ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 3, pp. 337–347. © Pleiades Publishing, Ltd., 2011.
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In memory of Mikhail Grigor'evich Kucherov, an outstanding organic chemist who discovered the first industrially important reaction catalyzed by metal complexes (to the 130th anniversary of the discovery in 1881 and to the 100th anniversary of the day he died in 1911).

Green Chemistry in the Bulk Chemicals Industry

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Received October 8, 2010

Abstract—The bulk chemicals industry is a branch of the chemical industry whose assortment includes key organic synthesis products and intermediates. The world output of these products is as large as millions of tons. This scale requires the use of not only maximally inexpensive raw materials but also the most selective and energy-efficient processes for converting them into target products. This paper considers the examples of changing the sources of raw materials and developing catalysts and processes to minimize environmental disruption. The majority of these new processes have been introduced into industry well before the appearance of the term *green chemistry*; their development has been stimulated by not only environmental protection but also economic reasons.

DOI: 10.1134/S0023158411030141

INTRODUCTION

Industrial organic synthesis had its genesis in the 19th century. In 1842, Zinin discovered the transformation of nitrobenzene into aniline [1]. This reaction became the basis of the aniline dye industry—one of the very rapidly developing branches of heavy organic synthesis. Needs for dyes and spices were driving forces that impelled seafarers to voyages, in the course of which great geographical discoveries were made. The Zinin's discovery placed the industry of dyes on a synthetic basis. The German chemist Hofmann, an outstanding contemporary of Zinin, highly appreciated this discovery and said that if Zinin had done nothing else but the conversion of nitrobenzene into aniline, his name would have nevertheless been written in golden letters in the annals of chemistry [2].

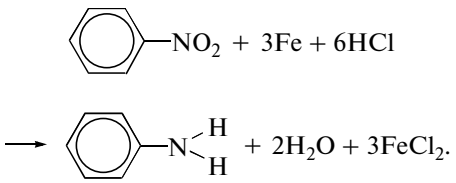
The aniline production rapidly increased. A leader of the industrialization of Germany intentionally introduced the word *aniline* into the company name Badische Anilin- und Soda-Fabrik AG (BASF). This concern rapidly organized the production of aniline dyes in various countries. In Russia, this was the famous Butyrskii chemical plant. Currently, the world production of aniline exceeds 3 million tons annually and grows at a rate of 5–7% per year. It is clear that it is unprofitable to reduce nitrobenzene with ammonium sulfide in accordance with the protocols of Zinin's experiments in order to manufacture aniline on this scale. Moreover, the utilization of colloidal sulfur, which is formed in the course of oxidation of the reducing agent, would become a considerable obstacle in the commercial production of aniline by this method.

The problem of utilization of wastes that cannot be efficiently used appeared more frequently during the development of chemical industry. Professor Sheldon (Delft University of Technology), who analyzed the situation in industry, concluded that the influence of chemical production on the environment should be quantitatively assessed [3]. He proposed the concept of the E-factor (environmental factor), which is calculated as $E = €(S_p/P)$, where S_p is the amount of nonutilizable waste (salts in the terminology of Sheldon), P is the amount of a useful product, and € is the unfriendliness factor of salts. In the ideal case, $E = 0$. In the calculation of the environmental factor, stoichiometric yields are used and the amount of the formed water is ignored. Thus, ideally, the production of aniline from nitrobenzene by the reaction

$$PhNO_2 + 3H_2 \longrightarrow PhNH_2 + 2H_2O,$$

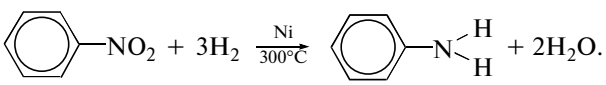
is a nonoffensive process ($E = 0$).

Initially, iron metal in a mineral acid was industrially used for nitrobenzene reduction. The resulting salt was consumed in the manufacture of pigments:



Iron reduction is also in current use when nitroaromatic compounds containing functional groups, which are readily removed under comparatively severe conditions of nitro group hydrogenation, at the benzene ring should be reduced. Thus, iron metal in supercritical CO_2 was used for the highly selective reduction of *p*-chloronitrobenzene [4]. The yield of *p*-chloroaniline approached 100% at 6 MPa, 120°C, the ratio Fe : substrate = 3 : 1 after 8 h.

However, this process, which is unacceptable for the large-scale production of aniline, was replaced by a method in which hydrogen was used as a reducing agent (Bayer & Allied, *S* (selectivity) >99%, $E = 0$):



At the current level of the production of aniline (more than 3 million tons per year), the areas of application of which are far beyond the chemistry of dyes, it would be necessary to consume 5.6 million tons of iron instead of 0.2 million tons of hydrogen.

The aim of this work was to demonstrate how the development of the industry of the basic organic synthesis is related to the environmental science. The changes caused by life were by no means always justified by environmental problems—the economy was at the head. The importance of environmental protection for sustainable development has been realized later.

PETROLEUM CHEMISTRY REPLACES COAL CHEMISTRY

From the early 20th century up to the 1960s, more than 50% of the total output of the heavy organic synthesis was obtained from coal and coal processing products. Nearly half a century ago, an event occurred that became a turning point after which the fraction of coal in the raw-material base of the heavy organic synthesis began to decrease sharply. In September 1959, a group of German chemists headed by Jurgen Smidt [5] reported a new process for the manufacture of acetaldehyde, in which ethylene served as a raw material. The work of these scientists ideologically and even chronologically coincided with the works carried out by Soviet chemists in the laboratory of Academician Syrkin by that time [6].

