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History in the Making

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Acetaldehyde from Ethylene—A Retrospective on the Discovery of the Wacker Process**

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acetaldehyde · history of science · technical chemistry · Wacker process

The Wacker process for manufacturing acetaldehyde from ethylene is one of the most important and successful processes developed by the chemical industry after World War II. This year marks the fiftieth anniversary of the initial publication of the process in *Angewandte Chemie* (Figure 1)[1]—the reason why I, as co-author, was asked to describe the situation at that time.

This year marks the fiftieth anniversary of the initial publication of the process.

During the rebuilding of the chemical industry following the ravages of World War II and the war-related dismantling of the factories, engineers reverted mainly to familiar prewar processes. The most important raw material for the synthesis of low-molecular-weight aliphatic compounds was acetylene, which was typically obtained by hydrolyzing calcium carbide. However, it was soon recognized that olefins, in particular ethylene, were less expensive starting materials for the industrial synthesis of aliphatic compounds because they require less energy. The most important derivatives of acetylene in terms of quantity were acetaldehyde and a whole range of secondary products, as well as vinyl chloride and vinyl acetate. The aim was to develop processes for obtaining these products from ethylene. While this situation was being discussed—at least at the executive level—in the chemical industry, Wacker-Chemie and Farbwerke Hoechst were planning to cooperate in the field of ethylene-derived acetaldehyde.

The economic boom in the industrialized countries was accompanied by an increasing demand not only for fuels, such as gasoline, diesel, heating oil, and kerosene, but also for plastics. As a result, refineries were being erected around the globe. In industrialized countries, these were equipped with cracking facilities for the production of low-molecular-weight olefins.

In the summer of 1956, a delegation from Esso AG informed the Wacker-Chemie management that Esso was intending to build a refinery north of Cologne, and that it could supply the chemical industry with low-molecular-weight olefins. A suitable site bordering on the refinery, so they said, was also available. Wacker-Chemie's central research

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[**] In the Minireview following this article J. A. Keith and P. M. Henry give a modern overview of the reaction mechanism of the Wacker oxidation.[7]

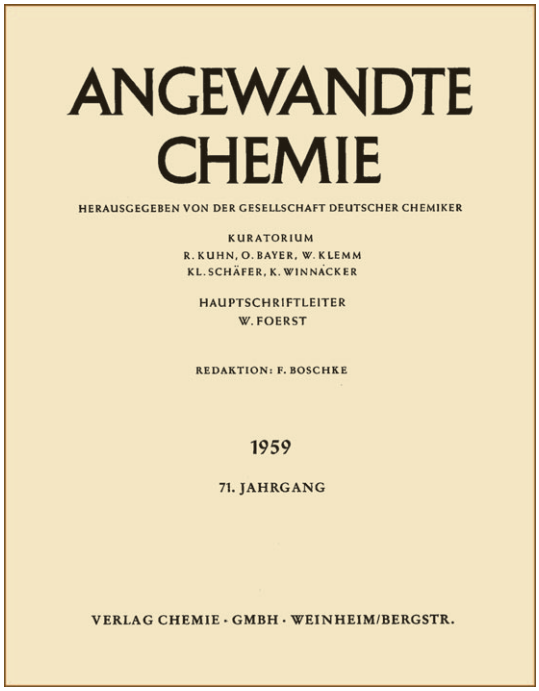

Figure 1. Cover of *Angewandte Chemie* in 1959.

facility, Consortium für elektrochemische Industrie, and the Consortium's young, newly graduated chemist Walter Hafner were commissioned with finding applications for ethylene. Hafner hit on the idea of oxidizing ethylene to ethylene oxide with oxygen activated by atomic hydrogen. (The production of ethylene oxide from ethylene and oxygen using a silver catalyst was known.) To this end, he passed a mixture of ethylene, oxygen, and a trace of hydrogen over a palladium-on-charcoal catalyst, and was able to smell acetaldehyde in the gas evolved. At that time, the Consortium did not have a gas chromatograph. A brief search through Chemical Abstracts led to a research paper by J. Chatt,[2] which described the decomposition of Zeise's salt, the long-known ethylene–platinum complex, with water to give acetaldehyde and platinum metal. A further search through the literature, this time the palladium volume of Gmelin's Handbuch der Anorganischen Chemie, produced a reference to an 1894 publication by F. C. Phillips,[3] who, on passing ethylene into an aqueous solution of palladium chloride, detected acetaldehyde while metallic palladium precipitated.

