The crude acidic product was purified by filtering through a 1-inch layer of anhydrous potassium carbonate and was fractionated to give a neutral product.

Cyclohexylamine Salt of C_8 Chlorofluorocarboxylic Acid. A solution of 24 grams (0.05 mole) of C_8 chlorofluorocarboxylic acid in 25 ml. of ethvl ether was added to 5 grams (0.05 mole) of cyclohexylamine in 15 ml. of ethyl ether. The solvent was evaporated and the remaining solid was recrystallized from cyclohexane to give 14 grams (48%) of white solid.

Decarboxylation of C_8 Chlorofluorocarboxylic Acid. A 27-gram charge of C_8 chlorofluorocarboxylic acid was neutralized with sodium hydroxide, concentrated under a stream of nitrogen, and dried at 105 °C. in a vacuum oven. A 10.7-gram (0.0214 mole) sample of the dry sodium salt was heated in a small distillation apparatus. A liquid product (8.3 grams) distilled at ca. 160 °C. as the pot temperature rose from 160° to 300 °C. and gave a positive unsaturation test with aqueous potassium permanganate. A redistilled portion had a molar refractivity confirming the structure $CF_2Cl(CFClCF_2)_2CF{=}CF_2$. $CF_2Cl(CFClCF_2)_2CCl{=}CF_2$ is indicated by the presence of fluoride in the pyrolysis residue.

APPLICATIONS

The chlorofluorocarboxylic acids are resistant to thermal decomposition and are very stable toward strong acids, bases, and oxidants. This stability indicates that the acids or their derivatives will be excellent surfactants in some environments where hydrocarbon surfactants fail.

The large number of derivatives of the chlorofluorocarboxylic acids potentially available should provide new classes of materials useful as hydraulic fluids, lubricants, plasticizers, and for other applications where a nonflammable, stable material is required.

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Pyrolytic Degradation Products of Cellulose

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This work represents the first phase of a study designed to elucidate the nature of the pyrolytic degradation of cellulose and the mechanism by which the reaction proceeds, in order to understand better the larger problem of the flame and glow resistance of cellulosic materials. This is of high priority in the Department of Defense for clothing purposes. A knowledge of the degradation of cellulose may ultimately give a solution of the problem.

The decomposition of the cellulose polymer in the solid state at temperatures greater than 250 °C. has been studied extensively (*3, 4, 6, 7, 9–11, 20–22, 25–28*). The products of decomposition have usually been divided into three main categories (*7*).

1. **Gas Phase Products.** This phase consists of carbon monoxide, carbon dioxide, methane, and hydrogen, usually constituting 20 to 25% of the total products of pyrolysis (*3, 6, 7, 20, 25, 26*).
2. **Solid Phase Products.** A carbonaceous residue or char is produced in approximately 15% yield (*9, 11, 17, 20, 26*).
3. **Liquid Phase Products.** An aqueous distillate (the pyrolyzate) is obtained, consisting of tars, water, and volatiles condensable at 0° C., and comprising approximately 65% of the total products. According to Coppick (*7*), the aqueous distillate obtained from the pyrolysis or controlled combustion of cellulose contains the tarry primary dissociation products which appear to be critically related to the flaming characteristics of fabrics.

At elevated temperatures then, cellulose decomposes to form considerable amounts of flammable products. It has been suggested that when a cellulosic material burns, the volatile decomposition products arising from pyrolytic decomposition of the cellulose actually cause flaming (*4*).

A mechanistic theory of the pyrolytic degradation of cellulose (*21*) suggests that the reaction proceeds through a common intermediate, 1,6-anhydro-β-D-glucopyranose (levoglucosan), resulting from initial depolymerization. Levoglucosan is then thought to participate in two competing reactions: repolymerization in a dehydration process to form char and decomposition to volatile, flammable products. The degradation reactions of cellulose at temperatures of pyrolysis are not clearly understood at present, and the chemical literature lacks information and data as to the nature of the products in the cellulose pyrolyzate.

