Although no effect of particle ejection from times earlier than 45 days before perihelion could be detected, the dust emission rate nearer the perihelion became apparently large enough to dim the solar illumination of the nucleus.

3) Initial particle velocities, v_d (in kilometers per second), can be approximated by

$$v_d = \frac{0.80}{1 + 0.38\, r\, (1 - \mu)^{-1/2}}$$

where $1 - \mu$ is the particle acceleration caused by the solar radiation pressure (in units of the solar gravity). Comparison of the observed v_d with that predicted in Probstein's theory (*2*) indicates that the drag force must have essentially been due to water vapor, that the ratio of the rate of emission of dust to the rate of emission of gas at the time of observations was about 0.5, and that the radius of the nucleus of Comet Bennett was about 2.6 km. Furthermore, the production rate of molecules with a molecular weight of 18 at 1 astronomical unit from the sun (extrapolated from the working solar distance of ~ 0.6 astronomical unit with the use of the r^{-2} law) is 4×10^{17} molecule cm^{-2} sec^{-1}, which compares most favorably with the theoretical rate of vaporization of water snow, calculated from the energy balance equation (*3*).

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Isocyanate Intermediates in Ammonia Formation over Noble Metal Catalysts for Automobile Exhaust Reactions

Abstract. *Isocyanate species have been detected on the surface of noble metal catalysts during the reactions of carbon monoxide with nitric oxide. The intensity of the surface isocyanate infrared band correlates with the known ammonia-forming tendencies among the noble metals. The discovery of this isocyanate species suggests a new mechanistic pathway to the ammonia formed during catalytic reduction of nitrogen oxides in automobile exhaust.*

Recent interest in the chemistry of nitric oxide reduction in automotive exhaust gas (*1–3*) has prompted study of the infrared spectra of species adsorbed on the surface of noble metal catalysts during the reaction of NO with CO. When reaction mixtures of CO, NO, and N_2 were contacted with catalysts consisting of noble metals on alumina at elevated temperatures, very strong infrared absorption bands were observed in the region from 2260 to 2270 cm^{-1}. After a number of auxiliary experiments, including some in which ^{15}NO was used, it was concluded that these intense bands are due to

