

A SHORT HISTORY OF THE DUTCH SCHOOL OF CATALYSIS

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Edited by J.J.F. Scholten
Emeritus Professor of Catalysis
Delft University of Technology, Delft, The Netherlands

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H. van Bekkum

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1. THE BÖESEKEN PERIOD (1907-1938)

Before being appointed to the chair of organic chemistry at Delft Jacob Böeseken (born 1868, Rotterdam) served a secondary school at Assen as a teacher and the University of Groningen as a lecturer, working together with professor A.F. Holleman.

Böeseken was graduated as a chemical engineer ("technoloog") at Delft (prof. S. Hoogewerff, founder of the faculty of Chemical Technology and also one of the founders of the *Recueil des Travaux Chimiques des Pays-Bas*). At that time the Delft degree together with the non-classical secondary school education of Böeseken did not give access to the defense of a thesis in the Netherlands and through Holleman's mediation [1] Böeseken obtained his doctoral degree at the University of Basel (on research carried out at Groningen!)

At the time Böeseken joined Delft he was already interested in reactions of the Friedel Crafts type. His first publication in this field - based on experiments carried out at Assen - was: J. Böeseken, "Note sur la formation des cétones grasses aromatiques à l'aide du chlorure d'aluminium" [2]. Some years later a series - mainly published in the *Recueil* - starts entitled: "Contribution à la connaissance de la réaction de Friedel et Crafts".

At Delft Böeseken was able to intensify the Friedel-Crafts work. Aromatic alkylation as well as acylation were on the program. Delft theses on these subjects include:

- 1912 J.G.W. Sieger, "Het aethyleeren van chloorbenzol" ("The ethylation of chlorobenzene")
- 1912 H.J. Prins, "Bijdrage tot de kennis der katalyse. De katalytische werking van aluminiumhalogeniden" ("Contribution to the knowledge of catalysis. The catalytic action of aluminum halides")
- 1913 S.C.J. Olivier, "Snelheidsmetingen bij de reactie van Friedel en Crafts" ("Rate measurements in the reaction of Friedel and Crafts")
- 1919 G.E. Hoeffelman, "De acetylering van nitrophenolen onder den invloed van eenige katalysatoren" ("The acylation of nitrophenols under the influence of several catalysts")

and

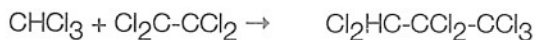
- 1922 E. van Thiel, "Acetyleringen met azijnzuuranhydried onder invloed van katalysatoren" ("Acylation with acetic anhydride under the influence of catalysts").

Essential features of Friedel Crafts catalysis were already recognized in the thesis of Sieger:

- di- and higher alkylation as a consequence of the activation of electrophilic substitution by alkyl groups;
- transalkylation as a means to enhance the amount of mono-alkylated product, and also (!)
- oligomerization of ethene under special Friedel-Crafts conditions.

The thesis of Prins contains a review of the Friedel Crafts reactions together with experimental work on the AlCl_3 -catalyzed addition of small polyhalogen compounds (CHCl_3 , CCl_4) to olefins. The latter most intelligent sequence of experiments (starting with a side product found by Böeseken, then to identification of a role of the solvent CHCl_3 ,

subsequently experiments with CCl_4) led to the discovery of the Prins reaction:



Induced by the AlCl_3 catalyst an electrophilic mechanism is assumed to apply.

Actually two Prins' reactions exist, the other being the acid-catalyzed addition of an olefin to formaldehyde leading to 1,3-diol systems [3]. The latter and best-known Prins reaction [4] was discovered by H.J. Prins in 1919 [5].

It may be noted that the first Prins-reaction is (again) under investigation at Utrecht since 1980 (G. van Koten/D.M. Grove) applying homogeneous nickel-catalysts. The mechanism seems well-understood now.



Fig. 1. H.J. Prins (1912), discoverer of two catalytic reactions.

Böeseken started a general series of publications on catalysis [6] under the heading: "L'action catalytique", but gradually some other fields of more stoichiometric character caught the main part of his attention. These fields were:

- borate complexes of diols and conformational deduction and consequences
- oxidation using peroxides and peracids.