Gillet and Urlings (*9–11*) have made a thorough investigation of the pyrolysis of wood and cellulose. True pyrolysis was found to begin at 250° C. and adjudged complete at 360° C. Glyoxal and glycolic aldehyde were suggested as products from the pyrolysis of cellulose, but no experimental data were presented. Coppick (*7*) reports the existence of hydroxyl, methylene, methyl, carbonyl, ethylene, and ester groups in the cellulose pyrolyzate on the basis of infrared analysis. In 1918 Pictet and Sarasin (*22*) identified levoglucosan as a product in high yield from the destructive distillation of cotton cellulose. Tischenko and Fedorischev (*28*) decomposed cellulose in the dry state in an autoclave and reported that the products consist largely of levoglucosan.

The work reported here is primarily concerned with the exact nature of the tarry products present in the cellulose pyrolyzate. A detailed knowledge of these critical compounds would appear basic to an understanding of the complex process of pyrolytic degradation, as it proceeds in the case of cellulose. Quantitative data are presented on the production of char and pyrolyzate as gross decomposition products. Data on the pyrolyzate constituents are reported and new products identified.

EXPERIMENTAL

Samples. The cellulose studied was an unmodified cotton fabric. The work sample selected was a desized and alkali-scoured, cotton oxford fabric (6 ounces per square yard) of 80 × 80 construction.

The pyrolysis equipment consisted of a demountable combustion tube and train. A thick-walled borosilicate glass tube 2.8 cm. in inside diameter and 25.4 cm. long constituted the pyrolysis chamber, which was heated electrically to the desired temperature by a Nichrome winding which enclosed the entire length of the tube. One end of the pyrolysis chamber was open to the air, while the efflux end was connected by a ground-glass joint lubricated with graphite through an adapter to two traps placed in series and maintained at 0° C. The efflux tube leading from the second cold trap contained a glass wool filter. The apparatus was then connected through a filter flask to a water aspirator. A sample mounted on a hollow, stainless steel tube could be introduced into the chamber in such a manner as to preclude any contact with the walls. Temperatures in the pyrolysis chamber were estimated by iron-constantan thermocouples.

Samples of cotton fabric were pyrolyzed in air at 350° to 375° C. The decomposition products were moved into the cold traps by an air stream at flow rates greater than 500 cc. per minute. Products condensable at 0° C. were trapped as an aqueous distillate consisting of tars and water. The volatile gases were allowed to escape. Weights were obtained on the aqueous distillate (pyrolyzate) produced and the carbonaceous residue (char) remaining in the pyrolysis chamber. The pyrolyzate was then treated with excess water, which dissolved most of the tar to yield an aqueous fraction. A small water-insoluble residue remained, which was soluble in acetone or ethyl alcohol.

Chromatographic Analysis. Paper partition chromatography was used to determine the levoglucosan and organic acid components. The capillary descent technique with *Whatman* No. 1 paper as the support was used throughout.

Levoglucosan Determination. A qualitative analysis was performed using a modified Partridge solvent system consisting of 5:4:1, 1-butanol, water, and ethyl alcohol to develop the chromatograms. Then the developed chromatogram was dried and sprayed with a 1% aqueous solution of potassium permanganate containing 2% sodium carbonate (*19*) to reveal spot locations. Quantitative estimation was accomplished by an indirect method, based on the fact that levoglucosan is hydrolyzed in acid media to D-glucose. Aliquot portions of the aqueous fractions were hydrolyzed by refluxing 1 hour with dilute sulfuric acid. After hydrolysis the acid was removed either by precipitation as barium sulfate or by a weak anion exchange resin (Amberlite IR-4B, Rohm & Haas, Philadelphia, Pa.) in the hydroxyl form. The glucose content of the deacidified hydrolyzates was then determined by quantitative paper chromatography (*23*). The amount of levoglucosan originally present could thus be accurately estimated.

