COMET OUTBURSTS AND POLYMERS OF HCN

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ABSTRACT

Dramatic cometary outbursts have been noted by observers for many years. These outbursts can sometimes increase the apparent brightness of a comet up to 9 mag and release energy on the order of 10^{19} ergs. A number of mechanisms have been suggested for outburst activity; however, none has been generally accepted. HCN is a known constituent of both interstellar icy grain mantles and cometary nuclei, and HCN polymers have been postulated to exist on the dark surface of comets such as P/Halley. Since polymerization is a strongly exothermic process, we investigate the possibility that HCN polymerization can provide the energy needed for outbursts. Polymerization may be continuing in the inhomogeneous interior of comets. In addition, the reactive CN groups in these oligomers can be hydrolyzed and may contribute to CO_2 and CO pressure buildup in the interior of comets.

Subject headings: comets: general — molecular processes

1. INTRODUCTION

Cometary outbursts have puzzled astronomers since the 1920s when comet P/Schwassmann-Wachmann 1 with a nearly circular orbit at a heliocentric distance of 6 AU was seen to brighten by 5 mag (Whitney 1955). These outbursts contradict the expectation that comets should be relatively inactive beyond 3 AU if water ice dominates the sublimation process. Since the 1920s cometary outbursts have been shown to be relatively common (Delsemme 1985; Wyckoff 1982). Outbursts, usually resulting in a brightening of up to 9 mag within a few days or even hours, have been observed at a rate of 1–3 per year. No completely satisfactory mechanism has been found to explain outbursts (Hughes 1991).

Many outbursts of P/Schwassmann-Wachmann 1 have been recorded since the initial outburst observation, sometimes indicating a preferred brightness on one hemisphere of the coma and at times showing jets indicating localized production of excess material, probably from a limited region of the nuclear surface. CO^+ has been detected in some outbursts (Cochran, Barker, & Cochran 1980; Larson 1980). Outbursts in P/Halley were enriched in other species, for example, CO_2 (Feldman et al. 1986), CN, NH_2, and C_2 (Rettig et al. 1987), and H_2O (Mumma, Weaver, & Larson 1987; Larson et al. 1990). These outbursts occurred during the active phase of comet P/Halley, and showed a brightness increase of 1 mag at 1 AU while an outburst of approximately 8 mag was observed during an inactive phase at 14.3 AU (West et al. 1991; Meech 1991). As discussed here, outbursts do not include brightness variations due to rotation or changes in spin-axis orientation.

Comets are thought to form with amorphous water ice as the most abundant molecule and frozen methanol (CH_3OH) and carbon monoxide (CO) next in abundance. The volatile composition seems to agree with the abundances in interstellar ice (see Mumma, Weissman, & Stern 1992 for a recent review); both CH_3OH and CO seem to vary in abundance within comets. The CH_3OH/H_2O ratio was found to be 5% in new comets but only 1% in several short-period comets (Hoban et al. 1991; Reuter 1992; Bockelee-Morvan et al. 1991). CO/H_2O was 1%–3% in comet Austin (1990V), approximately 20% in comet Wilson 1987VII and approximately 15% in P/Halley where CO was produced from both direct and extended sources in roughly equal amounts (Eberhardt et al. 1987).

Smoluchowski (1981) has suggested cometary outbursts are due to energy released by the rapid transition of amorphous to cubic ice in localized regions. Jewitt (1990) suggested the persistent coma of comet P/Schwassmann-Wachmann 1 at 6 AU may be a sublimate of crystalline water ice and that the comet is at the critical heliocentric distance such that the subsolar temperature (140 K) is just high enough to trigger an exothermic amorphous-crystalline phase change for the observed outburst activity. Short-period comets with semimajor axes smaller than 4 AU are too warm for amorphous ice to exist within the nuclei (Herman & Weissman 1987), and comets with perihelia larger than 6 AU are too cold to trigger the amorphous-cubic phase transition (Jewitt 1990).

