

## OXIDATION OF CH<sub>3</sub>CN OVER SILVER: FORMATION OF SURFACE COMPOUNDS

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The oxidation of CH<sub>3</sub>CN over silver particles was examined between 200 and 300°C. The kinetic data exhibit an unusually abrupt change in activity between 270 and 300°C which is attributed to the oxidation/decomposition of surface AgCN and possibly AgOCN.

### 1. Introduction

Oxidation reaction studies over silver have shown that the surface chemistry of a particular reaction is determined by the functional group or groups contained in the reactant molecule [1-8]. Alcohols (R-OH) are oxidized to surface alkoxide intermediates (R-O<sub>ads</sub>) [1,2], aldehydes (R-C<sub>2</sub>H<sub>3</sub>) and carboxylic acids (R-C(=O)OH) are oxidized to surface carboxylate intermediates (R-C(=O)O<sub>ads</sub>) [2-5], and C<sub>2</sub> hydrocarbons (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) are oxidatively dehydrogenated to surface carbon [6-8]. No studies, however, have investigated the surface chemistry of nitriles (R-C≡N) during oxidation over silver. In the present investigation the oxidation of CH<sub>3</sub>CN over silver was examined to obtain information about the oxidation of nitriles over silver.

### 2. Experimental

Acetonitrile (Aldrich, >99%) was oxidized over silver particles in a fixed-bed flow reactor. The silver was prepared by reaction of KOH and AgNO<sub>3</sub> and had a surface area of 0.27 m<sup>2</sup>/g. The 10 cm<sup>3</sup> reactor was charged with 12.2 g of the silver particles. The acetonitrile was vaporized by bubbling helium through a saturator containing liquid acetonitrile. The total flow rate of the CH<sub>3</sub>CN-O<sub>2</sub>-He mixture was always 300 SCCM in order to maintain a constant residence

time of the gases in the reactor. The reaction products were analyzed with a HP-5830A gas chromatograph containing a Porapak Q column. The quantity of N<sub>2</sub>, NO, and CO produced could not be determined with this column since the retention time of these products coincided with the retention time of oxygen. The absence of homogeneous or wall initiated reactions was confirmed by replacing the silver catalysts with glass beads. Additional information about this reactor system is described elsewhere [9].

### 3. Results

Only the combustion products of acetonitrile (CO<sub>2</sub>, H<sub>2</sub>O, and NO<sub>2</sub>) were detected during the oxidation of CH<sub>3</sub>CN over silver. Temperature had a pronounced effect on the conversion of acetonitrile to its combustion products as shown in fig. 1A. Below 270°C the oxidation of acetonitrile was negligible, but above 270°C the conversion rapidly increased with increasing temperature. The increase in the conversion of CH<sub>3</sub>CN with temperature was very dramatic since conversion varied from 0 to 100% over an extremely narrow range of temperature, ≈25°C. An Arrhenius plot of the acetonitrile conversion data yielded an apparent activation energy on the order of 100 kcal/mole whereas typical activation energies for chemical reactions on metal surfaces vary from 10 to 35 kcal/mole. The oxygen partial pressure also had an unusually pronounced effect

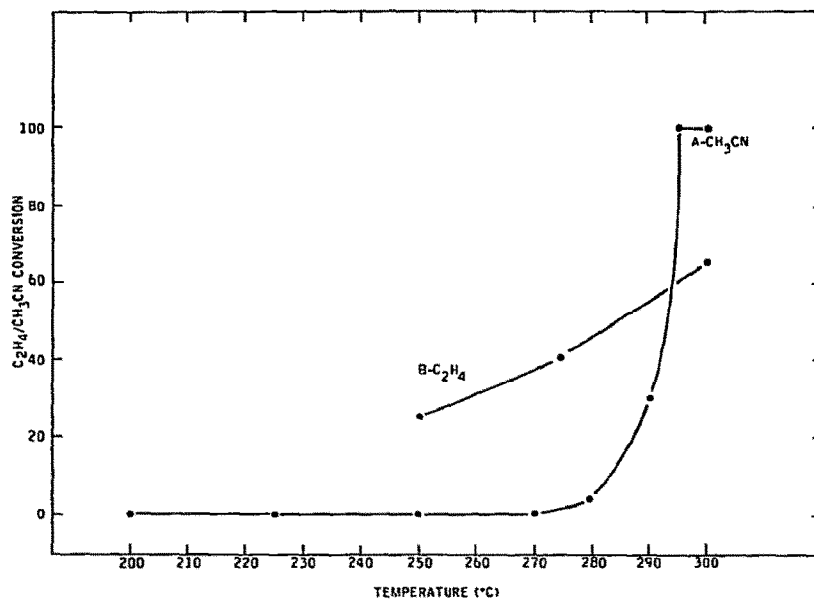


Fig. 1. (A) Oxidation of  $CH_3CN$  over silver as a function of temperature (5 SCCM  $CH_3CN$ , 30 SCCM  $O_2$ , and 265 SCCM He at 130 kPa); (B) oxidation of  $C_2H_4$  over silver as a function of temperature (5 SCCM  $C_2H_4$ , 30 SCCM  $O_2$ , and 265 SCCM He; 130 kPa)

