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# Pressure-induced dimerization of fullerene C<sub>60</sub>: a kinetic study

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## Abstract

The kinetics of pressure-induced dimerization of fullerite C<sub>60</sub> at 1.5 GPa in the 373–473 K temperature interval was studied by X-ray diffraction, infrared and Raman spectroscopy. Kinetic curves of the dimerization reaction in the fcc and sc phases of C<sub>60</sub> were obtained by monitoring the dimeric (C<sub>60</sub>)<sub>2</sub> IR line at 796 cm<sup>-1</sup>. The value of the dimerization activation energy was determined to be  $E_{a(\text{dim})} = 134 \pm 6$  kJ mol<sup>-1</sup>, assuming the second order irreversible reaction. The peculiarities of the dimerization processes in the fcc and sc phases of C<sub>60</sub> fullerite are also discussed. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The dimerization of C<sub>60</sub> has attracted considerable interest of investigators as an elementary act of C<sub>60</sub> polymerization proceeding through the (2+2) cycloaddition reaction induced by light irradiation [1] or pressure action [2,3]. To date, theoretical consideration of the phenomena has predominated over experimental work [4–17], in part because of the absence of unambiguous criteria for the identification of the dimeric (C<sub>60</sub>)<sub>2</sub> molecules. As a result, the first conclusions about the presence of (C<sub>60</sub>)<sub>2</sub> molecules in the products of photo- and pressure-induced polymerization carried out on the basis of a qualitative comparison of

computed and experimental Raman spectra [14,18] remained, strictly speaking, tentative. However, the mechanochemical synthesis of the (C<sub>60</sub>)<sub>2</sub> dimer [19–21] made it possible to determine the main individual characteristics of the molecule and to identify it by infrared (IR) and Raman spectroscopy. It has opened up the opportunity of detailed experimental investigation of C<sub>60</sub> dimerization. Recently we have shown that the dimerization as the first stage of pressure-induced C<sub>60</sub> polymerization was observed in the broad pressure interval above ~1 GPa even at room temperature. At elevated temperature and duration of treatment the polymerization proceeds further, resulting in the formation of the linear or two-dimensional polymers of C<sub>60</sub> depending on the  $p$ ,  $T$  parameters of the synthesis [16,22].

This work presents a thorough kinetic study of the pressure-induced dimerization of C<sub>60</sub> fullerite

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at 1.5 GPa. Bearing in mind that at this pressure the temperature of the  $sc \leftrightarrow fcc$  phase transition is about 425 K [23–25], the temperature interval of the study was chosen within  $\pm 50$  K of this value in order to carry out the dimerization both in the  $sc$  and the  $fcc$  phases of  $C_{60}$ .

## 2. Experimental

The experimental part of the work consisted in the high-pressure synthesis of the dimerized states of  $C_{60}$  at 1.5 GPa and temperatures of 373, 383, 393, 403, 413, 423, 433, 453, and 473 K and different treatment times from 1 to 50 000 s. High-purity (99.98%) twice-sublimed small-crystalline  $C_{60}$  supplied by Term USA was taken as a starting material. The standard scheme of high-pressure experiments was used in the work. Heating was performed with a temperature control module which set the prescribed rate of heating ( $15 \text{ K s}^{-1}$ ). The details of the synthesis performed using the ‘Maxim’ (piston-cylinder type) and ‘Toroid’ high-pressure apparatus have been described earlier [18,26]. High-pressure states were conserved at ambient conditions quenching them down to room temperature under pressure and were analyzed by IR spectroscopy. The transmission spectra of the samples pelleted in KBr were recorded on a Specord M80 (Carl Zeiss) spectrophotometer.

As already found [16,22], the structural changes of the system associated with the dimerization manifest themselves in a broadening of the powder diffraction peaks and their shifts to the greater angle values, thus the disordered structure retains on an average the  $fcc$  lattice. In this situation the X-ray data are hardly applicable to the precise measurement of the dimer concentration in the system. At the same time the vibrational spectra are more informative and allow one to measure quantitatively the content of the dimer.

