cosities, thicknesses of unimolecular films and surface pressures) and studies of other series, including appropriate non-cyclic ones, may be of assistance in developing an authentic explanation of the abnormality. Further investigation is contemplated.

In Fig. 2, refractive indices of the 1-*n*-alkylcyclohexanols are plotted against numbers of carbon atoms in the alkyl groups; here, also, there is an abrupt break at the hexyl. Where the densities of the members of an homologous series drop suddenly, other factors remaining constant, the rate of change of index of refraction with respect to increase in the number of carbon atoms should decrease. A curve of this sort, therefore, was to be expected.

Experimental

1-*n*-Alkyl-cyclohexanols.—These compounds were prepared from cyclohexanone and the appropriate alkyl bromides by the method of Zelinski and Gutt.[5] The ethyl, butyl, hexyl and octyl compounds were purified by repeated fractional distillation at pressures ranging from 760 to 0.2 mm.

It was impractical to purify the 1-*n*-heptylcyclohexanol adequately in this manner, because at no pressure at which distillation was possible without marked decomposition was there more than two degrees difference between its boiling point and that of *n*-tetradecane formed in the original synthesis. The crude product was distilled, therefore, and a fraction collected at 116–118° (11 mm.) was dissolved in twice its volume of 95% ethyl alcohol and cooled to −30°. At this temperature white plates of *n*-tetradecane precipitated. The supernatant liquid was removed by suction through a fritted glass crucible. The chilling and separation were repeated five times, until no more solid tetradecane separated. The ethyl alcohol was then distilled off under reduced pressure, and the remaining liquid containing the 1-*n*-heptylcyclohexanol redistilled.

The dodecyl member of the series could not be purified by fractional distillation, because of the ease with which it underwent dehydration when heated. Its ethereal solution was shaken several times with saturated sodium bisulfite solution, and then washed repeatedly with warm water. The ether was removed by evaporation and the crude tertiary alcohol purified by selective solvent action, employing, first, 95% ethyl alcohol at −25°, and, second, an ethyl alcohol–water mixture at room temperature, each step being repeated several times. The ethyl alcohol and water were distilled off under reduced pressure at a temperature of 50°, and the residual 1-*n*-dodecylcyclohexanol was desiccated at 5 mm. for forty-eight hours.

All members of this series were colorless liquids with camphor-like odors. Some, if not all, were supercooled liquids at room temperature. Yields varied from 41 to 72% with the exception of the octyl member, which suffered relatively large loss during purification.

1-*n*-Alkylcyclohexylphenyl Urethans.—Avoidance of elevated temperatures reduced dehydration of these tertiary alcohols sufficiently to permit satisfactory formation of their urethans. In a typical instance, the alcohol (0.01 mole) and phenyl isocyanate (0.02 mole) were placed in a tightly-stoppered 25-ml. flask, kept at room temperature for two days, and then placed in an ice-bath, where, after approximately twenty-four hours, the entire solution solidified, forming a crystalline mass. This was extracted with warm, high-boiling petroleum ether, the extract filtered with suction, and the greater part of the petroleum ether evaporated. The alkyl-cyclohexylphenyl urethan precipitated, forming snowy-white crystals. These were recrystallized from the same solvent, and dried in a vacuum desiccator.

Determination of Boiling Points.—Boiling points were determined by distillation of the purified compounds. Thermal dehydration prevented such determinations over a complete range of pressures with members of the series higher than butyl.

Summary

1. The 1-*n*-alkylcyclohexanols have been characterized as a series through preparation and study of four new members, together with additional characterization of two members previously reported. New phenyl urethans have been prepared from five of these.

2. Densities and refractive indices of these alcohols have been plotted; the former have been compared graphically to densities of other related series; and the peculiar forms of these graphs have been discussed.

BATON ROUGE, LA. RECEIVED JULY 15, 1946

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[5] Zelinski and Gutt, *Ber.*, **34**, 3950–3952 (1901).

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

The Kinetics of the Alkaline Dehydrochlorination of the Benzene Hexachloride Isomers. The Mechanism of Second-Order Elimination Reactions[1,2]

BY STANLEY J. CRISTOL[2a]

The existence of the four known geometric isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) was first demonstrated by the work of van der Linden.[3] The group working in the laboratories of the Imperial Chemical Industries under Slade[4] has recently confirmed the findings of van der Linden and has reported various physical and chemical properties of the several isomers. Interest in the compounds arises from the fact that the *gamma* isomer of benzene hexachloride is a very effective insecticide.[4]

The problem of the structure of the various isomers of benzene hexachloride is similar to that

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[1] The work described in this paper was part of a program conducted under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

[2] This paper was presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 8–12, 1946.

