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Molecular Dynamics Study of C-C Bond Dissociation in Linear Alkanes and Polyethylene: Effects of Condensed Phase

Konstantin V. Popov and Vadim D. Knyazev

*Research Center for Chemical Kinetics, Department of Chemistry,
The Catholic University of America, Washington, D. C. 20064, USA*

Molecular dynamics modeling of C-C bond dissociation is performed for linear alkanes - polyethylene macromolecules under the conditions of isolated molecules in the gas phase and those of condensed phase hydrocarbon melt. The rate constants are obtained as functions of temperature and density. The results of simulations demonstrate significant effects of density on the rates of C-C bond scission. Per-bond rate constant values decrease with the increasing density, by up to an order of magnitude. These effects are consistent with an earlier proposed hypothesis of the effects of torsional motions in linear hydrocarbon chains on the rates of chain scission.

1. Introduction

Detailed modeling of chemical kinetics as a tool of prediction and control of complex chemical processes has achieved great success in the chemistry of many types of gas phase processes (e.g., combustion, atmospheric modeling) and is currently being used for understanding and control of pyrolysis of polymers (see below). One critical requirement for the success of such modeling is availability of reliable database of rate coefficients of elementary reactions involved in a particular type of chemical processes being modeled. However, existing database of gas-phase reaction rate coefficients primarily includes reactions involving relatively small molecules. Similarly, existing computational methods of predicting reaction rates have been developed and validated using experimental data for small-molecule reactions as experimental data for gas phase elementary reactions of large species are, generally, unavailable. As a result, modeling efforts directed at elucidation of such complex phenomena as combustion of real fuels (relatively large long-chained, branched, and cyclic hydrocarbon molecules) and pyrolysis of polymers are hindered by the lack of data on the rates of important elementary reactions. Nevertheless, modeling efforts continue, largely motivated by the need to develop computational tools of prediction and control, for both large hydrocarbon combustion (e.g., [1-4]) and for pyrolysis of polymers (e.g., [5-14] and references cited therein).

In the vast majority of the existing models of polymer pyrolysis, most of the rate coefficients used are derived from the corresponding gas phase values of chemically similar but smaller species. One of the most important reaction types in polymer pyrolysis is the backbone scission, i.e., dissociation of C-C bonds forming the polymer chain. These reactions are generally believed to be responsible for initiation of polymer pyrolysis. In evaluating the rate constants for polymer C-C bond dissociation, an approach based on analogy with gas phase small molecule chemistry (decomposition of small alkanes) leads to preexponential factors of approximately $10^{16} - 10^{17} \text{ s}^{-1}$

and activation energy values close to the C-C bond strength, $\sim 348 \text{ kJ mol}^{-1}$. The deficiency of this approach becomes apparent when one compares the calculated temperature dependence of the rate constant with known experimental data on polymer pyrolysis. For example, the above Arrhenius parameters predict that the per-bond C-C bond scission rate constant, k_{CC} , will achieve the value of 1 s^{-1} at $T \cong 1070 - 1140 \text{ K}$ and that of $1 \times 10^{-3} \text{ s}^{-1}$ at $T \cong 910 - 960 \text{ K}$. At the same time the typical temperature range for the onset of polyethylene pyrolysis is $300 - 400^\circ\text{C}$ ($573 - 673 \text{ K}$), [8,15] where the above Arrhenius parameters would give $k_{\text{CC}} \cong 2 \times 10^{-16} - 1 \times 10^{-10} \text{ s}^{-1}$. Clearly, to explain the initiation of pyrolysis, rate constants of C-C bond scission need to have much larger values (also, see a discussion of rate constants in [8]).

In a recent reactive molecular dynamics study (RMD), Nyden et al. [16] observed surprisingly low values of activation energies for chain scission of three alkane-based polymers: polyethylene, polypropylene, and polyisobutylene. These simulations were conducted under the conditions of polymer melt; the reactive force field used included several types of elementary reactions, including C-C backbone scission. The activation energy values obtained from the temperature dependences of the observed rate constant values were in the $40 - 190 \text{ kJ mol}^{-1}$ range, which is much lower than the above typical value of the C-C bond strength. Furthermore, in a related RMD study of polyisobutylene (PIB) pyrolysis Stoliarov et al. [17] demonstrated that the activation energy of the C-C scission decreases with the increased size of the polymer model. These authors reported that the activation energy for C-C scission decreased from 239 kJ mol^{-1} in PIB-4 to 170 kJ mol^{-1} in PIB-150 (here and below, the number in polymer notation is that of the monomer units that form the polymer chain).

In an earlier work, we performed a systematic molecular dynamics study of the C-C bond scission in a series of linear alkanes and polyethylene macromolecules [18]. In this work, increasing chain length was shown to result in significant acceleration of the decomposition reaction, by up to an order of magnitude. This effect was tentatively attributed to centrifugal effects of torsional motions about the C-C bonds in the alkane chains. The absolute values of the per-bond rate constants, however, were not dramatically different from those expected for small molecules in the gas phase. These values, thus, are not in the range required to explain the phenomenon of low-temperature polymer pyrolysis.

