Thus it is seen that amylose behaves as a coil in the solvents used and as a nearly ideal random coil in aqueous KCl near room temperature. If the θ temperature of amylose in neutral aqueous solution is indeed near 25° it would be anticipated that precipitation should take place from such solutions at significantly lower temperature. Under some conditions amylose does indeed precipitate reversibly at temperatures near the freezing point. However, it is normally impossible to maintain any appreciable concentration of polymer at a temperature even a few degrees below the θ temperature. It is suggested as a possible explanation that amylose, in view of its known propensity for adopting a helical conformation in various complexes, may revert to a helix at temperatures below the θ point in water, thus satisfying polymer–polymer contacts intramolecularly. Attempts have been made to find evidence for such a change in conformation by measuring the optical rotation of an amylose solution over the temperature range 9 to 41° in 0.5 N KCl. No evidence for any transition was seen, the specific rotation (sodium D line) decreasing almost linearly with increasing temperature, by about 0.5° per degree centigrade, over the entire range. This result is in accord with the expected behavior for a coil.[15] The fact that amylose slowly crystallizes (retrogrades) at temperatures even above the θ temperature is, at first thought, somewhat surprising. However, the usual treatment of polymer precipitation and the concept of the θ temperature are based on amorphous phase separation and are not strictly applicable to crystallization phenomena.[16] It seems possible that polymer-polymer interactions are increased through slowly attained preferential contacts so that nucleation and crystallization may ensue at temperatures appreciably above the θ temperature. In a general way the difficulty of dissolving amylose in water and the instability of aqueous solutions of amylose are compatible with the fact that water is a relatively poor (indifferent) solvent for this polymer.

(15) J. Schellman, *Compt. rend. trav. Lab. Carlsberg. Serie Chim.*, **30**, 363 (1958).

(16) P. J. Flory, "Principles of Polymer Chemistry," Chap. 8, Cornell University Press, Ithaca, N. Y., 1953.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Controlled Thermal Decomposition of Cellulose Nitrate. VI. Other Polymeric Nitrates[1,2]

BY M. L. WOLFROM, ALAN CHANEY AND K. S. ENNOR

RECEIVED DECEMBER 17, 1958

The reduced pressure ignition products (formaldehyde, formic acid, glyoxal, hydrogen cyanide, α-hydroxynitrile, and volatile and total acid) of amylose and amylopectin nitrates were found to correspond in identity and yield with those produced by cellulose nitrate. Under the same conditions, the nitrates of polyvinyl alcohol and dextran afforded similar products but the yields were distinctively altered. These alterations in yield are correlated with the variations in structure of the polymeric nitrates ignited. The general mechanistic sequences previously utilized to interpret the ignition decomposition of cellulose nitrate appear to be applicable with minor variations to the interpretation of all polymeric nitrate ignition reactions. The intrinsic viscosity and optical rotation of dextran nitrate were determined.

Our investigations[2-6] of the ignition of cellulose nitrate under reduced pressure indicated that additional valuable information might result from similar studies employing other polymeric nitrates. It has been found that the pyrolytic method employed, in which the polymeric nitrate sample is subjected to a nearly instantaneous increase in temperature of several hundred degrees, institutes a self-sustaining, normally non-luminous,[5] decomposition reaction. The initial reaction products, which are expelled violently from the hot reaction zone, are cooled as rapidly as possible in an attempt to quench secondary reactions between the several substances formed. The investigation, herein described, was initiated in the belief that a study of the products of ignition of the nitrates of dextran, starch and polyvinyl alcohol would provide further insight concerning the important initial decomposition reactions of polymeric nitrates.

The recent commercial availability[7] of two starch fractions, amylose and amylopectin, simplified the study of two considerably different polymeric carbohydrate nitrates. Although similar starch fractions have been nitrated previously,[8,9] the methods appeared experimentally tedious or afforded products that required considerable effort to stabilize. In the current work, both amylose and amylo-

---

(1) This work was carried out under contract (DA-33-019-ord-2025, technical supervising agency, Ballistic Research Laboratories, Aberdeen Proving Ground, Md.) between the Ordnance Corps and The Ohio State University Research Foundation (Project 675). Preliminary communication: *Abstracts Papers, Am. Chem. Soc.*, **134**, 10E (1958).

