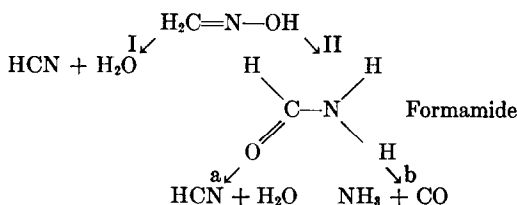


Decomposition of Formaldoxime by Oxide Catalysts

The solid trimer of formaldoxime ($\text{H}_2\text{C}=\text{NOH}$, subl. point, 134°C) is evaporated in a nitrogen stream and passes over the catalyst at 180°C . The gaseous and water-soluble decomposition products are collected in two washing bottles containing water. Carbon monoxide, if formed, is traced with PdCl_2 solution.

The decomposition of formaldoxime is possible in two directions:



HCN and NH_3 are measured by titration. A characteristic parameter for comparison of different catalysts is the ratio $f = \text{NH}_3/\text{HCN}$. For discrimination of reaction paths I and IIa, formamide has been decomposed on the same catalysts as formaldoxime (compare ref. 1). The principal results are given in Table 1.

TABLE 1
VALUES OF f FOR FORMALDOXIME AND FORMAMIDE

Catalyst	MgO	Al_2O_3	SiO_2
Formaldoxime	0.43	56	1.3
Formamide	23.5	>185	3.6

With MgO , f is opposite for the two substrates. Here, formamide cannot be an intermediate of the formaldoxime decomposition. This reaction follows path I on MgO . However, on Al_2O_3 , both decompositions appear to have a common step, both giving nearly exclusively NH_3 and CO . Hence, on Al_2O_3 , formaldoxime is decomposed by reaction IIb. For SiO_2 , the values of f are again of the same order of magni-

tude, and it appears to be probable, that here too formamide is an intermediate according to scheme IIa and IIb.

A suitable conclusion would be that on basic catalysts (MgO with $f = 0.43$, CaO with $f = 0.35$) formaldoxime is mainly decomposed according to I, whereas on acidic catalysts II is the main path. Here, the effect of the catalyst is essentially the isomerization since it has been shown (1) that the formamide decomposition according to IIb is not influenced by any usual catalysts but is a spontaneous monomolecular process.

In search for a relationship between the characteristic factor f and the cation radius of the catalyzing oxide, a series of oxide catalysts has been applied (Table 2).

TABLE 2
DECOMPOSITION OF FORMALDOXIME

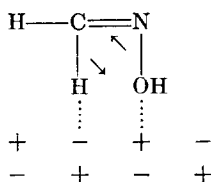
Catalyst	r_+ (Å)	f	Catalyst	r_+ (Å)	f
BeO	0.30	4.0	Al_2O_3	0.45	56
MgO	0.65	0.43	Fe_2O_3	0.53	5.1
CaO	0.94	0.35	Cr_2O_3	0.55	2.9

It may be seen that a predominant formation of HCN occurs only on basic catalysts with large cation radius whereas in all the other cases reaction path IIb is the prevalent one.

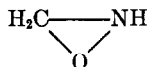
It may be added that the formaldoxime decomposition is always accompanied by the formation of a brown by-product which after a certain time leads to a resin-poisoning of the catalyst. A part of the by-product is transported by the nitrogen stream and is condensed in the cool part of the reaction tube. Finally it polymerizes giving a solid lacquer. The IR spectrum of this product and its solution behavior are very similar to those of polymers of hydrocyanic acid, especially azulmine. The poi-

soned catalysts can be regenerated by heating to 500°C.

Reaction path I is comparable with a great many examples of heterogeneous elimination reactions, e.g., dehydration of alcohols and HCl elimination from alkyl chlorides. For these types of "salt catalysis," a mechanism based on the surface polarity of the catalyst has been brought forward (2) which, in our case, would be:



with an anti-clockwise shift of electron pairs. When the polarity of the catalyst is not sufficient to bring about this shift, isomerization to formamide is the catalyzed step, possibly through adsorbed oxazirane



as an intermediate. Formamide then gives, as is known (1), ammonia and carbon monoxide without influence of the catalyst.

An alternative explanation would be a primary reaction, I, in all cases with following equilibration of the hydrolysis of hydrocyanic acid, the latter being poisoned by formaldoxime depending on the nature of the catalyst. The authors think, however, that the presentation given above allows a better coordination of the findings with known experience.

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