# 23. Relationships Between Acidity Functions, Rates of Reactions of Formaldehyde with Cellulose and of Cellulose Hydrolysis

## 28th Communication on investigations in textile chemistry[1])

### by Angelika Mohn-Wehner, H. K. Rouette and H. Zollinger

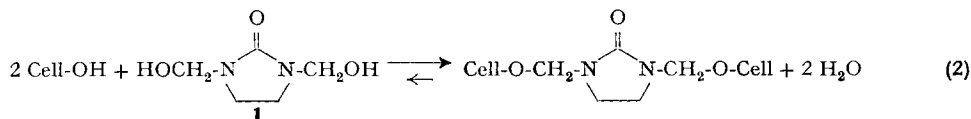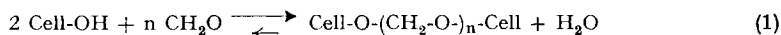Technisch-Chemisches Laboratorium, Eidg. Technische Hochschule, Zürich

(3. VI. 72)

*Summary*. The rates of hydrolysis of cellulose and the rates of formation of cellulose formal were measured in heterogeneous systems consisting of cotton cellulose and solutions of formaldehyde in aqueous hydrochloric acid and in solutions of hydrochloric acid in various water/acetic acid mixtures. The rates were related to the acidity functions ($H_0$) of the solutions. Although fairly good linear relationships between the logarithms of the rates and $H_0$ were obtained in most cases, no conclusions concerning the reaction mechanism could be drawn.

**1. Introduction.** – Crosslinking reactions of cellulose molecules (Cell-OH) with formaldehyde (1) and cyclic derivatives of N,N'-dimethylolurea, e.g. with 2,5-di-methylol-imidazol-1-one **1** (2), are important processes for improving the crease resiliency of cotton fabrics. These reactions are characterized

1. by catalysis, using either certain metal salts (e.g. $MgCl_2$) or moderately concentrated solutions of mineral acids,

2. by diffusion phenomena due to the fact that the reactions take place either in liquid/solid or gas/solid heterogeneous systems.

$$2 \text{ Cell-OH} + \text{n CH}_2\text{O} \rightleftharpoons \text{Cell-O-(CH}_2\text{-O-)}_n\text{-Cell} + \text{H}_2\text{O} \qquad (1)$$

$$2 \text{ Cell-OH} + \text{HOCH}_2\text{-N} \overset{\text{O}}{\underset{\displaystyle 1}{\diagdown}} \text{N-CH}_2\text{OH} \rightleftharpoons \text{Cell-O-CH}_2\text{-N} \overset{\text{O}}{\diagdown} \text{N-CH}_2\text{-O-Cell} + 2 \text{ H}_2\text{O} \qquad (2)$$

These phenomena enormously complicate a thorough mechanistic evaluation of these reactions. In particular, rationalization of apparent kinetic data becomes very complex.

In a preceeding paper [2] we discussed the influence of the composition of formaldehyde solvents (water/acetic acid mixtures in various ratios) on reaction (1). It was shown that, depending on the water content, either the rate of swelling, diffusion, physisorption of formaldehyde in the cellulose, hemiformal formation (Cell–OCH$_2$OH) or formal formation (Cell–O–CH$_2$–O–Cell) could become the rate determining step.

In this paper we describe the correlation of the rate of formal formation with the acidity of the reaction system. Formal formation is an acid catalyzed, reversible reaction. At the same time, hydrolysis of the glucosidic bonds between anhydroglucose units of cellulose is also acid-catalysed. Since the crosslinking reaction with

---

[1])   27th Communication: *O. Annen, P. Rys, Y. Terada & H. Zollinger* [1]. Presented at the VIth IUPAC Symposium on Carbohydrate Chemistry, Madison (Wisconsin), August 15th, 1972.

formaldehyde is most often performed in moderately strong mineral acid solutions (mainly in hydrochloric acid), acid concentrations or pH-values are useless for a fundamental analysis of experimental data. This conclusion may appear trivial, yet it was only quite recently applied to the hydrolysis of cellulose in solution [3], and not – with the exception of some brief comments in our previous papers [2, 4] – to our knowledge, to crosslinking reactions and the hydrolysis of cellulose in heterogeneous phase.

**2. Acidity functions used.** – We are interested in formaldehyde/cellulose reactions and cellulose hydrolysis in purely aqueous systems as well as in water/ acetic acid mixtures with hydrochloric acid.

Since acidity functions were not available for the water/acetic acid/hydrochloric acid systems used, they were determined in the usual way by spectrophotometry using 4-chloro-2-nitroaniline as an indicator base following the procedure of *Torck et al.* [5]. Results for 4.41 M HCl and 4.80 M HCl in water/acetic mixtures containing 23 to 95% (v/v) water are given in Fig. 1.
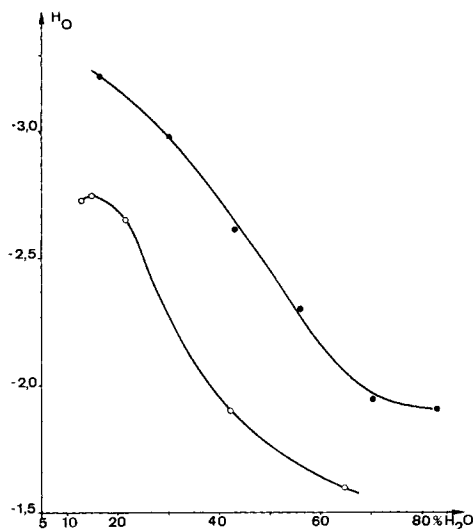


Fig. 1. *Acidity functions of 4.41 M HCl and 3.80 M HCl in water/acetic acid mixtures*

**3. Rates of hydrolysis cellulose.** – Following proposals by *Ott et al.* [6] and *Vink* [3] we determined the rate constants of cellulose hydrolysis by plotting the logarithm of the fluidity (reciprocal viscosity) of treated cotton cellulose taken from the hydrolytic system, nitrated and dissolved in acetophenone [7] as a function of time of hydrolysis.

The results with cotton fibres are shown in Fig. 2 for purely aqueous systems, containing 5 to 22 g HCl/100 ml (1.3 to 6.02 M): After an induction period a roughly linear relationship is obtained which is consistent with a (pseudo)-first order reaction.

---

[2]   Introduction of more than one unit of such crosslinking reagents between two cellulose hydroxyl groups also occurs; it is, however, not considered here.

