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The Controlled Thermal Decomposition of Cellulose Nitrate. II[1,2]

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When propellent type cellulose nitrate is ignited under reduced pressure, the white solid (a nitrated oxycellulose of low degree of polymerization), obtained as a major product in the pressure range of 2–3 mm., is succeeded by a liquid mixture as the pressure is raised. This mixture forms in maximum amount at *ca.* 30 mm. and decreases thereafter. It consists in the main of water, formic acid, formaldehyde and glyoxal. Other carbonyl products are present, among which two oxidation stages of glyceraldehyde (without carbon fragmentation) were detectable. All of these products (and acetic acid from the ethyl acetate solvent) were established by isolation procedures and quantitative assays were devised for the major products by means of which their formation as a function of increasing pressure was determined. The amounts of the major products (formic acid, formaldehyde and glyoxal) attain a maximum below 60 mm. pressure and then decrease to give a plateau in the pressure region of 200–500 mm., falling off rapidly thereafter with increasing pressure. Some hydrogen cyanide was found at all pressures investigated and may originate in residual solvent. Formaldehyde is formed in amounts directly proportional to the primary nitrate content of the material ignited, therefore the formaldehyde arises from this function. The amounts of formic acid, formaldehyde and glyoxal produced decrease inversely with the nitrogen content of the cellulose nitrates employed. The results are interpreted on the basis of homolytic bond scission.

The decomposition of cellulose nitrate (of a high degree of nitration), in the absence of chemical agents, can be divided into three distinct classes (excluding decompositions initiated by irradiation). The first, thermal decomposition, increases in rate with increasing temperature below 190–200°. Furthermore, the rate will decrease if the temperature is subsequently reduced by removal of the external heat source. At temperatures above 190–200° or after prolonged heating at lower temperatures, thermal decomposition may progress to either of the other types, according to controllable governing conditions. The second class, ignition decomposition, occurs on initiation by contact with sources of intense heat and is self-sustaining under most conditions. The last class, detonation, occurs normally when cellulose nitrate is subjected to severe shock in a confined space but may develop under the proper conditions from either of the other classes. It is sometimes difficult to distinguish between the last two types. The products arising from each of these classifications are different.

The detonation of cellulose nitrate affords only carbon monoxide and dioxide, nitrogen, hydrogen and water, the proportions being dependent on the pressure of the reaction system.[4] The products isolated from the thermal decomposition of cellulose nitrate are more complex. Degraded and oxidized cellulose nitrates[2,5,6] are the only[7] non-volatile products. Among the volatile products afforded by the thermal decomposition of cellulose nitrate are[8–11] carbon monoxide and dioxide, nitric oxide, nitrous oxide, nitrogen dioxide, nitrogen, methane, hydrogen,[12] formaldehyde[12] and water. The very recent work of Phillips, Orlick and Steinberger[13] on the kinetics of the thermal decomposition of cellulose nitrate provides a new body of data which clarifies much of the earlier and somewhat contradictory reports in this field.

The ignition decomposition of cellulose nitrate at pressures greater than atmospheric affords carbon monoxide and dioxide, nitric oxide, hydrogen, methane and water.[14] Formaldehyde,[15,16] cyanide ion[17,18] and ammonia[15] have also been detected in minor amounts. At very high pressures, no methane or nitric oxide are found.[19] Apparently all of the oxides of nitrogen are consumed in the conversion of the carbon to its oxides since the only nitrogen-containing substance found is nitrogen gas.

The ignition of cellulose nitrate under reduced pressure was investigated by Abel[17] in 1864 and he reported a reduction in burning rate and observed the formation of "a considerable portion of a white vapour, slowly dissolved by water." Rideal and Robertson[12] also observed "the deposition of some white body on the walls of the bulb," when they initiated the "explosion" of cellulose nitrate thermally under reduced pressure at temperatures above

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[2] Paper I: M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, D. O. Hoffman, R. S. Bower, A. Chaney, Eloise Carpenter and P. McWain, THIS JOURNAL, **77**, 6573 (1955); preliminary paper: M. L. Wolfrom, *Abstracts Papers Am. Chem. Soc.*, **127**, 9E (1955).

[3] Aberdeen Proving Grounds, Maryland.

[4] E. Sarrau and P. Vieille, *Compt. rend.*, **89**, 165, 169 (1879).

[5] A. P. Sy, THIS JOURNAL, **25**, 549 (1903).

[6] J. Desmaroux, R. Vandoni, L. Brissaud and Therese Petipas, *Mém. poudres*, **39**, 134 (1939).

[7] S. DeLuca, *Compt. rend.*, **53**, 298 (1861); **59**, 487 (1864), reports the isolation of oxalic acid and glucose from the prolonged photochemical degradation of cellulose nitrate, but these are not the initial products.

[8] R. Robertson and S. S. Napper, *J. Chem. Soc.*, **91**, 764 (1907).

[9] A. Koehler and M. Marqueyrol, *Mém. poudres*, **18**, 101, 106 (1921).

[10] A. V. Saposhnikoff and M. Borisoff, *J. Russ. Phys. Chem. Soc.*, **36**, 836 (1904).

[11] R. Vandoni, *Compt. rend.*, **201**, 674 (1935).

[12] E. K. Rideal and A. J. B. Robertson, "Third Symposium on Combustion," Williams and Wilkins Co., Baltimore, Md., 1949, p. 536.

[13] R. W. Phillips, C. A. Orlick and R. Steinberger, *J. Phys. Chem.*, **59**, 1034 (1955).

[14] E. Sarrau and P. Vieille, *Compt. rend.*, **90**, 1112 (1880).

[15] B. L. Crawford, Jr., C. Huggett and J. J. McBrady, *J. Phys. Chem.*, **54**, 854 (1950); experiments performed with cellulose nitrate containing glycerol trinitrate; also unpublished work of these authors, see O. K. Rice and R. Ginell, *ibid.*, **54**, 885 (1950).

[16] E. Trapani, *Atti reale accad. Lincei*, **26**, [I] 332 (1917).

[17] F. A. Abel, *Proc. Roy. Soc.* (London), **13**, 204 (1864).

[18] B. Pfyl and P. Rasenack, *Arb. kaiserl. Gesundh.*, **32**, 1 (1909); *C. A.*, **3**, 2752 (1909).

[19] E. Sarrau and P. Vieille, *Bull. soc. chim.*, [2] **33**, 581 (1880).

200°. The fragmented oxycellulose nitrate, which we reported previously,[2] is probably essentially identical with the materials of both Abel and of Rideal and Robertson, although they report no characterizations of their products. Methane,[20] carbon monoxide and dioxide,[20] nitric oxide,[20] nitrogen dioxide[20] and cyanide[17] have been found in the gases produced by the ignition of cellulose nitrate under reduced pressure. At very low pressures, ignition with a hot wire fails to initiate the self-sustaining decomposition of cellulose nitrate.[21]

Except for the residual oxidized and degraded cellulose nitrates,[2,5,6,13] no substance having a carbon–carbon bond has hitherto been isolated from the decomposition of pure cellulose nitrate under any conditions of a thermal nature. The elucidation of a mechanism for the decomposition reaction would be simplified considerably if such materials could be recovered and their origins determined. The investigation herein described reports the isolation of several substances containing carbon–carbon bonds. An investigation of the products of the ignition decomposition of cellulose nitrate (11.0–13.9% N) at 2-700 mm. and the quantitative estimation of the variations in yield of the major organic components with decomposition pressure and nitrogen content of the nitrate is also reported.

