

has an intercept near zero time, thus indicating that the assumption regarding step (5a) is valid to the extent that k_1 is much greater than k_2 . Table I gives the values found for k_2 .

If it is correct that (5b) is the slow step in the dehydrochlorination of the *delta* isomer, then it should be possible to isolate the $C_6H_5Cl_5$ compound produced as a result of step (5a). Study of the products of partial dehydrochlorination is planned, so that this evidence may be obtained.

Materials Used.—Samples of each of the isomers were kindly furnished by M. C. Swingle, of E. I. du Pont de Nemours and Co., Inc., and were purified by recrystallization to constant melting point and dried in vacuum before use. The melting points of the materials were: *alpha*, 157–158° (cor.); *beta*, 305–307° (dec.); *gamma*, 112.5–113° (cor.); *delta*, 137–138° (cor.).

Acknowledgment.—The author wishes to acknowledge the support and interest of Dr. H. L. Haller in this work.

Summary

A kinetic study has been made of the dehydrochlorination of the four isomers of benzene hexachloride by ethanolic sodium hydroxide. The results establish conclusively the steric requirement of *trans* elimination in the E_2 -type elimination. A mechanism has been suggested for *trans* elimination which indicates its superiority as a reaction path over *cis* elimination.

The kinetics of elimination for the *alpha* and *gamma* isomers suggest that the rate-determining step in the elimination is the loss of the first mole of hydrogen chloride which is followed by relatively rapid loss of the next two moles of hydrogen chloride. The *delta* isomer does not have the same kinetics, and evidence is presented to suggest that the elimination of the second mole of hydrogen chloride is the rate-determining step in the process of elimination in this isomer.

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Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. II. The Evolution of Carbon Dioxide from Uronic Acids and Polyuronides¹

BY E. W. TAYLOR, W. F. FOWLER, JR., P. A. MCGEE AND W. O. KENYON

The evolution of carbon dioxide from uronic acids upon treatment with hydrochloric acid at elevated temperatures has long been known and is the basis for their estimation.^{2,3} The present investigation was undertaken to determine the rate of decomposition of various monomeric uronic acids for comparison with the rates of evolution of carbon dioxide from certain natural and synthetic polyuronides. Such data are used here to corroborate and compare the polyuronide structures, especially those of the celluronic acids resulting from the treatment of cellulose by nitrogen dioxide.^{4,5,6}

Harris⁷ and his co-workers have found that carbohydrates also evolve carbon dioxide under the same conditions as do uronic acids, but their rates of evolution are slow and linear. These observations bear on the present experiments which entail the interpretation of carbon dioxide evolution data from materials containing both uronic acid units resulting from oxidation and unchanged

anhydro-D-glucose units. Illustrative of such materials are certain partially oxidized celluloses. Rates of carbon dioxide evolution have been determined for several structures, other than *combined* carbohydrate and *combined* uronic acid, which might conceivably be present in oxidized celluloses.

Experimental

Apparatus and Technique.—The apparatus used was similar to that described by Yackel and Kenyon,⁴ except that in the evaluation of the reaction rates of uronic acids, nitrogen was used to sweep carbon dioxide through the absorption train. This change in technique necessitated a stopcock to regulate the nitrogen input and a flow-meter at the outlet. Duplicate apparatus were used in the same oil-bath. Certain of the non-uronic acid materials of low carbon dioxide evolution were run by the older technique using slight vacuum, and are so indicated in Table II.

The operating technique paralleled that of Harris.⁷ Samples (all 100-mesh or finer, in particle size), weighing approximately 0.2500 g. on the air-dried basis, and a few clay chips, previously boiled in 3.290 *N* hydrochloric acid, were placed in the boilers. Seventy-five ml. of 3.290 *N* (12%) hydrochloric acid were introduced into each. The same stock acid was used for all runs. Nitrogen was passed through the apparatus for one-half hour at 2 liters per hour with the boiling flasks at room temperature to sweep carbon dioxide from the train. Zero time weighings of absorption tubes were made, and the heating unit then was turned on. The bath temperature rose in 1.4 hours to 130°, where it was held throughout the experiments. Subsequent weighings were at one-half-hour intervals. In our apparatus it was found best to maintain a flow of nitrogen of 2.0 liters per hour. At faster rates, *i. e.*, 10 liters per hour, which have been advocated,⁷

(1) Presented before the Division of Cellulose Chemistry at the 110th Meeting of the American Chemical Society, September 1946, Chicago, Illinois.

