PHOTODISSOCIATION AND RECOMBINATION OF HALOGENS IN THE GAS PHASE AT PRESSURES UP TO 1.4 KBAR

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Dissociation and recombination reactions of halogens under variable pressure conditions are well suited examples for studies on the influence of third bodies on the dynamics of diatomic molecules. Different phenomena are observed which elucidate the role of the carrier gas: The effective quantum yield of the photodissociation drops with increasing gas density. This can be interpreted in terms of a photolytic cage effect. The importance of weakly bound complexes between a halogen atom X and one or more carrier gas particles M for the mechanism of atom recombination is clarified by wide range measurements on the pressure dependence of recombination rate constants. Application of high gas densities allowed further a gradual transition from the normal gas dynamic regime of reaction to diffusion control.

Experiments were performed on the laser induced dissociation (Nd YAG, 2nd harmonic, 4MW, 15ns) of bromine and the following recombination in different gases: He, N_2, CO_2, C_2F_8. A stainless steel reaction cell with sapphire windows allowed us to use permanent gas pressures up to 1400 bar. Bromine concentrations were monitored in a beam in beam alignment via the Br_2-continuum absorption at λ =436nm.

For the recombination of halogen atoms two mechanisms have been postulated; energy transfer mechanism and a complex mechanism involving intermediates XM or XM_n. The energy transfer mechanism predicts as pressure dependence a smooth transition from a reaction order of 3 to an order of 2. Qualitatively similar results can be derived for different versions of a complex mechanism.

In the pressure dependence of the Bromine recombination in Helium the influence of both mechanisms can well be separated. A reaction order of 3 is observed at pressures up to 150 bar. With increasing pressure the reaction order drops markedly to about 2,5 and reaches again a value of 3 in the range 400 to 1400 bar. Such a behaviour was also observed in an earlier work on the iodine recombination[1] and may be interpreted in the following way: At low pressures of Helium about 40% of the bromine atoms recombine via the energy transfer mechanism (65% in the case of iodine). The "fall-off" region of the energy transfer mechanism is approached above 100 atm and the corresponding rate constant finally reaches its constant high pressure value. Consequently recombination occurs nearly exclusively via complex formation at pressures above 400 bar. The reaction order 3 in this domain demonstrates that the Br-He is so weakly bound, that even at 1400 atm the equilibrium is still on the side of the separated atoms.

Experiments with molecular third bodies show a smooth transition of the reaction order from 3 to 2 at high densities. It is shown that energy transfer is of minor importance in these cases and that the decreasing reaction order is due to a saturation of the complex mechanism when almost all atoms are attached to chaperons in BrM or BrM_n complexes.

From our results we can derive equilibrium constants for $Br+M \rightleftharpoons BrM$ which are in good agreement with expectations on the basis of potential parameters for similar weakly bound species from molecular beam measurements.
A photolytic cage effect in the gas phase dissociation of bromine was observed similar to that one which was measured in iodine earlier[2]. The onset of the observed drop in the effective quantum yield of dissociation lies at rather low pressures of several atmospheres.

1) H. Hippler, K. Luther, and J. Troe, Ber. Bunsenges. Physik. Chem. 77, 1104 (1973).

2) K. Luther and J. Troe, Chem. Phys. Letters, 24, 85 (1974)