Inhibition of Hydrocyanic Acid Evolution from Polyurethanes during Oxidative Degradation*

H. H. G. JELLINEK, A. CHAUDHURI,** and K. TAKADA***

Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

(Received September 17, 1977)

ABSTRACT: It has been shown that the evolution of hydrocyanic acid during the thermal oxidative degradation of aliphatic and aromatic polyurethanes is inhibited by metals such as Cu and Co powders, their oxides, and decomposable compounds. Other metals are much less efficient inhibitor. The inhibition efficiency also depends on the degree of dispersion. Cu or its oxides and decomposable compounds are the most powerful inhibitors; very effective are copper films (400 to 1000-Å thick) deposited on polymer films. It is shown that HCN evolved from NaCN is catalytically decomposed in an air stream; if the velocity of such a stream is low and the HCN concentration is small, then the main decomposition product is N_2 (ca. 90%) plus small amounts of nitrogen oxides, H₂O, and CO₂. The catalytic decomposition reaction of HCN evolved from polyurethanes is exactly analogous to that for NaCN, i.e., at low air flow rates and low HCN concentrations mainly N_2 is the decomposition product. The results obtained for HCN evolved from NaCN agree well with those of previous workers. It can be definitely concluded that the inhibition by copper of HCN evolution from polyurethanes and other nitrogen containing polymers is not due to a change in the oxidative degradation mechanism of the polymers but is due to the catalytic decomposition of HCN evolved from polymers.

KEY WORDS Oxidative Degradation / Hydrocyanic Acid / Polyurethenes / Copperoxide Catalysis / Inhibition /

The kinetics and mechanism of the evolution of hydrocyanic acid from aliphatic and aromatic polyurethanes during oxidative degradation have recently been investigated by Jellinek and Takada.¹ During this work it was found that copper powder and easily decomposable copper compounds dispersed in the polymer films inhibit the evolution of hydrocyanic acid almost completely during the thermal oxidation of the polymers. Other metals and metal compounds are less efficient for this inhibition process. In the present paper the mechanism of this inhibition reaction has been studied. It emerges that HCN, as soon as it is evolved from the polymer, is catalytically oxidized and decomposed. About fifty years ago this catalytic oxidation of HCN was investigated by various authors.²⁻⁴ It is shown here that the mechanisms of inhibition of HCN evolution from polymers agrees well with the catalytic oxidative decomposition mechanism of HCN. The results obtained by modern methods such as chromatography and measurements by specific ion electrodes are in accordance with results obtained in the past.

EXPERIMENTAL

Materials

Polyurethanes were prepared (1) from tetramethylene glycol and diisocyanate in solution according to Marvel and Johnson⁵ (linear aliphatic polyurethane) and (2) from tetramethylene glycol and methylene bis(4-phenylisocyanate) according to Lyman⁶ (linear aromatic polyurethane). The polymers were, after purification, thoroughly dried

^{*} Paper Presented at 26th International Congress, IUPAC, Tokyo, September 4–10, 1977.

^{**} Present Address: Research Laboratories, American Cyanamide Co., New Jersey, U.S.A.

^{***} Present Address; Research Center, Sanyo Chemical Industries Ltd., Kyoto, Japan.

under high vacuum ($\langle 10^{-5}$ torr) at 50°C for at least 72 hr.

APPARATUS AND TECHNIQUES

The principle of the degradation techniques was as follows. An air stream was passed over the polymer film heated to the desired temperature. This stream was then led into a 1-N NaOH solution where all of the HCN gas was absorbed and transformed to NaCN. The concentration of $CN^$ ions was continuously monitored with a specific CN^- ion electrode (Orion Inc.). The respective e.m.f. values were reproducible within ± 5 mV (depending somewhat on the total CN^- ion concentration) or 2% to 5%. Plotting data *vs.* time averages them and makes them more accurate.

The quartz reaction vessel for this thermal oxidative degradation of polymer films (usually 15 μ thick; at these thicknesses diffusion control by O₂ is negligible¹) is shown in Figure 1. It is provided with a gas inlet (A) and outlet (B); its diameter is 6 cm. All joints connecting this vessel to the rest of the apparatus assembly were at least 6 cm removed from the hot surface of the liquid metal bath (Pb/Sn 1: 1 by weight) into which the vessel is eventually immersed. The temperature of the thermostated bath was constant to $\pm 0.5^{\circ}$ C. The vessel was completely submerged in the liquid metal bath at time t=0; its bottom was touched by the point of a chromel-alumel thermocouple and the temperature indicated was taken as the reaction temperature.

A polymer film was deposited at the bottom of this reaction vessel as follows. Usually a solution of 50 mg to 100 mg of polymer was prepared (in freshly distilled *m*-cresol for the aliphatic polyurethane and in DMF for aromatic polyurethane). This solution was slowly evaporated in the reaction vessel; a film of 15 μ (50 mg) thickness was formed; it was thoroughly dried under high vacuum (10⁻⁵ torr or better) for at least 72 hr.

Metal powder was mixed into the polymer solution before evaporation for the inhibition experiments; also easily decomposable metal compounds were used in a number of cases. Some experiments were performed with copper films vacuum deposited on polymer films. These were oxidatively heated in a tube furnace (see Figure 2). The thickness of these copper metal films was between 400 A to 1000 A.