Experimental

Preparation and Decomposition of the Cellulose Nitrate.—Cast sheets of cellulose nitrate containing 10.99, 11.35, 12.09, 12.26, 12.60,[22] 13.20,[22] 13.42[22] and 13.90% N[23,24] were prepared as described previously,[2] employing ethyl acetate as the solvent. No attempt was made to remove the last residual traces of solvent and it is estimated[25] that about 5% by weight of the prepared sheet was ethyl acetate. The sheets were decomposed in the apparatus illustrated in Fig. 1. The section A-I (Fig. 1) was dried at 110° before use. The procedure was to place a 2 × 10 cm. strip of cellulose nitrate sheet in contact with the igniter loop (D, Fig. 1). With stopcocks A and L closed, the system was evacuated to a pressure somewhat below the pressure required. The stopcock L was then opened and the pressure in the system was adjusted with the bleeder valve attached at L until a constant pressure slightly below that required was attained. Nitrogen gas was then admitted through stopcock A at a rate sufficient to increase the pressure to somewhat above that desired. After sweeping the system with nitrogen for several minutes, stopcock A was closed and when the pressure dropped to that desired, a current was applied to the igniter loop D until the sheet began to decompose. After the decomposition was complete (1 to 2 sec.), the stopcock F was closed (pumping was continued on the system F-M) and a flow of nitrogen through A was used to increase the pressure in A-E to that of the atmosphere. The apparatus was opened at C and a new strip was inserted as before. The system was closed and stopcock F was opened slowly until the pressure could be adjusted as before. This process was repeated until about 20 g. of cellulose nitrate had been ignited. The best yields were obtained in the experiments in which the sheets were ignited at a single point at the end adjacent to stopcock F. Considerable difficulties were encountered in the initiation of self-sustaining decomposition at 200 mm. (presumably at other pressures also) with samples containing 10.99, 11.35 and 13.90% nitrogen. Preliminary investigations using the methods reported below indicated no qualitative differences between the components of the product found in the combustion tube and that retained by the spiral traps. Insertion of a water-filled Fisher–Milligan gas-washer between the last spiral trap and the pumping system demonstrated that the only products not retained in the cold traps were gases which condense only below −60° and small amounts of the oxides of nitrogen which were detected as their corresponding acids.

The above condensate, a red liquid, was removed from the ignition tube and spiral traps (allowed to stand at 0° for 1 to 2 hr. prior to removal) by dissolving it in water. After filtration through medium-porosity sintered glass, the solution was diluted to volume with water (final volume, 20 ml. per g. of cellulose nitrate ignited). The amounts of the water-insoluble solid product retained by the filter are given in Fig. 2. Condensate yields were 250–450 mg. per g. of cellulose nitrate decomposed as estimated from the gain in weight of the condensing system. The yield varied with the decomposition pressure and the nitrogen content of the cellulose nitrate in an apparently non-systematic manner.

The evaporation of aliquots of the condensate solutions to dryness using a 250-watt infrared lamp, followed by drying to constant weight under reduced pressure over calcium chloride and sodium hydroxide, was used to determine the yield of non-volatile, water-soluble solids. The results are presented in Fig. 2.

Experiments at 200 mm. Pressure with 12.6% N Cellulose Nitrate

Water Content of the Condensate.—Samples of the condensate were removed from the combustion system prior to the dilution with water. Weighed portions were added to a mixture containing 2 ml. of pyridine and 10 ml. of a 1.5 *M* solution of acetyl chloride in dry toluene, following the general method of Smith and Bryant.[26] The resulting mixture was shaken for 2 min. and the excess reagent was decomposed with absolute ethanol. The acid formed was titrated with 0.1 *N* sodium hydroxide to a phenolphthalein end-point. After correction for the blank and the acidity due to acids in the sample, including the anomalous reaction due to formic acid, the water content of the condensate was found to be 1.1 mmoles per mmole of cellulose nitrate (12.6 and 13.4% N) ignited.[27]

Effect of the Film Casting Solvent on the Condensate.—Sheets of cellulose nitrate cast[2] by the evaporation of acetone solutions were ignited and the condensate aqueous solution obtained was neutralized with 2.5 *N* sodium hydroxide. An aliquot of the neutral solution was steam distilled and 0.1 *N* potassium permanganate was added to the distillate (150 ml.) until the color persisted. After filtration, the solution was added to an excess of 2 *N* hydrochloric acid saturated with 2,4-dinitrophenylhydrazine, following the general procedure of Iddles and Jackson.[28] The precipitate which formed after 1 hr. at 0° was recrystallized once from nitrobenzene to afford acetone 2,4-dinitrophenylhydrazone, m.p. 127–128°,[29] undepressed on admixture with authentic material.

The residue from the steam distillation was acidified with 0.5 *N* phosphoric acid and an excess of mercuric oxide was added. The mixture was refluxed for several hours to destroy any formic acid and was then treated with 0.5 *N* sulfuric acid to dissolve excess mercuric oxide. After filtration, the solution was steam distilled and the distillate (1200 ml.) was neutralized with 0.1 *N* sodium hydroxide and concentrated under reduced pressure. The concen-

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[20] L. v. Karolyi, *Ann. physik. Chem.*, **118**, 544 (1863); *Phil. Mag.*, [4] **26**, 266, 272 (1863).

[21] H. Muraour and W. Schumacher, *Compt. rend.*, **199**, 140 (1934).

[22] These samples were blends; the others were unblended.

[23] Nitrogen analyses were obtained with the du Pont nitrometer; see W. W. Scott, "Standard Methods of Chemical Analysis," N. H. Furman, ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, pp. 650–655.

[24] The penultimate sample was obtained from the E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., while the ultimate sample was furnished by Dr. B. T. Federoff, Picatinny Arsenal, Dover, N. J.

[25] F. D. Miles, "Cellulose Nitrate," Interscience Publishers, Inc., New York, N. Y., 1955, p. 205.

[26] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 841 (1935).

[27] The millimoles of cellulose nitrate were calculated by division of the grams decomposed by the sum of the millimolecular weight of one anhydro-D-glucose unit (0.162) and the increase in millimolecular weight caused by the nitrate ester groups (0.045 times the degree of substitution).

[28] H. A. Iddles and C. E. Jackson, *Anal. Chem.*, **6**, 454 (1934).

[29] All melting points were determined with a Fisher-Johns apparatus.

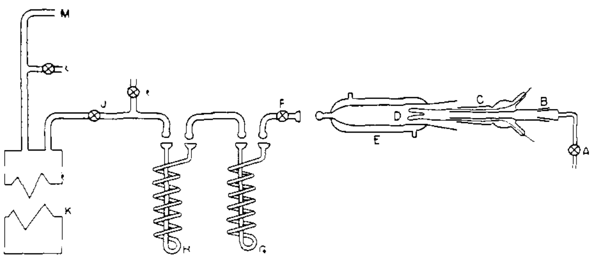

Fig. 1.—Apparatus for the thermal decomposition of cellulose nitrate: A, stopcock for nitrogen introduction; B, 19/38 ground glass joint for insertion of cellulose nitrate; C, feeder tube, glass, 20 mm. o.d.; D, double loop of No. 24 Chromel wire connected to leads sealed through glass and connected to a variable potential control; E, cold water-jacketed glass combustion chamber, 25 cm. long inside, 34/45 ground glass joint at one end and reduced to a 28/15 glass spherical joint at the other end; F and J, 15 mm. bore stopcocks; G and H, spiral traps of 12 mm. o.d. glass tubing connected by 28/15 spherical joints and inserted into Dewar-held baths of solid carbon dioxide and acetone; G was filled with 2 mm. diam. glass helices; I, stopcock to differential manometer; K, surge tank, a steel pipe (0.3 × 1.3 m.) with gasketed fittings and flanges; L, take-off to a fine adjusting Meeker burner valve serving as a bleeder in adjusting pressure; M, connection to a high capacity Cenco Megavac pump. The pressure in the system could be reduced to 0.5 mm. or lower.

trated salt solution (10 ml.) was treated with an excess of p-bromophenacyl bromide under reflux for 1 hr. The precipitate which formed on cooling was recrystallized once from dilute ethanol to afford p-bromophenacyl acetate, m.p. 85-86°, unchanged on admixture with an authentic specimen.

Anal. Calcd. for $C_{10}H_9O_3Br$: C, 46.72; H, 3.52. Found: C, 46.67; H, 3.68.

The condensate produced by the decomposition of cellulose nitrate sheets cast from ethyl acetate solution afforded no acetone derivative by the method described. The acetic acid content (determined by titration of the second steam distillate) was greater than that produced by the acetone cast films and the distillate from the neutralized solution contained a saponifiable material which probably was ethyl acetate. The presence of ethyl alcohol was also detected in trace amounts.

