# Homomolecular Reactions: A New Field of Study in Chemistry

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Among the interesting new researches which have been made possible by the ready availability of enriched stable isotopes and mass spectrometers is the reaction of a molecule with itself. More rigorously stated, this is a reaction of a molecule with an identical molecule during which identical atoms are interchanged. It is proposed that these reactions be called homomolecular exchange reactions.

An interesting example is the homomolecular reaction of oxygen which we have studied (1) using a sample (2) of oxygen enriched to twenty-five per cent oxygen —18. Initially this sample contained a non-equilibrium mixture of the molecular species O_2^{32}, O_2^{34}, and O_2^{36}. Mass spectrometric measurements were used to follow the approach to a random distribution of the heavy isotope. An example of one of the exchange reactions producing this change is

$$O_2^{18-18} + O_2^{16-16} \rightarrow O_2^{18-16} + O_2^{18-16} \tag{1}$$
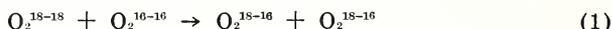
We have shown that this reaction does not proceed thermally, even in the presence of the specie, O_4, in the liquid state. On the other hand a rapid photochemical exchange is produced by appropriate ultraviolet radiation.

In general in the case of a one-element diatomic molecule, the use of two stable isotopes makes possible the preparation of a non-equilibrium mixture of the three molecular species. Such an initial non-equilibrium distribution will approach equilibrium through a simple exchange reaction according to the equation (3),

$$\ln(1-\alpha) = \frac{-2Q}{N} \cdot t \tag{2}$$

where Q is the rate of exchange, N is the number of molecules, and t is the time for a measured fraction of exchange, α. The expression for α is

$$\alpha = \frac{f_1° - f_1}{f_1° - f_1\infty} \tag{3}$$

in terms of the change in the fraction of any one of the molecular species, i, and its complete change to the equilibrium fraction corresponding to a random isotopic distribution. In this expression $f_1°$ and $f_1\infty$ are the initial and equilibrium fractions, respectively.

It is interesting to note that the rate of exchange, Q, in Equation (2) refers to the overall rate of exchange independent of change in isotopic composition. Thus this equation allows us to obtain the actual rate of reaction between identical one-element molecules. Similar expressions apply to a two-element molecule, such as nitric oxide; however, they necessarily involve double tagging or the use of an enriched isotope of each element.

Another homomolecular reaction which we have studied is that of the nitrogen molecule (4). In view of the great strength of the nitrogen bond it is perhaps not surprising that no reaction was observed in days at 850°C. However, a reaction does occur in a glow discharge (4, 5) in the presence of active nitrogen.

In the homomolecular exchange of oxygen, photochemically, and of nitrogen in a glow discharge the kinetics of these reactions confirm the derived law, Equation (2). These kinetics make possible an understanding of the mechanisms of these reactions and provide interesting kinetic data for the application of absolute rate theory to extremely simple chemical reactions in which there is no change in stoichiometry. Despite this simplicity it is interesting to observe in conclusion that many of our studies show that even these reactions probably occur chiefly through heterogeneous processes. This new field of study again emphasizes the importance of kinetics in modern chemistry.

Literature Cited

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