# Formation of Carbon Nanoparticles by the Condensation of Supersaturated Atomic Vapor Obtained by the Laser Photolysis of C<sub>3</sub>O<sub>2</sub>

E. V. Gurentsov<sup>*a*</sup>, A. V. Eremin<sup>*a*</sup>, and C. Schulz<sup>*b*</sup>

<sup>a</sup> Institute of Thermal Physics of Extreme States, Russian Academy of Sciences, Moscow, 125412 Russia <sup>b</sup> Institut für Verbrennung und Gasdynamik, 47048 Duisburg, Germany

> *e-mail: gurentsov@ihed.ras.ru* Received November 11, 2005

Abstract—A new technique is suggested for obtaining nanoparticles from highly supersaturated vapor resulting from the laser photolysis of volatile compounds. The growth of carbon nanoparticles resulting from C<sub>3</sub>O<sub>2</sub> photolysis has been studied in detail. Absorbing UV quanta (from an Ar-F excimer laser),  $C_3O_2$  molecules decompose to yield atomic carbon vapor with precisely known and readily controllable parameters. This is followed by the condensation of supersaturated carbon vapor and the formation of carbon nanoparticles. These processes have been investigated by the laser extinction and laser-induced incandescence (LII) methods in wide ranges of experimental conditions (carbon vapor concentration, nature of the diluent gas, and gas pressure). The current and ultimate particle sizes and the kinetic parameters of particle growth have been determined. The characteristic time of particle growth ranges between 20 and 1000 µs, depending on photolysis conditions. The ultimate particle size determined by electron microscopy is 5-12 nm for all experimental conditions. It increases with increasing total gas pressure and carbon vapor partial pressure and depends on the diluent gas. The translational energy accommodation coefficients for the Ar, He,  $\hat{CO}$ , and  $C_3O_2$  molecules interacting with the carbon particle surface have been determined by comparing the LII and electron microscopic particle sizes. A simple model has been constructed to describe the condensation of carbon nanoparticles from supersaturated atomic vapor. According to this model, the main process in nanoparticle formation is surface growth through the addition of separate atoms to the nucleation cluster. The nucleus concentrations for various condensation parameters have been determined by comparing experimental and calculated data.

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## INTRODUCTION

The problem of quantitatively describing the formation of carbon nanoparticles is important for a wide variety of applications ranging from combustion to the manufacture of new materials. Although this problem has been the subject of numerous studies, both experimental and theoretical, it is still far from being solved. The potential of numerical simulation of the growth of carbon nanoparticles is limited by the uncertainty of the structure and thermodynamic properties of small carbon clusters. The main difficulties in experimental studies (including experiments dealing with flames, electric arcs, laser ablation of carbon, and pyrolysis of carboncontaining compounds) arise from uncertainties in experimental conditions (temperature, pressure, and carbon concentration) and from the effects of active impurities [1–4].

Thus, the main prospects for the detailed investigation of the formation of condensed carbon particles are establishing experimental conditions under which it will be possible to obtain carbon vapor with precisely known, homogeneous, and readily controllable properties and developing methods for diagnostics of growing nanoparticles during their formation.

Here, we report a radically new approach to producing supersaturated vapor, specifically, the photolysis of volatile compounds under the action of UV radiation. This technique was for the first time suggested for the preparation and examination of nanoparticles [5]. Supersaturated carbon vapor was obtained from carbon suboxide (C<sub>3</sub>O<sub>2</sub>), a volatile carbon-containing compound. Under the action of UV radiation with  $\lambda <$ 207 nm, the C<sub>3</sub>O<sub>2</sub> molecule decomposes into a carbon atom and two inert CO molecules [6]. This provides a means of obtaining supersaturated carbon atom vapor with a precisely known and readily controllable carbon concentration.