Acidity of the Condensate.—Colorimetric analysis of a freshly prepared condensate aqueous solution for nitrite ion with dimethylaniline[30] indicated the presence of less than 0.003 mmole of nitrite per mmole of cellulose nitrate ignited[27] and none could be detected several weeks after preparation.

A 30-ml. aliquot of the condensate solution was acidified with 0.5 ml. of 16 *N* sulfuric acid and the solution was refluxed. Nitron solution (6 ml. of a solution containing 10% 4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole in 5% aqueous acetic acid) was added following the procedure of Cope and Barab.[31] After cooling at 0° for 2 hr., the crystalline precipitate was filtered, dried and weighed; yield, calculated as nitric acid, 0.014 mmole per mmole of cellulose nitrate ignited.[27]

Although it was considered possible that oxalic acid would be formed on the ignition of cellulose nitrate, all efforts to establish its presence among the decomposition products failed.

Gases Produced by the Action of Mercury and Sulfuric Acid on the Condensate.—A standard du Pont nitrometer apparatus[23] was employed. The weighed sample of the condensate was transferred to the reaction bulb with concentrated sulfuric acid (15 ml.). The gases were generated and transferred to the measuring buret in the normal way.[23] The gases were then returned to the reaction bulb and shaken successively with 33% aqueous ferrous sulfate, 50% potassium hydroxide and 1% cuprous chloride. Measurement of the volume decrease effected by each of these treatments afforded a measure of the amounts of nitric oxide, carbon dioxide and carbon monoxide, respectively.

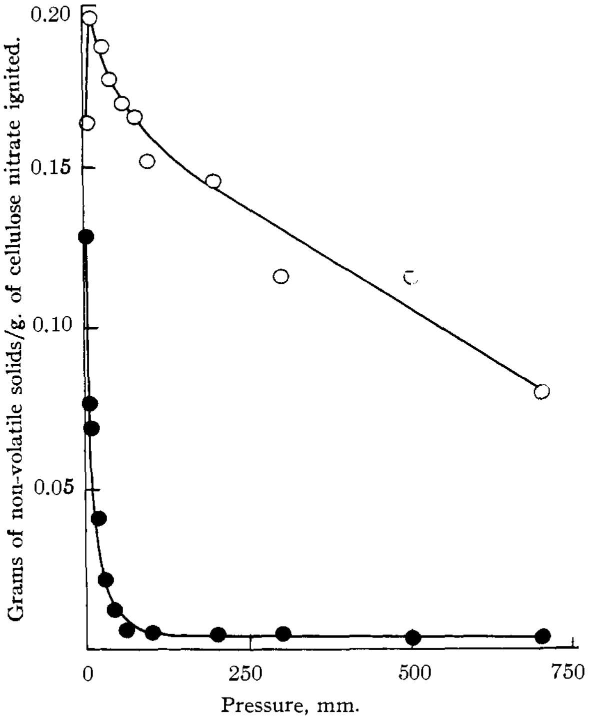

Fig. 2.—Pressure dependency of non-volatile solid formation from ignited cellulose nitrate (13.4% N): ○, water-soluble solids; ●, water-insoluble solids.

Found.—CO_2, 1×10^{-2} mmole; NO, 1.7×10^{-2} mmole; CO, 42×10^{-2} mmole (all per mmole of cellulose nitrate ignited[27]). The precursors of the gases in the condensate are believed to be an organic acid (decarboxylation), nitrate and nitrite ions (see above) and formic acid (see below), respectively.

Determination of Cyanide Ion.—The addition of excess 0.1 *N* silver nitrate to aqueous solutions of the condensate afforded a white, curdy precipitate which darkened on exposure to light. After removal of this precipitate by filtration, no further precipitation was caused by the addition of small amounts of the other components of the condensate herein reported. The white water-washed precipitate was treated with dilute sulfuric acid (no effervescence) and the supernatant solution gave positive reactions for cyanide ion with ferric thiocyanate,[32] mercuric chloride–methyl orange test paper[33] (vapors on heating the solution), and alkaline picrate.[34] A portion of the white precipitate was extracted with 3 successive 100-ml. aliquots of 5% nitric acid. The insoluble residue was transferred to a tared porcelain crucible and dried to constant weight at 100°. The residue was analyzed for silver by ignition to constant weight.

Anal. Calcd. for AgCN: Ag, 80.6. Found: Ag, 79.8.

The condensate solutions prepared by the ignition of 12.6 N cellulose nitrate (cast films prepared under identical conditions) at pressures between 8 and 750 mm. were analyzed for cyanide ion by the addition of silver nitrate solution and weighing of the washed and dried (110°) precipitate. A small variation with ignition pressure was observed (Fig. 3).

Isolation of N-p-Bromophenylformamide.—Fifty ml. of the condensate solution was neutralized (pH 9) with 5 *N* sodium hydroxide and steam distilled at constant volume

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[30] E. H. Miller, *Analyst*, **37**, 345 (1912).

[31] W. C. Cope and J. Barab, THIS JOURNAL, **39**, 504 (1917).

[32] R. K. McAlpine and B. A. Soule, "Prescott and Johnson's Qualitative Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1933, p. 459.

[33] J. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 534.

[34] Ref. 33, p. 30.

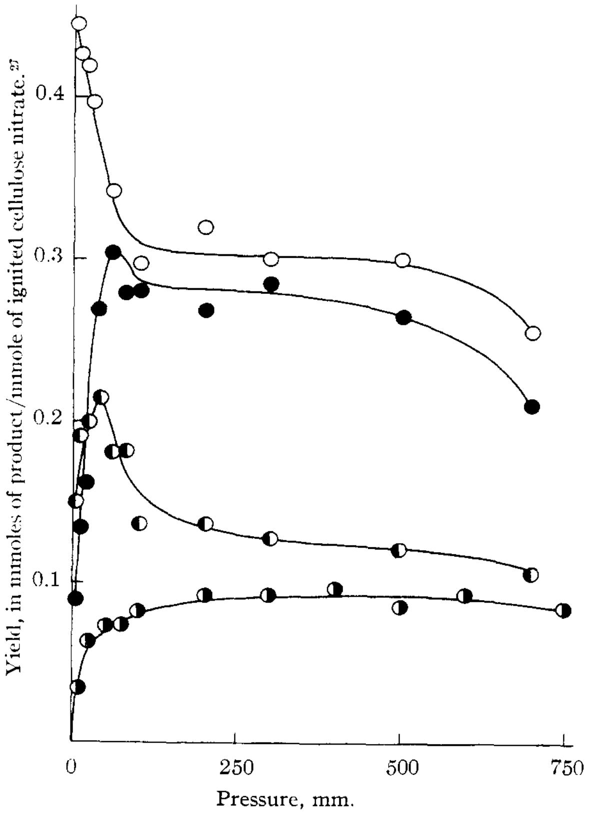

Fig. 3.—Pressure dependency of product formation from ignited cellulose nitrate (13.4% N): ○, formic acid; ●, formaldehyde, ◐, glyoxal; ◑, cyanide (12.6% N cellulose nitrate).

until 3 liters of distillate was collected. The residual solution was acidified (*p*H 2) with 0.5 *N* phosphoric acid and again subjected to steam distillation. This distillate (1.5 liters) was neutralized with 0.5 *N* sodium hydroxide and evaporated to dryness at 100°. The salts remaining were treated with slightly less than the stoichiometric amount of 2 *N* sulfuric acid. The resulting solution was frozen and sublimed at 0.03 mm. pressure into a trap cooled with solid carbon dioxide and acetone. The liquid which formed on warming the trap was transferred to a distillation apparatus containing twice its volume of trichloroethylene. This mixture was distilled at 75–80° employing the codistillation technique of Petersen and Engelbrecht.[35] The distillate was redistilled, employing the same method, and the distillate was neutralized with 0.5 *N* sodium hydroxide. The salt obtained by evaporation to dryness at 100° was treated with thionyl chloride and then with *p*-bromoaniline as described by Cheronis and Entrikin.[36] After two recrystallizations from dilute ethanol, there was obtained N-*p*-bromophenylformamide of m.p. 118.5–119.0°. This material did not depress the melting point of a pure sample prepared directly from sodium formate or the product obtained by the same procedure from a solution containing equal amounts of formic and acetic acids.

