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Thermal stability of a fullerene-amine adduct

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Abstract

A fullerene-diethylamine adduct has been prepared by an addition reaction at room temperature and is characterized by FTIR, UV–VIS Spectroscopy, X-Ray Diffraction and HPLC techniques. After repeated recrystallisation from hexane the purified adduct has been studied by Thermogravimetry and Differential Scanning Calorimetry. Thermal Analysis and associated characterisation studies indicate that on heating the adduct undergoes an elimination reaction, i.e., the secondary amine which adds on to C_{60} at room temperature is eliminated between 100 and 650°C. This leads to the formation of the retro product C_{60} which has been characterized by spectroscopic studies on quenched samples. Kinetics studies indicate that in contrast to the addition reaction which is fast (almost instantaneous) the elimination reaction is sluggish and the process is associated with an activation energy of only 12–13 kJ mol^{-1}. Possible reasons for this unusual kinetic behaviour are suggested. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fullerene-amine adduct; Thermal elimination

1. Introduction

Fullerenes and their derivatives possess a number of interesting physical, biological and chemical properties [1]. With respect to chemical reactivity, C_{60} behaves as a giant electron deficient alkene rather than as an aromatic entity and undergoes reactions like addition, cycloaddition and polymerisation characteristic of such unsaturated molecules [1]. The amine addition is particularly interesting because of the possibility of some charge transfer in some of the amine complexes and modified electronic properties. A dramatic increase of conductivity has been observed during exposure of a fullerene film to volatile polar substances such as gaseous ammonia or amines and this has led to a proposal for its use as a sensor material [2]. However, the detailed physical properties of the amine adducts have not been investigated so far since it is difficult to synthesize single phase adducts with well defined stoichiometries and also separate the different regio-isomers. From the chemical point of view the amine adducts may be useful precursors for the synthesis of large fullerene polymers and macromolecules.

The thermal elimination reaction of the amine adduct is the reverse of the addition reaction of C_{60} with amines. The latter, namely the addition reaction, has been extensively studied in literature [3–9]. It is found to be facile and proceeds efficiently even at low temperature and is exothermic in nature [7,9]. The addition is generally believed to go through an ion radical intermediate [3].

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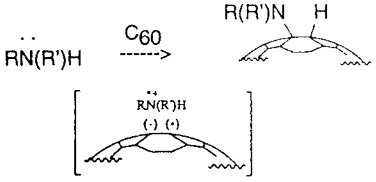

However, the thermal elimination reaction has not been studied in literature. On the other hand the thermal elimination reaction of the bromo adduct has been studied [10].

In our present work, we have synthesized a fullerene-diethylamine adduct $C_{60}[(C_2H_5)_2NH]_x$ (x=10–13) by solution route. The product has been characterized by XRD, FTIR, Optical absorption and HPLC studies. Results of our characterisation studies unambiguously confirm adduct formation and purity. X-ray diffraction studies indicate that the adduct exhibits an amorphous structure; however, the basic cage structure of the C_{60} molecule is retained. Thermal analysis studies and associated characterisation studies indicate that the adduct is unstable on heating and undergoes an elimination reaction in which the secondary amine viz., diethylamine which adds on to C_{60} at room temperature is eliminated between 100 and 650°C. This reaction apparently involves a low energy change and leads to the formation of the retro product C_{60} which is amorphous and sublimes above 600°C. The kinetics of this elimination reaction is very sluggish in contrast to the addition reaction which is very fast (almost instantaneous) and the process is associated with an activation energy of only 12–13 kJ mol^{-1}. Possible reason for this unusual kinetic behaviour is suggested.

2. Experimental

C_{60} was first prepared by arc evaporation of graphite followed by chromatographic separation the details of which have been reported earlier [11]. The adduct was synthesized by the solution route starting from C_{60} and diethyl amine [3]. A 2×10^{-5} mol solution of C_{60} in toluene is stirred with 15 ml of diethyl amine for 24 h at room temperature. A green solution is obtained which turns orange red after 0.5 h. This is vacuum dried for 24 h to remove any unreacted amine. The crude product is dissolved in 5 ml of $CHCl_3$ and precipitated by adding hexane dropwise. It is then centrifuged, washed with hexane repeatedly and vacuum dried to give a purified brown amine adduct.

