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Environmentally Safer Processes: Opportunities for Catalysis & Process R&D

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Abstract

Increasing awareness over the environmental impact of chemical processes and products is having a profound impact on the petroleum and chemical industry. In addition to remediation, there are tremendous opportunities for catalysis and process research in four main areas: 1) more selective and active catalysts to reduce waste and energy consumption; 2) waste minimization through conversion of byproducts to coproducts; 3) processes which minimize the use, transportation and storage of hazardous materials; 4) development of environmentally safer products. Examples from recent Du Pont research will illustrate the potential in each of these areas.

Introduction

The general public is becoming much more concerned over environmental issues, and decisions are being made that are not necessarily based on science. For the chemical industry it is becoming increasingly difficult to obtain permits, eliminate waste, construct incinerators and receive and ship toxic materials. The effect will clearly increase the relative importance of environmental vs variable costs for current and future plants. As a result, the following will become increasingly important: processes with 100% yield (by whatever means); catalyst recovery, regeneration and recycle; heterogenization of homogeneous catalysts; increasing importance of chiral pharmaceutical and agrichemicals; polymer recycle and environmentally safer processes. Several of these aspects, from Du Pont R&D will be highlighted during this seminar.

High Yield-Low Waste Processes

Elimination of byproducts and process waste is becoming a major issue and will clearly determine the viability of future chemical processes. Those processes which strive for zero emissions and very high process yields at the lowest cost will be winners in the 21st century. It is difficult to project the total effect of environmental issues much into the future, other that to say that they will become increasingly important. I will describe one process which is illustrative of a low waste processes.

The synthesis of HCFC-141b, results from Du Pont's work on the development of alternatives to the ozone depleting chlorofluorocarbons (CFCs). It is a replacement for several solvent blends and azeotropes, and for blowing foams:

$$\underset{\mathit{VCl_2}}{CH{=}CCl_2} + HF \longrightarrow \underset{\mathit{141b}}{CH_3CFCl_2} + \underset{\mathit{142b}}{CH_3CF_2Cl} + \underset{\mathit{143b}}{CH_3CF_3} \quad (1)$$

Historically, low yields to 141b have been reported since the reaction is thermodynamically in favor of HFC-143a. We discovered[1] that a specially prepared AlF_3 catalyst was remarkably selective in producing 141b in nearly quantitative yield. The reactor was divided into two stages such that a high degree of conversion of VCl_2 was obtained in the first step. The second stage conditions are adjusted to provide a liquid film on the catalyst. As a result, the yield of 141b is 99.5%, with <500 ppm of VCl_2 remaining in the product. As a result, it is possible to go directly from the reactor into a product tank with no refining and recycle. The product directly from the reactor meets the purity specifications defined by an international toxicity panel.

Waste Minimization and Resourcing

The ultimate objective of industrial scientists is to develop chemical processes that have 100% yield and operate under conditions that require minimal energy. Unfortunately, modern technology does not allow us to economically achieve these goals. Our challenge is to effectively manage process byproducts and waste through minimization or conversion to salable products (resourcing). Unused products have traditionally be disposed of by incineration, atmospheric venting or underground injection. Historically there has been little incentive to recover and utilize these byproducts. Increasing environmental awareness and concern is now providing the initiative to reconsider these disposal options. Several examples will be discussed.

Hydrofluoric acid is currently produced in very large volume for the production of many specialty fluorochemicals and fluoropolymers. It is produced by reaction 2:

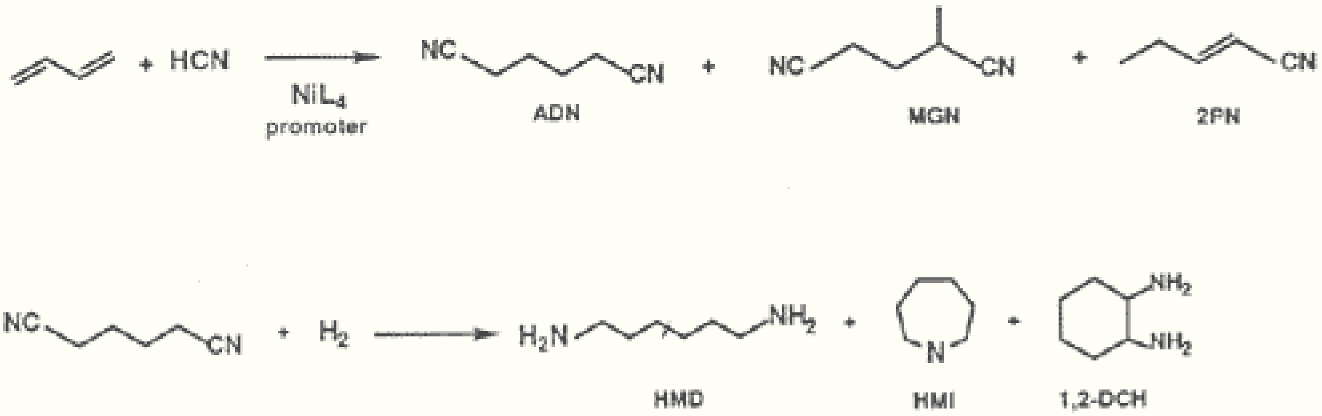
$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4 \quad (2)$$

The stoichiometry shows that 3.4 lbs of $CaSO_4$ are produced for every pound of HF produced. At the Du Pont LaPorte Texas site, since the early 1960's over 4 million tons have been stockpiled over an area covering 60 acres. With the need approaching to develop a new site, plant technical evaluated process improvements which took advantage of the unique forms of $CaSO_4$ produced in our process. By working with the Texas Water Commission, the byproduct was found to pass all leachate tests and was reclassified from a byproduct to a coproduct. In collaboration with a Gulf States, Inc., new applications for this material were found as substitutes for limestone and gypsum in road base and drywall applications. As a result of that effort, approximately 50% of new road construction in Houston uses this plant product and the size of the $CaSO_4$ stockpile has been reduced to pre-1978 levels, a new landfill has been avoided and waste material as been utilized.

Du Pont's adiponitrile process is used to manufacture hexamethylenediamine, a precursor to nylon 6.6. The main process steps are shown in Figure 1.

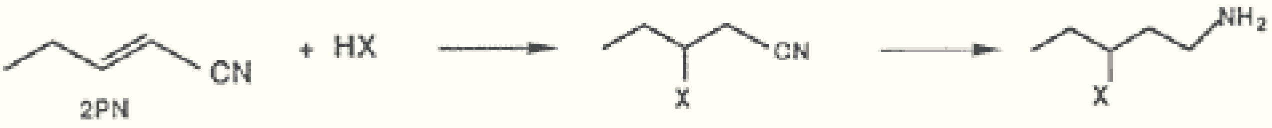
Figure 1. Du Pont Hexamethylenediamine Process

Main Chemistry



Two moles of hydrogen cyanide are added to butadiene, in a two-step process, using a zero valent nickel phosphite catalyst to produce the linear (ADN) and branched (MGN) C_6-dinitriles in very high yield. A small amount of the conjugated, undesirable, 2-pentenenitrile (2PN) has historically been separated and incinerated. The ADN is catalytically hydrogenated to hexamethylenediamine (HMD) is very high yield, although small amounts of other cyclic amines such as HMI, and 1,2-DCH are produced. Several years ago we began searching for opportunities to convert these minor byproducts into usable products instead of incinerating them.

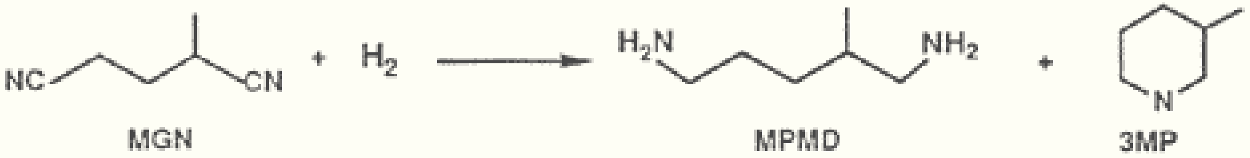
The linear, conjugated, 2PN, was found to react readily with amines, (HX) to give 2-cyanobutylated amines as shown in equation 3.



(3)

Hydrogenation of the aminonitrile with a Raney® catalyst leads to a family of branched diamines. Because of the branching, most of the aminonitriles and diamines are liquids at low temperature and have low freezing points. They have found markets as comonomers or curatives, since they lower polymer viscosity, crystallinity, and glass transition temperature.