Isolation of Formaldehyde Dimethone.—A 10-ml. aliquot of the condensate aqueous solution was added to 100 ml. of a 0.4% aqueous solution of dimedon (5,5-dimethyl-1,3-cyclohexanedione). The resulting solution afforded crystals after cooling overnight at 4–5°. After a single recrystallization from aqueous ethanol, the crystals showed the m.p. 191–192° which was not depressed on admixture with authentic formaldehyde dimethone.

Isolation of Glyoxal Bis-(phenylhydrazone).—A 10-ml. aliquot of the solution containing the condensate was added to 2 ml. of 10% aqueous sodium bisulfite. After heating the mixture at 100° for 30 min., 4 ml. of a 11% aqueous solution of sodium acetate and 6 ml. of a 5% aqueous solution of phenylhydrazine hydrochloride were added and the solution was heated for 30 min. at 100°. After cooling to room temperature, 0.1 g. of Celite[37] was added to the mixture and the solids were removed by filtration. The solids were washed on the filter 5 times with 4-ml. portions of water and then with acetone until the last washing was colorless. Evaporation to dryness of the acetone washings afforded *ca.* 50 mg. of derivative mixture.

The derivative mixture was dissolved in 15 ml. of warm benzene and adsorbed on a 23 (diam.) × 180 mm. column of silicic acid-Celite[38] which had been prewet with benzene. The column was developed with benzene (*ca.* 100 ml.) (omission of the sodium bisulfite treatment leads to a more complex system) at 500 mm. until a wine-red and a bright yellow zone had been collected in the effluent. The yellow zone at the bottom of the column (after extrusion) was eluted with acetone and the yellow crystals obtained on evaporation of the eluate were recrystallized once from benzene; yield 20 mg., melting point and mixed melting point with an authentic sample of glyoxal bis-(phenylhydrazone), 167–169°.

Isolation of Triose Phenylosazone.—Several chromatograms identical to the one described above were prepared and the yellow zones at the top of the columns were eluted with acetone. After evaporation of the acetone, the solid residue was rechromatographed by the same procedure. Recrystallization from benzene of the material obtained from the second chromatogram afforded 15 mg. of yellow crystals of m.p. (and mixed melting point with authentic triose phenylosazone from D-glyceraldehyde) 131–132°. Comparative chromatograms of the authentic derivative and the material derived from the condensate further indicated their identity.

Isolation of Mesoxaldehyde 1,3-Bis-(phenylhydrazone).—The orange zones (third from the top of the column) from several of the chromatograms described above were eluted with acetone. The orange-red crystals obtained after evaporation of the eluates were crystallized from benzene to afford mesoxaldehyde 1,3-bis-(phenylhydrazone) of m.p. (and mixed melting point with authentic material) 173–174°. Although the m.p. 175–176° has been reported,[39] our purest sample had m.p. 173.5–174.5°. The identity of the material from the condensate with the pure mesoxaldehyde derivative was further demonstrated by means of comparative chromatograms.

Identification of the Gases Formed Concomitantly with the Condensate.—The traps G and H (Fig. 1) were replaced by other traps (equivalent to those listed as No. J-4310 by the Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.). Dewar-held baths of liquid nitrogen were employed as condensing agents. After decomposition of the cellulose nitrate, the traps were attached (air excluded) to a previously evacuated glass system into which the condensed gases were transferred on warming the traps to room temperature. After permitting the system to attain equilibrium, the pressure and temperature were measured. Since the volume of all parts of the system had been determined, sufficient data were available for calculation of the yield. Thus, the decomposition of cellulose nitrate (13.20% N) at 200 mm. pressure was shown to afford 55.5 ml. (S.T.P.) of condensable gases (100–130°K.) per mmole of nitrate ignited.[27] The nitric oxide and nitrogen dioxide contained in known volumes of the condensable gases were separated from the other constituents and their quantities determined following the general procedure of Johnson.[40] The yields of nitric oxide and nitrogen dioxide were 1.01 and 0.14 mmoles, respectively, per millimole of cellulose nitrate (13.20% N) ignited.[27]

The residual gases from these analyses were transferred (air excluded) to a cell with sodium chloride windows (5 cm. path length). Spectral absorption bands were found with a Baird infrared spectrophotometer at 2.68, 2.74, 4.21, 4.30, 4.45, 4.51, 6.12, 6.23, 7.70, 7.85, 13.74, 13.96 and 15.0 (broad) μ. The intensity of the absorption band at

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(35) I. Petersen and C. Engelbrecht, U. S. Patent 1,813,636 (1931).

(36) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, pp. 210–211.

(37) No. 535, a product of the Johns-Manville Co., New York, N. Y.

(38) See ref. 2, footnote 65.

(39) H. von Euler and C. Martius, *Ann.*, **505**, 73 (1933).

(40) C. L. Johnson, *Anal. Chem.*, **24**, 1572 (1952).

7.70 μ^{41} was selected for comparison with that of known concentrations (pressures) of nitrous oxide. This comparison indicated that 0.2-0.3 mmole of nitrous oxide was produced per mmole of cellulose nitrate (13.2% N) ignited.[27] If one sums the amounts (1.01, 0.14 and 0.25) of these oxides of nitrogen and subtracts this total from the total moles of gases produced (2.5, calculated from the ideal gas law), the value of 1.1 mmoles of gas per mmole of cellulose nitrate (13.2% N) ignited[27] is obtained. This value affords a crude estimate of the yield of carbon dioxide since it is the major (other components were present only in traces) undetermined constituent of the condensable gases on the basis of the spectra recorded.

Variation of the Constituents of the Condensate with Pressure and Nitrogen Content

Since the main organic constituents of the liquid condensate are formic acid, glyoxal and formaldehyde (other than cyanide ion, see above), it was considered important to investigate the variation in the yields of these substances arising from cellulose nitrates of different degrees of nitration on ignition at pressures between 2 and 700 mm. The analyses described below were carried out immediately after preparation of the condensate solutions. Although the analytical methods employed herein are believed to be accurate (±5%, see below), and not subject to interference by the other components in the mixture being analyzed, the condensate is an extremely sensitive and reactive mixture arising from an attempt to halt in mid-course the conversion of cellulose nitrate to completely gaseous products. In spite of employing the same cellulose nitrate and ignition pressure, two operators following the same written instructions have on occasion obtained results differing by 20% for the same component. However, with sufficient cooperation and experience, one or more operators can obtain self-consistent and reproducible (±5%) results. For example, the results obtained by one operator employing 13.2% N cellulose nitrate at 200 mm. were as follows for separate decompositions: glyoxal, 0.130 and 0.138; formic acid, 0.321 and 0.331; formaldehyde, 0.279 and 0.281; total carbonyl, 0.91 and 0.96 mmole (all per mmole of cellulose nitrate ignited[27]), the largest discrepancy being *ca.* 5%.

Analysis for Formic Acid.—A 10-ml. aliquot of the condensate solution was diluted with 10 ml. of 0.3 *N* phosphoric acid and the mixture was distilled to dryness under reduced pressure at 50°. The distillate was collected in a trap immersed in a Dewar-held bath of solid carbon dioxide and acetone. After warming the distillate to room temperature, 175 ml. of 5% aqueous mercuric chloride, 4 ml. of commercial anhydrous acetic acid and 4 g. of sodium acetate were added following the general procedure of Fincke.[42] The mixture was refluxed for 2 hr. and then cooled. The crystalline precipitate was collected on a tared sintered-porcelain crucible and dried at 110° for 1 hr. The amounts of mercurous chloride were converted to mmoles of formic acid produced by the decomposition of cellulose nitrates with various degrees of nitration and at the different ignition pressures. The results are given in Figs. 3 and 4. In several instances these results were confirmed by the volume of carbon monoxide produced on treatment of the condensate with concentrated sulfuric acid and mercury (described above) and by the difference in the quantities of the steam-volatile acids obtained with and without prior refluxing with mercurous oxide (which destroys the formic acid present).