Let us evaluate the efficiency of this process in a simple way. Suppose that the volume containing original molecules is exposed to a photon flux of density F (photon/cm<sup>2</sup>). The absorbed part of the flux will be expressed as

$$\Delta F = F[1 - \exp(-C_{C_2O_2}l)] \tag{1}$$

and, for an optically thin layer,

$$\Delta F \approx F \sigma C_{\rm C_2O_2} l, \qquad (2)$$

where  $C_{C_3O_2}$  is the concentration of absorbing molecules and  $\sigma$  is the absorption cross section, which is estimated at  $10^{-17}$ – $10^{-18}$  cm<sup>2</sup> for  $C_3O_2$  and  $\lambda = 190$ – 200 nm [6]. Each absorbed photon produces one carbon atom [6] (i.e., the quantum yield of photolysis is 1). It is interesting that the total photolysis yield *Y*, defined as the total number of atoms formed (which is equal to the number of absorbed photons) divided by the total number of molecules encountered by the photon beam,  $\Delta F/M$  (photon/molecule), where  $M = C_{C_3O_2}l$ , is independent of the concentration of original molecules (*C*) and is expressed as

$$Y = \frac{\Delta F}{M} \approx F\sigma. \tag{3}$$

Thus, for complete  $C_3O_2$  dissociation followed by nanoparticle formation, the quantum flux density should be of the order  $10^{18}$  photon/cm<sup>2</sup>. For a photon energy of about 6 eV, the radiation energy density should be of the order 1 J/cm<sup>2</sup>.

However, carbon vapor condensable into nanoparticles will still form at a lower energy density, with the difference that the environment will contain undissociated  $C_3O_2$  molecules, which do not exert any significant effect on condensation at room temperature [7], and the total yield of nanoparticles will be lower. By varying the initial conditions (the concentration of the carboncontaining compound, the diluent gas, and pressure), it is possible to study the kinetics of condensation and of the formation of carbon nanoparticles.

The new method suggested here for obtaining nanoparticles has the advantages of low energy demand, a wide variety of means of controlling the synthesis outcomes, and readily variable and reliably controllable photosynthesis conditions. These features make the process very promising for fundamental research in nanoparticle condensation and growth and offer the prospect of producing nanomaterials with controllable properties.

Here, we report a detailed experimental study of the kinetics of carbon nanoparticle growth by condensation from highly supersaturated vapor and describe the observed kinetics in terms of a simple cluster growth model.

### EXPERIMENTAL PROCEDURES

Experiments were carried out at room temperature in a rectangular quartz cell with a volume of  $0.5 \text{ cm}^3$  $(10 \times 10 \times 5 \text{ mm})$ . The cell was pumped and was then filled with C<sub>3</sub>O<sub>2</sub> premixed with an inert gas. The formation of nanoparticles was studied by the laser extinction and the laser-induced incandescence (LII) methods using the setup shown in Fig. 1. The C<sub>3</sub>O<sub>2</sub> concentration was varied between 1 and 100%; the diluent gas was Ar, He, Co, or Kr; and the total pressure was varied



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**Fig. 1.** Experimental setup: (1) excimer laser, (2) reactor cell, (3–5) energy meters, (6) dielectric mirror, (7) photodiode, (8) He–Ne laser, (9) quartz plate, (10) converging lens, (11) Nd:YAG laser, (12) photomultiplier, (13) filter ( $\lambda = 694$  nm), and (14) ( $\lambda = 633$  nm).

between 10 and 1000 mbar. The source of photons for  $C_3O_2$  photodissociation was an argon-fluorine excimer laser (Lambda Physik EMG 150TMSC) generating  $\lambda =$ 193 nm UV light with a pulse duration of ~20 ns and a pulse energy of 100 mJ. The laser beam, with a rectangular cross section, was focused so that its cross section coincided with one of the cell walls. The optical path length was 10 mm. In order to determine the energy absorbed by the  $C_3O_2$  molecules, we measured, in each experiment, the radiation energy before and after the pumped cell, using a calibrated photodiode and a calibrated calorimeter. From these measurements, the absorption cross section of  $C_3O_2$  at  $\lambda = 193$  nm was determined to be  $9 \times 10^{-19}$  cm<sup>2</sup>. This value is in good agreement with previous data [6]. At this absorption cross section and a cell length of 1 cm, the optically thin layer conditions were stringently fulfilled only at  $C_3O_2$ pressures of  $\sim 10$  mbar. It is at these pressures that most of our experiments were conducted. At higher  $C_3O_2$ pressures, the concentration of the resulting vapor was somewhat nonuniformly distributed along the cell length. The average carbon atom concentration resulting from  $C_3O_2$  photolysis was derived from energy absorption data under the assumption that the absorption of a photon with  $\lambda < 207$  nm yields one C atom and two CO molecules [6]. The carbon atom concentrations and the partial pressures of carbon vapor resulting from

| C <sub>3</sub> O <sub>2</sub> partial pressure, mbar | Concentration of C atoms $\times 10^{-16}$ , cm <sup>-3</sup> | Partial pressure<br>of C atoms, mbar |
|--|---|--------------------------------------|
| 10   | 1.15  | 0.50                                 |
| 30   | 1.85  | 0.85                                 |
| 100  | 3.40  | 1.50                                 |

**Table 1.** Carbon vapor concentration and partial pressure as a function of the  $C_3O_2$  pressure

 $C_3O_2$  photolysis are listed in Table 1. The error in carbon atom concentration measurements was 25%.

