

Development of a Pulsed Mixing Source for Bimolecular Reaction

Chan Ho Kwon

Department of Chemistry, Kangwon National University, Chuncheon, Kangwon 200-701, Korea

E-mail: chkwon@kangwon.ac.kr

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Photoinitiated reactions between molecules and reactive atoms that occur within supersonic expansion¹ elucidate the basic features of reaction steps going from reactants, through the transition state, to products. Thus, such reactions are the subject of many experimental and theoretical studies.²⁻⁴ Many of these studies concentrate on the hydrogen-abstraction reactions of hydrocarbons and halocarbons with the electronic ground state chlorine atom generated by photolysis to produce HCl and polyatomic radicals, which are very important in combustion and atmosphere.^{5,6} But these studies have suffered from the fact that most reagent gases in such reactions are reactive and hence can prereact in the mixture. Also, a cold expansion of the reagent gases is necessary before photoinitiation to successfully study their reaction dynamics. To be precise, 1) the reagents should be coexpanded to ensure that their relative translational energy is near zero in the region of interaction with the photolysis laser and 2) they must not react with one another before photoinitiation.

Robertson *et al.*⁷ have designed an ion source for the preparation of cold ion-molecule complexes by using the principle of supersonic entrainment, demonstrating the ion complexes formed in the expansion. However, we doubt whether this source can produce high enough concentrations of the entrained gas, especially at a distance from the orifice equal to several multiples of the nozzle diameter, which is where the photoinitiated reaction typically occurs. Orr-Ewing and coworkers⁸ have built dual pulsed nozzles whose front faces attach to Teflon tubes running in parallel and touching at their ends, allowing the merger of the expanding gases. They have studied some bimolecular reactions by utilizing the double expansion source attached to Teflon tubes. Subsequently, DeBoer *et al.*⁹ have constructed a dual pulsed valve source in a concentric arrangement for production of reactive clusters. In fact, the two designs mentioned above utilize a two pulsed valve system to produce the dense molecular species. This valve system features short opening times, which reduces the pumping load of the vacuum system, an essential requirement in a photoinitiated reaction. While, the relative translational temperature of the mixed species in expansion had to be cold enough to well-define the collision energy between the species. To generate a colder beam, Camden *et al.*¹⁰ have designed a late-mixing source to introduce the second gas upstream into the expansion orifice. In this arrangement, the faceplate of one

valve with an orifice 0.8 mm in diameter is connected to a capillary tube of 1.6 mm in outer diameter to the additional channel bored into the side of the custom machined faceplate of the other valve. They have demonstrated the usefulness of the source by examining the photoinitiation reaction of Cl + CH₃OH. However, installing two valves coupled to a capillary tube of 4 cm long might be difficult, considering the fact that the extraction region in the electrode assembly of a linear Wiley-McLaren time of flight (TOF) mass spectrometer is very narrow. In addition, it seems that a capillary tube between the two might interfere with the effective generation of a cold molecular beam. Accordingly, we will demonstrate a simpler and more efficient pulsed mixing source.

The pulsed mixing source we introduce here has the distinctive feature that all parts except only the faceplate are commercially available products. In addition, our custom machined faceplate was designed to be very compact and simple as well as compatible with the standard Series 9 valve assembly, which means the two valves can be directly combined with no capillary tube. This allows for easy assembly as shown in Figure 1. The source was attached to the translator for easy positioning just in front of the electrode assembly in our existing vacuum chamber. Then, the translator and the gas feedthrough for the pulsed valve 1 (PV1) were held on a flange placed along the flight axis and the gas feedthrough for pulsed valve 2 (PV2) and the electrical feedthroughs were mounted on the topside flange. The rest of the experimental apparatus and techniques were similar to those described previously.⁶ Our pulsed mixing source compared with the double expansion source, proving the D³⁷Cl products from the reaction of C₂D₆ + Cl (²P_{3/2}) under identical conditions. The reasons for this choice are, first, that this reaction yields products with cold rotational distribution¹¹ that is comparable with the rotational temperature by the instrumental and it is possible to observe the condition of the expansion. Second, the detection of DCI was chosen to avoid disturbances by HCl contamination of the valve PV2 due to the chlorine. Third, we expected to examine whether the reagents can be mixed efficiently through our source. After optimizing the expansion from PVs with the timing of the lasers and valves, the C₂D₆ (98%, Cambridge Isotope) of ~10% and the Cl₂ (99.997%, AGA-Linde) of 10% in He (99.999%, AGA-Linde) were expanded with the backing pressures of 650 Torr and 760 Torr