The metal and corresponding polymer films were



Metal bath

Figure 1. Apparatus assembly for monitoring HCN evolution: A, reaction vessel; B, inlet of reaction vessel; C, outlet of reaction vessel; D, connection tube; E, metal bath; F, thermocouple, G, absorption bottle; H, absorption medium; I, cyanide electrode; J, reference electrode; K, thermistor; L, heater; M, stirrer; N, polymer film.



Inhibition of Hydrocyanic Acid Evolution from Polyurethanes

Figure 2. Apparatus assembly for studying the effect of thin copper films on inhibition of HCN from polyurethanes.

prepared as follows: aliphatic polyurethane was taken for these experiments. A few drops of a 5% by weight of polymer solution in DMF were placed on a microscope slide $(24 \times 50 \times 2 \text{ mm})$. The solution was spread over the whole surface of the glass plates, which were placed in a desiccator until the solvent had evaporated. Complete drying of the polymer films was achieved under high vacuum (ca. 10^{-5} torr) at 60°C for 24 hr. The thickness of the films was between 6 μ to 15 μ . Copper films were vacuum deposited onto the polymer films from a Mo-boat (standard Velco -V5-9 vacuum station). The deposition was carried out after a pressure of 10^{-6} torr was reached. The pressure was kept below 5×10^{-6} torr throughout the deposition process. The thickness of the copper deposit was monitored with a quartz crystal oscillator. The films were uniform in thickness within about 3% (this percentage is based on calculations of the incident flux from a point source).*

Degradation of the metal covered polymer films were carried out in a Lindberg Heavi Duty electric tube furnace (see Figure 2). A pyrex glass tube served as the reaction vessel into which the copperpolymer coated slides were placed. The temperature was 400° C and an air stream was passed through the tube during the experiment. The CN⁻ ion concentration was continuously monitored by a specific CN⁻ ion electrode. The Cu film remained as a coherent black CuO film on the polymer substrate during oxidation.

Next, the apparatus and techniques will be described for the evolution of HCN from NaCN and polyurethanes, for the catalytic oxidation of HCN, and for the analyses of the product gases.

The first apparatus used for these investigations is shown in Figure 3. H_2SO_4 (1:1) was stored in the side arm of the reaction vessel C. At the start of the experiment, H₂SO₄ was pressed over into the reaction vessel where it mixed with highly concentrated aq. NaCN. The evolved HCN was carried by an air stream through copper powder located in an horizontal tube furnace (Heavi-Duty), which was heated to 300°C. The NaCN-H₂SO₄ mixture was eventually boiled to expel all dissolved HCN. The air, HCN, and other product gases were bubbled through 1-N NaOH, where all HCN was absorbed. The concentration of CN⁻ ions was continuously monitored by a specific CN⁻ ion electrode (Orion Inc.). Experiments were carried out at 300°C.

A slight modification was made to the first apparatus (see Figure 3) for general chromatographic analysis. Two traps (see Figure 4) were connected

^{*} Our thanks are due to Dr. A. Czanderna, Physics Dept., Clarkson, for having these depositions carried out.



Figure 3. Apparatus assembly for generation of HCN from NaCH— H_2SO_4 and catalytic oxidation of HCN by Cu/CuO powder at 300°C: A, compressor for air supply; B, heating & stirring unit; C, reaction vessel; D, drying tower of CaCl₂; E, heating tape; F, horizontal furnace; G, absorbing bottle, 1-*N* NaOH; H, exhaust.



Figure 4. Double-trap for condensing gaseous products from HCN oxidation.

to it, in which reaction products and also unreacted HCN were condensed after the catalytic reaction had taken place in the hot copper zone. The first trap was cooled to about -78° C by a dry ice—acetone mixture; the second trap, which contained Poropak Q, was also cooled to *ca*. -78° C. The first trap condenses water, while the second one absorbs gases such as N₂, NO₂, CO, CO₂, etc. After condensation or absorption of the product gases, the traps were closed and warmed to room temperature. The contents of the first trap were sampled by a gas tight syringe $(ca. 500 \ \mu l)$ and chromatographed; the carrier gas was N₂.

A second apparatus (see Figure 5) was used at 300° C for the detection of N₂ in the product gases of the catalytically decomposed HCN. A mixture of pure oxygen plus He (80: 20 by volume) was

Inhibition of Hydrocyanic Acid Evolution from Polyurethenes



A. Gas container (O₂+He)

Figure 5. Apparatus assembly for oxidation of HCN: A, gas container $(He+O_2)$; B, HCN generator; 1000 ml; C, reaction zone; D, absorbing bottle; E, gas receiver; F, outlet; G, to gas cylinder (O_2, He) .

passed through the apparatus. The absence of N_2 in the apparatus was proved chromatographically; only traces of N_2 could be detected. Usually 1.2 g to 2.0 g of NaCN were dissolved in a few mlof aq. NaOH for the catalysis experiments conducted at 300°C. The furnace tube (pyrex) had a diameter of 0.5 cm; 3 cm of its length in the middle were filled with Cu-powder (1 g of Cu-dust, 325 mesh). Unreacted HCN was absorbed in NaOH(D). The 1 l gas receiver (Figure 5), which was provided with a three way tap (F), was evacuated. The gas flow was kept constant manually.

The chromatograph for the gas analysis was a Gow-Mac Dual Column (series 550) one with a thermal conductivity detector.

The products obtained in the second apparatus (see Figure 5, E) were sampled with a syringe (ca. 2500 μ l) and injected into the chromatograph. The carrier gas in this case was He and oxygen; analysis for N₂ only was performed in this case.