The average size of growing nanoparticles was determined by the LII method [8, 9]. This method is based on measuring radiation from nanoparticles heated with a laser pulse as short as a few nanoseconds. The radiation from the particles peaks in a short time owing to heating and then declines because of cooling. A typical profile of the incandescence signal is shown in Fig. 2. The determination of the particle sizes from the time profiles of incandescence intensity is based on the energy and mass conservation equations for a spherical particle. The absorbed energy of laser radiation is dissipated by radiative and conductive heat transfer to the environment and is spent on the evaporation of the material of the particles. The heating and cooling periods do not overlap. The radiation heat flux and evaporation were not taken into account in our experiments because the particle were heated to relatively low temperatures ( $\leq$ 3500 K) and, therefore, their cooling was mainly due to collisions with surrounding gas molecules. Under conditions of free molecular heat transfer between the particles and the gas (Kn  $\leq 1$ ), considering that the laser-heated volume was small (0.03 of the cell volume), the temperature of the gas around the particle was invariable and was equal to the ambient temperature.



Fig. 2. Observed profile of the LII signal.

The source of radiation was a pulsed Nd:YAG laser (Quanta Ray DCR11) generating  $\lambda = 1064$  nm light with a pulse duration of about 10 ns. The profile of the laser beam was a disc 1 mm in diameter, and the energy density in a pulse was set below 0.4 W/m<sup>2</sup> to avoid particle evaporation [10]. The time profiles of incandescence were recorded using a system consisting of a photomultiplier (Hamamatsu R7400 U-4), a narrow-bandpass filter with a transmission peak at 694 nm placed before the photomultiplier, and a digital oscillo-scope (LeCroy LT 342) with a frequency bandwidth of 500 MHz. The time-resolving power of this system was 2 ns or better.

The absorbance of the gas medium containing a condensed phase was measured using the laser extinction method [1, 4]. The source of radiation was a continuous-wave He–Ne laser. The laser beam was passed through the cell, and the transmitted beam intensity was recorded using a system consisting of an active photodiode (E2VUV, Spindler & Hoyer) with a time-resolving power of 1  $\mu$ s or better, a narrow-bandpass filter with a transmission peak at 633 nm, and a digital oscilloscope (LeCroy 9314 AM) with a frequency bandwidth of 400 MHz. A typical extinction profile is presented in Fig. 3.

#### EXPERIMENTAL DATA

**Optical measurements.** In extinction measurements, we used the absorbance of the medium (D) determined as

$$D = -\ln(I/I_0), \tag{4}$$

where I is the beam intensity transmitted by the medium and  $I_0$  is the beam intensity in vacuo (Fig. 3). The time dependence of D for one experimental mode is plotted in Fig. 4 (curve I). Particle growth can



Fig. 3. Observed extinction profile.

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**Fig. 4.** Time variation of the absorbance of the carbon nanoparticles for the 10 mbar  $C_3O_2 + 1$  bar Ar mixture: (1) experimental data and (2) fitted curve.

roughly be described by the following relaxation equation:

$$\frac{\mathrm{d}D}{\mathrm{d}t} = k_{\mathrm{eff}}(D_{\mathrm{max}} - D(t)), \tag{5}$$

where  $k_{\text{eff}}$  is the effective particle growth rate and  $D_{\text{max}}$  is the maximum absorbance. The experimental absorbance data were fitted to the exponential function (Fig. 4, curve 2)

$$D = D_{\max}[1 - \exp(-k_{\text{eff}}t)].$$
(6)

