25 May 2001

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Chemical Physics Letters 340 (2001) 1–6

CHEMICAL PHYSICS LETTERS

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Influence of nitrogen on carbon arc plasma and formation of fullerenes

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Received 23 January 2001; in final form 6 March 2001

Abstract

The influence of nitrogen on the process of fullerene formation in the carbon arc discharge in a helium/nitrogen atmosphere has been studied. Applying optical emission spectroscopy and using the self-absorption effect, the spatial distribution of the temperatures and chemical species, i.e. $C_2(a^3\Pi_u,\ v''=0)$ and $CN(X^2\Sigma^+,\ v''=0)$ radicals produced by the d.c. arc discharge between pure graphite electrodes, were determined across the arc gap. The soot product was analyzed spectrophotometrically to determine C_{60} content. C_{60} was detected even when pure nitrogen was used (at about 0.5 wt%). The relative content of higher fullerenes was measured by mass spectrometry and their formation was found to be significantly enhanced in the presence of nitrogen. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The properties of carbon vapor are of interest in several areas of theoretical chemistry and physics as well as for a variety of technologies and industrial uses. While much of the chemical interest in carbon vapor has been recently connected with the formation of novel carbon nanostructures, i.e. the fullerenes [1] and nanotubes [2], the physical interest has been largely connected with the spectra of the stellar atmosphere or of flames, in which spectral lines assigned to various carbon species have been observed [3]. From the considerations regarding the d.c. carbon arcs it seems probable that the distribution of C_n species leaving the anode crater resembles, but is not equal to, an equilibrium relationship. What happens to these species in the arc itself is, of course, quite another matter and various processes like ionization and fragmentation can either remove them or generate non-equilibrium species distributions. Thus, the composition of the vapor resulting from the arc ablation of carbonaceous bodies in high temperature environments is of interest, with respect to the formation mechanism and yield of nanocarbons.

A great deal of work has been reported that correlates fullerene species production and yields with the operational parameters involved, providing an extensive and very useful body of engineering data. These parametric studies have provided, however, little insight into the detailed mechanism of fullerene formation, indispensable for synthesis scale-up. The process involves some interesting and unusual chemistry [4]. Fullerene formation represents growth from an initial species with perhaps 1–10 carbon atoms to nanoparticles,

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PII: S0009-2614(01)00333-5

with hundreds of 'well ordered' carbon atoms (the higher fullerenes). Such rearrangements take place at high temperatures, where the driving force from entropy strongly opposes such atomic aggregations. With increasing pressure in the arc reaction chamber the formation of chains from carbon species becomes more extensive. At the optimal pressure of 13.3 kPa [5] the development of the three-dimensional network that is characteristic of fullerenes is observed, while at higher pressures, over-saturation in the system may lead to the creation of graphite sheets and nanotubes.

Fullerenes have been routinely produced in the helium carbon arc plasma for more than 10 years. The involvement of other gases in the process may result in decreased production costs. In the case of nitrogen, the heterohedral substitution of carbon atom(s) by nitrogen in the fullerene structures could also yield novel compounds with properties of amazing interest [6]. In the present study, the formation of fullerenes in He/N_2 mixtures was investigated.

To obtain knowledge of the plasma characteristics, the temperature and the plasma composition were evaluated by optical emission spectroscopy [7]. The spectral characterization of the arc zone can provide new insights into the mechanism involved in the transformation of fullerene nanostructure precursors [8,9]. The C_2 and CN radical distributions were measured across the arc plasma. Of the numerous possible intermediate carbon/nitrogen species these radicals are the only ones that can be quantitatively measured using conventional optical emission spectroscopy. The C_2 radical, as is generally accepted, plays an important role in the formation mechanism for fullerenes and nanotubes. Hence, it is of considerable interest to be able to quantitatively study its presence in the reaction zone [10]. It should be mentioned here that there have been several studies [11–13] on the application of emission spectroscopy to the characterization of the carbon arcs in the process of fullerene formation, but these studies all deal with helium plasma and qualitative data only were reported.

In the present Letter, which we believe is the first account of research on the quantitative diagnostics of the carbon arc in a chemically reactive environment, the influence of nitrogen on the plasma characteristics and the formation of fullerenes are reported. The composition of the arc generated solid products was also studied by means of various techniques.