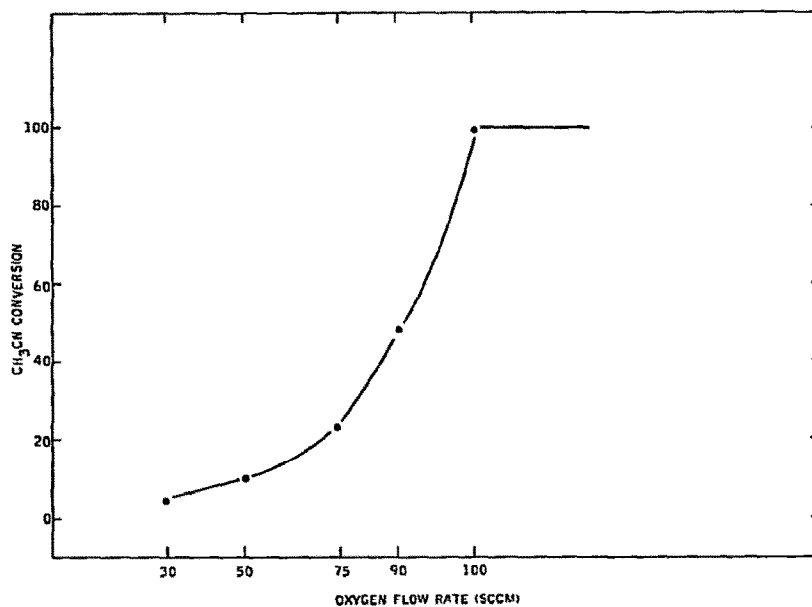


Fig. 2. Oxidation of  $CH_3CN$  over silver as a function of oxygen partial pressure (5 SCCM  $CH_3CN$ , 295 SCCM He and  $O_2$ ; 130 kPa and 279 $^{\circ}C$ )

upon the conversion of acetonitrile as shown in fig. 2. A tripling of the oxygen flow rate from 30 to 90 SCCM produced an order of magnitude increase in the conversion of acetonitrile. At 279°C the CH<sub>3</sub>CN conversion varied from ≈0 to 100% as the oxygen partial pressure was increased. The dramatic influence of oxygen partial pressure and temperature upon the oxidation of CH<sub>3</sub>CN to combustion products over silver contrasts with the behavior of hydrocarbon oxidation reactions over silver.

The oxidation of C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>CHCH<sub>3</sub> was examined over the silver catalysts in order to compare their oxidation characteristics to that of CH<sub>3</sub>CN. Oxidation of C<sub>2</sub>H<sub>4</sub> over silver produced C<sub>2</sub>H<sub>4</sub>O, CO<sub>2</sub>, and H<sub>2</sub>O as reaction products. The influence of temperature on the C<sub>2</sub>H<sub>4</sub> oxidation reaction is presented in fig. 1B. The conversion of the C<sub>2</sub>H<sub>4</sub> oxidation reaction varied from 25 to 65% over a very wide range of temperature in comparison to CH<sub>3</sub>CN oxidation over silver. An Arrhenius plot of the ethylene conversion data yielded an apparent activation energy of ≈13 kcal/mole. The oxygen partial pressure also increased the rate of ethylene oxidation, but the enhancement was minimal in comparison to the effect of oxygen upon CH<sub>3</sub>CN oxidation over silver. The CH<sub>2</sub>CHCH<sub>3</sub> oxidation over silver produced only combustion products and behaved very similarly to C<sub>2</sub>H<sub>4</sub> oxidation over silver. These studies confirm that the presence of the -CN group in acetonitrile has a significant impact on its oxidation characteristics over silver.

The oxidation of CH<sub>2</sub>CHCN over silver was also examined to determine whether other nitriles exhibit the same oxidation characteristics [10]. CH<sub>2</sub>CHCN combusted very similarly to CH<sub>3</sub>CN: conversion dramatically rose with increasing temperature as 300°C was approached and the oxygen partial pressure exerted a strong influence on conversion. Comparison of the oxidation characteristics of the nitriles, CH<sub>3</sub>CN and CH<sub>2</sub>CHCN, and the olefins, C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>CHCH<sub>3</sub>, over silver confirms that the -CN group present in the nitriles is responsible for their unique kinetic characteristics.