Characterisation of the adduct has been carried out by IR and UV spectroscopy, HPLC and X-ray diffraction. techniques. IR spectra have been recorded in the range 400–4000 cm^{-1} under a resolution of 4 cm^{-1} using a Bomem (Model MB100) FTIR spectrometer on samples pelletized with potassium bromide. The X-ray diffractograms have been taken using a Siemens model D-500 diffractometer and a zero background sample holder comprising of a Si (9 1 1) single crystal wafer specially developed in our laboratory [12]. The slit dimensions have been reduced to 0.3° in order to minimize background due to air scattering. UV–VIS absorption spectra were recorded using a Shimadzu make (Model-UV 3101PC) UV–VIS–NIR spectrophotometer.

The thermal elimination reaction has been studied by carrying out thermogravimetry runs in pure helium atmosphere at a heating rate of 1°C min^{-1}. Portions of the sample were quenched at 300, 400, 550°C and characterized by IR, Optical absorption and XRD measurements to study the progress of elimination. The thermal analysis equipment used was a Simultaneous Thermal Analyser Model PL STA-1500 in the TG mode. The sample chamber was evacuated to a pressure of 60 μbars before purging with helium gas, to remove any trapped oxygen. The helium flow rate was maintained low, at 10 ml min^{-1} to minimise buoyancy error. DSC measurements were carried out using a Seiko Thermal Analyser in the range 30–600°C in sealed aluminium crucibles at a heating rate of 2°C min^{-1}.

3. Results and discussion

The IR spectrum of the adduct is shown in Fig. 1a. The spectra of C_{60} and diethylamine have also been taken for comparison (Fig. 1b and c, respectively). It is well known [13] that pristine C_{60} has only four IR modes of T_{1u} symmetry and these occur at 1428, 1183,577 and 527 cm^{-1} [13]. Our experimental spectrum for C_{60} (Fig. 1b) shows peaks at 1427, 1182, 576 and 527 cm^{-1} and is in good agreement with literature. Similarly it is observed that the experimental spectrum of diethylamine (Fig. 1c) is also in good

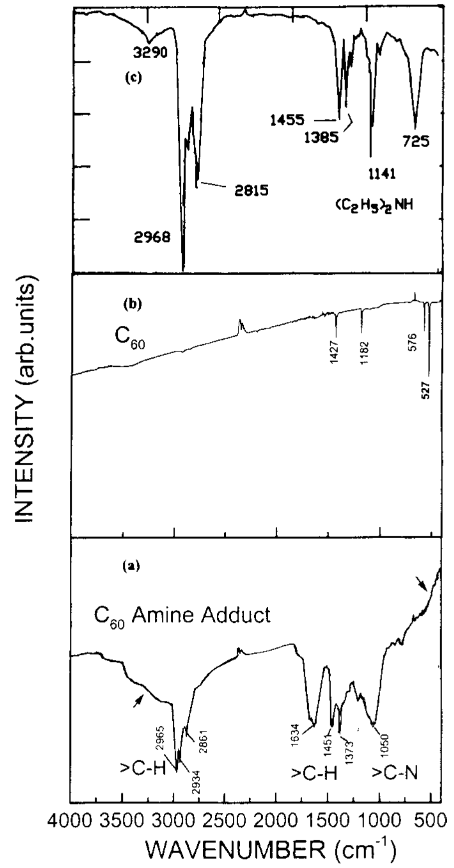

Fig. 1. IR spectra of (a) C_{60}-diethylamine adduct (b) C_{60} and (c) diethylamine.

agreement with the spectrum reported in literature [14]. The IR spectrum of the adduct in comparison with the spectra of $(C_2H_5)_2NH$ and C_{60} indicates absence of pristine modes of $(C_2H_5)_2NH$ and absence of unreacted C_{60}. Analysis of this spectrum (cf. Fig. 1a) indicates that it exhibits peaks at 1050, 1373, 1451, 1634, 2861, 2934 and 2965 cm^{-1}. The peak at 1050 cm^{-1} corresponds to the C–N mode and all the other bands refer to the C–H modes. It is clear that the C–N mode which occurs at 1141 cm^{-1} in diethylamine is shifted to 1050 cm^{-1} in the case of the adduct. This is an evidence for adduct formation. Similarly the C–H modes are also considerably shifted in the adduct compared to diethylamine. It is important to note that a new mode is observed for the adduct which appears at 1634 cm^{-1} and which is absent in the diethylamine spectrum. This may correspond to the new C–H bond which forms when amine adds on to C_{60}. The region between 3000–4000 cm^{-1} has been subjected to peak fitting analysis taking into account background subtraction. It is noted that there is no peak corresponding to N–H at 3290 cm^{-1}. The absence of peak due to N–H stretch (3290 cm^{-1}) in the adduct compared to diethylamine is consistent with the formation of a tertiary amine product. All the above features observed in the IR spectrum including the absence of the strong line of C_{60} at 527 cm^{-1} indicate adduct formation.

