J. Phys. Chem. A **1997,** *101,* 3367−3370

Dimer and Trimer Formation in Dense Gaseous Argon: A MD Study

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Received: December 23, 1996[⊗]

Formation and dissociation rates of dimers and trimers in relatively dense ((0.61−1.21) × 10^{21} atoms/cm^3) argon at 100−140 K were studied by MD simulation. Rate constants and equilibrium constants were evaluated, and their magnitudes and behavior agreed with previous values and predictions where available. The effects of local densities on the kinetics are discussed.

Introduction

In recent years there has been much interest in nucleation theory: studying the detailed mechanism of gas condensation to a liquid. A number of workers,[1−3] most notably Bauer and his co-workers,[4−7] endeavored to replace classical nucleation theory by a kinetic model leading progressively from dimers to trimers to higher oligomers until, finally, clusters large enough to act as nuclei for condensation are formed.

Such models necessarily contain rate constants (or overall rate constants if passage through a collision complex is considered) for the formation and dissociation of dimers, trimers, etc. Such constants are not easy to come by experimentally. They may be calculated using either trajectory calculations or MD simulations. Trajectory calculations have indeed been published in the past. Such calculations, for the reaction $A + A_n \rightarrow A_{n+1}^*$, focus naturally on the metastable A_{n+1}^*, which requires another collision for stabilization.[8−10] Calculations considering the exchange reaction $Ar' + Ar_2 \rightarrow A + Ar'Ar$ (the prime denoting the originally monomer Ar) and $Ar' + Ar_2 \rightarrow Ar + Ar'Ar^*$ have also been published.[11,12] Trajectory calculations have the advantage of being able to deal in a straightforward way with larger clusters but are not geared to take into account numereous interactions of the collision partners with other particles such as would occur under high-density conditions. MD simulations, as used in this study, are particularly attractive, with oligomer formation and dissociation occurring in, as it were, their natural habitat: a system in which oligomers of various sizes exist at the same time. The use of a MD simulation obviously limits the study to systems sufficiently dense that the mean free path is significantly shorter than the box length and the time between collisions is sufficiently short. It also becomes possible, in such a simulation, to check whether the various oligomer formation and dissociation reactions do have the orders predicted by theory.

For our first model system we chose the simplest, that of a rare gas.

Computational Section

The simulation was a classical MD simulation using 256 particles and a 2.5 × 10^{-15} s time step. Two box lengths were used, 59.92 × 10^{-8} and 75.49 × 10^{-8} cm, the ratio of the volumes of the boxes being 2. The particles were assumed to interact via a 12−6 Lennard-Jones (LJ) potential with parameters chosen to roughly simulate argon: $\epsilon/k_B = 120$ K and $\sigma = 3.42 \times 10^{-8}$ cm.[13] The cutoff separation was 3σ, and the potential was shifted to equal zero at this value of the separation. The molar mass of the particles was 40. Each simulation started with the particles occupying sites on a fcc lattice. With a spacing of 7.49 × 10^{-8} cm (or, for the larger box, 9.44 × 10^{-8} cm) this means we always start from the monomeric, albeit artifically ordered, gas. Fifty thousand steps were allowed for equilibration. Simulations were usually run for 600 000 steps, amounting to 1500 ps. With 256 particles the overall number density was 1.19 × 10^{21} particles/cm^3 for the smaller box and 0.595 × 10^{21} particles/cm for the larger one.

The mean free path for our LJ gas is 15 × 10^{-8} cm at the high density and twice that at the lower density so that the ratio of box length to free path is 4 at the high density and 2.5 at the low density.

Temperatures were constant to ±2−3 K and pressures to ±10−15%.

We consider a bond to have formed between two atoms whenever the sum of their interaction potential and the kinetic energy of the motion about their center of mass is less than zero. The number density of such bonds we denote n_b, which would equal the density of dimers n_d in the absence of trimers and higher oligomers. Similarly we define the number density of trimers n_t as the number density of bonds between atoms at least one of which is already bound to another atom. Clearly our definition of n_t corresponds to the true number density of trimers only in the absence of tetramers and higher oligomers. We note here that the trimers we find are almost always of the type Ar−Ar−Ar (linear), the concentration of cyclic trimers being negligibly small.

