

data with those obtained by Goodeve and Powney [*J. Chem. Soc.*, 2078 (1932)]. The agreement was excellent. In addition we have the qualitative observations that the melting point is below 190°K ., and that the liquid dissolves slowly in water to give an acid solution which does not react with sulfurous acid (indicating perchlorate rather than lower valences of chlorine). The amount of this oxide produced in a given reaction mixture seems to be proportional to the initial ozone pressure and to increase somewhat with the chlorine pressure; it is only slightly dependent on temperature between 20 and 30° . It is obvious that the formation of these oxides, Cl_2O_7 and ClO_3 , invalidates any interpretation of the behavior of chlorine and ozone mixtures which assumes that the pressure change measures the oxygen formed.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

A. C. BYRNS
G. K. ROLLEFSON

RECEIVED APRIL 12, 1934

CHAINS IN THE ACETALDEHYDE DECOMPOSITION

Sir:

A recent paper by F. O. Rice and Herzfeld [*THIS JOURNAL*, **56**, 284 (1934)] gives an explanation of the kinetics of the homogeneous thermal decomposition of certain organic compounds on the basis of chain mechanisms, involving in some cases very long chains. In many cases this theory comes into direct conflict with the generally accepted explanation [L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chapter V] of these reactions as unimolecular decompositions "falling off" at low pressures. In fact, most supposed examples of the latter theory, such as the ethers and azo compounds, must now be regarded as under suspicion of being due to chain mechanisms.

There is a simple test, applicable in many cases, for the existence of such chains. One step in these chains will nearly always be the reaction of a methyl radical with the molecule of the substance, and the activation energy for this must be lower than that for the primary decomposition into free radicals. Hence if we introduce free methyl radicals from some extraneous source into an organic vapor at a temperature somewhat below that at which it ordinarily decomposes, a chain decomposition should be set up. Thus, these decompositions should be induced at an

abnormally low temperature by mixing our compound with another that decomposes at this lower temperature to give methyl radicals.

We have tried this experiment with a mixture of acetaldehyde and azomethane. Decomposition is actually induced in the aldehyde; a few per cent. of azomethane is sufficient to cause complete decomposition of the aldehyde at 300° , at which temperature the aldehyde alone is quite inert. Chain lengths, calculated from rate measurements, are found of the order of 30. The rate of the reaction is found, within the accuracy of our few preliminary experiments, to be proportional to the first power of the aldehyde pressure and to the square root of the pressure of the azomethane, just as the chain theory predicts.

Our result strongly confirms the above explanation of the decomposition of pure acetaldehyde as a chain reaction, but this is not yet definitely proved since there may be some other faster reaction superimposed upon the chain reaction at higher temperatures. We expect, however, by further experiments with azomethane-aldehyde mixtures to establish this point by getting the activation energies of the chain steps. These experiments may also throw light on the question of whether the azomethane decomposition is a chain reaction.

MALLINCKRODT CHEMICAL
LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

DARRELL V. SICKMAN
AUGUSTINE O. ALLEN

RECEIVED APRIL 16, 1934

THE LOW PRESSURE EXPLOSION LIMITS OF DEUTERIUM AND OXYGEN

Sir:

We have compared the explosion limits of deuterium-oxygen and hydrogen-oxygen mixtures at low pressures at 500° and 520° in potassium chloride-coated Pyrex according to our original technique [*THIS JOURNAL*, **55**, 3227 (1933)]. Deuterium was generated by electrolysis of pure heavy water; in some cases additional care was taken to purify it by diffusion through palladium. Tank hydrogen was used in alternate experiments. From Fig. 1 and Fig. 2 it is seen that the deuterium curve is much broader. At high pressures where there is no appreciable deactivation at the wall of the vessel, the negative reciprocal slope of the explosion limit curve represents the relative deactivation efficien-

cies ZH_2/ZO_2 and ZD_2/ZO_2 in the chain-breaking processes $X + O_2 + M$, where X is the chain-carrier and M is H_2 , D_2 or O_2 . Experimentally these values are 3.1 and 2.1, respectively; whence $ZH_2/ZD_2 = 1.5$. This value compares favorably with the value $ZH_2/ZD_2 = \sqrt{\mu D_2/\mu H_2} = \sqrt{4/2} = 1.4$, roughly calculated from the simple theory of