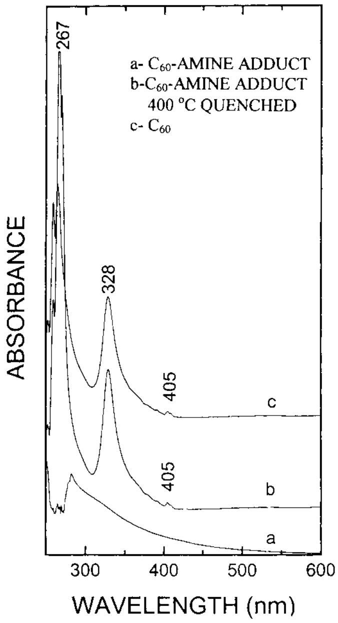

Fig. 2. UV–VIS absorption spectra in solution of (a) C_{60}-diethylamine adduct in $CHCl_3$ (b) hexane soluble extract of C_{60}-diethylamine adduct, 400°C quenched and (c) pure C_{60} in hexane.

The UV–VIS absorption spectrum of the adduct in $CHCl_3$ solution is shown in Fig. 2a. The spectrum of C_{60} in hexane (Fig. 2c) has also been taken for comparison. The UV–VIS absorption spectrum of C_{60} is known to exhibit strong peaks in the region around 210, 260, and 329 nm depending upon the solvent, a weak peak at around 404 nm and a weak broad absorption between 450 and 600 nm [15]. Our spectrum for C_{60} exhibits peaks at 267, 328, and 405 nm and is in close agreement with literature. In the case of the adduct it is observed that the absorption bands are completely modified compared to C_{60}. The absorption spectrum (Fig. 2a) shows a broad continuum until the absorption edge and there is a riding absorption from 600 nm to the UV region. Most of the bands characteristic of C_{60} are no longer present in the spectrum of the adduct. This result indicates that the energy levels of C_{60} are significantly affected on adduct formation. This is dramatically illustrated by the fact that even on visual observation while C_{60} exhibits a magenta colour in solution the adduct exhibits a deep yellowish orange colour and diethylamine a pale yellow colour.

High pressure liquid chromatography studies have also been carried out to characterize and determine the purity of the fullerene-diethylamine adduct. The HPLC measurements were carried out under two experimental conditions both using C18 column and flow rate 1.5 ml min^{-1} but with different solvents, one using 30% toluene, 70% isopropanol as mobile phase and detector at 330 nm, and the other using as mobile phase pure isopropanol and detector at 255 nm. The HPLC chromatograph of optical absorption as a function of retention time has been plotted for both experimental conditions (Fig. 3a and b). Studies have been carried out on the adduct, C_{60} as well as diethylamine. The results indicate that there is no trace of unreacted C_{60} or diethylamine or any other impurity present within the limits of detectability of 0.1%. A new compound has formed with solubility characteristics very different from C_{60}.

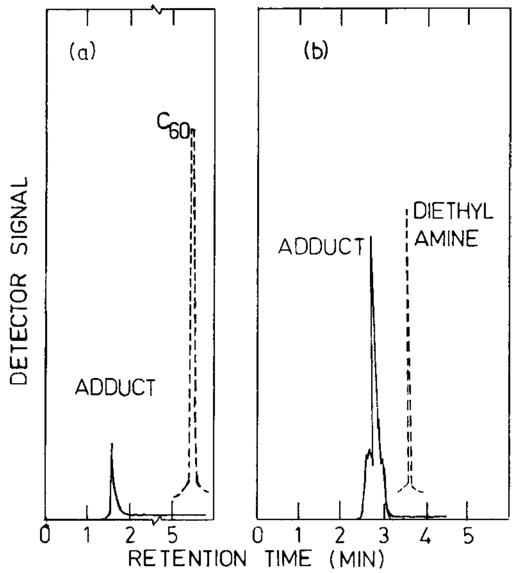

Fig. 3. Results of HPLC measurements: panel (a) corresponds to measurements using 30% toluene, 70% isopropanol with detector at 330 nm. Panel (b) corresponds to measurement using pure isopropanol as mobile phase and the detector at 255 nm. Solid line corresponds to the adduct and dotted lines to C_{60} and diethylamine. Notice that there is no signal in the HPLC of the adduct at the positions corresponding to C_{60} in panel (a). Notice also that there is no signal in the HPLC of the adduct at the positions corresponding to diethylamine in panel (b). Hence the samples are pure.