In order to derive the nanoparticle size from the observed LII signal, it is necessary to know the physical properties of the nanoparticles, namely, thermal conductivity, density, and the radiation absorption coefficient, as well as thermal energy accommodation coefficient ( $\alpha$ ) data for collisions of the particles with molecules of various diluent gases. In this study, we used the same physical data for soot particles and the same accommodation coefficient ( $\alpha = 1$ ) as in previous studies of  $C_3O_2$  pyrolysis [11, 12], although it has recently been demonstrated that  $\alpha$  can differ significantly from 1, depending on the diluent gas [13, 14]. (The variation of  $\alpha$  will be discussed below.) Figure 5 shows the time profile of the size of the growing nanoparticles according to LII data (the points represent experimental data, and the solid curve is an exponential fit similar to the fit used in absorbance data processing (Eq. (6)). A simultaneous analysis of the absorbance and particle size (Figs. 4, 5) time profiles demonstrated that, under fixed conditions, both can be fitted to one exponential function (like that defined by Eq. (6)) with the same coefficient  $k_{\rm eff}$ . In other words, the absorbance of the condensed phase and the particle size increase at the same rate.

From the LII time profiles of the particle size obtained at different  $C_3O_2$  pressures or at different carbon vapor concentrations in the mixture, we derived  $k_{eff}$  as a function of the initial concentration of carbon atoms

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**Fig. 5.** Time variation of the carbon nanoparticle size for the 10 mbar  $C_3O_2 + 1$  bar Ar mixture. The points are experimental data, and the solid line is the fitted curve.

and pressure for argon-diluted mixtures (Figs. 6, 7). Approximation of the experimental data indicated that  $k_{\text{eff}}$  is a quadratic function of the initial concentration of carbon atoms ( $C_0$ ),

$$k_{\rm eff} = BC_0^2, \tag{7}$$

where  $B = 2 \times 10^{-28}$  cm<sup>6</sup>/s (Fig. 6), and that the particle growth rate increases progressively less rapidly (Fig. 7). Furthermore,  $k_{\text{eff}}$  is nearly pressure-independent starting at P = 200-300 mbar. The pressure dependence of  $k_{\text{eff}}$  (Fig. 7) can be fitted to the exponential equation

$$k_{\rm eff} = 0.018 \left( 1 - \exp\left(-\frac{P}{80}\right) \right), \tag{8}$$

where *P* is expressed in millibars.



**Fig. 6.** Growth rate of the carbon nanoparticles as a function of the initial concentration of carbon atoms in the  $C_3O_2$ -Ar mixture. P = 100 mbar. The points are experimental data, and the solid line is the fitted curve.



**Fig. 7.** Growth rate of the carbon nanoparticles as a function of the  $C_3O_2$ -Ar mixture pressure. P = 100 mbar. The points are experimental data, and the solid line is the fitted curve.

Electron microscopy. In some experiments of each series, we deposited nanoparticles onto a microscope grid placed on the bottom of the quartz cell. The particles were examined to determine their size distribution and structure. Figure 8 shows a micrograph of nanoparticles produced in one experiment. Clearly, the particles are near-spherical. From the micrographs of the nanoparticles obtained in all experiments, we derived the final particle size of the nanoparticles. The observed particle size distribution is close to the lognormal distribution with a geometric deviation from the mean of  $\delta = 1.2-1.4$  (Table 2).

**Table 2.** Average size of carbon particles (*d*) obtained under various conditions and the corresponding geometric deviations ( $\delta$ )

| Mixture composition                    | <i>d</i> , nm | δ   |
|--|---------------|-----|
| 10 mbar $C_3O_2$                       | 5.7           | 1.2 |
| 10 mbar $C_3O_2$ + 100 mbar Ar         | 5.5           | 1.2 |
| 10 mbar $C_3O_2$ + 100 mbar CO         | 5.5           | 1.2 |
| 10 mbar $C_3O_2$ + 100 mbar He         | 4.6           | 1.2 |
| 10 mbar $C_3O_2$ + 1 bar Ar            | 12            | 1.4 |
| $30 \text{ mbar } C_3O_2$              | 5.5           | 1.2 |
| 30 mbar $C_3O_2$ + 1 bar Ar            | 12            | 1.4 |
| 100 mbar C <sub>3</sub> O <sub>2</sub> | 9             | 1.3 |
| 100 mbar $C_3O_2$ + 1 bar Ar           | 11            | 1.4 |
| 10 mbar $C_3O_2$ + 300 mbar Ar         | 5.7           | 1.2 |
| 10 mbar $C_3O_2$ + 1 bar He            | 5.5           | 1.2 |
| 40 mbar $C_3O_2$ + 400 mbar Kr         | 5.5           | 1.2 |
|  |               |     |



**Fig. 8.** Micrograph of the carbon nanoparticles obtained by photolysis in the 30 mbar  $C_3O_2 + 1$  bar He mixture (×100000).