The comparative analysis of the IR and Raman spectra of the monomeric and different polymeric forms of  $C_{60}$  carried out by us earlier [27] showed that the IR spectra of these species (Fig. 1) were more suitable for analytical purposes because they had very distinctive bands that characterize each form well. For example, the  $(C_{60})_2$  dimer demon-

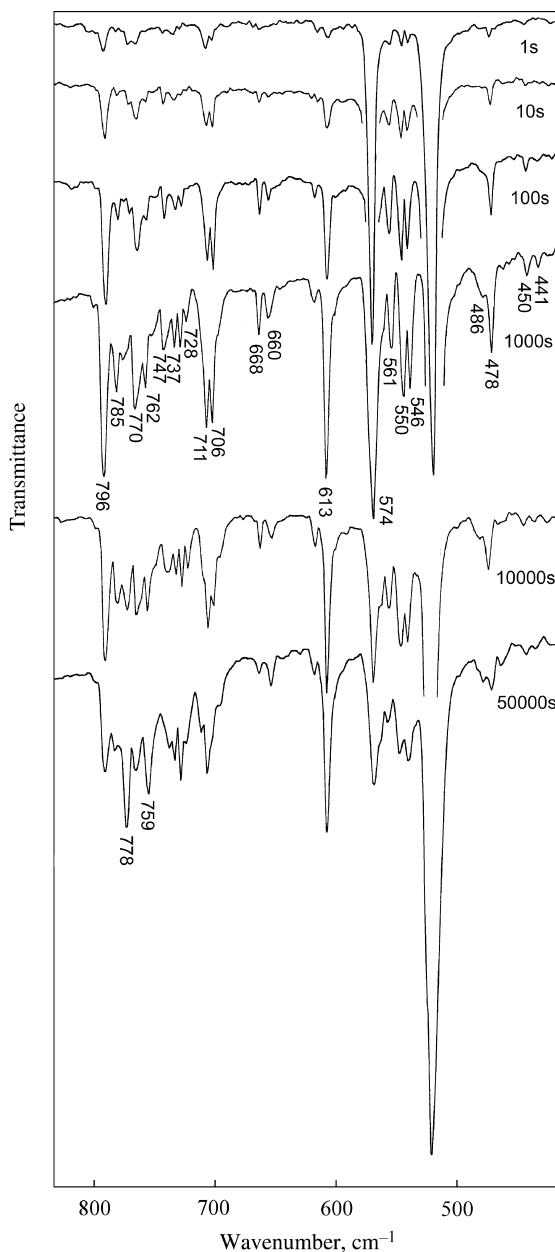


Fig. 1. IR transmission spectra of the samples obtained by treating the  $C_{60}$  fullerite at 1.5 GPa, 423 K and the treatment times from 1 to 50 000 s.

strates an intense IR line at  $796 \text{ cm}^{-1}$  that was employed in the present study. The fraction of the dimer in the sample was determined as follows. The absorbance in the maximum of the analytical

band was measured, corrected for the content of the sample in the pellet and its thickness, and was then made proportional to the corresponding value for the relevant pellet containing pure  $(C_{60})_2$ . This procedure made it possible to express the experimental data through the conversion extent ( $\alpha$ ) of the dimerization reaction. The extents of conversion analyzed fell within the interval of 0.1–0.8 as normally occurs in a kinetic study.

The subsequent treatment of the kinetic curves was made under the assumption that the pressure-induced dimerization  $2C_{60} = (C_{60})_2$  can be considered as an irreversible second-order reaction. In this case, the integral equation for the reaction rate takes the form:

$$kt = \alpha / (1 - \alpha),$$

where  $k$  is the rate constant,  $t$  the treatment time.

Using this equation, the rate constants of the dimerization reaction were calculated at different temperatures using the linear fit in the appropriate set of coordinates.

### 3. Results and discussion

Fig. 2 shows the changes in the absorbance at  $796\text{ cm}^{-1}$  vs HTHP treatment time at several temperatures. The forms of the curves point clearly to the difference in the process below and

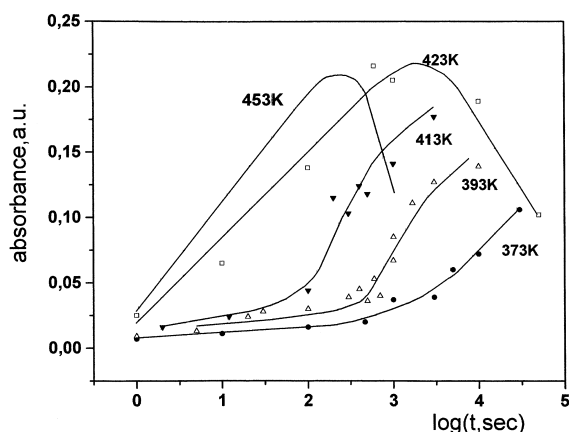


Fig. 2. Time dependence of the intensity of the dimer IR line at  $796\text{ cm}^{-1}$  for the samples obtained at 1.5 GPa and the indicated temperatures.