Before these publications, acetaldehyde has been mainly produced in industry from acetylene, that is, actually, using coal carbon:

$$CaO + 3C \xrightarrow{\text{arc}} CaC_2 + CO,$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2.$$

Both of the stages of acetylene generation are unacceptable from the positions of ecology ($E = 1.86$). At the first stage, carbon monoxide was obtained as waste, which was released into the atmosphere because it could not be used rationally at that time. Calcium carbide after electric furnaces was cooled to cause thermal pollution. At the second stage, a so-called white sea—a suspension of slaked lime in an excess of water—was formed. The process was characterized by an increased water consumption. However, the main expenditures consisted of coal and power costs (10 kW h/(kg C_2H_2)).

The chain from coal to acetaldehyde was finished by the following reaction, which was discovered in 1881 by the prominent Russian chemist Kucherov [7]:

$$C_2H_2 + H_2O \longrightarrow CH_3CHO.$$

The reaction is highly selective and ideal in terms of stoichiometry. However, actually, this stage was mainly hazardous to human beings because the catalyst industrially used for many years was a solution of mercury(II) sulfate in sulfuric acid. A portion of the mercury salt was reduced with time, and another portion was bound to acetylene and/or acetaldehyde and precipitated as slime. In spite of safety aids, mercury vapor penetrated into the workplace air to poison it. From time to time, it was necessary to move away and burn all doors and other interior components made of wood for the recovery of mercury. For the same purpose, slime from the reactor was dissolved in hot nitric acid. The enterprise was considered extremely harmful because of the released nitrogen oxides. The factor of harmfulness exceeded the limit.

The new method for the production of acetaldehyde (Wacker process) was free of all of the above disadvantages:

$$C_2H_4 + 1/2O_2 \xrightarrow[\text{20–100°C, 1–10 atm}]{\text{Pd(II), Cu(II), Cl}^-} CH_3CHO. \quad (1)$$

Moreover, acetaldehyde was prepared from ethylene in place of acetylene in this process. Ethylene is less expensive than acetylene.

Economy rather than ecology was mainly responsible for the rapid use of this reaction in industry. This is

one of a few processes in which the reaction product can be easily separated from the reaction solution. At the reaction temperature, acetaldehyde evaporates from solution. The catalytic system for the industrially important process was first discovered theoretically and designed based on well-known thermodynamic data rather than experimentally found.

Ethylene oxidation in the presence of palladium and copper salts played an important role in the development of catalysis. By the time of this discovery, the works of Halpern [8], Flid, Sokol'skii, Roelen, Reppe, Breslow [7], and many other scientists who actively worked in the area of the kinetics and mechanism of liquid-phase catalysis, have been well known. However, there were no books and periodicals that published information on catalysis by metal complexes and no specialized scientific forums at which problems equally related to coordination chemistry and catalysis were discussed. In this sector of catalysis, studies of the reactions in strong acids were predominant.

A study of the kinetics and mechanism of alkene oxidation by palladium salts led to a conclusion on the participation of organopalladium compounds as intermediates in this and many other reactions. At the same time, the existence of the organic derivatives of platinum group metals in the absence of phosphine ligands, which stabilize complex compounds, seemed very doubtful. The results of Soviet chemists shook this stereotype. More recently, many reactions in which similar complexes play the role of active intermediates were discovered. The term *metal complex catalysis* appeared [9].

For the first time, it became clear that a catalytic reaction is a sequence of stoichiometric steps. Thus, reaction (I) can be divided into the following three steps:

(1) ethylene oxidation

$$C_2H_4 + PdCl_4^{2-} + H_2O \rightarrow CH_3CHO + Pd^0 + 4Cl^- + 2H^+;$$

(2) palladium salt reoxidation

$$Pd^0 + 2CuCl_2 + 4Cl^- \rightarrow Pd\,Cl_4^{2-} + 2CuCl_2^-;$$

(3) copper salt oxidation

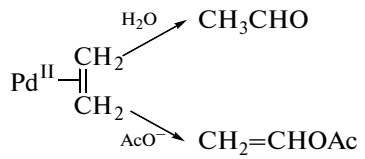
$$2CuCl_2^- + 1/2O_2 + 2H^+ \rightarrow 2CuCl_2 + H_2O.$$

In actual practice, reactions (1) and (2) are occasionally performed in a single apparatus, whereas reaction (3) is performed in another apparatus. In this case, air rather than oxygen can be uses as a consumable oxidizing agent. The method under consideration is highly selective because, unlike many other oxidation processes, the oxygen molecule does never directly contact the oxidized substrate. Moreover, the compounds of palladium with an oxidation number between zero and 2+ are the precursors of palladium metal. Even if free oxygenyl radicals appeared in this system, they decayed at the complexes of palladium with a decreased valence [10] to prevent the development of oxidation chains in reaction solutions.

