ADVANCES IN CATALYSIS

VOLUME 33

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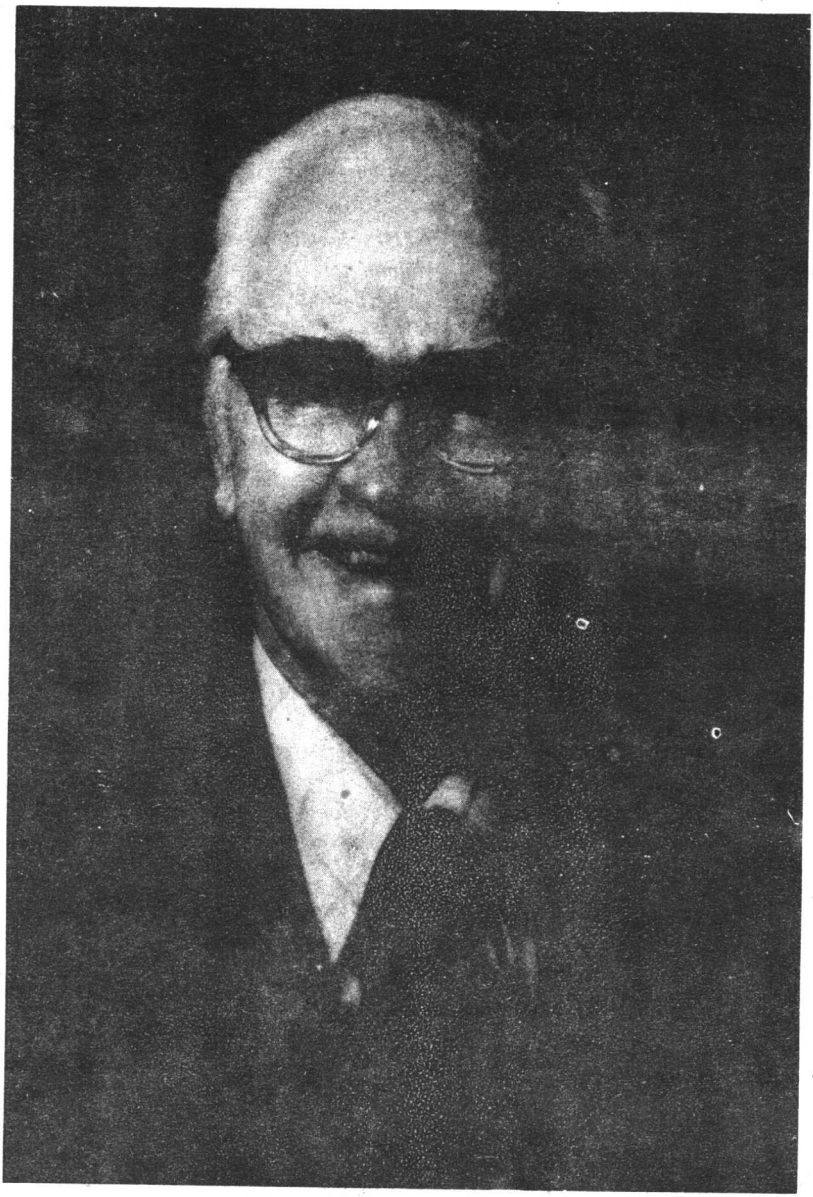

Paul Hugh Emmett, 1900–1985

Catalysis has lost a great leader. For over 60 years the creative genius of Paul Hugh Emmett challenged and stimulated the catalysis community worldwide. The techniques he developed and the mechanistic studies he directed have been vitally important in transforming catalysis from an empirical art into a highly sophisticated science. Loved and admired by all who knew him, Paul Emmett is remembered as a pioneer whose guidance will be sorely missed.

Born on September 22, 1900 in Portland, Oregon, Emmett graduated from the local Washington High School and received a B.S. degree in chemical engineering from Oregon Agricultural College (now Oregon State University) in 1922. His Ph.D. was earned in physical chemistry from the California Institute of Technology under the direction of Dr. Arthur F. Benton, who had been a student of Sir Hugh Taylor at Princeton. After a year of teaching chemistry at his alma mater in Oregon, Emmett joined the Fixed Nitrogen Research Laboratory of the U.S. Department of Agriculture (USDA) in Washington, D.C., where he spent eleven of his most productive years. In 1937 he was appointed as the first chairman of the Department of Chemical Engineering at The Johns Hopkins University in nearby Baltimore. For 5 years he served on the National Research Council's committee on contact catalysis and as a USDA consultant.

