

## Determination of Primary and Secondary Xanthate Groups in Cellulose Xanthate

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### Synopsis

Various kinetic methods for the determination of primary and secondary xanthate groups have been compared. With certain types of viscoses all methods give an excellent agreement and are superior to the purely chemical methods which are unreliable. The field of application of a kinetic method based upon decomposition in a slightly acid buffer is limited due to the appearance of a turbidity upon prolonged dexanthation. A modified technique in which the decomposition is carried out at elevated temperature in sodium hydroxide solution is both rapid and versatile.

Studies of the ripening of viscose carried out in this laboratory have shown that the redistribution of xanthate groups during the ripening can be eliminated if the ripening is carried out in the presence of an anion-exchange resin.<sup>1</sup> The dexanthation can in this case be expressed as the sum of two first order reactions; the faster one is ascribed to the decomposition of secondary xanthate groups and the other to the decomposition of 6-xanthate. A determination of the number of primary xanthate groups in the original viscose is obtained by plotting  $\log \gamma$  against time where  $\gamma$  denotes the number of xanthate groups per 100 glucose units and extrapolation of the linear portion of the curve to zero time.<sup>2</sup>

The slope of the straight line, i.e., the rate constant for the decomposition of 6-xanthate, is independent of the degree of substitution of the viscose, provided that the sodium hydroxide concentration is kept constant.<sup>3</sup> Moreover, the rate of dexanthation in the presence of resin is independent of the cellulose concentration. Since the rate of ripening without added resin increases when the viscose is diluted with sodium hydroxide,<sup>4</sup> it could be assumed that the dexanthation could be eliminated simply by diluting the viscose and the distribution determined from a plot of  $\log \gamma$  against the time of ripening of the diluted solution. Experiments carried out at 0.1% cellulose in the solution confirm that the  $\gamma_6$  value determined according to this dilution method agrees very well with that obtained by the resin method.<sup>5,6</sup> In a recent work the dilution method has been employed to study the influence of the sodium hydroxide concentration upon the actual rate of decomposition. Straight lines with varying slopes were obtained, but the  $\gamma_6$  value determined by extrapolation was found to be

independent of the sodium hydroxide concentration.<sup>6</sup> All these observations lend strong support to these kinetic methods.

A different kinetic technique for the determination of the relative amounts of primary and secondary substitution has been suggested by Miller and Geerdes.<sup>7</sup> Their paper is still unpublished, but a copy has recently been made available with kind permission of Dr. J. D. Geerdes enabling us to make use of their results in our work. A comparison between their method and the dilution method described previously will, therefore, be made in this paper. The chief difference between their method and the dilution method is that in their work the decomposition is carried out in a buffer at pH 6.5. In addition, higher temperature is used. Both changes contribute to a more rapid decomposition.

The aim of this work was to compare the buffer method devised by Miller and Geerdes with our dilution method. Based upon the experience gained during the course of this investigation a simplified dilution method which is more reliable than the buffer method and more rapid than the original dilution method has been worked out.

## PROCEDURES

### Buffer Method

A sample of viscose (e.g., 0.5 g.) from which low molecular anions had been removed according to the anion-exchange method<sup>8</sup> was diluted with 0.1*M* sodium hydroxide solution to 50 ml. A 5-ml. portion of this solution was diluted with cold 1*M* sodium hydroxide to 250 ml. and the  $\gamma$  value determined spectrophotometrically.<sup>9</sup> Another 5-ml. portion was diluted with a potassium phosphate buffer solution (pH 6.5, 50°C.) to 250 ml. and the flask was placed in a thermostat at 50°C. The absorbance at 303 *m* $\mu$  was measured (without treatment with resin) after various lengths of time, and the  $\gamma$  value calculated as usual. The logarithm of the  $\gamma$  value was plotted as a function of time and the straight-line portion of the curve extrapolated to zero time. The intercept on the ordinate corresponds to the number of xanthate groups in the 6-position.

### Dilution Method

The determinations were carried out as described in a previous paper.<sup>5</sup> If not otherwise mentioned, the sodium hydroxide concentration during the decomposition step was 0.1*M*. Some experiments were run at elevated temperature. In these runs the solution was cooled rapidly and passed through an ion exchange column cooled with ice.

### Simplified Dilution Method

The experiments were carried out as described for the buffer method, with the exception that 0.1*M* sodium hydroxide solution of 50°C. was used instead of the phosphate buffer.