At that time, the Consortium did not have a gas chromatograph.

The following observation supplied important information regarding the underlying reaction mechanism: During the reaction, the initially black grains of catalyst sometimes became covered with a silvery coating. As metallic palladium does not migrate, it must have been temporarily present in water-soluble form, enabling it to diffuse to the surface. It was thus only logical to suspect the presence of an intermediate olefin complex.

In view of what had gone before, Consortium head Jürgen Smidt immediately recognized the importance of this discovery. He devoted a major part of the Consortium's research potential to developing a process for manufacturing acetaldehyde from ethylene, giving precedence to the development of a gas-phase catalyst to support the reaction. The researchers also investigated compounds of other platinum group metals and brought other olefins to reaction. They also contemplated a reaction in aqueous solution. This part of the investigation was headed by the writer of these lines.

Building on the findings available at that time, the researchers passed a mixture of ethylene and oxygen over a supported catalyst impregnated with palladium chloride. Catalytic activity decreased rapidly, but additions of cupric and ferric chloride accelerated the reaction considerably. This was ascribed to reoxidation of metallic palladium, an explanation substantiated by references found in the literature.[4]

The first patent application, essentially describing a gas-phase reaction, was filed on January 4, 1957,[5] and a pilot plant was planned, naturally for a gas-phase process (Figure 2). However, liquid-phase experiments involving a homogeneous catalyst were also producing promising results. An extensive patent application was drafted for the process, but, following internal discussions, was split up into three applications. This decision was fatal for Wacker-Chemie, as is described below.

BUNDESREPUBLIK DEUTSCHLAND
DEUTSCHES PATENTAMT

PATENTSCHRIFT 1 049 845

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ANMELDETAG: 4. JANUAR 1957
BEKANNTMACHUNG DER ANMELDUNG UND AUSGABE DER AUSLEGESCHRIFT: 5. FEBRUAR 1959
AUSGABE DER PATENTSCHRIFT: 6. AUGUST 1959

Verfahren zur Herstellung von Carbonylverbindungen

Patentiert für:
Consortium für elektrochemische Industrie G. m. b. H., München

Dr. Jürgen Smidt, München-Solln,
Dr. Walter Hafner, München,
Dr. Josef Sedlmeier, München,
Dr. Reinhard Jira, München-Pasing,
und Dipl.-Ing. Rudolf Rüttinger, Deisenhofen bei München,
sind als Erfinder genannt worden

1

Die Erfindung betrifft ein Verfahren zur Herstellung von Carbonylverbindungen aus Olefinen.

Carbonylverbindungen, wie z. B. Acetaldehyd und Ketone, werden nach bekannten Verfahren aus Olefinen in einem Zweistufenprozeß hergestellt. Im allgemeinen wird dabei das Olefin zum Alkohol hydratisiert, der dann in einem weiteren Verfahren zum Aldehyd bzw. Keton dehydriert oder oxydiert wird.

Für die Hydratisierung werden im wesentlichen zwei Verfahren angewandt, ein Flüssig-Phase-Verfahren mit Alkylschwefelsäure als Zwischenprodukt und ein Gas-Phase-Verfahren mit Phosphorsäure- oder Wolframoxydkatalysatoren.

