Estimation of the allyl group in starch derivatives

K. TIHLÁRIK, V. KÉRY, and M. PAŠTEKA

Institute of Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 38 Bratislava

For estimation of the allyl groups in allylstarch a method which involves addition of mercury(II) acetate to double bonds and the subsequent acidimetric titration has been applied. The method was verified by the allyl alcohol estimation and the results obtained in the estimation of two allylstarch samples were compared with the values of elemental analyses and with the degree of substitution values calculated from these analyses. There was a good agreement between both approaches. The method is especially suitable for the derivatives with low degree of substitution. The results have been evaluated statistically.
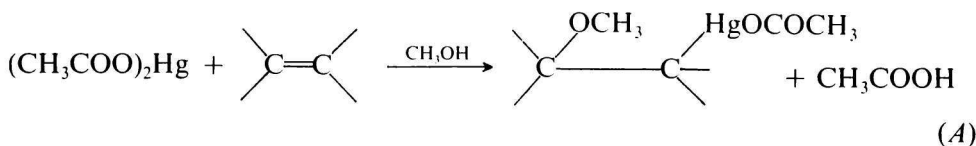
Для определения аллильных групп в аллилкрахмале был применен метод присоединения уксуснокислой ртути по двойным связям с последующим ацидиметрическим титрованием. Метод был проверен путем определения количества аллилового спирта, и результаты, полученные при анализе двух образцов аллилкрахмала, были сопоставлены с результатами элементарного анализа этих образцов и с величинами степени замещения, рассчитанными исходя из результатов элементарного анализа. Было обнаружено хорошее совпадение. Данный метод особенно пригоден для производных с низкой степенью замещения. Полученные результаты были статистически обработаны.

Estimation of the double bonds is of importance in the products of petrol and food industries, in pharmacy, and is also important in polysaccharide derivatives, *e.g.* in allylcellulose and allylstarch. The latter derivatives are applied not only for technical purposes but serve as intermediates, mainly in the controlled polymerization, for the production of mixed polymers for special purposes. In our work, there was a need for derivatives with a very low degree of substitution (less than 0.05). Using routine methods, the estimation of such a small amount of allyl groups may cause serious problems.
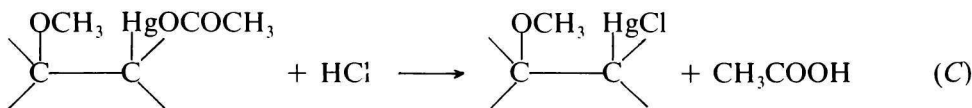
In the chemistry of polysaccharides, most methods of the allyl group estimation are based on halogen addition to the double bond. The addition of bromine to olefins in acetic acid has been used for a long time [1]. Several modifications have been reported in literature and among them also the method of the direct double bond estimation by titration with bromine solution in acetic acid [2]. Thus far, we have used in our works a modified Lucas and Pressman method for double bond estimation in polysaccharide derivatives which is also based on

bromine addition [3]. In the work with halogens, especially with bromine, side reactions may take place in dependence on the conditions used, *e.g.* substitution or oxidation. This is of importance mainly with the derivatives of very low double bond content.

Among the methods of double bond estimation one has been developed which is based on mercury(II) salts addition, especially of mercury(II) acetate to a double bond. Mercury(II) salts react quite easily with the low-molecular compounds [4] mainly in methanol, slower in higher alcohols and poorly in water. The method gives excellent results in the case of terminal double bonds [5], *i.e.* with allylstarch, too. *Das* [6] and *Mallik* [7] have reported on the mechanism of mercury(II) acetate addition to double bonds in methanol

$$
(CH_3COO)_2Hg + \;\; \underset{}{>}C{=}C\underset{}{<} \;\; \xrightarrow{CH_3OH} \;\; \underset{}{>}C\underset{\overset{|}{OCH_3}}{-}C\underset{\overset{|}{HgOCOCH_3}}{<} \;\; + CH_3COOH
$$

$$(A)$$

The estimation involves titration of the mixture of unconsumed reagent and adduct using hydrochloric acid and determination of the differences in consumption of hydrochloric acid on the reagent amount given and of its part, unconsumed in the addition

$$
(CH_3COOH)_2Hg + 2HCl \;\; \rightarrow \;\; HgCl_2 + 2CH_3COOH \qquad (B)
$$

$$
\underset{}{>}C\underset{\overset{|}{OCH_3}}{-}C\underset{\overset{|}{HgOCOCH_3}}{<} \;\; + HCl \;\; \longrightarrow \;\; \underset{}{>}C\underset{\overset{|}{OCH_3}}{-}C\underset{\overset{|}{HgCl}}{<} \;\; + CH_3COOH \qquad (C)
$$

As it is evident from eqns (*B*) and (*C*), a mole of mercury(II) acetate consumes two moles of hydrochloric acid while the adduct only one mole and thus the difference value indicates the amount of double bonds present.