2. Experimental

The reaction system and the experimental procedures employed have been presented elsewhere [14]. Graphite electrodes, 6 mm in diameter, were subjected to d.c. arcing in He/N_2 gas mixtures under static conditions and pressures of about 13.3 kPa. The electrode gap was held within 1 mm by means of an opto-electronic system [14]. Table 1 contains the averaged processing variables. Compared to the pure helium plasma [8] higher anode erosion can be related to the chemical etching of graphite by the plasma activated nitrogen.

Table 1
Operating parameters and anode sublimation rates

No.	$He + \%N_2$	I (A)	U (V)	p (mb)	m_{sub} (mg s^{-1})
1	0	76	20.8	128	5.3
2	0	74	20	140	5.6
3	10	78	21.5	132	6.2
4	10	81	19.9	144	9
5	25	73	21.8	123	6.3
6	25	80	20.5	150	8
7	50	70	20.4	134	6.2
8	50	75	20.2	161	8
9	100	67	21.7	152	5
10	100	75	24	166	10

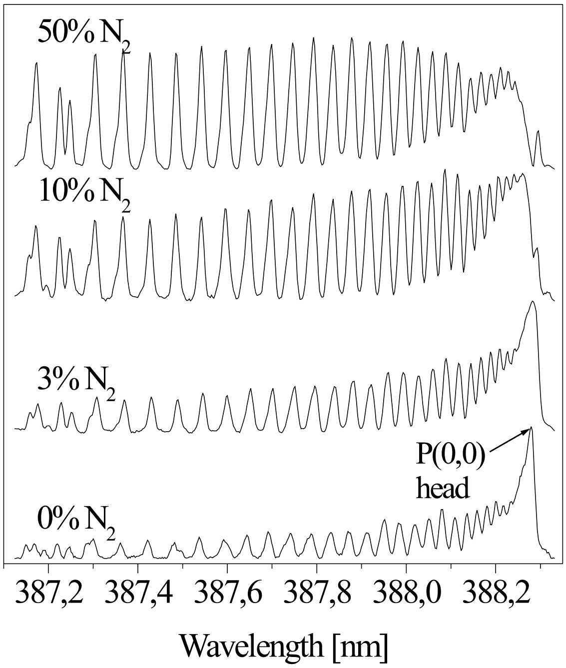

Fig. 1. Experimental examples of CN($B^2\Sigma^+$, $v' = 0 \rightarrow X^2\Sigma^+$, $v'' = 0$; 388, 3 nm) emission band emitted by arc discharge in He/N_2 atmosphere.

The CCD ST8 camera, coupled with a spectrograph, was used for the plasma diagnostics. The C_2 contents were determined using the well-pronounced self-absorption effect in the $d^3\Pi_g$, $v' = 0 \rightarrow a^3\Pi_u$, $v'' = 0$, (516.5 nm) transition. The column densities of C_2 (the product of average concentration and column length along a given chord in the arc cross-section) were calculated on the basis of the temperatures and integrated intensities of the normalized C_2 (d–a, 0–0) band using an a priori calculated functional dependence of the integrated intensities on the C_2 column density for various temperatures [7]. Temperatures were evaluated from the Boltzmann plots, using the resolved rotational components of this band. Since CN($B^2\Sigma^+$, $v' = 0 \rightarrow X^2\Sigma^+$, $v'' = 0$; 388, 3 nm) band is also strongly self-absorbed, a similar procedure was elaborated and applied in order to find the CN($X^2\Sigma^+$, $v'' = 0$) column density across the arc [15]. Examples of the experimental intensity distributions within this band emitted from the $C/N_2/He$ arc plasma for different nitrogen contents are shown in Fig. 1. The self-absorption is clearly visible in the position of the P(0–0) band head where many rotational lines overlap and cause a disappearance of the band head in the case of a high nitrogen content in the gas mixture.

The soot produced by the arc sublimation of the anode was subsequently refluxed in dry toluene prior to C_{60} determination by the conventional spectrophotometric measurements performed at 329 nm [8]. For the identification of the content of higher fullerenes, the soot was analyzed by the Laser Desorption TOF MS technique.