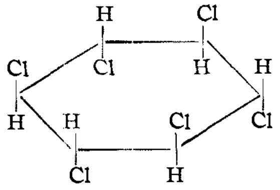
[2a] Present address: Department of Chemistry, University of Colorado.

[3] van der Linden, *Ber.*, **45**, 236 (1912).

[4] Slade, *Chem. Ind.*, 314 (1945).

of the inositols,[5] where there are eight[6] possible geometric isomers, one of which may exist in a *d* and an *l* form.

Of the four isomers, which have been given the designations *alpha*, *beta*, *gamma* and *delta*, only one, the *beta* isomer, is of established configuration. X-Ray data[7] have shown that the *beta* isomer is the one in which all adjacent chlorine (or hydrogen) atoms are *trans* to each other (see structural formula).



β-benzene hexachloride

The structures of the *alpha*, *gamma*, and *delta* isomers have not been established. It has been pointed out by Slade[4] that only four strainless forms of benzene hexachloride may be constructed when the cyclohexane ring is in the *trans* or "chair" form. Of these permitted forms, one may exist in optically active forms; the others are *meso*. Slade has assigned each of these structures to a given isomer, but, except in the case of the *beta* isomer, satisfactory reasons for the assignment have not been indicated.

The reaction studied in the present work is the elimination of three moles of hydrogen chloride from the benzene hexachloride isomers according to equation (1)

$$C_6H_6Cl_6 + 3\,OH^- \longrightarrow C_6H_3Cl_3 + 3\,Cl^- + 3\,H_2O \quad (1)$$

van der Linden has shown that the *alpha*, *beta* and *gamma* isomers give slightly different ratios of 1,2,4-, 1,2,3- and 1,3,5-trichlorobenzenes in this reaction, but that in each case the 1,2,4-isomer greatly predominates. The present work was restricted to a study of the kinetics of the elimination; the products of the reaction were not reinvestigated.

Measurement of Reaction Rates.—The following procedure was used to follow the rates of the reaction of the various isomers with sodium hydroxide: A solution in 76.1% (by wt.) ethanol containing the hexachloride, about 0.001 *M*, was prepared at 20.11° by dissolving the required weight of the hexachloride in 92.6% (by wt.) ethanol in a 500-ml. volumetric flask, adding 75 ml. of water, equilibrating the solution in a thermostat, and then adding, by means of a pipet, a measured volume of standard ethanolic sodium hydroxide brought to temperature before mixing. The solution was then made up to volume, mixed well by shaking, and replaced in the thermostat. Temperature control was constant within ±0.03°. During the course of a run seven to nine 50.0-ml. aliquot samples were transferred to a glass-stoppered Erlenmeyer flask at bath temperature and the reaction was then stopped by the addition of about 50 ml. of 1.5 *N* nitric acid. The solutions were then treated with 5.00 ml. of standard 0.03 *N* silver nitrate solution, and the precipitate was coagulated by vigorous shaking with nitrobenzene. The excess silver ion was titrated with standard 0.02 *N* ammonium thiocyanate with the use of a microburet and ferric sulfate as indicator in the customary Volhard procedure. The experiments were carried out in a room held at 20° to minimize errors arising during the period of transfer, which was approximately one and one-half minutes. Relatively dilute solutions were necessary to slow the reactions to measurable rates and, for the same reason, 76% ethanol was used as solvent rather than stronger ethanol.[8]

Mechanism of Second-Order Elimination Reactions.—Figure 1 is a plot of the amount of chloride ion produced (assuming that 3 moles of chloride are eliminated per mole of benzene hexachloride) *versus* time. It may be seen that, whereas under similar conditions the *alpha*, *gamma*, and *delta* isomers react very rapidly (50% of the hydrogen chloride eliminated in thirty to seventy minutes) the *beta* isomer is completely inert, no hydrogen chloride being eliminated in seventy-two hours at 20°.