### COMPARISON BETWEEN THE BUFFER AND THE DILUTION METHODS

In all methods employed in this work the cellulose xanthate is determined spectrophotometrically at  $303\text{ m}\mu$ . A prerequisite for a reliable determination is that no other substances which exhibit an absorption at this wavelength, be present in the solution. In the dilution method the interfering ions are, before each determination, removed by the ion-exchange method. In the buffer method the interfering substances are removed by ion exchange before the decomposition of the cellulose xanthate at about pH 6.5. The absorption spectra given in Figure 1 show that within the interval of interest in this connection the absorbance curves taken after various times of decomposition at pH 6.3 have the same shape

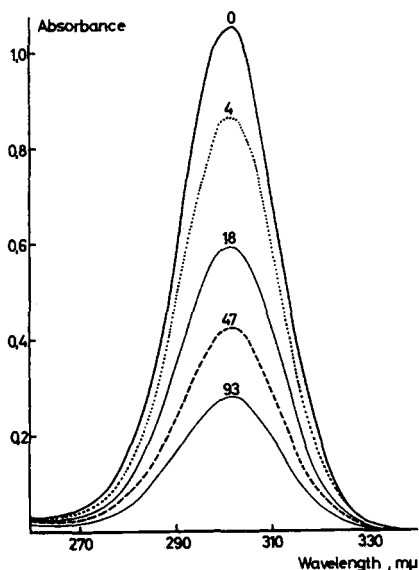


Fig. 1. Absorption spectrum of a viscose solution after decomposition at pH 6.5. The figures indicate the approximate time of reaction (in minutes).

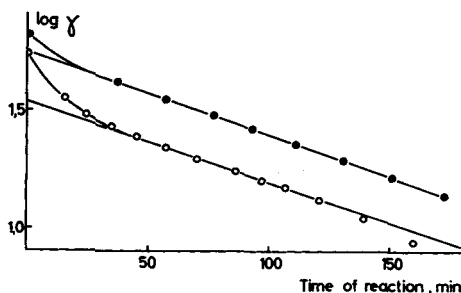


Fig. 2. Decomposition of two viscose samples according to the buffer method: (●)  $\gamma = 65$ ; (○)  $\gamma = 55$ .

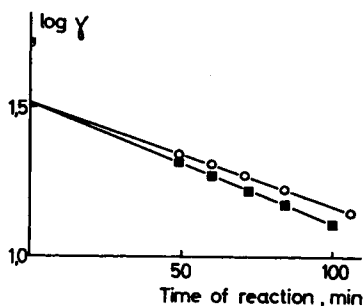


Fig. 3. Influence of the pH upon the determination of  $\gamma_8$  according to the buffer method: (O) decomposition at pH 6.5; (■) decomposition at pH 6.1.

as that of the original viscose from which trithiocarbonate and other interfering substances had been removed by ion exchange. Trithiocarbonate is known to exhibit an absorbance maximum at  $336 \text{ m}\mu$ . It is seen that no interfering trithiocarbonate is formed at this pH. The results indicate that a reliable determination of the xanthate groups is obtained by a direct determination of the absorbance at  $303 \text{ m}\mu$ .

The results of the decomposition in buffer solution of two different ion-exchanged viscose samples are given in Figure 2. It is seen that the shape of the curves is the same as observed in the ripening of viscose in the presence of anion-exchange resin and in ripening of a diluted viscose. Within a large interval, a linear relationship exists between  $\log \gamma$  and the time of reaction. Just as in the ripening experiments, the overall decomposition is explained as the sum of two independent reactions. The linear portion of the curve which represents the first-order decomposition of the more stable xanthate groups is extrapolated to zero time, and the intercept gives the initial amount of these groups.

With most viscose samples there is a deviation from linearity at very long times of reaction (see lower curve in Fig. 2). When the cellulose xanthate has a high initial  $\gamma$  value, the linear portion of the curve is with most samples large enough to permit a reliable extrapolation to zero time.

Sometimes, the slope of the straight lines differs somewhat, which is explained by the fact that buffers of different pH have been used. A study of the influence of the pH (Fig. 3) shows that a decrease in the pH from 6.5 to 6.1 results in a significantly increased rate of decomposition. An extrapolation to zero time gives, however, the same intercept.

