Bergmann[17] has made an extensive study of mixtures of mercury and cadmium halides with Ag, Tl, NH_4, Li, Na and K nitrates, using thermal methods. This study is interesting because of the low ionization of mercury and cadmium salts. Bergmann concludes that in the case of the mercury halides almost no double decomposition occurs but that the cadmium halides show a tendency toward double decomposition in case no complex compounds are formed.

Summary

1. X-ray patterns have been determined for a series of mixtures containing KCl–NaBr, KCl–NaF, KCl–NaI, KCl–$NaNO_3$ and KCl–AgBr.

2. Evidence of double decomposition in the absence of a solvent has been obtained for mixtures containing KCl–NaBr, KCl–NaI and KCl–$NaNO_3$.

3. Equimolar mixtures of KF–NaCl have been shown to go to KCl and NaF when melted and equimolar mixtures of AgCl–KBr have been shown to form AgBr and KCl when melted.

4. KCl–NaBr mixtures have been examined below the fusion temperature and double decomposition found to occur.

5. Within the limit of error all double decompositions examined have been found to go to completion and the final products to be insoluble in each other in the solid state.

ST. LOUIS, MO.

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[17] Bergmann, *Z. anorg. allgem. Chem.*, **157**, 83 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Some Chemical Reactions Involving Active Nitrogen[1]

BY R. H. EWART AND W. H. RODEBUSH

In the course of some investigations of the reaction of atomic hydrogen with hydrogen bromide a yellow luminosity was observed which was finally discovered to be due to traces of nitrogen present in the hydrogen which passed through the electrodeless discharge. In order to confirm this, hydrogen bromide at low pressure was introduced into a tube through which glowing nitrogen likewise at low pressure was flowing. The point of introduction of the hydrogen bromide was about 30 cm. from the discharge bulb. The nitrogen used in the experiment contained a trace of water vapor and the afterglow was quite brilliant and extended with no apparent diminution in intensity from the electrodeless discharge bulb to the liquid air trap.

At the point where the hydrogen bromide was admitted the afterglow became a brilliant orange of greatly increased intensity and all afterglow ceased in the tube below the point of admission of the hydrogen bromide. After a few minutes a white deposit appeared on the walls of the tube at the point of admission of the hydrogen bromide. The solid proved to be ammonium bromide and at the end of the run the liquid air trap was found to contain free bromine.

When the hydrogen bromide flow was stopped the brilliant orange flame diminished in intensity and moved at the rate of a few centimeters per minute. By the time the flame had moved some 20 cm. its intensity was apparently reduced to zero and the normal yellow afterglow suddenly swept through the apparatus as though a valve had been opened. When the flame was allowed to "die out" in this way no white deposit remained in the tube. In order to obtain samples of the white deposit it was necessary to stop the flow of active nitrogen at the same time that the flow of hydrogen bromide was stopped.

When hydrogen iodide is introduced in place of hydrogen bromide the same phenomena were observed and the flame was even more intense and of a brilliant blue color. With hydrogen chloride no effect was observed except that the afterglow ceased below the point of admission.

It is possible to offer a plausible explanation for this phenomenon. The ordinary bands in the nitrogen afterglow involve transitions from the 11th level of the B state to the 7th, 8th and 9th levels of the A state of the molecule. When the orange colored flame was examined with the spectroscope it was found to owe its color to strong bands of 5900–6000 Å. which probably correspond to transitions from the 9th level of the B state to the 6th or 7th levels of the A state.

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[1] For references to work on active nitrogen see Kneser, *Ergebnisse der exakten Naturwissenschaften*, **8**, 229 (1929); also publications by Kaplan in *Phys. Rev.* (1931–1932).

Now the vibrational spacing for hydrogen bromide is nearly twice that of the nitrogen molecule in the B state and it seems plausible that nitrogen molecules lose 2 vibrational quanta on collision to hydrogen bromide on collision and thus drop from the 11th to 9th level.

