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Reactions of Nitrogen Oxides with Isocyanide

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Various types of oxidizing agents, such as metal oxides,[1] ozone,[2] peracid,[3] *etc.*, are known for the oxidation of isocyanide to isocyanate. We wish to report the reduction of nitrogen oxide and dinitrogen oxide with isocyanide. Nitrogen oxides are reduced to elementary nitrogen and the isocyanide is oxidized to isocyanate.

Nitrogen oxide is reduced more readily than dinitrogen oxide. The results are shown in Table 1 (Exp. No. 1—4). The main gaseous product was nitrogen, whose amount roughly satisfies the stoichiometric relation:

$$RNC + NO \longrightarrow RNCO + \tfrac{1}{2} N_2$$

Small amounts of dinitrogen oxide (yield=about 10%; based upon nitrogen oxide) and carbon dioxide (less than a few percent) were formed as by-products. The production of carbon dioxide may be attributed to the hydrolysis of the product isocyanate with water which is present as impurity. The amine from the isocyanate hydrolysis may have been converted into the corresponding urea by the second molecule of isocyanate. In fact, a small amount of urea was isolated from the reaction mixture.

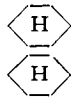
The nitrogen oxide-isocyanide reaction proceeded even at atmospheric pressure. Nitrogen oxide gas was passed at rate of 1.5 *l*/hr through a mixture of 50 mmol of cyclohexyl isocyanide and 10 m*l* of toluene (solvent) at 95°C for 10 hr. Cyclohexyl isocyanate was produced in 56% yield.

Dinitrogen oxide also oxidized isocyanide into isocyanate. Only 22% of cyclohexyl isocyanide was converted into isocyanate even after the reaction at 120—130°C for 16 hr (Exp. No. 5).

$$RNC + N_2O \rightarrow RNCO + N_2$$

From the reaction conditions and the conversion rate, we see that the oxidizing reactivity of dinitrogen oxide is much lower than that of nitrogen oxide. This finding does not support a mechanism of

Table 1. Reaction of nitrogen oxides with isocyanide

Exp. No.	RNC	(mmol)	Solvent	(m*l*)	Nitrogen Oxide	Reaction Temp. (°C)	Reaction Time (hr)	Yield of RNCO[a] (%)	N_2 (mmol)
1	 -NC	10	C_6H_6	3	NO	80	5	77	3.3
2	*t*-C_4H_9NC	20	$(C_2H_5)_2O$	5	NO	120	8	50	—
3	*n*-$C_6H_{13}NC$	10	C_6H_6	3	NO	100	8	62	—
4	 -NC	10	C_2H_5OH	5	NO	110	8	80[b]	—
5	-NC	13	C_6H_6	3	N_2O	120—130	16	22	—

a) Based on the isocyanide initially charged.
b) Isolated as ethyl *N*-cyclohexylurethane which is the reaction product of *N*-cyclohexyl isocyanate and ethanol (solvent).

1) A. Gautier, *Ann. Chim.* (Paris) [4], **17**, 229 (1869).
2) H. Feuer, H. Rubinstein and A. T. Nielsen, *J. Org. Chem.*, **23**, 1107 (1958).
3) T. Shono, M. Kimura, Y. Ito, K. Nishida and R. Oda, This Bulletin, **37**, 635 (1964).

stepwise reduction of nitrogen oxide to nitrogen through the intermediate stage of dinitrogen oxide.

It is interesting to compare the reaction of phosphite with nitrogen oxide with that of isocyanide. It has been reported that nitrogen oxide reacts with triethyl phosphite to produce triethyl phosphate and dinitrogen oxide in liquid phase at room temperature, and that dinitrogen oxide has no tendency to oxidize triethyl phosphite under the same reaction conditions.[4)]

$$(EtO)_3P + 2NO \rightarrow (EtO)_3PO + N_2O$$

However, we found that dinitrogen oxide also has the capacity of oxidizing triethyl phosphite to triethyl phosphate at higher temperatures and pressures. Thus, triethyl phosphate was obtained in more than 80% yield by the triethyl phosphite-dinitrogen oxide reaction under the same reaction conditions as described in the cyclohexyl isocyanide-dinitrogen oxide reaction.

$$(EtO)_3P + N_2O \rightarrow (EtO)_3PO + N_2$$

4) L. P. Kuhn, J. O. Doali and C. Wellman, *J. Amer. Chem. Soc.*, **82**, 4792 (1960).

Experimental

General Procedure. A mixture of isocyanide and solvent was placed in a 50 m*l* stainless-steel pressure tube, to which nitrogen oxide (or dinitrogen oxide) was compressed to 20 kg/cm^2 at room temperature. The pressure tube was closed and the content was heated without shaking or stirring. After the reaction, the gases were trapped and analyzed by glpc with a column of silica gel (column temp. -78°C for nitrogen and nitrogen oxide and 40°C for dinitrogen oxide and carbon dioxide). Isocyanide and isocyanate were analyzed also by glpc with columns of silicone DC 550 and PEG 6000.