(2) Lefèvre and Tollens, *Ber.*, **40**, 4513 (1907).

(3) Norman, *Nature*, **143**, 284 (1939).

(4) Yackel and Kenyon, U. S. Patent 2,232,990 (1941); British Patent 531,283 (1942); *THIS JOURNAL*, **64**, 121–127 (1942).

(5) Unruh and Kenyon, *ibid.*, **64**, 127–131 (1942).

(6) Unruh and Kenyon, *Textile Research*, **16**, 1–12 (1946). This reference further defines the term celluronic acid.

(7) Whistler, Martin and Harris, *J. Research Natl. Bur. Standards* **34**, 13 (1940).

small variations produced differences in the internal temperature of the boilers, rendering precision in kinetic measurement impossible. Excellent checks resulted at lower rates of flow. The heating and weighings were continued until the one-half-hour increments became very small or ceased.

Materials.—The crystalline compounds were Eastman Kodak Company products, except D-galacturonic acid monohydrate, D-glucuronic acid, D-gluconic acid, potassium acid saccharate and glyoxylic acid. D-Galacturonic acid monohydrate was prepared according to Isbell's procedure⁸ from the sodium calcium salt.⁹ The D-gluconic acid was secured from the MacKay Company. Potassium acid saccharate was prepared by the well-known method of oxidizing glucose with nitric acid and isolating the salt.

A 50% aqueous solution of crude D-gluconic acid (Eastman Kodak Company) was neutralized with sodium carbonate. The sodium salt crystallized upon concentration. The free acid was liberated by acidification with a mixture of dichloroacetic acid and glacial acetic acid. Glyoxylic acid was prepared in aqueous solution by the method of Benedict¹⁰ through the reaction of magnesium on oxalic acid and liberation of the free glyoxylic acid with acetic acid. The resultant solution was analyzed for glyoxylic acid using hydroxylamine hydrochloride.

Melting points of the crystalline substances examined in this study are given in Tables II and IV.

The celluronic acids were prepared by immersing surgical cellulose gauze, ground to 100-mesh, in a solution of nitrogen tetroxide in carbon tetrachloride for different periods of time,¹¹ washing the product free of reactants and diluent, and air-drying to constant weight at room temperature. The oxidized starch was similarly prepared from corn starch, the oxidation time being six hours. Alginic acid was isolated by treating commercial sodium alginate (Kelgin) in aqueous solution with hydrochloric acid, isolating the precipitated acid, and drying. The pectic acid contained 0.305% methoxyl.¹² The free carboxyl contents of these polymeric materials were determined by the calcium acetate method⁴ and the nitrogen contents of the celluronic acids by the DeVarda method. These data are summarized in Table I.

TABLE I

ANALYTICAL DATA FOR THE POLYURONIDE SAMPLES

Polymer	% COOH by calcium acetate (dry basis)	% N (dry basis)
Celluronic acid I	7.32	0.37
Celluronic acid II	10.78	.28
Celluronic acid III	18.68	.44
Celluronic acid IV	22.70	.20
Oxidized starch	22.40	.36
Alginic acid	22.32	
Pectic acid	21.25	

Each of the substances was analyzed for moisture by the Karl Fischer technique,^{13,14} immediately prior to use, and the percentage of carbon dioxide evolved in all subsequent experiments was calculated to the dry basis.

Results

Data for evolution of the carbon dioxide from substances other than uronic acids or polyuron-

(8) Isbell, *J. Research Natl. Bur. Standards*, **32**, 77 (1944).

(9) Supplied through the courtesy of Mr. C. M. Ingram and the Chas. Pfizer Company.

(10) Benedict, *J. Biol. Chem.*, **6**, 51-52 (1909).