In the current study, we expand our molecular dynamics investigation of alkane and polyethylene decomposition to include the effects of condensed phase. Simulations are performed for the conditions of hydrocarbon melt, as well as for isolated molecules in vacuum. Effects of density on the observed rate constants are studied.

2. Computational Methods

Molecular dynamics (MD) calculations were carried out for isolated single molecules as well as using periodic boundary conditions. Potential energy surfaces (PES) given by the all-atom OPLS-AA force field [19,20] with C-C stretch terms replaced by the Morse function were used. MD calculations were performed using GROMACS program package, version 3.2 [21,22]. Initial linear structures of molecules were obtained by potential energy minimization. The time integration step size of 1 fs was used in the simulations. Overall translational motion of the center of mass and rotation around the center of mass were removed in all calculations.

Each MD calculation was continued until one carbon-carbon bond dissociated; time required to achieve dissociation (t) was recorded. The value of t was averaged over ~ 40 trajectory runs to

obtain $\langle t \rangle$ and the value of the rate constant was obtained as the inverse of $\langle t \rangle$; per-bond rate constant k_{CC} was calculated by further dividing by the number of bonds in the chain. Separation of the two carbon atoms forming a bond by the distance of $R_0 = 0.45$ nm was used as the criterion of bond dissociation. For condensed phase simulations, the choice of the critical separation R_0 is not straightforward and selecting a different value would result in different rate constant values. Unlike the gas phase, where virtually no recrossing of trajectories was observed, simulations performed for the conditions of condensed phase were affected by the cage effect. Every broken C-C bond resulted in fragments of the molecule separating temporarily but then eventually recombining. To develop a meaningful criterion of bond dissociation, the dependences of the rate constants on the value of R_0 were studied. Typical results are illustrated in Figure 1 for the cases of single molecule in the gas phase (open circles) and for the same molecule in the liquid polymer melt (filled circles, calculations performed using periodic boundary conditions). Both plots display steep dependences of the rate constants on R_0 on the left sides of the plots, at $R_0 \leq 0.4$ nm. These data points have R_0 values located on the slope of the Morse potential and corresponding to incompletely dissociated C-C bonds. The behavior of the gas phase and the liquid phase plots at large R_0 values, however, shows significant differences. In the case of a single molecule in the gas phase, the rate constant value is virtually independent of R_0 at $R_0 \geq 0.5$ nm. In the condensed phase, the rate constant displays a monotonic negative dependence on R_0 even at large separations. While the steep k_{CC} vs R_0 dependences at low R_0 values are caused by incompletely dissociated bonds, the weak decrease in k_{CC} at large R_0 present only in the liquid phase case can be attributed to the cage effect that does not allow the bond fragments to separate and leads to eventual recombination. The selection of $R_0 = 0.45$ nm as the criterion of bond dissociation in both the gas and the liquid phase calculations was based on the analysis of such k_{CC} vs R_0 dependences obtained under various conditions and the resultant separation of the cage effect from that of incomplete bond dissociation.

Temperatures used in modeling ranged from 2300 to 3000 K; such high temperatures were necessary to make the MD reaction rates observable within the practicable range of times of molecular dynamics simulations.

3. Results and Discussion

The results of molecular dynamics simulations of the reaction of C-C bond dissociation in PE-500 (a polyethylene macromolecule consisting of 500 ethylene monomers) are presented in Figure 2. Calculations were performed for the conditions of the gas phase, liquid phase with the density of 0.75 g cm^{-3} (experimental density of polyethylene melt at 800 K), and liquid phase with the reduced density of 0.5 g cm^{-3} . As can be seen from the presented Arrhenius plots, the reaction of C-C bond dissociation in the condensed phase is noticeably slower than in the gas phase, with the differences of up to an order of magnitude. The condensed phase rate constants also demonstrate a strong dependence on the density, with much of the difference between the gas-phase rate constants and those obtained for the density of 0.75 g cm^{-3} recovered if simulations are performed for the reduced density of 0.5 g cm^{-3} .

Our earlier systematic molecular dynamics study of the C-C bond scission in a series of linear alkanes and polyethylene macromolecules [18] demonstrated that increasing chain length results in significant acceleration of the reaction, with increases of up to an order of magnitude in the values of the per-bond rate constant, k_{CC} . This effect was tentatively attributed to centrifugal

effects of torsional motions about the C-C bonds in the alkane chains. The differences between the gas phase and the condensed phase values of k_{CC} observed in the current study are similar to those found in [18] between the smallest molecule considered (C_2H_6) and long-chain alkanes; both are approximately a factor of 10. It can be proposed that the effect of reaction deceleration in the condensed phase is caused by the obstruction of the torsional degrees of freedom of alkane chains. Thus, reaction acceleration observed in the gas phase with the chain length increasing from PE-1 (C_2H_6) to PE-25 and longer chains (up to PE-1000) does not occur in the condensed phase of polymer melt. Additional simulations involving shorter alkane chains are currently being performed to evaluate the validity of this explanation.

