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30 May 1975

Hydrogen Cyanide Production During Reduction of Nitric Oxide over Platinum Catalysts

Abstract. *The catalytic reduction of nitric oxide with carbon monoxide and hydrogen was studied with a bench-scale flow reactor at 400° to 800°C over platinum to determine the yield of hydrogen cyanide. An opto-acoustic infrared absorption technique was applied to the analysis of hydrogen cyanide. In mixtures of nitric oxide, carbon monoxide, hydrogen, and water vapor, with all concentrations in the range of 0.1 to 5 percent, up to 80 parts per million (ppm) of hydrogen cyanide is formed over platinum at 600° to 800°C. In the absence of water vapor, the hydrogen cyanide concentration rises to 700 ppm. With 6 to 60 ppm of sulfur dioxide in the gas mixture, hydrogen cyanide production is suppressed to less than 5 ppm. No significant differences were found between a platinum sponge and platinum supported on cordierite. The implications of our results for the catalytic treatment of automotive exhaust are examined.*

The chemistry of NO at low concentrations is of importance in atmospheric chemistry and in air pollution abatement. For these reasons, we have measured the kinetics of the reactions of NO with CO and H over metallic (*1*) and oxidic (*2*) catalysts, employing synthetic mixtures of the pure compounds diluted with He and using bench-scale catalytic flow reactors. For similar reasons, we have developed selective and sensitive opto-acoustic (OA) infrared absorption techniques, using tunable (*3*) and fixed-frequency lasers (*4*). In the work reported here we combined these techniques to study the formation of HCN in synthetic mixtures of NO, CO, H_2, H_2O, and SO_2 diluted with He (when reduced over Pt catalysts at 400° to 800°C). The choice of the Pt catalyst was based on the following considerations.

Abatement of automotive exhaust emissions in the United States relies heavily on the use of catalytic converters in which CO and hydrocarbons are oxidized to CO_2 and H_2O (*5*). Presently used catalysts contain Pt as the active ingredient. They operate predominantly under net *oxidizing* conditions. However, under some driving modes, net *reducing* conditions may prevail, for example, in deceleration or downhill coasting. Indeed, H_2S derived from the reduction of SO_2 in the exhaust has been observed during such transients (*6*, p. 92). Future application of catalytic converters for the reduction of NO_x (oxides of nitrogen) is a strong possibility, especially in the remainder of this decade (*5*). In some proposed devices for NO_x reduction, a Pt catalyst is used in a reducing exhaust mixture as an oxygen scavenger upstream from the proper NO_x catalyst (*6*, p. 41). We have recently observed HCN in the reaction products from the reduction of NO by CO and H_2 in synthetic gas mixtures over Pt catalysts. In the following we describe the identification of HCN by gas chromatography (GC), mass spectrometry (MS), highly selective infrared (IR) absorption, and chemical analysis. Also, we report the parameters affecting the yield of HCN, such as temperature, gas composition, and flow rate (*7*).