The more rapid reaction, which occurs during the ripening in the presence of resin and in a viscose diluted with sodium hydroxide, has been identified as the decomposition of secondary xanthate groups, whereas the slower reaction is ascribed to the decomposition of primary groups.<sup>2</sup> Miller and Geerdes have come to the same conclusion as far as the decomposition at pH 6.5 is concerned. Their identification is based upon model experiments with some simple carbohydrate xanthates. The xanthate of methyl D-xylopyranoside was found to have a rate constant close to that of the least

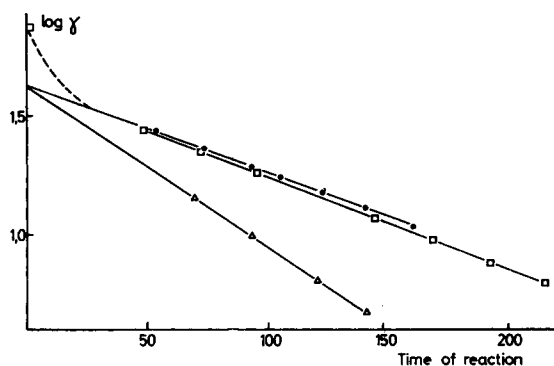


Fig. 4. Comparison between the buffer method and the dilution method: (●) buffer method, pH = 6.5, time in minutes; (□) dilution method, 20°C., 1M NaOH, time in hours; (Δ) dilution method, 25°C., 1M NaOH, time in hours.

stable form of cellulose xanthate, whereas the xanthate of methyl 2,3,4-tri-*O*-methyl-*D*-glucopyranoside was decomposed at about the same rate as the more stable form of cellulose xanthate. Methyl *D*-glucopyranoside, in which both types of hydroxyl groups are present, showed a behavior similar to that of cellulose.

If both methods are correct, the extrapolated value obtained in the two methods should, therefore, coincide. Figure 4 shows the results from parallel experiments carried out with one viscose sample. With both methods a linear relationship exists between  $\log \gamma$  and the time of reaction. Moreover, the value extrapolated to zero time shows good agreement. Similar experiments were carried out with other viscose samples, and, as can be seen from Table I, both methods give a good estimate of  $\gamma_6$  with these types of viscoses.

With samples of ripened viscose and other types of viscose with low  $\gamma$  values, the linear portion of curve is quite often so short that no reliable extrapolation to zero time can be made. A typical example is given in

TABLE I  
Relative Amount of Xanthate Groups in the 6-Position in Various Viscose Samples

Cellulose, %	NaOH, %	Added CS <sub>2</sub> , %	$\gamma_{tot}$	$(\gamma_6/\gamma_{tot}) \times 10^3$	
				Dilution method	Buffer method
7.4	5.5	34	51	66	64, 65
7.2	5.5	34	55	65	64
5.1	2.5	50	65 <sup>a</sup>	88	86
5.1	2.5	50	37 <sup>a</sup>	98	96
7.1	6.0	45	72	59, 60	60, 59
0.8	8.0	500 <sup>b</sup>	63	56	55

<sup>a</sup> Ripened.

<sup>b</sup> Excess CS<sub>2</sub> removed by evacuation after xanthation for 60 min.

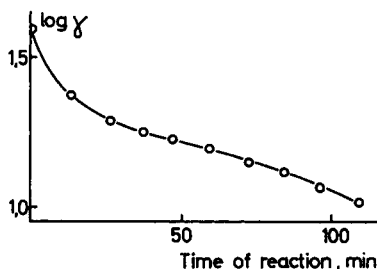


Fig. 5. Decomposition of a viscose sample with low  $\gamma$  value (40) according to the buffer method. Cellulose xanthate prepared by xanthation with 500%  $\text{CS}_2$  for 30 min.

Figure 5. This is a serious limitation in the applicability of the buffer method.