## DISCUSSION

Analyzing the particle size data, we found that the particle sizes determined by LII under the assumption that  $\alpha = 1$  far exceed the electron microscopic particle sizes (Table 2). The unlikely assumption that, late in the process, the particles change their structure so that their effective size decreases severalfold was disproved by LII measurements at long particle formation times (up to 0.1 s), which demonstrated that the particle size was almost invariable. An analysis of the dependence of the LII particle size data on the properties of the particles demonstrated that the LII and electron microscopic data cannot be reconciled by varying the thermal conductivity, density, or the radiation absorption coefficient of the particle within any reasonable range. Therefore, the only plausible cause of this discrepancy is that the accommodation coefficient  $\alpha$  is not equal to unity and depends on the diluent gas. By equating the LII particle sizes measured at a long nanoparticle formation time to the corresponding electron microscopic particle sizes, we arrived at the following accommodation coefficients: for Ar and CO,  $\alpha = 0.44$ ; for C<sub>3</sub>O<sub>2</sub>,  $\alpha = 0.51$ ; for He,  $\alpha = 0.1$ . These results are illustrated in Fig. 9, which shows how the true particle size changes with time in various diluent gases and presents the ultimate particle sizes measured by electron microscopy. The ultimate particle size is almost independent of the initial concentration of carbon vapor (note, however, that the initial concentration was varied only in a rather narrow range of  $1.15 \times 10^{16}$  to  $3.4 \times 10^{16}$  cm<sup>-3</sup>), but it depends on pressure in a way depending on the diluent gas.

This result allows some important assumptions to be made as to the role of the diluent gas in the formation of carbon nanoparticles. We will proceed from the concept that the carbon vapor condensation process consists of two steps, namely, the formation of nucleation clusters and the surface growth of the nucleation clusters by the addition of separate atoms to their surfaces [7, 15]. (This is followed by the nanoparticle coagulation (agglomeration) stage, which proceeds on a much longer time scale and, therefore, can be ignored here; furthermore, the LII method allows one to determine only the size of a separate particle, not the size of an agglomerate.)

In the framework of these concepts, it can be deduced that not only the particle growth rate at the late stages of the process (Fig. 7) but also the concentration of nucleation clusters depend on pressure and the nature of the diluent gas. Indeed, the surface growth of particles does not change the number density of these particles and comes to an end as the carbon atoms are consumed. Therefore, the higher the concentration of nucleation clusters, the smaller the ultimate size of the particles. This assumption seems quite plausible considering the significant role of deactivating collisions in the recombination and coagulation of small carbon clusters consisting of  $n < n_{cr}$  atoms, where  $n_{cr}$  is the number of atoms in a nucleation cluster. The kinetics of these processes is beyond the scope of this study. Here, we will attempt only to develop the numerical model describing the evolution of the size and number density of the clusters as a function of the carbon atom concentration in the gas phase and the nature and pressure of the diluent gas.

#### Numerical Simulation

Let us construct a simple model to qualitatively describe the experimental data that refer to the late stages of the growth of the particles that are detectable by LII (i.e., particles with d > 1 nm). Consider the condensation of homogeneous, highly supersaturated atomic vapor diluted with a nonreactive gas at various pressures. Suppose that some concentration  $C_0$  of carbon atoms (spheres of diameter d and volume  $V = \pi d^3/6$ , whose temperature is T and thermal velocity is  $u_c$ ) has formed instantaneously in some volume containing a diluent gas, whose concentration is  $C_g$ . Assume that nucleation clusters containing  $n_{cr}$  atoms form rather rapidly in the atomic vapor, resulting in the cluster number density  $N_p$ .