All gases were identified by comparing their chromatograms obtained under identical conditions with those of pure gases.

The retention times in seconds were as follows:

 $O_2 = 17.6$, CO = 17.7 (negative peak), $CO_2 = 38.8$ (negative peak), $NO_2 = 317.6$, $H_2O = 341.2$. Column temperature 51°C, injector temperature 57°C, detector temperature 87°C; carrier gas N_2 : speed 35.4 ml/min; filament current 110 ma; recorder expansion 1 mo, recorder speed 1/5''/min. The column was $1/8'' \times 6'$ stainless steel, Poropak Q 80/100 mesh.

The following conditions were chosen for the separation of HCN from air and moisture: column temperature 70°C, injector temperature 70°C, detector temperature 90°C, carrier gas N_2 , speed 40 ml/min, filament current 105 ma.

As pointed out above, the second apparatus was used for the determination of N_2 in the product gases. The conditions were as follows: column temperature 65°C, carrier gas He, 40 atm., at 600 ml/min, recorder speed 1''/min, column B (molecular sieve 5A).

IR spectra of a solid reaction product in the form of KBr pellets were measured with a Beckman Spectrophotometer No. 12.

Ozone was produced by passing dry air through an ozonator (03V1 Ozonator, Ozone Research and



Figure 6. Apparatus assembly for detection of oxides of nitrogen produced by catalytic oxidation of HCN by copper/copper oxide: 1, air compressor pump; 2, anhyd CaCl₂ tower; 3, silica gel; 4, ozonator; 5, metal thermostat; 6, reaction vessel; 7, anhyd CaCl₂ tubes; 8, anhyd Mg(ClO₄)₂ tube; 9, 3-*l* mixing flask; 10, absorbing bottle; 11, flow meter; 12, fritted glass; V, valves for flow control.

Equipment Co.).

Specific CN⁻ ion and NO₃⁻ ion electrodes were obtained from Orion Research Inc.; e.m.f. measurements were made with a Corning pH meter; the values given by the electrodes were reproducible within ± 5 mV or 2% to 5% depending on the concentration range.

The apparatus for the analyses of the product gases from polyurethane films is depicted in Figure 6. NO is determined by oxidation of NO_2 by O_3 to N_2O_5 .

EXPERIMENTAL RESULTS

Inhibition of HCN-Evolution from Polyurethanes

Figure 7 shows some experimental results for HCN evolution (281° C) from aliphatic polyurethane films cast from formic acid and *m*-cresol, respectively, without addition of Cu or Cu-compounds. An air stream was passed continuously over the polymer films.

The data are plotted as m_{HON} vs. time, where m_{HON} are the moles of HCN evolved from one unit mole of polymer. The molecular weights for the repeating units for the polyurethanes investigated are: aliphatic about 258 and aromatic about 340. Each unit mole can produce at most 2 mol of HCN, since there are two urethane groups in each repeating unit.



Figure 7. Inhibition of HCN evolution by Cu-powder Cu-phenolate, and Cu-formate in presence of air, aliphatic polyurethane, 281° C: \diamond , polymer film (60 mg) made from formic acid; \bigcirc , polymer film (70 mg) made from *m*-cresol; \bullet , polymer film (60 mg) from *m*-cresol+10% Cu-phenolate; \bullet , polymer film (70 mg) from formic acid+15% Cu-formate; \blacktriangle , polymer film (70 mg) from formic acid+50 mg copper dust.

If one mole of the repeating unit is considered as representing 100% of the weight, then the weight percentage of HCN evolved from one unit mole of polymer is given by

% w/w of HCN =
$$\frac{m_{\text{HCN}}MW_{\text{HCN}} \times 100}{MW_{\text{repeat unit}}}$$
 % w/w

MW stands for molecular weight. The maximum amounts of HCN in % weight which can be evolved from one unit mole are 20.93% w/w and 15.88% w/w for the aliphatic and aromatic polyurethane, respectively.

Figure 7 shows also the results of experiments (281°C) with the addition of Cu-phenolate, Cuformate and copper dust, respectively. These and the subsequent experiments were carried out in the apparatus shown in Figure 1. Figures 8 and 9 give results obtained at 300°C and 400°C. Cu and Co and their compounds are very efficient inhibitors. The efficiency, in part, also depends on the degree of dispersion of the inhibitor in the polymer film. Experiments showed that coarse copper powder is less efficient than fine powder for to equal weights. Compounds after decomposition in the polymer film have the metal in a very fine dispersed state. The polymer in this case is aliphatic polyurethane.

Figure 10 shows the effect of copper and some of its compounds for the case of the aromatic polyurethane (400°C). The results are similar to those for the aliphatic polymer. These experiments were carried out in the apparatus depicted in Figure 1. Figure 11 gives results for various Co compound inhibitors (400°C). These experiments were performed with the aromatic polymer (apparatus, see Figure 1). Figure 12 gives the effect of various metal salts and oxides on HCN evolution from aromatic polyurethane (400°C). It



Figure 8. Hydrogen cyanide evolution from aliphatic polyurethane, degradation in air at 300°C in the presence or absence of copper, copper formate, and cobalt formate: \bigcirc , 70-mg polymer; \bigcirc , 70-mg polymer +7-mg copper formate; \bigcirc , 70-mg polymer +7-mg cobalt formate; \square , 70-mg polymer+about 50-mg copper metal dust.