Diese Verfahren sind jedoch nicht voll befriedigend. Deshalb hat man sich bemüht, die erwähnten Verbindungen durch direkte Oxydation von Kohlenwasserstoffen herzustellen. Nach der deutschen Patentschrift 168 291 wird durch Oxydation von Äthylen mit Sauerstoff in Gegenwart von Wasserdampf bei 400°C Formaldehyd erhalten. Bei der weiteren Verfolgung älterer Arbeiten von Willstätter und Bommer sowie von Bone wird festgestellt, daß Acetaldehyd das erste faßbare Zwischenprodukt der Oxydation von Äthylen ist (Journal Soc. Chem. Ind., 41, S. 303 bis 310).

Nach der deutschen Patentschrift 664 879 gelingt es, bei Zusatz katalytischer Mengen von Stickoxyden Formaldehyd und Acetaldehyd durch Oxydation von Äthylen und anderen Olefinen zu erhalten. Außerdem ist in den französischen Patentschriften 891 209 und 1 001 377 ein Verfahren beschrieben, bei dem Acetaldehyd durch Oxydation von Äthylen in Gegenwart von viel Kohlendioxyd als Hauptprodukt erhalten wird. Als Katalysator wird dabei Silber auf Metalloxyden verwendet.

In keinem Falle ist es gelungen, Olefine mit hohen Ausbeuten in die entsprechenden Carbonylverbindungen gleicher Kohlenstoffzahl zu überführen oder gar Acetaldehyd und höhere Carbonylverbindungen in wirtschaftlich interessanten Ausbeuten zu erhalten.

Es wurde nun gefunden, daß man Olefine mit Sauerstoff oder Sauerstoff enthaltenden Gasen bei Gegenwart von Wasser in hoher Ausbeute zu den entsprechenden Carbonylverbindungen oxydieren kann, wenn man Katalysatoren verwendet, welche Verbindungen der Platinmetalle enthalten.

Die Bildung der Carbonylverbindungen erfolgt bereits bei niedriger Temperatur mit merklicher Geschwindigkeit und kann durch erhöhte Temperatur noch begünstigt werden. Die Wahl der optimalen Reaktionstemperatur hängt auch von den Siedepunkten der Olefine und der entsprechenden Carbonylverbindungen ab.

Katalytisch wirksam sind Verbindungen der Platinmetalle, insbesondere des Palladiums. Man kann auch die Metalle selbst verwenden, die in Gegenwart von sauren Substanzen, insbesondere von HCl, während des Verfahrens zu den wirksamen Verbindungen oxydiert werden.

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Die Aktivität der Katalysatoren kann durch verschiedene Zusätze noch wesentlich gesteigert werden. Als Zusätze sind Metallsalze und die bereits erwähnten sauren Substanzen geeignet. Besonders geeignete Metallsalze sind solche, die entweder hygroskopisch sind, wie Calciumchlorid, oder durch Übergang in verschiedene Wertigkeitsstufen die Oxydation fördern, wie z. B. Ferrichlorid. Diese Katalysatorsubstanzen werden vorzugsweise auf Träger mit großer Oberfläche aufgebracht. Geeignete Träger sind z. B. Aktivkohle, Tonerde, Kieselerde, Bimsstein und Silikate.

Es ist bekannt, daß wäßrige Lösungen von Palladiumchlorid durch Äthylen unter Abscheidung von metallischem Palladium reduziert werden und daß dabei Acetaldehyd gebildet wird. Diese Reduktionsreaktion hat seither vielfache analytische Anwendung gefunden, doch blieb die Bildung von Aldehyd unbeachtet.

H. Wieland (B., 45, S. 2607) hat festgestellt, daß Acetaldehyd in wäßriger Lösung durch feinverteiltes Palladium sogar bei Ausschluß von Luft zu Essigsäure oxydiert wird. Überraschenderweise kann diese Folgereaktion bei dem Verfahren der Erfindung fast völlig vermieden werden.

Figure 2. Patent application on the Wacker process (1959).