Organic Acid Determination. The acid components of the aqueous fraction were removed by an ion exchange resin column (Amberlite IRA-400, Rohm & Haas, Philadelphia, Pa.) in the hydroxyl or carbonate form. The free acids were recovered by elution from the column with dilute sulfuric acid. These eluates were then analyzed by paper chromatography for volatile and nonvolatile organic acids.

Volatile acids were determined as described by Brown (*1*); the acids were converted to their sodium salts and samples of the unknowns run against the knowns. The solvent system was 4:1:5, 1-butanol-ethyl alcohol-3*N* ammonia, and the spray reagent was bromothymol blue adjusted to pH 7.6.

Nonvolatile Acids. The free acids were applied directly to the paper, according to the method of Buch, Montgomery, and Porter (*2*). The solvent system was 1-pentanol-5*M* aqueous formic acid in a 1 to 1 ratio and the spray reagent was a 0.04% solution of bromophenol blue in 95% ethyl alcohol. Prior to development, the chromatograms were equilibrated with the vapor from the aqueous phase of the solvent system. When the dry chromatogram was sprayed, the acid components were revealed as yellow spots against a blue background.

Aldehyde and Ketone Determination. Qualitative tests were made using Schiff's reagent and Fehling's solution on the aqueous solutions of the pyrolyzates. Crystalline derivatives of aldehyde products were obtained by dimedone (5,5-dimethylcyclohexane-1,3-dione) precipitation in 50% ethyl alcohol solutions. Derivatives were recrystallized from aqueous ethyl alcohol. Carbon and hydrogen and molecular weight determinations were obtained on the derivatives from commercial microanalytical laboratories. Melting point data were obtained and the ultraviolet spectra of the compounds were measured in 95% ethyl alcohol at a uniform concentration of 12 mg. per liter, with a Model DU Beckman spectrophotometer.

p-Nitrophenylhydrazine derivatives of the unknown products were prepared and melting points determined.

The 2,4-dinitrophenylhydrazones of the unknown carbonyl products were prepared by techniques described by Iddles and his coworkers (*14*, *15*). Preliminary determination was accomplished by adsorption chromatography, using kieselguhr-bentonite columns (*8*).

All experimental melting point data are uncorrected.

RESULTS AND DISCUSSION

Quantitative estimates of the yield of the gross decomposition products, except the volatile gases, were made on a series of fabric samples. These samples were pyrolyzed at 350° to 375° C. in a limited air supply. The pyrolyzates produced were determined by weight differences, whereas the incident chars were measured by direct weighing. The results are presented in Table I.

Table I. Pyrolyzate-Char Data on 6-Ounce Cotton Oxford Cloth

Sample Wt., G.	Pyrolyzate Wt., G.	Pyrolyzate, %	Char Wt., G.	Char, %
7.25	4.50	62.1	0.94	13.0
7.22	4.80	66.5	0.76	10.5
7.24	4.90	67.7	0.82	11.3
7.39	5.32	72.0	1.36	18.4
7.45	5.01	67.2	0.62	8.3
7.25	4.94	68.1	0.80	11.0
7.26	5.22	71.9	0.71	9.8
7.20	4.89	67.9	1.01	14.0
7.15	4.86	70.0	0.87	12.2

Based on the data in Table I and employing the arithmetic mean, the average pyrolyzate yield is 68.1% and the average char yield is 12.1%. Carbon and hydrogen determination showed 85.42% carbon and 3.38% hydrogen content, as compared with 85.28% carbon and 3.40% hydrogen found by Coppick (*7*) for the pyrolytic chars of an untreated cotton fabric.

The first step in the pyrolytic degradation of cellulose appears to be the formation of the β-glucose anhydride, levoglucosan (*21*). Therefore the pyrolyzate was first analyzed for this compound. An aqueous solution of authentic levoglucosan and aqueous solutions of the cellulose pyrolyzate were examined qualitatively by paper chromatography. The known and unknown solutions, run simultaneously on the same chromatograms, gave rise to prominent spots of the same R_f value.

