

Pyrolysis and Combustion of Acetonitrile (CH₃CN)

Phillip F. Britt

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Chemical Sciences Division

PYROLYSIS AND COMBUSTION OF ACETONITRILE (CH₃CN)

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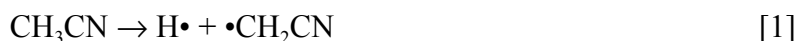
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Abstract

Acetonitrile (CH_3CN) is formed from the thermal decomposition of a variety of cyclic, noncyclic, and polymeric nitrogen-containing compounds such as pyrrole and polyacrylonitrile. The pyrolysis and combustion of acetonitrile have been studied over the past 30 years to gain a more detailed understanding of the complex mechanisms involved in the release of nitrogen-containing compounds such as hydrogen cyanide (HCN) in fires and nitrogen oxides (NO_x) in coal combustion. This report reviews the literature on the formation of HCN and NO_x from the pyrolysis and combustion of acetonitrile and discusses the possible products found in an acetonitrile fire.

PYROLYSIS

The pyrolysis of acetonitrile (CH_3CN) has been studied in a tubular flow reactor from 447 to 760°C in nitrogen (Metcalf et al. 1983), in a stirred-flow reactor from 880 to 960°C in helium (Asmus and Houser 1969), and in a shock tube from 1027 to 1827°C in argon with residence times of 0.7–1.7 ms (Lifshitz, Moran, and Bidani 1987; Ikeda and Mackie 1996). In all the studies, the major products from the pyrolysis of acetonitrile were hydrogen cyanide (HCN) and methane (CH_4). Smaller quantities of ethylene, acetylene, and acrylonitrile were reported in addition to trace quantities of cyanogen, ethane, diacetylene, fumaronitriles, dicyanomethane, and cyanoacetylene at high temperatures ($>1000^\circ\text{C}$) (Ikeda and Mackie 1996). Pyrolysis at lower temperatures (i.e., $<1000^\circ\text{C}$) also produced nitrogen-containing polymeric residue, which reduced the yield of HCN (Metcalf et al. 1983). The Arrhenius parameters for the decomposition of acetonitrile based on two sets of data are $\log k (\text{s}^{-1}) = 8.73 - 56.4/\theta$, where $\theta = 2.303RT$ in kcal mol^{-1} (Metcalf et al. 1983; Asmus and Houser 1969). The yield of HCN was found to increase with temperature, with almost quantitative yields (ca. 94%) reported in the shock tube studies, while lower yields were reported in the flow pyrolysis studies [68% (Chaigneau 1977) and 90% estimated (Metcalf et al. 1983)]. The reaction pathways for the primary products are shown below:



Subsequent reactions of the cyanomethyl radical give rise to the additional products listed above as well as HCN. In support of this mechanism, the pyrolysis rate of deuterated acetonitrile (CD_3CN) was 40% slower than that for acetonitrile, indicating that H–C homolysis was a rate-controlling step in the reaction (Asmus and Houser 1969).

The pyrolysis of CH_3CN has been modeled with a reaction scheme containing 46 species using the Sandia CHEMKIN code, together with a shock tube code, and an ordinary differential

equation solver LSODE (Ikeda and Mackie 1996). The model reproduced the experimental shock tube pyrolysis data for HCN and CH₄ yields reasonably well and predicted a maximum HCN yield of ca. 86% at 1727°C. Recently, another reaction scheme for the pyrolysis of acetonitrile has been developed containing 23 species and 43 reactions, which predicts the yields of the major and minor products in the temperature range from 1077 to 1677°C (Lifshitz and Tamburu 1998). There was very good agreement between the model and the experimental data. The model predicts the yield of HCN to increase with temperature until a maximum yield of ca. 76% is reached at 1630°C. Sensitivity analysis of the reactions scheme showed that HCN production was most sensitive to the initiation reaction 1. The cyanomethyl radical ($\bullet\text{CH}_2\text{CN}$), which was the dominant radical in the reaction, was consumed by recombination with the methyl radical ($\bullet\text{CH}_3$) to form propynitrile (CH₃CH₂CN) and by dimerization to make succinonitrile (NCCH₂CH₂CN). Independent pyrolysis of succinonitrile in a stirred flow reactor yielded equal quantities of HCN and CH₂CHCN at temperatures as low as 427°C with a 1-s residence time. At higher temperatures, secondary reactions produced fumaronitrile, dicyanoacetylene, ethyl cyanide, methane, and some polymeric material (Ikeda and Mackie 1996).