(11) Yackel and Kenyon, Patent Application No. 571,012.

(12) Supplied through the courtesy of Dr. Z. I. Kertesz, Geneva Experiment Station, Geneva, New York.

(13) Wernimont and Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1943).

(14) Mitchell, *ibid.*, **12**, 390 (1940).

ides are shown in Table II. As the weight percentage evolved was in each case essentially linear with respect to reaction time, only the final average values are tabulated.

TABLE II

EVOLUTION OF CARBON DIOXIDE FROM NONURONIC SUBSTANCES WHEN TREATED WITH 3.29 N HYDROCHLORIC ACID

Material	M. p., °C. (uncor.)	Method	Total reaction time, hr.	CO ₂ evolved (% by wt.)
D(+)-Xylose	141-143	Nitrogen	15	1.39
D-Glucose	146	Nitrogen	15	1.18
Cellulose		Nitrogen	15	0.81
Starch		Nitrogen	15	1.29
Cellobiose	225	Nitrogen	15	1.04
Maltose	102-103	Nitrogen	15	1.18
Potassium acid saccharate		Nitrogen	15	4.50
Tartaric acid	141-143	Vacuum	21.5	0.44
D-Gluconic acid	145-147	Vacuum	24	8.16
D-Glucono-γ-lactone	136-137	Vacuum	24	7.72
Oxalic acid	192	Vacuum	23	4.97
Glyoxylic acid		Vacuum	23	1.83

The results using alginic acid are given in their entirety in Table III as illustrative of typical results for materials having uronic acid structures.

TABLE III

CO₂ EVOLUTION DATA FOR ALGINIC ACID WHEN TREATED WITH 3.29 N HYDROCHLORIC ACID

Time, hr.	Apparatus A		Apparatus B	
	Wt. CO ₂ , g.	Total % CO ₂	Wt. CO ₂ , g.	Total % CO ₂
0.5	0	0	0	0
1.0	0	0	0	0
1.5	0.0016	0.34	0.0029	0.61
2.0	.0173	3.97	.0190	4.60
2.5	.0120	7.16	.0122	7.16
3.0	.0103	9.33	.0104	9.35
3.5	.0085	11.12	.0093	11.30
4.0	.0074	12.67	.0074	12.86
4.5	.0069	14.12	.0065	14.23
5.0	.0057	15.32	.0057	15.43
5.5	.0052	16.41	.0052	16.52
6.0	.0043	17.31	.0043	17.42
6.5	.0037	18.09	.0034	18.13
7.0	.0025	18.62	.0033	18.82
7.5	.0031	19.27	.0026	19.37
12.0	.0147	22.36	.0133	22.16
15.0	.0057	23.56	.0055	23.32

In this as well as the other determinations, duplicate runs were made, using different apparatus, to detect instrumental divergences. The evolution curves of several uronic-acid type materials are shown graphically in Fig. 1. The curves of several celluronic acids of different carboxyl contents are collected in Fig. 2 for comparison between themselves and with D-gluconic acid.

