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HNO as an Intermediate in the Catalytic Reduction of Nitric Oxide

The catalytic reduction of nitric oxide with hydrogen has been reported by several workers (*1–5*). Most of these investigations have been carried out at or above room temperature, the reduction products being reported as water, ammonia, nitrogen, or hydroxylamine. More recently, Kokes (*5*) has studied the reduction of nitric oxide with hydrogen on an alumina supported platinum catalyst over a wide range of temperatures. In these studies, it has been found that at low temperatures nitrous oxide is the main product with only traces of ammonia formed; however, ammonia formation increases with increasing temperature. At temperatures above 400°K only ammonia and water are found in the reduction products. It is assumed that hydrogen is activated on the platinum sites and migrates from particle to particle until encountering a nitric oxide molecule to form HNO, a well characterized species in the gas phase (*6*), the dimer of which has been found to be stable below 183°K (*7*). This initial HNO formation is followed by one of the subsequent steps.

$$(HNO)_2 \rightarrow N_2O + H_2O \qquad (1)$$

$$HNO + 2H_2 \rightarrow NH_3 + H_2O \qquad (2)$$

The high nitrous oxide yields at low temperatures might possibly be attributed to the stability of the dimer of HNO below 183°K. If this be true, the reaction products obtained from the reaction of hydrogen atoms with nitric oxide at low temperatures should be similar to those obtained for the catalytic system studied by Kokes. Preliminary studies (*8*) carried out on the addition of hydrogen atoms generated in the gas phase to nitric oxide physically adsorbed on silica gel at 77°K have shown this to be a particularly reactive system. This reaction has now been studied in more detail.

Method

The reaction vessel used has been extensively described elsewhere (*9*). The adsorbent, Cab-O-Sil M2 obtained from the Cabot Corporation, Boston, Massachusetts, was spread over the bottom of the flask to form a layer roughly 2 mm thick. A chromel-alumel thermocouple was inserted in the adsorbent to enable adjustment to the desired surface temperature during the adsorption and desorption process. In the following discussion, it will be assumed that θ is the volume of nitric oxide adsorbed at 77°K divided by the B.E.T. monolayer volume obtained from nitrogen adsorption. All gases were C. P. grade or better and were purified by standard gas purification techniques. Prior to each run, the Cab-O-Sil was outgassed at 400°C for 3 hr. In a typical run, the desired volume of nitric oxide was measured out and adsorbed on the surface at 77°K. Following adsorption, the liquid nitrogen dewar was adjusted so that the entire reaction vessel was immersed in liquid nitrogen. The reaction was then started by admitting hydrogen and letting it come into contact with a heated tungsten filament. The hydrogen atomizes on the hot filament and

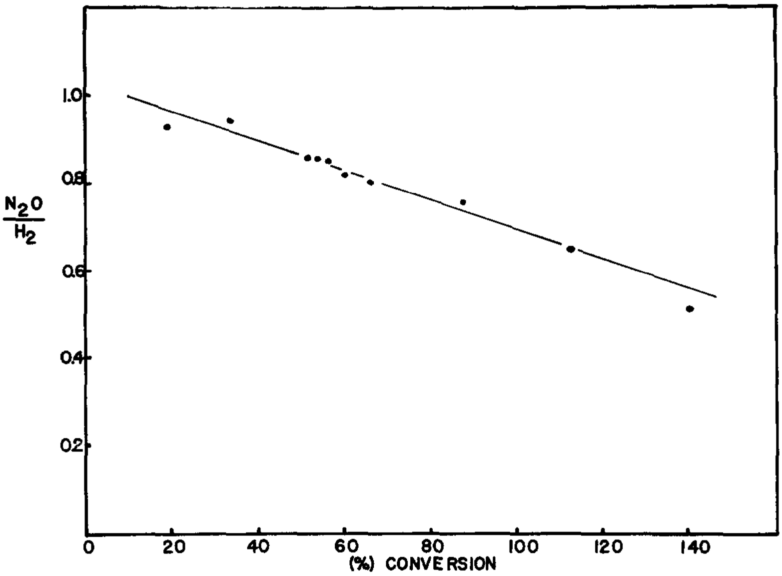

Fig. 1. Nitrous oxide hydrogen uptake ratio as a function of percent conversion; $V_m = 242$ μmoles, $\theta_{NO} = 0.09 \pm 0.01$. Tungsten filament temperature, 1700°K. Reaction temperature, 77°K.

diffuses to the surface where reaction occurs. Following reaction, the products were analyzed for nitrous oxide by gas chromatography, nitrogen and water being identified indirectly. An analysis of the condensable fraction carried out on a mass spectrometer showed no ammonia in the products.