Soon after the publications dedicated to the oxidation of ethylene in aqueous solutions, in the Soviet Union, Moiseev et al. [11] reported the results of a study on the oxidation of ethylene in acetic acid containing sodium acetate. They assumed that the nucleophilicity of this solvent was insufficient for an inner-sphere attack on the coordinated ethylene molecule. For this reason, they introduced sodium acetate into the solution and for the first time obtained vinyl acetate from ethylene and acetic acid:

$$C_2H_4 + AcOH + PdCl_2 \xrightarrow{AcONa} CH_2{=}CHOAc + 2H^+ + Pd(0).$$

Using this observation, BASF and Celanese [12] developed catalysts that operate in the absence an oxygen carrier and selectively catalyze the oxidation of ethylene into vinyl acetate. The reaction of ethylene with acetic acid in a liquid phase is very sensitive to the presence of water, which competes with acetic acid (acetate ion) in an attack on the coordinated molecule of ethylene:



Unlike this reaction, heterogeneous catalysts from BASF and Celanese very selectively afforded vinyl acetate, to 94% on an ethylene basis and 98–99% on an acetic acid basis, even in the presence of 10% water. The giant palladium cluster $Pd_{561}Phen_{60}AcO_{180}$ exhibited analogous catalytic properties [13, 14]:

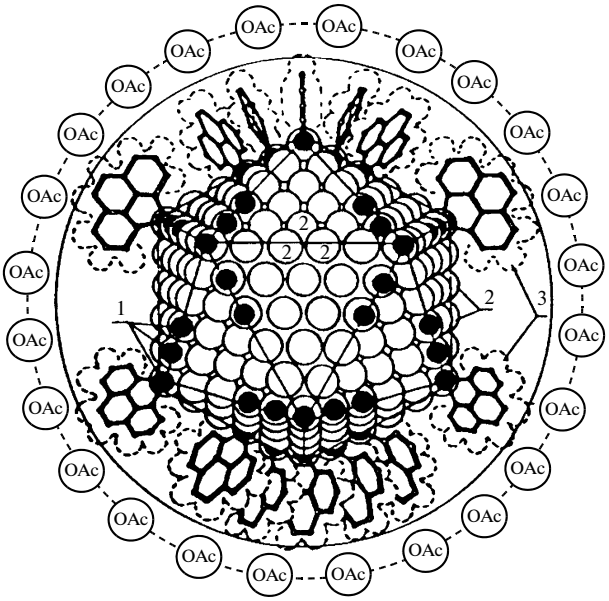


Table 1. If there would be no alkenes: World need for acetylene for the production of chemicals (in the absence alkenes)

Product	World output, million ton per year	Need for acetylene, million ton per year
$CH_2{=}CHCl$	35	14.56
$CH_2{=}CHOAc$	5	1.51
CH_3CHO	1	0.6
$CH_2{=}CHCN$	6	2.94
Total		19.6 million ton

The current world production of vinyl acetate by the oxidation of ethylene and acetic acid exceeds 4.5 million tons per year, and that of acetaldehyde, 1 million tons per year.

Following the oxidation of ethylene into acetaldehyde and vinyl acetate, the production of vinyl chloride from ethylene [7, 15]

$$C_2H_4 + HCl + 1/2O_2 \longrightarrow CH_2{=}CHCl + H_2O$$

and the production of acrylonitrile from propylene and ammonia [12]

$$CH_2{=}CH{-}CH_3 + NH_3 + 1\frac{1}{2}O_2 \xrightarrow[\text{2 atm, 460°C}]{\text{Mo/V (Bi)}} CH_2{=}CH{-}CN + 3H_2O$$

have been developed. As a result, acetylene was substantially displaced from the raw-material base of the basic organic synthesis. The production of calcium carbide sharply decreased, and it was not terminated completely because of the needs of acetylene welding.

In the absence of new processes, it would be necessary to produce about 20 million tons of acetylene per year in order to satisfy a demand for the products specified in Table 1. Note that 0.5 and 0.7 million tons of acetylene were produced in 1960 and 1998, respectively.

A change of the raw-material base is a sign of scientific and technical revolution in chemistry. The driving force of these revolutionary transformations was economy rather than ecology.

ALKENE OXIDATION

The epoxidation of ethylene on a silver catalyst was improved during the 20th century, and it became a highly selective process. Unlike ethylene, propylene cannot be directly converted into oxirane by a direct reaction with oxygen up to now. Only the oxidative ammonolysis of propylene and the direct oxidation to acrolein are used in industry (Table 2) [12]:

$$CH_2{=}CH{-}CH_3 + O_2 \longrightarrow CH_2{=}CH{-}CHO + H_2O.$$

The attempts to develop a process for the direct epoxidation of propylene remained unsuccessful. The reaction selectivity is unacceptable for industrial production (Table 3).

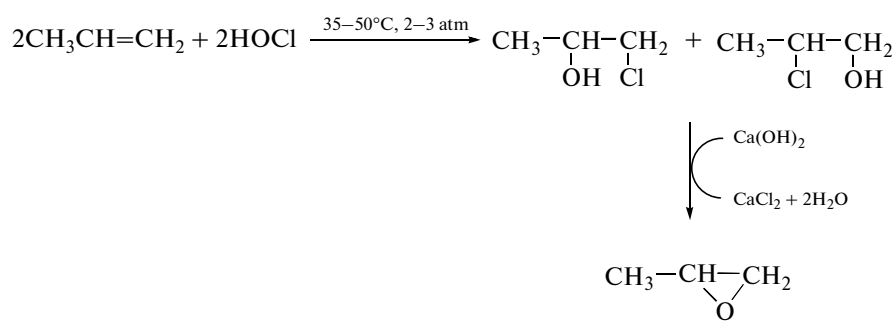
For this reason, indirect oxidation is industrially used. Historically, the first process of this kind was oxidation by a chlorohydrin method with 87–90% selectivity for propylene (Table 4):

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl,$$

$$2CH_3CH{=}CH_2 + 2HOCl \xrightarrow{\text{35–50°C, 2–3 atm}} CH_3{-}\underset{OH}{CH}{-}\underset{Cl}{CH_2} + CH_3{-}\underset{Cl}{CH}{-}\underset{OH}{CH_2}$$

$$\downarrow \; Ca(OH)_2,\ CaCl_2 + 2H_2O$$

$$CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2}$$



Currently, this method has been almost completely displaced from the industry in spite of its high selectivity. Its main disadvantages are a high *E*-factor (40.25) and a high consumption of expensive chlorine.