A second mechanism suggested for outbursts is the rapid release of gas from pockets rich in molecules more volatile than H_2O (Whipple 1980; Cowan & A'Hearn 1982; Feldman et al. 1986) such as CO and CO_2 (Sandford & Allamandola 1988). CO can provide limited sublimation at temperatures just below 70 K. If cometary surfaces are not porous, the released gaseous CO and CO_2 may accumulate in pockets within the ice. The buildup and sudden release of gas from these pockets triggered by sublimation of the surrounding nonporous ice or by macroscopic displacements within the nucleus might then produce outburst activity (Sandford & Allamandola 1988).

However, if cometary surfaces are porous, CO and CO_2 may diffuse through the surface quiescently, avoiding the necessary pressure buildup of these gases for cometary outbursts.

Flammer, Jackson, & Mendis (1986) showed that many of P/Halley's small outbursts at large heliocentric distances could be correlated with the passage of high-speed streams in the solar wind. They proposed that electrostatic levitation of charged dust from the nucleus causes an increase in effective scattering area, hence in brightness. Recently Intrilligator & Dryer (1991) have suggested the 1991 February outburst of P/Halley was caused by a flare-induced shock (3×10^{-9} dyn cm^2) impacting the surface of the comet. Even though the physics of cometary surfaces is not well known, the explanation that solar-wind shock pressure at 14.3 AU is responsible for outbursts does not seem sufficient. Weissman (1991) points out that the energy density in the shock calculated by Intrilligator & Dryer (1991) is less than the energy density of solar radiation and questions why P/Halley did not outburst during a series of similar flares in late 1989.

2. EVIDENCE FOR HCN POLYMERS IN COMETS

The occurrence of organic materials on comets has been predicted as far back as 1961 by Oro and again in 1980 by Gradie and Veverka. Spacecraft investigations of P/Halley showed that organic material comprised nearly one-third of the dust by mass (Kissel et al. 1986; McDonnell et al. 1987; Jessberger & Kissell 1991). This and other investigations showed that the volatile (gas) fraction of P/Halley is approximately 14% organic (by mass), and that the overall cometary organic composition is approximately 25% (Delsemme 1988).

Kissel et al. (1986) showed that cometary dust grains collected by the *Giotto* and *Vega* spacecraft were composed of two chemical end types: a Mg-rich silicate phase, and an organic phase rich in H, C, N, and O. The high abundance and complex chemical nature of the CHON grains suggest the possible presence of polymeric organic material. Further, observations from *Giotto* (Keller et al. 1987) confirmed the existence of a dark surface on P/Halley which could be a result of extreme microporosity, or of electronic band absorption in the surface material. Matthews & Ludicky (1986) proposed this dark crust was composed largely of hydrogen cyanide polymers. Recently Cruikshank et al. (1991) spectroscopically detected a dark CN bearing material in the dust of new comets and on a class of asteroids which may have originated from old comets. The CN spectroscopic identification was made through the detection of the 2.2 μm CN overtone of the stretching fundamental mode. Also, Encrenaz et al. (1988) and Combes et al. (1988) reported a marginal detection of a 4.4 μm emission band in infrared spectra of P/Halley acquired by IKS on *Vega 1*. They tentatively identify this 4.4 μm band as a CN stretch, but probably not of CN in small grains which have a signature near 4.6 μm. We suggest, in agreement with Cruishank et al. (1991), that the 2.2 and 4.4 μm bands are possibly associated with hydrogen cyanide (HCN) polymers. HCN polymers are not the only species that can explain this dark material. Huebner (1987) in a discussion of the PICCA mass spectrum also suggested that small particles emanating from the nucleus of P/Halley may originate at least partially from H_2CO polymers (polyoxymethylene). Others have suggested other macromolecules including kerogen-like material that has been identified in meteorites and interplanetary dust (Sagan & Khare 1979; Gradie & Veverka 1980; Chyba & Sagan 1987; Arakawa

et al. 1989). We note that the presence of polymers of HCN would produce an extended source for CN in the coma. A'Hearn et al. (1986) observed CN jets in P/Halley and suggested grains as the source for CN in the jets, however, Combi (1987) argues that a volatile parent is possible since outgassing material is azimuthally confined by the background water.