In summary, the pyrolysis of acetonitrile produces HCN and methane as the dominant products. The yield of HCN increased with temperature and reaches a maximum of ca. 90–95% at 1677°C with a residence time of 1.4 ms, but mechanistic models predicted slightly lower HCN yields (76–86 %). At lower temperatures (<1000°C) and long residence times (>2 s), a polymeric residue was formed from the polymerization of the initial products, reducing the yield of HCN.

COMBUSTION

The thermal decomposition of acetonitrile has been studied in a flow reactor in air from 400 to 1200°C (Chaigneau 1977; Dellinger et al. 1984), in a single-pulse shock tube at 1027–1827°C at pressures between 1.1 and 2.0 MPa and residence times of 0.7 to 1.4 ms with 1, 2, and 3.5 moles of oxygen per mole of acetonitrile (Ikeda and Mackie 1996), in an acetonitrile-oxygen diffusion flame diluted with argon at ca. 1940°C (where excess oxygen was present) (Crowhurst and Simmons 1984), and in a methane–acetonitrile–oxygen diffusion flame diluted

with argon at ca. 2160°C (Crowhurst and Simmons 1985). The ignition delay times of acetonitrile–oxygen mixtures diluted in argon have also been studied behind reflected shock waves at 1147–1447°C (Lifshitz, Tamburu, and Carroll 1997). In these studies, oxygen was found to enhance the decomposition of acetonitrile and alter the distribution of products compared to experiments in an inert atmosphere. The onset of decomposition of CH₃CN in air occurs at 760°C with a 2-s residence time, while 99.99% is decomposed at 950°C with a 2-s residence time (Dellinger et al. 1984). The Arrhenius parameters for decomposition of acetonitrile in air are $\log k(\text{s}^{-1}) = 7.67 - 40/\theta$, where $\theta = 2.303RT \text{ kcal mol}^{-1}$ (Dellinger et al. 1984). HCN yields increase at low oxygen concentrations at temperatures below 900°C (Chaigneau 1977), while excess oxygen decreased the yield of HCN and increased the yield of NO (Ikeda and Mackie 1996). The major products from the ignition of acetonitrile in excess oxygen were CO, CO₂, H₂O, N₂, and NO. Significant amounts of isocyanic acid (HNCO), which is considered an important intermediate in the formation of NO, were observed in reactions that were quenched at the onset of ignition (Ikeda and Mackie 1996). Production of NO occurred at least 200°C below that at which HCN was rapidly oxidized to NO, indicating that reaction intermediates were oxidized to form NO. In runs in which ignition did not take place (in the shock tube experiments with oxygen), the major products were HCN, CH₄, acetylene, and hydrogen with smaller amounts of acrylonitrile and cyanoacetylene.

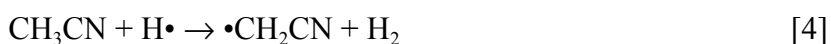
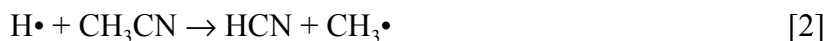
In the combustion of acetonitrile in an oxygen diffusion flame diluted in argon, the flame can be divided into three different zones:

- a. a fuel-rich zone in which pyrolysis of CH₃CN to form HCN, competes with diffusion into the
- b. main reaction zone in which CO and CO₂ are formed from combustion of CH₃CN, and
- c. an oxygen-rich zone in which NO arises from oxidation of HCN

On the oxygen side of the main reaction zone, there is a competition between NO formation and destruction (to N₂) depending on the CH₃CN to oxygen ratio. The residence time in the pyrolysis zone was estimated as 0.1 s.