The deviations from linearity cover an induction period which seems to become longer with increasing concentration of hydrochloric acid. This may be due to the influence of rate-determining diffusion processes[3]).
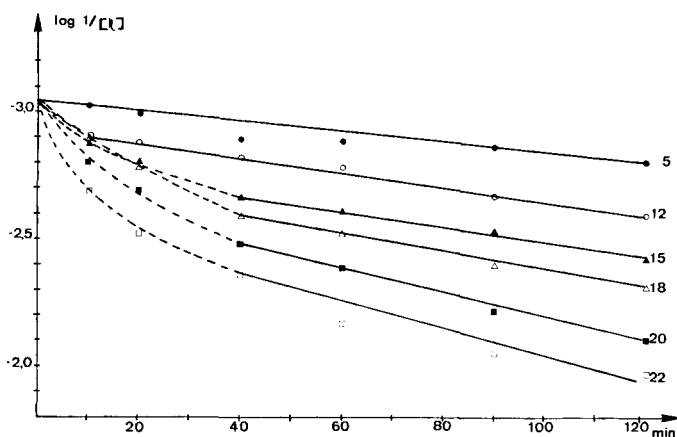


Fig. 2. *Depolymerisation (Hydrolysis) of cellulose in aqueous HCl.* (Fig. refer to g HCl/100 ml)

The slopes of the linear portion of the curves increase with higher acid concentration, resulting in larger first-order rate constants ($k_{hy}$). The rate constants are plotted in Fig. 3 as a function of $H_o$. Considering the inaccuracy brought into the evaluations of the rate constants by the induction period (Fig. 2), a reasonably good linear relationship is indicated, giving a slope of 0.288 (r = 0.938). A plot of log $k_{hy}$ + $H_o$ vs. $H_o$ + log [$H^{\oplus}$], as suggested by *Bunnett & Olson* [8] yields a slope $\Phi$ = 1.29 (r = 0.895).
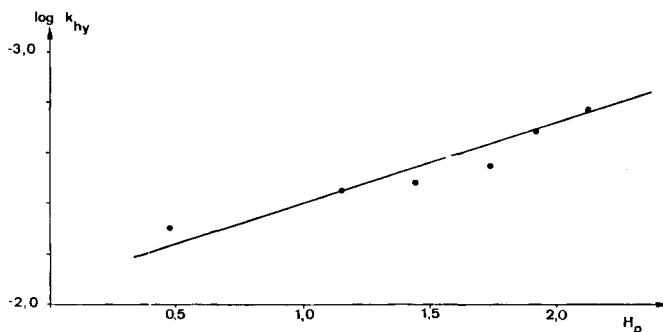


Fig. 3. *Rate of hydrolysis of cellulose in aqueous HCl vs. the acidity function*

The rates of the hydrolysis of cellulose in mixtures of water and acetic were measured by keeping the hydrochloric acid concentration constant [4.41 M) and varying the solvent composition (10 to 70% $H_2O$, 83.1 to 23.5% HOAc).

---

[3]    Based on our previous investigations [2], rates of swelling of cellulose in water have relaxation times of 1 to 2 minutes and, therefore, they probably do not influence the rate of hydrolysis.

A reasonably good linear relationship between the logarithm of the rate constant $k_{hy}$ and the acidity function is obtained (Fig. 4, slope $= 0.740$, $r = 0.983$).
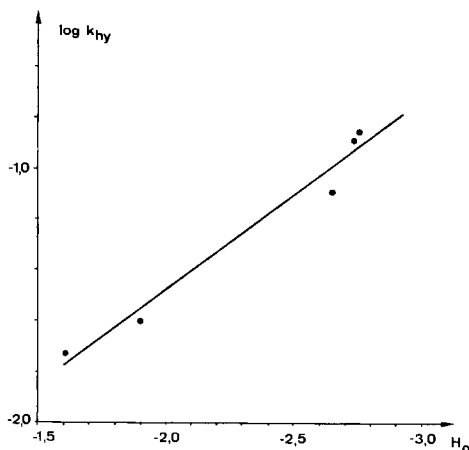


Fig. 4. *Rate of hydrolysis of cellulose in 4.41 M HCl/water/acetic acid mixtures*

**4. Rates of crosslinking of cellulose with formaldehyde.** – In previous papers [2, 9] we studied the rates of swelling of viscose fibres and cotton fabrics, sorption of formaldehyde, hemiformal formation (Cell–O–CH$_2$OH) and crosslinking (formal formation) in water/acetic acid systems in the presence of 14% hydrochloric acid (3.95 M HCl). These investigations demonstrated that

1. for viscose and cotton cellulose swelling is rate-limiting in systems with less than 50% and 30% water, respectively,

2. the rate of formal formation was, in spite of the constant concentration of hydrochloric acid, highest in that medium in which the acidity function indicated the highest activity of the acid (highest value of $-H_o$).

We are primarily interested here in the rate of formal formation as a function of the acidity function in an aqueous system with changing concentrations of hydrochloric acid and, based on that information, on the rates in water/acetic acid mixtures containing hydrochloric acid.

In order to eliminate swelling effects, preswollen cotton fibres were used. In Fig. 5 the logarithm of 1–f (where f corresponds to the fraction of formaldehyde reacted as formal at time t relative to the bonded formaldehyde after completion of the reaction) is plotted as a function of time.

For a first-order reaction, one expects straight lines. As with the results on the hydrolysis of cellulose (Fig. 2) there is an initial faster reaction and, at high degrees of substitution, a decrease in rate (Fig. 5).

First-order rate constants for formal formation ($k_{cx}$) were obtained from the linear part of the curve in Fig. 5.

On the basis of the graphical similarity of the hydrolysis and the formalisation rate curves (Fig. 2 and 5, respectively) one might argue that a pseudo-first order rate law (namely first-order with respect to those glucosidic bonds of cellulose which are

on the surface of the micro- [and perhaps the elementary] fibrils[4]) and zero-order with respect to water and hydroxonium ions [which are present in practically constant concentration]) is appropriate for the hydrolysis, but not for the reaction with
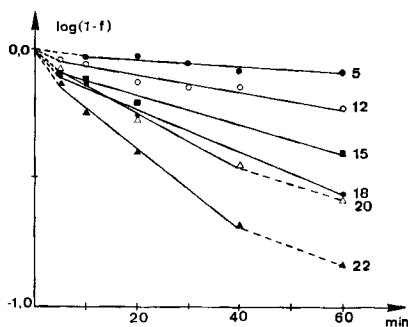


Fig. 5. *Rate of cellulose formal formation in aqueous HCl.* (Fig. refer to g HCl/100 ml)

formaldehyde. However, since the formation of formal is a reversible reaction whose equilibrium is not on the side of the formal, a pseudo-first order rate law becomes a sufficiently good approximation as long as f is not too large. The deviations observed at higher degrees of substitution (Fig. 5, runs with $> 5$ M HCl) are probably due to non-pseudo-first order conditions.

A good linear relationship of log $k_{cx}$ vs. $-H_0$ is obtained (Fig. 6, slope s = 0,634, r = 0.998). A *Bunnett-Olson* plot [8] yields $\Phi = 0.57$.
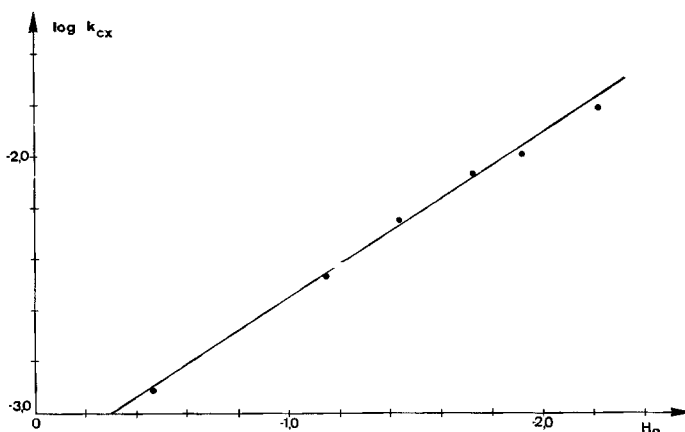