(2) Previous communication in this series: F. Shafizadeh, M. L. Wolfrom and P. McWain, THIS JOURNAL, **81**, 1221 (1959).

(3) M. L. Wolfrom, A. Chaney and P. McWain, *ibid.*, **80**, 946 (1958).

(4) M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, R. S. Bower, G. G. Maher, J. D. Murdock, A. Chaney and Eloise Carpenter, *ibid.*, **78**, 4695 (1956).

(5) 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, *ibid.*, **77**, 6573 (1955).

(6) F. Shafizadeh and M. L. Wolfrom, *ibid.*, **80**, 1675 (1958).

(7) Stein, Hall and Co., New York, N. Y.; the fractionation process of Coöperatieve Verkoop- en Productievereniging van Ardappelmeel en Derivaten "Avebe" G. A., Dutch Patent 78,328 (1955).

(8) G. V. Caesar and M. Goldfrank, THIS JOURNAL, **68**, 372 (1946); G. V. Caesar, N. S. Gruenhut and M. L. Cushing, *ibid.*, **69**, 617 (1947).

(9) W. R. Ashford, L. M. Cooke and H. Hibbert, *Can. J. Research*, **24B**, 238 (1946); W. R. Ashford, T. H. Evans and H. Hibbert, *ibid.*, **24B**, 246 (1946); W. R. Ashford and H. Hibbert, *ibid.*, **25B**, 151 (1947).

pectin were nitrated in absolute nitric acid at 0°. Nearly complete nitrations (13.9% N) were readily obtained and the nitrates obtained were sufficiently stable. This nitrating agent is much less effective with cellulose.[10] Although nitrates of starch have been known for more than a century, primary interest has centered on the preparation of stable nitrates.[11] The stability tests employed for cellulose nitrate have been applied to starch nitrate,[8,9] but no comprehensive investigation has been made of the degrading action of various chemical reagents or thermal treatments similar to those reviewed for ceullulose nitrate.[4,5]

Attempts to employ absolute nitric acid for the nitration of polyvinyl alcohol resulted in fires and other difficulties. Excellent results were obtained with the acetic anhydride–absolute nitric acid technique described by Deans and Nicholls.[12] Other than the application of standard cellulose nitrate stability tests,[12] only a single investigation of the chemical and thermal properties of polyvinyl nitrate has been published and this work is not generally available.[13]

Save for a single citation,[4] dextran nitrate has not been reported previously. Hence, it was deemed pertinent to determine the intrinsic viscosity and optical rotation of the sample prepared for the ignition studies. The viscosity data obtained have been plotted in Fig. 1. The utilization of the intrinsic viscosity obtained for dextran nitrate for the calculation of the molecular weight would be questionable without further investigation. For dextran itself, it has been shown[14] that the relation between intrinsic viscosity and molecular weights (above 100,000) is complex as a result of the branching in the polymer chains. The conclusions drawn concerning the structure of dextran[14] appear to be valid for the dextran nitrate sample. Furthermore, a minimum value of 100,000 for the molecular weight of the dextran nitrate would seem to be a reasonable assumption. Other pertinent physical data have been included in the Experimental section.

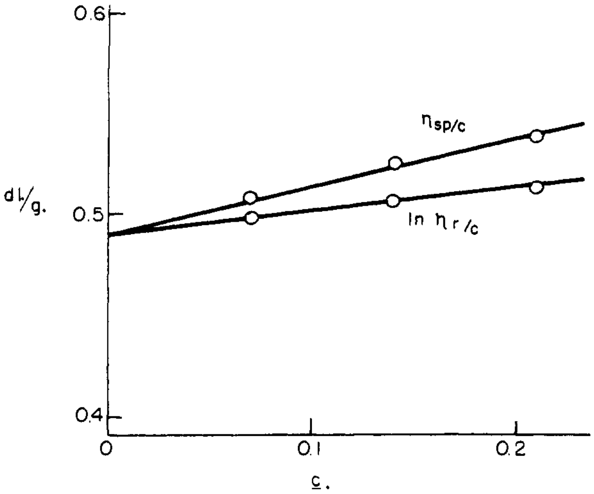

Fig. 1.—Variation of viscosity with concentration for dextran nitrate in N,N-dimethylformamide at 25.5°.