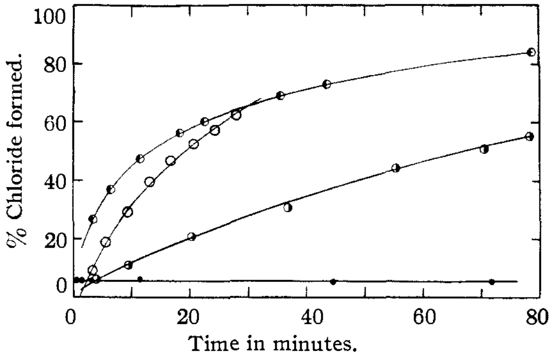
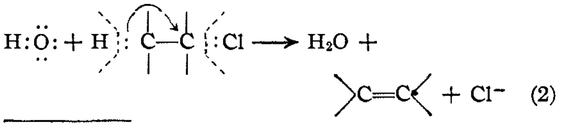


Fig. 1.—Rate of dehydrochlorination of benzene hexachloride isomers: (Halide) = 0.001 *M*, (OH^-) = 0.005 *M*: O, alpha; ●, beta (time in hours); ◑, gamma; ◐ delta.

This observation demonstrates the steric requirement of *trans* elimination in the removal of hydrogen halide in a second-order E_2-type reaction. Hughes and Ingold[8] have represented this type of reaction according to equation (2)



$$H{:}\ddot{\underset{..}{O}}{:} + H{:}\,C\!-\!C\,{:}Cl \longrightarrow H_2O + \;>C{=}C< + Cl^- \quad (2)$$

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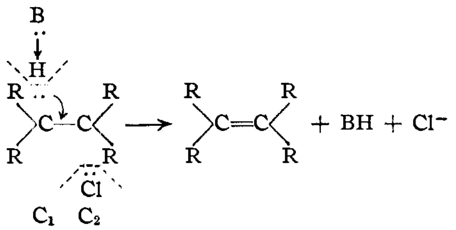
[5] Shriner, Adams and Marvel in Gilman, "Organic Chemistry," vol. 1, p. 251, John Wiley and Sons, New York, N. Y., 1938.

[6] This assumes that the cyclohexane ring may be represented by a planar ring. Although this concept is not strictly valid, it is true that, without exception, the maximum number of isomers found in six-ring systems may be calculated on the basis of a planar ring (see ref. 5, pp. 237–239).

[7] Hendricks and Bilicke, THIS JOURNAL, **48**, 3007 (1926); Dickinson and Bilicke, *ibid.*, **50**, 764 (1928).

[8] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

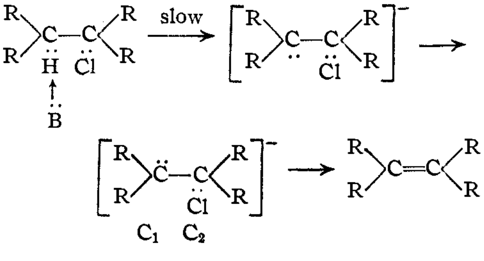
without reference to its steric course. If free rotation around the carbon–carbon bond is not permitted, as in the cyclohexane ring, and if one assumes that normal second-order reactions always go with Walden inversion,[9] then *trans* elimination may be pictured as follows



(3)

The base attacks the hydrogen atom on C_1, displacing the electron pair forming the carbon–hydrogen bond, which may invert C_2 directly, forming the C_1—C_2 double bond and displacing chloride ion. This may be considered as a smooth simultaneous reaction, the entire process occurring essentially together so that removal of the proton by base is greatly facilitated by the departing chloride ion. This picture of *trans* elimination is analogous to that of the second-order nucleophilic displacement reaction with the entire process going smoothly through the transition state.

cis Elimination cannot go smoothly, however, since C_2 cannot be directly inverted by the electron pair of the carbon-hydrogen bond undergoing rupture. Instead a possible reaction path for *cis* elimination involves removal of the proton by base without aid from the chlorine atom, except for its inductive aid, leaving a carbanion, which then may racemize rapidly with inversion of C_1, followed by displacement of chloride ion from C_2, as pictured in equation (4)



(4)

This process clearly may not go smoothly, since the chlorine atom may not facilitate the removal of the proton by simultaneous departure.

These considerations suggest that a *trans* elimination process should be greatly favored over *cis* elimination and that this effect might be observed when the C_1—C_2 bond is not free to rotate. Inspection of the structural formula for β-benzene hexachloride discloses that there are no hydrogen atoms *trans* to adjacent chlorine atoms; hence only the less-favored *cis* elimination is possible. As all the other isomers must have configurations in which one or more of the carbon atoms are inverted as compared with the *beta* form,[10] it is evident that each must have at least one pair of hydrogen atoms adjacent and *trans* to chlorine atoms; hence *trans* elimination is possible in these cases. Since these isomers react rapidly with base (see Fig. 1), whereas the *beta* isomer is almost inert at 20°, the results establish conclusively the steric requirement of *trans* elimination in the E_2 type at moderate temperatures. As the *beta* isomer does react with base in refluxing ethanol,[3] and very slowly at 20°, it is apparent that *cis* elimination may occur when *trans* elimination is impossible.