X-ray diffraction studies indicate that the adduct is amorphous with two broad peaks at $2\theta=5.52°$ ($d=16.10$ Å) and $2\theta=18.98°$ ($d=4.67$ Å). The first peak may be associated with the C_{60}–C_{60} correlation distance which is increased due to the shell of amine molecules and the second corresponds to C–C correlation distance in the adduct. This C–C correlation distance is much larger than those for the amorphous carbon products prepared by us earlier [16] by low temperature oxidation of C_{60} and by vacuum annealing of C_{60} in a sealed tube at 900°C. The amorphous pattern of the amine adduct obtained in this work is consistent with the literature report [17] on the structure of C_{60}-aliphatic diamine adducts which indicate amorphous structures with essentially two peaks, the broader one being observed at $2\theta=18°$ for all samples while the relatively sharp one appears in the range $2\theta=4$–$8°$.

The thermal elimination has been studied by thermogravimetry of the adduct in pure helium atmosphere at 1°C min^{-1} and is presented in Fig. 4. As can be seen from the figure the TG curve is very broad and extends even beyond the sublimation temperature of C_{60}. This indicates that the kinetics of elimination of the amine molecules is very sluggish. This is quite surprising as the reverse process namely, the addition reaction is very fast. Portions of the sample have been quenched at 300, 400, 550°C and characterized by IR and XRD measurements. FTIR spectra of the quenched samples clearly show the evolution of the peak of C_{60} at 527 cm^{-1} which is absent in the as prepared adduct (Fig. 5). The 527 cm^{-1} peak is well known to correspond to the strongest peak of C_{60} with T_{1u} symmetry and it has been observed in our spectrum for pure C_{60}. (Fig. 1b). In addition the quenched samples are sonicated in toluene in order to further confirm the presence of C_{60} obtained by the retro-reaction. UV absorption of the supernatant sonicated solution clearly indicates the presence of C_{60} in the

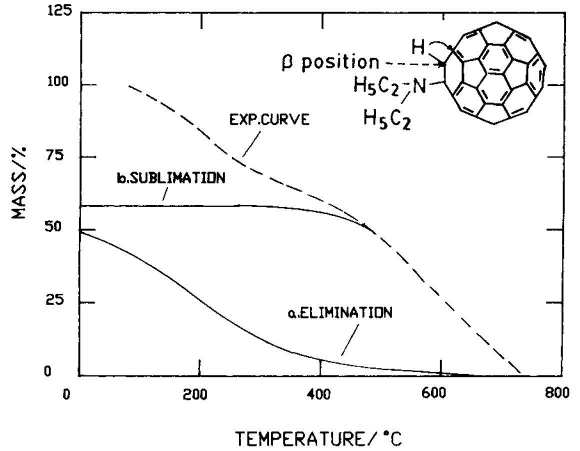

Fig. 4. Measured thermogravimetric curve of C_{60}-diethylamine adduct in He atmosphere at a heating rate of 1°C min^{-1}. Sigmoidal fits for the first step corresponding to elimination (a) and the second step corresponding to sublimation (b). The inset shows the possible attachment of the hydrogen and nitrogen of the amine to the C_{60} cage.

samples as all the UV–VIS absorption peaks characteristic of C_{60} are observed (Fig. 2b). The XRD of the quenched samples indicate that the samples are amorphous. A systematic shift of the lower angle peak corresponding to C_{60}–C_{60} correlation distance, from 16.10 Å for the adduct towards pure C_{60} value of 14.19 Å is observed with increasing quench temperature. It may be noted that the retro product C60 is amorphous and the reaction is therefore noted to be topotactic.