The nitrates of amylose, amylopectin, dextran, polyvinyl alcohol and cellulose were each ignited under reduced pressure in an all-glass apparatus employing the techniques reported previously.[4] The resulting easily condensable (−60°) decomposition products were dissolved and the aqueous solutions obtained were analyzed. The results of these analyses are given in Table I. Contrary to previous practice,[2–6] the results have been recorded in terms of millimoles of product obtained per gram of nitrate derivative ignited. This selection was made to facilitate comparison between the yields arising from the polymeric nitrate derivatives of grossly different structure and nitrogen content.

The yields of vicinal dicarbonyl in Table I are equivalent to glyoxal as recorded[3] previously. The recent identification of methylglyoxal[15] as one of the low yield ignition products of cellulose nitrate[4] coupled with the known interference[16] of vicinal dicarbonyl compounds in the hydrogen peroxide analysis employed[3] for glyoxal has necessitated this correction. This lack of specificity in the glyoxal assay probably has introduced an inexactness of no more than 5% in the reported[3] glyoxal yields from cellulose nitrate since the amount of methylglyoxal present was relatively low.[15]

It has been noted[4,5] that the ignition of cellulose nitrate afforded small amounts of water- and methanol-insoluble products. Previously,[3–5] the weight

Table I

Yield of Products in Mmoles per Gram of Nitrate Ignited at 200 Mm. Pressure

	Nitrate of[a]				
Product	Cellulose, 14.09% N	Amylose, 13.85% N	Amylopectin, 13.96% N	Polyvinyl alcohol, 14.35% N	Dextran,[d] 11.91% N
Formaldehyde	0.81	0.82	0.92	0.93[b,c]	0.24[e]
Formic acid	.91	.79	.99	.57	2.37
Cyanide (ion)	.11	.08	.13	.24	0.08
Nitrile (total)	.41	.36	.38	.52	.20
Vicinal dicarbonyl	.19	.20	.28	.16	.67
Volatile acid	1.17	.92	1.02	.70	2.66
Total acid	1.57	1.37	1.22	1.02[c]	3.81

[a] Cast as films from acetone and the major amount of the residual casting solvent removed by steeping in hot water. [b] Calculated after estimation of the purity of the precipitate obtained; see Experimental. [c] Values for formaldehyde and total acid were also obtained for 14.79% N polyvinyl nitrate, 0.89 and 0.99 mmole per g., respectively. [d] These values should be compared with those for cellulose nitrate[4] of similar nitrogen content: formaldehyde, 1.2; vicinal dicarbonyl, 0.4; formic acid, 1.9; and total acid, 3.2. [e] This value represents a minimum amount; an extremely rapid aging process reduced this yield to 0.07 mmole per g. in less than 2 hr. following the initial analyses.

---

(10) J. Chedin and A. Tribot, *Mem. services chim. état (Paris)*, **34**, 277 (1948); T. Urbanski and J. Hackel, *Tetrahedron*, **2**, 300 (1958).

(11) G. V. Caesar, *Advances in Carbohydrate Chem.*, **13**, 331 (1958).

(12) S. A. V. Deans and R. V. V. Nicholls, *Can. J. Research*, **27B**, 705 (1949).

(13) B. L. Crawford, Jr., a series of quarterly reports describing work done at the University of Minnesota under Naval Ordnance Contract 10346 during the years 1948–1950.

(14) F. R. Senti, N. N. Hellman, N. H. Ludwig, G. E. Babcock, R. Tobin, C. A. Glass and B. L. Lamberts, *J. Polymer Sci.*, **17**, 527 (1955).

(15) G. P. Arsenault, Ph.D. Dissertation, The Ohio State University, 1958; this work is being prepared for publication.

