Synthesis of Isocyanic Acid from Nitric Oxide over Palladium and Iridium Catalysts

Abstract. *A novel and convenient synthesis of isocyanic acid (HNCO) and its trimer isocyanuric acid has been obtained by the conversion of nitric oxide (NO). Nitric oxide, carbon monoxide, and hydrogen mixed in helium at the level of 0.3 to 5 percent reacted over iridium and palladium catalysts at 280° to 450°C to form HNCO in 60 to 75 percent yield. Major side products were ammonium cyanate at low temperature and ammonia or nitrogen at high temperature. Total conversion of nitrogen from NO to NCO reached 73 percent over palladium and 86 percent over iridium.*

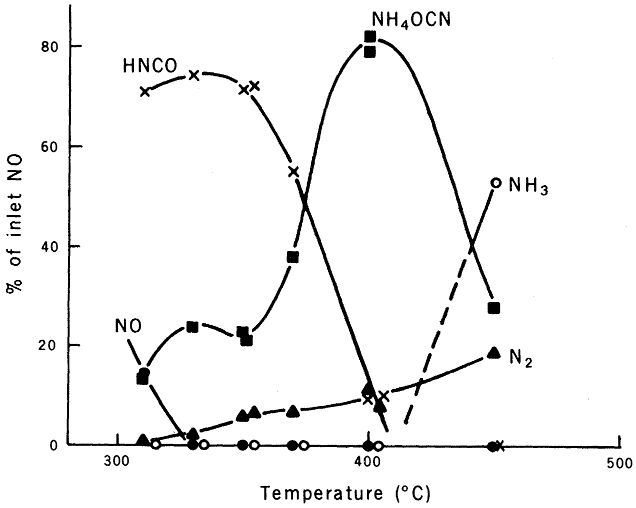
Use of the catalytic reduction of NO for environmental protection measures has prompted extensive studies of its interaction with CO on noble metals. Interaction on small noble metal particles dispersed on Al_2O_3 (*1, 2*) or SiO_2 (*3*) produced adsorbed species identified as isocyanate groups by infrared absorption. In ultrahigh-vacuum studies (*4*) of the coadsorption of CO and NO, no evidence was found for adsorbed isocyanate species. However, the presence of NCO groups on the surfaces of bulk metals under reaction conditions was conclusively shown by the production of ammonium cyanate (NH_4OCN) when NO, CO, and H_2 reacted over Pt and Rh surfaces (*5*). The formation of NH_4OCN was also of interest as a novel synthesis of NH_4OCN and its isomer urea, since NH_4OCN was being produced with yields as high as 95 percent over a substantial range of operating conditions. Curiously, free isocyanic acid (HNCO) was not produced. This suggested that a reaction such as

$$\text{HNCO (adsorbed)} + NH_3 \rightarrow NH_4OCN \text{ (gas)} \qquad (1)$$

was the rate-limiting step in the formation of NH_4OCN, while the desorption of HNCO per se was slow. We have now found that on Ir and Pd, HNCO is desorbed as the primary product and is produced in yields of 60 to 75 percent, calculated on the basis of converted NO. Moreover, we have found (*6*) that on a Pt-Rh alloy, gas phase NH_3 will strongly promote the desorption of NCO as NH_4OCN (Eq. 1). The results on Ir and Pd are significant because they show a novel and convenient synthesis of HNCO (and, by implication, of its trimer, isocyanuric acid) from NO. We know of no other direct synthesis of HNCO.