Catalytic hydrogenation of MGN with a Raney catalyst gives the branched-amine methylpentamethylenediaminee, MPMD, or 3-methylpiperidine (3MP) (4):



(4)

The product is dependent on conditions and choice of catalyst. The MPMD was initially isolated from plant streams to develop the market. Many applications were found as a polymer additive in urethanes and epoxies to reduce crystallinity and viscosity, as a water treatment chemical and as a monomer is polyamides. This material was once incinerated for its fuel value but after a 10 year development effort it's use has grown so that a dedicated commercial facility is now used to produce this valuable coproduct, on purpose.

Two byproducts, 1,2-diaminocyclohexane (DCH) and hexamethyleneimine (HMI) are produced during ADN hydrogenation[2], resulting from a cyclic deamination reaction. These compounds were initially isolated from plant streams and slowly introduced into the marketplace. Through a long development program they have found growing applications as epoxy-curing agents and agricultural intermediates. A new dedicated commercial catalytic process has been started up to satisfy this new market.

Many other examples from Du Pont's polyester, Kevlar®, and adipic acid processes could be presented to show the clear value of catalytic technology to convert waste byproducts to valuable coproducts. Even a 1% yield loss, in a billion lb/year process can generate 10 million lbs/yr of material that can be burned as a byproduct or converted to a higher value in use coproduct. Waste resourcing makes sense if there is a very strong, long term corporate commitment to do so. This commitment by Du Pont for the HMD process, for example has taken over 15 years. These efforts across the entire coproduct business, currently generate several hundred million dollars in sales. Further efforts are expected to expand this new business to $ 1 billion/year in sales by 2000, an effort that relies very heavily on catalysis and process R&D.

Hazardous and Toxic Materials Management

Hazardous and toxic materials such as HCN, HF, HCl, Cl_2, acrylonitrile, formaldehyde, ethylene oxide, sulfuric acid and phosgene, for example, are essential building reagents in the chemical industry since they often contain functionality or reactivity required for further chemical reactions. Future business practices must avoid or minimize the inventory and transportation of these materials.

Methylisocyanate (MIC) is familiar to us as a result of the tragic incident at Bhopal. It was produced by the phosgenation of methylamine:

$$CH_3NH_2 + COCl_2 \longrightarrow CH_3NCO + HCl \quad (5)$$

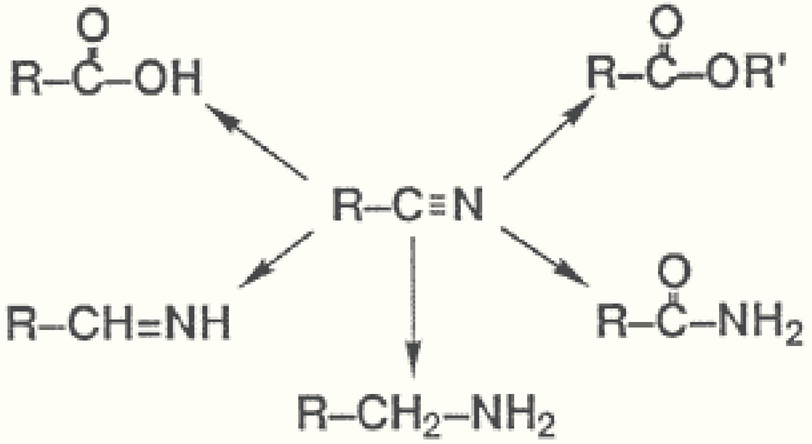
As a consumer of MIC, Du Pont was concerned over the use and storage of this toxic material. Prior to Bhopal, we began research on a new process that would produce MIC from less hazardous materials and minimize its handling and storage. The proprietary[3] catalytic oxidative-dehydrogenation process, shown in equations 6-7 was discovered:

