K. In figure 1 we present the infrared spectra showing the formation of C_{60} from $C_{60}Br_{24}$ as a function of temperature. Decomposition is observed at 363 K as noticed by the appearance of the IR band of C_{60} at 527 cm^{-1}. None of the prominent bands of $C_{60}Br_{24}$ at 546, 606, 720, 751, 776, 850, 912, 946, 1050, 1117, 1244 and 1400 cm^{-1} undergo any change either in their peak-widths or positions. A monotonic decrease in the intensities of $C_{60}Br_{24}$ and a corresponding increase in the C_{60} features are observed as we increase the sample temperature. The sample was held at each of the temperatures reported, for 30 minutes. Kinetic information derived this way gives rate constants of $5{\cdot}75 \pm 0{\cdot}43 \times 10^{-5}\,s^{-1}$, $7{\cdot}46 \pm 0{\cdot}39 \times 10^{-5}\,s^{-1}$, and $8{\cdot}30 \pm 0{\cdot}91 \times 10^{-5}\,s^{-1}$, at 393, 406

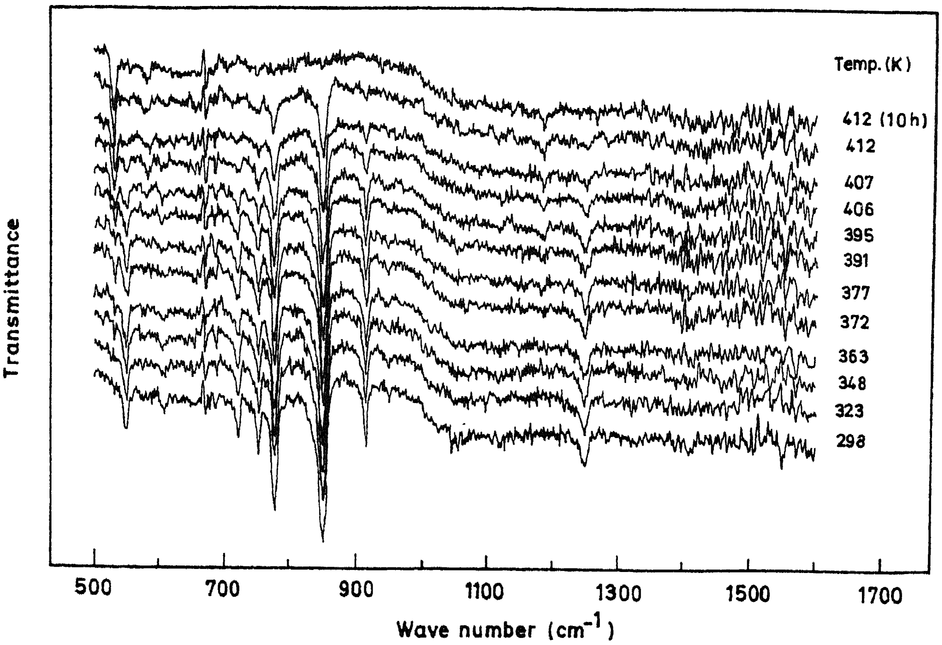

Figure 1. Infrared spectrum of $C_{60}Br_{24}$ as a function of temperature. Each spectrum corresponds to the first measurement at a given temperature. $C_{60}Br_{24}$ intensity was taken as proportional to the peak area of the $851\ cm^{-1}$ band.

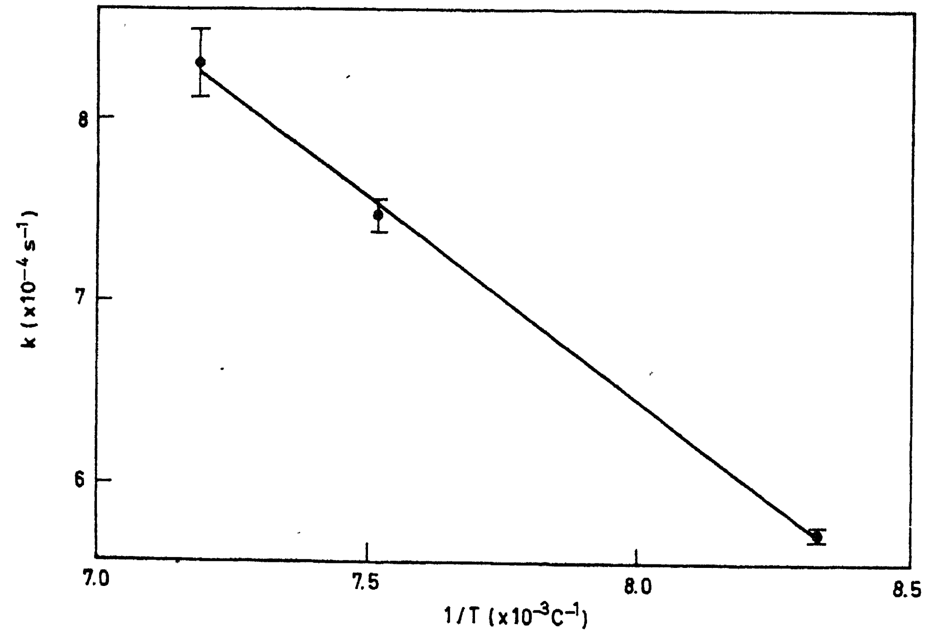

Figure 2. Plot of the variation of the rate constant k for the decomposition of $C_{60}Br_{24}$, with inverse of temperature ($1/T$). Energy of activation $E_a = 6{\cdot}2 \pm 0{\cdot}8$ kcal/mol.

and 412 K respectively as plotted in figure 2. It is important to note that, in the temperature range investigated, $C_{60}Br_{24}$ does not undergo any structural phase transition as evidenced by the absence of changes in the peak positions and intensities.