For some compounds (esters of methacrylic acid), several authors recommend addition of a small amount of perchloric acid as the catalyst [7].

The original method of mercury(II) acetate estimation by titration with hydrochloric acid was performed in the mixture of glycol—chloroform. Hydrochloric acid solution was prepared in the same solvent system and mercury(II) acetate solution was applied in methanol. It has been confirmed that mercury(II) chloride, which precipitates during estimation, does not interfere in the estimation of equivalent point [8]. However, easily hydrolyzable esters may interfere and therefore, they should not be present.

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The methods of double bond estimation based on morpholine addition [9] have not found a widespread application. Some derivatives of acrylic acid were estimated on the basis of hexamethylenimine [10] addition. They are applied mainly in pharmaceutical chemistry.

We have decided to reinvestigate the method of double bond estimation with mercury(II) acetate in allylstarch derivatives with the aim to determine very small amounts of allyl groups in these derivatives.

Experimental

Methanol, isopropyl alcohol, and allyl alcohol of anal. grade were the preparations of Lachema, Brno. They were freshly distilled before the use. Mercury(II) acetate, anal. grade, purchased from BHD Chemicals, Pools, England, was used as a reagent ($c = 0.125$ mol dm^{-3}) in methanol and hydrochloric acid ($c = 0.1$ mol dm^{-3}) in isopropyl alcohol was used as a titration reagent.

A solution of allyl alcohol ($\varrho = 20$ mg cm^{-3}) was prepared on dissolution in methanol.

The samples of allylstarch (A, B, C) were prepared in laboratory according to [11]. In samples A and B, the degrees of substitution (DS) were calculated from the elemental analysis data. For sample A w_i(found): 46.72 % C, 6.21 % H, which corresponded to DS = 0.220. For sample B w_i(found): 51.05 % C, 6.98 % H, which corresponded to DS = 0.710.

A pH-meter TTT2b Titrator (Radiometer, Copenhagen) equipped with glass G-202 C and calomel K-401 electrodes (Radiometer, Copenhagen) was used.

Estimation of the allyl group with mercury(II) acetate

To methanol (20 cm^3), an allyl alcohol solution (1 cm^3) containing 20 mg of allyl alcohol or a sample of allylstarch (20 mg of allylstarch with DS = 1.0 or an amount proportional to other DS expected) were added. A solution of mercury(II) acetate (4.0 cm^3) in methanol was then added and the mixture was stirred at room temperature in a closed vessel for 30 min (allyl alcohol) or 90 min (allylstarch samples).

Samples were titrated with hydrochloric acid in isopropyl alcohol using a potentiometric indication (consumption b cm^3). Similarly, the amount of mercury(II) acetate solution (4.0 cm^3) was titrated (consumption a cm^3).

The difference between the two consumptions is equivalent to the content of the allyl group in the sample, $m = 4.1(a - b)$ mg. DS $= 16.1(a - b)/(m_s - 4.1(a - b))$, where m_s is the mass of sample/mg.

Results and discussion

The method of double bond estimation, which is based on mercury(II) acetate addition in methanol and the subsequent estimation of the unconsumed

reagent and adduct by the hydrochloric acid titration has been applied for the determination of DS of allylstarch. The method has been proved with allyl alcohol and examined with three samples of allylstarch. In samples A and B, a time dependence of reagent addition to a double bond of the allyl group was determined. From ten parallel estimations, both the standard deviation and variation coefficient have been calculated for sample A (reaction time of addition 90 min). The results are given in Tables 1—4.

Table 1

Time dependence of the addition of mercury(II) acetate to the allyl alcohol (20 mg), expressed by the results of the standard estimation

| Reaction time | Estimation | |
| | m(alcohol) | w(sample) |
min	mg	%
1	10.42	52 10
5	15.31	76.55
10	18.23	91.15
30	19.99	99.95
60	20.02	100.10
120	20.58	102.90

Table 2

Time dependence of the addition of mercury(II) acetate to allylstarch (samples A and B), expressed by the results of the standard estimation

| Reaction time | Sample mass | Equivalent of HCl | Estimation of allyl group | | |
| | | | m | w | w(sample) |
min	mg	cm³	mg	mass %	%
		Sample A*			
10	100.50	0.98	4.01	3.99	75.71
30	101.00	1.18	4.83	4.75	90.13
60	100.60	1.27	5.20	5.16	97.91
90	101.20	1.31	5.37	5.30	100.56
120	100.40	1.33	5.45	5.41	102.65
		Sample B*			
10	70.10	1.85	7.58	10.81	70.79
30	71.00	2.25	9.22	12.98	85.22
60	71.05	2.58	10.57	14.87	97.63
90	70.90	2.66	10.90	15.37	100.91
120	70.25	2.67	10.94	15.57	102.23

*Content of the allyl group calculated from the elemental analysis data:
For sample A $w = 5.27$ mass %; for sample B $w = 15.23$ mass %.