It was noted earlier that molecular dynamics simulations performed for single molecules in the gas phase yielded per-bond rate constant values that are too low to explain the experimental phenomenon of low-temperature polymer pyrolysis [18]. Transition from the conditions of the gas phase to those of liquid polymer melt did not result in any acceleration of the C-C bond scission reaction. Rather, as can be seen from the plots in Figure 2, the reaction becomes slower. Activation energies obtained from the slopes of the Arrhenius plots of the $\ln(k_{CC})$ vs $1/T$ dependences (Figure 2) are similar to those obtained for gas phase conditions, which, in turn, are close to the C-C bond dissociation energy [18]. Thus, the results of the current study differ with those of [16] and [17], where activation energies of C-C bond scission were found to decrease with increasing alkane chain length.

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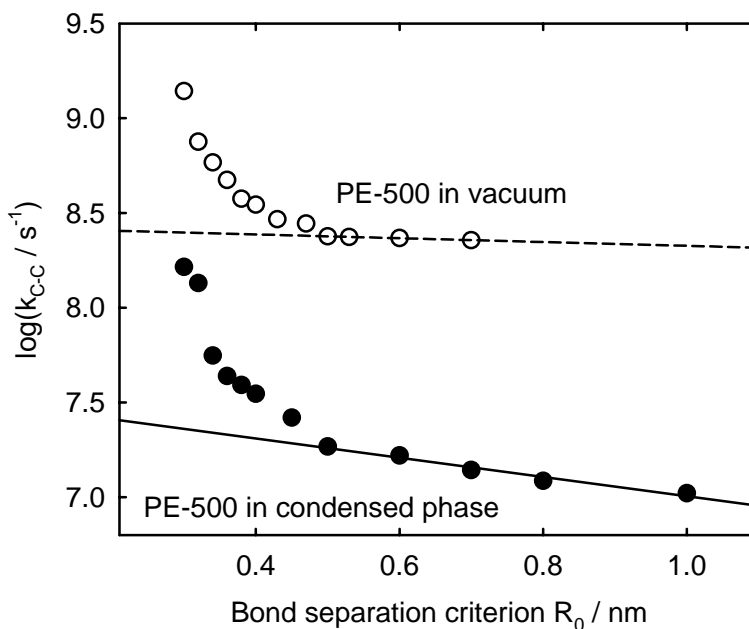


Figure 1: Dependences of the per-bond C-C dissociation rate constants on the values of the bond dissociation criterion R_0 obtained in molecular dynamics simulations of decomposition of PE-500 (polyethylene chain consisting of 500 ethylene monomers). Open circles, gas phase conditions; filled circles, condensed phase simulations.

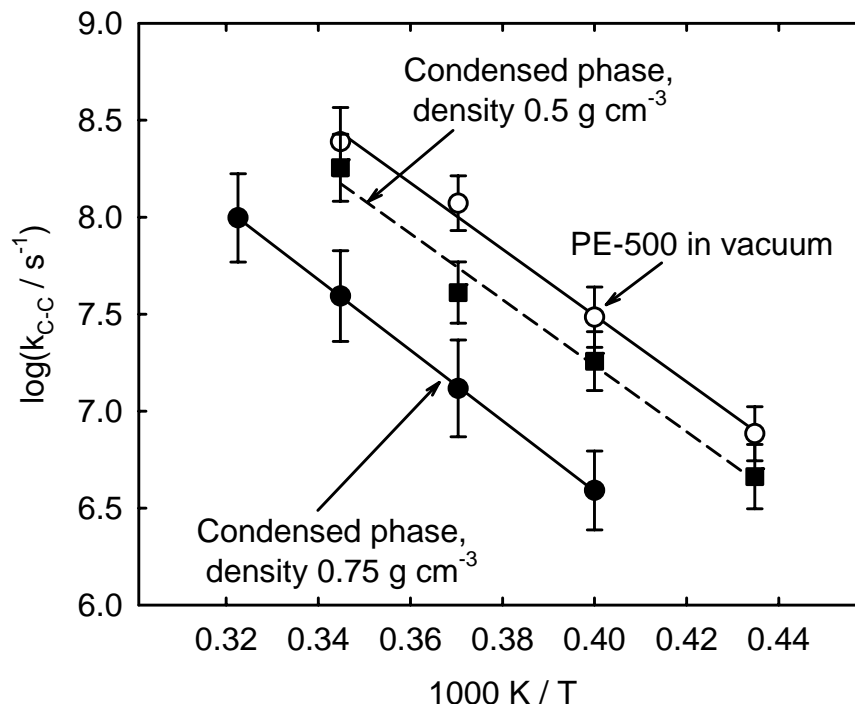


Figure 2: The Arrhenius plots of the dependences of the per-bond C-C dissociation rate constants on temperature obtained in molecular dynamics simulation of PE-500 decomposition. Open circles, gas phase conditions; filled circles, condensed phase with the density of 0.75 g cm^{-3} ; filled squares, condensed phase with the density of 0.5 g cm^{-3} .

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