(16) T. E. Friedemann, *J. Biol. Chem.*, **73**, 331 (1927); see Experimental also.

of this material has been determined and deducted from the weight of cellulose nitrate taken to give the amount of cellulose nitrate actually ignited. The water-insoluble solid, 2% by weight of the cellulose nitrate (12.6% N) taken, has now been investigated. Extraction with acetone followed by evaporation of the acetone extract afforded apparently unchanged cellulose nitrate, 1.3% of the weight taken. The undissolved solid remaining after washing with water, aqua regia and water and drying was elemental carbon, 0.55% of the weight taken. This corresponds to 2.1% of the carbon introduced as cellulose nitrate and increases the carbon recovery[3] to 90%. The yields of ignition products (Table I) obtained from the 14.1% N cellulose nitrate sample coincide with the values that result from extrapolation of the yield data given previously.[4]

In addition to the products listed in Table I, polyvinyl nitrate on ignition afforded acetaldehyde (0.16 mmole per g. ignited), isolated and characterized as the dimedon (5,5-dimethyl-1,3-cyclohexanedione) derivative, and both glyoxal and methylglyoxal, identified as their bis-(2,4-dinitrophenylhydrazones). If the carbon recoveries for the polyvinyl nitrate ignition products (Table I) are summed[3] together with the values reported[13] for carbon monoxide and dioxide (0.86 and 0.23 mmole, respectively, per mmole ignited at 1 atm.), a total carbon recovery of about 65% is obtained. This is considerably lower than the 90% (see above) recovery for cellulose nitrate and indicates the formation of unidentified carbon-containing products. No evidence for significant amounts of unidentified carbon-containing materials was noted in the study of the easily condensable fraction of the ignition products. The unidentified products are probably gaseous in nature; in particular, methane, which would not be detected, has been shown to be a product of ethyl nitrate flames.[17] The products of the polyvinyl nitrate ignitions were similar to those reported[17] for the ethyl nitrate flames. The minor differences appear to be explicable in the light of the recent studies with flames of the nitrates of 1,4- and 2,3-dihydroxybutane.[18]

The yields of the various ignition products of the starch nitrates (Table I) were in general accord with those determined for cellulose nitrate. These nitrates undoubtedly decompose under ignition conditions by mechanistic processes identical with those proposed for cellulose nitrate.[2-6] One reaction process, which has not been considered previously, should be mentioned in view of the results herein. Malmberg's[19] isolation of the 2,4-dinitrophenylhydrazine derivatives of glyoxal and methylglyoxal from the cool-flame combustion products of methane requires that recombination of the initially formed carbon intermediates occurs during burning. Although the yields of these carbonyl derivatives from the polymeric nitrate ignitions are larger by several orders of magnitude, recombination reactions of the intermediate ignition products may be of considerable importance. Possibly only the minor products, methylglyoxal,[15] mesoxaldehyde and triose,[4] arise by recombination reactions rather than by the involved sequences presented previously[3,4] (see below). Attempts to elucidate this matter could be made employing the potential radiochemical[2,6] or optical activity of certain of the low yield oxygenated ignition products,[15] but these methods appear experimentally formidable.

Based on studies[4] of cellulose and dextran nitrates, it had been implied that formaldehyde was produced only from the carbon of primary nitrate moieties. Subsequent radiochemical investigation[2,6] demonstrated that about 35% (0.12 mmole per mmole ignited) of the formaldehyde arose from the five carbons of the anhydro-D-glucose unit other than the primary. The data now available for the nitrates of dextran, pectic acid,[4] xylan[4] and polyvinyl alcohol (0.064, 0.036, 0.073 and 0.076 mmol. of formaldehyde formed per mmol. ignited, respectively) support this finding. The yields of formaldehyde obtained from the ignition of the polymeric nitrates which contain no primary nitrate groups are only about half that indicated by the cellulose-C^{14} experiments. Since the radiochemical method is not subject to the loss of formaldehyde resulting from the aging process in the isolative method,[3] this difference is to be expected. In every case, the yields of formaldehyde from the polymeric nitrates were much greater than could be produced by the small amount of primary nitrate occurring at the chain ends of these polymers. The postulations in the succeeding paragraph represent an attempt to rationalize these phenomena.