Fig. 6. *Rate of cellulose formal formation in aqueous HCl vs. the acidity function*

We also measured the rates of hydrolysis of the glucosidic bonds of the cellulose chain in the aqueous crosslinking solutions used for the data in Fig. 5, i.e. in the presence of formaldehyde. The decrease in intrinsic viscosity showed a similar time-dependence as in systems without formaldehyde given in Fig. 2. First-order rate

---

4)    For the definition of elementary fibrills see *Mühlethaler* [10]; for their accessibility to chemical reactions see *Haworth, Roberts & Robinson* [11].

constants ($k_{hy}$) calculated from that linear part of the log $[\eta]$ vs. time curves are not very different from those obtained in the absence of formaldehyde. The plot of log $k_{hy}$ vs. $-H_0$ (Fig. 7), however, shows a smaller slope (s = 0.219, r = 0.936) than the hydrolyses without formaldehyde.
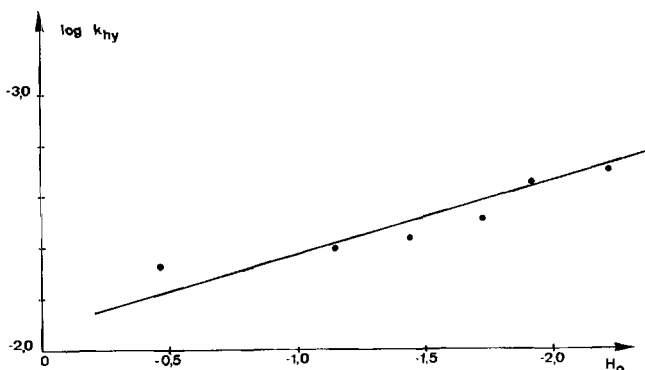


Fig. 7. *Rate of hydrolysis of cellulose in aqueous HCl in presence of formaldehyde vs. the acidity function*

The rate of formal formation was also measured in water/acetic acid mixtures, containing 20 to 70% water. Fig. 8 shows the experimental data. It becomes quite clear that a linear relationship between log (1–f) and t is, at best, only roughly indicated, and that induction periods are present, but not in all cases. The assignment of linear relationships in order to calculate rate constants as indicated by the straight lines is therefore questionable.
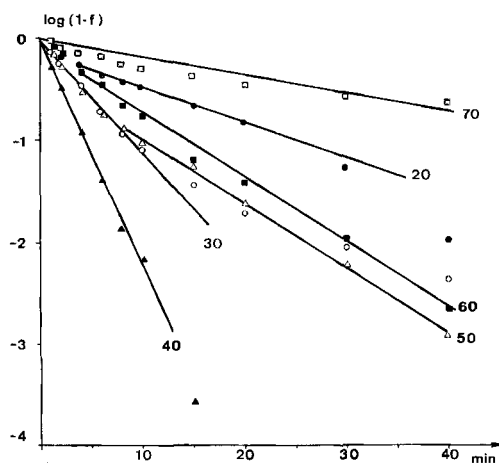


Fig. 8. *Rate of cellulose formal formation in 4.41 M HCl/water/acetic acid mixtures*
(Fig. refer to the water content of the solution)

We evaluated approximative rate constants $k_{cx}$ in this way, in order to check their relationship to the acidity functions of the systems used. Fig. 9 shows the results: There is clearly no simple correlation between $H_0$ and log $k_{cx}$ in water/acetic acid

mixtures with a constant concentration of hydrochloric acid. Only the increased rate at lower water content (70 to 40% water) and, therefore, increased acidity $(-H_0)$ is qualitatively understandable for an acid-catalysed reaction; the decreased rate observed for systems containing less than 40% water is not understandable.
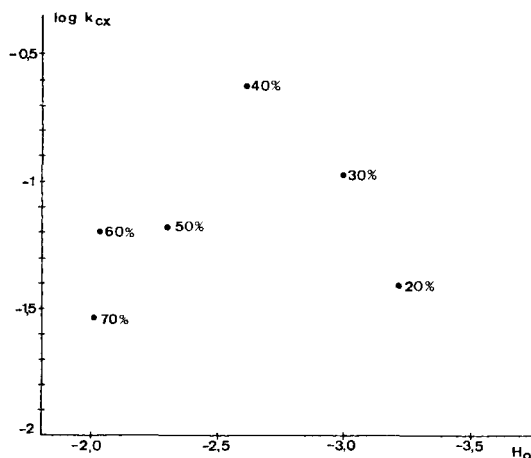


Fig. 9. *Rate of cellulose formal formation in 4.41 M HCl/water/acetic acid mixtures vs. the acidity function*

(Fig. refer to the water content of the solution)

**5. Discussion of the results.** – For the rates of both cellulose reactions studied – hydrolysis of glucosidic bonds and crosslinking with formaldehyde – a correlation with the acidity function of the system can be observed. Due to the fact that the kinetics of these reactions were studied as a function of the acidity function $H_0$ in heterogeneous systems, a quantitative interpretation is, however, not possible.

In particular we think that an interpretation of the mechanism of these acid-catalysed reactions is impossible for the following reasons:

1. In spite of intensive attempts in the last decade, particularly by *Bunnett* [8, 12], conclusive mechanistic interpretations of acid-catalysed reactions in moderately too highly concentrated mineral acids are possible only in cases where evidence in addition to log k vs. $H_0$ relationships is available.

2. $H_0$ is not identical with the activity of the hydroxonium ion, but contains the logarithm of the ratio of activity coefficients of the indicator acid/base pair used for its determination. This ratio again may be very specific for each indicator pair and different from that for the substrate investigated. This is particularly true for $H_0$ values determined in mixed solvents.

It is almost trivial to mention the difficulties of mechanistic studies in heterogeneous systems. In our case they are magnified by the fact that the heterogeneous phase is not static, but swells or, if preswollen cellulose is used, is in a dynamic equilibrium between swollen (chemically accessible) and ordered, unaccessible segments of macromolecules.

In spite of these reservations some conclusions are possible: First of all it is interesting to note that the slope in the log $k_{hy}$ vs. $-H_0$ relationship (Fig. 3) is

significantly less than 1. For related hydrolyses of glucosidic bonds in homogeneous systems in most cases slopes around 1 were found, e.g. by *Vink* [3] for the hydrolysis of hydroxyethylcellulose (s = 1.06), by *Timell* [13] for the hydrolysis of methyl-d-D-glucopyranoside in aqueous HCl and by *Hammett & Paul* [14] for the hydrolysis of sucrose[5]). It should be mentioned here, however, that *Timell* obtained smaller slopes when using other acids ($HClO_4$, $H_2SO_4$, $H_3PO_4$; e.g. s = 0.6 for aqueous $H_3PO_4$).

The slope of our hydrolysis relationship in the presence of formaldehyde is smaller (s = 0.219) than without formaldehyde (s = 0.288). This difference is caused essentially by the smaller rates of hydrolysis at higher acid concentrations where the extent of crosslinking by formaldehyde becomes greater. We think that this effect is due to a decrease in accessibility of glucosidic oxygen atoms when cellulose becomes cross-linked.