Figure 9. Hydrogen cyanide evolution from aliphatic polyurethane; degradation in air at 400°C in the presence or absence of varying amounts of cobalt oxide, cobalt formate, and copper formate: \bigcirc , 70-mg polymer; \square , 70-mg polymer+15-mg copper formate; \bigcirc , 70-mg polymer+12.6-mg cobalt formate; \triangle , 70-mg polymer+20 mg cobalt formate; \bigcirc , 70-mg polymer+50-mg cobalt oxide.



Figure 10. Effect of copper compounds on inhibition of HCN evolution from aromatic polyurethane (400°C, air); \bullet , blank; \bigcirc , 30-% copper dust; \blacktriangle , 100-% copper dust; \triangle , 10-% copper acetate; \Box , 10-% copper formate; \triangle , 10-% copper phenolate.



Figure 11. Effect of cobalt compounds on inhibition of HCN evolution from aromatic polyurethane (400°C, air): •, blank; \bigcirc , 10-% cobalt acetate; \square , 10-% cobalt oxide; \triangle , 10-% cobalt formate.

emerges from all these results that Cu-dust is the most effective inhibitor.

Figure 13 shows results for aliphatic polymer films covered with thin Cu-films. The weight percentages relate to the amount of copper on the polymer film (weight 100%). The 10-% Cu-film is quite an efficient inhibitor. The Cu-film



Figure 12. Effect of various metal compounds on inhibition of HCN evolution from aromatic polyurethane (400°C, air): •, blank; \bigcirc , 10-% nickel formate; \blacksquare , 10-% nickel acetate; \Box , 10-% lead oxide; \blacktriangle , 10-% magnesium oxide; \bigcirc , 10-% chromium oxide; \triangle , 10-% ferric oxide.



Figure 13. Effect of thin copper films on inhibition of HCN from polyurethane: \bigcirc , blank; \Box , 2.6% of copper film; \triangle , 4.7% of copper film; \bullet , 10.3% of copper film.

is completely oxidized to black CuO during degradation but remains behind as a coherent film.

Table I.	Relative effectivenesses of thin films
of Cu,	Cu-dust, and Cu-formate for the
inh	ibition of HCN evolution from
	aliphatic polyurethane

Copper film or compounds Cu as % of polymer	Evolution s of HCN, %	Temp, °C	Remarks (thickness)
Blank	100	400	
2.6	34	400	Cu, about 431 A; polymer, about 15μ
4.7	9	400	Cu, about 1000A; polymer, about 19µ
10.3	5		F J , , -
Copper forma	ite,		
20	10	400	
10	13	300	
Copper dust,			
10	23	261	

Relative effectivenesses of thin films of Cu, Cudust, and Cu-formate are given in Table I. Cuformate can be more evenly dispersed in the polymer film than Cu-dust.

Catalytic Oxidation of HCN Evolved from NaCN

HCN Evolution and Carrier Flow Velocity. HCN was evolved as described above by the reaction of H_2SO_4 with NaCN solution (apparatus, see Figure 3). The amount of HCN absorbed in the NaOH solution in the absence of Cu-powder was always 85% to 95% of the theoretical amount for experiments carried out at 300°C. At these temperatures HCN is not oxidized at all. The reason for the somewhat smaller than theoretical amount of HCN obtained is probably due to some adsorption of HCN in the drying chamber and some remaining in the reaction mixture.

Experiments carried out in the presence of copper or its oxides showed conclusively that HCN is catalytically oxidized. This is demonstrated below.

If the flow rate is high, *i.e.*, if the contact time between HCN and the catalyst is rather short, then the amount of HCN absorbed in the 1-N NaOH solution is relatively large.

Some of the results obtained are given in Table II below.

Solid Oxidation Product. A solid white product in very small amounts (ca. 1% by weight) is formed when the air flow velocity is high. However, when these velocities are small, all HCN is catalytically decomposed and it can no longer be detected with the CN^- ion electrode (1% of the theoretical amount can easily be detected, *i.e.*, 2 mg of HCN evolved from 0.35 g of NaCN). At the same time,

(a) In a	absence of copp	er powder		
NaCN, g	1:1 H ₂ SO ₄ , m <i>l</i>	Velocity of air flow	Yield of HCN, %	Remarks
0.49	1.0	medium	96	HCN not dried, and not passed through furnace.
0.35	1.0	medium	90	HCN dried, passed through furnace.
0.35	1.0	medium	84	HCN dried, passed through furnace containing glass wool in tube.
(b) In 1	presence of cop	per powder		
NaNC, g	1:1 H ₂ SO ₄ , m/	Velocity of air flow	Yield of HCN, %	Remarks
0.35	0.9	medium	1.3	HCN was not dried; small amount of white powder at exit of tube.
0.35	1.0	high	20	HCN dried; some yellowish crystalline material formed at exit of tube.
0.35	1.0	medium	4	HCN dried; small white crystals at exit of tube.
0.35	1.0	low (<i>ca</i> . 80—90 air bubbles per minu	0 ute)	HCN dried; no crystalline products.
0.35	1.0	high (<i>ca</i> . 600—900 air bubbles per minu	15 r ute)	HCN dried; appreciable amount of white crystal- line product.

Table II. HCN gas carried by air through a 300°C zone

the solid product is no longer formed. This seems to indicate that this solid product is due to insufficient oxidation of HCN. In any case, the solid is always a negligible fraction of the total amount of HCN.