The Pt catalysts used included a gently crushed honeycomb catalyst (Pt-I) containing approximately 0.2 percent Pt (by weight) on an alumina wash coat on cordierite support (*8*). The Pt area per gram of catalyst Pt-I was 0.07 m^2, as determined by chemisorption of H_2 (*9*). The other catalyst used was a Pt "sponge" (Pt-II) with a specific surface area of 0.12 m^2/g, as determined by the BET (Brunauer, Emmett, and Teller) N_2 adsorption technique (*9*). The HCN was produced in a continuous-flow, fixed-bed quartz reactor, when mixtures of CO (3 to 5 percent), NO [1500 to 3000 parts per million (ppm)], H_2 (0.2 to 0.5 percent), H_2O (0 to 4 percent), and SO_2 (0 to 60 ppm) diluted with He were passed through the catalyst, which was supported by a porous quartz disk. Automatic sampling of the effluent at 15-minute intervals was coupled with on-line injection into two gas chromatographs. In one gas chromatograph, incorporating a 4.9-m Porapack R column at 109°C, HCN, NH_3, H_2O, and CO_2 were measured. The HCN was identified by the calibrated retention time and peak shape; HCN in He (approximately 1000 ppm) served for calibration (*10*). This method was applied only for low concentrations of H_2O in the effluent ($\leqq$ 0.5 percent) because of the reduced sensitivity for HCN in the presence of H_2O. The second gas chromatograph contained molecular sieve 13x and Porapack Q columns at 30°C for the separation of N_2, NO, CO, H_2, N_2O, and CO_2 in the dried effluent (*1*). For both gas chromatographs, thermal-conductivity detectors were used. Samples of the reactor effluent were analyzed and HCN was identified therein by MS, yielding peaks at a mass-to-charge ratio m/e of 26 and 27 (*11*). The identifications by MS and GC were not considered sufficient, since other compounds might fortuitously yield the same retention time in the gas chromatograph or the same peaks in the mass spectrometer. Therefore, in several instances, the effluent from the reactor was bubbled through an excess KOH solution to bind CO_2 and HCN for 16 hours and the solution was analyzed for CN^- by the Liebig method (*12*).

Table 1. Relative sensitivities for the detection of HCN and H_2O (normalized to power level on each of the laser lines) at a total gas pressure of 60 torr in the OA cell.

CO laser		OA signal	
Line	Frequency (cm^{-1})	HCN (1000 ppm)	H_2O (10000 ppm)
$P_{27-26}(12)$	1442.15	50.0	$<10^{-3}$
$P_{26-25}(15)$	1456.02	$<10^{-5}$	4.8

Definitive identification and quantitative determination of HCN were made by IR absorption with OA detection. The effluent gas flowed continuously through the OA cell, which was connected to the reactor by stainless steel tubing. The IR detection of minute concentrations of pollutant gases has recently been studied with both tunable-frequency (*3*) and fixed-frequency (*4*) IR lasers. Detection of HCN, however, is difficult, especially in the presence of high concentrations of H_2O vapor, because of the relative inaccessibility of the IR active fundamental vibrational bands of HCN. The ν_2 fundamental centered at ~712 cm^{-1} (*13*) and the ν_3 fundamental centered at ~3312 cm^{-1} (*14*) are in ranges where tunable lasers with continuous wave (cw) power output sufficient for OA spectroscopy are not available. The alternative, a dense packing of fixed-frequency laser lines, is also not available in these ranges (*15*). We have therefore used the coincidence of the HCN $2\nu_2$ absorption band at ~1411 cm^{-1} (*13*) with the fixed-frequency lines of a CO laser (*16*).

The weakness of the absorption due to the $2\nu_2$ band relative to that arising from

Table 2. Comparison of the analysis of the HCN content in the effluent from Pt catalysts as determined by different techniques.

Catalyst, temperature; gas mixture in He	Analysis* (ppm)			
	IR absorption	GC	Chemical analysis	MS
Pt-I, 709°C; NO, H_2, CO, H_2O	33†		(48)	
Pt-I, 695°C; NO, H_2, CO	700	(302)	(710)	
Pt-II, 633°C; NO, H_2, CO	175	(230)		(520)
Pt-I, 709°C; NO, H_2, CO	642	(590)		

*Figures in parentheses are semiquantitative only, because of tailing of the HCN peak in the gas chromatograph and sampling procedures used in MS and chemical analysis. In-line IR analysis proved very reliable, with better than 5 percent reproducibility. †Measured at slightly lower space velocity than the value of 48 ppm.

the ν_2 band is compensated by the density of CO laser lines in the 1400-cm^{-1} range. Moreover, the use of the CO laser has the additional advantage that H_2O (and other constituents of interest, if any) could be simultaneously monitored because of the numerous lines available. We found an extremely good match of the $P_{27-26}(12)$ CO laser line at 1442.15 cm^{-1} and the HCN $3\nu_2$-ν_2 R(12) line located at 1442.15 cm^{-1} (*17*). This was seen by observing the OA cell output signal induced by the absorption of the $P_{27-26}(12)$ CO laser line by the ~1000-ppm HCN (in He) sample as a function of total pressure.