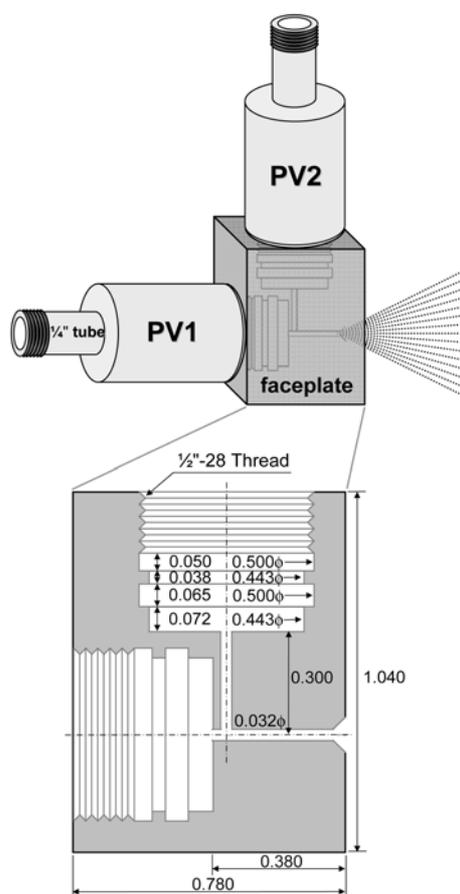


Figure 1. Schematic drawing of the pulsed mixing source. The faceplate of 1.040 in. \times 0.680 in. \times 0.780 in. is a custom machined.

through PV1 and PV2, controlled by separate drivers. The pressure in the vacuum chamber was held at 3×10^{-5} Torr and that in the TOF chamber at 2×10^{-6} Torr during the operation. Figure 2 shows 2+1 REMPI spectrum of a section of the R and S branches of the $F^1\Delta_2 - X^1\Sigma^+$ (0, 0) transition of nascent $D^{37}Cl$ products from the reaction of C_2D_6 with Cl ($^2P_{3/2}$) atoms generated by the photolysis of Cl_2 at 355 nm, using the mixing source. (The spectrum obtained with the double expansion source is not shown) By simulating the spectra implied by the rotational distribution of the $D^{37}Cl$ products,¹² the rotational temperatures were determined to 72 ± 5 K for our setup and 90 ± 5 K for the double expansion source, which means that colder expansion of the reagent gases can be obtained by the mixing source. Most of all, the remarkable thing is that the signal-to-noise of spectrum by the mixing source was 3–4 times larger than that of double expansion method, which indicates the efficient mixing.⁸ To examine any interruption by prereaction, the reaction of $CD_2Cl_2 + Cl$ was investigated. DCl by prereaction was virtually absent during operation of the source. These results

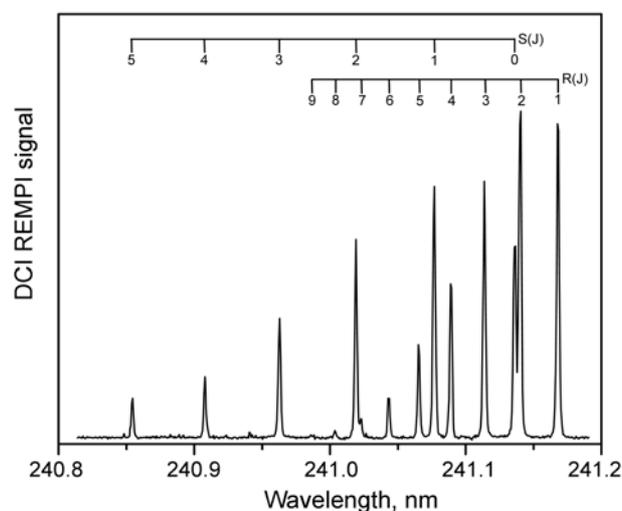


Figure 2. 2+1 REMPI spectrum of nascent $D^{37}Cl$ product from the reaction of $C_2D_6 + Cl$ ($^2P_{3/2}$) using the mixing source. The photolysis laser at 355 nm was fired alternatively for shot-to-shot subtraction of any signal from the contaminants by the Cl_2 .

demonstrate that the pulsed mixing source reported here is reliable for studying the bimolecular reaction between the reactive gases. This source will be applied to studies of various bimolecular reaction systems.

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