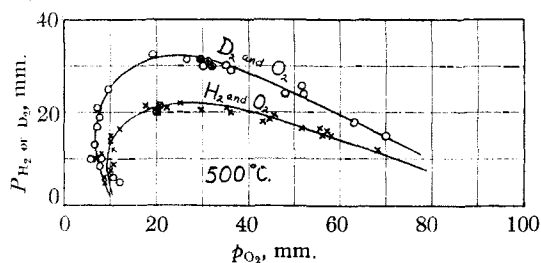


Fig. 1.—Explosion limits at 500°: \times , hydrogen and oxygen; \circ , deuterium and oxygen; $\boxed{\times}$, hydrogen diffused through palladium; \odot , deuterium diffused through palladium.

three-body collision frequency [Grant and Hinshelwood, *Proc. Roy. Soc. (London)*, **A141**, 29 (1933)], assuming equal collision diameters for H_2 and D_2 . For according to this, the ratio ZH_2/ZD_2 is a function only of the reduced masses, μ , of the respective complexes ($X + O_2 + H_2$) and ($X + O_2 + D_2$); and the reduced masses are

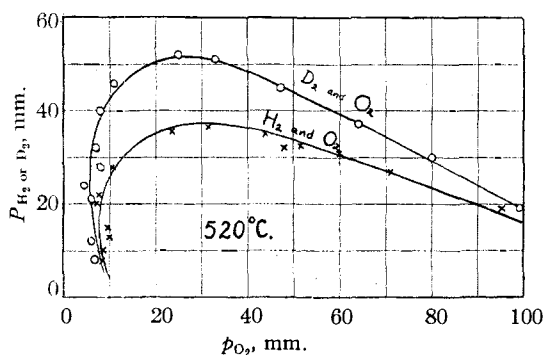


Fig. 2.—Explosion limits at 520°: \times , hydrogen and oxygen; \circ , deuterium and oxygen.

approximately the masses of H_2 and D_2 when $X + O_2$ is large compared with H_2 and D_2 . The whole of the observed change due to deuterium, therefore, can be accounted for on the basis of relative deactivating efficiencies. This leads to the observation that any additional changes, due to the substitution of deuterium for hydrogen, in the

relative rates of chain branching and chain breaking process controlling the explosion limit, must cancel one another. It is unlikely that this would be the case if D and H or D_2 and H_2 were the chain carriers.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

ARTHUR A. FROST
HUBERT N. ALVEA

RECEIVED APRIL 17, 1934

THE PREPARATION OF HYDROGEN COMPOUNDS OF SILICON

Sir:

In our studies on the kinetics of the catalytic decomposition of the hydrogen compounds of some of the fourth and fifth group elements it became necessary to prepare rather large quantities of silane, SiH_4 . Being acquainted with the very favorable results obtained in the preparation of the germanes in liquid ammonia [Kraus and Carney, *THIS JOURNAL*, **56**, 765 (1934)], it was thought advisable to follow the same procedure in an attempt to prepare some of the silicon compounds, since the former were obtained in unusually high yields, three to four times as great as those found in the aqueous method [Dennis, Corey and Moore, *ibid.*, **46**, 657 (1924)].

Magnesium silicide, prepared by the direct combination of the elements, was dropped into a solution of ammonium bromide in liquid ammonia. A reaction was noticed to proceed immediately with the liberation of considerable quantities of gases, which upon examination were found to consist chiefly of hydrogen, silane and disilane, and of small amounts of trisilane. To date approximately 30 liters of these silanes have been prepared by this method, with yields ranging from 65 to 80% based on the silicon used in the preparation of the magnesium silicide. The yield obtained here is about three times as great as that found by Stock and co-workers [Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933, p. 21], who employed the analogous aqueous method.

THE GEORGE HERBERT JONES
LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

WARREN C. JOHNSON
T. R. HOGNESS

RECEIVED APRIL 18, 1934