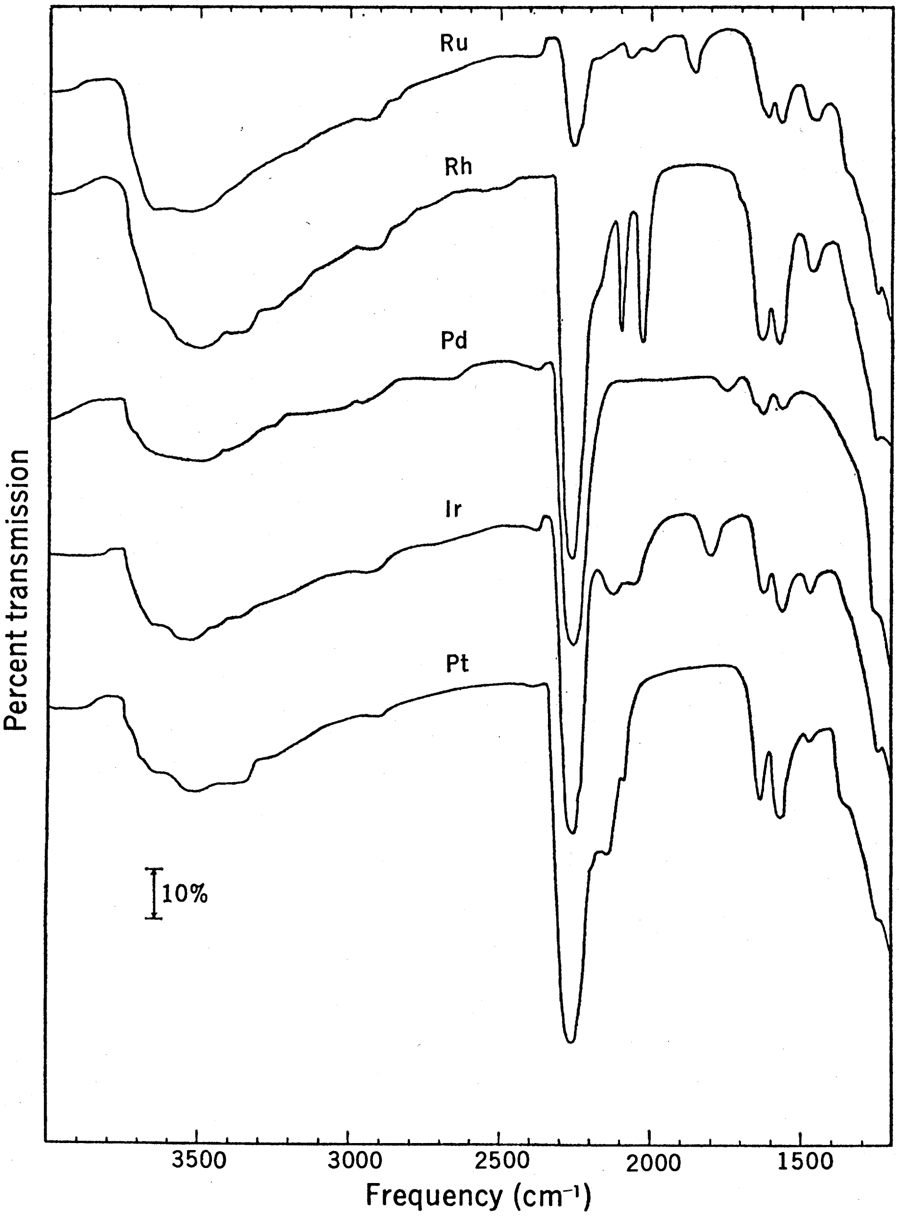

Fig. 1. Spectra observed at room temperature and a pressure of 1 torr after dosing the clean sample of noble metal (5 percent) on Al_2O_3 with 100 torr of a blend containing CO (10 percent), NO (5 percent), and N_2 (85 percent) at 400°C.

Table 1. Major bands as shown in Fig. 1; the numbers are frequencies, in reciprocal centimeters. The assignments in parentheses are considered tentative.

Metal	-NCO	(NCO^-)	-CO	-CO	-NO	(-NH_3)	(CO_3^{2-})	CO_3^{2-}
Ru	2259	2238	2070	2009	1856	1620	1568	1457
Ru*					1882	1610	1575	1536
					1861			1445
					1715			
Rh	2269	2175	2106	2036		1633	1570	1466
Pd	2264				1751	1635	1571	
Ir	2267	2239	2126	2050	1807	1627	1568	1475
Pt	2267	2148	2090			1631	1570	1465

* Spectrum not shown in Fig. 1. This was the same sample after it had been heated under a variety of gases a number of times. The experiment was identical, but it is obvious that the sample has changed. The Ru/Al_2O_3 was the only sample which changed under repeated experiments.

surface isocyanate (-NCO) species and that, in the presence of water, these species can be intermediates in the formation of ammonia. The route usually postulated (*3*) for ammonia formation over automobile exhaust catalysts involves the reduction of NO by the molecular hydrogen normally found in the exhaust or by the molecular or atomic hydrogen formed through the water-gas shift reaction ($CO + H_2O \rightleftarrows CO_2 + H_2$). The results reported here suggest a new mechanistic pathway to ammonia formation involving previously unreported isocyanate intermediates. The results do not permit one to assess the relative participation of the isocyanate route as compared to the hydrogen reduction route to ammonia formation in a practical automotive emission control system. A correlation between the relative intensity of the surface isocyanate band and the ammonia-forming tendencies among the various noble metals has been observed, although the significance of this correlation has not yet been established.

The infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer equipped with ordinate and abscissa scale expansion. The instrument was calibrated against polystyrene film, and the accuracy of the reported peaks is ± 2 cm^{-1} for very sharp bands and ± 5 cm^{-1} for the broader bands. A quartz cell similar to that described by Peri and Hannan (*4*) was used in conjunction with a conventional vacuum and gas handling system capable of evacuation to 10^{-6} torr. The samples can be moved from the heated section of the cell into the infrared beam without opening the cell. The alumina used in these studies, "Baymal" (*5*), was chosen because it is possible to cast a smooth film of the material plus an appropriate noble metal salt onto a smooth CaF_2 disk from an aqueous dispersion. Further, air-drying and subsequent vacuum calcination at 400°C does not usually cause severe loss of the sample through flaking. Because of the small diameter of the fibrils (*5*), transmission of the infrared beam is quite good. The Pt and Ir samples were prepared from chloroplatinic acid and iridium trichloride, respectively, while the Rh, Ru, and Pd samples were prepared from the corresponding nitrate salts. Each sample contained a nominal 5 percent (by weight) of the metal on alumina after calcination and had a thickness estimated as 1.0 to 1.5 mg/cm^2. All spectra were obtained at a sample temperature of $\leqq 50°C$ and a pressure of 1 torr after the cleaned (*6*) sample was contacted at 400°C with 100 torr of the gas or gas mixture for a period of 30 minutes.