Analysis for Glyoxal.—Although several excellent methods for the analysis of glyoxal are described in the literature,[43-45] none of these was completely satisfactory when applied to the condensate solutions because of serious interference caused by the variety of components present. For this reason we investigated a chromatographic method essentially identical with that described above under "Isolation of Glyoxal Bis-(phenylhydrazone)." It was found that under the conditions employed for hydrazone formation (presence of sodium bisulfite), no formaldehyde derivative was formed. Modifications were made to effect quantitative transfers in all of the steps and the recrystallization was omitted. Analysis of authentic glyoxal solutions (1 mg./ml.) by the alkaline hydrogen peroxide method[45] and by our method indicated that quantitative results were obtained. The results obtained for the series of condensate solutions are given in Figs. 3 and 4.

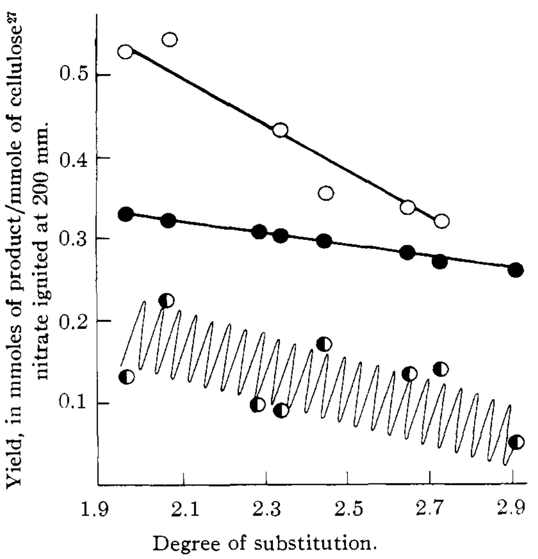

Fig. 4.—Variation in yield of product formed from ignited cellulose nitrate samples of varying nitrogen content: ○, formic acid; ●, formaldehyde; ◐, glyoxal.

Analysis for Formaldehyde.—Although Yoe and Reid[46] report that the precipitation of formaldehyde with dimedon is quantitative only in the *p*H range 4.2-5.0, it appeared that different conditions might permit quantitative precipitation at a lower *p*H. Since the condensate solutions contained other carbonyl compounds which would interfere above *p*H 4, a solution (*p*H 3.2) was prepared which was 0.02 *M* in dimedon (5,5-dimethyl-1,3-cyclohexanedione), 0.0057 *N* in hydrochloric acid and 0.0143 *M* in potassium hydrogen phthalate. Solutions containing 5-40 mg. of formaldehyde were added to 140 ml. of the buffered dimedon solution and the total volume was brought to 180 ml. with water. After 24 hr. at room temperature, the precipitate which had formed was filtered, washed with a small amount of water, dried for 12 hr. at 80° and weighed as formaldehyde dimethone. The amounts of formaldehyde so isolated were 100 ± 2% of that added. No greater deviations were observed when 5-20 mg. of glyoxal were added to the precipitation mixtures. In separate experiments with reductone, glyceraldehyde and mesoxaldehyde, under the same conditions, no precipitate was formed in 48 hr. If a known amount of formaldehyde and 10 ml. of the condensate solution were added to the buffered dimedon solution, the precipitate obtained was heavier than that afforded by the condensate solution alone by the amount required by the known amount of formaldehyde (agreement 100 ± 2%). The results obtained for a series of condensate solutions are given in Figs. 3 and 4.

Determination of Total Carbonyl.—The hydroxylamine hydrochloride method of Bryant and Smith[47] as modified by Gladding and Purves[48] was employed to determine the total carbonyl content of the condensate. Thus, a 2-ml. aliquot of the condensate solution (*p*H adjusted to 3.2 with dilute base) was added to 25 ml. of a solution containing 50 g. of hydroxylamine hydrochloride and 3.4 g. of sodium hydroxide per liter. After 24 hr., the mixture was titrated potentiometrically to *p*H 3.2 with standard sodium hydroxide. The results, corrected for simultaneously run blanks,

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(41) R. E. Nightingale, A. R. Downie, D. L. Rotenberg, B. L. Crawford, Jr., and R. A. Ogg, Jr., *J. Phys. Chem.*, **58**, 1047 (1954).

(42) H. Fincke, *Biochem. Z.*, **51**, 253 (1913).

(43) P. A. Shaffer and T. E. Friedmann, *J. Biol. Chem.*, **61**, 599 (1924).

(44) D. H. Grangaard, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **116**, No. 7, 41 (1943).

(45) W. H. Hatcher, G. W. Holden and F. J. Toole, *Trans. Roy. Soc. Canada*, [3] **20**, III, 399 (1926).

(46) J. Yoe and L. Reid, *Anal. Chem.*, **13**, 238 (1941).

(47) W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

(48) E. K. Gladding and C. B. Purves, *Paper Trade J.*, **116**, No. 14, 26 (1943).

TABLE I

RELATION BETWEEN FORMALDEHYDE FORMATION AND PRIMARY NITRATE CONTENT INCORPORATED IN THE IGNITED CELLULOSE NITRATE

Sample	Mmoles per g. decomposed H_2CO, found	$-CH_2ONO_2$, calcd.	Ratio[g] $H_2CO/$ $-CH_2ONO_2$
myo-Inositol hexanitrate, 25%[a]	0.82[b]	2.75[c]	0.30
D-Mannitol hexanitrate, 20%[a]	1.24	3.82[c]	0.32
Erythritol tetranitrate, 25%[a]	1.37	4.41[c]	0.31
Pentaerythritol tetranitrate, 21%[a]	1.52[b]	5.57[c]	0.27
Dextran nitrate, 11.53% N[d,h]	None[e]	None	...
2-*O*-Methylcellulose nitrate, 9% N[f,h]	1.10	3.99	0.28
Cellulose nitrate, 10.99% N	1.32	3.99	0.33
Cellulose nitrate, 11.35% N	1.27	3.92	0.32
Cellulose nitrate, 12.09% N	1.16	3.77	0.31
Cellulose nitrate, 12.26% N	1.13	3.74	0.30
Cellulose nitrate, 12.60% N	1.09	3.67	0.30
Cellulose nitrate, 13.20% N	1.00	3.55	0.28
Cellulose nitrate, 13.42% N	0.94	3.51	0.27
Cellulose nitrate, 13.90% N	0.90	3.41	0.26

[a] The percentage is the part of the total weight ignited due to the component specified, the remainder being 12.6% N cellulose nitrate. [b] These results were obtained from ignitions at 100 mm. pressure; all the others were at 200 mm. [c] The number of mmoles of total nitrogen per gram in these four mixtures is constant (9.9 ± 0.2). [d] A polymer formed by a *Leuconostoc dextranicum* strain producing essentially only α-D-(1 → 6) glycosidic linkages; hence no primary nitrate groups. [e] Nitrated pectic acid and xylan, which if pure should contain no primary nitrate groups, afforded 0.14 and 0.39 mmole of formaldehyde, respectively, per gram ignited; the purity of these samples was not known. [f] See ref. 49 for preparation. [g] Several other ratios may be calculated from the data in Figs. 2–5 but no other constant ratio was found. [h] Not admixed with cellulose nitrate.

are given in Fig. 5 for cellulose nitrate (13.4% N) ignited at pressures between 2 and 700 mm.

Analysis of Known Mixtures.—An aqueous solution 0.570 *M* in glyoxal, 1.33 *M* in formaldehyde and 1.11 *M* in formic acid was frozen on the walls of a pear-shaped flask cooled in a bath of solid carbon dioxide and acetone. A small amount of an equimolar mixture of nitric oxide and nitrogen dioxide was generated from sodium nitrate and sulfuric acid and was condensed in the flask. After warming the contents of the flask and permitting the gases to evolve at room temperature for several hours, the residual solution was diluted 50-fold with water and analyzed by the methods described above. Thus, the diluted solution was so found to be 0.0116 *M* in glyoxal, 0.0259 *M* in formaldehyde and 0.0217 *M* in formic acid, the deviations from the original known concentrations being 1.7, 2.6 and 1.8%, respectively.