above 423 K. Below 423 K, the curves are characterized by the pronounced induction period (slow acceleration) and by the relatively rapid period, thus recalling the so-called S-curves of the auto-catalytic chemical reaction. At higher temperatures, a considerable fraction of the dimer was formed very rapidly (after a few seconds of treatment). At the same time, the presence of the maxima on the kinetic curves indicates that this species is only an intermediate product of the reaction and transforms further at these conditions into the chain polymer of  $C_{60}$ . The formation of the latter is clearly seen from the bottom spectrum of Fig. 1 by the presence of the bands at  $778$  and  $759\text{ cm}^{-1}$  which are characteristic of the O phase [27]. Taking into account the observed peculiarities of the kinetic curves, their quantitative treatment was carried out at intervals excluding the induction periods and the regions with detectable content of the chain polymer. In practice, synthesis duration longer than 1000 s at 373–383 K, longer than 100 s at 393–403 K, within the 100–3000 s interval at 413 K and less than 1000 s at 423 K and 100 s at 433–453 K was considered. Data obtained from the samples synthesized at 473 K were excluded from the analysis altogether.

The temperature dependence of the rate constant logarithm is given in Fig. 3. The squares

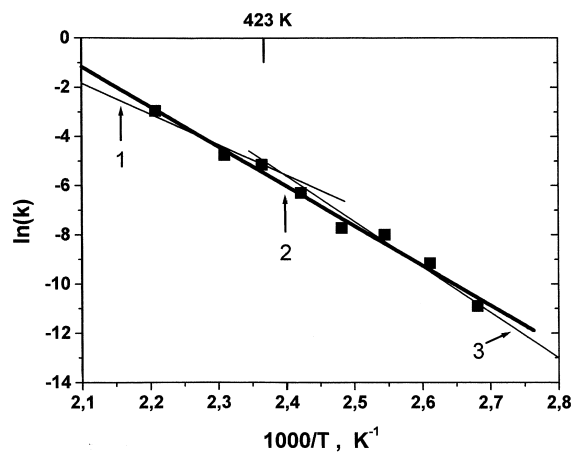


Fig. 3. Temperature dependence of the  $C_{60}$  dimerization rate constant at 1.5 GPa. The bold line 2 is obtained using the complete set of the data. The thin line 1 corresponds to the 373–413 K temperature range. The thin line 3 is related to the 423–453 K temperature range.

represent the experimental data and the lines are the result of a linear least-squares fit. From the complete set of these data (bold line 2) using the Arrhenius expression

$$k = A \exp(-E_a/RT),$$

the activation energy  $E_{a(\text{dim})}$  was determined to be  $134 \pm 6 \text{ kJ mol}^{-1}$ .

Although no indication of the change of the dimerization mechanism at 423 K is evident from the data of Fig. 3, these data may be analyzed separately for the two treatment temperature intervals of 373–413 K (thin line 1) and 423–453 K (thin line 3). In this case the following values of activation energies are:  $E_{a(\text{sc})} = 137 \text{ kJ mol}^{-1}$ , and  $E_{a(\text{fcc})} = 121 \text{ kJ mol}^{-1}$ . Note that the precision of the  $E_{a(\text{sc})}$  and  $E_{a(\text{fcc})}$  determination is not high ( $\pm 19 \text{ kJ mol}^{-1}$ ) because of the narrow temperature intervals, but the difference in these values correlates satisfactorily with the enthalpy of the  $\text{sc} \rightarrow \text{fcc}$  phase transition in the  $\text{C}_{60}$  that is equal at atmospheric pressure to  $7.46$  [28] or  $9.0 \text{ kJ mol}^{-1}$  [29]. This fact makes it possible to suggest that in both cases the dimerization reaction proceeds through the same transition state. That is, despite of the low precision of the determination, the difference between  $E_{a(\text{dim})}$  values in the fcc and sc phases should at least be kept in mind at a discussion of the  $\text{C}_{60}$  polymerization processes.

The  $E_{a(\text{dim})}$  value ( $134 \text{ kJ mol}^{-1}$ ) obtained in this study is much greater than that obtained for the  $\text{C}_{60}$  polymerization on the basis of the measurement of the thermal conductivity time dependence ( $38.6 \text{ kJ mol}^{-1}$ ) [31]. On the other hand, our value is significantly less than the theoretical estimation of  $400 \text{ kJ mol}^{-1}$  obtained by Ozaki et al. [13].