With these definitions and in the absence of tetramers the true number density of monomers n_m is

$$n_m = n_{total} - 2n_b + n_t \qquad (1)$$

where $n_{total} = 256/V$, V being the central simulation box volume. (The addition of n_t is necessary because a (linear) trimer has two bonds but only three atoms.) Similarly

$$n_d = n_b - 2n_t \qquad (2)$$

In addition to the densities of dimers and trimers we calculated r_b, which is the rate of formation or dissociation of bonds (as a check, we actually ascertained that the two equal one another). In the absence of trimers and higher oligomers, r_b would equal r_d, the rate of formation—or dissociation—of dimers, via the reaction

$$Ar + Ar \rightarrow Ar_2 \qquad (3)$$

Similarly r_t is the rate of formation or dissociation of trimers (in the absence of tetramers and higher oligomers) through the

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S1089-5639(97)00057-1 CCC: $14.00

TABLE 1: Temperatures, Pressures, Number Densities of Bonds, Trimers, Monomers, and Dimers, and Rates of Formation and Dissociation of Bonds, Trimers and Dimers

run no.[a]	T (K)	P (atm)	S (super saturation)	$n_b \times 10^{-19}$ (bonds/cm^3)	$n_t \times 10^{-19}$ (trimers/cm^3)	$n_m \times 10^{-19}$ (monomers/cm^3)	$n_d \times 10^{-19}$ (dimers/cm^3)	$r_b \times 10^{-32}$ (bonds/(cm^{3}s))	$r_t \times 10^{-32}$ (trimers/(cm^3 s))	$r_d \times 10^{-32}$ (dimer/(cm^3 s))
1	101	11.6	3.3	28.8	5.5	66.9	17.8	3.4	0.49	2.9
2	110	13.8	2.1	22.2	2.8	77.4	16.6	2.3	0.27	2.0
3	120	15.8	1.3	18.6	1.8	83.5	15.0	1.9	0.19	1.7
4	129	17.5		16.1	1.3	88.1	13.4	1.6	0.15	1.5
5	141	20.1		13.3	0.84	93.3	11.6	1.3	0.10	1.2
6	101	7.2	2.1	6.3	0.40	47.2	5.6	0.38	0.037	0.34
7	110	8.1	1.2	5.3	0.23	49.1	4.9	0.30	0.026	0.28
8	120	9.0		4.3	0.12	51.0	4.1	0.25	0.017	0.23
9	129	9.8		4.1	0.09	51.4	3.9	0.23	0.015	0.21
10	141	10.9		3.3	0.07	52.9	3.2	0.19	0.012	0.18

[a] Runs 1−5 are with the small simulation box, runs 6−10 with the large one.

TABLE 2: Ratio of Rates of Dimer Formation (and Dissociation) at High and Low Density Compared to Ratios of n_{total}^3 , of $n_m^2 n_{total}$, and of n_d n_{total} at High and Low Density

T (K)	ratio of rates	ratio of n_{total}^3	ratio of $n_m^2 n_{total}$	ratio of $n_d n_{total}$
101	8.6	8	4.0	6.4
110	7.3	8	5.0	6.8
120	7.4	8	5.4	7.3
129	6.9	8	5.9	6.8
141	6.7	8	6.2	7.2

reaction

$$Ar_2 + Ar \rightarrow Ar_3 \tag{4}$$

The rate of formation or dissociation of dimers, r_d, is then given by

$$r_d = r_b - r_t \tag{5}$$

Results and Discussion

The results of our simulation runs for pure argon are summarized in Table 1. Runs 1−5 were made with the smaller simulation box (box length = 59.92 Å) and runs 6−10 with the larger one (box length = 75.48 Å), which has twice the volume of the smaller box. Error estimates are for n_b about ±10%, for n_t about ±30%, for r_b about ±10%, and for r_t about ±30%. The results are more accurate at the lower temperatures, where concentrations and rates are higher, and less so at the higher temperatures. The supersaturation, S, was calculated as the ratio of the simulation pressure to the known vapor pressure of argon at the corresponding temperature.

As we shall see below, reactions 3 and 4 have short relaxation times so that equilibrium (or steady state) values for n_d and n_t are reached within a short time. Plateau values for large clusters, on the other hand, are reached much more slowly,[4−7] and actual condensation takes still longer. This explains the existence of the supersaturated systems, which within 1.5 ns have no time to condense. We did not notice, during the simulations, any systematic changes in the concentrations and rates we monitored (beyond the equilibration period).

Reaction 3 requires a third body to stabilize a dimer that is forming, and similarly a third body is required to dissociate a stable dimer. Should we however construe Ar to mean only Ar monomers or should we also consider Ar bound to other Ar atoms in dimers and trimers as possible reactant? Given the weakness of the Ar−Ar bond, this may well be the case.

To try to decide this question, we collected in Table 2 the ratios of the rates of formation of dimers in the two simulation boxes, at the various temperatures, along with the ratio of n_{total}^3, $n_m^2 n_{total}$ (and $n_d n_{total}$). It is clear that, although a trend with temperature seems to exist, the ratio of rates agrees with the ratio of n_{total}^3 within the stated uncertainties of the rates and definitely not with the ratio of $n_m^2 n_{total}$. This then means that kinetically free and bound Ar behave similarly. There is no such ambiguity regarding dimer dissociation, and indeed the ratio of $n_d n_{total}$ agrees well with the ratio of rates (except at the lowest temperature).