Attempts were made to identify this white product. In all probability it consists of a mixture of two or more compounds. This is substantiated by the following observations:

- (1) The solid product is usually white but sometimes it is slightly yellowish in color.
- It does not have a sharp melting point, but only a melting range (97°C to 115°C).
- (3) The product is soluble in NaOH and partly soluble in water, ethanol, and acetone; it is insoluble in toluene and dioxane.
- (4) Its IR spectrum (KBr pellets) shows the bands given in Table III (all within ±10 cm⁻¹); cyanuric acid is probably one of the compounds in the solid mixture: its IR spectrum was published by Newman and Badger.⁷ Table III shows the spectral characteristics of this solid product.

The IR spectrum does not fit the characteristics of any simple compound. The product is pro-

Table III. IR spectrum of solid product

Wave number, cm ⁻¹	Wave- lengths, μ	Remarks
3440	2.9	Very strong; degenerate N-H stretch
3340	3.0	Very strong; degenerate N-H stretch
2170	4.60/4.63	Very weak; (Absence of strong bands between 2700 cm^{-1} and 1850 cm^{-1} proves absence of of $-C \equiv N$ groups)
1692/1685	5.9	Very strong; degenerate C=O stretch
1630/1610	6.2/6.12	Very strong
1463	6.82	Strong; degenerate in plane ring stretch
1400	7.13	Medium; degenerate N-H in plane bend
1330	7.5	Medium
1195	8.33	Weak
1157	8.6	Medium
1070		Very weak; degenerate in plane ring stretch
760	13.15	Weak
705		Very weak
560/530	17.9/18.8	Medium; degenerate $C=O$ in plane bend

bably a mixture of compounds such as cyanuric acid and cyamelide,



HCN seems to be converted to HNCO during oxidation catalyzed by Cu or CuO; HNCO poly-



Figure 14 (a). Typical chromatogram of gas (*i.e.*, water) condensed in first trap.



Figure 14 (b). Typical chromatogram of gaseous products absorbed in the second trap.

merizes quite rapidly. If the contact time with copper is long enough, HNCO, instead of being partially polymerized, is quickly oxidized further to N_2 , its oxides, and water.

Product Gases from the Catalytic Oxidation of HCN

Chromatographic Determination of CO, CO_2 , and NO_2 . The apparatus used for these experiments is shown in Figure 4. A typical chromatogram of the content of the first trap obtained by oxidation at 300°C is given in Figure 14a. This was identified as water. The gas mixture in the second trap was also chromatographed (see Figure 14b) and was identified as a mixture of CO, CO_2 , and NO_2 , plus one unknown peak, probably SO_2 , originating from H_2SO_4 .

The peaks of the chromatograms were identified through their retention times by chromatographing pure gases.

Chromatographic Determination of N_2 . These experiments were carried out in the apparatus depicted in Figure 6. A mixture of He and O_2 (20: 80 by volume) was the carrier gas. After sweeping the apparatus out with this carrier gas, the absence of N_2 in the apparatus was checked by chromatography. Only trace amounts of N_2 were left in the apparatus (see Figure 15). This figure also shows that N_2 is produced during catalytic oxidation.

Two sets of experiments were performed at dif-



Molecular sieve 5A , 65°C

Figure 15. Gas-chromatogram of reaction products of catalytically (Cu) oxydized HCN gas: (1) 15 min, (2) 75 min; 300°C.

Polymer J., Vol. 10, No. 3, 1978

ferent carrier gas flow times, *i.e.*, different contact times of HCN with Cu (*i.e.*, CuO). These reaction times were 15 min and 75 min at 300°C. The experimental results are summarized in Table IV. As expected, the longer the reaction time, the greater is the conversion of HCN into N_2 .



Figure 16 (a). A typical chromatogram of volatile degradation products of polyurethane as separated by Poropak Q at 37° C: 1, hydrogen; 2, oxygen (air); 3, carbon dioxide; 4, ethylene; 5, unidentified (may be propylene).



Figure 16 (b). Chromatogram of volatile degradation products as separated by Molecular Sieve 5A Column at 23°C: 1, hydrogen; 2, oxygen.

Table IV. Chromatographic N₂ determination from catalytically (Cu) oxidized HCN evolved from NaCN (300°C); carrier gas. He+O₂

Amount of NaCN	1.8 g	1.5 g		
Reaction time, min	15	15		
Conversion to N ₂	8%	90%		
Remaining HCN	30%ª	8 % ^a		
Other Products ^b	42%	2%		
Decrease in O ₂	26%	55%		

^a Percentage of maximal evolved HCN from NaCN.

^b Polymerized products of HCN, NO, NO₂, etc.

 N_2 is practically the only product under the conditions of the experiments, *i.e.*, if the flow rate is low or the reaction time is long.