During the early years of the Second World War, Emmett directed an important National Defense Research Committee project at Hopkins that involved the use of adsorbents in gas masks to remove poison gases. In 1943 he became a division chief in the Manhattan Project, dealing with enrichment by diffusion of uranium isotopes for use in nuclear weapons. From 1945 until his death he was a consultant to the Atomic Energy Commission on peacetime uses of atomic power.

For the next eleven years (1944–1955), Emmett directed the Gulf Oil-sponsored Multiple Petroleum Fellowship at the Mellon Institute in Pittsburgh. In 1955 Emmett returned to Hopkins, but this time as the W. R. Grace Professor of Chemistry; there he remained until his retirement in 1971. His last 14 years were spent back in his beloved state of Oregon, where he held the title of Research Professor at the Portland State University. Dr. Emmett died on April 22, 1985. He is survived by his wife, Mrs. Pauline Pauling Emmett.

Paul Emmett is best known for the leading role he played in developing, along with Steven Brunauer and Edward Teller, the BET theory for measuring the surface area of porous materials. This fundamental technique laid the foundation which ushered in the modern era of catalysis in the mid-1930s.

A large fraction of Emmett's research centered around iron catalysts and the application of both radioactive and stable isotopic tracers in catalysis. His studies of the iron–synthetic ammonia system led to conclusions that remain unchallenged to this day.

At the Mellon Institute he applied ^{14}C tracers to examine the behavior of intermediates in Fischer–Tropsch synthesis over iron catalysts. By adding small amounts of radioactively labeled compounds to the CO/H_2 synthesis gas mixtures, he was able to prove that some of these compounds (e.g., small alcohols) are involved in the initiation step of the chain growth process that leads to larger hydrocarbon products. It was during this era that his associates first placed a catalytic reactor into the carrier gas stream of a gas chromatograph and developed the "microcatalytic pulse reactor," which is now a standard piece of equipment for mechanistic studies with labeled molecules. While at Mellon Institute Emmett began editing his comprehensive set of seven volumes called *Catalysis*, which he continued at Hopkins.

Nor did catalytic cracking escape the probing attention of Paul Emmett. At Johns Hopkins his students used labeled molecules extensively to examine the nature of secondary reactions in the cracking of cetane over amorphous silica–alumina and crystalline zeolites. They demonstrated that small olefins (e.g., propylene) are incorporated extensively into higher-molecular-weight molecules, especially aromatics, and are the primary source of coke formation on these catalysts.

A member of the National Academy of Sciences, Paul Emmett received numerous honorary degrees, awards, and medals in the United States, Europe, and Japan. His name has been immortalized through the Paul H. Emmett Award in Fundamental Catalysis administered by the Catalysis Society of North America. With over 150 research publications during his lifetime, Emmett was for 10 years an associate editor of the *Journal of the American Chemical Society*. His membership in the ACS spanned over 60 years, and he served as a Councilor from the Pittsburgh section during the early 1950s. Emmett attended the very first Gordon Research Conference in 1931 and occupied a front row seat at each of the GRC Conferences on Catalysis until his death. Twice he served as chairman of that annual conference.

One of the most notable attributes about Paul Emmett was his incredible memory. He was literally a walking encyclopedia of useful references from the chemical literature. This in-depth knowledge caused him to be in great demand as a consultant. Those of us who had the opportunity to study under the tutelage of this creative man will always remember and appreciate the personal interest he

took in our career development. While his death is a time of sadness, Emmett's life was filled with a multitude of insightful innovations that have greatly expanded the horizons of science and have had a positive impact on all of mankind.

