Four-Center Reactions Induced by Cluster Impact

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Molecular dynamics simulations showing that high-barrier, four-center reactions can be readily induced by cluster impact[1] are reported, with special reference to the $N_2 + O_2$ reaction. In this proposed method, the reactants are placed within a cluster of, for example, rare gas atoms, and the cluster is accelerated toward a hard surface.[2,3] Upon impact, the atoms at the front of the cluster reverse the direction of their velocity while the rest of the cluster is still moving forward. High relative velocities can thereby be achieved for a short period of time (~200 fs). Beyond that time, the cluster fragments and the reaction products separate. We show that the duration of the impact-induced compression and the energies that are thereby available suffice to induce a bond-switching reaction, even for a barrier that is quite high. The $N_2 + O_2 \rightarrow 2NO$ reaction in a variety of rare gas clusters is used as an example. At realistic velocities of impact, the yield of this four-center reaction can be quite high, as the products are stabilized first by collisions with the surrounding rare gas atoms and shortly thereafter by the fragmentation of the cluster. Moreover, the solvation of the reactants by the atoms of the cluster plays a central role in promoting the reaction so that the identity of the rare gas has a marked effect on the yield.

The classical[4] molecular dynamics simulations determine not only the yield but also the entire time history of the reactive event. They serve to elucidate the mechanism whereby the cluster activates the reactants and reveal that the cluster also plays a role in stabilizing the products. It was previously shown[1b,c] that the short period during which the energy density is high suffices for a dissociation of a diatomic molecule embedded in the cluster. That process was determined to occur via a single impulsive collision[5] between a rare gas atom which

has been reflected from the surface and the molecule which is still moving in the initial direction. When the four-center reaction occurs within the cluster, there are at least three stages. The reactants need to be activated, and then a bimolecular reaction has to take place, and finally stabilization of the products takes place, while at the same time the constituents of the cluster diverge as the cluster fragments. It turns out that, despite the high velocities typical during cluster impact heating (e.g., 0.1 A/fs; 1 fs = 10^{-15} s), there is time not only for two but also for a third or even fourth intracluster collision and that these subsequent collisions have a marked effect on the net outcome.[6]

Four-center reactions[7,8] are expected to have a high barrier due to considerations of electronic orbital symmetry.[9] Beyond this, the $N_2 + O_2$ reaction is very endoergic (180 kJ/mol) and so provides a good probe for activation by cluster impact heating. The burning of nitrogen was first studied by Cavendish in 1780 and has since been extensively studied in electrical discharges[10] and in shock waves.[11] In the bulk and at lower energies, the reaction occurs primarily by the Zeldovich mechanism,[11] in which either the N_2 or the O_2 reactant first dissociates into atoms, and the atom of one kind reacts with the diatomic. The atom−diatom reaction also has a high activation energy. The rapid fragmentation of the cluster precludes a true Zeldovich-type mechanism. However, we find that there are collision events where there is an incipient dissociation of one diatomic during the approach of the other.

Figure 1 is a typical output for a single trajectory from the simulation.[4] Shown is the time history of the $N_2 + O_2 \rightarrow 2NO$ reaction in a 125-atom Ne cluster, at an initial velocity of 12 km/s.

The role of the cluster in inducing the reaction is conveniently discussed in terms of three stages in the time evolution: before, during, and after the bond switching, cf. Figure 1. In the gas phase,[7] the reaction cross section is not large because the reactants need to collide nearly "head on" (i.e., with a low impact parameter) in order to react. An important role of the cluster is to constrain the possible geometries of the reactants and thereby favor a fruitful collision. The conversion efficiency in the cluster can indeed be as high as 70% of all impacts. Not only the position but also the momentum of the reactants is strongly influenced by the cluster: a rare gas atom which has been reflected from the surface collides with the diatomic and thereby changes both its center of mass velocity and the relative

(1) Beuhler, R. J.; Friedman, L. *Chem. Rev.* **1986**, *86*, 521. Schek, I.; Raz, T.; Levine, R. D.; Jortner, J. *J. Chem. Phys.*, in press. Raz, T.; Schek, I.; Ben-Nun, M.; Even, U.; Jortner, J.; Levine, R. D. *J. Chem. Phys.*, in press.