In the absence of any other  $E_{a(\text{dim})}$  values, we compare our data with the experimental and calculated values of the activation energy for the reaction of dimer dissociation ( $E_{a(\text{diss})}$ ). Setting the value of the dissociation enthalpy of ca  $16 \text{ kJ per } (\text{C}_{60})_2 \text{ mole}$  and  $E_{a(\text{dim})} = 134 \text{ kJ mol}^{-1}$ , we obtain  $E_{a(\text{diss})} = 150 \text{ kJ mol}^{-1}$ . Obviously, this estimation suggests the single reaction path for the direct and reverse reaction and a weak pressure dependence of their energetic characteristics. Despite the provisional character of this estimate, we can note that our result agrees with the experimental  $E_{a(\text{diss})}$

values found by Wang et al. ( $120.7 \text{ kJ mol}^{-1}$ ) [6], Nagel et al. ( $167 \text{ kJ mol}^{-1}$ ) [17] and the theoretical value ( $154.5 \text{ kJ mol}^{-1}$ ) calculated by Porezag et al. using a DF-TB method [9]. The height of the depolymerization barrier was also calculated by other authors, mainly by means of molecular dynamics methods based on semi-empirical (AM1[10] and MNDO/PM3 [13]) approaches, tight-binding scheme [5] or local-density approximation [8]. The value of the barrier at which the inter-cage bonds break was estimated to be  $193$ – $386$  [5],  $232$  [8],  $338$  [10] or  $273 \text{ kJ mol}^{-1}$  [13]. Though the comparison of the barrier heights calculated by different approaches should be made with care [10], it can be seen that the theoretical values, as a rule, exceed our experimental one.

The qualitative discrepancy of the kinetic curves for the dimerization reaction in the fcc and sc phases testifies that the molecular orientation and mobility in the fullerite lattice affect the pressure-induced polymerization as they do in the case of photopolymerization [1,6,30]. But if the transition from the fcc to the sc phase causes the suppression of a photo-process (one could use the expression ‘temperature threshold for the photopolymerizability’ near the orientational ordering temperature of  $260 \text{ K}$  [1,14,30]), the pressure-induced dimerization in the sc phase proceeds as an autocatalytic reaction. It may be connected with the different content of the two (so called P and H) orientational states [32,33] in the sc phase under the conditions of photo- (at atmospheric pressure) and pressure-induced polymerization. It is known that  $\text{C}_{60}$  (2+2)-polymerization demands the specific orientation of the double bonds (DB) in the adjacent molecules: they should be parallel to one another with the ‘edge-to-edge’ configuration [1,30]. Within the fcc phase, a small fraction of molecules with favorable orientation is available at any particular moment in consequence of the almost isotropic distribution of molecular orientations. Thus, the orientational disorder in the  $\text{C}_{60}$  lattice favors the polymerization. Vice versa, in the sc phase where the adjacent molecules are related through a  $2_1$  screw rotations, no suitable DB contacts are available in the both P and H states, the former being the most adverse. The predominance of the P state in the sc phase at atmospheric

pressure [33] explains why the photopolymerization is suppressed [6].

The increase of pressure reduces the fraction of the unfavorable P state in the sc phase. At 1.5 GPa the H state content becomes overpowering [34,35]. At these conditions the auto-catalytic character of the dimerization is probably associated with the formation of only a small fraction of the properly oriented  $C_{60}$  molecules which enter into reaction. The appearance of the dimeric molecules supplies some orientational disorder to the sc lattice that favors the reaction; hence the accumulation of the  $C_{60}$  dimers and polymers. Thus, the (2+2) reaction is ‘catalyzed’ by the disorder which has appeared, so that at some moment the process becomes similar to that which occurred in the fcc phase.

