THE CHEMICAL PRODUCTION OF EXCITED SPECIES

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ABSTRACT

The mechanism of formation of electronically excited species in elementary gas reactions is discussed in some detail. It is shown that three-body recombination is normally a more efficient source of electronically excited molecules than two-body association. The formation of electronically excited molecules in atom transfer reactions is considered in terms of the potential surfaces involved and their intersections. A brief comparison is made with the mechanisms of chemiluminescence in organic reactions and biological systems.

I. INTRODUCTION

The energy released in an exothermic chemical process normally exceeds the average thermal energy of the products as given by the Boltzmann distribution law for the reaction temperature. In this sense, many chemical reactions could be regarded as yielding excited species and only strongly exo-energetic processes where the energy distribution in the products shows a strong departure from equipartition or from the Boltzmann law are normally classified as such. The strong interactions between molecules in condensed media give very short relaxation times (~10^{-12}s for vibrational energy) and attention is therefore concentrated on gas phase processes.
Apart from the use of flash photolysis which was discussed in a previous chapter (1), these processes have been commonly investigated by using the visible or infrared chemiluminescent emission from the electronically or vibrationally excited species produced. Here attention is concentrated on reactions which yield electronically excited products and can therefore give visible or ultraviolet chemiluminescence. Such reactions occur via a potential surface which is not the lowest energy surface of the system in the product region. Such reactions are few in number, since most elementary reactions proceed by the lowest potential surface, which connects the electronic ground states of the reactants and products. Most of the elementary reactions studied involve the transfer of an atom, for instance between an atom and a diatomic molecule:

\[ A + BC = AB + C \quad (1) \]

Here, much of the energy released in the reaction can appear as vibrational excitation of the newly formed bond, giving infrared chemiluminescence by AB.

The calculation of trajectories for such systems on an empirical or semi-empirical potential surface using Monte Carlo methods enable experimental measurements of the vibrational and rotational excitation of ground state molecules or of reactive scattering in molecular beam systems to be transformed into information about the general form of the potential surface connecting ground state reactants and products. This topic has a considerable literature (2) but such methods have not yet been applied to the formation of electronically excited products either by reaction along a single potential surface, or by the more common situation where the emitting state is formed by a transition between different potential surfaces. Nevertheless, the qualitative findings of such calculations for ground state products can be used to characterize chemiluminescent reactions which are sometimes described as 'direct', 'occurring via a long-lived complex' and so on.

Electronically excited products are commonly formed in combination reactions, where little is known about the production of vibrationally excited ground state species. For two-body atomic combination, the potential surface leading to electronically excited products is simply the appropriate potential curve of the diatomic molecule and the spectral distribution of the emission can be analyzed theoretically to yield information about this potential, whether attractive or repulsive. However, more commonly, and es-