It has been shown mathematically¹⁵ that, in the

(15) Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

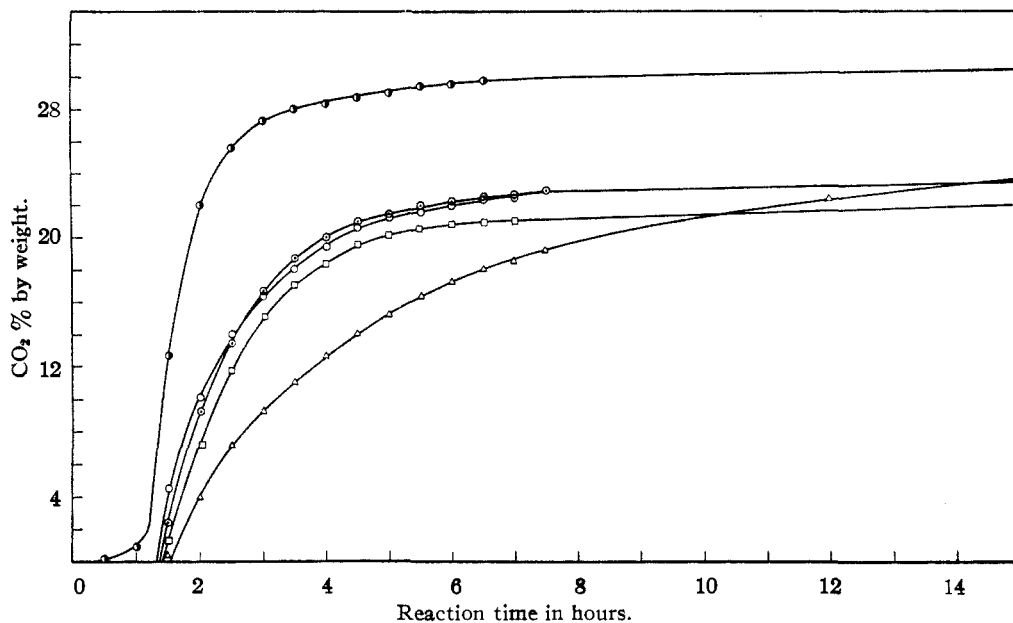


Fig. 1.—Carbon dioxide evolution as a function of time: Δ , alginic acid; \circ , oxidized starch; \square , pectic acid; \bullet , ascorbic acid; \odot , galacturonic acid.

determination of the velocity constant of a unimolecular reaction, it is necessary only to plot $\log_{10} (v_1' - v)$ against t_2 and the straight line so obtained will have a gradient $-k \log_{10} e$. Applying this principle here, $\log_{10} (v_1' - v)$ becomes the weight of carbon dioxide evolved in an interval of time, Δt . The weight increments were plotted semilogarithmically against one-half-hour reaction intervals in Figs. 3 and 4. The equation for the straight line for each run on each substance

was determined by analysis of the experimental values according to the method of least squares, to obtain the best possible mathematical conformance. The individual values for k (\log_e base), shown in Table IV, give an index to the degree of kinetic precision obtained.

Discussion

The carbon dioxide evolution values of several nonuronic structures including tartaric, D-glu-

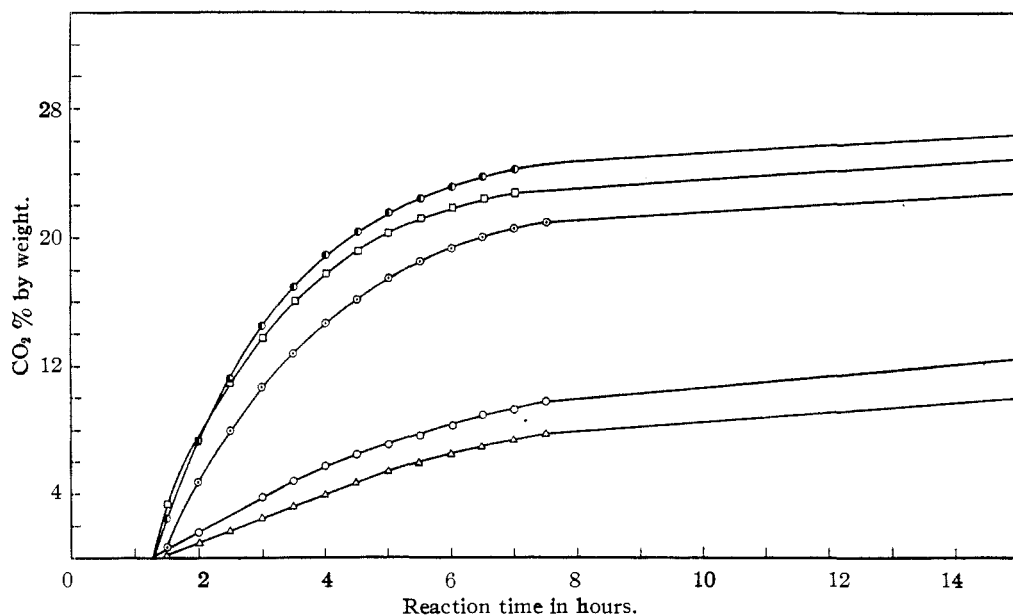


Fig. 2.—Carbon dioxide evolution from *d*-glucuronic acid and various celluronic acids: Δ , celluronic acid I; \circ , celluronic acid II; \odot , celluronic acid III; \square , celluronic acid IV; \bullet , *d*-glucuronic acid.