Accessibility in a dynamically changeable porous system is related to the viscosity of the liquid. This can be demonstrated particularly well in systems containing lower percentages of water and different acids: In Fig. 10 fluidities ($1/[\eta]$) of cellulose, treated for 30 min. in water/acetic systems containing 16.1% HCl or 31.5% $H_2SO_4$
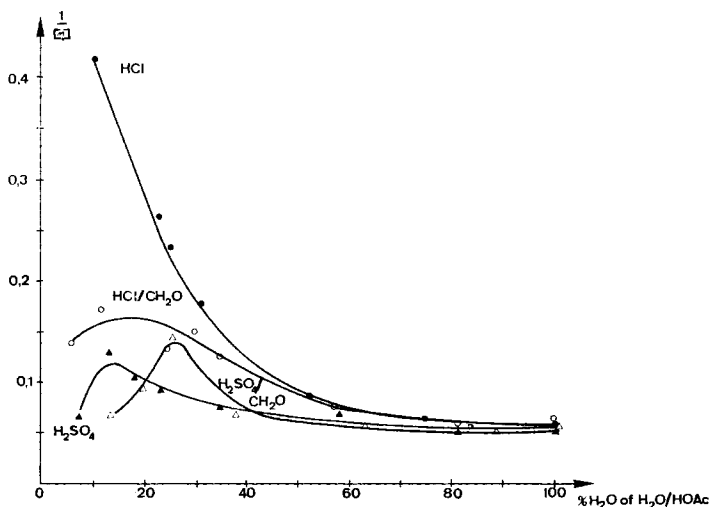


Fig. 10. *Hydrolysis of cellulose after 30 min in 4.41 M HCl (or 4.81 M $H_2SO_4$)/water/acetic acid mixtures with and without formaldehyde*

with or without formaldehyde (7.5%) are plotted against the water/acetic acid ratio of the system used. As Fig. 11 shows, the viscosity of the sulfuric acid solutions is similar to that of the hydrochloric acid solutions only if the water/acetic ratio is higher than ca. 0.30; at low water contents of the water/acetic acid mixtures sulfuric acid solutions are significantly more viscous than the respective solutions of hydrochloric acid.

The results of Fig. 10 can be understood well if one takes into account the dependence of diffusion coefficients ($D_{real}$) on the viscosity (*Stokes-Einstein* equation) in the pore model of diffusion developed by *Weisz* [15] in our laboratory. These results

---

[5]    For other related reactions see [8] and [12].

will be discussed in a paper on the influence of the viscosity of the formaldehyde solution made in our laboratory [16].

The reaction of polyvinylalcohol with formaldehyde in aqueous solution which was studied by *Kormanovskaya & Vlodavets* [17] as a function of $H_0$ is related to our
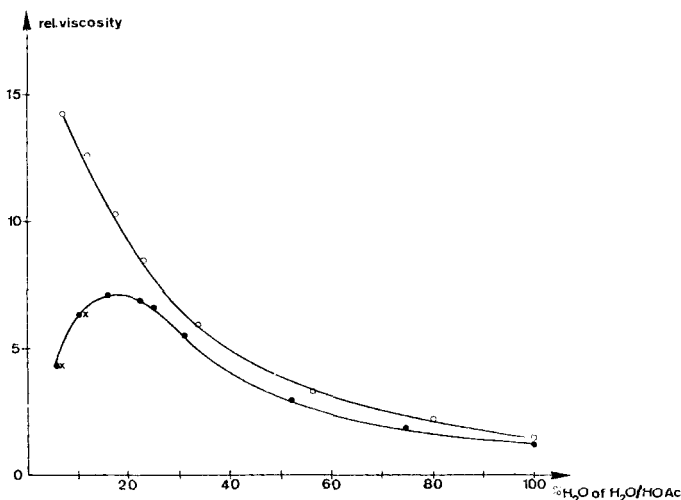


Fig. 11. *Relative viscosities of HCl and $H_2SO_4$ in water/acetic acid mixtures*
● 4.41 M HCl; × 1.70 M HCl; ○ 3.32 M $H_2SO_4$

reaction and leads to a value $\Phi = 0.0$ in a *Bunnett-Olson* plot. In *Bunnett & Olson's* interpretation [8] this result indicates that no water molecules are involved *as reactants* in the rate-determining step of the reaction. This result was, of course, to be expected since formal formation is not a hydrolysis, but a reaction in which water is *formed*. On the basis of the reservations made above a comparison of the slope of the cellulose-formal formation ($\Phi = 0.57$) with that of the respective reaction with polyvinyl-alcohol is impossible.

The speculations of various authors [18, 19] concerning the mechanism of the crosslinking reaction of cellulose with formaldehyde are, therefore, on a weak basis: A mechanism in which cellulose hydroxyl groups form oxonium ions and release water molecules, the cellulose carbonium ion reacting with the hemiformal [18], violates all experience in our knowledge of acetal chemistry, whereas a mechanism in which the hemiformal is protonated (Cell–O–CH$_2$–$\overset{\oplus}{O}$H$_2$) and forms a carbonium ion (Cell–O–CH$_2^{\oplus}$) seems to be much more feasible [19].

We have to emphasize, however, that this mechanism is neither supported nor eliminated by this or by other investigations.

The results shown in Fig. 9 are supported by another investigation from our laboratory [2] in which it was shown by a $^{14}CH_2O$ tracer technique that the rate of formal formation goes through a maximum at about 30% water content (at constant mineral acid concentration).

## Experimental Part

*Materials.* 100% cotton popeline, 130 g/m², bleached and mercerised, was washed with 2 g/l soap for 30 min. at the boil before use.

As a source of formaldehyde, paraformaldehyde (purum, *Fluka*) was used. Hydrochloric acid (37%), acetic acid (100%), acetic anhydride and sulfuric acid (95–97%) were pro analysis grade (*Merck*).

*Solutions.* The solutions in Table 1 were used for the measurements of the rates of hydrolysis and formal formation.

Table 1. *Solutions used* (R = Rest to 100 ml)

| Solution No. | Paraformal-dehyde g/100 ml | HCl (100%) g/100 ml | $H_2O$ g/100 ml | HOAC g/100 ml | $H_2O$ in % of $H_2O+$ HOAc |
|---|---|---|---|---|---|
| 1 | 7.5 | 5 | R | – | – |
| 2 | 7.5 | 12 | R | – | – |
| 3 | 7.5 | 15 | R | – | – |
| 4 | 7.5 | 18 | R | – | – |
| 5 | 7.5 | 20 | R | – | – |
| 6 | 7.5 | 22 | R | – | – |
| 7 | 7.5 | 17.5 | 20 | R | 26.3 |
| 8 | 7.5 | 17.5 | 30 | R | 40.0 |
| 9 | 7.5 | 17.5 | 40 | R | 53.2 |
| 10 | 7.5 | 17.5 | 50 | R | 66.7 |
| 11 | 7.5 | 17.5 | 60 | R | 80.0 |
| 12 | 7.5 | 17.5 | 70 | R | 93.2 |
| 13 | – | 5 | R | – | – |
| 14 | – | 12 | R | – | – |
| 15 | – | 15 | R | – | – |
| 16 | – | 18 | R | – | – |
| 17 | – | 20 | R | – | – |
| 18 | – | 22 | R | – | – |
| 20 | – | 16.1 | 21.8 | 73.1 | 23.0 |
| 21 | – | 16.1 | 24.1 | 71.6 | 25.2 |
| 22 | – | 16.1 | 30 | 65.5 | 31.4 |
| 23 | – | 16.1 | 50 | 45.7 | 52.2 |
| 24 | – | 16.1 | 70 | 23.5 | 74.9 |

**Acidity function determinations.** – *Indicator.* 4-Chloro-2-nitro-aniline (*Schuchardt*, München) was used to determine the $H_0$ functions (p$K_{BH}^{\oplus} = -1.11$) [21]. This was purified by recrystallizing twice from water/ethanol mixtures (m.p. = 117°). A standard solution of this indicator was made by dissolving accurately 0.01 moles of the purified indicator in one litre of glacial acetic acid.