3. Results and discussion

3.1. Thermodynamic considerations

To evaluate the composition of reactants the thermodynamic equilibrium calculations of a carbon/nitrogen mixture have been carried out for the temperature range between 1000 and 6000 K, with pressure fixed at 15 kPa and the input C/N ratio equal to 1 (as an example). From the results presented in Fig. 2 one can predict that at the temperatures prevailing in the arc, i.e. between 4000 and 6000 K, the plasma consists mainly of C, N_2,

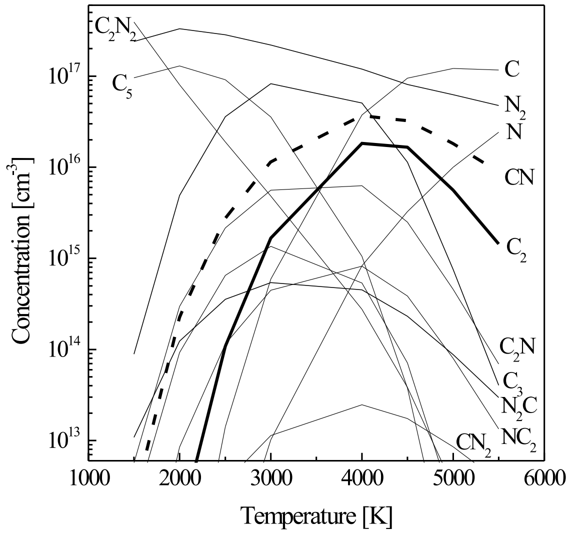

Fig. 2. Equilibrium composition of carbon/nitrogen plasma: $p = 15$ kPa, [C]/[N] = 1.

N, CN and C_2 species. The lower temperatures favor the formation of higher carbon species, e.g. C_5 and C_2N_2. The temperature dependence for the stability of the CN and C_2 radicals is much the same, with a maximum concentration at around 4200 K. Obviously, the starting molar ratio of the reactant will change the relative content of species under consideration.

It must be noted, however, that in the actual arc plasma system different process variables can distinctly influence the theoretical reaction course. For example, rapid quenching may lead to the final concentrations far exceeding those predicted from the equilibrium conditions [16]. Thus, equilibrium thermodynamics are often of limited use in predicting the final compositions, owing to sublimation, condensation, and kinetic barrier effects but they do contribute to a better understanding of the complex plasma phenomena.

3.2. Plasma temperature and C_2 content

The average temperature distributions across the arc gap are shown in Fig. 3A. Regardless of the nitrogen content in the arc chamber, the temperature profiles are similar with a maximum close to 6000 K along the chord crossing the arc axis, and 3500 K on the plasma edge. The observed minima in the region close to the arc center are a consequence of a systematic error which results from the self-absorption effect. It was shown earlier [15] that an increase in the C_2 density (and, consequently, an increase in self-absorption) can lower the temperature values, evaluated from the Boltzmann plots, by about 10%. This is exactly the case for the higher contents of N_2 (50% or 100%) in the present study.

The radial distributions of the column density of the $C_2(a^2\Pi_u,\ v''=0)$ radicals are shown in Fig. 3B. Both for pure carbon plasma and under the presence of nitrogen, the C_2 species are mostly concentrated near the arc axis, with the distributions being slightly expanded in the latter case. At lower nitrogen concentrations (up to 25% N_2) the C_2 column densities are close to the one without nitrogen with slightly different radial distributions only. It must be admitted, however, that because of the smaller gap, the accuracy of the positioning