The first mentioned investigations (with theses of Chr. van Loon (1919), H.G. Derox (1922), P.H. Hermans (1924), and C.J. Maan (1928)) afforded much insight into the conformations of cyclic systems, especially of sixmembered rings. Over 30 years later Hassel and Barton were awarded the Nobel Prize for their work on cyclohexane conformational analysis, but in essence the Delft people had disposal of this knowledge long before. Apparently the publication policy and skills (rather modest French) of Böeseken c.s. were not

very efficient. Borate complexes of glucose also allowed (theses of R. Verschuur (1927) and of N. Vermaas (1931)) the first assignment of the structure of α - and β -glucose, the α -epimer giving the more stable borate ester.

Of the oxidation work we mention the oxidation of catechol with peracetic acid towards cis,cis, muconic acid, at that time a remarkable aromatic-to-aliphatic transition, and the study of the Fenton system, $\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$ (thesis M. K  chlin).

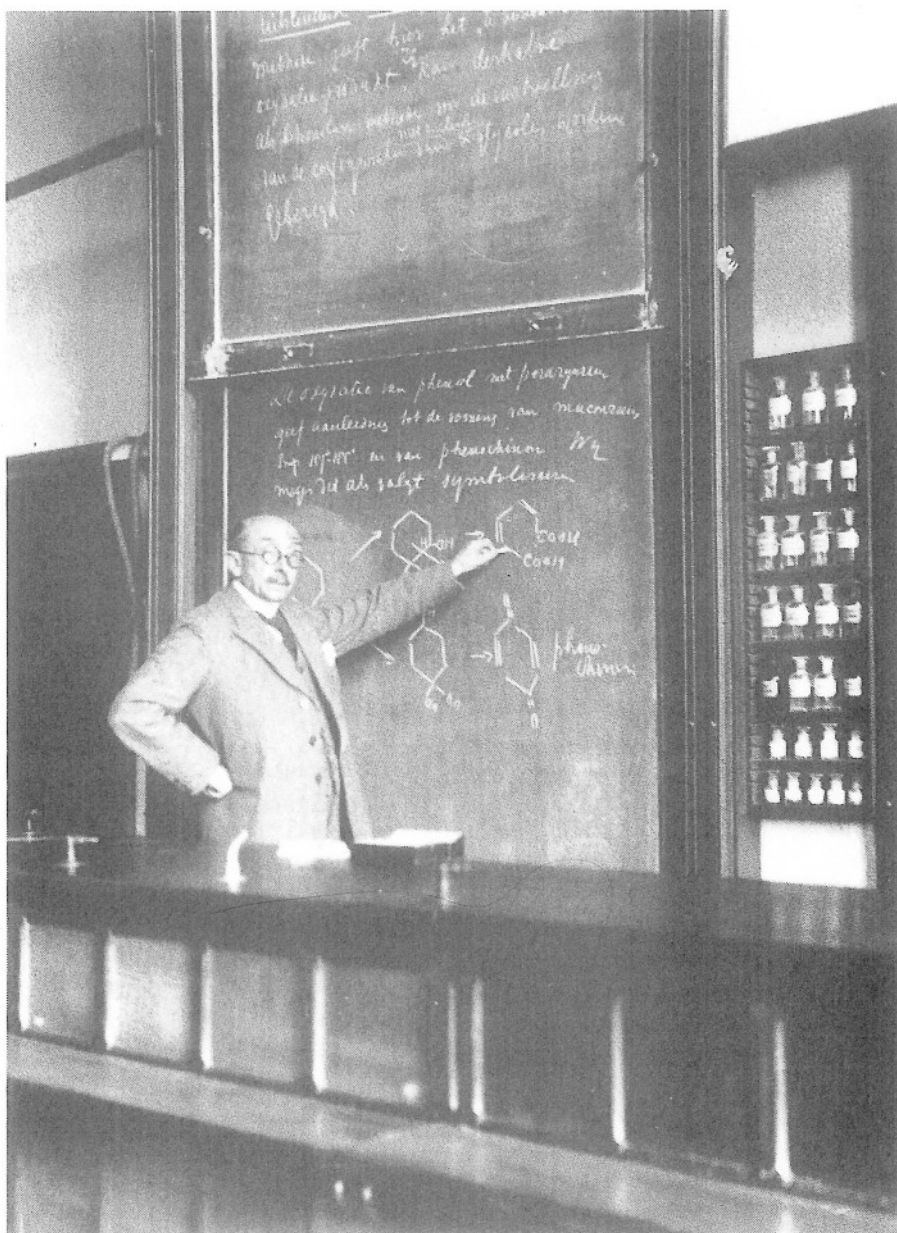


Fig. 2. J. B  seken (1932), teaching on oxidation.