A *Beckman* model DB-G spectrophotometer with 1 cm pathlength quartz cells was used to determine the absorption maxima in the visible region.

*Standardization of the indicator.* Acetic acid (3 ml) was placed in each of the cells. To the sample cell known amounts (1–10 $\mu$l) of the standard indicator solution was added, shaken thoroughly and its optical density at the maximum wavelength in the visible region was measured. From this, $\varepsilon_N$, which represents the concentration of the indicator in neutral solvent, was calculated. In general two determinations were carried out and the average taken.

*Measurements of $H_0$ in different acid solutions.* 3 ml of the acid solution was placed in each cell. To the sample cell known amounts of standard indicator solution was added, shaken thoroughly

and its optical density was measured at the maximum wave length in the visible region. From this, $\varepsilon_A$, which represents the concentration of the indicator in its basic form in the acid solution was calculated. The determinations were twice repeated and the average value was taken.

$H_0$ *calculation.* Acidity functions were calculated following equation (3) [21].

$$H_0 = pK_{BH^\oplus} - \log_{10}[BH^\oplus]/[B] .\qquad(3)$$

To calculate the term $[BH^\oplus]/[B]$ the method of *Pentii Salomaa* [22], using equation (4), was employed where $\varepsilon_N$ and $\varepsilon_A$ are the extinction coefficients of the indicator solutions at the wavelengths of maximum absorption in the neutral solvent and in the acid solution in question, respectively, and $\varepsilon_S$ is a small correction term which denotes the extinction coefficient of the conjugate acid of the indicator in the acid solution. In order to estimate $\varepsilon_S$ (which cannot be measured directly) *Pentti Salomaa* [22] took advantage of the fact that, in the near ultraviolet region, the absorption of the conjugate acid of an aromatic amine is of the same order of magnitude as that of the corresponding hydrocarbon lacking the amino group, by substituting the extinction coefficients of nitrobenzene for those of the conjugate acid of $p$-nitroaniline. In our case we measured the extinction coefficients of $m$-chloro-nitrobenzene in the different acid solutions under study, however, since the extinction the coefficients were negligible, the term $\varepsilon_S$ could be neglected.

$$[BH^\oplus]/[B] = \varepsilon_N - \varepsilon_A/\varepsilon_A - \varepsilon_S .\qquad(4)$$

*Treatments of cellulose* were carried out at room temperature in a fabric/liquor ratio of approx. 1:(100 to 200). For aqueous systems the fabric samples were preswollen in an aqueous formaldehyde (7.5%) solution (without HCl) for 3 h. Cotton samples were kept in the treating solution for appropriate periods of time (1 to 60 minutes), then rinsed and afterwards following the procedure already described [20]. For the determination of formaldehyde at equilibrium the reaction time was extended to 72 hours.

*Hydrolysis experiments* were carried out under the same conditions as crosslinking; the treating time for each solution varied from 1 to 120 minutes. Since no formaldehyde was present no aftertreatment was necessary.

*Hydrolysis* effects were expressed in viscosity changes of nitrated samples in acetophenon, following the *Swiss Standard Method* for the determination of the degree of polymerisation of cellulose [23]. The results are given in Table 2 together with the values for the rate constants $k_{hy}$ which were calculated from the slope of the function $\log(1/[\eta]) = f(t)$.

Table 2. *Rate of depolymerisation of cellulose*

| Solution No. | Time (min) | $[\eta]$ | $\log(1/[\eta])$ | $k_{hy}$ | $H_0$ [a] |
|---|---|---|---|---|---|
| 1 | 20 | 20.8 | − 3.03 | $2.10 \times 10^{-3}$ | − 0.47 [b] |
|   | 30 | 20.2 | − 3.02 | | |
|   | 40 | 19.8 | − 3.00 | | |
|   | 60 | 19.3 | − 2.96 | | |
| 2 | 20 | 20.0 | − 3.00 | $2.5 \times 10^{-3}$ | − 1.15 [b] |
|   | 40 | 18.9 | − 2.94 | | |
|   | 60 | 18.3 | − 2.90 | | |
| 3 | 20 | 19.1 | − 2.96 | $2.7 \times 10^{-3}$ | − 1.44 [b] |
|   | 60 | 17.5 | − 2.85 | | |
| 4 | 20 | 18.0 | − 2.89 | $3.2 - 10^{-3}$ | − 1.73 [b] |
|   | 60 | 15.8 | − 2.76 | | |
| 5 | 20 | 18.1 | − 2.90 | $4.5 \times 10^{-3}$ | − 1.92 [b] |
|   | 40 | 16.3 | − 2.80 | | |
|   | 60 | 15.1 | − 2.72 | | |
| 6 | 20 | 16.5 | − 2.80 | $5.0 \times 10^{-3}$ | − 2.12 [b] |
|   | 40 | 14.8 | − 2.68 | | |
|   | 60 | 13.5 | − 2.60 | | |