Levoglucosan was quantitatively determined as D-glucose (Table II). One mole of levoglucosan (molecular weight 162) produces 1 mole of D-glucose (molecular weight 180) on acid hydrolysis.

Table II. Levoglucosan in Cellulose Pyrolyzate

Sample	Pyrolyzate, G.	D-Glucose, Mg.	Levoglucosan, Calcd. Mg.	Levoglucosan, Calcd. %
IV	4.90	609	548	11.2
V	5.32	746	672	12.6
VI	5.01	535	482	9.6
VII	...	743	669	...
VIII	4.94	768	691	14.0
IX	5.22	877	790	15.1

Under the stated conditions of pyrolysis levoglucosan is confirmed as a major product, constituting 12.5% of the total pyrolyzate based on the quantitative data obtained.

Aqueous solutions of the pyrolyzates proved strongly reducing on testing with Fehling's solution and Tollen's reagent. A positive test for the presence of aldehydes was obtained with Schiff's reagent. Crystalline derivatives of the aldehyde products were obtained on treatment of the unknown solutions with excess 5,5-dimethylcyclohexane-1,3-dione (dimedone) in 50% ethyl alcohol solution. Two derivatives, I (melting point 190° C.) and II (melting point 230° C.), were thus found. I was readily prepared, coming down within a few minutes at room temperature as a yellow solid which yielded a flaky, white, crystalline compound melting at 189.5-91° C. on recrystallization from 75% ethyl alcohol. II was obtained from the mother liquor of I, after 120 hours under refrigeration. Recrystallization was effected from 85% ethyl alcohol to yield white needles melting at 229.3-30.3° C.

The identification of I and II posed unexpected problems and revealed the existence of serious defects in the literature on the dimedone derivatives of aldehydes. The melting point data obtained on I indicated formaldehyde, glyoxal, or acrolein as the aldehyde present. A standard work on qualitative organic analysis (*12*) gave a single dimedone derivative each for glyoxal, formaldehyde, and acrolein with melting points of 186°, 189°, and 192° C, respectively. Authentic derivatives of formaldehyde and glyoxal were prepared using the commercially available compounds. In the case of glyoxal this was a 30% aqueous solution, technical (Eastman). Data were then secured on melting points, mixed melting points, and carbon and hydrogen content for the known and unknown compounds (Table III).

Table III. Physical Data on Dimedone Derivatives

Derivative	Melting Point, °C. Lit. (*12*)	Melting Point, °C. Found	C,% Calcd.	C,% Found	H, % Calcd.	H, % Found	Mol.Wt., Calcd.
I		189.5-191		69.9		7.9	309[a]
Formaldehyde	189	190-191	69.8		8.3		292
Glyoxal	186	190-191.5	67.5	70.0	7.6	8.1	320
Formaldehyde-glyoxal[b]		188.5-192					
I-Glyoxal[b]		187.5-190					
I-Formaldehyde[b]		190-191.5					
Acrolein	192		71.6		8.2		318

[a] Exptl. data. MW by ebullioscopic method.
[b] 1: 1 mixtures for mixed melts.

The data in Table III indicated either formaldehyde or glyoxal, but no clear distinction could be made in view of the data on the authentic derivatives. The striking similarity between formaldimethone and the glyoxal derivative prepared in the laboratory led to a careful scrutiny of the glyoxal sample. It became apparent that no glyoxal derivative had been prepared and that the "authentic" glyoxaldimethone was in fact formaldimethone, as substantial formaldehyde impurity was shown to be present in the commercial glyoxal preparation.