It is likely that the deviations from linearity are due to the turbidity which appears in the viscose upon prolonged decomposition in the buffer. A measure of the turbidity was obtained by determination of the transmitted light with the cuvet placed at various distances from the photo-cell.<sup>10</sup> With a fresh viscose sample, prepared by xanthation with a large excess of  $\text{CS}_2$  for a very short time, turbidity appeared at a  $\gamma$  value of 21, whereas with a sample of ripened textile viscose no turbidity could be detected before the  $\gamma$  value had dropped to 14. The differences are probably due to variations in xanthate group distribution along the cellulose chains. This distribution must be assumed to be more uniform in the textile viscose than in the other sample.<sup>1</sup> The deviations from linearity were less pronounced with the textile viscose. It is worth mentioning that the light scattering caused by the turbidity would result in deviations in the direction opposite to that observed in the experiments. The probable explanation of the deviations from linearity is, therefore, that the agglomeration of the cellulose xanthate affects the light absorption.

An attempt was made to vary the composition of the buffer solution in order to displace the flocculation point to lower  $\gamma$  values. Phosphate buffers with the following cations were tried:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $(\text{CH}_3)_4\text{N}^+$ . No appreciable improvement was achieved in comparison with potassium phosphate buffers.

The most important conclusion which can be drawn from the experiments presented above is that kinetic methods permit a reliable determination of the amounts of primary and secondary xanthate groups in cellulose xanthate. This is very important, since certain results reported from purely chemical investigations, even in some recent papers, are confusing. Among the chemical methods, the most widely used methylation method<sup>11-15</sup> gives figures which are contradictory to those obtained by the kinetic methods. The probable explanation is that the methylation procedure does not result in a selective replacement of xanthate groups by methyl groups. With the procedure devised by Swan and Purves<sup>16</sup> it seems possible to

obtain some valuable information, but, as pointed out by the authors themselves, various difficulties reduce the reliability of the method, a statement which is confirmed by experiments carried out in this laboratory.

Great difficulties are also involved in the method by Philipp and Liu.<sup>17</sup> However, many of the results reported in the two aforementioned papers, are, as far as comparison is possible, in qualitative agreement with those arrived at by the kinetic methods. The fact that a disagreement is observed in certain instances<sup>3</sup> is to be expected, since several sources of error are involved in the purely chemical methods.

### APPLICATION OF THE DILUTION METHOD AT ELEVATED TEMPERATURE

The chief purpose of our earlier studies with the resin and dilution methods was to determine the rate constants within the temperature interval used in conventional viscose production. In order to speed up the determination of primary xanthate groups, experiments with the dilution method were carried out at elevated temperature. A comparison between the results achieved at 20 and 25°C. is included in Figure 4. It is seen that straight-line plots were obtained at both temperatures and that the extrapolated values, i.e. the determinations of  $\gamma_6$ , coincide. A similar comparison was made at 20 and 50°C. At both temperatures straight lines were obtained. As can be seen from Table II, the agreement between the two methods is excellent.

TABLE II  
Relative Amount of Xanthate Groups in the 6-Position in Various Viscose Samples

Cellulose, %	NaOH, %	Added CS <sub>2</sub> , %	$\gamma_{tot}$	$(\gamma_6/\gamma_{tot}) \times 10^2$			
				Dilution method		Simplified dilution method	
				At 20°C.	At 50°C.	With resin	Without resin
6.2	7.5	~60	80	63	64	61, 61	62, 62
6.2	7.5	~60	66 <sup>a</sup>	82	82	81	81
5.1	2.5	50	37 <sup>a</sup>	98		97	
7.4	5.5	34	47	69		68 <sup>b</sup>	

<sup>a</sup> Ripened.

<sup>b</sup> Experiment run at 35°C. instead of 50°C. gave the same value (68%).

The increase in the temperature from 20 to 50°C. resulted in a shortening of the time of reaction from about 3 days to 3 hr. When working with 0.1M sodium hydroxide solutions a turbidity appeared after a long time of reaction. Under unfavorable conditions (fresh viscose) a turbidity was observed at a  $\gamma$  number equal to 12. With the same viscose no turbidity was observed even at  $\gamma = 2$ , when the sodium hydroxide concentration was

increased to  $1M$ . In most instances the appearance of a turbidity at  $\gamma = 12$  does not prevent a reliable extrapolation to zero time, but with viscoses with very low  $\gamma$  values it is recommended either to work at higher sodium hydroxide concentration or to use the simplified dilution method described below.

### SIMPLIFIED DILUTION METHOD

In the buffer method only one ion-exchange operation is carried out, whereas in the dilution method an anion-exchange purification of the dilute xanthate solution is carried out before each determination of the absorbance.