Considerable advances in the selective and environmentally friendly epoxidation of propylene have been achieved, when chemists turned themselves to organic peroxides.

Prilezhaev was the first to perform the epoxidation of alkenes using peroxy acids [16]. This reaction was named after the discoverer:

$$R{-}CH{=}CH_2 + AcOOH \longrightarrow R{-}\underset{\diagdown O \diagup}{CH{-}CH_2} + AcOH.$$

The catalysis of peroxide reactions by metal compounds is well known since the discovery of Fenton

Table 2. Direct oxidation of propylene to acrolein

Company	Temperature, °C	Catalyst	Characteristics*
Shell	350–400	Cu_2O/SiC, I_2	$X_{C_3H_6} = 20\%$ $S = 70–85\%$
BP	–	Cu_2O/support	–
Montecatini	–	Cu/steel	–
Sohio	300–360	Bi_2O_3/MoO_3	–
Ugine-Kuhlmann Nippon Shokubai	350–450	Mo, Bi, Fe, Co, W+...	$X_{C_3H_6} = 96\%$ $S = 90\%$

* $X_{C_3H_6}$ is the conversion of propylene, and S is selectivity.

[17]. Hydroperoxides can undergo a variety of reactions depending on the nature of the metal [18]. Some of them have found practical use.

In the early 1960s, Brill [19] found that *tert*-butyl peroxide in the presence catalytic amounts of molybdenum, vanadium, and chromium acetylacetonates can be used for the epoxidation of propylene. The complexes of molybdenum were used as a commercial catalyst by Halcon and ARCO, which were joined to form Oxirane Chemical in 1967. A homogeneous process consisted of two stages, at the first of which an organic compound (RH), which easily forms hydroperoxide, was oxidized (Table 5). At the second stage, the resulting hydroperoxide (epoxidizing agent (EA)) was consumed in the epoxidation of propylene:

$$CH_2{=}CH{-}CH_3 + ROOH \xrightarrow{Cat} CH_2{-}\underset{\diagdown O \diagup}{CH}{-}CH_3 + ROH.$$

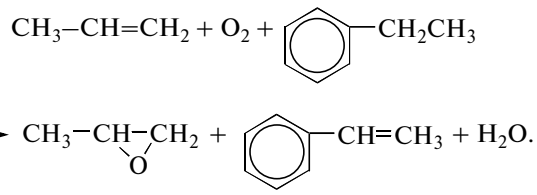
Acetaldehyde, isobutene, and ethylbenzene are most commonly used in the industry. These compounds are oxidized under comparatively mild conditions to low degrees of conversion in order to minimize the formation of by-products. A hydroperoxide solution is used for epoxidation without separation and purification. Oxirane Chemical uses higher carboxylates of molybdenum as a catalyst.

A detailed study of the kinetics of oxidation of propylene dissolved in ethylbenzene showed that propylene reacts with ethylbenzene hydroperoxide coordinated to the molybdenum(VI) atom [20–25]. The results of the kinetic study are consistent with the conclusions that follow from general observations [26].

In the industry, the alcohol formed at the stage of epoxidation is subjected to hydrogenation with the formation of an alkane, or it is used to obtain large-scale products. Methyl *tert*-butyl ether (an antiknock additive for fuel) is the end product in a process where isobutane (60% of cases) is used as an EA, whereas styrene is the end product with the use of ethylbenzene as an EA. Thus, the stoichiometric equations of the industrial processes of propylene epoxidation can be represented in the form

$$CH_3{-}CH{=}CH_2 + O_2 + (CH_3)_3CH + CH_3OH$$
$$\longrightarrow CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_2 + (CH_3)_3COCH_3 + H_2O$$

or



At a propylene conversion of 10%, the selectivity of alkene conversion into an oxirane was as high as 90%. Because there is a market for all of the main products, the *E*-factor of these industrial processes is close to zero.

The ability of titanium compounds with silicon dioxide to catalyze propylene epoxidation with peroxides has been known since the 1970s [27]. In the late 1980s, the chemists of EniChem found that this ability is due to the formation of titanium silicalite (TS-1 on the catalyst surface) [28]. In recent years, this catalyst has attracted considerable industrial attention (Degussa and Uhde). Degussa, which is one of the largest manufacturers of hydrogen peroxide, developed a process for the epoxidation of propylene by hydrogen peroxide generated at the same production plant. The selectivity of propylene oxide formation at 65°C and 15 atm is as high as 95%. The process efficiency seems very attractive because of a locally available supply of the oxidizing agent. Degussa and Uhde use TS-1 as a catalyst. The ability of this catalyst to activate H_2O_2 in very dilute solutions makes it possible to avoid the stage of concentrating the oxidizing agent [29].