| Solution No. | Time (min) | $[\eta]$ | $\log(1/[\eta])$ | $k_{hy}$ | $H_0$ [a] |
|---|---|---|---|---|---|
| 13 | 10 | 20.6 | − 3.02 | $2.0 \times 10^{-3}$ | − 0.47 [b] |
|  | 20 | 19.9 | − 2.99 |  |  |
|  | 40 | 18.1 | − 2.89 |  |  |
|  | 60 | 18.0 | − 2.88 |  |  |
|  | 90 | 17.6 | − 2.86 |  |  |
|  | 120 | 16.4 | − 2.80 |  |  |
| 14 | 10 | 18.3 | − 2.90 | $2.82 \times 10^{-3}$ | − 1.15 [b] |
|  | 20 | 17.8 | − 2.88 |  |  |
|  | 40 | 16.9 | − 2.82 |  |  |
|  | 60 | 16.1 | − 2.78 |  |  |
|  | 90 | 14.5 | − 2.67 |  |  |
|  | 120 | 13.4 | − 2.59 |  |  |
| 15 | 10 | 17.9 | − 2.88 | $3.0 \times 10^{-3}$ | − 1.44 [b] |
|  | 20 | 16.4 | − 2.80 |  |  |
|  | 40 | 14.4 | − 2.66 |  |  |
|  | 60 | 13.7 | − 2.61 |  |  |
|  | 90 | 12.6 | − 2.53 |  |  |
|  | 120 | 11.8 | − 2.42 |  |  |
| 16 | 10 | 18.1 | − 2.90 | $3.5 \times 10^{-3}$ | − 1.73 [b] |
|  | 20 | 16.1 | − 2.78 |  |  |
|  | 40 | 13.4 | − 2.59 |  |  |
|  | 60 | 12.4 | − 2.52 |  |  |
|  | 90 | 11.0 | − 2.40 |  |  |
|  | 120 | 10.1 | − 2.31 |  |  |
| 17 | 10 | 16.4 | − 2.80 | $4.75 \times 10^{-3}$ | − 1.92 [b] |
|  | 20 | 14.8 | − 2.69 |  |  |
|  | 40 | 12.0 | − 2.48 |  |  |
|  | 60 | 10.9 | − 2.38 |  |  |
|  | 90 | 9.2 | − 2.22 |  |  |
|  | 120 | 8.2 | − 2.10 |  |  |
| 18 | 10 | 14.8 | − 2.69 | $6.71 \times 10^{-3}$ | − 2.12 [b] |
|  | 20 | 12.4 | − 2.52 |  |  |
|  | 40 | 10.7 | − 2.36 |  |  |
|  | 60 | 8.8 | − 2.17 |  |  |
|  | 90 | 7.8 | − 2.05 |  |  |
|  | 120 | 7.2 | − 1.97 |  |  |
| 20 | 1 | 17.0 | − 2.83 | $1.3 \times 10^{-1}$ | − 2.73 |
|  | 2 | 16.0 | − 2.77 |  |  |
|  | 4 | 12.0 | − 2.48 |  |  |
|  | 6 | 9.0 | − 2.19 |  |  |
|  | 15 | 4.8 | − 1.57 |  |  |
| 21 | 1 | 17.0 | − 2.83 | $1.4 \times 10^{-1}$ | − 2.75 |
|  | 2 | 15.1 | − 2.71 |  |  |
|  | 4 | 11.0 | − 2.40 |  |  |
|  | 6 | 10.5 | − 2.34 |  |  |
|  | 15 | 4.6 | − 1.53 |  |  |
| 22 | 1 | 18.0 | − 2.88 | $8.0 \times 10^{-2}$ | − 2.65 |
|  | 2 | 13.7 | − 2.62 |  |  |
|  | 4 | 13.0 | − 2.56 |  |  |
|  | 6 | 12.0 | − 2.48 |  |  |
|  | 15 | 6.4 | − 1.85 |  |  |

| 23 | 1 | 20.0 | −2.99 | $2.5 \times 10^{-2}$ | −1.90 |
|----|-----|------|-------|------------------|-------|
|    | 4 | 18.9 | −2.93 | | |
|    | 7 | 17.3 | −2.84 | | |
|    | 15 | 6.5 | −1.87 | | |
| 24 | 3 | 20.8 | −3.03 | $1.87 \times 10^{-2}$ | −1.60 |
|    | 8 | 20.1 | −3.00 | | |
|    | 15 | 17.9 | −2.88 | | |
| unheated sample | 0 | 23.9 | −3.16 | − | − |

a)  Values in absence of formaldehyde. b) Literature values [21].

In Table 3 the fluidities $(1/[\eta])$ of cellulose samples after a treatment during 30 min. at room temperature in $HCl/H_2O/HOAc$ and $H_2SO_4/H_2O/HOAc$ systems with and without formaldehyde are given. These results are the basis for Figure 10 of this paper.

Table 3. *Fluidities of cellulose samples* (in acetophenone after nitration) treated for 30 min. in the systems given

| Solution No. | Paraform-aldehyde g/100 ml | HCl (100%) g/100 ml | $H_2SO_4$ g/100 ml | $H_2O$ g/100 ml | HOAc g/100 ml | $H_2O$ in % of $H_2O$-HOAc | $1/[\eta]$ (cellulose) | Relative viscosity of solution |
|----|------|------|------|------|------|------|-------|-------|
| 25 | – | 16.1 | – | 10 | 83.1 | 10.7 | 0.416 | – |
| 26 | – | 16.1 | – | 21.8 | 73.1 | 23.0 | 0.263 | 6.93 |
| 27 | – | 16.1 | – | 24.1 | 71.6 | 25.2 | 0.232 | 6.57 |
| 28 | – | 16.1 | – | 30 | 65.5 | 31.4 | 0.178 | 5.46 |
| 29 | – | 16.1 | – | 50 | 45.7 | 52.2 | 0.087 | 2.95 |
| 30 | – | 16.1 | – | 70 | 23.5 | 74.9 | 0.064 | 1.80 |
| 31 | – | 16.1 | – | 92.2 | 0 | 100 | 0.060 | 1.17 |
| 32 | 7.5 | 16.1 | – | 5 | 82.6 | 5.7 | 0.139 | – |
| 33 | 7.5 | 16.1 | – | 10 | 76.8 | 11.5 | 0.172 | – |
| 34 | 7.5 | 16.1 | – | 21.8 | 66.5 | 24.7 | 0.133 | – |
| 35 | 7.5 | 16.1 | – | 24.1 | 64.3 | 27.3 | 0.149 | – |
| 36 | 7.5 | 16.1 | – | 30 | 58.6 | 34.8 | 0.125 | – |
| 37 | 7.5 | 16.1 | – | 50 | 37.4 | 57.3 | 0.076 | – |
| 38 | 7.5 | 16.1 | – | 70 | 16.6 | 80.9 | 0.059 | – |
| 39 | 7.5 | 16.1 | – | 86.4 | 0 | 100 | 0.062 | – |
| 40 | – | – | 31.5 | 6.3 | 84.2 | 7.0 | 0.064 | 14.30 |
| 41 | – | – | 31.5 | 11.3 | 76.6 | 12.9 | 0.135 | 12.59 |
| 42 | – | – | 31.5 | 16.3 | 73.2 | 18.2 | 0.106 | 10.27 |
| 43 | – | – | 31.5 | 21.3 | 69.4 | 23.4 | 0.094 | 8.46 |
| 44 | – | – | 31.5 | 31.3 | 59.0 | 34.6 | 0.075 | 5.90 |
| 45 | – | – | 31.5 | 51.3 | 37.0 | 58.0 | 0.068 | 3.32 |
| 46 | – | – | 31.5 | 71.3 | 16.8 | 80.8 | 0.052 | 2.11 |
| 47 | – | – | 31.5 | 85.9 | 0 | 100 | 0.051 | 1.50 |
| 48 | 7.5 | – | 31.5 | 11.3 | 73.4 | 13.3 | 0.069 | – |
| 49 | 7.5 | – | 31.5 | 16.3 | 66.3 | 19.7 | 0.094 | – |
| 50 | 7.5 | – | 31.5 | 21.3 | 62.5 | 25.4 | 0.147 | – |
| 51 | 7.5 | – | 31.5 | 31.3 | 51.5 | 37.8 | 0.069 | – |
| 52 | 7.5 | – | 31.5 | 51.3 | 30.3 | 62.8 | 0.059 | – |
| 53 | 7.5 | – | 31.5 | 71.3 | 8.9 | 88.8 | 0.058 | – |
| 54 | 7.5 | – | 31.5 | 80.6 | 0 | 100 | 0.057 | – |

The rate of *cellulose formal formation* was measured by determinations of bonded formaldehyde by *Schiff*'s method [24]. The results are collected in Table 4 together with the rate constants which were calculated from the slope of a plot of log (l-f) vs. t (f = formaldehyde bonded as cellulose formal at time t relative to the bonded formaldehyde after 72 h).