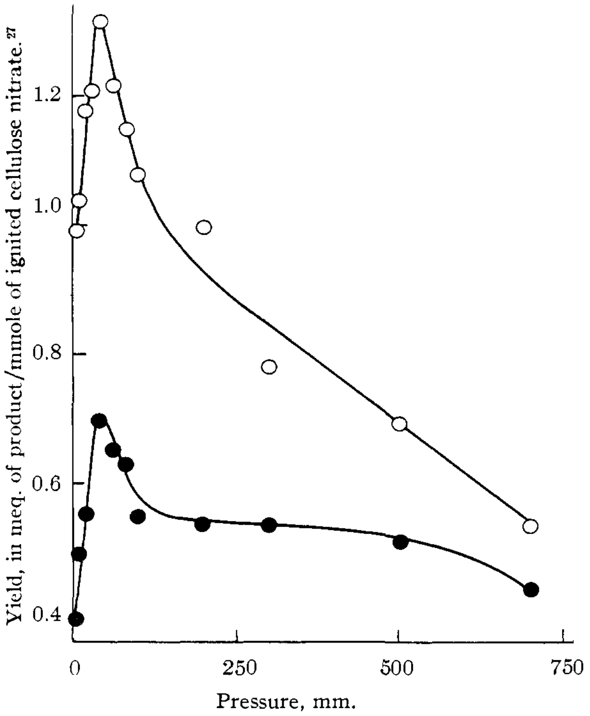

Fig. 5.—Pressure dependency of carbonyl compound formation from ignited cellulose nitrate (13.4% N): ○, total carbonyl; ●, formaldehyde + glyoxal, see Fig. 3.

Relation between Formaldehyde and Primary Nitrate.—The effect of primary nitrate groups on the yield of formaldehyde was investigated by the ignition of 2-*O*-methylcellulose[49] nitrate (9% N), dextran nitrate (11.35% N), cellulose nitrate (12.6% N) in admixture with known amounts of nitrated sugar alcohols, and cellulose nitrates containing from 10.99 to 13.90% N. The results are given in Table I, the primary nitrate value being calculated on the assumption that all of the primary hydroxyl groups in all of the samples were nitrated.

Discussion

While the self-sustaining decomposition of cellulose nitrate cannot be initiated at extremely low pressures,[21] a white, water-insoluble, fragmented oxycellulose nitrate (9% N) has been isolated at pressures of 1–60 mm. in this Laboratory.[2] The yield of this solid substance decreases rapidly with increasing pressure as indicated in Fig. 2. The maximum yield (Fig. 2) is lower than that previously reported[2] for two reasons: (a) the nitrogen content of the cellulose nitrate employed is higher, hence more complete decomposition is to be expected; (b) the decomposition products were not removed from the combustion chamber after the ignition of each strip, as before,[2] which permitted further decomposition of the solid products by the gases generated in subsequent ignitions. The traces of water-insoluble material found above 60 mm. pressure are probably unburned cellulose nitrate and carbon.[15]

At pressures between 5–700 mm. a water-soluble red oil is obtained as a condensate (−80°), the non-volatile portion of which (Fig. 2) is obtained in maximum yield at 40–60 mm. pressure. Since

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(49) J. M. Sugihara and M. L. Wolfrom, THIS JOURNAL, **71**, 3509 (1949).

water has been found as a decomposition product of cellulose nitrate under a variety of conditions,[4,10,15] the water content of the red oil condensate obtained from the ignition of cellulose nitrate (12.6 and 13.4% N) at 200 mm. pressure was investigated and shown to be *ca.* 1.1 mmole per mmole.[27] Since cyanide ion has been reported as a decomposition product of cellulose nitrate under a variety of conditions,[17,18,20] its presence in the condensate was demonstrated and the precipitation of silver cyanide was employed to determine the amounts of cyanide ion in the condensate. The yield of cyanide was essentially pressure-independent above 100 mm. but decreased at lower pressures (Fig. 3).

The presence of acidic components in the condensate solutions was indicated by the *p*H of 2. Analysis for nitric acid by precipitation with Nitron reagent[31] and for nitrous acid by a colorimetric method,[30] demonstrated that the condensate contained only 0.017 mmole of these acids per mmole of cellulose nitrate (12.6% N) ignited[27] at 200 mm. pressure. Since this value was identical with that calculated from the volume of nitric oxide liberated in the du Pont nitrometer,[23] the condensate contains no organic nitrates or nitrites. Known mixtures of the major organic constituents (formaldehyde, formic acid and glyoxal) of the condensate were treated with dinitrogen trioxide under conditions similar to those prevailing during the preparation of the decomposition products. The effect of this treatment on the organic components was negligible. Thus, the alteration of the condensate by the oxides of nitrogen is not sufficient to produce significant errors. This procedure also demonstrated the specificity of the analytical methods.

Separate experiments were made in which the decomposition gases condensable at −180° and above were retained for analysis. Chemical methods of analysis[40] indicated that 1.01 mmoles of nitric oxide and 0.14 mmole of nitrogen dioxide were formed per mmole of cellulose nitrate (13.2% N) ignited.[27] Infrared absorption studies of residual gases (at 760 mm. pressure) after chemical removal[40] of the nitric oxide and nitrogen dioxide indicated absorption arising from carbon dioxide,[50] 2.68, 2.74, 4.21, 4.30, 13.96 and 15.0 (broad) μ; and nitrous oxide,[41,50] 4.45, 4.51, 7.70 and 7.85 μ (in some of the spectra, weak absorption at 6.12 and 6.23 μ was noted, this being caused by residual traces of nitrogen dioxide[41]). Absorption at 13.74 μ was also observed but its source has not been determined.

The intensity of the absorption at 7.70 μ was compared with that of known concentrations of nitrous oxide and the yield was estimated to be 0.2–0.3 mmole per mmole of cellulose nitrate (13.2% N) ignited[27] (at 200 mm. pressure). By difference, the yield of carbon dioxide was estimated to be about 1.1 mmoles per mmole of cellulose nitrate ignited.[27]

Since the acid components of the condensate (*ca.* 0.6–0.7 mmole per mmole, at 200 mm. pressure) were not completely accounted for by the nitrogen acids and hydrogen cyanide, the presence of organic acids was suspected. Investigation demonstrated that formic acid, isolated as N-*p*-bromophenylformamide, and acetic acid, isolated as *p*-bromophenacyl acetate, were present in quantities sufficient to account for *ca.* 95% of the other acids present. The formation of carbon monoxide in the du Pont nitrometer[23] also indicated formic acid in amounts in excellent agreement with the values obtained from analyses employing the mercuric chloride procedure of Fincke.[42] The variations in yield of formic acid with both pressure of ignition (Fig. 3) and nitrogen content of the cellulose nitrate (Fig. 4) are presented.

Since about 0.15 mole of ethyl acetate per mole of cellulose nitrate may have been retained by the films cast from this solvent under the drying conditions employed,[25] the acetic acid found in the condensate may be formed either by acid-catalyzed hydrolysis or by thermal decomposition of the ethyl acetate itself since it is known that ethyl acetate affords acetic acid,[51–53] acetone,[52] ethanol,[53] ethylene[51–54] and ketene,[53,54] depending on the reaction conditions. If acetic acid is formed under our conditions from ethyl acetate, which is present in varying quantities, the amounts of acetic acid and thus the total acidity in the condensate will be independent of the cellulose nitrate employed and will not be directly related to the ignition pressure. Thus, the shape of the pressure dependency curve for total acidity is similar to that of formic acid (Fig. 3) but is displaced toward larger values along the ordinate.