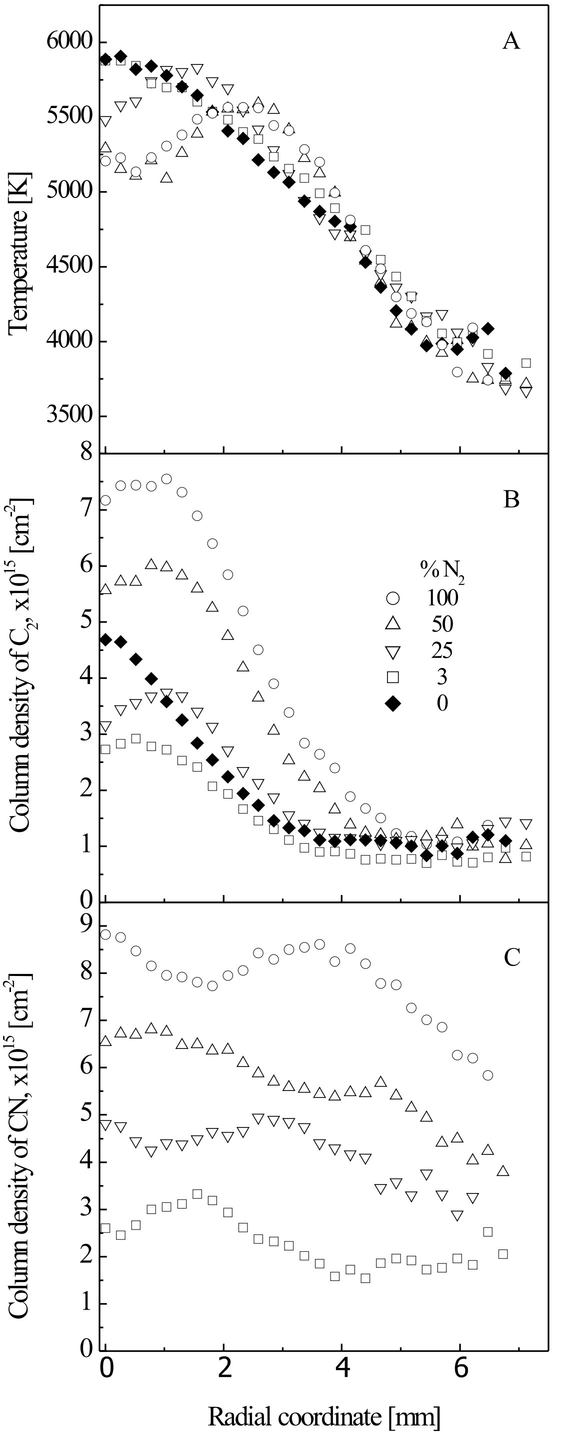

Fig. 3. Radial distributions of A: temperature, B: column density of $C_2(a^3\Pi_u,\ v''=0)$ and C: column density of $CN(X^2\Sigma^+,\ v''=0)$ in the arc plasma.

of the plasma cross-section image onto the spectrograph slit was within ±0.2 mm. Thus even a small horizontal displacement can yield results from a different arc cross-section than was intended.

At higher nitrogen contents a distinct increase of C_2 radicals is observed. Since the dissociation energy of C_2 (6.2 eV) is significantly lower compared to that of CN (7.8 eV) such a feature was rather unexpected. As it follows from thermodynamics (Fig. 2), the presence of N_2 should rather lower somehow the C_2 equilibrium concentration because of the CN formation. It is also very likely that the expansion of carbon species is hampered by the heavier nitrogen atoms and molecules (compared to helium) thus resulting in the higher local C_2 concentrations in the arc gap.

3.3. CN and C_2N_2 content

The column density distributions of $CN(X^2\Sigma^+, v'' = 0)$ radicals are shown in Fig. 3C. As expected, with an increase of the nitrogen in the gas mixture the CN densities are higher. Formation of CN radicals depends on the penetration of the nitrogen within the carbon cloud expanding from the arc gap. The mixing of the oppositely directed fluxes of nitrogen and carbon species, and also inherent temporal instabilities of the arc discharge [17], are responsible for the observed non-regular radial distribution of the CN radicals.

One can see that, in contrast to C_2, the CN species are widely spread beyond the arc region and are abundant at the plasma edge. A transition from the column densities to the average local concentrations can be simply made by dividing column densities by the radial coordinates of the radicals, which for CN are much greater ($\gg$7 mm) than for C_2 ($\approx$5 mm). Since the column densities of both radicals are close to each other, one can conclude that the expanding carbon gas effectively constrains the penetration of the nitrogen into the relatively narrow arc gap. It also shows that the CN radicals are formed mainly in the cooler zone just outside the electrodes where the mixing of carbon gas with nitrogen is not spatially disturbed.

The recombination of CN radicals results in the formation of the stable C_2N_2 gas. Surprisingly, it was found from the IR measurements of the gaseous reactants that the concentration of cyanogene after 15 min of the arc operation in nitrogen was relatively small. The amount of C_2N_2 formed in the arc discharge in the pure N_2 gas was only about three times higher in comparison to the amount detected in the case of the discharge in pure helium, contaminated by nitrogen only (<0.05%). This effect can be related to such factors as low dissociation degree of N_2 at the prevailing temperatures (Fig. 2) and the relatively ineffective gas mixing due to the limited convection and diffusion processes in the arc gap. Also, the real carbon arc discharge conditions may not strictly match the conditions of the local thermodynamic equilibrium [18] as mentioned earlier.