3. MECHANISMS FOR POLYMERIZATION

If we assume HCN polymers are present in comets, the question remains as to how these molecules are produced. One possibility is that HCN polymers may have originated either in the solar nebula or in the natal interstellar cloud core that predated the solar nebula. HCN is a familiar interstellar molecule, and polymers may form on icy grains irradiated by UV photons or ions (see § 4). Such grains likely accreted to form comets, and hence HCN polymers (a dark material) may have been incorporated throughout the interior of comets. Being less volatile than water they could experience additional processing during the comet's active phase and in time could accumulate to form an inactive crust. It is interesting to note that the abundance of XCN relative to H_2O in icy mantles of interstellar grains is 4% (d'Hendecourt et al. 1986; Tegler et al. 1992) which exceeds the HCN/H_2O abundance in comets (0.1%) (Schloerb et al. 1987). This could mean that most CN was complexed in forms other than HCN—possibly as polymers by processing in the natal cloud core—prior to incorporation into cometary nuclei. If the XCN abundance in icy grain mantles represents the original abundance of HCN, then HCN/H_2O is approximately 4% before polymerization. For amorphous ices, two HCN molecules will be in nearest-neighbor contact approximately 24% of the time; thus the probability of dimerization is high when the amorphous ice is warmed.

Creation of HCN polymers may also result from continuing chemical evolution of the cometary nucleus. HCN has been detected spectroscopically in the coma of comets (Huebner, Snyder, & Buhl 1974; Schloerb et al. 1987; Bockelee-Morvan et al. 1990) and presumably exists as a frozen primordial component of the nucleus. Schloerb et al. (1987) determined the abundance of HCN/H_2O in the nucleus of comets to be 0.1% by number, whereas Delsemme (1988) interprets the HCN/H_2O to be approximately 1% by mass, mainly in the form of CHON grains. Assuming an inhomogeneous nucleus, exposure of a concentrated fresh patch of frozen HCN to UV or high-energy photons can provide the necessary trigger to initiate polymerization.

Polymerization can be initiated by photoexcitation where the absorption of a UV photon by an HCN molecule produces an HCN molecule in an electronically excited state:

$$H-C\equiv N + hv \rightarrow [H-C\equiv N]^* .$$
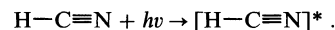
The electronically excited state of HCN will possess free-radical character largely localized on the carbon atom. Once the radical is formed, it may combine with another HCN molecule to produce an HCN dimer. The dimerization of HCN is an exothermic process (Evans et al. 1991). High-level ab initio calculations on HCN and the two HCN dimers shown in Figure 1 indicate that the formation of these initial dimers, a critical first step in the polymerization of HCN, is exothermic releasing 7.65×10^9 ergs g^{-1} (4.97 kcal $mole^{-1}$) and 8.32×10^9 ergs g^{-1} (5.41 kcal $mole^{-1}$), respectively (Evans et al. 1991). These very reactive HCN dimers can combine to

FIG. 1.—Probable HCN dimers in the initial formation of the HCN polymers.

form oligomers and polymers in a rapid chain polymerization process ultimately producing ladder structures (Fig. 2).

Polymerization of HCN can also be initiated via a free-radical chain reaction. The chain reaction process is initiated by the addition of a free radical (a species possessing an unpaired electron) to a molecule of HCN. The initiating radical can be formed from potentially any species present. This formalism has been suggested to be the preferred pathway for the formation of the simple ladder structures possessing conjugated —C=N— bonds (Figs. 2c, 2d) (Volker 1960). In comets or precometary icy grains, the free radical could be OH from photolysis of H_2O, or any radical from other species.