$$CH_3NH_2 + CO \longrightarrow CH_3NHCHO \quad (6)$$

$$CH_3NHCHO + O_2 \longrightarrow CH_3NCO \quad (7)$$

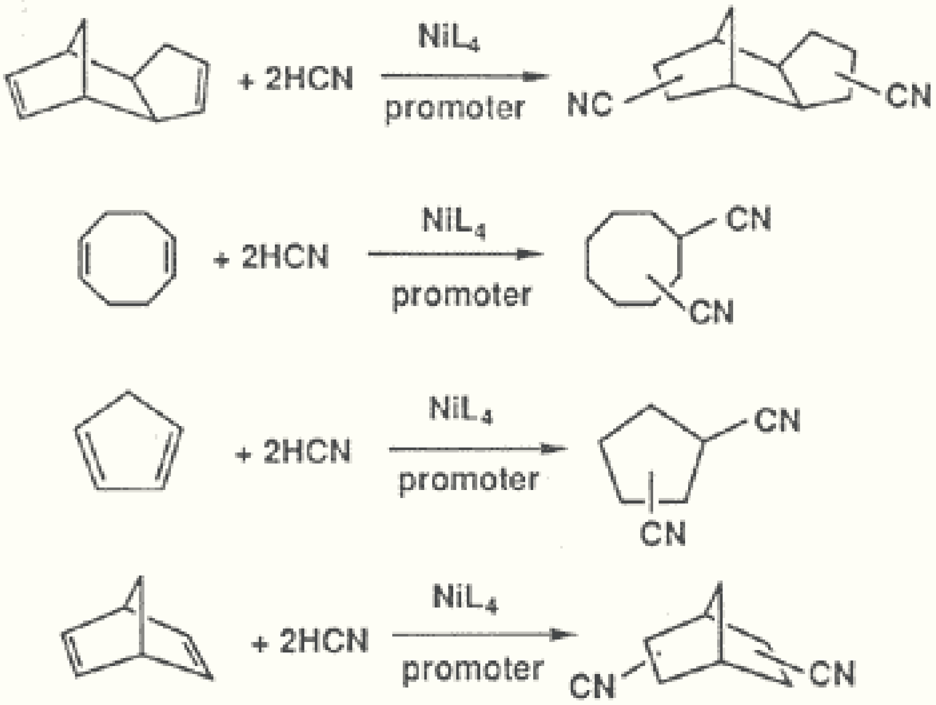
This innovative research has resulted in a commercial Du Pont process that makes MIC and converts it *in-situ* to an agrichemical product. Consequently, the potential for exposure is greatly reduced. This trend in *in-situ* manufacture and derivatization is clearly the way of the future for hazardous chemicals. Another example involves HCN. Du Pont is a large producer of HCN for internal use and external sales. The nitrile functionality is extremely versatile in organic synthesis since it is easily converted to amides, acids, amines, esters, etc as shown in Figure 2.

Figure 2. Versatility of Organic Nitriles



Conversion of the HCN, at our manufacturing sites would provide an environmentally safer option. We are using our proprietary hydrocyanation technology (similar to that shown in Figure 1) to prepare nitriles for transportation and customer functionalization. A vast number of nitriles have been produced by catalytic homogeneous hydrocyanation of mono, di, tri or polyolefins. Some representative examples are shown in Figure 3. The mono, di and tri nitriles

Figure 3: Examples of Diene Hydrocyanation



are currently being evaluated in the market place. Non-phosgene routes to isocyanates, and use of solid acids to avoid HF and H_2SO_4 as alkylation catalysts are other examples of research in progress to further minimize the use of hazardous materials.