The spectra obtained for Ru, Rh, Pd, Ir, and Pt samples after treatment at 400°C with 100 torr of a gas mixture of CO (10 percent), NO (5 percent), and N_2 (85 percent) are shown in Fig. 1. The locations of the major band centers and tentative assignments are given in Table 1. The main feature is the very intense band located at 2260 to 2270 cm^{-1} for each metal. In assigning this band to a surface isocyanate, facts learned from several other experiments were taken into account. For example, reference spectra, obtained under similar conditions, of adsorbed NO, CO, NO_2, N_2O, or CO_2 failed to produce the 2267-cm^{-1} band, so that it cannot be attributed to the chemisorption of any of the reactant or product molecules. Experiments in which the reaction mixture was contacted with the catalyst at various temperatures showed that the species is not formed until about 300°C. Experiments in which the proportions of the reactants were varied showed that when gas blends with equimolar or excess NO were used the intense bands in question were not observed. A frequency of 2267 cm^{-1} is reasonable for an isocyanate species since it is known that organic isocyanates have extremely intense characteristic absorptions at 2269 ± 6 cm^{-1} (*7*).

The most revealing experiments involved the use of ^{15}NO in the reaction mixture. For the Pt sample, isotopic shifts to lower frequencies of 15 and 17 cm^{-1} were found for the bands at 2267 and 2148 cm^{-1}, respectively. These shifts are very close to the ^{15}N shift of 17 cm^{-1} observed by Maki and Desius (*8*) for the ν_3 absorption of a cyanate ion in a KI host lattice, and therefore confirm the presence of nitrogen in the surface species and are good evidence for their assignment as isocyanate species. The isotope shift data also tend to rule out the -C≡N species since $KAu(CN)_2$ (*9*) and $Hg(CN)_2$ (*10*) both show ^{15}N shifts of 31 cm^{-1}. The possibility of an NO^+ species was also considered but was ruled out because of the absence of the 2267-cm^{-1} band in NO reference spectra, the isotopic shift data, and the irrationality of making NO^+ formation dependent on the presence of CO.

The discovery of a surface isocyanate species raises questions about the mechanism of its formation. For example, the initial step may be the dissociation of the NO molecule on the surface, and this may be followed by attack of a CO molecule to form -NCO; alternately, the breaking of the NO bond may be directly assisted by the attack of a CO molecule to form a surface nitride species, which then reacts with CO to form -NCO. It is, of course, not possible to determine the mechanism of surface isocyanate formation from the work reported here. However, once isocyanate is formed, the following reactions are possible in the presence of water:

$$MNCO + H_2O \rightarrow MOH + HNCO \qquad (1)$$

$$HNCO + H_2O \rightarrow H_2NCOOH \rightarrow NH_3 + CO_2 \qquad (2)$$

Here M stands for Ru, Rh, Pd, Ir, or Pt. In line with the consideration of reactions 1 and 2, an experiment was conducted in which the species giving rise to the bands at 2267 and 2148 cm^{-1} were formed on the Pt/Al_2O_3 sample by the NO + CO reaction. Then, at room temperature, 5 torr of water vapor was admitted to the sample cell and equilibrated for 30 minutes; the cell was then evacuated to $\leqq 0.01$ torr, and a spectrum was obtained. It was found that the 2148-cm^{-1} band was completely removed and the 2267-cm^{-1} band was sharply reduced in intensity. These observations are in accordance with the known sensitivity of isocyanates to hydrolysis. The net result of reactions 1 and 2 is to provide a pathway to NH_3 in mixtures of NO, CO, and H_2O which does not involve molecular hydrogen, whether it is already in the stream or generated in situ over the catalyst by means of the water-gas shift reaction.