From laboratory studies, liquid hydrogen cyanide is known to be very reactive and can be polymerized by various methods. Spontaneous polymerization of hydrogen cyanide can result from heating or prolonged storage and can be catalyzed by any base or by free radicals created through light irradiation, high-energy radiation, or an electric charge. Most laboratory experiments are done with a concentration of 10% HCN relative to H_2O plus a trace of a base such as ammonia or an amine. Complete polymerization to a dark solid occurs within several hours (Volker 1960). The polymers are relatively stable to 200°C and eventually decompose with the release of HCN, CN, NH_3, and CO_2 (Volker 1960). The laboratory HCN molecular concentrations and temperatures are inappropriate for cometary conditions, but these experiments demonstrate that HCN polymerization is highly exothermic and can occur under a variety of circumstances. Laboratory experiments representative of cometary conditions are needed to determine the rate of polymerization and length of polymers as a function of temperature and concentration for HCN as well as other molecules.

With the knowledge that HCN polymers are black (Volker 1960) and the surfaces of comets appear to be covered with a dark, low-albedo material and the fact that HCN is present in comets, we investigate the possibility that energy released during polymerization of HCN and/or closure of the polymer side groups (Figs. 2c, 2d) can provide the energy observed in cometary outbursts.

4. MODEL CALCULATIONS

We calculated the energy released by the polymerization of a gram of HCN in the following manner. The structure of the dimer and oligomers capped with terminal C—H bonds were calculated with complete geometry optimization (Fig. 3a–3c). The calculations were carried out at the minimal-basis set

FIG. 2.—Suggested pathway for the formation of HCN polymers. Dimers of HCN lead to the tetramer (a), and to the polymer (b) which readily undergoes ring closure to give the ladder polymers (c–d). Fig. 2b is referred to as polyaminocyanomethylene; (c) and (d) are black polymers.

STO-3G level using the Gaussian88 program (Frisch, et al. 1988). The geometries of panels (a)–(c) are schematic three-dimensional representations of the lowest energy structures. Calculations on higher oligomers were not feasible due to computational limitations. The calculated total energy for each structure (in atomic units or hartrees) is given in column (2) of Table 1, and the total energy for each structure divided by the number of HCN molecules contained in each structure is given in column (3), E_{tot}/n. The difference in energy (ergs g^{-1}) between one molecule of HCN and E_{tot}/n is given in column (5).

Structures a, b, and c (Fig. 3 and Table 1) should not be construed as structures in a chemical pathway to the octamer: they are strictly used as mathematical points in the extrapolation to eliminate the effect of the terminating C—H bonds. In the model structures (Figs. 3a–3c), the terminating C—H bonds are much lower in energy than internal C—C bonds in the ladder polymer and result in higher calculated energies on a per HCN basis than for the dimer calculated by Evans et al. (1991). As the number of —$(NH_2)C(CN)$— units in a ladder polymer increases, the relative contribution of the lower energy C—H bonds decreases. Values for E_{tot}/n-E_{HCN} converge quickly, with an extrapolated value of E_{tot}/n-E_{HCN} for an octamer reasonably representing the value of E_{tot}/n-E_{HCN} in an infinitely long ladder polymer. The large E_{tot}/n-E_{HCN} extrapolated value of the octamer is consistent with the known extremely exothermic polymerization of HCN. The resulting extrapolation provides a lower limit of 1.85×10^{11} ergs as the energy released during the polymerization of 1 g of HCN.

Other species are present in the matrix and may contribute radicals to end each polymer. Depending on intermediate
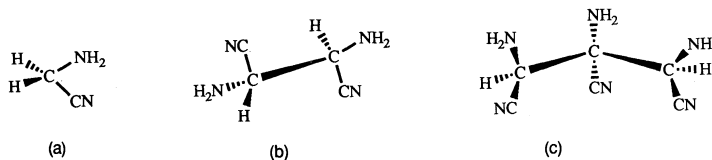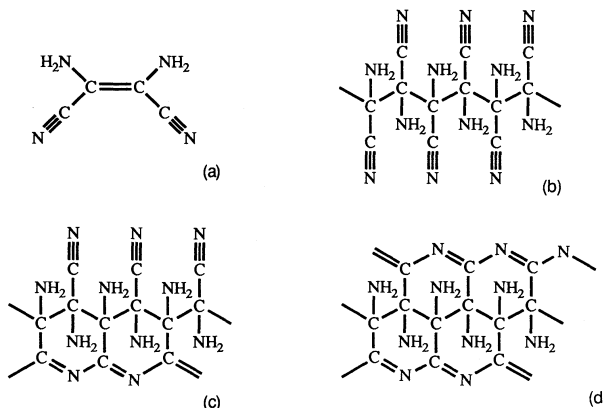

FIG. 3.—Structures representing the minimum energy and geometry of the dimer, tetramer, and hexamer with terminal H atoms on the end of each oligomer. The effect of the terminal C—H bond is minimized in the calculations. The plain bonds lie in the plane of the page, while the dark wedged-shaped bonds project forward, and the cross-hatched bonds project inward.