A close examination of the TG curve (Fig. 4) indicates two partially overlapping steps. The experimental TG curve has been fitted to two sigmoidal curves Fig. 4a and b. It is observed that the weight loss in the experimental TG curve (Fig. 4) starts at a temperature as low as 100°C. A priori, such a reduction in mass could arise due to the presence of residual solvents, but this can be ruled out as the sample has been vacuum dried for several hours and IR spectrum of the sample does not indicate the presence of any residual solvent. Also, our DSC studies on the sample presented in Fig. 6 do not reveal any endothermic peak corresponding to solvent evaporation. The signal due to solvent evaporation would be expected to be quite large and easily detectable in DSC studies (heat of vapourisation of diethylamine=29.1 kJ mol^{-1} [18]). On the other hand a broad and weak exotherm is observed between 120 and 300°C in the DSC curve perhaps due to some structural relaxation associated with the elimination reaction. This cannot be reconciled with solvent evaporation. Hence, the curve 4a must correspond to the thermal elimination reaction. The broad curve indicates that the kinetics is very sluggish. The extremely slow kinetics may be attributed to the dynamic behaviour of hydrogen and its

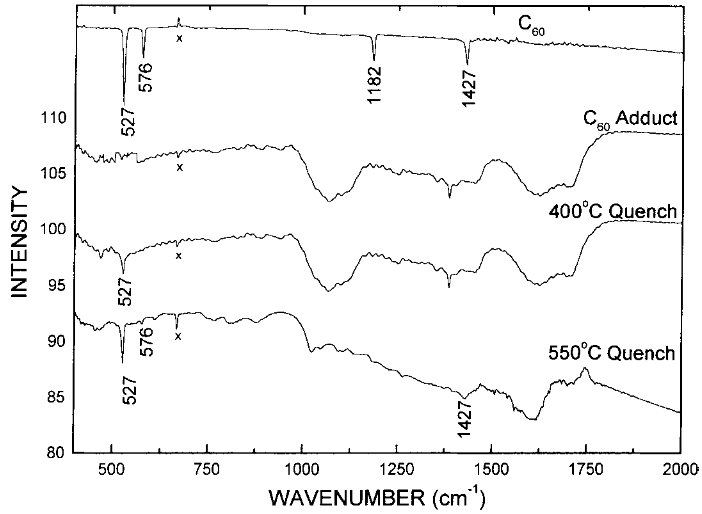

Fig. 5. IR spectra of (a) C_{60}-diethylamine adduct, as prepared (b) 400°C quenched (c) 550°C quenched and (d) pristine C_{60}. Notice the increase in intensity of the 527 cm^{-1} peak with heat treatment.

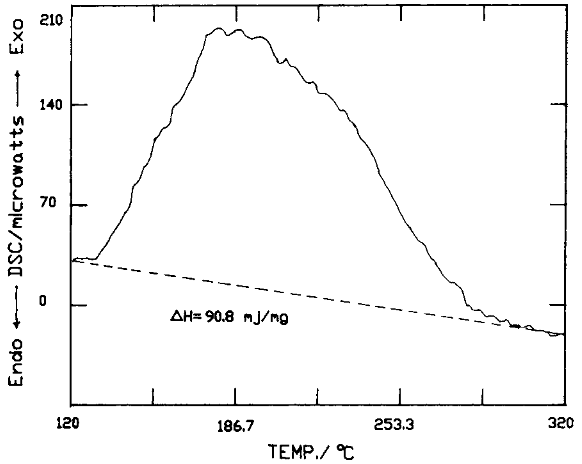

Fig. 6. DSC curve of C_{60}-diethylamine adduct in a sealed aluminium crucible at a heating rate of 2°C min^{-1}.

globe trotting around the C_{60} cage. The observation of globetrotting of proton was first made on $C_{60}H$ and C_{60}-morpholine adduct using high resolution NMR [19,20]. We propose that as a consequence of this sigmatropic hydrogen shift from the β position (see inset Fig. 4) to other positions on the C_{60} cage, only a small fraction of hydrogen atoms are available at the β position for elimination. Hence the kinetics is retarded. The second step in the TG curve of Fig. 4 corresponding to Fig. 4b is due to sublimation. It may be noted that the sharp drop in mass due to sublimation of pure C_{60} reported in literature [21] above 550°C is not observed here. This could arise due to the fact that the elimination reaction is still not complete (the tail of curve 4a extends up to around 650°C) and the unreacted amine adduct modifies the sublimation kinetics considerably as the product C_{60} vapour has to diffuse through the layer of the amine adduct.

The DSC curve of the fullerene-amine adduct in a sealed aluminium crucible at a heating rate of 2°C min^{-1} shows a broad exotherm in the range 120–300°C with an associated enthalpy change of 90.8 J g^{-1} (Fig. 6). The broad exotherm in the DSC curve may be attributed to some structural relaxation process associated with elimination. As the addition reaction of an amine to C_{60} is expected to be exothermic with associated heat of reaction calculated in literature to be approximately 30 kcal mol^{-1} [7,9] the reverse reaction namely the elimination is expected to be endothermic. However the DSC curve shows a broad exotherm. As the endothermic change corresponding to the elimination reaction is not expected to be very large (around 30 kcal mol^{-1}) it may be overshadowed by a broad exothermic structural relaxation process also associated with the elimination.