The conclusions reached in the present work are similar to those reached by Hückel[11] from a study of the reaction of sodium ethoxide upon *l*-menthyl chloride and other similar compounds. In that paper, which is outstanding for its definition of the steric requirements of first- and second-order elimination, as well as intramolecular elimination, the basis for the assignment of *trans* elimination in the E_2 reaction rests upon a violation of the Saytzeff rule; the results on the benzene hexachloride isomers are independent of this rule and are therefore more clear-cut. Consideration of Chavanne's[12] work on the dichloroethylenes leads to similar conclusions.[11]

Hückel has suggested that *trans* elimination—that is, the preference of one direction for the attack of the alcoholate ion—rests upon the electrostatic repulsion which would be involved between the alcoholate ion and the negative end of the dipole of the carbon–chlorine bond if the alcoholate ion were to approach from the side on which the chorine is bonded. Although it is likely that the steric and electrostatic properties of the neighboring chlorine atom are of considerable importance in the reaction, Hückel's mechanism does not consider the necessity for carbon C_2 to undergo Walden inversion by the electron pair of the C_1–H bond, which seems to us to be the essential characteristic of and requirement for *trans* elimination.

The process outlined for *trans* elimination of hydrogen halide is similar to that proposed by Young and co-workers[13] for the elimination of bromine from olefin dibromides with iodide ion or with zinc.

Reaction of α-, δ-, and γ-Benzene Hexachlorides.—The *alpha*, *gamma*, and *delta* isomers of benzene hexachloride lose three moles of hydrogen chloride to base, according to the following equations

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(9) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 181.

(10) In the structures proposed by Slade,[4] the positions of the chlorine atoms above and below the "plane" of the cyclohexane ring are as follows: *alpha*, $\frac{1,2,5}{3,4,6}$; *beta*, $\frac{1,3,5}{2,4,6}$; *gamma*, $\frac{1,2,3,5}{4,6}$; *delta*, $\frac{1,2,3}{4,5,6}$.

(11) Hückel, Tappe and Legutke, *Ann.*, **543**, 191 (1940).

(12) Chavanne, *Bull. soc. chim. Belg.*, **26**, 287 (1912).

(13) Winstein, Pressman and Young, THIS JOURNAL, **61**, 1645 (1939); Young, Cristol and Skei, *ibid.*, **65**, 2099 (1943).

$$C_6H_6Cl_6 + OH^- \xrightarrow{k_1} C_6H_5Cl_5 + Cl^- + H_2O \quad (5a)$$

$$C_6H_5Cl_5 + OH^- \xrightarrow{k_2} C_6H_4Cl_4 + Cl^- + H_2O \quad (5b)$$

$$C_6H_4Cl_4 + OH^- \xrightarrow{k_3} C_6H_3Cl_3 + Cl^- + H_2O \quad (5c)$$

It is theoretically possible for any of these steps to be slow and rate-determining. Analysis of the rate equation for the second-order reaction represented by (5a) as the rate-determining step–first-order with respect to both hydroxide ion and hexachloride concentration—and followed by rapid steps (5b) and (5c) gives the following equation connecting initial hexachloride concentration a, initial hydroxide concentration b, fraction φ of hexachloride reacted, and time, t.

$$\mathrm{d} \log \frac{1 - 3a\varphi/b}{1 - \varphi} \Big/ \mathrm{d}t = \frac{b - 3a}{2.303} k_1 \qquad (6)$$

If these kinetics hold, then a plot of the values of $\log (1 - 3a\varphi/b)/(1 - \varphi)$ corresponding to the various samples of a run against corresponding values of time, t, should give a straight line. The plot of one run with the *alpha* isomer and of one with the *gamma* isomer is shown in Fig. 2. Excellent correspondence to the straight-line relationship was found, and the lines intersect the time axis at zero time within the uncertainty of its determination. The slope of the line multiplied by the value of $2.303/(b - 3a)$ for the run gives the rate constant k_1. This method for calculating the rate constant does not give undue weight to the first analysis made, nor is the value of k_1 affected by uncertainties involved in the time taken as the start of the reaction. Values for k_1 are given in Table I.