The ultraviolet spectra of the dimedone derivatives prepared from reagent formaldehyde and 15% glyoxal were compared with the spectral curve obtained for compound I. The curves, shown in Figure 1, indicate the three derivatives to be identical—i.e., formaldimethone—and substantiate the conclusion that the glyoxal reagent was contaminated with formaldehyde. This result and the data in Table III identify I as formaldimethone, thus establishing formaldehyde as a pyrolysis product.

In the case of unknown compound II, carbon, hydrogen, and melting point data indicated a derivative similar to that reported by Rezek (*24*) as glyoxaltetramethone. The data on the unknown, with literature data on other derivatives, are shown in Table IV.

Attempts at molecular weight determination by both Rast and Signer (*5*) methods proved unsuccessful, in that no satisfactory solvent could be found. The negative results indicated a compound of high molecular weight. In Figure 2 the ultraviolet spectral curves of formaldimethone, compound II, and dimedone reagent are shown. The wave length of maximum absorbancy for compound II is not greatly shifted from the values found in the case of formal-

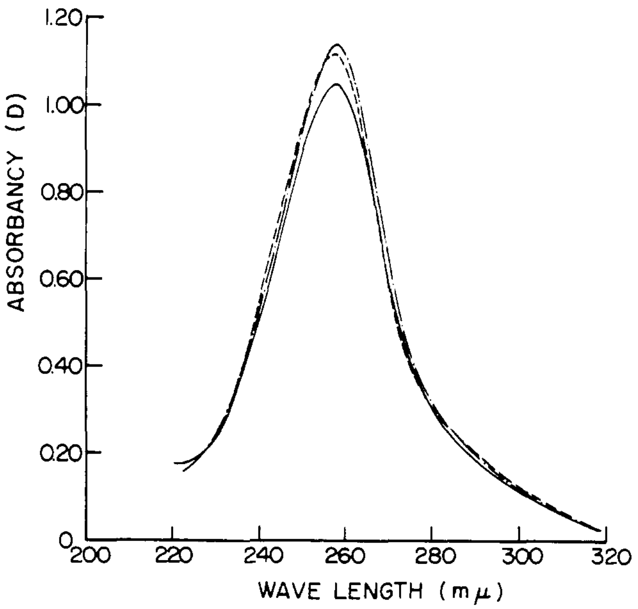

Figure 1. Ultraviolet absorption curves for dimedone derivatives
——— Dimedone derivative obtained from 15% glyoxal solution
- - - - Dimedone derivative I
······· Formaldimethone

Table IV. Physical Data on Dimedone Derivatives

Derivatives	Melting Point Data			
	°C.	Lit. ref.	C, %	H, %
II	229.3-230.3[a]		70.7[a]	7.7[a]
Glyoxaldimethone	228	(*13, 16*)	...	...
Glyoxaltetramethone	235-236	(*24*)	70.1	8.0
Glyoxal (mono)	186	(*12, 29*)	67.5	7.6
Cinnamaldehyde	219	(*12*)	76.1	7.7
2,4-Dihydroxybenzaldehyde	226	(*12*)	68.9	7.1

[a]Experimental data.

dimethone and dimedone. Therefore the same group is probably responsible for absorption in each case. The differences exhibited by the curves with respect to maximum absorbancy appear related to the molecular weights of the compounds. The height of curve III could indicate a compound of three to four times the molecular weight of the material represented by curve I. As dimedone represented by curve I has a molecular weight of 140, this would give the unknown compound a molecular weight of 500 to 600. Glyoxaltetramethone has a molecular weight of 582.

The data in Table IV indicate II to be glyoxaltetramethone and show that Klein and Linser's glyoxal derivative (*16*) melting at 228° C. is probably the tetramethone and not the dimethone.

Table V. Melting Point, Carbon, Hydrogen, and Molecular Weight of Known and Unknown Derivatives

Derivative	Melting Point, °C.	Found, %		Mol. Wt.
		C	H	
I	189.5-191	69.87	7.89	309
Formaldimethone	189	69.83	8.27	292
II	229.3-230.3	70.67	7.73	...
Glyoxaltetramethone	228 235-236	70.08	7.96	582

The data available on I and II are summarized in Table V and compared with literature data on formaldimethone and glyoxaltetramethone.