In some preliminary investigations, acetone was employed as the film casting solvent and acetone was isolated from the ignition products as its 2,4-dinitrophenylhydrazone. Acetic acid was also isolated (*p*-bromophenyl acetate) from the acetone-cast sheets of cellulose nitrate but in lesser amounts than from the ethyl acetate castings. The thermal decomposition of acetone alone affords acetic acid[55] and higher yields of this substance may be expected in the presence of the oxides of nitrogen. No acetone could be detected among the ignition products of cellulose nitrate cast from ethyl acetate. Thus, acetone does not arise from the ignition of cellulose nitrate. Although the data herein reported do not permit a conclusive decision on the point, acetic acid does not appear to be a cellulose nitrate ignition product. However, since formic acid is found in amounts (Figs. 3 and 4) much greater than could be produced by the quantity of solvent believed to be present,[25] formic acid must be, at least in part, a product of the ignition decomposition of cellulose nitrate.

Although formaldehyde has been detected[12,15,16] among the decomposition products of cellulose nitrate, no quantitative study has been reported. The results in Figs. 3 and 4 were obtained by precipitation of the formaldehyde with dimedon. The precipitation was effected under conditions of *p*H

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(50) D. F. Eggers, Jr., and B. L. Crawford, Jr., *J. Chem. Phys.*, **19**, 1554 (1951).

(51) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

(52) R. D. Obolentsev and Y. N. Usov, *Doklady Akad. Nauk S. S. S. R.*, **71**, 489 (1950); *C. A.*, **45**, 547 (1951).

(53) K. K. Georgieff, *Can. J. Chem.*, **30**, 332 (1952).

(54) Lonza Elektrizitätswerke und chemische Fabriken A.-G., Swiss Patent 233,176 (1944).

(55) M. Nakajima, *J. Electrochem. Assoc. Japan*, **10**, 112 (1942); *C. A.*, **45**, 1509 (1951).

and time such that the dimedon derivative of glyoxal (and, presumably, related carbonyl compounds) did not separate.

Silicic acid column chromatography was employed to separate the mixture obtained by treatment of the condensate aqueous solution with phenylhydrazine. This treatment was effected in the presence of sodium bisulfite which prevented the formation of the phenylhydrazone of formaldehyde and generally reduced the complexity of the chromatogram. Crystalline glyoxal bis-(phenylhydrazone), triose phenylosazone and mesoxaldehyde 1,3-bis-(phenylhydrazone) were so obtained. Since only the glyoxal derivative was present in appreciable quantities, an analytical procedure based on the chromatographic separation was established and verified against known mixtures. The results obtained by this method are presented in Figs. 3 and 4.

The hydroxylamine hydrochloride method[47,48] was employed to determine the free carbonyl present in the condensate solution. The results are given in Fig. 5 together with a curve obtained by summation of the amounts of carbonyl ascribed to formaldehyde and glyoxal.

Although the analytical methods presented herein are dependable to the precision required (±5%) it should be emphasized that the formation of the condensate is an extremely rapid process in which we attempted to halt the decomposition of the cellulose nitrate at the same relative point in a large number of ignitions. This is a very difficult undertaking and in one case we have observed that two operators following the same written instructions have disagreed by as much as 20% on the quantity of a component of the condensate. The results reported herein represent only a small part of those obtained in the course of this investigation and are believed to be self-consistent since they were obtained under conditions that were reproduced from one experiment to the next as closely as possible. However, in comparison with other data, it may be found that while the relative shapes of the curves (Figs. 2–5) will be the same, the curves may be displaced with respect to either or both axes.

Early in the course of this investigation, a relation between the nitrogen content of the cellulose nitrate and the yields of the three major organic components of the condensate was recognized. This relation is depicted in Fig. 4 and follows the expected pattern. An increase in nitrogen content of the cellulose nitrate is accompanied by a decrease in the yields of the organic components of the ignition (at constant pressure) products since more nitrogen oxides are formed which are reduced at the expense of the organic materials. A probable reason for the scattering of the results obtained for glyoxal (Fig. 4) is that the samples of cellulose nitrate employed were not substituted uniformly at positions 2 and 3 of the anhydro-D-glucose units. A more striking relationship was discovered when the ratios (Table I) between the formaldehyde yields and the primary nitrate content of the nitrate ignited were computed. The ratios are almost constant, 0.30 ± 0.03 mmole of formaldehyde per mmole of primary nitrate ignited, over a wide range of nitrate compositions. The constancy of the ratios, especially for the first four examples in Table I wherein the total nitrogen content remains constant while the primary nitrate content increases twofold, together with the fact that a nitrated dextran (containing no primary nitrate) afforded no formaldehyde on ignition, provides definitive evidence of a linear correlation between the primary nitrate content and the formaldehyde produced. Here then is presented another instance of selective rather than random reactivity of a substituted cellulose hydroxyl group. The ratios (Table I) were calculated employing the assumption that none of the cellulose nitrate samples contained non-esterified primary hydroxyl groups. If any assumption requiring non-esterified primary hydroxyl groups be made, the ratios would deviate from constancy. For example, if a random distribution were assumed, the ratio for the 13.9% N cellulose nitrate would be 0.27, an insignificant change, but the ratio for the 10.99% N cellulose nitrate would be 0.51, which cannot be correlated with any of the data indicating the linear relation between formaldehyde and primary nitrate content. The best assumption is the one which produces ratios in closest agreement with the ratio which is least affected by the assumption chosen. These considerations offer supporting evidence for the tentative suggestion of Murray and Purves[56] that essentially all of the primary hydroxyl groups are esterified in cellulose nitrates containing more than 10–11% N.

Figures 2, 3 and 5 record the pressure (2–700 mm.) dependency of the yields of the major organic products formed by the ignition decomposition of 13.4% N cellulose nitrate. Inspection of these figures suggests that an initial product at any pressure is the fragmented oxycellulose nitrate described previously.[2] The higher the ambient pressure, the greater is the proportion of this initial product undergoing additional degradation, nitrate cleavage and oxidation, with the formation of formaldehyde, formic acid, cyanide, glyoxal and the other organic substances isolated. As the pressure increases above 60 mm., all of the fragmented oxycellulose nitrate disappears and the rate of change in the yields of the organic products with pressure decreases, producing a range of pressures (200–500 mm.) in which the yields are almost pressure independent. The value for the total carbonyl (Fig. 5), however, decreases steadily with pressure which suggests that the formaldehyde, glyoxal and formic acid may be further oxidized but that the more complex entities (trioses and others), which are the source of the total carbonyl, are being degraded to these substances, thus maintaining their amounts essentially constant. As the ignition pressure increases above one atmosphere, all of the carbon compounds present at lower pressures are oxidized to carbon monoxide or dioxide at the expense of the nitrogen oxides. No oxides of nitrogen can be detected among the products formed at pressures above 100 atmospheres.[4,15,19]

In the previous paper of this series,[2] evidence was presented for the belief that the initial reaction

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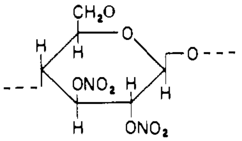
[56] G. E. Murray and C. B. Purves, This Journal, **62**, 3194 (1940).