TABLE 1

ENERGY RELEASE FOR FORMATION OF HCN OLIGOMERS

Oligomer (1)	E_{tot} (hartrees) (2)	E_{tot}/n (hartrees) (3)	$E_{tot}/n\text{-}E_{HCN}$ (hartrees) (4)	$E_{tot}/n\text{-}E_{HCN}$ ($\times 10^{11}$ ergs g^{-1} HCN) (5)
HCN	-91.67521	-91.67521	...	...
Structure a	-184.57906	-92.28953	0.61432	5.92
Structure b	-367.98133	-91.99533	0.32012	3.09
Structure c	-551.42497	-91.90416	0.22895	2.22
Octamer[a]				1.85

NOTE.—$E_{tot}/n - E_{HCN}$ for structures a, b, and c are not energetically realistic values because of the C—H terminating bonds. They are used only as points in an extrapolation to determine $E_{tot}/n - E_{HCN}$ for the octamer.

[a] Extrapolated value.

radical lifetimes and the concentrations of HCN, polymerization may preferentially produce the shorter oligomers when the HCN radical interacts with other species in the matrix. If the oligomer ends with the dimer, then the resulting energy release will be less than if the reaction proceeds to a polymer. Only if the concentration of HCN is relatively high in icy patches or the lifetimes of other intermediates is long will HCN polymerization produce the maximum energy release through this mechanism.

If the nucleus of P/Halley has an inhomogeneous composition arising from planetesimals produced at various solar distances, small regions with enriched HCN might be expected. Estimates of HCN/H_2O in comets and the interstellar medium range from 0.1% (Schloerb et al. 1987) to 4% (d'Hendecourt et al. 1986; Tegler et al. 1992). The extent of inhomogeneity of a comet nucleus is still in dispute, but variations in planetesimal composition and grain evolution are expected in the presolar disk, so inhomogeneities in comet accretion are not unexpected.

The energy released by HCN polymerization (1.85×10^{11} ergs g^{-1} of HCN) may be sufficient to initiate H_2O sublimation in comets. A comet that has a region with HCN/H_2O = 4% releases approximately 8×10^9 ergs g^{-1} as a result of polymerization. For a comet with a subsurface icy matrix at a temperature of 100 K and a specific heat of 0.25 cal g^{-1} K^{-1}, 5×10^8 ergs g^{-1} are needed to raise the temperature of the icy matrix to 150 K. Sublimation of H_2O becomes significant at about 150 K. Only 6% of the energy released from the polymerization of HCN is required to raise the temperature of the subsurface icy matrix to the H_2O sublimation temperature. Sandford & Allamandola (1990) have determined the volume binding energy of H_2O—H_2O ($\Delta H/k \approx 5000$ K) from which we calculate the latent heat of sublimation ($\approx 10^{10}$ ergs g^{-1}). The energy of polymerization is not quite sufficient to sublimate the entire mass of H_2O, but in a scenario where only a portion of the mass expelled is sublimated, a much smaller total energy will be required. Using the energy released by HCN polymerization to provide the estimated energy released in outbursts (10^{19}–10^{21} ergs) and a density of 0.3 g cm^{-3} (Krasnopolsky et al. 1987), the required diameter of the outbursting region ranges from 20–100 m.

The 1.85×10^{11} ergs g^{-1} released by HCN polymerization can be compared to other exothermic processes. Specifically the phase transition of amorphous to cubic ice at 140 K releases 8.4×10^8 ergs g^{-1}, and the explosion of dynamite releases 4.2×10^{13} ergs g^{-1}.