The catalytic reactions of NO, CO, and H_2 were carried out in a flow system incorporating a fixed-bed quartz reactor, an on-line gas chromatograph (GC) to analyze for NO, CO, H_2, and N_2 (*7*), and an absorber and on-line colorimetric analyzer for gaseous OCN in NH_4OCN and HNCO (*8*). A flow of 0.3 percent NO, 0.5 percent H_2, and 5 percent CO in He was directed over Pd or Ir catalyst (*9*) supported on a fritted quartz disk. The effluent was split for on-line GC and colorimetric analysis. The NCO produced as NH_4OCN or HNCO was absorbed in an alcoholic solution of ammonium acetate to convert all OCN into NH_4OCN, which was then converted into urea and analyzed as the yellow complex with diacetyl monoxime (*8*). The conversion of NO into NH_3 was calculated from the nitrogen balance, using the analysis of inlet gas and effluent for NO, N_2, and total NCO. This is permissible since in the temperature range of interest other nitrogen-containing products, namely, N_2O and HCN, were negligible (*10*). Since NH_3 is bound as NH_4OCN if sufficient HNCO is present, the results are reported as NH_4OCN and HNCO. NH_4OCN and HNCO were isolated in consecutive condensers at room temperature (~25°C) and −30°C, respectively. After trapping of NH_4OCN, HNCO was also isolated by the precipitation of its silver salt.

Figure 1 shows the formation of HNCO, NH_4OCN, and NH_3 over Ir as a function of the reaction temperature. We plot the fraction of N from NO in the inlet gas recovered as NO, HNCO, and so on in the outlet gas. The catalyst was prereduced at 450°C in a flowing mixture of 80 percent H_2 and 20 percent He for 100 minutes. Without such prereduction a somewhat higher activity and a significantly lower selectivity were observed. The maximum yield of HNCO in Fig. 1 is 75 percent at 330°C and the total NCO yield is 86 percent. At these conditions, the reaction products were trapped in the two condensers for several hours. The product in the second condenser was dissolved in CCl_4 at −30°C. After the solution was warmed to room temperature, its infrared spectrum showed a high con-



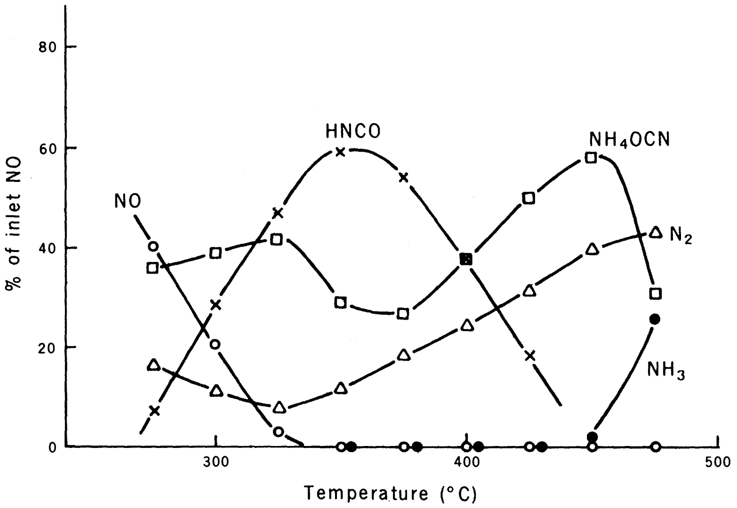


Fig. 1 (left). Iridium-catalyzed conversion of NO, CO, and H_2 to HNCO and NH_4OCN. The gas mixture consisted of 0.3 percent NO, 0.5 percent H_2, and 5 percent CO in He and the flow rate was 40 liter/hour per square meter of Ir. The nitrogen in nitrogen-containing compounds in the effluent is plotted as atomic percentage of N in inlet NO. Fig. 2 (right). Palladium-catalyzed conversion of NO, CO, and H_2 to HNCO and NH_4OCN. The flow rate and composition of the gas were as described for Fig. 1. The nitrogen in nitrogen-containing compounds in the effluent is plotted as atomic percentage of N in inlet NO.

0036-8075/78/1103-0525$00.50/0

centration of HNCO, identified by absorptions at 3495 cm^{-1} (strong, vibrational frequency ν_1), 2265 cm^{-1} (very strong, ν_2), and 790 cm^{-1} (strong, ν_4), all of which show small shifts to shorter wavelengths compared with the spectrum of gaseous HNCO (*11*).