Kinetic analysis of the elimination reaction which corresponds to step 1 of Fig. 4 has been carried out. This has been done using several methods used in literature including Coats and Redfern, Mc Carthy and Green and Phadnis and Deshpande [22,23]. The dynamic equation for non-isothermal conditions can be generally expressed as

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

where α is the fraction of weight loss, A is the frequency factor, β the heating rate, E the reaction activation energy and $f(\alpha)$ is a function related to the reaction mechanism which depends on whether the kinetic control mechanism is nucleation and growth, diffusion, or phase boundary interface motion [24]. In the Coats and Redfern method $f(\alpha)$ has been assumed to be $(1-\alpha)^n$ and the integral form of the above equation has been solved to give [22]

$$\ln\left\{\frac{[-\ln(1-\alpha)]}{T^2}\right\}=\ln\left\{\frac{AR}{\beta E}\right\}-\frac{E}{RT} \quad \text{for } n=1$$

So a plot of $-\ln\{[-\ln(1-\alpha)]/T^2\}$ versus $1/T$ should yield a straight line whose intercept and slope give $-\ln(AR/\beta E)$ and E/R. For the sigmoidal curve corresponding to the elimination reaction Fig. 4a, the plot of the term $-\ln\{[-\ln(1-\alpha)]/T^2\}$ versus $1/T$ is shown in Fig. 7. The activation energy is evaluated from a least square fit of the points to a straight line and is found to be around 12.6 kJ mol^{-1}. The same value, which is arrived at using the other methods, is surprisingly low.

One possible reason for the unusually low activation energy is the globe trotting of proton around the C_{60} cage which occurs even at low temperature [19,20]. Literature studies estimate that the activation enthalpies for sigmatropic hydrogen shifts on the surface of C_{60} must be extraordinarily low and lie below 10 kcal mol^{-1} since a rapid exchange is occurring above −25°C [19]. In the case of the elimination reaction being studied at present, it may be noted that

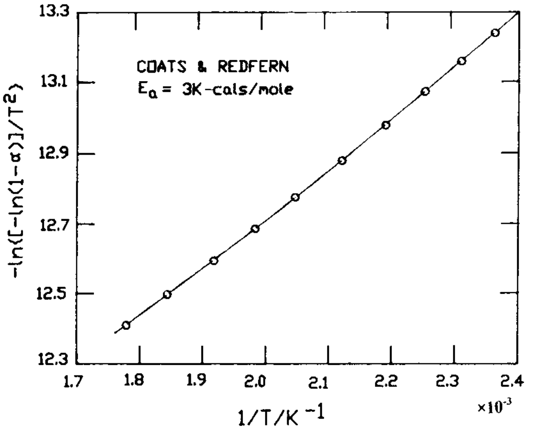

Fig. 7. Coats and Redfern plot of $-\ln\{-\ln(1-\alpha)/T^2\}$ versus $1/T$ for the first step corresponding to elimination reaction in Fig. 4.

the presence of hydrogen in the vicinity of the attached nitrogen atom is required for elimination to occur. The rate of the reaction is therefore limited by the hydrogen shift which is the slow step followed by the cleavage of the amine molecule which is perhaps the fast step. The activation energy for the elimination reaction of around 3 kcal mol^{-1} determined in this study corresponds quite closely to the activation energy for the hydrogen shift which is also noted to be very low. Therefore, this hydrogen shift is perhaps the rate determining step for the elimination of the amine.

4. Conclusions

A fullerene-diethylamine adduct has been synthesized by the solution route starting from C_{60} and diethylamine and purified. The UV–VIS spectrum of the adduct is significantly modified compared to that of C_{60}. The IR spectrum indicates a new C–H mode at 1634 cm^{-1}, and a shift in the C–N mode. This may be due to the new C–H and C–N bonds formed when diethylamine adds on to C_{60}. Thermogravimetry and associated characterisation studies on the adduct indicate a mass loss between 100 and 650°C corresponding to the elimination reaction. The globe-trotting of proton in this complex molecule gives rise to an unusually low value for the activation energy for the elimination reaction.

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