In the spring of 1957, Wacker-Chemie began negotiations with the city of Cologne concerning the acquisition of an industrial site. At that time, the Wacker family owned 50% of the company's shares. The other 50% was owned by Farbwerke Hoechst. A site purchase of this kind had to be approved by the shareholders and the supervisory board. At the shareholders' meeting of June 5, 1957, a motion to buy the Cologne site was introduced because, as is documented in the minutes, "a process developed at Consortium makes it possible …. to anticipate the production of acetaldehyde from ethylene," and "this process will likely be suitable for industrial-scale production within the foreseeable future." The minutes continue: "Acquisition of the Cologne site was approved as the project was considered sufficiently likely to succeed."

"This process will likely be suitable for industrial-scale production within the foreseeable future."

That was pushing our luck, since we still had no knowledge of process conditions, catalyst lifetime, yields, space–time yields, profitability, etc. But inevitably Hoechst received knowledge of the Consortium's work, including details of the catalyst. Hoechst naturally resumed work immediately and lost no time in filing a patent application. The

ensuing patent was granted at a time between our second and the vital third, liquid-phase patent. Hoechst thus acquired a share in the process, forcing the two firms to collaborate and, following numerous tedious negotiations during which Wacker was accorded initial publication status, to establish the joint patent exploitation company "Aldehyd GmbH," which then conducted all licensing negotiations. This comprehensive publication appeared in early 1959.[1]

A gas-phase pilot plant had been commissioned in the summer of 1957. This process involved passing a water-saturated ethylene/oxygen mixture with a composition above the upper flammability limit over the heterogeneous catalyst. The trial runs failed. During preceding lab tests, the researchers had not been able to produce a catalyst with long-term stability. The same problem was encountered in the pilot-plant trials. A "hot spot" migrated through the catalyst bed, leaving the catalyst inactive.

In the meantime, however, acetaldehyde was being produced successfully in experiments in which the same ethylene/oxygen mixture as in the gas-phase trials was bubbled though an aqueous solution of the homogeneous catalyst mixture containing $PdCl_2$ and, in a larger proportion, $CuCl_2$. A pilot plant was erected without delay and was commissioned in autumn of 1957. Rudolf Mittag was initially in charge of the trials before Jobst Poßberg took over in January 1958. A larger pilot plant (for the production of roughly one metric ton of acetaldehyde per day) had already been planned for the Burghausen site, and started up in March 1958 under Poßberg's direction. The author took charge of the Munich plant. The idea behind having two pilot plants was to speed up the development process, during which the reactors' suitability had to be tested. To start with, these were packed towers in which gas and liquid were made to react in countercurrent and then cocurrent systems. Corrosion was the most serious problem. Rubber- and resin-lined pipes, reactors, and vessels were attacked by the aggressive catalyst solution, allowing the pressurized solution to spout out with intensity. Titanium, the only stable metallic material, was not yet available to us.

At this point, plans were already underway for the industrial-scale facility at the Cologne site. This was to have an annual production capacity of 15000 tons. During negotiations with potential oxygen suppliers, it transpired that oxygen could not be acquired at an acceptable price in Cologne at the scheduled commissioning date. So we had to modify the process once again and develop a two-stage process that used air instead of oxygen as oxidizing agent. This possibility had been considered before, and laboratory tests had shown such an approach to be feasible. We then modified both pilot plants accordingly. The underlying principle is as follows: first, ethylene is reacted with the catalyst solution under pressure to form acetaldehyde, whereby copper(II) is reduced to copper(I). In a flash tower, the catalyst is brought to atmospheric pressure, and water and acetaldehyde vaporize. The heat of reaction is utilized to increase the concentration of acetaldehyde in the water/acetaldehyde mixture to 70% to 90% in a distillation column. A pump conveys the spent catalyst to the second reactor, where it is reoxidized by air under elevated pressure. The residual air, mainly nitrogen, is separated, while the regenerated catalyst is reacted again with ethylene.[6]

It was a stroke of luck that titanium had become available (Krupp, Essen) as a material for constructing chemical apparatus, and that a pump manufacturer (Klaus, Bochum) was able to engineer a pump made of solid titanium. To my knowledge, it was the first time that large quantities of titanium were used as a construction material in the chemical industry. However, setbacks were encountered here, too. Not only Krupp but also our workshop staff had to learn how to work titanium.

