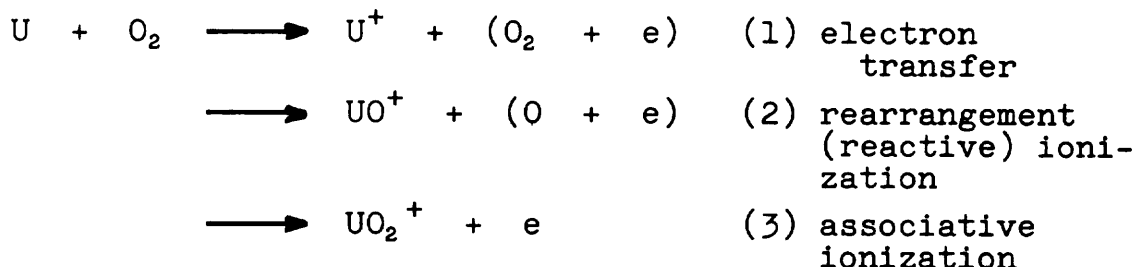


Chemi-Ionization Reactions in Accelerated Crossed-Molecular Beams

S. Wexler, C. E. Young, P. M. Dehmer and R. B. Cohen

Chemi-ionization reactions in more than 20 accelerated metal and non-metal atom collisions with O<sub>2</sub> molecules were studied by the crossed-molecular beam method. A detailed investigation was made of the processes in the uranium-oxygen system:



Relative cross sections for the various ionization channels were measured as a function of collision energy in the center of mass system from 0,2 to 60 eV. Throughout this range absolute cross sections were estimated to be below  $10^{-16}$  cm<sup>2</sup> for all channels. The cross section for associative ionization was observed to be nearly proportional to  $1/v$ ,  $v$  being the relative velocity of the U-O<sub>2</sub> collision. In the case of rearrangement ionization, the cross section rose rapidly at threshold (3,0 eV), corresponding to the UO<sup>+</sup> + O + e product channel, peaked near the threshold for the electron transfer process (6,1 eV), and then declined with increasing relative collision energy. The electron transfer cross section increased monotonically with collision energy throughout the entire range investigated.

Angular and energy distributions of product ions from uranium atom-oxygen molecule collision were obtained to elucidate the dynamics of the ionization processes. The data from both types of measurements support the conclusion that the rearrangement ionization reaction [reaction (2)] proceeds by a "spectator-stripping" mechanism over a wide range of collision energies. The U<sup>+</sup> product of the electron transfer process is also strongly peaked in the forward direction.

Less thorough studies of chemi-ionization processes were conducted for a large number of other elements with O<sub>2</sub> molecules. These included Al, B, Ba, C, Ca, Ce, Fe, Hf, La, Li, Mg, Mo, Nb, Sc, Si, Sr, Ta, Ti, Th, V, W, Y, and Zr. All three ionization channels were observed for Ba, Ce, Hf, La, Nb, Th and Zr. For the elements M = Sc, Ti and Y, moderately large yields of M<sup>+</sup> and Mo<sup>+</sup> were observed, the yields of the associative-ionization processes being very low or unobservable. Only M<sup>+</sup> ion product was detected for the elements Al, Ca, Fe, Mg, Si, Sr, Ta, V and W, with small yields of MO<sup>+</sup> also for M = B, C, Ta and V. The observation correlate well with the ordering of the energetics of the competing ionization processes for each pair of collision partners. Rearrangement and associative ionization channels may be prominent reaction pathways only when their thermodynamic thresholds are less than that for electron transfer ionization. When the threshold for electron transfer is less than those for the two (true) chemi-ionization processes, the former is dominant (and usually the only observed) reaction.

Dr. S. Wexler  
Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois  
USA