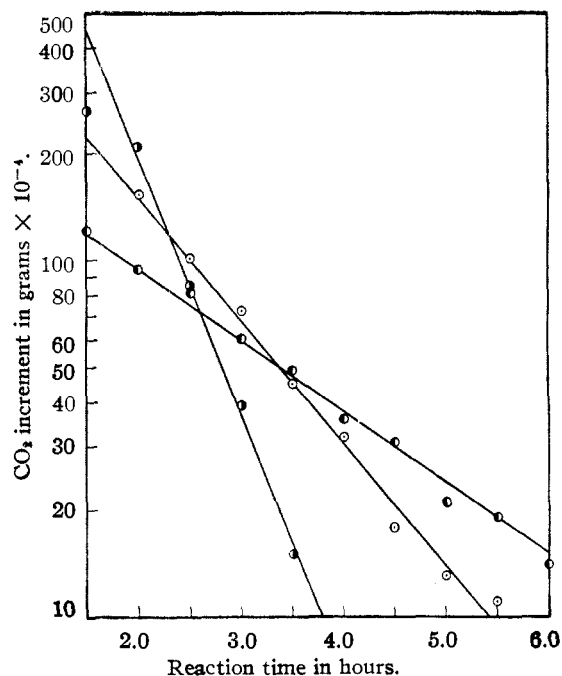


Fig. 3.—Log of increment carbon dioxide evolved as a function of time for simple molecules: ●, *d*-glucuronic acid; ○, *d*-galacturonic acid; ●, *l*-ascorbic acid.

TABLE IV
REACTION VELOCITY CONSTANTS FOR THE EVOLUTION OF
CARBON DIOXIDE FROM URONIC ACIDS
(log_e base)

Material	<i>k</i> , no. 1 hr. ⁻¹	<i>k</i> , no. 2 hr. ⁻¹	<i>k</i> , mean hr. ⁻¹
<i>l</i> -Ascorbic acid ^a	-1.690	-1.711	-1.700
<i>d</i> -Galacturonic acid monohydrate ^b	-0.783	-0.783	-0.783
Pectic acid	-.702	-.698	-.700
Oxidized starch	-.686	-.712	-.699
<i>d</i> -Glucuronic acid ^c	-.474	-.440	-.457
Celluronic acid IV	-.451	-.438	-.444
Celluronic acid III	-.396	-.412	-.404
Alginic acid	-.318	-.327	-.322

^a M. p. 190–192°. ^b M. p. 155°. ^c M. p. 153–155°. This m. p. is low and was not improved by recrystallizations.

conic, oxalic and glyoxylic acids, potassium acid saccharate and *D*-glucono- γ -lactone are shown in Table II. These structures could arise by oxidation at various points in the anhydro-glucose units. All the values were far from the theoretical. On treatment with strong hydrochloric acid, the celluronic acids of less than theoretical carboxyl group contents could yield cellobiose, *D*-glucose and *D*-xylose (the latter from decomposition and hydrolysis of polyanhydro-*D*-glucuronic acid) as well as uronic acid units. Oxidized starch could produce a mixture of maltose, *D*-glucose and *D*-xylose, as well as glucuronic acid. None of these nonuronic acid substances or their parent polymeric carbohydrates evolved as much as 1.50%