As already mentioned, there is no formation of interfering trithiocarbonate under the conditions used in the buffer method. Experiments similar to those represented in Figure 1 were carried out after decomposition at  $50^\circ C$ . of an extremely dilute solution of cellulose xanthate in  $0.1M$  sodium

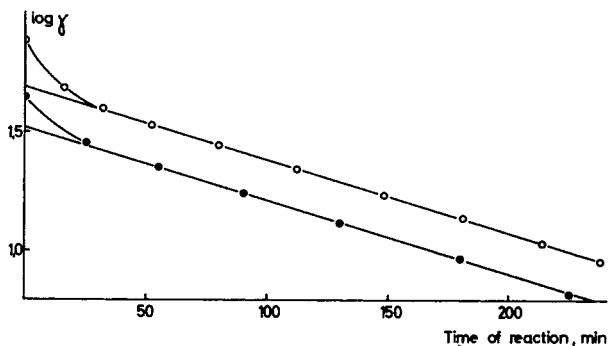


Fig. 6. Decomposition of two viscose samples according to the simplified dilution method: (O)  $\gamma_6 = 76$ ; (●)  $\gamma_6 = 44$ .

hydroxide. In these experiments, ion-exchanged viscose samples were immediately diluted to a cellulose concentration of about  $0.002\%$ . The absorption spectra taken after various times of reaction were, within the range  $270\text{--}340\text{ m}\mu$ , very similar to those reported in Figure 1. Hence, no interfering trithiocarbonate is formed at this low cellulose concentration.

As shown in Figure 6, plots of  $\log \gamma$  against the time of reaction give curves of the same type as observed in experiments carried out according to the resin and dilution methods. Systematic deviations from linearity at long times of reaction were not observed in any experiment in which this technique was employed. Turbidity measurements were made with five viscoses of different types after decomposition to a  $\gamma$  value of about 5. No indications of a formation of a turbidity were obtained. Hence, this method is more versatile than the buffer method. The time required for a determination of the xanthate distribution is about the same in both methods.



A comparison between the results achieved with this simplified dilution method (without resin) and the dilution method used earlier is given in Table II. It is seen that a good agreement was obtained.

Although there is no indication of a formation of interfering amounts of trithiocarbonate under the conditions used in the simplified dilution method, there are indications that some other by-product formed, can give a slight contribution to the absorbance at 303  $m\mu$  which is used in calculating the  $\gamma$  value. Experiments run at 0.1% cellulose in the viscose during the decomposition show that under these conditions interfering by-products are formed, and that it is necessary to remove these before the spectrophotometric determination. At higher cellulose concentration during the decomposition step but the same concentration during the measurement, the difference in absorbance of a solution before and after ion exchange is greater. Within the interval studied (6–0.1% cellulose) the interference due to the by-products decreased when the cellulose concentration was lowered, and it is therefore probable that this interference is very small at a concentration of about 0.002%. At this low concentration it is not possible to obtain an accurate determination of the contribution of the by-products to the absorbance at 303  $m\mu$ , since an interfering adsorption of cellulose onto the resin occurs.<sup>18</sup>

At this very low cellulose concentration the amount of resin necessary for a complete removal of interfering by-products must, however, be very small. Experiments with various amounts of resin present during the decomposition of a solution containing 0.002% cellulose were, therefore, carried out in order to estimate the error which can be anticipated due to the formation of by-products. Very small but reproducible differences in the absorbance were observed, the highest values being observed in the run without resin and the lowest values in the run with the largest amount of resin. From these determinations the relative amount of xanthate groups in the 6-position as well as the rate constant for the decomposition of 6-xanthate were calculated as usual. The values given in Table III show that very small but systematic variations occurred. It is likely that due to the adsorption of cellulose xanthate onto the resin the  $\gamma_6$  values obtained in experiments with added resin should be somewhat too low. Some further experiments carried out according to the simplified dilution method

TABLE III  
Influence of the Amount of Added Resin

Added resin, g./250 ml. solution	$(\gamma_6/\gamma_{tot}) \times 10^6$	$K_6^2 \times 10^4, \text{sec.}^{-1}$
0	76	1.19
0.2	76	1.20
1.0	75	1.21
5.2	75	1.22

\*  $K_6$  is the rate constant of the decomposition of primary xanthate groups.

with added resin (4 g./250 ml. viscose solution) are included in Table II. The results given in both tables show that the observed  $\gamma_6$  values are slightly lower in experiments with resin. The differences from the  $\gamma_6$  values obtained with the other methods are, however, small and hardly of any practical importance. From the results given in Table III it can also be concluded that in the simplified method without resin the interference due to the possible contribution of by-products to the absorbance at 303 m $\mu$  has hardly any influence upon the determinations of the  $\gamma_6$  values and the rate constants.

