

hope to obtain data on this in the near future by using a different method of pressure measurement.

¹ Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

² For a bibliography of experimental work on nitrogen pentoxide, and tests of the constancy of high pressure rate, see Rice and Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

³ Hirst and Rideal, *Proc. Roy. Soc.*, **109A**, 526 (1925).

⁴ Hibben, *J. Am. Chem. Soc.*, **50**, 940 (1928).

⁵ Loomis and Smith, *J. Am. Chem. Soc.*, **50**, 1864 (1928).

⁶ Sprenger, *Zeit. physik. Chem.*, **136**, 49 (1928).

⁷ F. O. Rice, Urey and Washburn, *J. Am. Chem. Soc.*, **50**, 2402 (1928).

⁸ O. K. Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); *Ibid.*, **50**, 617 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928).

⁹ Kassel, *J. Phys. Chem.*, **32**, 225 (1928); *Ibid.*, **32**, 1065 (1928).

¹⁰ D. F. Smith and Taylor, *J. Am. Chem. Soc.*, **46**, 1393 (1924).

¹¹ The flask was taken from stock but as far as we are aware had not previously had liquid in it.

¹² Obtainable from Metropolitan Vickers Electric Co., Ltd., Strafford Park, Manchester, England.

TYPES OF UNIMOLECULAR REACTIONS

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Recently certain writers have expressed the belief that chemical reactions are to be explained on the basis of the quantum mechanical resonance phenomenon.² There are a large variety of different types of chemical reactions, of different degrees of complication, some of which may be too complicated to treat directly by quantum mechanical methods, but some of which are so simple that they have already been treated in more or less detail on the basis of the new mechanics. In this situation it seems desirable to point out the relations between certain reactions, one of which has been considered on the basis of the quantum mechanics, and the others of which have been treated only by classical or old quantum theory methods. We hope later to consider some of these relations in more detail with a view to seeing whether we can make new inferences (even though they must necessarily be of a preliminary nature) about the more complicated reactions.

The types of reaction which we wish to consider are predissociation, unimolecular decompositions of complex organic compounds, and photochemical decomposition of the same compounds, all occurring in the gaseous state.

1. *Predissociation*.—Predissociation can occur when a molecule can

be excited by absorption of radiation of a given frequency in two different ways, i.e., by two different electronic jumps, accompanied by the corresponding changes in vibrational and rotational quantum numbers. If one of these electronic states has a lower dissociation limit than the other, the continuum corresponding to the former overlaps discrete vibration rotation levels of the other. Thus a molecule in one of these discrete states (a predissociated molecule³) may be able to go by a radiationless transition to the overlapping continuum, and dissociate. This is a purely mechanical process occurring after the molecule has been activated by light. The theory of this sort of transition has been treated by a number of writers.⁴

2. *Unimolecular Decompositions.*—At first sight it may seem a far cry between the decomposition of a complicated molecule and predissociation; but, though outwardly the differences appear great, there are certain striking similarities. In the first place the theory of the decompositions indicates that only those molecules may react which have energy greater than a certain minimal amount, i.e., the molecules must be activated. In these cases, however, the molecules presumably do not obtain the energy by absorption of light, but by collision with other molecules, and the energy is presumably not electronic energy, but simply the energy of vibration of the atoms within the molecule. These reactions have been extensively treated using classical and old quantum theory statistical methods.⁵ By these considerations it seems to have been rather conclusively proved (at least in the cases of azomethane⁵ and methyl isopropyl diimide⁶) that the actual decomposition of a molecule occurs only when the requisite energy becomes localized in a certain part of the molecule (say a certain oscillator). Thus there are certain states of the molecule in which it has sufficient energy but does not decompose until a radiationless transition from a discrete state to a continuous state takes place. This is seen to be in very close analogy with the case of predissociation, only in the present case the transition consists of a change from one vibrational state to another, rather than from one electronic state to another.

3. *Photochemical Decompositions.*—In the case of the photochemical decomposition of a complex molecule we have a still more complicated situation, there being presumably first an electronic excitation, very likely followed by transitions of the type mentioned in the preceding paragraph, in which exchanges of energy occur between oscillators. This is similar to the suggestion of Ramsperger⁷ made in connection with the photochemical decomposition of azomethane, but there is no necessity of a direct transfer of energy from the excited electron to the oscillators in the molecule, as the very fact that the electron is excited may very likely alter the binding forces in the molecule in such a way that oscillation is started which ultimately leads to decomposition. Thus after

excitation some of the oscillators will find themselves far from their new positions of equilibrium and will begin to vibrate so that some of the light absorbed actually goes to exciting atomic vibrations, as described by Franck in simpler cases, and, furthermore, it is not at all unlikely that the dissociation energy in the new state will be lowered. In the case of the photochemical decompositions, as in the other cases, the final reaction probably occurs as a transition from the predissociated condition just described to a continuous state with the same energy.