The chemical reactions with the hydrogen halides undoubtedly involve the nitrogen atom.[2] We may write the following reactions

$$N + HCl = NH + Cl + 5 \text{ cal.}$$
$$N + HBr = NH + Br - 15 \text{ cal.}$$
$$N + HI = NH + I - 35 \text{ cal.}$$

The heats of reaction given are only approximate since the heat of dissociation is not known exactly but it is obvious that there is little or no tendency for the nitrogen atom to react with hydrogen chloride while the second and third reactions take place readily since the heats of activation are probably small.

With the hydrogen bromide for example subsequent reactions take place

$$NH + HBr = NH_2 + Br$$
$$NH_2 + HBr = NH_3 + Br$$
$$NH_3 + HBr = NH_4Br$$

and ammonium bromide is deposited on the walls. The complete cessation of the afterglow below the point of admission must be attributed to the catalytic action of the ammonium bromide on the walls of the tube in deactivating the nitrogen, since this effect persists after the flow of hydrogen bromide is stopped. This deactivation, however, liberates heat and the ammonium bromide sublimes molecule by molecule and travels slowly down the tube. When the ammonium bromide sublimes, however, it dissociates into hydrogen bromide and ammonia and the above reactions occur again. The ammonium bromide is thus all used up and the bromine is eventually all collected in the liquid air trap.

A second experiment which still remains to be explained was suggested by the fact that pure dry nitrogen does not give the afterglow. The common impurity is water, oxygen or some oxygen compound. The afterglow increases in intensity with the increase in the percentage of nitrogen atoms and the highest percentage of atoms is to be obtained with enough water vapor present to render the walls inactive. On the other hand, we have observed several per cent. of atoms to be present in nitrogen which has been purified and dried to a point where the afterglow has practically ceased. Now there is no record of a photograph of the nitrogen afterglow spectrum which does not also show some of the β or γ bands of nitric oxide. This may be only a coincidence because of the oxygen usually present as an impurity but it appears rather significant. Accordingly, we have tried the experiment of introducing nitric oxide into a stream of pure dry nitrogen which has been passed through the electrodeless discharge but which shows no afterglow. When the nitric oxide is admitted a beautiful afterglow is obtained which extends throughout the apparatus. This afterglow is greenish in color and is not as intense as the regular nitrogen afterglow but it has the same property of disappearing in a part of the tube which is heated and reappearing beyond in the cooler part of the tube. Neither water nor oxygen give this afterglow. When this afterglow was examined with the spectroscope the regular afterglow bands if present were masked by what appears to be a continuous spectrum through the visible region. This continuum is attributed to the nitric oxide and may be considered to indicate dissociations since the metastable molecules present possess sufficient energy to dissociate nitric oxide. This experiment may be considered to prove that under certain circumstances at least nitric oxide enters into the cycle of reaction mechanisms involved in the nitrogen afterglow.

Active nitrogen contains both metastable molecules and metastable atoms but it is not known certainly whether the zero state of the A level of the molecule lies 8.2 volts above the ground state as proposed by Sponer[3] or about 6 volts above as is indicated by the work of Vegard[4] on solid nitrogen. Neither is the heat of dissociation of nitrogen known with certainty. Consequently, it is impossible to decide between several possible mechanisms because it is not known whether metastable atoms are involved in the excitation which produces the afterglow bands. It is of course equally difficult to say whether nitric oxide is a necessary ingredient in the luminous mixture but it appears to be a sufficient one. The nitric oxide was not carefully purified and undoubtedly contained traces of other oxides of nitrogen.

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[2] Willey, *J. Chem. Soc.*, 669 (1927), observed the dissociation of the hydrogen halides by active nitrogen but his explanation was quite the opposite of that given above.

[3] Sponer, *Z. Physik*, **41**, 611 (1927).

[4] Vegard, *ibid.*, **79**, 471 (1932).