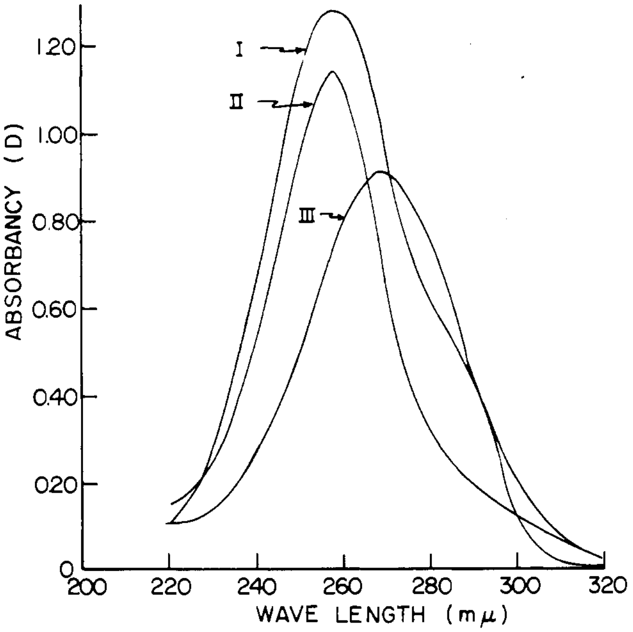

Figure 2. Ultraviolet absorption curves for dimedone and dimedone derivatives

I. Dimedone reagent
II. Formaldimethone
III. Dimedone derivative II

Compound II has been identified as glyoxaltetramethone, and glyoxal is thus believed to have been established as a pyrolysis product.

The status of the dimedone derivatives of glyoxal is not clear in the literature; this subject will be fully dealt with in a separate paper in an attempt to resolve the confusion.

Derivatives of the unknown carbonyls were also prepared by precipitation as the corresponding *p*-nitrophenylhydrazones (*12*). A red, crystalline material, assumed to be a complex mixture, was obtained. The unknown precipitate was partially soluble in ethyl alcohol in the cold, but a substantial alcohol-insoluble residue remained. The formaldehyde derivative is soluble in alcohol, whereas the glyoxal derivative of *p*-nitrophenylhydrazine is not. Melting point data and other information on the unknown compounds are compared in Table VI with comparable literature (*18*) and laboratory data on the formaldehyde and glyoxal derivatives of *p*-nitrophenylhydrazine. Unknown II is the alcohol-insoluble component of the *p*-nitrophenylhydrazine derivative mixture prepared from the unknown. The data in Table VI strongly suggest glyoxal as present in the pyrolyzate.

Table VI. Properties of *p*-Nitrophenylhydrazones

Derivative	Description	M.P., °C.	Color in Alcoholic KOH(*18*)
Unknown I[a]	Red-brown crystals	258-261 (d)	Deep purple
Unknown II[a]	Red-brown crystals	288-290 (d)	Deep blue
Glyoxal[a]	Dull red crystals	290.5-293.5 (d)	Deep purple-blue
Formaldehyde[a]	Yellow-brown crystals	177-178.5	Deep red-brown
Glyoxal[b]	Reddish crystals	311 (d) 302 (d)	Deep blue
Formaldehyde[b]	Yellow needles	181-182	...

[a]Experimental data.
[b]Literature data.

The cellulose pyrolyzate was observed to be weakly acidic, with pH in the range of 2.4 to 2.8. Aqueous solutions prepared therefrom were accordingly analyzed by paper partition chromatography to discover the acid components present. Volatile acid products were determined by using a method described by Brown (*1*). The results obtained are shown as R_f values in Table VII, where they are compared with literature values.