Table 4. *Rate measurements of formal formation*

| Solution No. | Time (min.) | $CH_2O$ % [a] | log (1-f) | $k_{ex}$ | $H_0$ [b] measured without $CH_2O$ |
|---|---|---|---|---|---|
| 1 | 10 | 0.01 | − 0.030 | $1.24 \times 10^{-3}$ | − 0.47 [c] |
|   | 20 | 0.01 | − 0.030 | | |
|   | 30 | 0.02 | − 0.060 | | |
|   | 40 | 0.03 | − 0.092 | | |
|   | 60 | 0.03 | − 0.092 | | |
|   | 72h | 0.34 | − | | |
| 2 | 5 | 0.02 | − 0.041 | $3.4 \times 10^{-3}$ | − 1.15 [c] |
|   | 10 | 0.04 | − 0.064 | | |
|   | 20 | 0.08 | − 0.136 | | |
|   | 30 | 0.08 | − 0.147 | | |
|   | 40 | 0.08 | − 0.152 | | |
|   | 60 | 0.12 | − 0.228 | | |
|   | 72h | 0.60 | − | | |
| 3 | 5 | 0.06 | − 0.094 | $5.63 \times 10^{-3}$ | − 1.44 [c] |
|   | 7 | 0.07 | − 0.099 | | |
|   | 10 | 0.09 | − 0.129 | | |
|   | 15 | 0.10 | − 0.149 | | |
|   | 20 | 0.14 | − 0.212 | | |
|   | 60 | 0.25 | − 0.403 | | |
|   | 72h | 0.75 | − | | |
| 4 | 1 | 0.04 | − 0.051 | $8.42 \times 10^{-3}$ | − 1.73 [c] |
|   | 2 | 0.06 | − 0.062 | | |
|   | 5 | 0.09 | − 0.104 | | |
|   | 7 | 0.12 | − 0.134 | | |
|   | 10 | 0.12 | − 0.136 | | |
|   | 20 | 0.21 | − 0.264 | | |
|   | 60 | 0.39 | − 0.566 | | |
|   | 72h | 0.91 | − | | |
| 5 | 2 | 0.03 | − 0.032 | $1.01 \times 10^{-2}$ | − 1.92 [c] |
|   | 5 | 0.08 | − 0.083 | | |
|   | 10 | 0.14 | − 0.142 | | |
|   | 20 | 0.24 | − 0.264 | | |
|   | 40 | 0.36 | − 0.437 | | |
|   | 60 | 0.44 | − 0.568 | | |
|   | 72h | 1.02 | − | | |
| 6 | 2 | 0.07 | − 0.067 | $1.56 \times 10^{-2}$ | − 2.12 [c] |
|   | 5 | 0.14 | − 0.136 | | |
|   | 10 | 0.24 | − 0.244 | | |
|   | 20 | 0.38 | − 0.391 | | |
|   | 40 | 0.56 | − 0.681 | | |
|   | 60 | 0.64 | − 0.830 | | |
|   | 72h | 1.13 | − | | |

| Solution No. | Time (min.) | $CH_2O$ % [a] | $\log(1-f)$ | $k_{cx}$ | $H_0$ [b] measured without $CH_2O$ |
|---|---|---|---|---|---|
| 7 | 1 | 0.40 | $-0.115$ | $3.8 \times 10^{-2}$ | $-3.21$ |
| | 2 | 0.57 | $-0.168$ | | |
| | 4 | 0.90 | $-0.280$ | | |
| | 6 | 1.12 | $-0.359$ | | |
| | 8 | 1.28 | $-0.424$ | | |
| | 10 | 1.44 | $-0.495$ | | |
| | 15 | 1.76 | $-0.646$ | | |
| | 15 | 1.76 | $-0.646$ | | |
| | 20 | 2.08 | $-0.826$ | | |
| | 30 | 2.66 | $-1.270$ | | |
| | 40 | 3.19 | $-1.985$ | | |
| | 50 | 3.54 | $-3.160$ | | |
| | 60 | 3.70 | – | | |
| 8 | 1 | 0.53 | $-0.147$ | $1.04 \times 10^{-1}$ | $-2.98$ |
| | 2 | 0.86 | $-0.248$ | | |
| | 4 | 1.50 | $-0.478$ | | |
| | 6 | 2.00 | $-0.718$ | | |
| | 8 | 2.37 | $-0.935$ | | |
| | 10 | 2.60 | $-1.094$ | | |
| | 15 | 2.97 | $-1.435$ | | |
| | 20 | 3.20 | $-1.714$ | | |
| | 30 | 3.40 | $-2.05$ | | |
| | 40 | 3.54 | $-2.38$ | | |
| | 50 | 3.60 | $-2.54$ | | |
| | 60 | 3.90 | – | | |
| 9 | 1 | 0.54 | $-0.296$ | $2.34 \times 10^{-1}$ | $-2.61$ |
| | 2 | 0.84 | $-0.488$ | | |
| | 4 | 1.28 | $-0.94$ | | |
| | 6 | 1.60 | $-1.39$ | | |
| | 8 | 1.78 | $-1.88$ | | |
| | 10 | 1.86 | $-2.17$ | | |
| | 15 | 2.04 | $-3.57$ | | |
| | 20 | 2.10 | – | | |
| | 30 | 2.14 | – | | |
| | 40 | 2.12 | – | | |
| | 50 | 2.10 | – | | |
| | 60 | 2.10 | – | | |
| 10 | 1 | 0.18 | $-0.129$ | $6.6 \times 10^{-2}$ | $-2.30$ |
| | 2 | 0.34 | $-0.258$ | | |
| | 4 | 0.62 | $-0.534$ | | |
| | 6 | 0.78 | $-0.734$ | | |
| | 8 | 0.88 | $-0.884$ | | |
| | 10 | 0.96 | $-1.02$ | | |
| | 15 | 1.06 | $-1.225$ | | |
| | 20 | 1.22 | $-1.675$ | | |
| | 30 | 1.34 | $-2.24$ | | |
| | 40 | 1.42 | $-2.92$ | | |
| | 50 | 1.47 | $-3.91$ | | |
| | 60 | 1.50 | – | | |

22

| Solution No. | Time (min.) | $CH_2O$ %[a] | log (l-f) | $k_{cx}$ | $H_o$[b] measured without $CH_2O$ |
|---|---|---|---|---|---|
| 11 | 1 | 0.06 | – 0.062 | $6.37 \times 10^{-2}$ | – 2.03 |
|    | 2 | 0.15 | – 0.163 | | |
|    | 4 | 0.28 | – 0.330 | | |
|    | 6 | 0.37 | – 0.461 | | |
|    | 8 | 0.46 | – 0.654 | | |
|    | 10 | 0.53 | – 0.755 | | |
|    | 15 | 0.70 | – 1.204 | | |
|    | 20 | 0.76 | – 1.425 | | |
|    | 30 | 0.86 | – 1.96 | | |
|    | 40 | 0.93 | – 2.66 | | |
|    | 50 | 0.96 | – 3.22 | | |
|    | 60 | 1.00 | – | | |
| 12 | 1 | 0.03 | – 0.039 | $2.88 \times 10^{-2}$ | – 2.02 |
|    | 2 | 0.08 | – 0.106 | | |
|    | 4 | 0.14 | – 0.193 | | |
|    | 6 | 0.18 | – 0.256 | | |
|    | 8 | 0.24 | – 0.356 | | |
|    | 10 | 0.28 | – 0.430 | | |
|    | 15 | 0.38 | – 0.644 | | |
|    | 20 | 0.46 | – 0.856 | | |
|    | 30 | 0.56 | – 1.204 | | |
|    | 40 | 0.64 | – 1.606 | | |
|    | 50 | 0.72 | – 2.106 | | |
|    | 60 | 0.80 | – | | |

[a]) Weight percent of cellulose.
[b]) Values in absence of formaldehyde.
[c]) Literature values [21].