METHYL METHACRYLATE: SULFATE CONTROL

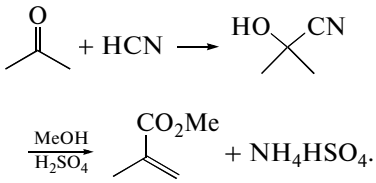
Methyl methacrylate is an important monomer, which is used in the production of organic glass for modern aviation. At the first stage of the production of

Table 3. Direct epoxidation of propylene*

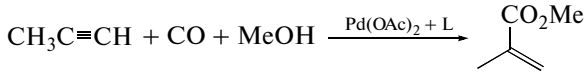
Company	Catalyst	S, %	$X_{C_3H_6}$, %
BP	Ag/CrO_3	50	15
Rhône-Progil	uncatalyzed liquid-phase	–	–
Jefferson Chemical	Mo/PhCl	59	12
Olin Corp.	$LiNO_3/KNO_3 + NaNO_3$, 180–250°C	57	24

* S is selectivity, and $X_{C_3H_6}$ is the conversion of propylene.

the monomer, hydrocyanic acid reacts with acetone in the presence of alkali metal cyanide to form acetone cyanohydrin. At the second stage, acetone cyanohydrin reacts with methanol in the presence of sulfuric acid to give methyl methacrylate and ammonium sulfate as a by-product ($E = 2.5$):

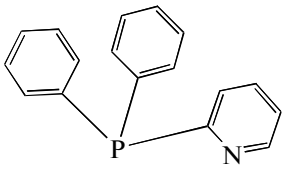


There is no market for acid ammonium sulfate. For a long time, chemists attempted to convert this salt, for example, to regenerate ammonia by thermolysis. The new technology was developed by Shell [30]:



($E \approx 0$).

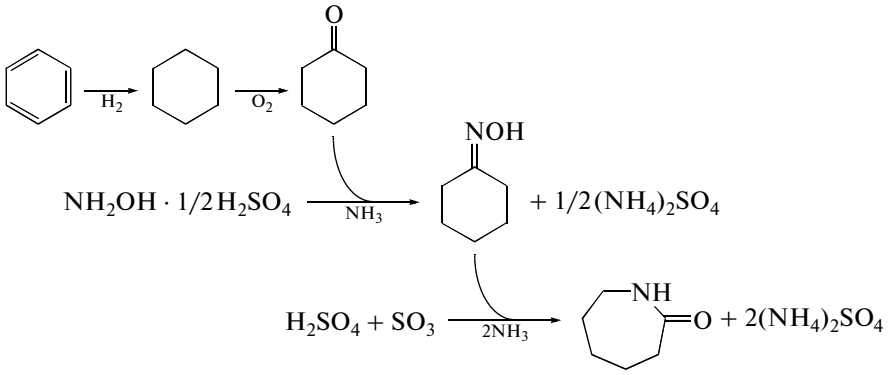
The selectivity of this process was high ($S = 98.9\%$) because of the following new ligand (L) found by the authors:



The proximity of phosphorus and nitrogen atoms coordinated to metal atom/atoms is very important. Thus, triphenylphosphine, which does not contain nitrogen atoms in the molecule, exhibits high selectivity but negligibly low activity, as compared with that of the Drent ligand. The same is observed for the ligands containing a nitrogen atom in the *para* or *meta* position with respect to the phosphorus atom. All of the available data indicate that complexes with the Pd–Pd bond are responsible for catalysis. It is likely that the presence of *ortho*-located phosphorus and nitrogen atoms is required for the stabilization of these complexes.

BECKMANN REARRANGEMENT: SUMITOMO BREAKS THE STEREOTYPES

In the classical version of the manufacture of caprolactam, cyclohexanone oxime undergoes rearrangement into caprolactam under the action of oleum; thereafter, the reaction solution is neutralized with ammonia:



The amount ammonium sulfate formed as a by-product varied depending on technologies, and it was as high as 2.6 and 1.6 t per ton of caprolactam in BASF and DSM processes, respectively [31]. The Beckmann

rearrangement is usually considered as a reaction in which the oxime molecule undergoes protonation followed by dehydration. The resulting cation with a positive charge on the nitrogen atom undergoes isomerization into a carbocation, which reacts with water to form caprolactam as the end product. This reaction scheme was undoubted; moreover, it served as a guiding star in searching for new catalysts.

The tendency to avoid sulfate formation and the use of a liquid phase resulted in searching for zeolites. For about two decades, chemists searched for zeolites capable of simulating oleum in terms of acidity. However, the solution was found in another sector. Isumi et al. [32] at Sumitomo found that, in the series of high-silica zeolites, both the conversion of cyclohexanone oxime and the selectivity of its rearrangement into caprolactam increased as the Si : Al ratio was increased up to 100000. Moreover, according to Isumi et al. [32], the additives of methanol, which is capable of esterifying silanol groups and thereby reducing the surface acidity, increased both the selectivity and the substrate conversion. They failed to monitor the dynamics of surface defect formation, which may play an important role in the reaction. Isumi et al. [32] hypothesized that the ensembles of silanol groups arranged in the mouths of channels that passed through the support participated in the reaction as a catalyst. The oxime conversion was higher than 99%, and the reaction selectivity was higher than 95%. The authors used the ammoxymation of cyclohexanone with ammonia and hydrogen peroxide in the presence of TS-1, which was discovered by Eni Chem (Syndial):

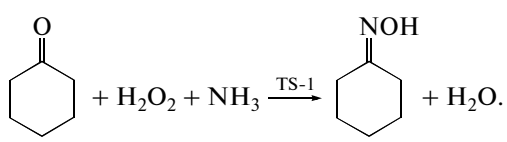


Table 4. Wastes of the chlorohydrin method of propylene epoxidation

Product	ΔE, kg/kg
1,2-Dichloropropane ($S = 8\%$ (C_3H_6))*	0.18
Bis(chlorodiisopropyl) ether ($S = 2\%$ (C_3H_6))	0.07
6% aqueous solution of $CaCl_2$, 0.1% $Ca(OH)_2$	40

* S is selectivity.