It is now known that Ru, of all the noble metals, is unique in its ability to remove NO from automobile exhaust without producing large amounts of ammonia (*2*). Reexamination of Fig. 1 will show that the isocyanate band is much weaker for Ru than for any of the other noble metals. Further, the isocyanate species on Ru could only be found on freshly prepared samples (see Table 1). These observations also correlate with the unique ability of Ru to switch between two metastable states one of which gives significant amounts of ammonia and one of which does not (*2*). The low ammonia-forming tendency of Ru can be due either to its ability to promote NO reduction without appreciable ammonia formation, or to its ability to promote facile decomposition of any ammonia formed. The observations (*2*) that "reduced" ruthenium gives low ammonia formation even at temperatures as low as 300° to 350°C whereas the same catalyst promotes appreciable ammonia decomposition only at temperatures above 400°C indicates that the ammonia decomposition route to low ammonia cannot be invoked under all conditions.

In reactor studies in our laboratory it has been observed that reaction mixtures containing NO, CO, and H_2O (no H_2) gave ammonia formation over a noble metal catalyst. Under similar conditions, a mixture containing CO and H_2O (no NO or H_2) gave no appreciable water-gas shift reaction over the same catalyst. Under these conditions, it seems possible that the observed ammonia formation may be due to the isocyanate mechanism. The situation in actual automobile exhaust is quite complex, and it is impossible from the spectral results alone to assess the relative contribution of the isocyanate mechanism to ammonia formation. Actual exhaust often contains both H_2 and CO, so that hydrogen reduction, CO reduction, and isocyanate mechanisms of NO reaction are competing. Moreover, nonequilibrium reaction conditions exist in a federal CVS (constant volume sampling) test, so that both the gas composition and the catalyst temperature are varying during a particular test and are, in addition, affected by parameters of the vehicle system that vary from one vehicle to the next. The results reported here indicate the existence of a previously unreported mechanism to ammonia formation over noble metal catalysts, and it will require additional work to determine the relative importance of this mechanism under the actual conditions encountered in a practical vehicle emission control system.

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Adenosine 3′,5′-Monophosphate in Pancreatic Islets: Glucose-Induced Insulin Release

Abstract. *Glucose-induced release of insulin from perifused rat islets is associated with elevated islet adenosine 3′,5′-monophosphate. If values for adenosine 3′,5′-monophosphate are compared to insulin release during theophylline or glucose stimulation and theophylline plus glucose stimulation, it suggests a minor role for adenosine 3′,5′-monophosphate in directly stimulating insulin release but a prominent role in modulating glucose-induced release of insulin.*

Intracellular regulatory phenomena in many endocrine systems are affected by adenosine 3′,5′-monophosphate (cyclic AMP) (*1*). Stimulation of insulin release by glucagon and inhibition by epinephrine are thought to be modulated by intracellular cyclic AMP (*2*). The following indirect evidence suggests that glucose-induced release of insulin also is in part influenced by perturbation of intracellular cyclic AMP. Infusion of cyclic AMP into the isolated perfused rat pancreas stimulates insulin release (*3*). Theophylline, a phosphodiesterase inhibitor, and glucagon, an adenyl cyclase stimulator, both elevate cyclic AMP and induce insulin release in the absence of glucose (*4*), and both potentiate glucose-induced release of insulin (*5*, *6*). Imidazole, an agent that decreases intracellular cyclic AMP by stimulating phosphodiesterase, inhibits glucose-induced release of insulin (*7*). It has also been demonstrated that if the terminal mechanisms of insulin release are inhibited, theophylline will only partially restore this release (*8*), which indicates that cyclic AMP has its mechanism of action before the final step of insulin release. Finally, direct evidence of glucose-induced increases in intracellular cyclic AMP in static islet incubation systems has been negative (*2*, *9*).

This report demonstrates elevated cyclic AMP during glucose stimulation in perifused rat islets, which suggests that cyclic AMP indeed may in part mediate glucose-induced release of insulin. Further observations suggest that cyclic AMP causes a synergistic action on this release.

Islets from fed Long-Evans male rats were isolated with collagenase and perifused at 37°C, according to the methods of Lacy (*10*). After a 35-minute stabilization period, stimulators were added and the perifusion was discontinued 2 or 20 minutes thereafter. Islets were removed from the perifusion chamber within 60 seconds and placed in boiling 1 m*M* theophylline for 10 minutes (*11*). The boiled extracts were centrifuged to remove particulate debris, lyophilized, and assayed in duplicate for cyclic AMP by a protein-binding radiodisplacement method (*12*). The perifusate was composed of 0.3 percent human serum albumin in phosphate-bicarbonate buffer (*p*H 7.4) containing 2.5 m*M* glucose, a concentration that does not stimulate phasic