The last assumption was analyzed by numerical calculations for the early stages of carbon vapor condensation. The kinetic scheme for the recombination and coagulation of small carbon clusters containing up to 30 atoms was taken from an earlier publication [7]. The thermodynamic properties of the small clusters were

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**Fig. 9.** Comparison between LII and electron microscopic particle size data for nanoparticles obtained from (a) pure  $C_3O_2$  and (b, c)  $C_3O_2$  diluted with (b) Ar and (c) He. (a): (*1*–3) LII and (4–6) electron microscopic data for samples obtained at  $C_2O_3$  pressures of (2, 5) 10, (1, 4) 30, and (3, 6) 100 mbar. (b): (1, 2) LII and (3, 4) electron microscopic data for samples 1, 2 obtained from the (1, 3) 10 mbar  $C_3O_2 + 1$  bar Ar and (2, 4) 30 mbar  $C_3O_2 + 1$  bar Ar mixtures. (c): (1, 2) LII and (3, 4) electron microscopic data for samples 1, 2 obtained from the (1, 3) 10 mbar  $C_3O_2 + 1$  bar He and (2, 4) 10 mbar  $C_3O_2 + 100$  bar He mixtures.

estimated by extrapolating available data, as was done by Krestinin et al. [15]. The calculations were carried out using the program package Chemkin II. The calculated data indicated that carbon molecules containing up to six atoms appear as early as 0.2  $\mu$ s after the appearance of carbon vapor in the gas phase consisting of an inert gas (1 bar) and a C<sub>3</sub>O<sub>2</sub> admixture.

Since the equilibrium state of carbon under the given conditions is a condensed phase, we will assume that a recombination event (or the surface growth of a particle) takes place each time a carbon atom collides against a nucleation cluster (or, at later stages, against a particle) and that the collision cross section is equal to the particle surface area S. The frequency of collisions between a carbon atom and a particle ( $Z_c$ ) will be expressed as

$$Z_{\rm c} = u_{\rm c} SC, \tag{9}$$

where *C* is the current concentration of carbon atoms. However, it will be assumed that the complex resulting from a collision between an atom and a particle is unstable and will break down after some time  $\tau$  unless a stabilizing collision between this complex and a molecule of the surrounding gas (which consists largely of a buffer gas) takes place within this period of time. The characteristic lifetime of the unstable complex,  $\tau$ , may be of the same order of magnitude as the characteristic time of the vibrations of the atom–particle bond. The particle–gas molecule collision frequency  $Z_g$  is expressed as

$$Z_{\rm g} = u_{\rm g} S C_{\rm g},\tag{10}$$

where  $u_g$  is the thermal velocity of the buffer gas molecules. The probability of a cluster colliding with a diluent gas molecule (X) within the time  $\tau$  will then be equal to

$$X = (1 - \exp(-Z_g\tau)), \tag{11}$$

and the kinetic equation for the increasing number of atoms in the particle (n) will appear as

$$\frac{\mathrm{d}n}{\mathrm{d}t} = XZ_{\rm c} = u_{\rm c}SC[1 - \exp(-u_{\rm g}SC_{\rm g}\tau)]. \tag{12}$$

The current carbon atom concentration balance is written as

$$C = C_0 - N_{\rm p} n, \tag{13}$$

and, under the assumption that the particles are spherical, n is related to the particle size as

$$n = \frac{\pi d^3}{6V}.$$
 (14)

Hence, we arrive at the following kinetic equation for the current particle diameter d at various initial concentrations of carbon vapor ( $C_0$ ) and diluent gas concentrations ( $C_g$ ):

$$\frac{\mathrm{d}d}{\mathrm{d}t} = 2u_{\mathrm{c}} \Big[ C_0 V - \frac{1}{6} N_{\mathrm{p}} \pi d^3(t) \Big]$$

$$\times [1 - \exp(-u_{\mathrm{g}} \pi d^2(t) C_{\mathrm{g}} \tau)].$$
(15)

In order to solve this equation, it is necessary to specify both initial conditions ( $C_0$  and  $C_g$ ) and the initial size of the nucleation cluster, which is defined as

$$d_0 = \frac{6n_{\rm cr}V^{1/3}}{\pi}.$$
 (16)

The value of  $d_0$  was varied over the  $n_{cr}$  range of 3 to 30, and these variations did not modify the calculated data to any significant extent.