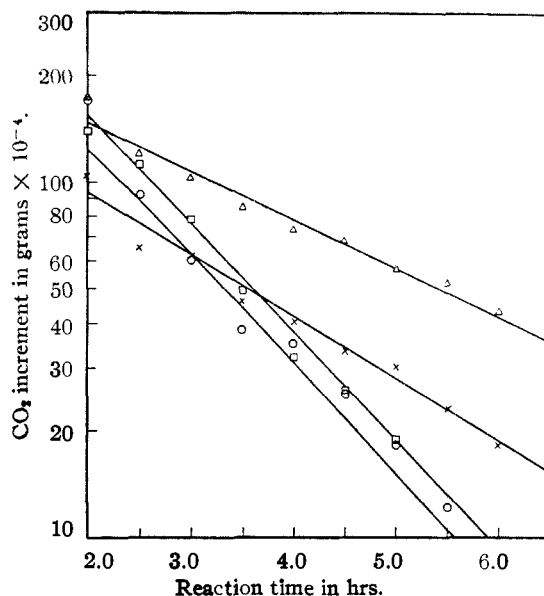


Fig. 4.—Log of increment carbon dioxide evolved as a function of time for polyuronides: X, celluronic acid IV; Δ, alginic acid; □, pectic acid; O, oxidized starch.

of carbon dioxide during fifteen hours in the uronic acid analysis (Table II). In all cases the very small quantity of carbon dioxide was linearly evolved, and only the terminal values are tabulated. The evolution data for celluronic acids and oxidized starch cannot be ascribed to such a source.

Oxidation of all primary hydroxyl groups in the anhydro-*D*-glucose units of cellulose would produce a polyanhydro-*D*-glucuronic acid, with a theoretical carbon dioxide evolution value of 25.00%. Celluronic acid, IV, yielded 24.80% (Fig. 2). Furthermore, if the carbon dioxide evolved comes from decomposition of uronic acid, one would expect the data to follow an *exponential* as opposed to a *linear* function, and such was the case for the highly oxidized celluloses, III and IV.

Kinetic consideration of the carbon dioxide evolution of the various celluronic acids offers strong evidence for their structure. The higher their carboxyl values, the more closely their evolution curves approached that of *D*-glucuronic acid. It is doubtful, however, if the two curves could be made to coincide even by exhaustive oxidation of the cellulose, because the celluronic acids are insoluble in the strong hydrochloric acid for a sufficient time to affect the rate of carbon dioxide evolution.

It is instructive to consider the curves of Fig. 2 in the light of the recent work by Harris,⁷ who found that evolution of carbon dioxide from a mixture of *D*-galacturonic acid monohydrate and *D*-glucose was intermediate between that for a linear and an exponential function. In other words, curves with slight curvature resulted. If cellu-

lose is only partially oxidized with nitrogen tetroxide, and if the product consists of anhydro-D-glucuronic acid units and anhydro-D-glucose units, as part of the same molecule or in different molecules, curves similar to those described by Harris should result. Celluronic acids, I and II, of intermediate degrees of oxidation exhibit evolution curves which meet this description and are both known by a variety of corroborative analyses to be only partially oxidized. It will be noted that celluronic acid, III, showed a lower reaction velocity constant than the most highly oxidized sample, IV. The latter closely approximated the constant of monomeric D-glucuronic acid.

The carbon dioxide evolution method always indicates higher carboxyl values for the celluronic acids, than does the calcium acetate method (compare Table I and Fig. 2). The celluronic acids contain small quantities of combined nitrogen. Secondary oxidations due to the presence of nitrate groups may account for a part¹⁶ of the observed differences. Two mechanisms may be involved. The nitrate group may hydrolyze to nitric acid, which oxidizes the celluronic acid during the carbon dioxide evolution evaluation. The nitrate groups may oxidize the celluronic acid as a part of the hydrolysis mechanism—a reaction which is known to occur during the alkaline saponification of cellulose nitrate.

Table V shows the effect of small amounts of nitric acid added to cellulose or celluronic acid in the carbon dioxide evolution determination. All other experimental conditions were as previously described.