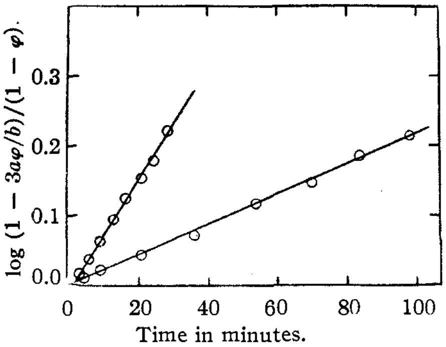

Fig. 2.—Treatment of data for rate constants for alpha-(upper line) and gamma-(lower line) benzene hexachloride isomers: (Halide) = 0.001 M; (OH$^-$) = 0.005 M.

The data obtained thus suggest that the reaction path for the *alpha* and *gamma* isomers involves the slow, rate-determining second-order removal of one mole of hydrogen chloride by *trans* elimination (represented by step 5a), followed by relatively rapid removal of the second and third moles of hydrogen chloride (represented by 5b and 5c). This reaction path is in agreement with the results of van der Linden,[3] who was unable to eliminate hydrogen chloride in a stepwise fashion when α-, β-, or γ-benzene hexachloride was treated with one mole of base; instead part of the material lost three moles of base, and the remainder of the starting material was unchanged.

TABLE I

DATA AND REACTION-RATE CONSTANTS FOR DEHYDROCHLORINATION OF BENZENE HEXACHLORIDE ISOMERS WITH SODIUM HYDROXIDE IN 76.1% ETHANOL AT 20.11°

Isomer	[Halide], a, M	[NaOH], b, M	Rate constant, k_1, liters/sec./mole	Rate constant, k_2, liters/sec./mole
Alpha	0.000760	0.00471	0.167	...
	.000980	.00471	.172	...
Beta	.000868	.00471	Inert[a]	...
	.000838	.03782	3×10^{-6}[b]	...
Gamma	.000972	.00471	0.0457	...
	.000939	.00471	.0435	...
Delta	.001007	.00471	Fast	0.112
	.001010	.00471	Fast	.106
	.000948	.00471	Fast	.113

[a] No measurable reaction in seventy-two hours.
[b] Eleven per cent. reacted in three hundred and seventy-two hours.

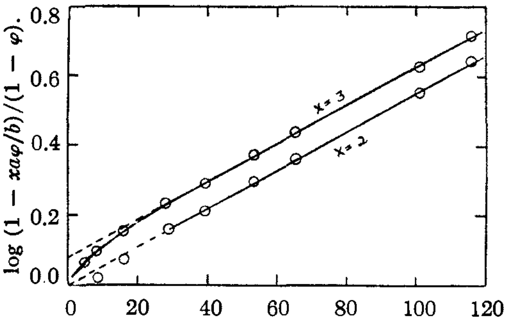

Fig. 3.—Treatment of data for rate constant of delta-benzene hexachloride: upper curve calculated for step (5a) slow; lower calculated for step (5b) slow.

The *delta* isomer did not give the same kinetics as the other two isomers. When a plot was made of values of $\log (1 - 3a\varphi/b)/(1 - \varphi)$ against corresponding values of time, the initial portion was a curve with a large slope which then flattened out to a straight line (see upper curve of Fig. 3). When the linear portion of the curve is extrapolated backward, the abscissa is not intersected at zero time, but instead the ordinate axis is intercepted at a value equivalent to 30–35% reaction. This suggested that in the case of the *delta* isomer step (5a) is fast compared with (5b) and that the slope of the line is a measure of k_2 rather than k_1. On the assumption, as a first approximation, that step (5a) is instantaneous, the data were recalculated using the second-order equation for step (5b)

$$\mathrm{d} \log \frac{1 - 2a\varphi'/b'}{1 - \varphi'} \Big/ \mathrm{d}t = \frac{b' - 2a}{2.303} k_2 \qquad (7)$$

where b' and φ' were corrected for the initial step (5a). The extrapolated line thus obtained (lower curve of Fig. 3) is parallel to the upper line, but 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.

BELTSVILLE, MARYLAND RECEIVED AUGUST 28, 1946

[COMMUNICATION NO. 1097 FROM THE KODAK RESEARCH LABORATORIES]

Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. II. The Evolution of Carbon Dioxide from Uronic Acids and Polyuronides[1]

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]

Harris[7] 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]

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[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* **24**, 13 (1940).