(2) Christen, W.; Kompa, K.-L.; Schroder, H.; Stulpnagel, H. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 1197.

(3) Even, U.; Schek, I.; Jortner, J. *Chem. Phys. Lett.* **1993**, *202*, 303.

(4) The potential that is used to generate the dynamics is the sum of five parts: a four-atom London−Eyring−Polanyi functional form for the reactants, where standard spectroscopic constants are used for the three possible diatomics [Altar, W.; Eyring, H. *J. Chem. Phys.* **1936**, *4*, 661]; the long-range interaction of the two reactants; the interaction of the reactants with the rare gas atoms that make up the cluster; and the interaction of the cluster atoms among themselves (all three of which are taken as sums over Lennard-Jones (12,6) atom−atom potentials using combination rules for the reactant atoms−rare gas atoms potential parameters); and the interaction at the hard surface, approximated by the hard cube model [Grimmelman, E. K.; Tully, J. C.; Cardillo, M. J. *J. Chem. Phys.* **1980**, *72*, 1039]. This allows for energy dissipation at the surface and was found to account well for the dynamics of the cluster as compared to a full atomic model of the surface. In this exploratory study, we do not allow for electronic excitation, which is certainly possible at the high velocities in question, and we intend to return to this point in detail. The mitigating circumstances are that, at these velocities, the atoms move as hard spheres and hardly notice any attractive part of their potential. The molecular dynamics simulations are standard [Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Clarendon Press: Oxford, 1987]. A cold (30 K) cluster is generated by equilibrating the reactants embedded in the cluster. The long-range attraction keeps the reactants about 3 Å apart and at the center of the cluster. No tendency of the reactants to migrate to the surface of the cluster was discerned. The long-range forces do not significantly constrain the relative orientation of the reactants but do keep them a finite distance apart, a distance too small to allow a rare gas atom to be inserted between them. A large number of trajectories is run, corresponding to different initial orientations of the reactants within the cluster, initial configurations of the cluster atoms, etc.

(5) Ben-Nun, M.; Raz, T.; Levine, R. D. *Chem. Phys. Lett.* **1994**, *220*, 291.

(6) Cluster impact heating is also of interest in principle, because it shares with electronic optical excitation the characteristic that it is a method of activation on a time scale which is comparable or shorter than the times needed for intramolecular motions. Like short time optical excitation, cluster impact can provide rather high energies over very short times and hence deserves the label "femtochemistry" [Zewail, A. H.; Bernstein, R. B. *Chem. Eng. News* **1988**, *66*, 24]. It is a method for the, so far [Pimentel, G. C. *Opportunities in Chemistry*; National Academy Press: Washington, DC, 1987], not extensively explored study of chemistry under extreme conditions. It is therefore of interest that, during the cluster impact, it is not only bond breaking but also bond forming that can take place. What our simulations suggest is that the short (~100 fs) duration of the "big bang" during which the cluster is hot and compressed is not too short for real chemistry. In part, the reason is the high velocities at which the atoms are moving, velocities which have hitherto only been experimentally available using atoms produced in nuclear recoil [Wolfgang, R. *Annu. Rev. Phys. Chem.* **1965**, *16*, 15. Willard, J. E. *Ibid.* **1955**, *6*, 141]. These high velocities help in visualizing the dynamics[7] because the atoms move as hard spheres and the bond-switching event is very sudden-like, lasting far shorter than a vibrational period.
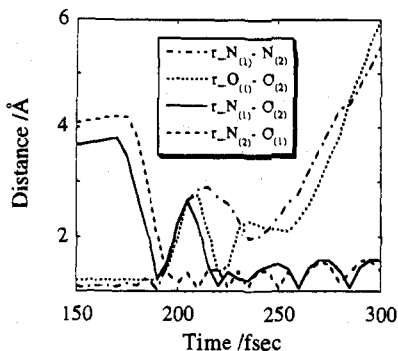
(7) Raz, T.; Levine, R. D. *Chem. Phys. Lett.* **1994**, *226*, 47.