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ADVANCES IN CATALYSIS, VOLUME 33

Homogeneous Nickel-Catalyzed Olefin Hydrocyanation

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I. Introduction and Scope

A. Old ADN[1] Technology

Adiponitrile (ADN) has been a molecule of considerable industrial importance ever since the development of Nylon 66 by du Pont during the 1930s. Adiponitrile is hydrogenated to hexamethylenediamine which in turn is condensed with adipic acid. Because of the large volume of Nylon 6,6 produced worldwide (6 billion lb/yr), it is not surprising that considerable time and resources have been dedicated to developing the most efficient process for the production of ADN. From a feedstock economics viewpoint, the addition of 2 mol hydrogen cyanide to butadiene to give ADN has always been very attractive. However, the technology for direct addition of HCN to butadiene was unknown until the late 1960s. Prior to that time, an indirect method was utilized.

The indirect hydrocyanation of butadiene as practiced by du Pont (*1*) involved the electrolysis of sodium chloride, formation of sodium cyanide from HCN using the NaOH, chlorination of butadiene to give 1,4-dichloro-but-2-ene, chloride displacement with sodium cyanide, and subsequent hydrogenation, as indicated in Eqs. (1)–(5), with the net result of Eq. 6.

$$2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} Cl_2 + 2NaOH + H_2 \quad (1)$$

$$2NaOH + 2HCN \longrightarrow 2NaCN + 2H_2O \quad (2)$$

$$C_4H_6 + Cl_2 \longrightarrow C_4H_6Cl_2 \quad (3)$$

$$C_4H_6Cl_2 + 2NaCN \longrightarrow C_4H_6(CN)_2 + 2NaCl \quad (4)$$

$$C_4H_6(CN)_2 + H_2 \longrightarrow NCC_4H_8CN \quad (5)$$

$$\text{Net: } C_4H_6 + 2HCN \longrightarrow NCC_4H_8CN \quad (6)$$

Though this process was used successfully for many years, the electrolysis of 2 mol NaCl to make 1 mol of ADN, and the corrosive nature of chlorine made the direct addition of HCN to butadiene highly desirable.

[1] Abbreviations: A, Lewis acid; ADN, adiponitrile; BD, butadiene; C2M2BN, *cis*-2-methyl-2-butenenitrile; Cp, cyclopentadienyl; C2PN, *cis*-2-pentenenitrile; Cy, cyclohexyl; DCN, deuterium cyanide; DN, dinitrile; ESN, ethylsuccinonitrile; HCN, hydrogen cyanide; L, a phosphorus ligand; 2M2BN, 2-methyl-2-butenenitrile; 2M3BN, 2-methyl-3-butenenitrile; MGN, 2-methylglutaronitrile; Ph, phenyl; PN, pentenenitrile; 2PN, 2-pentenenitrile; 3PN, 3-pentenenitrile; 4PN, 4-pentenenitrile; THF, tetrahydrofuran; T2PN, *trans*-2-pentenenitrile; T3PN, *trans*-3-pentenenitrile.

It should be noted that ADN is also synthesized commercially by electrolytic coupling of acrylonitrile (*2*).

B. Early Attempts to Hydrocyanate Olefins

The addition of hydrogen cyanide (HCN) to carbon–carbon double bonds activated by electron-withdrawing groups in the presence of a base as a catalyst (a variation of the Michael Reaction) has been known for a long time. Nitriles were also obtained by hydrocyanation of branched olefins, such as isobutylene and trimethylethylene, in vapor phase reactions; in particular the reactions over alumina (*3*) and cobalt-on-alumina (*4*) were reported in the late 1940s and early 1950s. Addition of HCN to conjugated dienes in the presence of cuprous salts (vapor and liquid phase) was reported as early as 1947 (*5*).

The first example of homogeneously catalyzed olefin hydrocyanation was reported by Arthur *et al.* in 1954 (*6*). Unactivated monoolefins, as well as conjugated dienes, were hydrocyanated in the presence of dicobalt octacarbonyl. Hydrocyanation of monoolefins appeared to become more difficult as the chain length of the olefin increased. For example, under similar conditions, ethylene, propylene, and 1-butene gave >65% conversion to nitriles whereas 1-octene gave only 13% conversion. Styrene gave >50% conversion to 2-phenylpropionitrile. 2-Butene, having an internal double bond, gave only 9% conversion to 2-methylbutyronitrile; only branched nitriles were formed. The addition of HCN to conjugated olefins such as butadiene and isoprene gave primarily 1,4-addition products—results similar to the copper halide catalyzed reaction. Interestingly, nonconjugated dienes isomerized *in situ* to allow 1,4-addition. Although some dinitrile was observed in these cases, it was always a branched isomer; no adiponitrile was observed in the reaction of butadiene.