The results for Pd are shown in Fig. 2. The maximum yield of HNCO was 60 percent at 350°C and the total yield of NCO was 73 percent. A prerequisite for a high yield is thorough reduction of the Pd. An effective procedure was to pass pure H_2 or H_2-He mixtures over the Pd at room temperature for several hours (*12*), followed by reduction in flowing pure H_2 at 450° to 500°C. A more moderate prereduction at 380°C was not effective. The effect of the concentrations of H_2 and H_2O in the inlet gas was studied. The yield of HNCO increased slightly when 3.4 percent H_2O was added to the standard NO-CO-H_2-He mixture with the Pd at 350°C. Replacing part of the H_2 with an equivalent concentration of H_2O decreased the yield of HNCO.

The reactions of NO, H_2, and CO over Ir or Pd described here provide a novel and practical synthesis of HNCO. Because of the large difference between the HNCO and NH_4OCN condensation temperatures, separation of the two products is simple. At a sufficiently low collection temperature (less than -20°C), HNCO is a stable liquid or solid, while at a higher temperature (20°C) it easily trimerizes to isocyanuric acid, cyanuric acid, and cyamelide (*13*). The mixture can simply be converted to pure isocyanuric acid (*14*) or reacted with NH_3 to melamine (*15*). Both are important raw materials in the chemical industry (*16*). In addition, conversion of HNCO to urea is long-known and straightforward (*17*). The mechanism of the formation of HNCO and NH_4OCN is under current investigation.

R. J. H. VOORHOEVE
L. E. TRIMBLE

Bell Laboratories,
Murray Hill, New Jersey 07974

References and Notes

1. M. L. Unland, *Science* **179**, 567 (1973); *J. Phys. Chem.* **77**, 1952 (1973); *J. Catal.* **31**, 459 (1973); R. A. Dalla Betta and M. Shelef, *J. Mol. Catal.* **1**, 431 (1976); F. Solymosi and J. Sarkany, *React. Kinet. Catal. Lett.* **3**, 297 (1975).
2. F. Solymosi, J. Sarkany, A. Schauer, *J. Catal.* **46**, 297 (1977); F. Solymosi and J. Rasko, *ibid.* **49**, 240 (1977).
3. M. F. Brown and R. D. Gonzalez, *ibid.* **44**, 477 (1976).
4. R. Ku, N. A. Gjostein, H. P. Bonzel, *Surf. Sci.* **64**, 465 (1977); G. Zhdan and H. Weinberg, *Appl. Surf. Sci.*, in press; H. Conrad, G. Ertl, J. Kuppers, E. E. Latta, *Faraday Discuss. Chem. Soc.* **58**, 116 (1974).
5. R. J. H. Voorhoeve, L. E. Trimble, D. J. Freed, *Science* **200**, 759 (1978).
6. R. J. H. Voorhoeve and L. E. Trimble, *J. Catal.* **53**, 251 (1978).
7. ——, *ibid.* **38**, 80 (1975).
8. W. R. Fearon, *J. Biochem.* **33**, 902 (1939); L. E. Trimble and R. J. H. Voorhoeve, *Analyst* **103**, 759 (1978).
9. The Pd catalyst was a sponge, surface area 0.4 m^2/g, from United Mineral and Chemical Corp. (lot 34515). The Ir catalyst was a sponge, surface area 0.58 m^2/g, from Engelhard Industries, Newark, N.J.
10. R. J. H. Voorhoeve *et al.*, *J. Catal.* **45**, 297 (1976).
11. G. Herzberg and C. Reid, *Discuss. Faraday Soc.* **9**, 94 (1950); C. Reid, *J. Chem. Phys.* **18**, 1544 (1950).
12. During the initial contact of Pd with H_2 at room temperature, a rapid uptake of H_2 to an atomic ratio $H/Pd \approx 1$ was observed.
13. P. Klason, *J. Prakt. Chem.* **33**, 129 (1886); E. A. Werner and W. R. Fearon, *J. Chem. Soc.* **117**, 1356 (1920); D. H. Chadwick and E. E. Hardy, in *Kirk-Othmer's Encyclopedia of Chemical Technology*, A. Standen, Ed. (Interscience, New York, 1967), vol. 12, p. 50.
14. E. M. Smolin and L. Rapoport, *s-Triazines and Derivatives* (Interscience, New York, 1959), pp. 25 and 34.
15. American Cyanamid Co., British Patent 598, 175 (12 February 1948).
16. R. N. Mesiah, in *Kirk-Othmer's Encyclopedia of Chemical Technology*, A. Standen, Ed. (Interscience, New York, 1969), vol. 20, p. 662.
17. J. Liebig and F. Wohler, *Ann. Phys. (Leipzig)* **20**, 393 (1830).
18. We thank D. J. Freed for the infrared spectra of HNCO in CCl_4 solution.