Table 5. Epoxidizing agents (EAs) in propylene oxidation processes

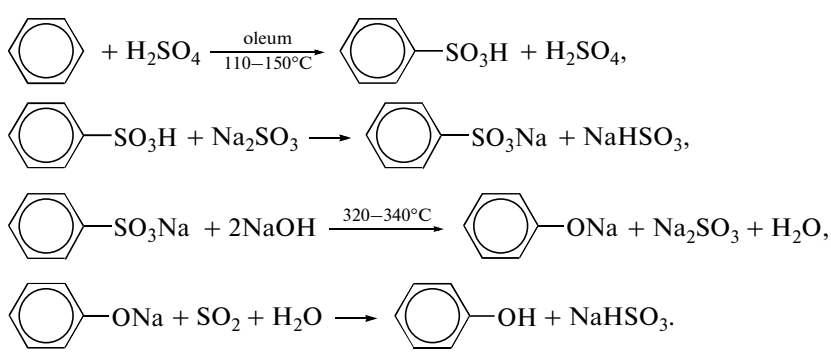
RH	EA	EA reduction product
Acetaldehyde	AcOOH	AcOH
Isobutane	$(CH_3)_3COOH$	Isobutanol
Isopentan	$C_5H_{11}OOH$	Isopentanol
Cyclohexane	$C_6H_{11}OOH$	Cyclohexanol or cyclohexanone
Ethylbenzene	$C_6H_5CHCH_3OOH$	Phenylethanol, styrene
Cumene	$C_6H_5C(CH_3)_2OOH$	α-Methylstyrene

This made it possible to completely remove ammonium sulfate emissions.

In April 2003, Sumitomo introduced a new process for the manufacture of caprolactam with a productivity of 60000 t/year into the industry [33].

PHENOL FROM BENZENE

For many years, chemists attempted to develop a direct method for the synthesis of phenol from benzene and to replace coal by raw materials of petroleum origin. One of the early methods was based on the sulfonation of benzene with oleum, and it was characterized by very unfavorable environmental safety parameters.



In spite of a sufficiently high yield (88%), the process is extremely unfavorable for the environment (E = 3.45; Table 6).

Another disadvantage of this process is the high consumption of sulfuric acid and sodium hydroxide. At the same time, the need for phenol is significant: 6.1 million tons was produced in 1999. It is clear that the sulfuric acid process, which is very harmful to the environment, is little used in actual practice. Its place is occupied by another reaction, which was discovered

Table 6. Process characteristics of the synthesis of phenol by the sulfonation of benzene with oleum (per ton of phenol)

Raw material (t)	Waste (t)
Benzene (1), H_2SO_4 (1.75), NaOH (1.7)	Na_2SO_3 (1.35), Na_2SO_4 (2.1)

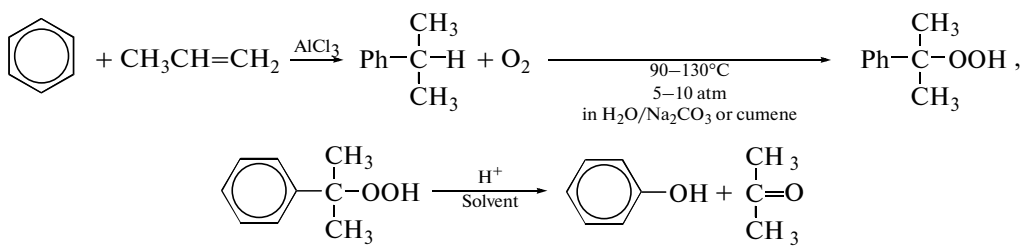
Table 7. Industrial conversion of cumyl hydroperoxide

Company	Solvent, conditions
Hercules BP	acetone, 60–65°C
Rhône-Poulenc Phenolchemie	phenol, two phases, 40% H_2SO_4, 50°C

by Sergeev and Udris in the Soviet Union in 1942 under dramatic circumstances. Nemtsov and Kruzhalov were responsible for the engineering design. The development of the industrial process won the Stalin Prize in 1951. For the first time, industrial production (Dzerzhinsk phenol–acetone, FAD) was implemented in Dzerzhinsk (Gorky oblast) and then at plants in Grozny (FAG) and a number of other cities.

In 1942, the authors of this process were kept in detention, and they could not patent or publish their results. Meanwhile, in 1944, Hock and Lang [34] published the acid-catalyzed conversion of cumyl hydroperoxide into phenol and acetone, which formed the basis of a new industrial process for the production of phenol and acetone. For this reason, the reaction discovered by Sergeev and Udris is referred to as the Hock and Lang reaction in the West.

Phenol results from the cooxidation of benzene and propylene. At the first step, benzene is alkylated with propylene in the presence of an acid catalyst (aluminum chloride was used in the early processes), and the resulting cumene was oxidized to form cumyl hydroperoxide. This latter decomposes in the presence of a mineral acid (usually, H_2SO_4) to give phenol and acetone.