TABLE V
EFFECT OF NITRIC ACID ON THE CARBON DIOXIDE EVOLUTION

Polymer	% HNO ₃ ^a		% CO ₂ ^c
	% HNO ₃ ^a	% N ^b	
Cellulose (Eastman filter cotton)			0.87
	2.2	0.49	2.5
	4.4	.98	4.8
	11.9	2.65	7.7
	14.5	3.22	9.0
Celluronic acid	22.0	4.90	13.6
	29.1	6.48	32.5
	29.3	6.52	34.2
Cellulose nitrate		11.89 ^e	19.84 ^d

^a In terms of actual HNO₃, calculated from the concentrated nitric acid (sp. gr. 1.42), added, and as per cent. by weight based on the amount of polymer sample employed. ^b As per cent. by weight from the nitric acid used. ^c Twenty-four hours reaction time except for cellulose nitrate. ^d Sixteen hours reaction. ^e By analysis of the cellulose nitrate.

Cellulose shows a considerable apparent carboxyl content due to the carbon dioxide resulting from the oxidizing action of nitric acid. Nitric acid increases the apparent carboxyl content of the celluronic acid. Cellulose nitrate in the absence of added nitric acid is decomposed with high

(16) Other factors which may be involved are to be described in subsequent papers.

carbon dioxide evolution. These results led to the choice of celluronic acids of low nitrogen contents for the experimental studies of this paper. Though even the small contents of combined nitrate group affect the ultimate apparent carboxyl values, it is believed that they may not seriously alter the kinetic considerations.

The structure of highly purified pectic acid has been conclusively shown to be polyanhydro- α -D-galacturonic acid containing the pyranose ring and linked glycosidically through positions 1 and 4.¹⁷⁻²⁰ Similarity of the reaction velocity constants for pectic acid and D-galacturonic acid would be anticipated and was found experimentally to be the case (Table IV). The order of magnitude of the constants for the two substances was the same, but again the value for the monomeric compound was somewhat higher.

The structure of alginic acid was first postulated^{19,21} and later shown conclusively by X-ray study²⁰ to be polyanhydro- β -D-mannuronic acid. This structure is epimeric with celluronic acid and its rate of evolution is valuable for comparative purposes. Alginic acid and the celluronic acids III and IV evolved carbon dioxide at slower rates than any of the uronic acid substances investigated. These three materials showed further similarities in that their rates of evolution were close to the same value. Also, their rates of evolution were logarithmic over the period of time required to evolve the bulk of the carbon dioxide. In contradistinction, oxidized starch and pectic acid showed logarithmic evolution only during the early part of the decomposition. This result with pectic acid corroborates the findings of Harris.⁷

L-Ascorbic acid was decomposed at a rate greater than twice that of its nearest neighbor in the scale, D-galacturonic acid. This indicates the profound effect of an enediol structure on the stability of the adjacent lactonized carboxyl group. If only the carboxyl group supplies the carbon dioxide, the evolution should be 25.0% by weight. However, the evolution rapidly reached 28%, after which it was slow for many hours more, finally attaining a total value in excess of 30% (Fig. 2). While the carboxyl group decomposed very rapidly, there was further slow decomposition evolving more carbon dioxide.

L-Ascorbic acid units presumably cannot be present in oxidized celluloses, as their formation would necessitate oxidation of the 4 and 5 positions of the anhydro-glucose units. Such oxidation has never been proved. There is no evidence from the carbon dioxide evolution data that celluronic acids contain any substantial quantities of such units.

The heterogeneity of constitution of starch as

(17) Smith, *Chem. Ind.*, **58**, 363 (1939).

(18) Beaven and Jones, *ibid.*, 363 (1939).

(19) Hirst, Jones and Jones, *J. Chem. Soc.*, Part II, 1880 (1939).

(20) Astbury, *Nature*, **155**, 667 (1945).

(21) Lunde, Heen and Oy, *Kolloid Z.*, **83**, 196 (1938).

compared with that of cellulose is substantiated by the evolution data for oxidized starch. Figure 1 discloses that the rate of evolution appeared logarithmic for the first three hours, followed by a slow linear evolution for two and one-half hours. Bearing in mind that the other polyuronic acids examined are made up essentially of long, unbranched chains, whereas starch is composed, in part at least, of branched chains assumed to involve the C₆ hydroxyl group, we find that interpretation of the velocity constant becomes difficult and speculative. Thus, the data may offer further evidence that starch is structurally more heterogeneous than cellulose, celluronic acids, purified pectic acid, or alginic acid.