The formyl radical is significant in the thermal reactions of many substances.[20] Both glyoxal and formaldehyde are believed[20] to afford formyl radicals during their thermal decomposition and to be formed by such radicals, as outlined below.

$$\mathrm{HCHO} \longrightarrow \mathrm{H\dot{C}O} + \mathrm{H\cdot} \qquad (1)$$

$$\mathrm{OHC - CHO} \longrightarrow 2\mathrm{H\dot{C}O} \qquad (2)$$

$$\mathrm{H\cdot} + \mathrm{HCHO} \longrightarrow \mathrm{H\dot{C}O} + \mathrm{H_2} \qquad (3)$$

$$\mathrm{H\dot{C}O} + \mathrm{H\dot{C}O} \longrightarrow \mathrm{HCHO} + \mathrm{CO} \qquad (4)$$

$$\mathrm{H\dot{C}O} + \mathrm{H\dot{C}O} \longrightarrow \mathrm{OHC - CHO} \qquad (5)$$

$$\mathrm{H\cdot} + \mathrm{H\dot{C}O} \longrightarrow \mathrm{HCHO} \qquad (6)$$

$$\mathrm{H\cdot} + \mathrm{H\dot{C}O} \longrightarrow \mathrm{H_2} + \mathrm{CO} \qquad (7)$$

Once formed (1 to 3), the formyl radicals may suffer several fates. Although the most energetically favorable (7) might be exclusive if the system were allowed to equilibrate, 4 to 6 may contribute under the quenching conditions employed. Thus, a fraction of the formaldehyde formed may arise from the carbons of the nitrate which also afford glyoxal, if the sequence 2 is succeeded by either 4 or 6. Although the reaction is less probable, glyoxal may be formed, in part, by the combination (5) of formyl radicals which arose, *via* 1 or 3, from the formaldehyde produced in the initial decomposition of the polymeric nitrate. That

---

[17] D. P. Needham and J. Powling, *Proc. Roy. Soc.* (*London*), **A232**, 337 (1955).

[18] J. Powling and W. A. W. Smith, *Combustion and Flame*, **2**, 157 (1958).

[19] E. W. Malmberg, THIS JOURNAL, **76**, 980 (1954).

[20] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954.

neither formaldehyde nor glyoxal arise exclusively from a particular carbon atom (or atoms for glyoxal) of the anhydro-D-glucose moieties has been shown by studies of the ignition of cellulose-C^{14} nitrate.[2,6] The reactions 1 to 7 appear to correlate these observations in addition to providing a possible explanation for the production of formaldehyde during the ignition of the nitrates of those polymers which contain no primary hydroxyl functions.

The ignition of dextran nitrate has been found (Table I) to generate considerably greater amounts of formic acid than cellulose nitrate of equal nitrogen content. This result may be explained on the basis of a relation which has been intriguing throughout our investigation of the ignition of cellulose nitrate. Namely, a similarity has been noted between the products formed by the decomposition of molecules containing vicinal nitrate ester functions and those resulting from the action of glycol-cleaving reagents on substances with vicinal hydroxyl groups. Since dextran nitrate is the only substance studied which contains three contiguous nitrate ester functions, the increased yield of formic acid is in accord with the postulated relation. Obviously other reaction paths leading to formic acid may be important. Similar relations have also been noted in a study of the vapor phase thermal decomposition of substances containing vicinal nitrite ester groups.[21]

Experimental

Preparation of Nitrates.—Flakes of amylopectin (10 g., Ramalin G[7]) were added in small portions to 133 ml. of absolute nitric acid stirred at −5 to −10°. After stirring at 0° for 2 hr., the heterogeneous mass was poured into ice and water (2 liters). The white precipitate was collected by filtration and washed with water. The dry solid was dissolved in acetone (100 ml.) and reprecipitated by addition of the solution to water (4 liters) containing a small amount of sodium chloride. The solid was again washed with water, dried in air, and dissolved in acetone. The acetone solution was dried with anhydrous calcium sulfate and the dissolved nitrate cast into a sheet as described previously.[5] The sheet obtained (14.5 g.) was extremely fragile and broke into small fragments which were extracted for several days with boiling water. Final drying was carried out at 1 mm. over phosphoric anhydride. Analysis of a portion of this amylopectin nitrate employing the nitrometer method[22] afforded a nitrogen content of 13.96% (degree of substitution, 2.93; polymerizing unit mol. wt., 294).