TABLE 3: Ratio of $P/(n_{total}$ - $n_b)$ and of P/n_{total} at High and Low Density

T (K)	ratio of $P/(n_{total}$ - $n_b)$	ratio of P/n_{total}
101	0.96	0.81
110	0.96	0.85
120	0.96	0.88
129	0.96	0.89
141	0.98	0.92

It is interesting that, as regards the pressure, a different conclusion might be reached. From eqs 1 and 2 the total density of the various species, $n_m + n_d + n_t$, is seen to be $n_{total} - n_b$. In Table 3 ratios of $P/(n_{total} - n_b)$ and ratios of P/n_{total}, at the various temperatures, are collected. It is seen that the former are much closer to the expected value of 1 than are the latter, which might indicate that as far as the presure is concerned it is $n_m + n_d + n_t$ that represents the relevant totality of particles and not n_{total}.

In Table 4 rate constants for the formation and dissociation of dimers and trimers and the corresponding equilibrium constants are presented. The rate constants are defined, in keeping with our conclusion that bound and free Ar behave kinetically in a similar fashion, as

$$k_{d,as} = r_d/n_{total}^3 \tag{6}$$

where $k_{d,as}$ is the rate constant for dimer formation and

$$k_{d,dis} = r_d/n_d n_{total} \tag{7}$$

where $k_{d,dis}$ is the rate constant for dimer dissociation. Similarly

$$k_{t,as} = r_t/n_d n_{total}^2 \tag{8}$$

and

$$k_{t,dis} = r_t/n_t n_{total} \tag{9}$$

where $k_{t,as}$ and $k_{t,dis}$ are the rate constants for trimer formation and dissociation respectively.

Equilibrium constants are given as

$$K_d = k_{d,as}/k_{d,dis} \tag{10}$$

and

TABLE 4: Temperatures, Rate Constants for Formation and Dissociation of Dimers and Trimers and Equilibrium Constants for Dimers and Trimers

run no.[a]	T (K)	$k_{d,as} \times 10^{32}$ (cm^6 molecule^{-2} s^{-1})	$k_{d,dis} \times 10^8$ (cm^3 molecule^{-1} s^{-1})	K_d x 10^{23} (cm^3 molecule^{-1})	$k_{t,as} \times 10^{32}$ (cm^6 molecule^{-2} s^{-1})	$k_{t,dis} \times 10^8$ (cm^3 molecule^{-1} s^{-1})	$K_t \times 10^{23}$ (cm^3 molecules^{-1})
1	101	17.3	0.14	12.5	19.6	0.07	26
2	110	12.0	0.10	11.8	11.6	0.08	14
3	120	10.1	0.095	10.6	9.1	0.09	10
4	129	8.8	0.093	9.5	8.0	0.10	8
5	141	7.2	0.088	8.2	6.2	0.10	6
6	101	16.1	0.10	15.7	18.7	0.16	12
7	110	13.2	0.096	13.8	14.8	0.18	8
8	120	10.9	0.094	11.6	12.0	0.25	5
9	129	10.1	0.091	11.1	10.7	0.27	4
10	141	8.6	0.095	9.1	10.7	0.29	4

[a] Runs 1−5 are with the small simulation box, runs 6−10 with the large one.

$$K_t = k_{t,as}/k_{t,dis} \tag{11}$$

where K_d and K_t are equilibrium constants for dimer and trimer formation, respectively.

As is the case with rate constants for atomic recombinations $k_{d,as}$ is seen to decrease with increasing temperature. The temperature dependence corresponds to an "activation energy" of −2.1 kJ/mol. Extrapolation (as ln $k_{d,as}$ vs $1/T$) to 298 K—to the extent that it is permissible—yields a value of 3×10^{-32} cm^6 molecule^{-2} s^{-1}, in good agreement with rough estimates predicting $(1-2) \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}.[14] Somewhat surprisingly $k_{d,dis}$ also decreases slightly with increasing temperature, although this seems to level off. The equilibrium constant K_d decreases, with increasing temperature, as expected. From the slope of ln K_d vs $1/T$ one obtains a binding energy for the dimer of 1.4 ± 0.2 kJ/mol, in good agreement with the 1 kJ/mol, corresponding to our ϵ_{LJ}.