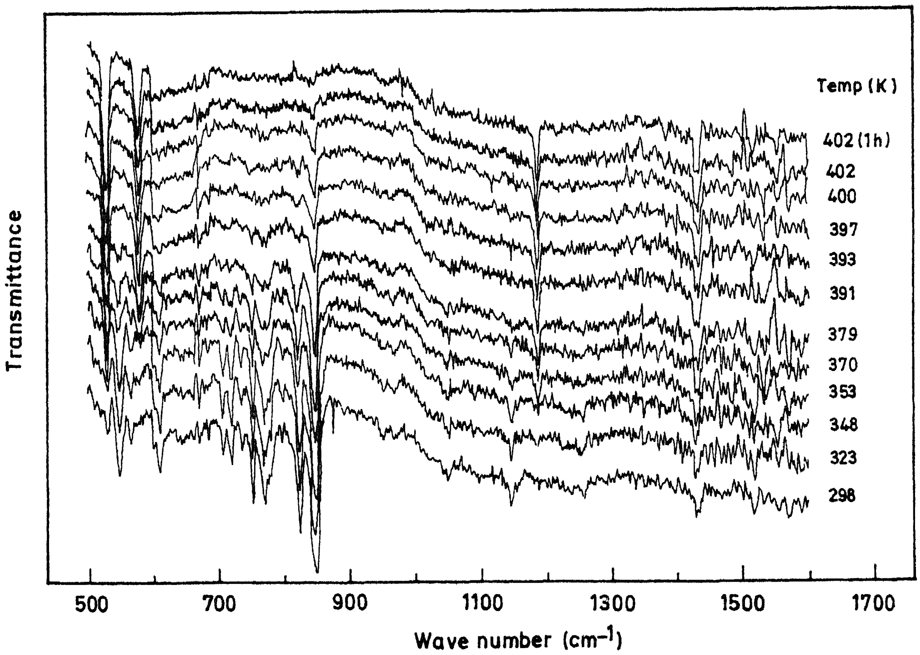

Figure 3. Infrared spectra of $C_{60}Br_8$ at various temperatures. Each spectrum refers to the first measurement at the given temperature. The integrated intensity of the $849\,cm^{-1}$ band was taken as proportional to the $C_{60}Br_8$ concentration.

The rate constants measured have been fitted to the Arrhenius expression giving an E_a of $6{\cdot}16 \pm 0{\cdot}8$ kcal/mol and a pre-exponential factor of $A = 3{\cdot}4 \pm 0{\cdot}6 \times 10^3$.

The decomposition of $C_{60}Br_8$ to yield C_{60} as a function of temperature is shown in figure 3. The decomposition of $C_{60}Br_8$ commences at 343 K. The appearance of the peak at $527\,cm^{-1}$ marks the onset of decomposition. Like in the case of $C_{60}Br_{24}$, $C_{60}Br_8$ also shows no change in the line-width or peak position on increasing the temperature. Details of the kinetics of the experiment are plotted in figure 4. The reaction gives rate constants of $1{\cdot}15 \pm 0{\cdot}96 \times 10^{-4}\,s^{-1}$, $1{\cdot}27 \pm 0{\cdot}91 \times 10^{-4}\,s^{-1}$, and $1{\cdot}36 \pm 0{\cdot}64 \times 10^{-4}\,s^{-1}$ at 377, 385 and 391 K respectively. These rate constants when fitted to the Arrhenius expression give a pre-exponential factor of $A = 5{\cdot}6 \pm 0{\cdot}02 \times 10^{14}$ and an E_a value of $4{\cdot}1 \pm 0{\cdot}06$ kcal/mol. From these values, it can be inferred that $C_{60}Br_{24}$ is much more stable than $C_{60}Br_8$.