Amylose (Superlose,[7] 10 g.) was nitrated and converted to a tough flexible sheet (15.7 g.) as described for amylopectin nitrate. The amylose nitrate contained[22] 13.85% N (degree of substitution, 2.89; polymerizing unit mol. wt., 292).

A sample of dextran[23] (12.5 g.) was added to 166 ml. of absolute nitric acid at −5 to −10°. After stirring the heterogeneous mixture for 2 hr. at 0°, it was poured into 3 liters of ice and water. The flaky white product was recovered, purified and converted to a tough, flexible sheet (19.3 g.) as described for amylopectin nitrate.

Anal. Calcd. for $C_6H_7O_2(ONO_2)_{2.23}(OH)_{0.77}$: C, 27.45; H, 2.98; N, 11.91. Found: C, 27.53; H, 2.81; N, 11.90 (Kjeldahl), 11.91 (nitrometer[22]).

Viscosity studies of the dextran nitrate in N,N-dimethylformamide solution at 25.5° (Fig. 1) employing a modified Ostwald viscometer yielded a value of 0.49 deciliter/g. for the intrinsic viscosity. Dextran nitrate was insoluble in water, ethanol, 2-methoxyethanol, acetonitrile and several alkyl acetates. Of the three solvents found for dextran nitrate, acetone, N,N-dimethylformamide and tetrahydrofuran, the latter was used to measure the optical rotation, $[\alpha]^{24.4}D$ + 199° (c 0.25). In the same solvent, only end absorption was observed in the ultraviolet; the infrared absorption was indistinguishable from that of cellulose nitrate.

Polyvinyl alcohol (30 g., Borden Co., Chemical Division, Lemol 60–98) was suspended in 180 ml. of acetic anhydride and added slowly to a mixture of 165 ml. of absolute nitric acid and 165 ml. of acetic anhydride[12] stirred at −5 to −10°. After stirring at −10° for 1 hr., the suspension was poured into ice and water (2 liters). The solid was stabilized and converted to sheet form (25 g.) as described for amylopectin nitrate. The polyvinyl nitrate was found[22] to contain 14.79% N (degree of substitution, 0.89; polymerizing unit mol. wt., 84.1).

Another sample of polyvinyl nitrate was prepared from Borden's Lemol 24–98 (lower degree of polymerization) employing the same method: nitrogen content,[22] 14.35% (degree of substitution, 0.84; polymerizing unit mol. wt., 81.7).

Cotton linters (13 g., Hercules Powder Co., High Viscosity) were added to a mixture of absolute nitric acid (350 ml.), acetic anhydride (250 ml.) and acetic acid (250 ml.) at 5°. The suspension was stirred for 5 hr. (5°) before the insoluble fibers were recovered by centrifugation and dropped into water and washed with water, cold 50% ethanol and cold absolute ethanol. After boiling the fibers twice with ethanol and drying, there was obtained 23.2 g. of 14.09% N cellulose nitrate[22] (degree of substitution, 2.98; polymerizing unit mol. wt., 296). These fibers were cast into sheet form by evaporation of an acetone solution.

The nitrates of dextran and amylose, stored at room temperature in the dark for several months, began to decompose as indicated by the evolution of nitrogen dioxide. At this time, all of the polymeric nitrates except that of cellulose (14.09% N) were destroyed. The cellulose nitrate sample had remained stable for more than five years. Since no determined attempt was made to completely stabilize the nitrates, the decompositions were not surprising. All of the nitrates could be detonated by a hammer blow on a steel anvil.

Ignition of Nitrates.—The polymeric nitrates were ignited at 200 mm. as described previously.[4] The apparatus was modified slightly for the ignitions of amylopectin nitrate due to its physical state. The ignition wire was wrapped around a 1″ by 3″ Pyrex microscope slide and the small pieces of sheet were placed on the slide in contact with the wire.