It was a stroke of luck that titanium had become available as a material for constructing chemical apparatus.

The equipment for the Cologne plant was ordered while process development was still going on. It was thus only natural that process modifications had to be taken into account continually. Trickle-bed reactors, for example, proved unsatisfactory because they kept getting plugged up by precipitating catalyst components. They were replaced by reactors with vertical, meander-type tube banks. The towers that had already been ordered were used as separators instead. Development work continued right up to the end. For example, a catalyst regeneration system was modified just weeks before the plant went on line. During operation of the pilot plants, copper oxalate was produced as a by-product. This not only removes copper from the catalyst, but is a nuisance in many other ways as well. The copper has to be recovered, and the plan had been to do this discontinuously. To this end, a centrifuge had been ordered to separate off the copper oxalate, and the plant's steel framework engineered to be especially rugged. It turned out, however, that it was easier to degrade the copper oxalate by heating a small shunt stream of catalyst solution.

The new plant was commissioned in early January 1960, little more than three years after the reaction had been discovered in the lab.

Unlike Wacker, Hoechst had developed a one-stage process using oxygen as the oxidizing agent. The plant went on line in early January 1960, like ours.[6]

The process attracted great interest around the globe. Acetaldehyde was an important intermediate in industrial chemistry, with a wide range of derivatives. The fact that a market already existed explains the keen interest. Both versions of the process were licensed in many countries. The production capacity of all the installed plants exceeds two million tons per year. Today, acetaldehyde is less important, as a number of its derivatives can be made in different ways. For example, the Aldol process for manufacturing C_4 compounds such as butyraldehyde has been replaced almost completely by the hydroformylation of propylene (oxo synthesis, Roelen). A different process (carbonylation of methanol, or Monsanto process) has also been developed for acetic acid. This process uses a rhodium catalyst. In some cases, however, the traditional process is still used. At Wacker, acetic acid remains the most important acetaldehyde derivative today.

It should be mentioned that Hoechst developed a process based on the same principle for producing acetone from propylene, and Wacker devised a process for making methyl ethyl ketone from butenes. Two acetone plants were built in Japan, but an industrial methyl ethyl ketone process was never realized.

Our publication[1] caused a boom in research on palladium compounds, which is still going strong. This work includes studies of the mechanism (see the recent Minireview by Keith and Henry),[7] reactions that utilize the synthesis principle of regiospecific oxidation of an olefinic double bond to a carbonyl group—today usually referred to as the "Wacker reaction"—in multistage organic syntheses, and new synthesis principles, for example, a C–C bond-forming process (Heck reaction), transalkenylation reactions,[8] etc. The wide variety of studies conducted by J. Tsuji[9] should also be mentioned in this context. The boom in palladium chemistry was reinforced still further when I. I. Moiseev and his team described the synthesis of vinyl acetate.[10]

As Moiseev filed no patents, many firms jumped at the opportunity to develop a method of synthesizing this important monomer. Today, however, vinyl acetate is produced industrially in the gas phase from ethylene, acetic acid, and oxygen on a palladium-containing heterogeneous catalyst. Corrosion problems in the non-aqueous medium prevented the use of a homogeneous catalyst, as is employed in the acetaldehyde process.

Finally, a class of compounds should be mentioned that Walter Hafner came across while working at the Consortium. He obtained a yellow, crystalline palladium compound which he described as an allyl complex of palladium. The allyl group occupies two of the palladium's coordination sites, making the compound a π-allyl complex.[11] That Hafner was the first to describe such a compound is largely ignored in today's chemical literature. π-Allyl compounds are intermediates in many catalytic processes. Additional information on the Wacker process and related reactions can be found in reference [12].

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