The Schlegel diagram of $C_{60}Br_{24}$ and $C_{60}Br_8$ brings out the difference in the additions patterns of these two molecules (Wang and Jansen 1995). In the former case, the bromine atoms are symmetrically disposed around the C_{60} sphere, whereas in the latter the bromine atoms are seen to occupy only one face of the ball. In $C_{60}Br_{24}$ and $C_{60}Br_8$ there are only 1,4-additions, but we also see 1,2-additions in derivatives such as $C_{60}Br_{12}$, $C_{60}Br_{16}$, $C_{60}Br_{18}$ etc. (Matsuzawa *et al* 1992c). The difference is that in 1,4-additions one double bond (per addition) shifts to a pentagon which destabilises the structure but this instability is more than overcome by the absence of steric interactions. Although in 1,2-additions there are no double bonds on the pentagons, there is considerable steric strain, especially if the substituent is bulky as is the case with bromine. Therefore, owing to dominating steric reasons such structures are not stable, though their existence has been predicted theoretically. ΔH^0 values for the 1,2- and

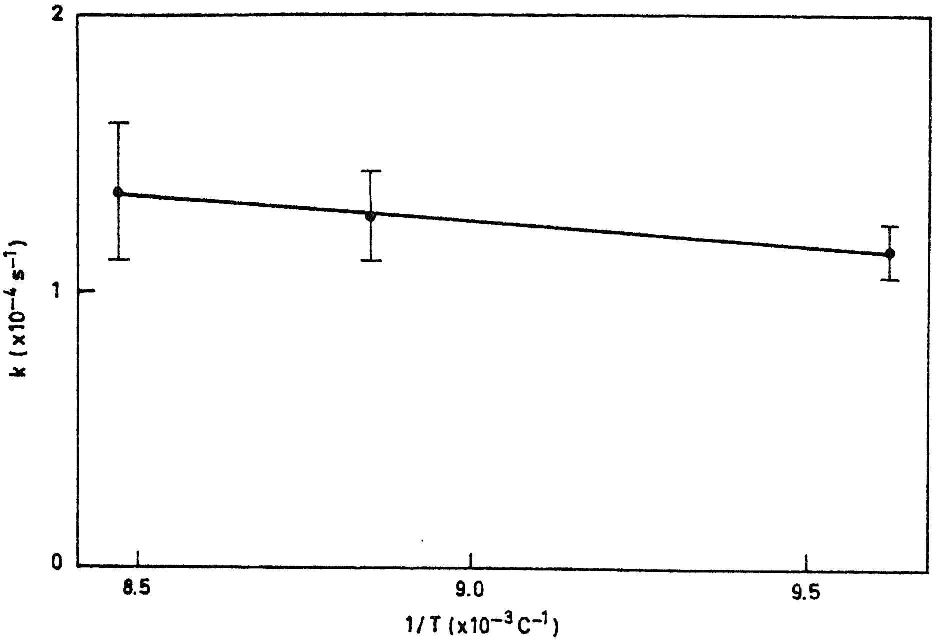

Figure 4. Variation of the rate constant *k*, for the decomposition reaction of $C_{60}Br_8$ with inverse of temperature (1/T). $E_a = 4{\cdot}1 \pm 0{\cdot}06$ kcal/mol.

1,4-addition of substituents have been calculated and, as the number of substituents added increases, the ΔH^0 values of the 1,4-addition increase rapidly, compared to those of the 1,2-addition. This is most prominent in the case of bromine addition. Another factor contributing to the instability is that in $C_{60}X_n$, where $12 < n < 24$, non-bonded interactions predominate, leading to unstable structures. For $n > 24$, deformation of the cage leads to destabilisation of the structure. The dominance of the non-bonded interactions in the lower derivatives and the structural instability of the higher derivatives dictate the kind of addition products experimentally observed.

The foregoing suggests that structural and electronic reasons are important in deciding the type of decomposition processes occurring in fullerene derivatives. Ion/surface (Beck *et al* 1991; McElvany *et al* 1991; Busmann *et al* 1993; Kane *et al* 1993) and ion/molecule (McElvany and Ross 1992) collision experiments indicate the high degree of structural stability of C_{60}, which is attributed to the resilience of the geodesic structure. Distortion caused by thermal or vibrational activation can get distributed geodesically very quickly within the cage. This is demonstrated by the simulation of C_{60} collision with hydrogen terminated diamond surface (Mowrey *et al* 1991). The study shows that within 1·4 ps of the impact, the fullerene regains the original structure. Even when high internal energy of the order of tens of electron volts is given to the molecule, it reverts to the original structure in a few picoseconds, keeping the cage structure intact. The energy provided in thermal activation, however, is inconsequential as far as fragmentation of the cage is concerned. Activation of the cage affects the vertices equally and since the C-Br bond energy is only of the order of a few electron volts, it is logical to assume that there is a high propensity for the derivatives to revert to the parent fullerene in a single step. This is the reason why almost all the derivatives upon mass spectrometric examination revert to the parent fullerene.

In conclusion, thermal decompositions of $C_{60}Br_{24}$ and $C_{60}Br_8$ occur via single-step eliminations and follow first-order kinetics. The theoretically predicted intermediaries, $C_{60}Br_{18}$, $C_{60}Br_{16}$ and $C_{60}Br_{12}$, are not stabilised possibly due to the dominance of non-bonded interactions. Single-step elimination can be attributed to the uniform distribution of energy to all the vertices of the ball. Resilience and the inherent structural stability of the cage also contribute to one-step decomposition. Analysis of the kinetic data for $C_{60}Br_{24}$ gives an activation energy value of $6{\cdot}2 \pm 0{\cdot}8$ kcal/mol and a pre-exponential factor of $3{\cdot}4 \pm 0{\cdot}6 \times 10^3\ s^{-1}$.

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