Many of Böeseken's students made an excellent industrial or academic career; we mention:

H.I. Waterman, served as professor of chemical technology (1919-1959) at Delft;

A.J. Kluyver, kept the chair of applied microbiology (1921-1956) at Delft;

J. Coops Jr., became the first professor of organic chemistry at the Free University at Amsterdam;

P.E. Verkade (1891, Zaandam) got a chair in "warenkennis" (product technology) at the Nederlandsche Handelshoogeschool at Rotterdam (at present the Erasmus University). In 1939 he succeeded Böeseken at Delft.



Fig. 3. H.I. Waterman (1913), Thesis "Over eenige factoren, die de ontwikkeling van *Penicillium glaucum* beïnvloeden" ("On some factors influencing the growth of *Penicillium glaucum*")

2. THE VERKADE YEARS (1939-1961)

In the Verkade period [7, 8] the attention shifted to natural products, particularly triglycerides, and phosphoglycerides and their accurate regioselective synthesis. Catalysis mainly played a role as synthetic tool such as Pd-catalyzed de-benzylation and proton-catalyzed (de)-acetalization.

Another line was in aromatic synthesis, leading, amongst others, to new sweetening agents such as P-4000, 2-amino-4-nitropropoxybenzene, 4000 times as sweet as sucrose on a wt. basis. P-4000, an orange compound, was - during a short time - commercially produced. In war time the German occupiers, thinking that a sweetening agent for gasoline was involved, gave some facilities to continue research on P-4000 and analogous compounds.

With the appointment (1948) of B.M. Wepster (1920, Dordrecht) on a new chair in

theoretical organic chemistry, the laboratory embarked on some new subjects. Thus the group started to study systematically substituent effects in some aromatic reactions (such as catalytic de-acylation of acetanilides). A review paper by B.M. Wepster, P.E. Verkade and H. van Bekkum (1959) [9] on substituent effects and how to deal with them in terms of the Hammett equation, became a "classic".

Another Wepster-line was a study of steric effects as exerted by ortho-substituents in aromatic systems.

A third organic chair (H.C. Beyerman, 1954) directed its research towards multistep synthesis of super-fine chemicals, peptides and alkaloids. Here too, catalysis was applied as a synthetic method.

3. THE VAN BEKKUM PERIOD (1961- up to now)

When Verkade retired, H. van Bekkum (1932, Rotterdam) returned from the Amsterdam Shell Laboratory to Delft, being appointed to teach general organic chemistry.

The first catalytic subjects, guided jointly by Van Bekkum and Wepster, dealt with catalytic hydrogenation of benzene and naphthalene derivatives. The accents were on partial hydrogenation over noble metal catalysts and on stereoselectivity in hydrogenation and how to understand and tune these.

It was found that bulky groups (*t*-butyl) or carboxylate groups strongly enhance the selectivity to intermediate cyclohexene compounds. Steric hindrance in the aromatic compound sometimes led to strongly enhanced rates of hydrogenation (theses Nieuwstad, Van Bekkum, Van de Graaf). The phenomena could be explained by combining the steric hindrance concepts of Wepster and the hydrogenation theories of Burwell and Siegel. A new Delft concept in hydrogenation was the trans-addition of hydrogen when hydrogenating bicyclic cyclo-alkene compounds over Pt, Pd and Rh (thesis F. van Rantwijk).

Several pairs of isomeric 1,4-substituted cyclohexane compounds, obtained by hydrogenation, could be separated using thiourea inclusion compounds which form only when the guest compound (i.e. the trans-1,4-isomer) fits into the thiourea host lattice. At Delft (J.D. Remijnse, MSc-work) the first selenourea inclusion compounds were made and studied.

Within the doctoral work of D.P. Roelofsen (thesis 1972) the step was made from thiourea complexes towards the stable pre-formed lattices of zeolites. Roelofsen applied, amongst others, zeolites for the first time successfully in the shifting of organic equilibria (transesterification, acetalization, enamine formation) by selectively adsorbing a small product molecule (water, methanol) into a suitable zeolite. A large pore zeolite can be used to catalyze the latter two reactions.

Roelofsen's work formed the start of a now 25 years lasting effort of the Delft group in the synthesis/modification/characterization/application of zeolites. Theses of Th.M. Wortel (1979), J.C. Oudejans (1984), F.J. van der Gaag (1987), R.A. le Fèvre (1989), Th.L.M. Maesen (1990), P. Voogd (1991), J.C. Jansen (1992), E. de Vos Burchart (1992), R. de Ruiter (1993), A. Arafat (1993), E.R. Geus (1993) and P.J. Kooyman (1993) reflect the results.