There have been multiple detailed kinetic models developed for the oxidation of acetonitrile. Ikeda and Mackie (1996) developed a model containing 73 reversible steps, which

combined a set of pyrolysis reactions for acetonitrile with the Miller-Bowman mechanisms for HCN-NH₃ oxidation to describe the oxidation of acetonitrile. The model reasonably reproduces the experimental data. Below the ignition temperature (i.e., at 1312°C), the most sensitive reactions for decomposition of CH₃CN are shown below. Analysis of the rate of production of HCN indicates that a large amount of HCN is formed by reaction 2.



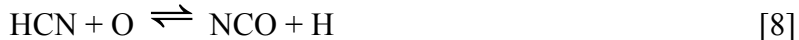
Above the ignition temperature (1427°C), the most sensitive reactions to CH₃CN decomposition were 1 and 2. The reactions that were most sensitive to NO production were 1, 2, 3, 4, and the chain branching reaction [H• + O₂ → HO• + •O (7)]. Oxygen lowers the decomposition temperature of CH₃CN and produces HCN at low temperatures as a consequence of reactions 5, 6, and 7. (HCN is produced from the combination of two cyanomethyl radicals to make succinonitrile which decomposes into HCN and acrylonitrile as described above.) It is predicted that at 727, 1227, and 1727°C, the ratio of $k_6[\text{CH}_3\text{CN}][\text{O}_2]/k_1[\text{CH}_3\text{CN}]$ is 2500, 0.9, and 0.015, respectively, indicating that at lower temperatures (<1000°C), reaction 6 will consume acetonitrile faster than reaction 1 [$\log k_6(\text{M}^{-1}\text{s}^{-1}) = 13.78 - 49.9/\theta$, where $\theta = 2.303RT$ in kcal mol⁻¹ and $\log k_1(\text{s}^{-1}) = 14.6 - 94.9/\theta$] (Ikeda and Mackie 1996).

Lifshitz, Tamburu, and Carroll (1997) modeled the ignition delay times of CH₃CN-O₂ mixtures by a reaction scheme containing 36 species and 111 elementary reactions and compared the results to experimental ignition delay times behind reflected shock waves at 1147-1477°C. From 70 experimental runs, the following correlation for the ignition delay times was derived: $t_{ign} = 9.77 \times 10^{-12} \exp(41.7/RT) [\text{CH}_3\text{CN}]^{0.12} [\text{O}_2]^{-0.76} [\text{Ar}]^{0.34}$ s, where concentration is expressed in units of mol cm⁻³ and R is expressed in kcal K⁻¹ mol⁻¹. There was good agreement between

the calculated and experimental delay times. Although many of the absolute rate constants for the reactions were slightly different from those used by Ikeda and Mackie (1996), similar conclusions were reached on the key reactions. The only new conclusion derived was that the branching step $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}\cdot + \cdot\text{O}$ played a more important role than reaction 7.

OXIDATION OF HYDROGEN CYANIDE

The mechanisms and rate parameters for the formation of NO from the combustion of nitrogen-containing compounds have been extensively studied. Miller and Bowman (1989) summarize the understanding of the mechanisms and rate parameters for the gas phase reactions of nitrogen-containing compounds at high temperatures ($>1000^\circ\text{C}$) found in coal- and oil-fired furnaces and gas turbines. In these studies, it was shown that up to an equivalence ratio ($\phi =$ fuel/oxygen ratio) of 1.2, HCN was rapidly converted to NO by the following reaction scheme:

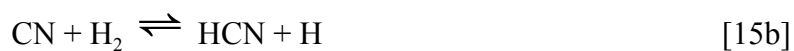


Under fuel-lean conditions, nitrous oxide (N_2O) can become an important product. The major reactions for the formation of N_2O are reactions 12 and 13, while nitrous oxide is removed by reaction 14 (Miller and Bowman 1989).