Table 3

Estimation of an average degree of substitution of sample C with a very low content of the allyl group

Estimation	Sample mass mg	Equivalent of HCl cm^3	Estimation of allyl group		DS
			$\dfrac{m}{mg}$	$\dfrac{w}{mass\ \%}$	
1	250.1	0.75	3.07	1.22	0.048
2	250.0	0.85	3.48	1.40	0.055
3	250.9	0.79	3.23	1.28	0.051
4	250.0	0.79	3.23	1.29	0.051
5	250.6	0.84	3.44	1.37	0.048
					$\overline{DS} = 0.050$

Table 4

Estimation of the content of allyl group (x_i) in sample A

Estimation	Sample mass mg	Equivalent of HCl cm^3	$\dfrac{x_i}{mass\ \%}$	$\{(x_i - \bar{x})^2\}$
1	101.20	1.31	5.30	0.0025
2	100.00	1.25	5.12	0.0529
3	100.90	1.30	5.28	0.0049
4	101.00	1.37	5.55	0.0400
5	102.00	1.40	5.62	0.0729
6	100.20	1.40	5.72	0.1369
7	101.20	1.33	5.38	0.0004
8	101.90	1.28	5.14	0.0441
9	100.80	1.29	5.23	0.0144
10	100.10	1.28	5.23	0.0144
			$\{\bar{x}\} = 5.35$	$\Sigma\{(x_i - \bar{x})^2\} = 0.1469$

Standard deviation $s = \sqrt{\dfrac{\Sigma(x_i - \bar{x})^2}{n - 1}} = 0.1276\,\%$.

Variation coefficient $v = \dfrac{s}{\bar{x}} 100\,\% = 2.38\,\%$.

Under the conditions given in [6], *i.e.* using the system glycol—chloroform, we have not obtained in the work with allylstarch the values expected even after 8 h. Similarly, we have shown that the mixture glycol—isopropyl alcohol, monomethyl ether of glycol, and dimethyl sulfoxide (in which the derivative is soluble) were not suitable.

Because of the substrate insolubility in most solvents examined, we had to

reinvestigate the method under heterogeneous conditions. Preliminary experiments have shown methanol to be the most suitable solvent, which also dissolves mercury(II) acetate. Because of its high volatility it could not be applied as the solvent for titration reagent, hydrochloric acid, and it was substituted by isopropyl alcohol.

Using our reaction conditions, the addition of mercury(II) acetate to the allyl double bond in allylstarch proceeds easily also in a heterogeneous phase due to the fact that the latter is sterically easily accessible terminal double bond where the addition proceeds well also with the low-molecular compounds [5].

With allyl alcohol, where the reaction proceeded in a homogeneous phase, the reaction time was short (Table 1). With allylstarch, theoretical values were obtained after 90 min under vigorous stirring at room temperature (Table 2). During the 8 h period the DS values increased only negligibly (therefore, they are not given in tables). Similarly, potato starch has not shown a noticeable consumption of mercury(II) acetate.

Validity of the method has been proved in samples A and B by calculation of DS from the elemental analysis data and by comparison with the values obtained by the method developed. There was a good agreement between both approaches. In sample C, an average DS was determined from five parallel estimations. The method gave a good reproduction also with a sample of very low DS (Table 3).

To indicate the equivalent point in the titrations with hydrochloric acid, thymol blue can be used as the indicator (pH = 1.0—2.5). As there is a need to investigate more deeply the influence of individual parameters, we have preferred to use the potentiometric indication. The curves obtained were of normal shape and are not presented. The indication is especially suitable for those samples having a very low amount of double bonds.

The method has been proved to be simple, rapid, it does not need a special equipment and has a good reproduction. Some care must be given to the preparation of mercury(II) acetate solutions in methanol as it is required in the work with poisons.

References

1. Uhrig, K. and McLevin, H., *Ind. Eng. Chem., Anal. Ed. 13*, 90 (1941).
2. Tomíček, O., Blažek, A., and Roubal, Z., *Chem. Zvesti 4*, 479 (1950).
3. Jureček, M., *Organická analysa.* (Organic Analysis.) P. 238. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1957.
4. Wright, G. F., *J. Am. Chem. Soc. 57*, 1993 (1935).
5. Martin, R. W., *Anal. Chem. 21*, 921 (1949).
6. Das, M. N., *Anal. Chem. 26*, 1086 (1954).

7. Mallik, L. and Das, M. N., *Chem. Ind. 1959*, 162.
8. Palit, S. R., *Ind. Eng. Chem., Anal. Ed. 18*, 246 (1946).
9. Critchfield, F. E., Funk, G. L., and Johnson, J. B., *Anal. Chem. 28*, 76 (1956).
10. Terentyev, A. P., Obtemperanskaya, S. I., Volodzko, V. E., and Buzlanova, M. M., *Zh. Anal. Khim. 19*, 135 (1964).
11. Tomecko, G. G. and Adams, R., *J. Am. Chem. Soc. 45*, 2698 (1923).