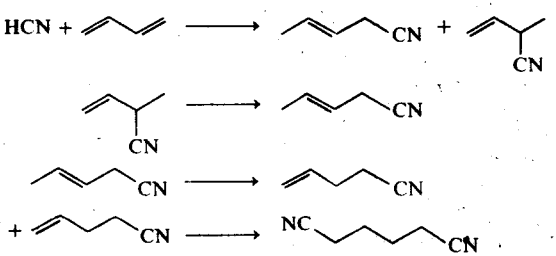
The problem of terminal addition (anti-Markovnikov) of HCN to isolated unactivated double bonds was not solved until carbon monoxide-free, low-valent transition metal complexes became available. During the mid 1960s, W. C. Drinkard allowed 1-hexene to react with HCN in the presence of tetrakis(triethylphosphite)nickel(0) and the resulting product mixture contained a small amount of the terminal addition product *n*-heptanenitrile, and Drinkard and Lindsey found that the reaction with 3-pentenenitrile produced ADN (*7*).

Irreversible oxidation by excess HCN during batch reactions limited Ni(0) catalyst lifetime and so further work was undertaken to improve catalyst utility. It was reasoned that the addition of $NaBH_4$, a reducing agent, might reduce Ni(II) *in situ* back to the active zero-valent form. Addition of $NaBH_4$

along with a very slow feed of the HCN (so-called semibatch feed) did result in a large improvement in catalyst activity and lifetime. However, $NaBH_4$ did not function by reducing oxidized nickel. Analysis of the reaction mixture showed that significant dinitrile production did not begin until $NaBH_4$ had disappeared; actually HCN, $NaBH_4$, and 3-pentenenitrile were reacting to form trialkylboron compounds (*8*)! The promotional effect of Lewis acids in the hydrocyanation of monoolefins had been discovered. A number of Lewis acid cocatalysts were found (*9*) which improved catalyst activity, and the hydrocyanation of 3-pentenenitrile to produce adiponitrile began to appear to have commercial significance. The first plant utilizing this technology began operation in 1971. The thirty years du Pont had spent scouting research in hydrocyanation had finally paid off!

C. The Current ADN Process

The current hydrocyanation process can be broken down into two major steps. In the first, HCN is added to butadiene in the presence of an NiL_4 catalyst to give 3-pentenenitrile (3PN) and 2-methyl-3-butenenitrile (2M3BN) [Eq. (7)]. Fortunately the branched 2M3BN may be isomerized to the linear 3PN isomer [Eq. (8)]. In the second step, a Lewis acid promoter is added to the NiL_4 (L = a phosphorus ligand) catalyst to effect the double bond isomerization of 3PN to 4-pentenenitrile (4PN) concurrently with the



selective addition of HCN to 4PN [Eqs. (9) and (10)]. By-products in the second step include 2-methylglutaronitrile (MGN), ethylsuccinonitrile (ESN), and 2-pentenenitrile (2PN) arising, respectively, from Markovnikov addition to 4PN, direct addition of HCN to 3PN, and isomerization of 3PN to its conjugated isomer which is not hydrocyanated.

D. Description of Semibatch, Pulse, and Continuous Reactors

Whereas many nickel-catalyzed olefin hydrocyanation reactions may be run in the batch mode (i.e., all reagents charged to the vessel at the beginning of reaction), it is often preferable to feed one or more components in a

controlled manner. For this reason, three different types of reactor system have been utilized to gather the data described below: semibatch, pulse, and continuous.