Equation (15) contains two unknown parameters, namely, the number density of nucleation clusters ( $N_p$ ) and the lifetime of the atom–particle complex ( $\tau$ ). The latter can be estimated from the experimental pressure dependence of the particle growth rate (Eq. (8)). Since all experiments were conducted at room temperature, Eq. (8) can be represented in terms of the diluent gas concentration:

$$k_{\rm eff} = 0.018 \left( 1 - \exp\left(-\frac{C_{\rm g}}{2.16 \times 10^{18}}\right) \right).$$
 (17)

With this representation, the exponential term in empirical equation (17) is very similar to Eq. (11). Therefore, the lifetime of the particles can be estimated from the condition

$$Z_{\rm g}\tau = u_{\rm g}\pi d^2(t)C_{\rm g}\tau = C_{\rm g}/2.16\times 10^{18}.$$
 (18)

For particle sizes between 1 and 10 nm, the lifetime is estimated at  $\tau \approx 5 \times 10^{-10}-5 \times 10^{-12}$  s. These values somewhat exceed the characteristic times of molecular vibrations. However, since the probability of energyexchange collisions is finite, this result seems quite plausible. Note that the real probability of an active atom-particle complex breaking down must decrease as the size (number of degrees of freedom) of this complex increases. However, for the particle sizes considered (n > 1000), this trend is weak. At the same time, the low probability of energy-exchange collisions seems to reflect the difference between the real mechanism of the deactivating collisions and the mechanism of strong collisions.

For this reason, in further calculations, we used the mean value of  $\tau \approx 5 \times 10^{-11}$  s, the initial size of a nucleation cluster was taken to be  $n_{\rm cr} = 6$ , and the only variable parameter was the number density of nucleation clusters  $(N_{\rm p})$ .

The time profile calculations using this equation were carried out by the Runge–Kutta method employing the Maple 9.5 program.

Figure 10 presents calculated and experimental data for the growth of carbon nanoparticles at a constant pressure (b) and at a constant concentration of carbon

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atoms (a) and compares the data obtained for two diluent gases, namely, argon and helium (c).

The calculated data indicate that the model adequately describes both the particle growth time and the ultimate particle size data at  $N_p = 10^{10}-10^{11}$  cm<sup>-3</sup>. For the mixtures diluted with argon at P = 1 bar, the best fit between the experimental and calculated data is observed for  $N_p = 10^{10}$  cm<sup>-3</sup>. For a lower argon or C<sub>3</sub>O<sub>2</sub> pressure,  $N_p = 10^{11}$  cm<sup>-3</sup>; for helium-diluted mixtures,  $N_p = 3 \times 10^{11}$  cm<sup>-3</sup>. Thus, according to our calculated data, the number of nucleation clusters decreases with increasing pressure for a given buffer gas and is 30 times larger in helium than in argon under the same conditions. Qualitatively, this result is in good agreement with the fact that the efficiency of the energyexchange collisions between small clusters and the surrounding gas molecules (which are necessary for nucleation) decreases with decreasing pressure or on passing from argon to helium, a lighter diluent. A quantitative analysis of this result should be made using a kinetic model of the growth and coagulation of small carbon clusters and is beyond the scope of this study.

## Number Density of Particles

Proceeding from the results of the above simulation, it is pertinent to attempt an analysis of the experimental  $N_p$  data. Using the results of the simultaneous measurements of the particle size and absorbance, it is possible to relate the number density of particles in a given volume to the particle formation time. The expression for  $N_p$  can be written as follows [16]:

$$N_{\rm p} = \frac{6f_{\rm v}}{\pi d^3},\tag{19}$$

$$f_{\rm v} = \frac{D}{H}.$$
 (20)

Here,  $f_v$  is the volume fraction of the particles, *D* is the observed absorbance, *d* is the particle diameter, and *H* is a function characterizing the optical properties of the particles [16]:

$$H = \frac{6\pi \operatorname{Im}[(m^2 - 1)/(m^2 + 2)]}{\lambda},$$
 (21)

where  $\lambda$  is the wavelength of absorbed light and m = k - iz is the refractive index, for which

$$\operatorname{Im}[(m^{2}-1)/(m^{2}+2)] = \frac{6zk}{(k^{2}-z^{2}+2)^{2}+4z^{2}k^{2}}.$$
 (22)

As is clear from these relationships,  $N_p$  is proportional to the function that accounts for the optical properties of the nanoparticles and is inversely proportional to the cubed particle size. The calculations were performed for two different refractive indexes. In the first case, the refractive index of soot particles was taken to be  $m_1 =$ 1.57 - i0.56, the value used in the LII determination of