5 July 1978

Phagocytosis of Light- and Dark-Adapted Rod Outer Segments by Cultured Pigment Epithelium

Abstract. *Pigment epithelial cells in culture retain their ability to phagocytize rod outer segments. These cells phagocytize rod outer segments isolated from light-adapted rats, or from dark-adapted rats killed after the time at which the lights would normally be turned on. However, they phagocytize far fewer rod outer segments prepared in the dark from the retinas of rats killed before the onset of the normal light cycle. Phagocytosis of dark rod outer segments is variable, but that of light outer segments is reproducible. It is postulated that the effect of light is to synchronize the chemical events that occur at the surface of the rods to prepare them for phagocytosis. These processes also occur in the dark, but more slowly and irregularly than in the light.*

Vertebrate rod photoreceptor cells continually renew their outer segments by a balanced process of synthesizing new disks at the base of the outer segment and shedding packets of disks from the tip of the outer segment. These shed packets of disks are subsequently phagocytized by the adjacent pigment epithelial cells to form phagosomes, which are degraded by hydrolytic enzymes contained within the lysosomes of these cells (*1*).

It has recently been reported that the shedding of disks in rats and frogs is coupled to the light-dark cycle in which the animals are kept. In the rat retina a burst of rod outer segment (ROS) disk shedding occurs soon after the onset of light. However, the same process occurs at the same time without the onset of light, suggesting that disk shedding in this animal follows a circadian rhythm (*2*). In frogs it appears that most disk shedding is directly initiated by light, although cyclic shedding does occur at a reduced level when animals are kept in constant darkness for prolonged periods (*3*).

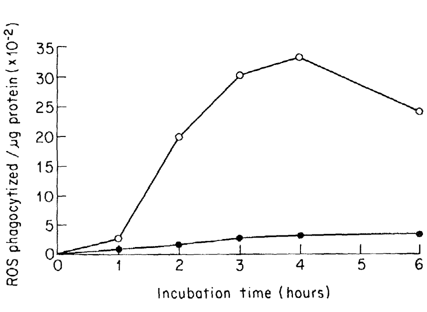


Fig. 1. Phagocytosis of ROS by PE cells. The ROS were isolated from rats killed (●) 60 minutes before the onset of light or (○) 30 minutes after the lights were turned on, and incubated with monolayer cultures of PE cells for the indicated periods. Each culture well received 2×10^6 ROS containing a measured amount of radioactivity. From the total radioactivity phagocytized by the monolayers, it was possible to calculate the number of ROS phagocytized at each time point.

Rod outer segment tips are not phagocytized by the pigment epithelium (PE) before being shed into the subretinal space. Since the phagocytic response of the PE cells appears to be triggered by this shedding, some chemical change must occur to the tip of the ROS that allows the PE to recognize the shed packet of disks as foreign and thus to initiate phagocytosis (*4*). This recognition must involve the plasma membranes of the shed outer segment fragments and the PE, and thus it is most probable that the plasma membrane of the ROS is chemically modified either before or just after shedding of a packet of disks.

To explore this problem, I examined the ability of PE cells grown in tissue culture to phagocytize ROS isolated at various times during the lighting cycle. I found that light acts as a trigger to prepare the ROS for phagocytosis by the PE.