Hydration of Acetylene: A 125th Anniversary

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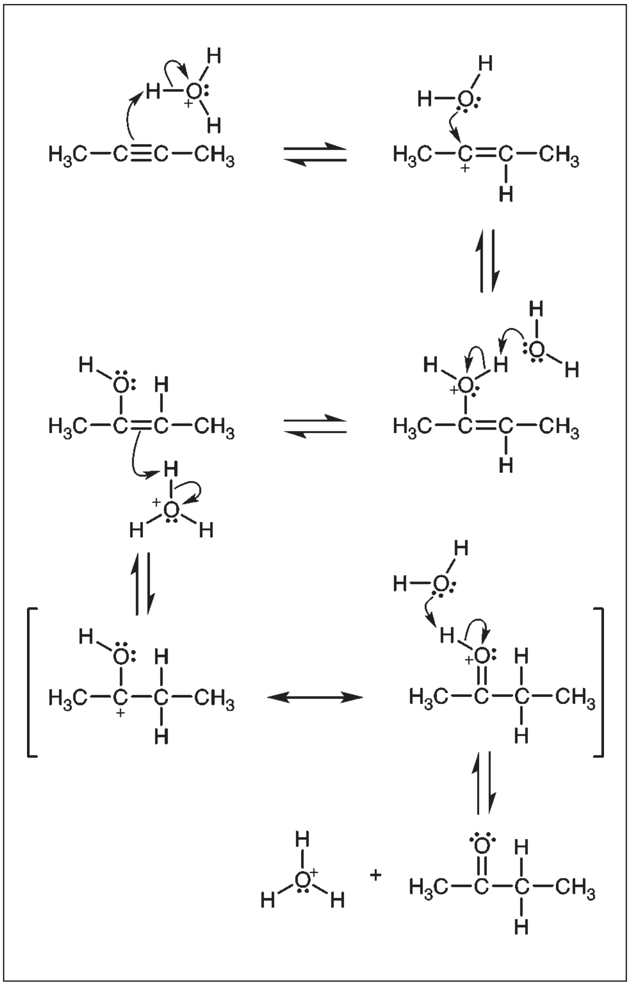
Without much celebration, an amazing anniversary occurred in 2006—the anniversary of a relatively obscure chemical reaction, whose discovery has had a profound effect on the development of industrial chemistry in the 19th and 20th centuries.

In 1881, Mikhail Kucherov, a Russian chemist from the Imperial Forestry Institute in St. Petersburg, published a paper documenting his discovery of hydration of alkynes catalyzed by mercury(II) bromide *(1)*. As a result of this hydration and subsequent rearrangement, acetaldehyde was produced from acetylene. Other alkynes yielded ketones. For example, conversion of propyne into acetone was remarkably easy, requiring just a few hours of heating on a water bath. The mechanism of the process involves an enol formation at the first stage, followed by the keto–enol rearrangement *(2)*.

$$HC{\equiv}CH \xrightarrow[H_2O]{Hg^{2+}} H_3CCHO \qquad (1)$$

$$RC{\equiv}CH \xrightarrow[H_2O]{Hg^{2+}} RC(O)CH_3 \qquad (2)$$

A stepwise reaction mechanism is illustrated in Scheme I.



Scheme 1. Hydration of alkyne involving an enol formation and keto–enol rearrangement.

This reaction opened the way to industrial production of acetaldehyde that began simultaneously in Canada and Germany in 1914. Acetaldehyde was a major industrial chemical until the 1970s (e.g., a raw material for acetic acid production), while the name of Kucherov, initially attached to the reaction (Kutscheroff hydration), was rarely mentioned. In recent decades, acetaldehyde production by this process has been largely replaced by the Wacker catalytic process that uses less expensive ethylene as a precursor *(3)*.

Kucherov was a colorful figure, which was not unusual among the "great generation" of chemists of the second half of the 19th century, people with broad educations and interests who founded chemistry, as we know it. The painting of the Chemical Laboratory at the Imperial Forestry Institute, one of the oldest such laboratories in Russia, was done by Kucherov (Figure 1).

Figure 1. A painting by M. Kucherov of the Chemical Laboratory at the Imperial Forestry Institute in St. Petersburg, Russia at the end of 19th century.

The chemistry of acetylene was the main subject of his research at the Chemical Laboratory at the Imperial Forestry Institute, which he combined with a parallel assignment at the Chemical Laboratory of the Ministry of Finance at St. Petersburg, where he had been developing and supervising analytical procedures for quality control of beverage alcohol and wines. The government of the Russian Empire at the time introduced a state wine monopoly that, strangely enough, stimulated development of chemistry in the country. The government was interested in raising standards for vodka, the staple of domestic alcoholic drinks. Therefore, many known scientists were involved in vodka-related projects, including Kucherov and D. I. Mendeleev, the father of the periodic table.

Even considering the insight and imagination characteristic of the chemists of the 19th century who were lacking modern instrumental tools, yet not knowledge and intuition, the discovery of the Kucherov reaction was a remarkable achievement. The earlier work of Linneman demonstrated that heating 2-bromopropene $CH_3CBr{=}CH_2$ in aqueous acetic acid in presence of mercury (II) acetate yielded acetone, while 2-bromo-3-methyl-2-butane $(CH_3)_2C{=}CBrCH_3$ yielded methylisopropylketone *(4)*. Linneman reported a smell of acetaldehyde during the process but never isolated it. Kucherov suggested that mercury(II) acetate catalyzes hydrogen bromide elimination from vinyl bromides thus transforming them into substituted acetylenes, and mercury(II) acetate becomes mercury(II) bromide. This logic led him to the idea of studying acetylene hydration in the presence of mercury(II) bromide. It was found later that the Kucherov reaction also opened the gate to synthesis of ethers, thioethers, and amides via hydration of acetylene ethers, thioethers, and enamines *(5)*.

$$\begin{array}{c} RC{\equiv}CX \xrightarrow{H_2O} RCC(O)X \\ \text{where } X = OR', SR', \text{and } NR'_2 \end{array} \qquad (3)$$

All these reactions, originating from an obscure discovery in the 19th century, remained important through most of the 20th century in the industrial chemical production of acetaldehyde, used as a starting material in the synthesis of acetic acid, *n*-butyl alcohol, ethyl acetate, and other chemical compounds. We think it is of some educational value to look occasionally at the time, place, and circumstances that led to modern chemical practices, normally taken for granted.

Literature Cited

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