Environmentally-Safer Products

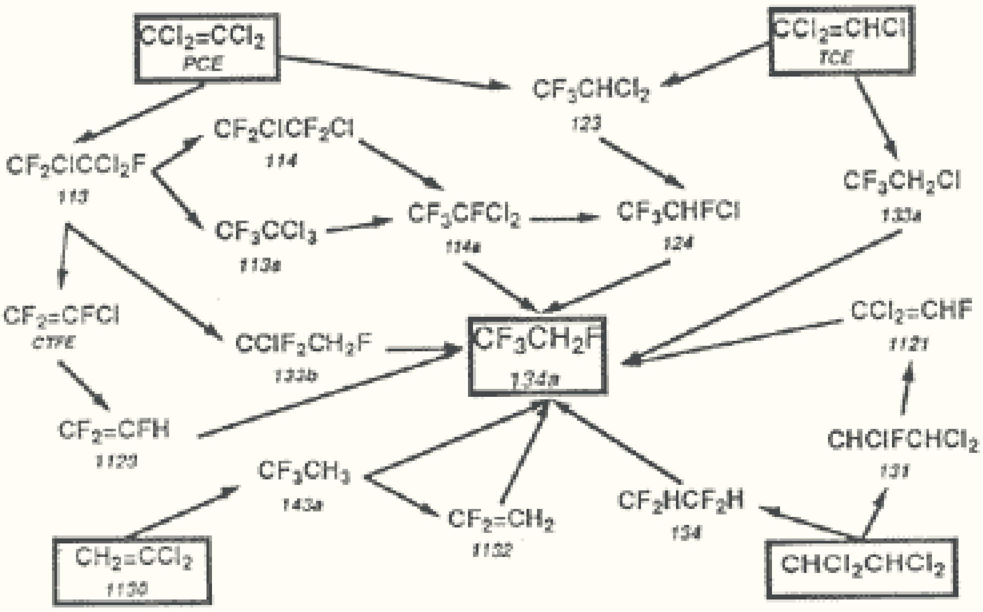
Although products are introduced into the market to serve societal needs, their impact on the environment is not always predictable. The use of tetraethyl lead in gasoline provided a high octane gasoline for many years. However, lead has now been phased out in certain parts of the world, in favor of environmentally safer oxygenated organics such as methyl-t-butyl ether (MTBE). New catalytic technology is providing more isobutylene and MTBE for this large volume chemical. Another recent example[4-5] involves the recognition that ozone is being depleted by man-made chlorocarbons such as methylchloroform, carbon tetrachloride and chlorofluorocarbons (CFCs). Although these chemicals have served society very well it was not until atmospheric science developed during the late 1980's provided scientific evidence that they were causing significant ozone depletion (nearly 50 years after they were first introduced). As a result, industry has responded rapidly and is currently developing and commercializing safer products. Some of the products currently under development by the CFC industry to replace chlorofluorocarbons are shown in Table 1.

Table 1. Potential CFC Substitutes

Market	Current CFC	CFC-Alternative
Refrigerants	CFC-12 (CF_2Cl_2)	HFC-134a (CF_3CFH_2) HCFC-22 (CHF_2Cl) HFC-32 (CH_2F_2) HFC-125 (CF_3CF_2H) HCFC-124 (CF_3CHFCl) HFC-152a (CH_3CHF_2) Blends/Azeotropes
Blowing Agents	CFC-11 ($CFCl_3$)	HCFC-141b (CH_3CFCl_2) HCFC-123 (CF_3CHCl_2) HCFC-22 (CHF_2Cl) Blends/Azeotropes
Cleaning Agents	CFC-113 ($CF_2ClCFCl_2$)	Blends/Azeotropes New Compounds

These new products are much more complex than the CFCs they are replacing and require much more complicated catalytic technology. Most CFCs are produced in a single catalytic step while alternatives such as HFC-134a can require 2-5 complex catalytic steps as shown in Figure 4.

Figure 4: Potential Routes to HFC-134a



The key to their reduced ozone and global warming potentials is that they contain hydrogen atoms. As a result they have significantly shorter atmospheric lifetime because they are less stable. However, this also creates problems in their synthesis because they decompose readily, resulting in rapid catalyst deactivation. Longer lived catalysts have subsequently been developed. A detailed summary[6] of the catalytic chemistry reported for the preparation of the most significant CFC alternatives has been reported. Without rapid development of these new catalytic processes, CFCs would continue to be produced, resulting in further ozone depletion. As a result of Du Pont's effects to date, over $ 400 million have been spent and projected costs for full conversion of CFCs to alternatives is estimated to be about $ 1 billion dollars.

Similar process development is underway to find environmentally-safer substitutes for a variety of chemicals, polymers and products currently used by society.

Conclusions

I hope that I have been able to show you the importance of catalysis and process research for developing environmentally safer processes and products for the future. This will become a condition for staying in business and those companies which commit resources will succeed. This provides an excellent opportunity for collaborations between government, academic and industrial laboratories. The long range research necessary to discover new chemistry and develop mechanistic understandings of current industrial processes can be exciting areas for joint collaboration. Universities and industry must work together to make this process easier.

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