There appears to be nothing in the carbon dioxide evolution data to contradict the previously published suggestion that celluronic acids are composed of anhydro-D-glucose and D-glucuronic acid units in varying amounts, dependent on the degree of oxidation.

Acknowledgment.--We wish to acknowledge the assistance of Dr. Delbert D. Reynolds in preparing the D-galacturonic acid monohydrate

and D-gluconic acid. The method described herein for preparing the latter was developed by him.

Summary

1. Kinetic data on the evolution of carbon dioxide from celluronic acids is submitted as evidence that cellulose, highly oxidized with nitrogen dioxide, is composed essentially of β -D-glucuronic acid units and unchanged D-glucose units.

2. Reaction velocity constants are given for evolution of carbon dioxide from D-glucuronic acid, D-galacturonic acid, L-ascorbic acid, pectic acid, alginic acid, celluronic acids and oxidized starch.

3. The close relationship existing between the rates of acid decomposition of monomeric and corresponding anhydro-polymeric acids is discussed.

4. With the exception of L-ascorbic acid, the nonuronic organic acids tested as reference compounds evolved small amounts of carbon dioxide linearly.

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Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. III. The Reaction of the Carboxyl Groups of Polyuronides with Calcium Acetate¹

BY P. A. MCGEE, W. F. FOWLER, JR., AND W. O. KENYON

Numerous investigators of oxidized celluloses have used the calcium acetate method to characterize their products. It was first used to measure the residual acidity of cellulose itself^{1a} and has since been employed in determining the equilibrium between cellulose and salts.² Calcium acetate is now utilized to estimate the carboxyl groups in celluloses which have been oxidized with nitrogen peroxide (NO₂-N₂O₄),^{3,4} *i.e.*, celluronic acids.⁵ The present study is to define and delimit the interpretation to be given to carboxyl values so obtained. The object is to use the calcium acetate method to investigate further the structure of celluronic acids rather than to develop it as an analytical procedure. Alginic acid, a naturally occurring polyuronide consisting of β -anhydro-D-mannuronic acid units, is used as a reference material against which celluronic acid, nitrogen tetroxide-oxidized starch, and other natural and synthetic polyuronides may be compared.

(1) Presented before the Division of Cellulose Chemistry at the 110th Meeting of the American Chemical Society, September, 1946, Chicago, Illinois.

(1a) M. Ludtke, *Biochem. Z.*, **233**, 25 (1931); **268**, 372 (1934); **285**, 78 (1936); *Z. angew. Chem.*, **41**, 650 (1935).

(2) Heymann and Rabinov, *J. Phys. Chem.*, **45**, 1152 (1941).

(3) Yackel and Kenyon, *THIS JOURNAL*, **64**, 121 (1942).

(4) Unruh and Kenyon, *ibid.*, **64**, 127 (1942).

(5) Unruh and Kenyon, *Textile Research*, **16**, 1 (1946).

Experimental

The alginic acid was liberated by the addition of hydrochloric acid to commercial sodium alginate solution, the free acid being precipitated as swollen gelatinous particles. These were leached in successive changes of distilled water, ethanol, and ether, and finally air-dried. The product, in a flaky condition, was ground in a Wiley cutting mill to 60-mesh size. Moisture was determined just prior to use by the Karl Fischer technique. All results are calculated to the dry basis.

Anal. Calcd. for alginic acid (C₆H₈O₆)_n: C, 40.9;

TABLE I
EFFECT OF REACTION TIME ON CARBOXYL CONTENT OF ALGINIC ACID BY CALCIUM ACETATE

Reaction time, hr.	% COOH on dry basis	Mean % COOH (dry)
0.5	23.10	23.05
0.5	23.00	
1.25	23.10	23.12
1.25	23.14	
2.0	23.00	23.05
2.0	23.10	
4.0	23.10	23.04
4.0	22.98	
7.0	22.87	22.90
7.0	22.94	
16.0	23.25	23.13
16.0	23.01	

Average 23.05