All viscosity measurements were carried out with an *Ostwald*-Viscosimeter (capillary diameter 0.7 mm) at constant temperature of 20°. Efflux times of solutions were divided by the efflux time of water to get the relative viscosity, neglecting the relative densities.

<div align="center">REFERENCES</div>

[1] *O. Annen, P. Rys, Y. Terada & H. Zollinger*, Melliand Textilber., in print (1972).
[2] *O. Annen, H. K. Rouette, P. Rys & H. Zollinger*, Textilveredlung 7, 528 (1972).
[3] *L. I. Novikova & A. A. Konkin*, Russ. J. Appl. Chemistry 32, 1104 (1959); *H. Vink*, Makromol. Chem. 94, 1 (1966).
[4] *O. Annen, K. Heinisch, M. Kimura, S. Kalyana Raman, H. K. Rouette, A. Wehner & H. Zollinger*, Textilveredlung 5, 327 (1970); *H. Zollinger*, Text. Chem. Col. 4, 248 (1972).
[5] *B. Torck, M. Hellin & F. Coussemant*, Bull. Soc. chim. France 1962, 1657.
[6] *E. Ott, H. M. Spurlin & M. W. Grafflin*, Cellulose and Cellulose Derivatives, Interscience, New York 1954, Part I, p. 122.
[7] *M. Lewin & S. Weinstein*, Text. Res. J. 37, 751 (1967).
[8] *J. F. Bunnett & F. P. Olson*, Canad. J. Chemistry 44, 1899, 1917 (1966).
[9] *O. Annen, P. Rys, Y. Terada & H. Zollinger*, Melliand Textilberichte 53, in print (1972).
[10] *K. Mühlethaler*, Annual Review of Plant Physiology 18, 1 (1967).
[11] *S. Haworth, J. G. Roberts & R. W. Robinson*, Textilveredlung 2, 361 (1967); *R. Jeffries, J. G. Roberts & R. W. Robinson*, Text. Res. J. 38, 234 (1968).
[12] *J. F. Bunnett*, J. Amer. chem. Soc. 83, 4956, 4968, 4973, 4978 (1961).
[13] *T. E. Timell*, Canad. J. Chemistry 42, 1456 (1964).

[14] L. P. Hammett & M. A. Paul, J. Amer. chem. Soc. 56, 830 (1934); L. P. Hammett, Chem. Reviews 16, 67 (1935).

[15] P. B. Weisz, J. S. Hicks & H. Zollinger, Trans Faraday Soc. 63, 1801, 1807, 1815 (1967), 64, 1693 (1968); P. Rys, Inaugural thesis, ETH Zürich 1970, R. Ott, Ph.D. thesis, ETH Zürich 1971.

[16] K. S. Unger & P. Rys, in preparation.

[17] G. N. Kormanoskaya & I. N. Vlodavets, Izvestiya Akademii Nauk SSSR, Seriya Khumcheskaya 10, 1748 (1964).

[18] R. S. Parikh, Text. Res. J. 37, 538 (1967); H. U. Metha, N. T. Baddi, R. S. Parmar, K. A. Patel & R. S. Patel, Text. Res. J. 39, 387 (1969).

[19] W. A. Reeves, J. Text. Inst. 53, P 22 (1962); R. H. Barker & S. L. Vail, Test. Res. J. 37, 1077 (1967).

[20] S. B. Patel, J. Rivlin, T. Samuelson, O. A. Stamm & H. Zollinger, Text. Res. J. 38, 226 (1968).

[21] M. A. Paul & F. A. Long, Chem. Reviews 57, 1 (1957); C. H. Rochester, Acidity Functions, Academic Press, London 1970, chapt. 2.

[22] Pentti Salomaa, Acta Chem. Scand. 11, 125 (1957).

[23] SNV 195596 (1969).

[24] S. Ramanathan, J. Rivlin, O. A. Stamm & H. Zollinger, Text. Res. J. 38, 63 (1968).

---

## 24. N, N'-Alkylidenpeptide: Peptidsynthese-Nebenprodukte bei Einwirkung von Carbonylverbindungen.[1])[2])

von F. Cardinaux und M. Brenner

Institut für Organische Chemie der Universität Basel

(5. X. 72)

*Summary.* Byproducts of peptide synthesis, formed in the course of accidental attack by Pd-activated oxygen on ethanol and triethylamine in reaction media, have been identified as products of condensation between peptides and acetaldehyde, and demonstrated to represent N, N'-alkylidenepeptides, i.e. derivatives of 4-imidazolidinones. The same products are obtained by direct action of acetaldehyde on the respective peptides, and analogs resulted in some cases when acetaldehyde was replaced by formaldehyde or acetone. The condensation is reversible, imidazolidinone stability depending on structural features of both the involved peptide and carbonyl compound. There are evidently implications of these findings with respect to the chemistry and biochemistry of peptides and proteins.

**1. Bildung und Struktur.** – Bei der Hydrogenolyse der Benzyloxycarbonylpeptidester Z-Pro-Leu-Glu(OBu$^t$)-Phe-OBu$^t$ **1a**, Z-Val-His-Pro-Phe-OMe **2a** und Z-Val-Tyr-Val-His-Pro-Phe-OMe **3a** zu den entsprechenden Peptidestern **1, 2** und **3** fiel schon vor Jahren die Entstehung von dünnschichtchromatographisch charakterisierbaren peptidartigen Nebenprodukten **1b, 2b** und **3b** auf [2]. Bemerkenswert war insbesondere, dass diese zwar gleiche Aminosäurezusammensetzung aufwiesen wie **1, 2** und **3**, aber nicht wie jene nach der peptidsynthetisch gebräuchlichen *p*-Nitrophenylestermethode acylierbar waren. Wir sind im Einverständnis mit den Herren *Rittel, Riniker & Sieber*[3]) diesem merkwürdigen und störenden Sachverhalt

---

[1])   Auszug aus der Dissertation *F. Cardinaux*, Basel 1972.

[2])   Teile dieser Arbeit wurden vorgetragen am «11. Europäischen Peptidsymposium» in Wien, 1971 [1].

[3])   Chemische Forschungslaboratorien der Division Pharmazeutika der CIBA-GEIGY AG., Basel.