At an equivalence ratios greater than 1.2 (i.e., 1.2-1.5), NO concentration decreases relative to HCN because the conversion of HCN to NO is no longer rapid (because of low O-atom concentration), the recycle of NO to HCN begins to inhibit NO production by reactions 15–18 (shown below), and the reaction of N with NO (reaction 18) becomes favorable.



At an equivalence ratios of greater than 1.5, OH concentration is so low that N reacts with CH₃ to form H₂CN, which decomposes to HCN, as shown in reactions 19 and 20. This provides a route to reform HCN.



Experimental studies have shown that a significant fraction of NO_x emissions from some combustion sources, such as gas turbines, can be NO_2 (Miller and Bowman 1989). The primary reaction that forms nitrogen dioxide is reaction 21; but in the presence of high radical concentrations, NO_2 will be converted back to NO by reactions 22 and 23. Thus, NO_2 is expected to exist only as a transient species unless there is quenching of NO_2 in the flame.



In summary, at high temperatures ($>1000^\circ\text{C}$), the products from the oxidation of HCN in a flame depend on the HCN/ O_2 ratio. The dominant reaction pathway for the formation and destruction of NO in a flame are summarized below. It is clear that the key reactive species, such as oxygen and hydrogen atoms, as well as hydroxyl radicals, must be present in the flame for the reactions to occur efficiently. In general, in excess oxygen (i.e., $\phi < 1.2$), HCN is oxidized to NO , but in oxygen-poor environments, nitrogen yields are greater and small amounts of HCN are formed. For example, in a $\text{H}_2/\text{O}_2/\text{Ar}$ flame at low pressure in which 1 or 2 % HCN was added, the ratio of NO/N_2 for $\phi = 0.5, 1.0,$ and 1.5 (i.e., oxygen rich to oxygen poor) was ca. 3.2, 0.73, and 0.34 respectively (at 2.5 cm from the burner). In the oxygen-poor case ($\phi = 1.5$), the ratio of NO/HCN was 53, indicating that HCN was found in the product gases (ca. 1.4% of the nitrogen containing species which were $\text{NO}, \text{HCN},$ and N_2) (Miller and Bowman 1989).

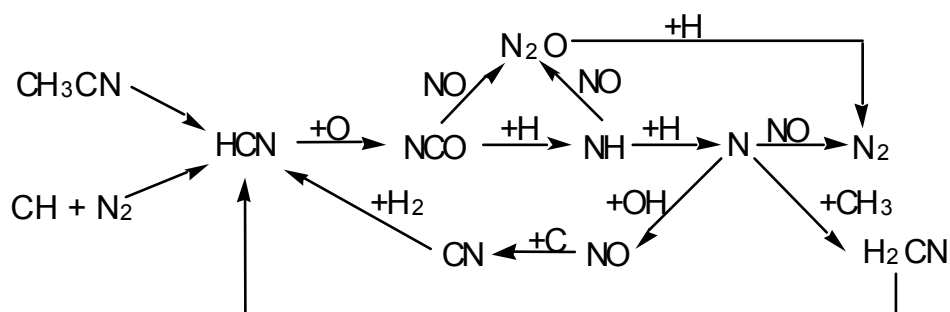


Fig. 1. Major reaction pathways for oxidation of HCN to NO , N_2 , and N_2O .

The low-temperature (i.e., <1000°C) oxidation of HCN has been studied by Houser, McCarville, and Zhuo-Ying (1988) in a plug flow reactor and a stirred flow reactor at 625–1000°C. The yield of products, NO, N₂O, and N₂, depended on reaction temperature, residence time, fuel type, and fuel (and oxygen) concentration. In general, HCN was quantitatively oxidized at 800°C with residence times of 1 s or less. In the oxidation of polyurethanes, oxidation of the evolved HCN became appreciable at temperatures as low as 550°C (Jellinek and Dunkle 1983). At temperatures of 700–800°C before ignition, N₂O yields are larger than NO yields; but after ignition, NO yields tend to dominate. Once N₂O is formed, it is not very reactive and only a small fraction can be further oxidized.