Catalytic Oxidation of HCN Evolved from Polyurethanes

Product Gases from Aliphatic Polyurethane in the Absence of a Catalyst. These experiments were carried out at 300°C. Polymer films were prepared as described before. A steady air flow was passed through the apparatus (see Figure 7). The air was dried by anhydrous CaCl₂ and silica gel and then passed through the reaction vessel $(300^{\circ}C)$. The volatile reaction products were dried by passing them through two tubes filled with anhydrous CaCl₂, followed by a tube with anhydrous MgClO₄. The gases were then condensed in a trap containing Poropak Q (50–80 mesh) cooled to -78° C; a second trap with either Molecular Sieve 5A (30-60 mesh) or silica gel (40-140 mesh) cooled to the same temperature was used as a precaution for trapping all volatiles which might have escaped from the first trap (these traps are not shown in this figure; they are depicted in Figure 5). As an additional precaution, the air stream is passed finally through a 1-N NaOH solution to make sure all HCN gas has been removed. This solution did not show any signs of CN⁻ ions. After a definite degradation time, the traps were closed (outlets were also closed by septums) and heated to 90°C to 120°C unit all volatiles were desorbed. Definite volumes were then withdrawn and chromatographed.

200 to 300 mg films of aliphatic polyurethane were degraded in this case. The analysis was done using either Poropak Q or Molecular Sieve 5A columns. It is very important to remove moisture from the product gases before condensation in



Figure 17 (a). A typical chromatogram of volatile degradation products as separated by Poropak Q column at 85° C: 1 oxygen (air); 2, carbondioxide. 3, ethylene; 4, unidentified (may be propylene); 5, water; 6, hydrogen cyanide; 7, unidentified (probably an amine).

Figure 17 (b). Chromatogram of volatile products when polyurethane is degraded in presence of copper/copper oxide; separation by Poropak Q column at 21° C: 1, oxygen (air); 2, nitric oxide; 3, carbon dioxide.

order to successfully detect the presence of HCN, as the latter is highly soluble in water. The response characteristics of the detector are rather low towards HCN.

The following gases were found in the volatile products (results were obtained by experiments where product gases were dried and not dried): (1), oxygen (from carrier air); (2), carbon dioxide; (3), ethylene; (4), unidentified (probably propylene) (5), water; (6), hydrogen cyanide; (7), unidentified (probably an amine); (8), hydrogen.



Figure 18. Gas-chromatogram of reaction products N_2 from polyurethane degradation in the presence of copper dust (3 hr degradation under 30 mmHg of O_2 , 300°C; 300 mg of aliphatic polyurethane).

Figure 16a shows some of the products separated by Poropak Q (37°C). The presence of H₂, which is only partially separated by Poropak Q is clearly, resolved by Molecular Sieve 5A (23°C), as shown in Figure 16b. The chromatogram of Figure 17a, obtained by the same Poropak Q column at a higher temperature (85°C) than used previously (Figure 16a), shows the presence of additional peaks to those observed at a lower temperature (CO and CH₄ were not detected in products analyzed by Molecular Sieve 5A). The additional peaks belong to ethylene, unidentified (may be propylene), water, HCN, and another unidentified one (probably an amine).

Product Gases from Catalytic Oxidation of HCN Evolved from Polyurethanes. The chromatographic resolution for nitric oxide (Figure 17b, Poropak Q, 21°C) is only partial. It was, therefore, decided to examine the presence of NO_x (*i.e.*, $NO+NO_2$) by an alternative method. This was done by degrading polymer films, and the evolved gas including HCN was catalytically oxidized with copper or its oxide. The lower oxides of nitrogen, if produced in this way, can be oxidized to nitrogen pentoxide in the gas phase by a strong oxidizing agent such as ozone. N_2O_5 can then be absorbed in water where it hydrolyzes to nitric acid. The presence of NO_3^- ions can be quantitatively determined with a specific NO_3^- ion electrode. Details of this procedure were described by D. Martini.⁸

The apparatus used for the degradation experiments is shown in Figure 6. The volatile products are mixed with a stream of ozonized air in a flask where oxidation of NO_x takes place to N_2O_5 . Then the gases are passed through a dilute NaNO₃ solution of known concentration. The flow rates of air, both through the ozonator and the degradation vessel, are controlled independently by suitable valves and measured. Finally, the increase in NO_3^- concentration is determined by the specific NO_3^- ion electrode.

Typical experimental conditions for this analysis were: polymer about 500 mg, CuO powder, about 300 mg; absorbing solution; initial concentration, 1×10^{-4} -M NaNO₃ in water; ozonator, 0.85 a; flow pressure, 2 psi; flow velocity in ozonator, 114 ml/min; flow velocity through degradation vessel, 40 to 50 ml/min; duration of experiment, 5 hr at 300°C.

In another set of experiments, the total amount of HCN which was evolved from the same amount of polymer and under the same experimental conditions as those given above was determined by absorbing HCN in 1-N NaOH solution and measuring the CN⁻ ion concentration with the specific CN⁻ ion electrode. This data and the results obtained from the ozone oxidation experiments give an indication of the extent of the oxidation of HCN in the presence of Cu or its oxide to nitrogen oxides. The results were as follows: amount of HCN from aliphatic polyurethane, about 3.9×10^{-5} mol; amount of NO₃⁻ obtained from ozone oxidation, about 1.2×10^{-6} mol.

These results are very surprising because they show that only about 3% of the total evolved HCN is oxidized to (NO+NO₂) by Cu or its oxide.

We know from our experiments that practically all HCN produced from polyurethane is inhibited (*i.e.*, oxidized) in the presence of excess CuO. It can therefore be reasonably assumed in view of the results given in Table IV (second column), that HCN under our experimental conditions (moderate air velocity and small concentrations of HCN in the air stream) is oxidized by the catalyst largely to free nitrogen and only to a small extent to oxides of nitrogen.