The ignition products were removed from the combustion system by dissolution in water[4] or 0.1 *N* sodium hydroxide.[3] Aliquots of the solutions were analyzed immediately by the methods reported[3] and the results are given in Table I. The current determination that dextran nitrate affords formaldehyde merits comment. This result contradicts a previous report.[4] Under the standard procedure evolved for the determination of formaldehyde,[4] the small amount of this substance produced from dextran nitrate would have been difficult to detect. Furthermore, at the time of the original study, no recognition had been given to the aging processes leading to loss of carbonyl compounds.[3] In the present work, it has been shown that the loss of formaldehyde in the aqueous solution of dextran nitrate ignition products occurs (Table I, footnote *e*) at a much greater rate than was the case[3] with cellulose nitrate. This variation probably was the consequence of the greater ratio of cyanide to formaldehyde found for the dextran nitrate ignition products.

Identification of Polyvinyl Nitrate Ignition Products.—Since the yields of the polyvinyl nitrate ignition products were quite different from those obtained from the carbohydrate nitrate ignitions, further confirmation of their identity seemed desirable. For example, the melting point range (110–170°) of the precipitate obtained in the analysis for formaldehyde with dimedon (5,5-dimethyl-1,3-cyclohexane-

---

(21) L. P. Kuhn and L. DeAngelis, This Journal, **76,** 328 (1954).

(22) 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.

(23) From *Leuconostoc mesenteroides* NRRL B-512-E (P.P. 55-B). This sample had 95% α-1,6-linked anhydro-D-glucopyranose units; the remainder were 1,3-linked. The sample and composition were very kindly furnished by Dr. Allene Jeanes of the Northern Utilization Research and Development Division of the U. S. Department of Agriculture. The intrinsic viscosity of the dextran, 1.02 deciliters/g. (water, 25.5°), as determined in this Laboratory is comparable to that determined by J. W. Van Cleve, W. C. Schaefer and C. E. Rist, This Journal, **78**, 4435 (1956), for a sample with a molecular weight of 30,000,000.

dione) was lower and greater than usual (185–190°). A single crystallization of this impure material (350 mg.) from 10 ml. of refluxing ethanol afforded a 64.5% yield of pure formaldehyde dimethone (2,2′-methylidenebis-[5,5-dimethyl-1,3-cyclohexanedione]), m.p. 194–195°. The mixed melting point with an authentic specimen was unchanged and identical X-ray powder diffraction patterns were obtained. Under the same conditions the recovery of pure formaldehyde dimethone from a mixture (2 to 1 by weight) of the authentic dimedon derivatives of formaldehyde and acetaldehyde was 95.3%. The yields of formaldehyde from polyvinyl nitrate recorded in Table I are those obtained by correcting the weight of dimethone derivative obtained in the standard analytical method for the formaldehyde dimethone content found by crystallization increased by the loss during purification: net correction factor, 66.7%.

The remaining 33.3% of the dimethone mixture was shown to be primarily acetaldehyde dimethone (2,2′-ethylidenebis-[5,5-dimethyl-1,3-cyclohexanedione]). A large aliquot (50 ml.), equivalent to 4.74 g. of polyvinyl nitrate, was steam distilled. The distillate, 800 ml., was treated with a slight excess of dimedon reagent in ethanol. The resulting crystals, 1.75 g., were dissolved in 20 ml. of refluxing ethanol. On cooling, 1.13 g. of pure formaldehyde dimethone was deposited. The mother liquor was diluted with water and cooled; 0.36 g. of solid was deposited. Two recrystallizations from methanol afforded pure acetaldehyde dimethone, 0.21 g., of m.p. 141–142°. The melting point was not depressed on admixture with an authentic sample and identical X-ray powder diffraction patterns were obtained. Since the recovery in pure form of acetaldehyde dimethone from a mixture with formaldehyde dimethone (above) was only 83%, the yield of acetaldehyde from polyvinyl nitrate was 0.16 mmol. per g. minimum. The remaining 0.4 g. of the original 1.75 g. of dimethone mixture was not investigated further; it undoubtedly contained about 0.2 g. of the identified dimethones which were not recoverable.