An achievement in the educational area was the organization of the first International Summerschool on Zeolites, Zeist, 1989, and the editing [10] of a new book on Zeolites (incl. an inexpensive Student Edition).

Some research highlights include: the successful application of modified zeolites in ammoxidation and pyridine synthesis (J.C. Oudejans, F.J. van der Gaag, R.A. le Fèvre), the direct conversion of aqueous fermentation alcohol to gasoline (J.C. Oudejans), the structural

analysis of MFI-zeolite containing the template (tetrapropylammonium) or p-xylene as an adsorbate (J.C. Jansen, H. van Koningsveld), the molecular mechanics calculations applied on zeolite/template combinations (B. van de Graaf/E. de Vos Burchart), the fast microwave induced synthesis of zeolites (A. Arafat), clean zeolite-catalyzed aromatic acylation (thesis A.J. Hoefnagel), the growth of zeolites onto stainless steel wire leading to new catalyst systems (C.H. Legein, J.C. Jansen), the first ceramic membrane containing a continuous zeolite (MFI) layer (E.R. Geus).

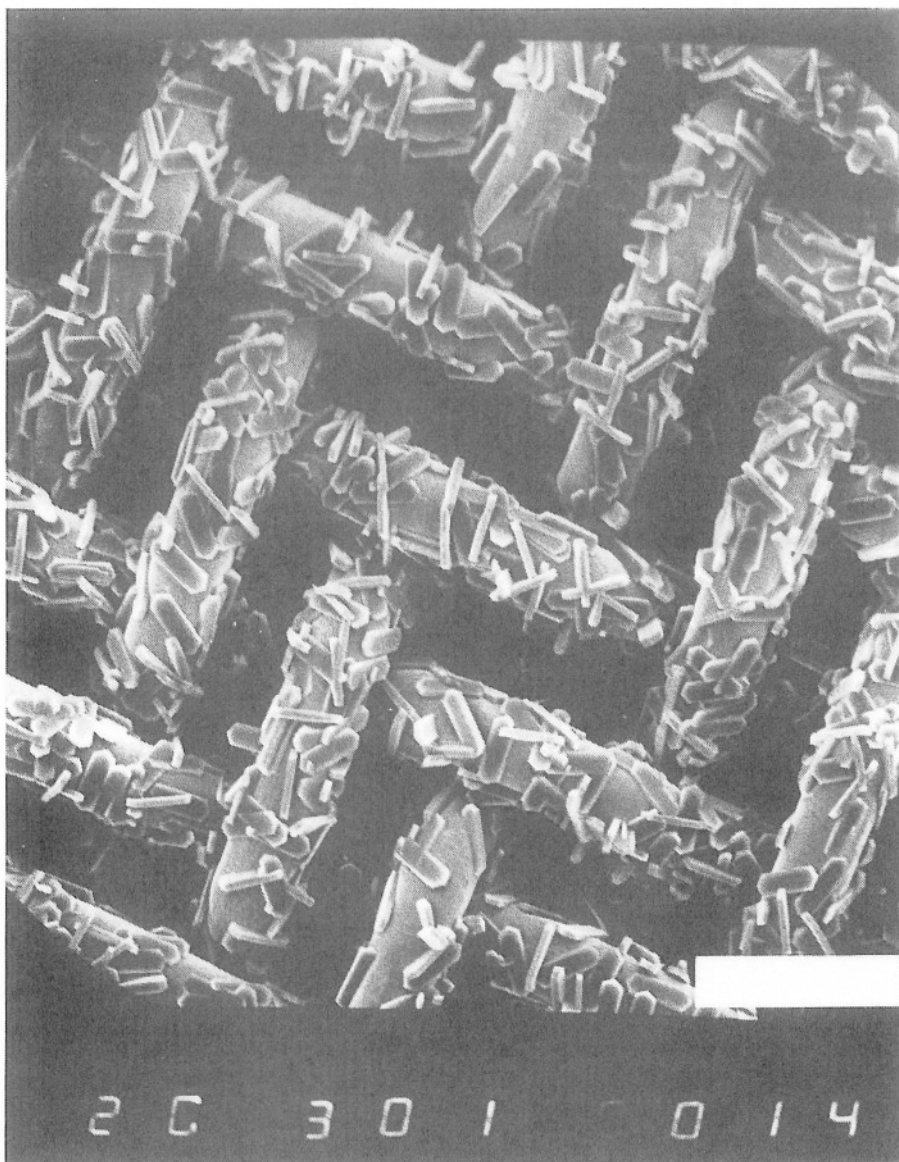


Fig. 4. Axial growth of zeolites onto a stainless steel gauze.