(8) Bauer, S. H. *Annu. Rev. Phys. Chem.* **1979**, *30*, 271.

(9) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971.

(10) Riegel, E. R. *Industrial Chemistry*; Reinhold: New York, 1951.

(11) Gardiner, W. C., Jr., Ed. *Combustion Chemistry*; Springer-Verlag: New York, 1984.

Figure 1. Time history of the old and new bond distances, as identified in the inset, for the reaction $N_2 + O_2 \rightarrow 2NO$ in a 125 Ne atom cluster following impact. Activation by collision with cluster atoms which have been reflected from the surface occurs at $t \approx 175$ fs. The first collision of the two reactants, which lasts for <10 fs, is at $t \approx 190$ fs and results in both the old bonds being broken and the formation of one NO molecule. The other NO molecule is too energy rich and begins to immediately fall apart. (One can argue[7] that the kinematics of a four-center reaction favor the formation of internally excited products.) The unstable NO molecule is stabilized by a collision with a Ne atom at $t \approx 205$ fs. There is a third collision with a Ne atom at about 240 fs, after which the cluster begins to fall apart, thereby insuring the kinetic stability of the products. (It is, of course, impossible to achieve such rapid separation of the products under electric arc heating conditions.) The entire event took place in less than 100 fs.

velocity of the two atoms. The rather different efficiencies of the different rare gases in inducing reaction are due to their efficacy for momentum transfer. The second time point at which the cluster plays a key role is after the reactants have collided for the first time. Often, this first collision does not lead to reaction. The reactants separate but are caged by the cluster and return to collide again. Finally, after bond switching, the nascent NO molecules are produced internally quite hot. In the gas phase, many of them would immediately dissociate.[7] In the cluster, those hot NO molecules that undergo impulsive collisions with the cluster atoms can be stabilized by an efficient energy transfer. What was quite unexpected by us is that this rather complex sequence of events will take place in the very short, cf. Figure 1, time interval before the cluster fragments. The resulting divergence of the nascent products ensures their ultimate kinetic stability.
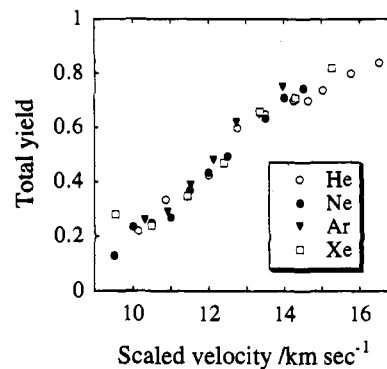
Figure 2. Yield of reaction (to form either stable or dissociated NO molecules) in impact heated clusters of 125 rare gas atoms vs the collision velocity for the Ne cluster. For the other rare gases (identified in the inset), the initial velocity has been scaled (down by 0.75 for He, up by 1.24 and 1.91 for Ar and Xe, respectively).

The high yield of NO in the cluster-induced reaction as opposed to the far lower yield in the electrical arc industrial process[10] is thus due not only to the unique means of activation but also to the two mechanisms of stabilization of the products: the instantaneous (within 10−30 fs) cooling by a collision and the fragmentation of the cluster within ~50 fs, whch insures the kinetic stability.

Clusters of different rare gases differ considerably in conversion efficiency as a function of impact velocity. A quantitative understanding of these differences is available and will be presented elsewhere. Suffice it here to say that, in terms of both the initial geometrical constraints and the efficacy for momentum transfer, a Xe cluster is most efficient. It is, however, possible to compensate for the mass effect by using a lighter rare gas at a higher velocity of impact. This is shown in Figure 2, where the yield, computed for 200 trajectories at each point, is plotted for four different rare gas clusters vs a common reduced energy scale.