The low activity for the oxidation of CH<sub>3</sub>CN over silver below 270°C was due to either (1) the stability of the CH<sub>3</sub>CN molecule towards oxidation in this temperature range or (2) the formation of a stable adsorbed layer on the silver surface that inhibited the adsorption of CH<sub>3</sub>CN and/or O<sub>2</sub>. To deter-

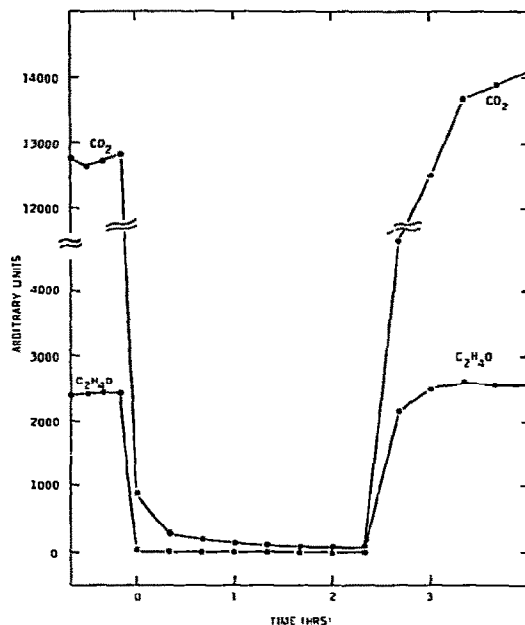


Fig. 3. Influence of CH<sub>3</sub>CN upon C<sub>2</sub>H<sub>4</sub> oxidation over silver (5 SCCM C<sub>2</sub>H<sub>4</sub>, 5 SCCM CH<sub>3</sub>CN, 30 SCCM O<sub>2</sub>, and 265 SCCM He; 130 kPa and 252°C)

mine the origin of the low CH<sub>3</sub>CN oxidation activity over silver the ethylene oxidation reaction was used to probe the chemical state of the silver surface. At 252°C the ethylene oxidation reaction readily proceeds over the silver surface to yield CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>O as shown in fig. 3. However, the addition of CH<sub>3</sub>CN to the ethylene feed inactivated the silver catalyst for C<sub>2</sub>H<sub>4</sub> oxidation. Removal of CH<sub>3</sub>CN from the ethylene feed restored the activity for ethylene oxidation. This experiment demonstrates that the low activity for the oxidation of CH<sub>3</sub>CN over silver is caused by the presence of a stable adsorbed layer on the silver surface that inhibits the adsorption of CH<sub>3</sub>CN and/or O<sub>2</sub>. Furthermore, the nature of the stable adsorbed layer on silver during nitrile oxidation is related to the -CN function of nitriles since a similarly adsorbed layer is not formed during the oxidation of olefins.

#### 4. Discussion

The oxidation of CH<sub>3</sub>CN and CH<sub>2</sub>CHCN over

Table 1  
Decomposition temperatures of bulk silver compounds

Silver compound	Bulk decomposition temperature (°C)
Ag <sub>2</sub> CO <sub>3</sub> – carbonate	218
AgOCN – cyanate	–
AgCN – cyanide	320
AgNO <sub>3</sub> – nitrate	444
AgNO <sub>2</sub> – nitrite	140

silver demonstrated that nitriles exhibit unique reaction kinetics which are related to the presence of the –CN group in these molecules. The low activity for the oxidation of nitriles over silver below 270°C is due to the formation of a stable surface layer during this reaction which inhibits the adsorption of the reactants. The dramatic increase in the rate of oxidation of nitriles over silver above 270°C with increasing temperature and increasing oxygen partial pressure is related to the oxidation/decomposition of the stable adsorbed layer on the silver surface under these conditions. The adsorbed layer is formed from the –CN function of nitriles since hydrocarbon oxidation reactions over silver do not exhibit the same unique characteristics.

The nature of the adsorbed layer present on the silver surface during nitrile oxidation can be tentatively assigned by comparison of the temperature at which the adsorbed layer decomposes, 270–300°C, with the decomposition temperatures of known bulk silver compounds. The silver surface compounds that can be derived from –CN and oxygen are Ag<sub>2</sub>CO<sub>3</sub>, AgOCN, AgCN, AgNO<sub>3</sub>, and AgNO<sub>2</sub>. The decomposition temperatures of their bulk analogs, in an inert atmosphere, are listed in table 1 [11]. Silver nitrite and silver carbonate decompose at temperatures that are low and silver nitrate decomposes at a temperature that is high relative to the decomposition of the adsorbed layer on the silver surface during nitrile oxidation. Additional information about the influence of carbonate upon oxidation reactions over silver is available from studies of C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>CHCH<sub>3</sub> oxidation [12–14]. The formation of carbonate on the silver surface exerts only a mild inhibiting effect upon the oxidation of olefins, and therefore cannot be responsible for the

formation of the stable surface layer during nitrile oxidation over silver. The decomposition of silver cyanide occurs in the temperature range where the stable silver surface layer is observed to oxidize/decompose during nitrile oxidation. The stability of the adsorbed surface layer is related to the oxygen partial pressure, as shown in fig. 2, and this might account for the slightly higher decomposition temperature of bulk AgCN in an oxygen-free environment. No information is available about the decomposition temperature of silver cyanate, but the absence of backbonding in the AgOCN structure and the presence of backbonding in the AgCN structure suggests that the decomposition temperature of AgOCN should be somewhat lower than AgCN. Without additional data the formation of AgOCN during nitrile oxidation over silver cannot be excluded. Thus, the stable surface layer formed on silver during nitrile oxidation most probably consists of AgCN and possibly AgOCN. Definitive identification of the nature of the surface layer formed during nitrile oxidation over silver can only be achieved with in situ surface techniques such as infrared spectroscopy and surface-enhanced Raman spectroscopy.

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