The selectivity for cumyl hydroperoxide is ≥90%.

Various companies use not only cumene but also its conversion products as a solvent (Table 7).

The stoichiometric equation of the process has the following form:

$$C_3H_6 + C_6H_6 + O_2 = C_3H_6O + C_6H_5OH \ (E \approx 0).$$

The disadvantage of this elegant process is the presence of two commercial products a demand for which not always coincides with stoichiometric yields. For this reason, the direct oxidation of benzene to phenol is under development.

Panov (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences) achieved the greatest success; he used the unique properties of N_2O as a selective donor of oxygen in oxidation reactions in the presence of Fe-containing zeolite catalysts [35]:

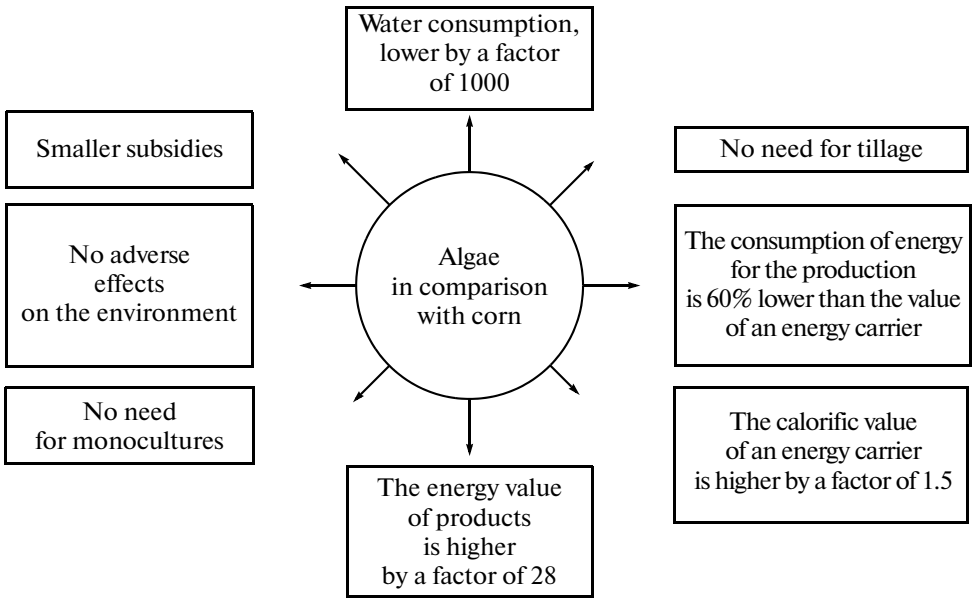
$$C_6H_6 + N_2O = C_6H_5OH + N_2,$$

$S(N_2O) = 75\%$, $S(C_6H_6) = 98\%$.

$E \approx 0$ because N_2 can hardly be considered as nonutilizable and environmentally hazardous waste.

SECOND GREEN REVOLUTION

Chemists have been familiar with the problem of environmental pollutant emissions for a long time. This resulted in a trend to develop industrial chemical processes that meet environmental requirements. The term *green chemistry* was born [3, 36, 37]. The attention of chemists was concentrated on searching for the methods that make it possible to obtain well-known products from well-known raw materials by new methods, which are characterized by the absence of harmful emissions and a smaller thermal load on the environment. However, note that, economy rather than ecology was responsible for the tendency toward resource and energy savings in the 20th century long before the appearance of the term *green chemistry*. In the 1940s, the minister of agriculture of Mexico combined the efforts of the Rockefeller and Ford Foundations and directed them toward studies in agriculture. This activity resulted in doubled gross grain yields in countries such as Mexico, Pakistan, and India [38]. This revolution in agricultural engineering and biology, which was called green revolution, became the basis of the world production of foods for a period of recent seven decades. Meanwhile, the expected



Scheme.

increase in the population (8.2 billion in 2030 in comparison with 6.8 billion in 2008) sets new problems for the world economy in the production of energy and the supply of freshwater, foodstuffs, and fodders for fishes and animals. In searching for rational solutions to these global problems, humankind hopes not only for an improvement in methods for the cultivation and processing of terrestrial plants [39] but also for the adaptation of aquaculture technology [40]. The green revolution acquires a distinct blue nuance in recent years.

The entire vegetable kingdom (both terrestrial and aquatic plants) depends on photosynthesis reactions in which carbon dioxide and water are converted into the fragments of carbohydrates, lipids, and proteins:

$$nCO_2 + nH_2O \xrightarrow{h\nu} C_n(H_2O)_n + nO_2,$$

$$nCO_2 + nH_2O \xrightarrow{h\nu} (CH_2)_n + 3/2nO_2.$$

These reactions occur much more rapidly in aquatic plants than in terrestrial plants. The high productivity of algae, a high lipid content of algae, and the almost complete absence of lignin from them are additional reasons that stimulate interest in aquacultures [41] (see the scheme).

Absorbing carbonic acid dioxide (greenhouse gas, the largest scale atmospheric pollutant), plants convert it into potentially useful products in the course of photosynthesis: into raw materials for the production of motor fuel components, plastics, organic acids, and a number of other chemicals. Biomass is referred to as a new paradigm of organic chemistry. Recently, the US Department of Energy (DOE) defined ten the most needed products, which, as expected, will be industrially produced from the biomass: ethanol, furans, glycerol and its derivatives, hydrocarbons (motor fuel components), lactic acid, succinic acid, hydroxypropionic acid and its aldehyde, levulinic acid, sorbitol, and xylitol [42].