Further, to verify the validity of the ozone oxidation results, a blank experiment (*i.e.*, no catalyst) with the same amount of polymer was performed under identical conditions. A stream of ozonized air was mixed with the volatile degradation products; the gas mixture was passed through NaNO₃ and the solution was analyzed as before. After the same reaction period, it was observed that practically no change took place in the measured initial NaNO₃ concentration. This shows that the volatile products do not interfere with the oxidation method or the NO₃⁻ ion determination.

Catalytic oxidation of HCN. Determination of A number of experiments were carried out N_2 . with a closed reaction system (see Figure 2). 300mg films of aliphatic polyurethane with different amounts of Cu-dust dispersed in them were degraded at 300°C for three hours under a partial pressure of oxygen of 30 mmHg. He gas was added after degradation until 1 atm was reached. The gaseous products were analyzed under the same conditions as described under C (b). Results are shown in Figure 18. The amounts of O₂ decrease in the closed system as thermal oxidative degradation proceeds. The amounts of N₂ produced are a function of the amounts of Cu added. Thus HCN evolved from degraded polyurethane produces N_2 in the presence of a catalyst, as does HCN evolved from NaCN. Actually the amounts of N₂ found indicate that in a closed vessel much more HCN is produced than in an open system. This is probably due to the presence of reaction products such as water which will induce further decomposition of the polymer by hydrolysis at 300°C.

DISCUSSION

Appreciable quantities of hydrocyanic acid, HCN, are evolved during thermal oxidative degradation of polyurethane in the range of temperatures from 200°C to 500°C.¹ The kinetics and mechanism of this gas evolution was investigated in detail previously.¹ Actual amounts of HCN produced in mol % (one unit mol about 100%) in air during 1 hr exposure at 311°C are: aliphatic polyurethane 1% and aromatic polyurethane 0.4%, or 2.84 g of HCN from 284 g and 1.36 g of HCN from 340 g of polymer, respectively.

It must be pointed out that from the point of view of mechanism, HCN is only a minor product of the oxidative degradation of polyurethanes due to a minor side reaction. However, it is an important reaction because of its high toxicity.

Figures 8 to 14 show conclusively that metal and their powders as well as their decomposable compounds are effective in inhibiting HCN evolution. Copper, its oxides, and its compounds are the most efficient inhibitors. Especially potent inhibitors are the decomposable Cu-compounds, for they can be very finely dispersed in the polymers; also copper films deposited on polymer films show quite potent inhibiting powers. It is noteworthy that these films remain coherent during oxidation.

The main gaseous products obtained during the oxidation of polyurethanes at high temperatures are CO_2 and CO. For instance, after 30 minutes exposure to 30 mmHg of O_2 at 438°C the following gases were evolved in $10^3 m_{gas}$ (*i.e.*, in moles/unit mole of polymer)¹:

	CO2	C_2H_4	C_2H_6	H_2O	CH ₄	СО
Aliphatic	807	95	39	15	46	411
Aromatic	1140	74	4	4	78	303

HCN evolved in either gas is about 50.

In the present paper, the following gases were found when the aliphatic polyurethane was oxidized at 300°C in air: CO_2 , C_2H_4 , C_3H_6 (?), H_2O , HCN, H_2 , and amine (?). The main products are CO_2 , C_2H_4 , and H_2O . CO and CH₄ were not found; if present, their quantities must be very small.

In the previous work¹ a mechanism was proposed for the oxidative degradation of polyurethanes, as follows:

$$\overset{\mathrm{H}}{\sim} \overset{\mathrm{O}}{\overset{\mathrm{V}}{\sim}} \overset{\mathrm{O}}{\overset{\mathrm{H}}{\sim}} \overset{\mathrm{O}}{\sim} + \operatorname{O}_{2} \overset{k_{1}}{\longrightarrow} \overset{\mathrm{O}}{\overset{\mathrm{N}}{\sim}} \overset{\mathrm{O}}{\overset{\mathrm{O}}{\sim}} - \operatorname{O} \overset{\mathrm{O}}{\sim} + \operatorname{HO}_{2}^{:}$$
 (1)

The following reaction will also be operative:

 CH_2 is usually adjacent to the NH-group. The subsequent reactions for reaction (1) and (1a) are analogous. The sequence of reactions for (1) is as follows:

$$\sim \dot{N} \sim + O_2 \xrightarrow{k_2} \langle Cage \rangle$$
 (2)

Chain scission becomes permanent when fragments (*i.e.*, chain radicals) escape from cages:

$$\langle \text{Cage} \rangle \xrightarrow{k_4} \rightarrow \text{Fragments} \frac{\text{FAST}}{\sum k_6} \rightarrow \text{Other Products} \\ \underset{\sim}{\text{H}} \qquad \begin{array}{c} \text{Fast} \downarrow k_5 & \text{H} \\ \sim \overset{\circ}{\text{C}} - \text{H} + \text{HCN} + \text{CO}_2 + \text{H}_2 \text{O} + \text{O}_2 + \overset{\circ}{\text{C}} \sim \\ \underset{H}{\overset{\circ}{\text{H}}} \qquad \begin{array}{c} \text{3} \end{array} \right)$$

Reaction step k_5 is only a relatively small side reaction resulting from chain scission; many other products are formed by the simultaneous reaction steps $\sum k_6$. The above scheme was quantitatively evaluated; for the initial stages of HCN evolution, the following final rate equation for HCN evolution is obtained:

$$\frac{\mathrm{d}m_{\mathrm{HCN}}}{\mathrm{d}t} = k_{\mathrm{exP}} \left[\mathrm{O}_2 \right] \tag{4}$$

HCN evolved from NaCN is decomposed catalytically by Cu or CuO-powder (all Cu is converted in the presence of air to CuO at 300°C). The amount of HCN decomposed depends on the flow or contact time of the oxidizing gas. If this is high (or long) relatively large amounts of HCN are left undecomposed. The flow rates were relatively slow in our experiments for the catalytic decomposition of HCN evolved from polyurethane. The concentrations of HCN in the oxidizing gas stream were small. Such conditions favor almost complete decomposition of HCN.