Pressure-broadening caused by a total pressure of 1.33×10^4 pascals (Système International units: 1 newton/m^2 = 1 pascal $\approx 7.5 \times 10^{-3}$ torr) was found to be sufficient to give the strongest absorption of the CO P_{27-26} (12) laser line by the HCN 3 ν_2-ν_2 R(12) absorption line. We simultaneously measured the concentration of H_2O, using the CO $P_{26-25}(15)$ laser line at 1456.02 cm^{-1}. The relative sensitivities at a total pressure of 8000 pascals, normalized to power on each laser line for HCN and H_2O, are given in Table 1. From this matrix we see that for HCN concentrations down to 1 ppm, H_2O vapor concentrations of 10 percent could be tolerated. For actual measurements a minicomputer controlled the frequency of a grating-tuned CO laser, collected the data, and reduced the data to values representing HCN and H_2O concentrations (*18*).

Using the IR technique, we measured the formation of HCN as a function of the temperature of the catalyst for both Pt catalysts (Fig. 1). The correspondence between the four methods to determine HCN is illustrated by examples in Table 2. The yield was insignificant below 500°C, peaked at 710°C, and decreased substantially at 800°C. In this range, NO conversion was complete. The main product of the NO reduction was NH_3 at lower temperature ($\leq 600°C$) and N_2 at higher temperature ($> 750°C$). The composition of the inlet gas strongly influenced the yield of HCN. The effects of H_2O and of SO_2 are shown in Fig. 1. The yield of HCN for conditions relevant to auto exhaust (with H_2O) was a maximum of 80 ppm in the absence of SO_2 and less than 5 ppm (*18*) in the presence of 3.5 percent H_2O and 6 to 60 ppm SO_2 (*19*). The effects of H_2O and of SO_2 were reversible (*20*). In the absence of SO_2 and with less than 500 ppm of H_2O in the feed mixtures, the yield of HCN rose to a maximum of 700 ppm on catalyst Pt-I.

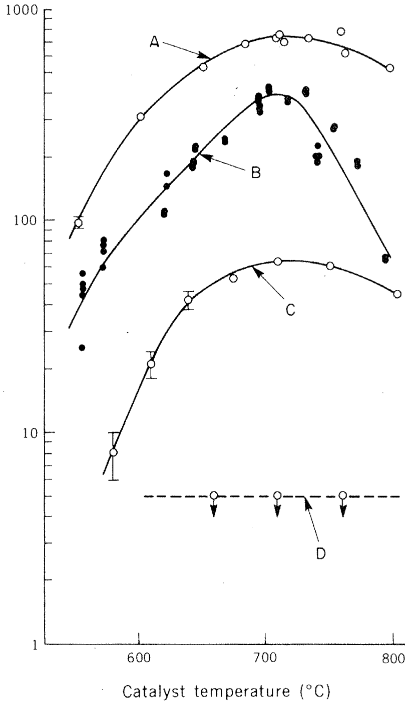

Fig. 1. Yield of HCN over Pt catalysts: curve A, dry mixture (5 percent CO, 0.5 percent H_2, 0.3 percent NO in He) at 4.8×10^5 ml m^{-2} $hour^{-1}$ over catalyst Pt-I (gently crushed PTX); curve B, same dry mixture at 2.3×10^4 ml m^{-2} $hour^{-1}$ over catalyst Pt-II ("sponge"); curve C, wet mixture (3.5 percent H_2O) at 3.8×10^5 ml m^{-2} $hour^{-1}$ over catalyst Pt-I; and curve D, upper limit of the HCN yield for wet mixture (3.5 percent H_2O, 6 to 60 ppm of SO_2) at 7.1×10^5 ml m^{-2} $hour^{-1}$ over catalyst Pt-I. Points for catalyst Pt-I are averages of eight to ten measurements with the mean deviation indicated. All measurements were made by IR absorption.