The latter two investigations were conducted in recent cooperation with groups of the Delft Laboratory of Chemical Process Technology, prof. C.M. van den Bleek et al., and prof. J.A. Moulijn c.s., respectively.

Earlier, around 1970, a request by prof. J.C. Vlughter, at that time professor of chemical technology at Delft, to cooperate in a project on catalytic hydrogenolysis of sucrose towards glycerol, induced us to make a start in carbohydrate hydrogenation. The doctoral work of A.P.G. Kieboom on metal-catalyzed hydrogenation of carbonyl compounds facilitated this step. One of our early findings in carbohydrate hydrogenation was in fact a catalytic dehydrogenation which takes place when aldehyde-sugars are brought in contact with Pt or Rh at high pH. Hydrogen is evolved under very mild conditions (room temperature or lower) and the aldonic acid is formed (MSc-work R. Laroy, thesis G. de Wit). Within the PhD work of M. Makkee a combined action of metal catalyst (Cu-on-SiO₂) and enzyme catalyst (glucose-isomerase) was applied so as to arrive at a one-pot conversion of glucose (via fructose) to mannitol.

Besides hydrogenation, also isomerization (thesis J.M. de Bruijn) and esterification (lipase-catalyzed) of carbohydrates and selective catalytic oxidation (theses M. Floor, H.E. van Dam, P. Vinke, A.C. Besemer) became part of the Delft program. Much work was devoted to the noble metal- (esp. Pt) catalyzed oxidation of carbohydrates; oxygen (air) is serving here as the oxidant and the pH should be 7 or higher. It was found, amongst others, that 1-O-alkylated aldohexoses could be selectively transformed into the 6-COOH systems. The Delft results and activities, including a review of the state of the art, persuaded the Dutch Ministry of Agriculture to finance (1991) a national program on catalytic oxidation of carbohydrates. It may be mentioned here that polycarboxylates obtained by glycolic oxidation of starch and of inulin, as studied at Delft, show great prospects as components in detergent formulations.

Several times areas studied by Böeseken et al. have been revisited, sometimes without being aware of this beforehand. A major example is the work on borate complexes, their structure, stability, preferred reaction position of a polyol etc. Böeseken used merely conductivity measurements as a tool; nowadays various advanced NMR techniques are available for the identification and quantification of borate esters in solution.

Recently a new oxidative method was found in which borate catalyzes the oxidation of a reducing sugar with H₂O₂ and protects the product for further oxidation by forming a stable borate ester (R. van den Berg, J.A. Peters).

In between the main catalysis research streams on zeolites and carbohydrate conversion some special catalyst systems were studied. These include Co(CN)₅³⁻ as hydrogenation catalyst (thesis J.D. Basters, co-guided by prof. L.L. van Reijen), supported Ru hydrogenation catalysts (thesis P.G.J. Koopman), metal catalysts equipped with a liquid film (thesis A.A. Wismeijer) and heteropolyacids (thesis M.A. Schwegler). The latter area is still under investigation with special attention for carbon-supported heteropolyacid catalysts; collaboration exists with prof. I.V. Kozhevnikov, Boreskov Institute, Novosibirsk.

4. ORGANIC CHEMISTRY AND CATALYSIS (from 1985)

Upon the retirement of professors Wepster (1985) and Beyerman (1984) the number of "organic professors" at Delft was reduced again to two. A.P.G. Kieboom (1945, Rotterdam), who had co-guided the carbohydrate research and part of the special catalyst systems, was appointed (1986) with a teaching commitment in Bio-organic chemistry and Bio-catalysis. After being embarked for two years, he preferred, however, to join industry. His successor became (1990) R.A. Sheldon (1942, Nottingham, U.K.) who had gained much experience in fine chemical synthesis including bio-catalysis during his work as a research director at Andeno (presently DSM-Andeno).

As nowadays both professors Van Bekkum and Sheldon devote their attention to organic chemistry and to catalysis, it was decided (1992) to change the name of the laboratory accordingly.

We finally mention that per January 1st, 1994, the total number of Delft organic theses amounts to 125, of which 47 were supervised by Böeseken and 42 by Van Bekkum. From these theses, some 45 were engaged with catalysis and catalysts.

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