3.4. Yield of C_{60} and higher fullerenes

The measured contents of C_{60} fullerene in the soot collected from the different tests are presented in Fig. 4. It is evident that the nitrogen drastically lowers the C_{60} formation yield. However, it is interesting to note that even in the case of pure nitrogen, C_{60} is still formed (ca. 0.5 wt%).

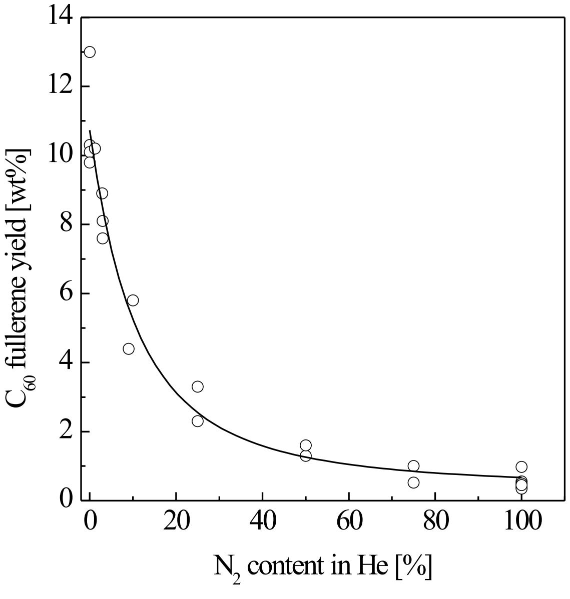

Fig. 4. Yield of C_{60} vs. N_2 content in He/N_2 mixtures.

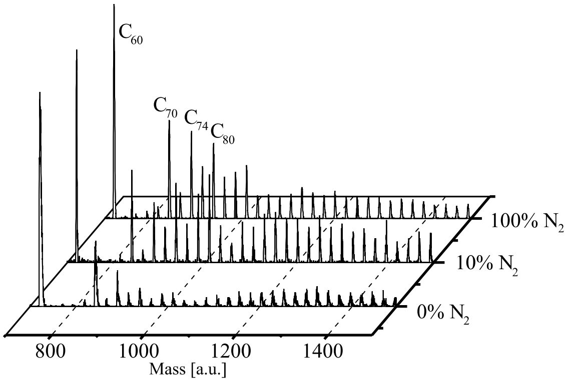

Fig. 5. MS of soot produced under different N_2 content in He/N_2 mixtures: 0%, 10% and 100%.

It is known that during the arcing of the graphite in helium not only C_{60}, but also the higher, mainly C_{70}, fullerenes are formed. Therefore the relative mass distributions of these species in the solid products were measured by LD TOF MS technique. The resulting mass spectra, normalized to the C_{60} peak, are presented in Fig. 5. The content of the higher fullerenes, particularly the so-called 'missing fullerenes' C_{72}, C_{74} and C_{80} [19], in the case of the pure He arc is, as expected, low. However, the positive influence of the nitrogen on the formation of these species is evident, and resembles the one observed earlier when an iron-doped graphite anode was arced in helium [20]. It is clearly seen that in the presence of nitrogen the formation of higher fullerenes is distinctly enhanced. Thus, one can conclude that nitrogen atoms or molecules play a role in generating these, otherwise 'missing', fullerene species.

In considering the fullerene composition in the soot, it has to be kept in mind that the final yields also depend on the efficiency of the extraction method. The spectral analyses of the toluene extracts from the collected soot samples did not reveal any new absorption features, which could be assigned to the nitrogen-doped heterofullerenes [6]. These relatively unstable species, if present, cannot, however, be extracted by the 'conventional' fullerene solvents such as toluene used in this study.

Acknowledgements

This work was supported by the Committee for Scientific Research (KBN) through the Department of Chemistry of Warsaw, under grant no. 7 T09A 020 20. Thanks are due to Prof. H. Shinohara and Dr. A. Koshio, Department of Chemistry, Nagoya University (Nagoya, Japan) for their important collaborative MS works.

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