The corresponding constants for the trimer behave as expected. $\mathrm{k}_{t\ as}$ decreases, like $k_{d,as}$, with increasing temperature and $k_{t,dis}$ increases. K_t decreases with increasing temperature. The point to note is that trimer rate constants (and, consequently, the equilibrium constant) do not differ much from the dimer constants. This is in keeping with the observation stated earlier that free and bound argon atoms behave similarly. It will be interesting and of importance for kinetic condensation models to know to what size of clusters this behavior continues.

It is also of relevance, in this connection, to note that, as stated in the Computational Section, we rarely see cyclic trimers. The short lifetime of trimers, about 1 ps, may well explain the rarity of cyclic trimers in terms of a linear trimer not having sufficient time to maneuver itself into the necessary position and get rid of the extra energy through another collision. Of course, the rarity of cyclic trimers may also be explained thermodynamically as an entropic effect.

The first-order rate constant for dimer dissociation, $k_{d,dis}n_{total}$, is on the order of 10^{12} s^{-1}, which corresponds to a lifetime of 1 ps. This compares reasonably (though see below) with a time between collisions for a dimer of about 2 ps. The relaxation times for the attainment of dimer and trimer equilibria, as obtained from the rate constants in Table 4, are both on the order of 1 ps so that we are assured that equilibria (or at least steady states) are indeed achieved during the time allotted for equilibration.

The picture obtained regarding the formation and dissociation of dimers and trimers is thus self-consistent and in good agreement with previous findings and predictions. It is however of interest to wonder about why it is that the lifetime of dimers is, at the high density, 1 ps, whereas the time between collisions for a dimer is on the order of 2 ps. To answer this, we consider that density fluctuations do of course exist and for sufficiently small regions of space could become considerable. Now during its lifetime a dimer will travel, on the average, ∼1.6 Å (at 100 K), so that we are indeed concerned with rather small regions of space.

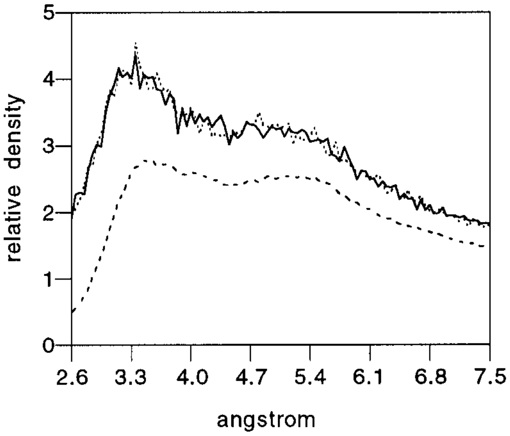

Figure 1. Radial distribution function of Ar atoms around a general dimer (---), a dimer that has just dissociated (—), and a dimer that has just formed (···). All functions for 101 K and the high density (1.19×10^{21} atoms cm^{-3}).

To have some picture of the magnitudes of the fluctuations, we have divided the central simulation box into 512 equal rectangular cells (cell length 7.49 Å) and found that at 111 K (and at the high density) on average 13.5% of the particles are, at any given moment, in cells where the density is 6 times the average and above. At 97 K this increased to 17.5%.

Dimers are naturally formed preferentially in the denser regions of space, where they also dissociate very quickly, upon collisions with their neighbors. Although the time needed for the averaging out and disappearance of such denser regions has not been measured in the present study, it stands to reason that it is considerably longer than the lifetime of dimers.

Convicing evidence for the correctness of these notions is provided by Figure 1 in which the radial distribution function of Ar atoms around the center of mass of a general dimer is compared with the distribution functions around a dimer that has just dissociated and a dimer that has just formed.[15] It is seen that the two latter distribution functions, which are practically identical, are always larger than the former, particularly at the small separation important for kinetic interaction, and approach one another (and the value of 1) at larger separations. Figure 1 is for 101 K (and the high density), but qualitatively similar results are obtained at the higher temperatures.

This would then explain the difference between the lifetime of a dimer and the time between collisions. It may also explain the decrease of $k_{d,dis}$ with temperature as due to a more uniform distribution of particles at the higher temperatures and, therefore, a decrease in size and local density of the denser regions. Finally, the trend in the ratio of formation rates at the two densities noted in the discussion of Table 2 may also be connected to the local density effect since it becomes clear that, strictly, it is local, not average, concentrations one should use in the discussion of the results for such short-lived species. Since, however, the trend we are talking about, is, as noted previously, within statistical uncertainty, further discussion of it does not seem warranted.

Conclusion

Rate constants and equilibrium constants for the formation and dissociation of Ar dimers and trimers have been obtained. It was found that for these reactions free and bound Ar atoms behave in a similar fashion. It was shown that for the discussion of the kinetics of very short-lived species consideration of local densities may be relevant.

Acknowledgment. The author thanks Dr. A. Litan of the Department of Chemistry at Ben Gurion University for critical reading of the manuscript and valuable comments.

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