in the decomposition of cellulose nitrate is the homolytic cleavage of the nitrogen–oxygen bonds to form nitrogen dioxide and intermediates of types I and II. Some evidence has been reported[13] which suggests that such intermediates may be generated simultaneously throughout the polymer molecule but at different rates. The data are conflicting and do not permit a conclusive decision as to which intermediate is formed at the greater rate. It was suggested previously,[2] that intermediate I could rearrange with the formation of formaldehyde and another intermediate III. The data, herein reported, correlating the formation of formaldehyde with the primary nitrate content, support this postulation. However, since not all of the carbon originally at position 6 of the anhydro-D-glucose unit is recovered as formaldehyde, the formation of formaldehyde is either not the exclusive reaction of the primary nitrate or the formaldehyde is destroyed in part by a subsequent reaction. Thus, the intermediate I may simply abstract a hydrogen atom from some other position to yield a stable entity IV. If a similar step occurred, intermediate III would afford the stable entity V. Alternatively, the formaldehyde may react with the nitrogen dioxide present, which affords both oxides of carbon, water, nitric oxide, nitrogen and possibly nitrous oxide,[57] or the formaldehyde may react with itself to give methanol and carbon monoxide (radical-sensitized)[58] or hydrogen and carbon monoxide (chain reaction).[59]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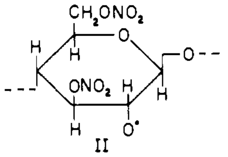
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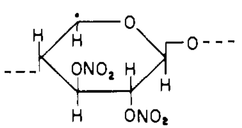
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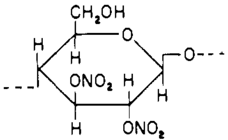
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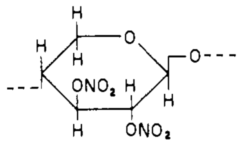
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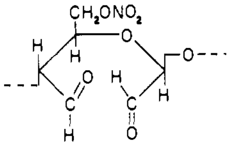
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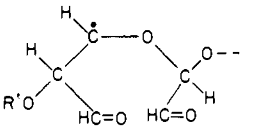
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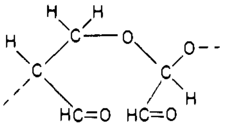
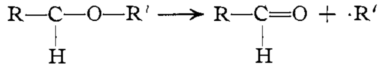
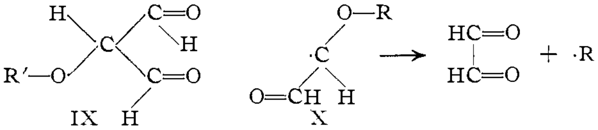

VIII

The rearrangement of II, with the elimination of nitrogen dioxide and the formation of the stable entity VI, was suggested previously[2] by analogy with the thermal cleavage of *trans*-1,2-cyclohexanediol dinitrite to produce adipic dialdehyde.[60] If the reaction sequences I → III and II → VI were to occur within the same anhydro-D-glucose unit, an intermediate such as VII may be expected. If VII were to extract a hydrogen atom from some other position, a stable unit VIII would result. Another fate of VII is suggested by the evidence[61] that a carbon possessing an odd electron and adjacent to an alkoxyl function may decompose as shown.

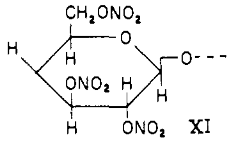


$$\mathrm{R{-}\underset{|}{\overset{\cdot}{C}}{-}O{-}R' \longrightarrow R{-}\underset{|}{C}{=}O + \cdot R'}$$

Thus, intermediate VII could rearrange with chain cleavage to afford glyoxal (through X) and the entity IX.

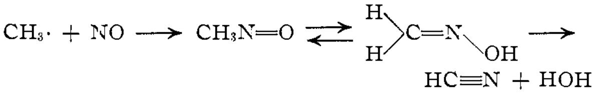


The action of the nitrogen dioxide on IX might afford the mesoxaldehyde which has been isolated in small yield. Intermediate III might also rearrange twice in the same manner to produce a greater number of R· groupings which are detailed as XI.


XI

If one compares the formic acid yield curve (Fig. 3) with the yield curve for the fragmented oxycellulose nitrate (non-volatile, water-insoluble solids, Fig. 2), it is apparent that at low pressures the rates of formation are parallel. Since chain cleavage is the main reaction required for the formation of the fragmented oxycellulose nitrate and formic acid appears concurrently, formic acid may very probably arise from an intermediate produced in the chain cleavage reaction. Intermediate XI has been postulated as one of the intermediates in all of the chain cleaving processes proposed and thus may be associated, in some as yet undefined manner, with the formation of formic acid.

Since it is known that the formation of hydrogen cyanide (Fig. 3) appears to proceed from methyl radicals[62] and since no source of methyl radical is apparent from the above intermediates, the hydrogen cyanide may not arise from the cellulose nitrate. A suitable precursor for the hydrogen cyanide would be the residual solvent,[25] ethyl acetate, which can afford a methyl radical[51–54] in the course of its decomposition. This supposition, now under further investigation, is supported by the constancy (except at the two lowest pressures) of yield of cyanide (Fig. 3) since the amount of residual casting



$$\mathrm{CH_3\cdot + NO \longrightarrow CH_3N{=}O \rightleftarrows H_2C{=}N{-}OH \longrightarrow HC{\equiv}N + HOH}$$

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solvent present is believed to be quite constant. However, it may be that formaldehyde oxime, postulated above as a precursor of the cyanide, can arise from the interaction of formaldehyde with one of the reduction products of the nitrogen oxides such as hydroxylamine. The presence of such nitrogenous intermediates is supported by the identification of ammonia as an ignition product at pressures above atmospheric.[15]

The role of the nitrogen oxides in the above processes cannot be ignored; however, their participation in the formation of the initially produced carbon fragments may be negligible compared to their major role in the further oxidation, to carbon monoxide and dioxide, of the entities first formed. This is particularly true of nitric oxide since it is not appreciably reduced to nitrogen at initial pressures below 20 atmospheres.[15]

The above discussion suggests possible modes of formation for the compounds isolated after the ignition of cellulose nitrate. However, except for formaldehyde, the data herein reported do not define either the modes of formation or the position of origin, in the original anhydro-D-glucose units, of the carbon isolated as small organic molecules. Accordingly, we are currently seeking further insight into these matters through the use of tracer techniques.[63]

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Action of Alkaline Hypochlorite on Corn Starch Amylose and Methyl 4-O-Methyl-D-glucopyranosides[1,2]

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Hypochlorite oxidation of corn starch amylose at 25° and at *p*H 9 and 11 with oxidant levels of 0.5 to 2.0 equivalents per anhydro-D-glucose unit shows that 75 to 88% of the polysaccharide remains non-dialyzable and that up to 27% of the oxidant is used for cleavage of the anhydro-D-glucose residues between carbons C2 and C3. From the hydrolyzate of the oxidized amylose can be isolated D-glucose, D-erythronic acid and its γ-lactone and glyoxylic acid. Likewise, by oxidation of methyl 4-*O*-methyl-β-D-glucopyranoside with sodium hypochlorite at *p*H 9 and 25°, there is obtained 43–47% of glyoxylic acid, isolated as the 2,4-dinitrophenylhydrazone and 10% of glyoxal as the 2,4-dinitrophenylosazone, again showing evidence of preferential oxidation at the C2 and C3 positions of the substituted D-glucopyranosidic ring. The corresponding α-D-glucopyranoside is oxidized similarly but more slowly.

Oxidative reactions are of importance in dealing with all polysaccharides but assume greatest industrial significance with starch and cellulose. Oxidative modification of starch to introduce new properties which widen its industrial application has been long practiced in the starch industry. Bleaching of cellulose pulps to improve whiteness by the destruction of color bodies subjects the cellulose molecules to oxidative degradation. In both of these industrial processes hypochlorite is the principal oxidant. While much information exists as to how the properties of these polysaccharides are altered by oxidants, little information exists either as to the sites at which oxidation occurs or as to the nature of the molecular fragments that may be produced. The present preliminary report describes some of the products formed when hypochlorite reacts with corn starch amylose and with the β- and α-anomeric forms of methyl 4-*O*-methyl-D-glucopyranoside, which may be regarded as models for cellulose and starch.

It is well known that specific oxidants such as periodate,[3] lead tetraacetate and perhaps one or two others[4] bring about cleavage between C2 and C3 of anhydro-D-glucose units of starch and cellulose. Nitrogen dioxide oxidizes starch[5,6] and cellulose[7] preferentially at C6, although some other non-specific oxidation also occurs.

Most other oxidants have far less specific action as indicated by various analytical procedures designed to measure the amounts of carbonyl and carboxyl groups which may be produced. Bromine water in the presence of calcium carbonate[8] and alkaline hypochlorite[9] react with starch to produce degradation products, among which are acids with less than six carbons. Hypochlorous acid, on the other hand, seems to oxidize starch preferentially[10] at C6 with little oxidation[11] occurring at C2 and C3.

At *p*H 11 sodium hypochlorite reacts with cellulose to give an abrupt rise in carboxyl content

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[1] Journal Paper No. 949 of the Purdue Agricultural Experiment Station, Lafayette, Indiana.

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