The semibatch reactor is the simplest. All reagents except the HCN are placed in a thermostated vessel (usually glass). HCN is then fed in a controlled manner by syringe pump as a pure liquid (or more usually as a solution). An even simpler method of adding HCN is vapor transfer; pure liquid HCN is maintained at 0°C in an ice bath and a controlled flow of nitrogen gas bubbled through it. The resulting vapor is about 35% HCN and may be fed directly into the reaction mixture or more commonly just above the mixture (the HCN is adsorbed from the vapor very efficiently). The reaction may be followed thermally (exothermic reaction), by IR spectroscopy (nitrile bands), or by gas chromatography (GC). Most of the nonspectroscopic results described below were obtained in this manner and indeed most of the scouting and optimizations were carried out this way. However, because kinetic studies are very difficult if not impossible by this method, a pulse reactor system was developed.

The pulse reactor method is similar to semibatch in that all the ingredients except HCN are placed in a small, well-mixed vessel in a thermostated bath. Very small amounts of HCN are then rapidly injected into the reaction mixture with vigorous mixing and the exotherm is monitored. Repeated pulses are made only after the reaction mixture has come back to temperature equilibrium with the bath. In this manner, kinetic information may be obtained.

Whereas much mechanistic information can be obtained by one of the above methods, any practical applications must be demonstrated under conditions similar to process operation, i.e., continuous flow. Small glass reactors which allow controlled addition of reagents by syringe pump and continuous removal and monitoring (IR spectroscopy) of product mixture have been developed. Much of the information obtained from semibatch operation has been reproduced under these continuous flow conditions.

E. Scope

In this article, we will discuss the chemistry behind the du Pont adiponitrile process from a mechanistic viewpoint (*10*). It is not intended to be a comprehensive review of the hydrocyanation literature. We will restrict ourselves rather to homogeneous nickel-catalyzed hydrocyanation of olefins and will depend primarily on du Pont studies. Reviews which explore hydrocyanation in a more general way include those of Brown (*11*), Hubert and Puentes (*12*), and James (*13*). A general review of low-valent organonickel chemistry has been published by Jolly and Wilke (*14*).

Before discussing hydrocyanation chemistry we will explore the interaction of zero-valent nickel phosphite complexes with various independent components of the catalytic system. Then, in turn, we will examine the catalyzed addition of HCN to butadiene, the isomerization of olefins, and the addition of HCN to monoolefins. Finally, a summary of the mechanism as it is now understood will be presented.

II. Equilibria Involving Nickel(0) Complexes

A. NiL_4 Dissociation

The development of the adiponitrile process has had considerable impact on the process of organometallic chemistry. The discovery that certain zero-valent nickel complexes catalyze the hydrocyanation of butadiene (*7*) led to extensive studies on the formation and reactions of NiL_4 complexes. In particular, a detailed understanding of the solution behavior of tertiary phosphine and phosphite complexes of nickel and their substitutional chemistry was developed at an early stage after it was discovered that the ability of phosphorus ligands to compete for coordination to Ni(0) was dominated by ligand size. This led to a heightened awareness of the general importance of steric effects in organometallic chemistry and Tolman and co-workers (*15–20*) quantified the steric and electronic factors which affect the reactivity of NiL_4 complexes for a broad variety of phosphorus ligands; steric factors of a ligand L were defined by cone angle whereas electronic factors were measured by the change in carbonyl vibrational frequency (ν_{CO}) in $Ni(CO)_3L$. Whereas electronic factors contribute to the substitutional reactivity of NiL_4 complexes, the strengths of the nickel–phosphorus bonds [which range between 32 and 39 kcal/mol in NiL_4 complexes (*20*)] are dominated by steric effects. For example, in the complexes $Ni[PPh_3]_4$ (Ph = phenyl) and $Ni[P(O\text{-}o\text{-tolyl})_3]_4$ the phosphorus ligands are electronically very different but sterically similar [cone angles of 145° and 141° for PPh_3 and $P(O\text{-}o\text{-tolyl})_3$, respectively] and both show extensive ligand dissociation in solution (*18*). While ligand exchange in the phosphine complex is so rapid that no ^{31}P resonance can be observed in the NMR spectrum until one gets to low temperatures (*21*), the phosphite complex spectrum shows distinct signals for NiL_4, NiL_3, and L even at room temperature and above (*17*). The complex $Ni[P(OEt)_3]_4$, with a smaller ligand cone angle of 109°, is not dissociated to any detectable extent even in highly dilute solutions at 70°C (Table I). Virtually all substitution reactions of NiL_4 complexes involve prior