Results and Discussion

The presence of noncondensables in the gas phase plus the fact that hydrogen up-

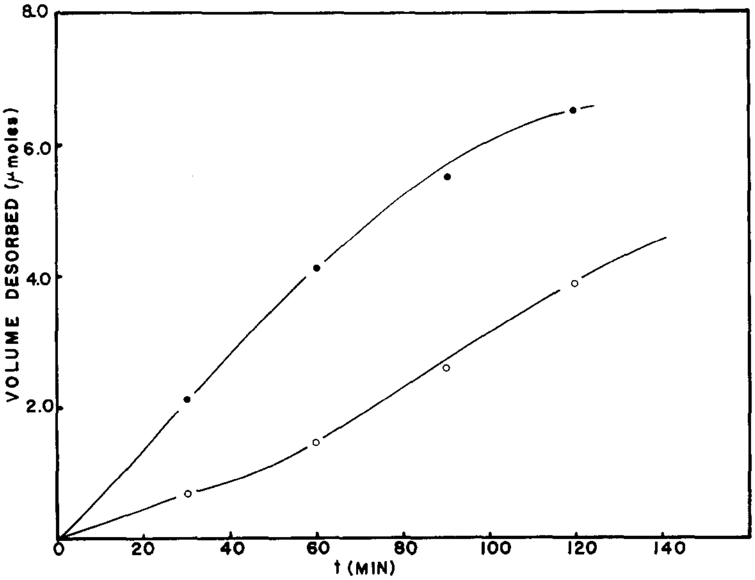

Fig. 2. Volume of N_2O desorbed as a function of time: ○ addition product; ● pure N_2O. Desorption temperature 153°K.

take in excess of that required for 100% conversion of nitric oxide to nitrous oxide could be obtained led us to believe that the reaction

$$(HNO)_2 + 2H \rightarrow 2H_2O + N_2 \qquad (3)$$

was occurring in addition to reaction (1). The presence of nitrogen was also confirmed mass spectrometrically. In order to study the extent of this reaction, the ratio of nitrous oxide to hydrogen uptake as a function of per cent conversion was obtained (100% being defined as the stoichiometric amount of hydrogen required to convert the nitric oxide to nitrous oxide with no nitrogen formation). The results are shown in Fig. 1. This ratio approaches unity at low conversions and decreases steadily as the conversion is increased, thereby showing an increase in nitrogen formation. The possibility that reaction (1) occurs at 77°K and that the nitrous oxide formed reacts further with the hydrogen atoms to yield nitrogen according to the equation

$$N_2O + 2H \rightarrow N_2 + H_2O \qquad (4)$$

was precluded, as adsorbed nitrous oxide exposed to hydrogen atoms showed no reaction. To investigate the stability of the intermediate, a series of desorption rates on the addition product and nitrous oxide was made. In these studies, the reaction was carried out to a predetermined percent conversion. Following reaction, the liquid nitrogen dewar was rapidly replaced by an ethanol-liquid nitrogen slush bath at 153°K. The desorption products were collected in a liquid nitrogen trap and the volume of nitrous oxide desorbed was measured periodically. These desorption rates were compared to those obtained for an equivalent amount of nitrous oxide adsorbed on the Cab-O-Sil. In one case the desorption products including water were readsorbed and the rate of desorption was determined. There was no significant difference between this rate and that for pure nitrous oxide in the absence of water. The results, shown in Fig. 2, show that the rate of desorption of adsorbed nitrous oxide is much faster than that for the addition product. Presumably this is due to the stability of the intermediate which must undergo reaction prior to desorption. These data suggest that the intermediate is most likely the dimer of HNO and that nitrous oxide is formed on warm-up. The high yields of nitrous oxide at low temperatures in the catalytic reduction of nitric oxide are probably due to the stability of $(HNO)_2$, a likely precursor to the formation of N_2O.

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