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### References

- [1] A.M. Rao, P. Zhou, K.A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.T. Lee, X.-X. Be, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, *Science* 259 (1993) 955.
- [2] M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Berthou, M. Perroux, *Phys. Rev. Lett.* 74 (1995) 278.
- [3] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter Jr., A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas, T. Yagi, *Science* 264 (1994) 1570.
- [4] D.L. Strout, R.M. Murry, C. Xu, W.C. Eckhoff, G.K. Odom, G.E. Scuseria, *Chem. Phys. Lett.* 214 (1993) 576.
- [5] M. Menon, K.R. Subbaswamy, M. Sawtarie, *Phys. Rev. B* 49 (1994) 13966.
- [6] Y. Wang, J.M. Holden, X. Bi, P.C. Eklund, *Chem. Phys. Lett.* 217 (1994) 413.
- [7] N. Matsuzawa, M. Ata, D.A. Dixon, G. Fitzgerald, *J. Phys. Chem.* 98 (1994) 2555.
- [8] G.B. Adams, J.B. Page, O.F. Sankey, M. O’Keeffe, *Phys. Rev. B* 50 (1994) 17471.
- [9] D. Porezag, M.R. Pederson, Th. Frauenheim, Th. Kohler, *Phys. Rev. B* 52 (1995) 14963.
- [10] J. Fagerström, S. Stafström, *Phys. Rev. B* 53 (1996) 13150.
- [11] J. Kurti, K. Nemeth, *Chem. Phys. Lett.* 256 (1996) 119.
- [12] K. Esfarjani, Y. Hashi, J. Onoe, K. Takeuchi, Y. Kawazoe, *Phys. Rev. B* 57 (1998) 223.
- [13] T. Ozaki, Y. Iwasa, T. Mitani, *Chem. Phys. Lett.* 285 (1998) 289.
- [14] B. Burger, J. Winter, H. Kuzmany, *Z. Phys. B* 101 (1996) 227.
- [15] Y. Iwasa, K. Tanoue, T. Mitani, T. Yagi, *Phys. Rev. B* 58 (1998) 16374.
- [16] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V.M. Senyavin, V. Agafonov, R. Ceolin, H. Szwarc, *JETP Lett.* 68 (1998) 928.
- [17] P. Nagel, V. Pasler, S. Lebedkin, A. Soldatov, C. Meingast, B. Sundqvist, P.A. Persson, T. Tanaka, K. Komatsu, S. Buga, A. Inaba, *Phys. Rev. B* 60 (1999) 16920.
- [18] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V. Agafonov, R. Ceolin, H. Szwarc, *Carbon* 35 (1997) 735.
- [19] G.W. Wang, K. Komatsu, Y. Murata, M. Shiro, *Nature* 387 (1997) 583.
- [20] K. Komatsu, G.W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, K. Yamamoto, M. Saunders, *J. Org. Chem.* 63 (1998) 9358.
- [21] S. Lebedkin, A. Gromov, S. Giesa, R. Gleiter, B. Renker, H. Rietschel, W. Kratschmar, *Chem. Phys. Lett.* 285 (1998) 210.
- [22] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V. Agafonov, H. Allouchi, R. Ceolin, A.V. Dzyabchenko, V. Senyavin, H. Szwarc, T. Tanaka, K. Komatsu, *J. Phys. Chem. B* 103 (1999) 1800.
- [23] G. Kriza, J.-C. Ameline, D. Jerome, A. Dvorkin, C. Fabre, D. Schuta, A. Rassat, P. Bernier, *J. Phys. I. Fr* 1 (1991) 1361.
- [24] G.A. Samara, J.E. Schirber, B. Morosin, L.V. Hansen, D. Loy, A.P. Sylvester, *Phys. Rev. Lett.* 67 (1991) 3136.
- [25] O. Andersson, A. Soldatov, B. Sundqvist, *Phys. Rev. B* 54 (1996) 3093.
- [26] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V. Agafonov, H. Allouchi, R. Ceolin, A.V. Dzyabchenko, V.M. Senyavin, H. Szwarc, *Phys. Rev. B* 58 (1998) 14786.
- [27] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V.M. Senyavin, R. Ceolin, H. Szwarc, H. Allouchi, V. Agafonov, *Phys. Rev. B* 61 (2000) 11936.
- [28] B.V. Lebedev, K.B. Zhogova, T.A. Bykova, B.S. Kaverin, V.L. Karnatsevich, M.A. Lopatin, *Izv. RAS, Ser. Khim.* (1996) 2229.
- [29] J. De Bruijn, A. Dvorkin, H. Szwarc, J. Goldard, R. Ceolin, C. Fabre, A. Rassat, *Europhys. Lett.* 24 (1993) 551.
- [30] P. Zhou, Z.H. Dong, A.M. Rao, P.C. Eklund, *Chem. Phys. Lett.* 211 (1993) 337.
- [31] A. Soldatov, K. Prassides, O. Andersson, B. Sundqvist, in: *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, vol. 6, Proceedings of the 193rd ECS Meeting, San Diego, 1998, p. 769.

- [32] P.A. Heiney, J.E. Fisher, A.R. McGhie, W.J. Romanov, A.M. Demenstein, J.P. McGauley, A.B. Smith, D.E. Cox, *Phys. Rev. Lett.* 66 (1991) 2911.
- [33] W.I.F. David, R.M. Ibberson, T.J.S. Dennis, J.P. Hare, K. Prassides, *Europhys. Lett.* 18 (1992) 219.
- [34] W.I.F. David, R.M. Ibberson, *J. Phys.: Condens. Matter* 5 (1993) 7923.
- [35] B. Sundqvist, O. Andersson, A. Lundin, A. Soldatov, *Solid State Commun.* 93 (1995) 109.