The effects of the partial pressures (p) of NO, CO, and H_2 in the inlet gas were studied at 710°C and 3.5 percent H_2O. At a constant p_{CO} (5 percent) and p_{H_2} (0.5 percent) the yield of HCN varied as $(p_{NO})^{0.3}$. At constant p_{NO} (0.3 percent) and p_{H_2} (0.5 percent) the yield varied as $(p_{CO})^{1.0}$, whereas at constant p_{CO} (5 percent) and p_{NO} (0.3 percent) the HCN yield varied as $(p_{H_2})^{1.0}$. The effect of H_2O was studied between 0 and 4 percent. On the basis of these data, some further reduction of the HCN yield is expected between 4 and 10 percent H_2O, a range that was inaccessible with our catalytic test equipment. For a dry mixture, the reduced space velocity (flow rate of gas over the catalyst per square meter of catalyst surface area) had little effect beyond 2×10^5 ml m^{-2} $hour^{-1}$, when NO was completely converted (710°C, 0.3 percent NO, 5 percent CO, 0.5 percent H_2). For a wet inlet mixture the HCN yield *increased* with flow rate from 60 ppm at 3.5×10^5 ml m^{-2} $hour^{-1}$ to 78 ppm at 7.1×10^5 ml m^{-2} $hour^{-1}$ (710°C, 0.3 percent NO, 5 percent CO, 0.5 percent H_2, 3 to 4 percent H_2O). The latter flow rate corresponds to a gas hourly space velocity of 37,000 $hour^{-1}$ (milliliters of gas per milliliter of honeycomb per hour) for an intact PTX honeycomb. At low space velocities, the HCN yields decreased, possibly indicating conversion of HCN at longer residence times.

In this complicated gas mixture, under conditions of total NO conversion, we can only speculate about the mechanism of HCN formation. However, on several noble metal and other metal catalysts, isocyanate groups, NCO, have been observed by IR absorption techniques (*21*), whereas thermal desorption data have indicated stable chemisorption layers with chemisorbed N/CO ratios of ≈ 1 (*7*). In addition, we have observed the formation of $(CH_3)_2NH$, tentatively identified by GC in the dry gas mixture. These results suggest that coupling of the C and N atoms on the surface takes place rather readily. The further reactions of the CN or NCO species presumably depend on the temperature and the composition of the gas.

The implications of our results for the use of catalytic conversion of automotive exhaust deserve some comment. We cannot state whether HCN forms when, under *reducing* conditions, actual exhaust is fed over Pt catalysts, since the composition of exhaust is more complicated than that of our feed mixtures (*22*). However, on the basis of our results, HCN formation over Pt under *reducing* conditions appears possible in the catalyst temperature range from 600° to 800°C, in the absence of SO_2 (*23*). Removal of SO_2 from the exhaust may enhance HCN production to significant concentrations (*24*). In view of the toxicity (*25*) of HCN, the determination of HCN in catalytically treated automotive exhaust is recommended. A much more comprehensive analysis of the effects of catalytic exhaust treatment than heretofore reported is warranted, since other potentially hazardous compounds may be found. For instance, in the present study, in addition to HCN, COS and $(CH_3)_2NH$ were tentatively identified (by GC) as components of dry reactor effluents.