Among the simplified methods described, that without resin is preferred to that with resin. Both methods are simple and rapid, and the deviations between the results achieved with these methods and those obtained with the dilution method are hardly of practical importance. The chief reason why the method with resin has been abandoned is that the adsorption error involved in this method may be different with different viscose samples dependent upon, among other things, the hemicellulose content in the viscose and the polymolecularity of the cellulose.

The financial support of the Swedish Technical Research Council is gratefully acknowledged.

### References

1. Lyselius, A., and O. Samuelson, *Svensk Papperstidn.*, **62**, 751 (1959); *ibid.*, **64**, 145 (1961).
2. Lyselius, A., and O. Samuelson, *Svensk Papperstidn.*, **64**, 815 (1961).
3. Dunbrant, S., and O. Samuelson, *Tappi*, **46**, 520 (1963).
4. Matthes, A., *Faserforsch. Textiltech.*, **5**, 127 (1952).
5. Dolby, I., S. Dunbrant, and O. Samuelson, *Svensk Papperstidn.*, **67**, 110 (1964).
6. Dolby, I., and O. Samuelson, *Svensk Papperstidn.*, **68**, 136 (1965).
7. Miller, I. K., and I. D. Geerdes, paper presented at 131st American Chemical Society Meeting, Miami, Fla., April 1957; *Abstracts of Papers*, p. 3E.
8. Samuelson, O., and F. Gärtner, *Acta Chem. Scand.*, **5**, 596 (1951).
9. Dux, J. P., and L. H. Phifer, *Anal. Chem.*, **29**, 1842 (1957).
10. Jullander, I., *Svensk Papperstidn.*, **53**, 719 (1950).
11. Lieser, Th., *Ann. Chem.*, **470**, 104 (1929).
12. Lauer, K., *Makromol. Chem.*, **5**, 287 (1950).
13. Lauer, K., R. Jaks, and L. Skark, *Kolloid-Z.*, **110**, 26 (1945).
14. Chen, C. Y., R. E. Montonna, and C. S. Grove, *Tappi*, **43**, 420 (1951).
15. Horio, M., R. Imamura, N. Komatsu, H. Sakata, and T. Kato, *J. Soc. Textile Cellulose Ind. Japan*, **19**, 102 (1963).
16. Swan, E. P., and C. B. Purves, *Can. J. Chem.*, **35**, 1522 (1957).
17. Philipp, B., and K.-T. Liu, *Faserforsch. Textiltech.*, **10**, 555 (1959).
18. Törnell, B., *Svensk Papperstidn.*, **67**, 756 (1964).

### Résumé

On a comparé différentes méthodes cinétiques pour la détermination des groupements xanthates primaire et secondaire. Avec certains types de viscoses toutes les méthodes donnent une excellente concordance et elles sont supérieures aux méthodes purement chimiques qui sont incertaines. Le domaine d'application d'une méthode cinétique basée sur la décomposition dans un tampon légèrement acide est limité à cause de l'appari-

tion d'une turbidité après une déxanthation prolongée. Une technique modifiée dans laquelle la décomposition est effectuée à température élevée dans une solution d'hydroxyde de sodium est en même temps rapide et souple.

### **Zusammenfassung**

Verschiedene kinetische Methoden zur Bestimmung von primären und sekundären Xanthatgruppen wurden verglichen. Bei gewissen Viskosetypen lieferten alle Methoden eine ausgezeichnete Übereinstimmung und sind den rein chemischen Methoden, die nicht verlässlich sind, überlegen. Die Anwendbarkeit einer auf der Zersetzung in einem schwachsauren Puffer beruhenden kinetischen Methode ist wegen des Auftretens einer Trübigeit bei längerer Dexanthierung beschränkt. Ein modifiziertes Verfahren, bei welchem die Zersetzung bei erhöhter Temperatur in Natriumhydroxydlösung ausgeführt wird, ist rasch und besitzt einen grossen Anwendungsbereich.

Received February 10, 1965