It should be noted that the reactions described above are not of the radioactive type, in which there is a leaking away over a potential energy hump. The energy curve of the oscillator which breaks *may* have such a hump in it, to be sure, but the *essential* process, in the belief of the present writer, contrary to the view recently expressed by Bourgin,³ is a quantum transition which cannot be properly described as a leaking over a hump, but must be described as we have done above.

In closing it may be well to mention briefly the probable nature of one inference regarding reactions of type 2 which we will be able to make from the quantum mechanical theory of reactions of type 1. When there is interaction between continuous states and discrete states (i.e., when it is possible for radiationless transitions to take place between discrete and continuous states in the manner we have described) it has the effect of broadening the discrete states. (The exact meaning of this statement is given in my article previously referred to.⁴) When there is interaction between a set of continuous states and several discrete states, these discrete states may be broadened till they overlap, even though the unperturbed discrete states were of different energies. This means that the perturbed eigenfunctions which correctly describe the conditions of the molecule will be functions of a number of unperturbed eigenfunctions corresponding to different energy values. (The unperturbed eigenfunctions are those which would correctly describe the molecule if the radiationless transitions could not occur.) The broadening of the discrete lines is probably in general inversely proportional to the life period of the molecule in the discrete state, so at least where the reaction rate is fast the result will be a considerable complication of the statistics of the molecule, which we hope to treat later in more detail.

The ideas expressed in this note seem to be in direct contradiction to the view expressed by Langer⁹ that reaction occurs when a molecule passes from one discrete state to another; it hardly seems possible that his views can be correct in the case of a decomposition, where the final state to be reached is one of a continuous series.

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² Oppenheimer, *Phys. Rev.*, **31**, 81 (1928); Langer, *Phys. Rev.*, **33**, 290 (1929); Kallmann and London, *Zeits. physik. Chem.*, **2B**, 207 (1929).

³ We have defined predissociation in possibly a slightly more specialized sense than that first used by Henri and Teves, *Nature*, **114**, 894 (1924).

⁴ See e.g., Kronig, *Zeits. Physik*, **50**, 360 (1928); Rice, *Phys. Rev.*, **33**, 748 (1929).

⁵ Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927), **50**, 617 (1928); Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928); Rice, *Comptes Rendus, Réunion Internationale de Chimie Physique*, Paris, October, 1928.

⁶ Ramsperger, *J. Am. Chem. Soc.*, in press.

⁷ Ramsperger, *Ibid.*, **50**, 123 (1928).

⁸ Bourgin, *Proc. Nat. Acad. Sci.*, **15**, 357 (1929).

⁹ Abstract No. 127 presented to the American Physical Society at the Washington meeting, April 18-20, 1929.

THE VALENCE OF SULFUR IN DITHIONATES

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It has been shown by Lindh¹ and others² that the shift in the K absorption edges for various compounds of sulfur, chlorine, phosphorous, iron, and some other substances, depends chiefly on the valence of the element in a given compound. With increasing valence in a given element the wave-length of the edge shifts to smaller values. Stelling³ has explained the effect of valence as being due to the screening effect of electrons in external parts of atoms. To be sure, other factors influence the position of the edges, such as other elements occurring in the compounds, and lattice structure, but these factors produce in general only minor fluctuations around a mean value, whereas the mean values for the several valences show rather wide divergences. For example, the wave-lengths of the principal K edge of a large number of 4- and 6-valent inorganic sulfur compounds practically all lie within half an X-unit of the means of their respective groups, whereas the means themselves are separated by 8 X. U. A similar state of affairs is observed in the 2-valent compounds. The edges do not lie quite so close to the mean, but the mean is 13 X. U. from that of the 4-valent compounds. All the substances thus far investigated bear out the general statements above.

In view of the rather large body of facts now before us, it seems legitimate to try to use x-ray absorption data to obtain information on the valence state of an element in a compound.

The substance used in the present investigation was potassium dithionate, the object being to determine the state of the two sulfur atoms in $K_2S_2O_6$. Lindh⁴ has already shown that for $Na_2S_2O_3$ and some other thio-sulfates there is not just a simple absorption edge, but two edges, corre-