Polymerization of HCN to the open-ended side chains (Fig. 2b) may have occurred within planetesimals or icy grains at a specific heliocentric distance (i.e., temperature) in the early solar disk. Further accretion with other planetesimals from various heliocentric distances may have resulted in inhomogeneous comet nuclei. Eventually, such comets may enter the inner solar system where exposure to increased solar radiation may trigger closure of the side chains (Fig. 2d) in localized regions of the nuclei. The energy of closure (approximately 3.1×10^{10} ergs g^{-1} or 20 kcal mole^{-1}) is roughly 17% of the HCN polymerization energy calculated previously and may provide additional energy to power outbursts.

5. POLYMER FRAGMENTATION

Figure 2 shows the structure of a polymer with CN and NH_2 bonded to each carbon atom of the carbon backbone. The photodissociation of the ladder polymers will result in the production of CN and NH_2 radicals and the formation of free-radical centers along the carbon backbone of the polymer. This photodissociation may be an important source of CN and NH_2 radicals observed in the comae of comets.

The dissociation of the polymer to release either CN or NH_2 is expected to occur through the initial electronic excitation of the C≡N band. The required excitation energy can be in the form of a UV photon near 170 nm ($\pi \rightarrow \pi^*$ excitation) (Pasto & Johnson 1979). Usually the UV photon is absorbed by the polymer, and the electronic excitation energy is transferred to high-energy vibrational modes that can result in bond dissociation. The absorption of this quantity of energy and transfer to vibrational modes would lead one to expect that both C—C≡N and C—NH_2 bonds might undergo dissociation. Calculations have been carried out on a large number of substituted methyl radicals (X—CH_2) in an attempt to evaluate the effect of substituents on the relative stability of the radical center (Pasto, Krasnansky, & Zercher 1987). Both the CN and the NH_2 groups stabilize a radical center, the former by 8.22×10^9 ergs g^{-1} (5.34 kcal mole^{-1}) and the latter by 1.58×10^{10} ergs g^{-1} (10.26 kcal mole^{-1}). The greater relative stabilization of a radical center by the NH_2 group would thermodynamically favor the loss of the CN radical in a photodissociation process relative to the loss of NH_2. It is interesting to note that in the outburst of UT 1986 March 24.7 CN was shown to be much more enhanced than NH_2 (Rettig et al. 1987).

Improved knowledge of photolysis rates and of kinetic energies of the products is required to determine whether NH_2 and CN are more likely to derive from NH_3 and HCN or from polymers. The photodissociation rates of NH_3 to NH_2 and H, and HCN to CN and H are well known (Gordon & Ford

1972). However, the photodissociation rates of HCN polymers into NH_2 and CN fragments are unknown. Because of the complexity of the molecular system only the relative thermodynamic energies have been calculated. The thermodynamic dissociation energy for H from NH_3 to produce NH_2 is known to be 1.58×10^{11} ergs g^{-1} (103 kcal $mole^{-1}$), whereas the thermodynamic dissociation energy calculated in this work for NH_2 from the polymer is approximately 7.23×10^{10} ergs g^{-1} (47 kcal $mole^{-1}$). Similarly, the dissociation of CN from HCN is known to require 2.00×10^{11} ergs g^{-1} (130 kcal $mole^{-1}$), whereas the calculated thermodynamic energy required for dissociation from the polymer is 1.38×10^{11} ergs g^{-1} (90 kcal $mole^{-1}$). These energies imply production of CN and NH_2 from the polymer may be easier than from HCN and NH_3. Laboratory experiments are needed to determine the photodissociation rates of HCN polymers into CN and NH_2 fragments and hence to verify whether HCN polymers are likely to be the dominant source of CN and NH_2 in the comae of comets.

If the observed CN is derived from photodissociation of polymers, the observations should show a distributed source. NH_2 jets similar to CN jets might be expected but as yet are undetected. If polymers are released and/or photodissociated from surfaces of small grains as they flow outward in the coma, the effective size of the grains will be reduced producing a steeper radial density gradient in the central regions of the coma. Alternatively, if polymers are the glue that holds small grains together, photodissociation of the polymers will result in an increase in the number of small grains in the outer coma. This could produce a surface brightness distribution varying less steeply than r^{-1} and may produce an observable radial color gradient in the continuum.