R. J. H. VOORHOEVE
Bell Laboratories,
Murray Hill, New Jersey 07974
C. K. N. PATEL
Bell Laboratories,
Murray Hill and *Holmdel, New Jersey*
L. E. TRIMBLE
R. J. KERL
Bell Laboratories, Murray Hill

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7. A paper detailing the results of kinetic and thermal desorption data for Pt and other catalysts will be published elsewhere (R. J. H. Voorhoeve, C. K. N. Patel, L. E. Trimble, R. J. Kerl, P. K. Gallagher, J. P. Remeika, in preparation).
8. The honeycomb catalyst was a PTX-3 catalyst obtained from Engelhard Industries, Newark, N.J. The Pt sponge was from the same source.
9. The H_2 chemisorption measurement was made by E. Vogel with a Micromeritics model 2100D Orr surface area analyzer, following the method of C. R. Adams, H. A. Benesi, R. M. Curtis, and R. G. Meisenheimer [*J. Catal.* **1**, 336 (1962)]. The N_2 adsorption was measured by F. Schrey with a Perkin-Elmer Sorptometer.
10. The HCN in He was obtained from Scientific Gas Products, Inc. Lots with analyses of 1040 and 1010 ppm, respectively, were used. The analysis was carried out according to the wet chemical method of M. B. Jacobs [*Analytical Chemistry of Industrial Poisons, Hazards and Solvents* (Interscience, New York, 1949), pp. 451–457]; accuracy, ± 2 percent of component.
11. Measurements were made at Gollub Analytical Service, Berkeley Heights, N.J.
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17. A preliminary theoretical search based on the only available high-precision determination of the $2\nu_2$ HCN vibrational-rotational frequencies by Brim *et al.* (*13*) indicated additional coincidence between (i) the $P_{25-24}(10)$ CO laser line at 1472.91 cm^{-1} and the HCN $2\nu_2$ R(19) line at 1472.97 cm^{-1} and (ii) the $P_{24-23}(7)$ CO laser line at 1506.99 cm^{-1} and the HCN $2\nu_2$ R(30) line at 1506.98 cm^{-1}. This could not be confirmed experimentally, however.
18. For the experiments reported here the absolute values of HCN concentrations obtained from the IR measurements have error limits of ± [(5 percent of the quoted HCN concentration) ± 5 ppm]. Plans are under way to improve these limits significantly. Further experimental details of this measurement technique will be published elsewhere (C. K. N. Patel and R. J. Kerl, in preparation).
19. In the presence of H_2O, the water gas shift reaction $CO + H_2O = CO_2 + H_2$ converts about 34 percent of the CO at 710°C. In the presence of SO_2, the shift reaction is largely inhibited.
20. The effect of H_2O may be due to hydrolysis of a NCO intermediate. The inhibition by SO_2 is understandable on the basis of the negative effects of S on the hydrogenation activity of Pt. However, these are speculations, since the mechanism of the formation of HCN is not known.
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22. After completion of this work, we found that the formation of HCN at a concentration of 1 to 15 ppm in automotive engines has been reported by M. Kaneko [*J. Jpn. Soc. Air Pollut.* **8**, 327 (1973); *Air Pollut. Abstr.* **5**, 22 (Sept. 1974)] and by R. W. Hurn, J. R. Allsup, and F. Cox [*Rep. Environ. Prot. Agency 650/2-75-014* (Dec. 1974)]. The reports by Kaneko indicate that the use of a catalytic converter diminishes the HCN emissions. Kaneko's work was done under oxidizing conditions, whereas our report deals with HCN formation in reducing conditions. We thank J. G. Cohn and K. Aykan (Engelhard Industries, Menlo Park, N.J.) for pointing out Kaneko's work to us and R. L. Bradow (Environmental Protection Agency, Research Triangle Park, N.C.) for the reference to the paper by Hurn *et al.*
23. This could happen during the transient conditions mentioned before and also if Pt were used in a "rich" mixture, for example, for the proposed use of Pt as an oxygen scavenger for a reducing Cu-Ni-Cr catalyst [see (*6*), p. 41]; temperatures of 600° to 800°C are within the normal operating range for both oxidation and reduction catalysts [see (*6*), pp. 39–41].
24. We have at present no data regarding the question of whether HCN is produced over other noble metal catalysts and, if so, whether that production is similarly suppressed by SO_2. Removal of S from gasoline has been proposed as a method of eliminating H_2SO_4 emissions caused by Pt catalysts.
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26. We thank C. A. Lambert for her help with the use of the computer; P. K. Gallagher, E. Vogel, and F. Schrey for determinations of surface areas by N_2 and H_2 adsorption; and J. P. Remeika for helpful discussions.