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**Fig. 10.** Effects of (a) pressure, (b) the  $C_3O_2$  concentration, and (c) the nature of the diluent gas on the growth of carbon nanoparticles. (a): (1) 10 mbar  $C_3O_2$ , (2) 10 mbar  $C_3O_2$  + 100 mbar Ar, and (3) 10 mbar  $C_3O_2$  + 1 bar Ar. (b): (1) 10 mbar  $C_3O_2$  + 1 bar Ar and (2) 30 mbar  $C_3O_2$  + 1 bar Ar. (c): (1) 10 mbar  $C_3O_2$  + 1 bar He and (2) 10 mbar  $C_3O_2$  + 1 ≤ bar Ar.

particle sizes. In the second case, we used the refractive index suggested for carbon particles smaller than 1 nm that are transparent to visible light:  $m_2 = 1.4 - i0.08$  [17]. Figure 11 illustrates the time dependence of the number densities thus calculated ( $N_{p1}$  and  $N_{p2}$ ) for one



**Fig. 11.** Comparison between the experimental and the calculated nanoparticle number densities as a function of the particle formation time for different optical properties assigned to the nanoparticles: (*I*, 2) experimental data processed using the refractive index of (*I*) soot particles ( $m_1 = 1.56 - i0.57$ ) and (2) ultrafine carbon particles ( $m_2 = 1.4 - i0.08$ ) [17] and (3) numerical simulation data. The starting mixture is 10 mbar C<sub>3</sub>O<sub>2</sub> + 1 bar Ar.

set of experimental conditions (curves 1, 2). Figure 11 also shows the  $N_p$  value that is used in the model as the initial concentration of nucleation clusters (line 3).

The initial portion of the experimental number density curve indicates that  $N_p$  (determined under the assumption that the refractive index is constant) falls from its maximum to its steady-state value within  $\sim$ 150 µs, while the theoretical number density is set to be equal. This difference is due to the fact that the particles radically change their optical properties as they grow from a few atoms to their ultimate size. The ultimate  $N_{\rm p}$  value determined using the optical properties of soot (Fig. 11, curve 1) is closer to the model value, and the  $N_{\rm p}$  curve calculated using the optical properties of ultrafine particles [17] (Fig. 11, curve 2) intersects the model  $\hat{N}_{\rm p}$  line at ~15 µs. Similar results were obtained for the other experimental conditions. These results seem to be significant for independent, laser extinction-based analysis of the growth kinetics of the particles and of the evolution of their optical properties.

#### CONCLUSIONS

The experimental data obtained in this study and the numerical model developed to describe these data suggest the following inferences:

(1) A new technique is developed for obtaining nanoparticles by the UV photolysis of volatile carboncontaining compounds. This technique can produce carbon nanoparticles in the gas phase at room temperature. (2) The ultimate yield of nanoparticles depends on the energy spent on the photodissociation of the starting molecules. The highest yield of nanoparticles is observed at an energy density of about 1 J/cm<sup>2</sup>.

(3) The current size of growing nanoparticles was measured by the laser-induced incandescence method in wide ranges of total pressures and  $C_3O_2$  concentrations and for a variety of diluent gases. The growth time of the carbon nanoparticles does not exceed 1 ms and depends strongly on the total gas pressure at P = 10-1000 mbar.

(4) The ultimate size of the nanoparticles was measured using an electron microscope. The average size of the particles resulting from the photolysis of carbon suboxide is 4–12 nm. The translational energy accommodation coefficients for the Ar, He, CO, and  $C_3O_2$ molecules colliding against a carbon particle were determined by comparing the particle sizes measured by LII and electron microscopy.

(5) The growth rate of the nanoparticles resulting from photolysis was determined. The growth rate is proportional to the squared initial concentration of carbon atoms and grows at a decreasing rate as the total gas pressure in the system is raised to 300 mbar. As the total pressure is further increased, the particle growth rate remains invariable.

(6) A simple model has been suggested to describe the condensation of carbon nanoparticles from supersaturated atomic vapor. According to this model, the main process in nanoparticle condensation from supersaturated vapor is surface growth through the addition of separate atoms to the nucleation cluster. The concentration of nucleation clusters for various pressures and diluent gases was determined by comparing experimental and calculated data.

(7) The number density of particles estimated from the experimental particle size and absorbance data is in satisfactory agreement with the model calculations.

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