The production of ethanol from corn and other starch-containing raw materials became the largest scale process. Ethanol from potato became the first product utilized by chemists for industrial purposes. In the early 1930s, Academician Lebedev developed the world's first industrial process for the manufacture of synthetic rubber. Butadiene for this product was obtained from ethanol, which was produced from potato.

The first portions of synthetic rubber were expensive: 5 or, more recently, 50 g of divinyl was obtained from 1 l of ethyl alcohol. However, even this absolute breakthrough did not solve the problem because, for example, 500 kg of potatoes was required for the production of a tire. The production of synthetic rubber became profitable after a lapse of a long time. Potatoes remained a raw material for the production of ethanol and (on this basis) ethylene up to the beginning of the era of petroleum chemistry. The discovery of Lebedev became a sensation for the West. At that time, neither Germany nor the United Kingdom was ready to propose a version to solve this industrial problem. In 1928, when the Soviet press reported the development of artificial synthetic rubber by Lebedev in Russia, Edison responded to this report and said that information that the Soviet Union was capable of obtaining synthetic rubber is improbable; this cannot be made; moreover, this communication is false. However, this

response only more pronouncedly emphasizes the value of the discovery made by Lebedev. Indeed, he exceeded the capabilities of science of that time and made an impossible thing. As early as 1932, the first synthetic rubber plant gave production in Yaroslavl.

Currently, the use of food raw materials (potatoes, corn, manioc, wheat, and barley) in the chemical industry causes a social protest. In connection with this, chemists turned themselves to lignocellulose raw materials. Thus, in Germany, Süd-Chemie AG builds an experimental plant for the production of cellulose ethanol—bioethanol of the second generation—from agricultural wastes, including straw, using biotechnology with an output of up to 2000 t of fuel bioethanol. The plant will be located not far from BioCampus in Straubing. The project is partially subsidized by the Bavarian government and the Federal Ministry of Education and Research (Germany). The production is based on the Sunliquid® technology, which has been tested by Süd-Chemie since 2009: plant wastes are converted into sugar components with the use of enzymes; then, these components are converted into bioethanol. This method makes it possible to convert not only cellulose but also hemicellulose into ethanol to increase the yield of ethanol by 50% in comparison with usual technologies. Furthermore, the utilized enzymes can be chosen depending on source materials and produced in necessary amounts directly at the plant.

The recent development of Danisco, which resulted in the bacterial synthesis of isoprene from lignocellulose raw materials, is also of considerable importance [43]. Isoprene is a favorite building block of nature, from which it builds many substances familiar to human beings since olden times. Natural rubber is built from the molecules of isoprene. The development of an inexpensive process for the production of isoprene from underfoot raw materials seems very attractive. Danisco evaluated the world market for isoprene as $1–2 billion and planned to invest $50 million in the further development of this project in the coming year. It is expected that the first large-scale production of isoprene will be released in 2012. In November 2009, Goodyear, which is one of the most important tire manufacturers, and Genencor, a subdivision of Danisco, declared the amalgamation of firms. Note that the production volume of mechanical rubber goods, primarily, automobile tires, is an indicator of the level of the development of chemical industry [44, 45].

The insufficiently high productivity of terrestrial plants forces one to more actively use algae, in particular, in the production of plastics. For example, in 2010, Cereplast, which is specialized in the manufacture of biopolymers, began to produce Cereplast Algae Plastics® from algae [46]. Cereplast currently uses agricultural raw materials: corn, manioc, wheat, and potatoes. The company considers the replacement of food raw materials by algae as a significant breakthrough. The fraction of agricultural raw materials used by the company should decrease to 30%, whereas the fraction of marine algae should increase to 30–40% for five years. In addition to a social aspect, there is an important technical aspect: corn requires 100 days for ripening, whereas the harvest of marine algae is ready in a week.

It is evident that the fuel sector will be the main area of application of algae. Carbohydrates and lipids are the two components of these plants and cyanobacteria. Both of these components are test materials for chemists and biochemists who study the conversion of both lipids and carbohydrates into motor fuels. Optimists believe [40] that algae will allow the United States to do away with the import of oil. DOE proposes to replace a half of diesel fuel produced from petroleum by biodiesel from algae by 2022 [47].

In this paper, I intentionally focused on the evolution of heavy organic synthesis, which operates with large-tonnage processes. The ideas of green chemistry are also of considerable importance for fine organic synthesis, where a source material may require 17 stages to be converted into the end product [48]. This area of organic synthesis has been considered in publications [37, 48, 49] and in numerous articles in the journal *Green Chemistry*, which has been issued since 1998.

The concept proposed by Sheldon played an important role in the attraction of the scientific and technical community to the problems of environmental protection.

In the 20th century, intensive studies were oriented toward replacing expensive raw materials by cheaper ones, performing syntheses under milder conditions, increasing the selectivity of reactions, and replacing multistage syntheses by direct syntheses. All the above factors led to a decrease in the thermal load on the environment and the protection of the environmental from harmful and nonutilizable emissions, but, primarily, material and energy savings. The new stage of going to biomass is dictated not only by the requirements of environmental protection. Sheikh Zaki Yamani, former Saudi Arabian oil minister, said that the Stone Age did not end for lack of stone, and the Oil Age will end long before the world runs out of oil.

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