Also, fragmentation of HCN polymers may explain the mass spectrum peaks at 45, 61, 75, 91, 105, and possibly 121 amu detected in the coma of P/Halley with the heavy-ion analyzer RPA2-PICCA aboard the *Giotto* spacecraft (Mitchell et al. 1987; Huebner 1987). The PICCA consists of an electrostatic analyzer that was designed to provide a mass resolution of approximately 1 amu for masses up to 210 amu. These systematic mass spectrum peaks suggest the presence of long repeating chain molecules that are rich in carbon, hydrogen, nitrogen, and oxygen that can dissociate into smaller fragments. Separation of the mass peaks is 14–16 amu for which Mitchell et al (1987) and Huebner (1987) suggest progressive dissociation of CH_2 (methylene) and/or oxygen from polymerized formaldehyde (polyoxymethylene or POM). According to Mitchell et al. (1987) the observed mass spectrum clearly shows the presence of other ions in the range from 63 to 67 amu and from 93 to 95 amu that cannot be produced by the breakup of POM. It is possible that the dissociation of NH_2 and CN from the polymer provides an alternative solution to the observed mass spectrum peaks, and the 2–4 amu width of the mass peaks as noted by Mitchell et al. (1987) probably results from the dissociation or prior attachment of hydrogen atoms to unsaturated bonds or from attachment of hydrogen to open end points of the polymer chains.

We further speculate that the HCN polymerization may contribute to the buildup of gas pressures beneath the comet surface. The HCN polymers are known to consist of CN ladder structures as well as less abundant polyamidine structures. These polyamidine structures formally derive from the trimer rather than the tetramer (Matthews & Moser 1966, 1967; Matthews & Ludicky 1986; Matthews 1992). H_2O is the dominant constituent of cometary ice and could react with the various HCN polymers to release quantities of CO_2 (Volker 1960). In particular, the polyamidines have nitrile groups that are readily hydrolyzed to carboxylic acids which spontaneously release CO_2 to provide a source of CO from the photodissociation of CO_2. It is interesting to note that Delsemme (1991) has proposed formic acid, the lowest member of the monocarboxylic acid homologous series, as a significant component of the cometary nucleus in order to bring the chemical inventory of H/O into better agreement with the observed production rates ($HCOOH/H_2O$ approximately 5%). Other members of the homologous series have been identified in the interstellar medium (Turner 1989) and have been isolated from the Murchison meteorite, a C2 chondrite (Yuen et al. 1984), so their presence in cometary nuclei is expected.

6. CONCLUSIONS

A number of mechanisms have been suggested as the energy source for cometary outbursts, but none has received general acceptance. In this paper we present calculations to provide an estimate of the energy released by HCN polymerization. We have chosen to investigate this mechanism because of the presence of HCN in comets and in the interstellar medium, the presence of possible polymeric dissociation products (NH_2, CN) in cometary comae, and the energetics and reactivity of the molecular components. We have shown that HCN polymerization in the nucleus of inhomogeneous comets is a possible source of energy for outbursts. Only 6% of the energy released from the polymerization of HCN (where $HCN/H_2O = 4\%$) is needed to raise the temperature of the subsurface icy matrix from 100 K to the H_2O—H_2O sublimation temperature ≈ 150 K. At this temperature the polymerization of HCN could provide sufficient sublimation of the H_2O matrix to drive outbursts.

To explain cometary outbursts, HCN polymerization requires inhomogeneity in the comet nucleus such that the concentration of HCN in the matrix is sufficient for polymerization. H_2O is a part of this matrix and will interact with the HCN oligomers to release quantities of CO_2 and CO. This standard reaction may provide a source for the enhanced CO_2 and CO observed in outbursts and may produce a variety of long chain molecules used in the building of proteins. Simulations appropriate to cometary conditions are needed to determine whether or not this is a reasonable method for producing the observed outbursts.

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