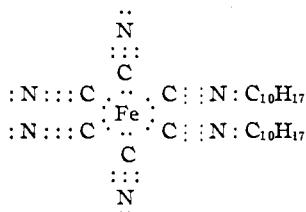


To obtain isobornylamine, however, we are led to the conclusion that there is some sort of connection between the nitrogen and the $C_{10}H_{17}$ group probably as follows



Tetra-covalent nitrogen is not unique; nevertheless, the experimental evidence presented by these investigators leads to conclusions which may be interesting as applied to the structure of the complex ferrocyanides.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO, N. Y.

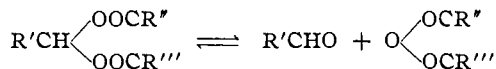
HOWARD W. POST

RECEIVED JULY 24, 1931
PUBLISHED OCTOBER 5, 1931

A NEW SERIES OF HOMOGENEOUS MONOMOLECULAR GAS REACTIONS

Sir:

In the course of a systematic investigation of equilibria and reaction velocities in gaseous and liquid "ester-acid anhydride-aldehyde" systems from points of view outlined elsewhere [Coffin and Maas, *Canadian Journal of Research*, **3**, 526 (1930); **3**, 540 (1930)], a new series of homogeneous monomolecular reactions has been found. Several examples of the gaseous decomposition represented by the general equation



have been found to be monomolecular in accordance with modern ideas regarding the break-up of complicated molecules. In the cases already investigated the reaction is homogeneous and follows the Arrhenius equation. The heats of activation and the absolute temperatures at which the reactions attain a given rate fall in well with the parallelism displayed by known examples of monomolecular change. Experiments are being carried out at present to determine whether or not the rate constant falls off as the pressure is lowered.

As the reaction appears to be particularly well adapted for an investigation of the influence of molecular structure on reaction velocity, the decomposition of as many as possible homologous and isomeric esters is being studied. A description of the experimental method together with the results obtained to date will be published shortly.

It is of interest in connection with the "dreierstoss" theory that in none

of the systems yet investigated does the reverse reaction occur at a measurable velocity. A special search is being made for a measurable equilibrium and a homogeneous bimolecular gas reaction between an aldehyde and an anhydride.

CHEMISTRY LABORATORY
DALHOUSIE UNIVERSITY
HALIFAX, CANADA
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C. C. COFFIN

THE SEPARATION OF THE RARE EARTHS BY FRACTIONAL CRYSTALLIZATION

Sir:

No one working on the fractional crystallization of the rare earths seems to have paid much attention to the differences in the ionic radii. The relative ionic radii in the oxides have been determined by Goldschmidt [Hevesy, "Die Seltenen Erden," Verlag von Julius Springer, Berlin, Germany, p. 111, 1927], and they have been found to differ by several per cent. The usual separations, however, are effected from solution and the ions, both in solution and in the hydrated crystals, are surrounded by water molecules, in most cases, probably, as $\text{La}(\text{H}_2\text{O})_6^{+++}$, $\text{Ce}(\text{H}_2\text{O})_6^{+++}$, etc. The *fractional* differences between these augmented ionic radii are certainly much less than those of the unhydrated ions.

It would be natural to attempt separation from molten salts so as to benefit by the maximum differences in the radii since relative solubilities, etc., are determined here by the radii of the bare ions. However, high temperatures may deprive one of most of the expected advantages, for they tend to smooth over factors associated with small energy differences. (This vague statement might be helped by a more precise example, the elementary law that the smaller the difference in energy between two states of a system in equilibrium the lower must be the temperature to bring about an appreciable concentration of the lower energy state.) Nevertheless, a study of molten salts may prove of value because the unknown thermodynamic magnitudes for the crystals and their molten solutions may not be altogether unfavorable.

On the other hand, one can turn one's attention to those salts crystallizing with so little of the solvent that the positive ion is not screened from the negative ions. The acetates, for example, crystallize ordinarily with only one and one-half molecules of water and hence the acetate ions are directly in contact with the positive ions. Fractional crystallization of the acetates has not appeared very promising in the past, perhaps on account of their high solubilities. Very concentrated solutions do not differ much from crystals, the positive ions are completely "acetated" and their distribution between the liquid solution and the solid solution is almost the