27 May 1975; revised 27 June 1975

The Cation $H_{13}O_6^+$: A Short, Symmetric Hydrogen Bond

Abstract. *The* $H_{13}O_6^+$ *ion has been found to exist as a discrete entity, forming when the cage compound* $[(C_9H_{18})_3(NH)_2Cl]^+Cl$ *is crystallized from hydrochloric acid solution. The aquo-cation* $H_{13}O_6^+$ *has crystallographic symmetry* 2/m (C_{2h})*. The central bond* $O \cdot\cdot H \cdot\cdot O$ *is symmetric, with a length of 2.39 ± 0.02 angstroms; the four outer hydrogen bonds are asymmetric, with a length of 2.52 ± 0.01 angstroms. The cage compound consists of a chloride ion encapsulated within a triply bridged diammonium species, with hydrogen bond distances* $N(H) \cdot\cdot Cl$ *of 3.10 ± 0.01 angstroms.*

As a serendipitous by-product of an investigation of the crystal structure of an interesting cage compound, we have identified and determined the structure of an unusual cationic species, $H_{13}O_6^+$, consisting of a cluster of six water molecules plus an additional H^+ ion.

The cage compound that we were investigating has been named "chloridekatapinato-*in*,*in*-1,11-diazabicyclo[9.9.9]nonacosanebis(ammonium)chloride"; it has the empirical formula $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$, and forms when a chloride ion is encapsulated within the "*in*,*in*-1,11-diazabicyclo[9.9.9]nonacosanebisammonium" ion (*1*). The compound was obtained from Drs. C. Park and H. E. Simmons (Central Research and Development Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware). When recrystallized from a 10 percent solution of HCl in water, it forms orthorhombic crystals, space group *Cmcm*, with unit cell dimensions $a = 15.73$ Å, $b = 9.46$ Å, and $c = 24.91$ Å; the unit cell contains four $[(C_9H_{18})_3(NH)_2Cl]^+$ ions, four $H_{13}O_6^+$ ions, and eight Cl^- ions. X-ray diffraction data were collected by θ–2θ scans (θ is the diffraction angle) to a maximum 2θ value of 100° (Cu$K\alpha$ radiation). The crystal was sealed inside a thin-walled glass capillary containing a water-saturated atmosphere. The structure was derived from Patterson and electron density maps and refined by full-matrix least squares to an R index

$$R = \frac{\Sigma \left| |F_{obs.}| - |F_{calc.}| \right|}{\Sigma |F_{obs.}|}$$

(where $F_{obs.}$ and $F_{calc.}$ are, respectively, the observed and calculated structure factors) of 0.086 for the 524 reflections having intensities greater than 3 standard deviations (σ) above background, an R index of 0.123 for the 879 reflections having positive net intensities, and a goodness of fit

$$\left(\frac{\Sigma \left[\frac{F_{obs.}^2 - F_{calc.}^2}{\sigma\ (F_{obs.}^2)} \right]^2}{(n-p)} \right)$$

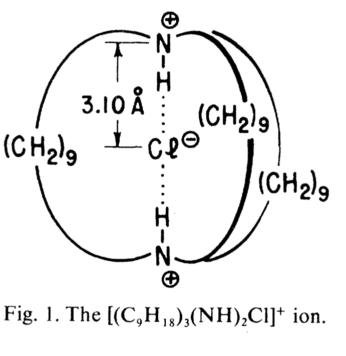

Fig. 1. The $[(C_9H_{18})_3(NH)_2Cl]^+$ ion.