CONSIDERATIONS IN A FIRE

In the combustion of acetonitrile, HCN is formed by pyrolysis reactions and is consumed by oxidation reactions. The distribution of products, such as HCN, NO, N₂O, N₂, CO, and CO₂, depends on the acetonitrile/oxygen ratio. Because most fires tend to be oxygen deficient, there is a potential for HCN release from the combustion of CH₃CN. The temperature and residence time control the extent of decomposition of acetonitrile and efficiency of HCN formation. The autoignition temperature of acetonitrile is 523°C (973°F), and the upper and lower explosive limits are 16% and 4.4% respectively (MSDS 2001). The adiabatic flame temperature (i.e., where no heat is allowed to leave the flame) from the stoichiometric combustion of acetonitrile is 1964°C (2237°F) (Crowhurst and Simmons 1984). Thus, an acetonitrile fire's temperature could range between 523°C and 1964°C depending on the reaction conditions. The heat of combustion of acetonitrile is 298.1 kcal mol⁻¹ at 25°C (CRC 2001). Taking the typical temperatures for a wood fire (760°C, 1400°F) and an oil fire (980°C, 1796°F) and using the Arrhenius parameters for the decomposition of acetonitrile in an inert atmosphere (nitrogen or helium) and in air (where excess oxygen is present), the wt % decomposition of acetonitrile can be calculated (see Table 1). This provides some limits for the expected extent of reaction of acetonitrile in a fire.

Table 1. Calculated acetonitrile decomposition (in wt %) as a function of residence time, temperature, and atmosphere

Residence time (s)	Nitrogen		Air	
	760°C	980°C	760°C	980°C
0.1	0.006	0.8	1.6	39.0
1	0.06	7.6	14.9	99.3
5	0.3	32.4	55.3	100
10	0.6	54.3	80.0	100
30	1.9	90.4	99.0	100
60	3.7	99.1	99.9	100

In a worst case scenario, the temperatures would be greater than 1000°C and there would be no oxygen present. Under these conditions, the acetonitrile would decompose by pyrolysis, and the HCN release would be almost quantitative (ca. 90 mol % or ca. 59 wt %). At lower temperatures (<1000°C), HCN yields would be reduced by polymer formation. The oxidation of HCN to NO, N₂O, and N₂ depends on temperature, residence time, and oxygen concentration. Under the worst case scenario (limited oxygen, short residence times, and low temperatures), no HCN would be oxidized to nitrogen oxides. In excess oxygen at temperatures greater than 750°C and residence times greater than 1 s, HCN yields should be less than 5 mol % (or less than 3 wt % based on CH₃CN). The yield of HCN would decrease with higher temperatures and longer residence times. The maximum yields of NO from the oxidation of HCN could be as high as 100 mol % or as low as 0% depending on the reaction conditions. Maximum N₂O yields appear to be limited to 50–60 mol % (Houser, McCarville, and Zhuo-Ying 1988). In all cases, nitrogen (N₂) is also formed from the oxidation of HCN.

In general,

- a. Fires that have an ample supply of air (fuel/oxygen < 1.2) will produce little if any HCN and more NO than fires that are oxygen deficient (fuel/oxygen > 1.2). Oxygen access to the fire is critical to reduce or eliminate HCN emission. Thus, small fires would trend to produce less HCN than larger fires, which would tend to be fuel rich and oxygen starved.

- b. Low-temperature ($<700^{\circ}\text{C}$) smoldering fires, which have long residence times (>60 s), have the potential to produce HCN under conditions in which HCN oxidation may be slow. Thus, low temperature smoldering fires should be avoided. Under these conditions, N_2O would be the dominant oxidation product of HCN rather than NO.

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