Table VII. R_f Values of Volatile Acid Ions

Ion	R_f
Unknown	0.15
Formate	0.15
Formate[a]	0.14
Acetate[a]	0.16
Propionate	0.26

[a]Literature data (*1*).

Only one unknown acid spot was indicated and from the data was tentatively identified as formic acid. Subsequently it was found that the possibility of acetic acid could not be ruled out. Tebbens and Torrey (*27*) found volatile acids present in the condensed gases obtained from the incineration of sawdust and wood. They noted the difficulty in separating acetic and formic acids by the chromatographic method and as a consequence reported their volatile acids as acetic and/or formic acid.

Determination of nonvolatile acid products was also undertaken by paper chromatographic techniques (*2*). The free acids were applied directly to the paper and chromatograms prepared. Identification was accomplished by a comparison of R_f values of the unknowns with R_f values obtained from the literature (*2*) and from known laboratory samples. The data (Table VIII) indicated the presence of

Table VIII. R_f and R_{lactic} Values of Known and Unknown Acids

Compound	R_f	R_{lactic}
Acid I	0.05	...
Acid II	0.17	...
Acid III	0.25	...
Acid IV	0.43	0.68
Glycolic acid[a]	0.44	0.69
Glycolic acid[b]	0.43	0.67
Acid V	0.63	1.00
Lactic acid[a]	0.64	1.00
Lactic acid[b]	0.62	1.00
Pyruvic acid[b]	0.65	1.03
Acid VI	0.76	1.20
Dilactic[a]	0.75	1.20

[a]Experimental data.
[b]Literature data.

six acid components. The unknowns found are designated by Roman numerals in order of their appearance on the chromatograms. On the basis of spot size and color intensity, acid IV was present in greatest quantity. The possibility of a keto acid such as pyruvic was checked by preparing the 2,4-dinitrophenylhydrazone of the unknown solution and testing the solubility of the derivative mixture in dilute sodium bicarbonate. The unknown hydrazones showed no solubility, indicating that no keto acid was present. In Table IX the R_f values obtained by running known acids suggested by the data in Table VIII on the same chromatograms with the unknown acid mixture are shown.

Table IX. R_f Values of Known and Unknown Acids

Compound	R_f
Acid IV	0.44
Glycolic acid	0.45
Acid V	0.67
Lactic acid	0.67
Acid VI	0.80
Dilactic acid	0.80

These data enabled three of the unknown acid components to be identified:

IV. Glycolic acid
V. Lactic acid
VI. Dilactic acid

Unknown acid components I, II, and III have not as yet been identified.

The aqueous solutions of the pyrolyzate were observed to react easily with 2,4-dinitrophenylhydrazine to produce copious precipitates assumed to be a complex mixture. These precipitates have been determined quantitatively and by assuming a conservative average mole weight have been estimated to represent at least 15% of the pyrolysis products. By dimedone precipitation, generally accepted as quantitative (*30*), aldehydes were estimated to constitute no more than 3% of the pyrolysis products. Therefore the presence of carbonyl products other than glyoxal and formaldehyde was clearly indicated. A reddish-orange, crystalline compound was obtained on addition of unknown aqueous solution to a reagent solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid (*14, 15*). This material proved to be partially soluble in ethyl alcohol and chloroform. Preliminary experiments have been carried out on the chloroform-soluble derivatives using the chromatographic method of Elvidge and Whalley (*8*). Concentrated solutions of the derivatives were added directly onto kieselguhr-bentonite columns. The chromatograms were developed with chloroform solvent and the derivative mixture separated down the column as discrete and distinctively colored bands. At least five separate components have thus been revealed as present, but not identified. This work is being continued and will be fully reported in a subsequent publication.

Water is of course a major constituent of the cellulose pyrolyzate and has been estimated to constitute approximately 55% of the products, but no precise quantitative data have yet been obtained.

In Table X the chemical constitution of the cellulose pyrolyzate based on data presented in this paper is shown.