The product gases from the decomposed HCN evolved from NaCN were found to be N_2 , CO₂, CO, H₂O, and NO₂; N₂ was determined by a special procedure. It was found that at small flow rates (long contact times) the main gaseous product was N₂ (*ca*. 90% or more; this corresponds also to the conditions for HCN evolution from polyurethanes). At high flow rates the amounts of N₂ decreased dramatically (to *ca*. 8%).

Analysis of the catalytic decomposition products of HCN from polyurethanes (low flow rates, small HCN concentrations) showed that the products consisted mainly of N₂ and small amounts of NO+NO₂ (*ca.* 3%), possibly mixed with small amounts of other gases such as H₂O, CO, and CO₂; in addition gases are present due to the oxidation of polyurethane, leading to products

Polymer J., Vol. 10, No. 3, 1978

other than HCN. Thus, it is seen that the catalytic oxidation of HCN evolved from NaCN yields under similar conditions the same products as the inhibition of HCN evolution from polyurethanes. This shows conclusively that the inhibition due to copper oxide is due to catalytic oxidation and decomposition of HCN evolved from the polymers and not to an alteration of the degradative oxidation mechanism.

The results presented here agree well with results for the catalytic decomposition of HCN gas or HCN evolved from NaCN by previous workers.²⁻⁴ Neumann and Manke⁴ found, with CuO as catalyst, that N₂ was the predominant decomposition product, along with some nitrogen oxides; they also found H₂O and CO₂ in the product gases (400°C). Sinozaki and Hara³ reported mainly N₂ as the product with CuO as catalyst at 700°C. All authors also found a small amount of a solid reaction product which they assumed to be a mixture of polymerized cyanuric acid (HOCN)₃ and cyamelide.

According to Neumann and Manke,⁴ the following exothermic reactions may take place for the oxidative and catalytic decomposition of HCN:

- (1) 2HCN+50 \longrightarrow H₂O+N₂+2CO₂ -317.12 kcal/m
- (2) $2\text{HCN}+70 \longrightarrow H_2O+2NO+2CO_2$ -274.0 kcal/m
- (3) $2NO+O_2 \longrightarrow 2NO_2-40.5 \text{ kcal/m}$
- (4) $4HCN+10NO \longrightarrow 7N_2+4CO_2+2H_2O$ -850.1 kcal/m

If sufficient air is present and the contact time is long (*i.e.*, small flow rates), then, reaction (1) will be predominant. If the gas velocities are high and the temperature low, reaction (2) will be the main one. These authors assume that as long as undecomposed HCN is still present, it reacts also according to step (4). They think that the oxidation proceeds *via* the imide (NH) as a transition product because they found small amounts of hydrazine, N_2H_4 . Sinozaki's and Hara's³ formulations are similar. Zawadski and Liechtenstein⁴ also found mainly N_2 , CO₂ and H₂O when the air flow rate was small.

The mechanism of the catalytic decomposition of HCN can be tentatively formulated as follows (following largely Neumann and Manke's⁴ suggestions):



Acknowledgement. Thanks are due to NASA, Ames Research Center, for financial assistance which made this work possible.

REFERENCES

- H. H. G. Jellinek and K. Takada, Toxic Gas Evolution from Polymers: Evolution of Hydrogen Cyanide from Linear Polyurethane, J. Polym. Sci., 13, 2709–2723 (1975); For Part II, H. H. G. Jellinek and K. Takada, *ibid.*, 15, 2269–2288 (1977); K. Takada, Ph.D. Thesis, Department of Chemistry, Clarkson College, July 1976.
- 2. R. Hara and H. Sinozaki, Tohoku Teikoku Dai-

 $\begin{array}{c} + & \mathrm{NH} \\ & & \uparrow & \mathrm{O}_2 \\ \mathrm{N}_2 \longleftrightarrow & \mathrm{N} + \mathrm{H} \longrightarrow \mathrm{H}_2 \mathrm{O} \\ & & \downarrow \mathrm{O}_2 \\ & \mathrm{NO}_2 \end{array}$

gaku, Japan; Technology Reports, Sendai, V, 5 (2), 71 (1925).

- 3. H. Sinozaki and R. Hara, *ibid.*, 6, 95 (1926).
- B. Neumann and G. Manke, Z. Elektrochem. Angew, Phys. Chem., 35, 751 (1929). See also: J. Zawadzki and I. Lichtenstein, Rocznikow Chemji, 1926, 831.
- C. S. Marvel and J. H. Johnson, J. Am. Chem. Soc., 72, 1674 (1950).
- 6. D. J. Lyman, J. Polym. Sci., 45, 49 (1960).
- R. Newman and G. M. Badger, J. Am. Chem. Soc., 74, 3545 (1952).
- 8. R. D. Martini, Anal. Chem., 42, 1102 (1970).