Table X. Cellulose Pyrolyzate Analysis

Compound	%
Levoglucosan	12.5
Carbonyl	Ca. 15.0
Formaldehyde	
Glyoxal	
Unknown I	
Unknown II	
Unknown III	
Acids	Ca. 7.5
Glycolic	
Lactic	
Dilactic	
Formic and/or acetic	
Unknown I	
Unknown II	
Unknown III	
Water	Ca. 55.0

SUMMARY

New data as to the nature of the tars and other compounds present in the aqueous distillate obtained from the pyrolysis of cotton cellulose have been obtained. Formaldehyde, glyoxal, formic and/or acetic acid, glycolic, lactic, and dilactic acids have been identified as new products. Levoglucosan has been confirmed as another product and quantitative data are presented. Ketones, as yet unidentified, are present as pyrolysis products. This investigation shows the cellulose pyrolyzate to be a complex mixture of organic acids, aldehydes, ketones, water, and levoglucosan representing 14 or more different compounds.

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Adsorption of Polyoxyethylated Detergents on Quartz

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Detergents prepared by condensation of ethylene oxide with an alkylphenol have attained widespread industrial usage. Because the mole ratio of ethylene oxide to phenol can be varied continuously above a value of 1, detergents with a wide range of properties may be prepared readily. Detergents of this type appear promising as additives to water injected into petroleum-producing formations to stimulate petroleum production. They have been investigated extensively for this specific application and for more general applications (*3, 4, 8–10*). The surface activities (*3, 8*), interfacial activities (*4, 8*), and critical micelle concentrations (*7*) of these detergents have been investigated recently.

Because of the extremely large surface areas of petroleum-producing formations, adsorption of detergents may cause their use to be economically prohibited. However, application of the chromatographic theory (*2, 11*) to detergent movement in such reservoirs indicates that adsorption may not be an insurmountable obstacle. The basic data for calculations according to the chromatographic theory, and of many other surface functions (*1*), are obtained as adsorption isotherms.

A comparative study of the adsorption of Igepal CO-710 on sand was made recently in an investigation of the mechanism of adsorption (*6*). No general study of the adsorption characteristics of series of polyoxyethylated detergents has been made, although the data would be of considerable practical value. The adsorption of six members of series based on nonylphenol and of three members of the octylphenol series has been investigated with a fine quartz powder. The data afford comparisons of the effects of composition on adsorption and allow generalizations of the behavior of similar detergents.

MATERIALS

The quartz powders were sized carefully by sedimentation from a crushed sample of commercial quartz. They were cleaned with hot chromic acid, washed extensively with deionized water, rinsed with reagent grade acetone, and dried at 110° C. The quartz powder used in most of the experiments contained particles ranging from about 0.5 to 4 microns and averaging 2 to 3 microns in diameter. A coarser powder used for a few of the experiments ranged from 3 to 13 microns and averaged about 8 microns in diameter. The surface areas of the powders were 3.9×10^4 and 1.1×10^4 sq. cm. per gram, respectively, as determined by the B.E.T. nitrogen-adsorption method.

The detergents were of the polyoxyethylated alkylphenol type and represented homologous series based on nonyl- and octylphenol in which the hydrophilic polyoxyethylene chains varied in length. Two of these series were described previously and were designated "Series II" and "Series III", respectively (*3*). Series II comprises Igepal CO-710 homologs (General Aniline and Film Corp., New York) and series III, Triton X-100 homologs (Rohm and Haas Co., Philadelphia). The various detergents are designated "NR" or "OR" to indicate nonyl- or octylphenol, and by a numeral to indicate mole ratio of ethylene oxide to phenol.

Thus, NR-20 is a detergent composed of 1 mole of nonylphenol and an average of 20 moles of ethylene oxide. Two of the detergents, NR-7.9 and NR-11.5, were molecularly distilled samples similar to those described by Mayhew