An aqueous solution (120 ml.) of the ignition products produced by 11.4 g. of polyvinyl nitrate was added, immediately after preparation, to 680 ml. of 30% perchloric acid containing 17 g. of dissolved 2,4-dinitrophenylhydrazine.[15] The mixture was immediately centrifuged for 90 min. The supernatant liquid was filtered and after standing overnight had deposited an added 0.73 g. of solid after washing and drying. The solid from the centrifugation vessels was transferred to a filter and washed with water; yield 5.78 g. About 3 to 4 times this weight would have been produced by cellulose nitrate.[15] A portion (4.5 g.) of the larger fraction was dissolved in about 40 ml. of hot (210°) nitrobenzene, treated with activated carbon, and the solution cooled. The crystals which deposited (400 mg.) were recrystallized four times from hot nitrobenzene giving 210 mg. of glyoxal bis-(2,4-dinitrophenylhydrazone) with m.p. 331–334° dec. The infrared spectrum in a potassium bromide pellet was identical with that reported.[24] Identical X-ray powder diffraction patterns were obtained from this material and authentic glyoxal bis-(2,4-dinitrophenylhydrazone); for the latter: 7.90[25]m,[26] 6.92m, 6.49m, 4.25m, 3.98w, 3.74m, 3.36m, 3.28s, 2.91m.

The nitrobenzene solution was diluted to 300 ml. with benzene and added at the top of a 7 (diam.) by 12 cm. column of silicic acid–Celite (5/1) containing 8% free water.[15] This column was developed successively with 2 liters of benzene, 2 liters of 5% ether in benzene, 2 liters of 10% ether in benzene, and 2 liters of 25% ether in benzene. The combined effluents were evaporated under reduced pressure and the residual nitrobenzene solution was diluted to 200 ml. with benzene. This solution was rechromatographed in 35-ml. portions using the same absorbent, 5.5 (diam.) by 25 cm., employing about 3 liters of benzene developer. The orange-red zones at the bottom of the extruded columns were sectioned and eluted with ether. The combined eluates from six columns were evaporated to dryness under reduced pressure and the red crystals were chromatographed on a single column by the same technique. The material (10 mg., 2×10^{-3} mmol. per g. ignited) obtained from the eluate was crystallized four times from hot nitrobenzene. The infrared absorption spectrum of this material (m.p. 299–300°) was identical with that recorded[24] for methylglyoxal bis-(2,4-dinitrophenylhydrazone). This material afforded an X-ray powder diffraction pattern identical with that obtained from authentic methylglyoxal bis-(2,4-dinitrophenylhydrazone); for the latter: 6.65,[25]s,[26] 6.03s, 5.25w, 4.14w, 3.74w, 3.60m, 3.43m, 3.16s, 3.07w, 2.94m, 2.24w.

The orange-red zones immediately above the methylglyoxal zones were eluted and purified in the same manner. The crystals obtained were identified as glyoxal bis-(2,4-dinitrophenylhydrazone) by the techniques described above. Following the chromatographic method detailed below, formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazone were identified in the column effluents. The material at the top of the columns was separated partially by chromatography.[15] Two crystalline derivatives were isolated in very low yield after purification by crystallizing the material from the eluates from nitrobenzene. Attempts to identify these materials by study of their infrared absorption spectra were unsuccessful; no similar spectra were found in our files[15] or elsewhere[24] but it was concluded from the spectra that these substances were bis-(2,4-dinitrophenylhydrazones).

A part of the larger fraction of the 2,4-dinitrophenylhydrazine derivative mixture was extracted with several portions of boiling water. The combined extracts were evaporated under reduced pressure. The solid remaining was sublimed at 100° and 0.2 mm. pressure. Part of the sublimate (1 mg.) was dissolved in chloroform and added at the top of a silicic acid–Celite column (5/1, 0% free water,[15] 1 by 20 cm.). Development[15] with 10% ether in petroleum ether (b.p. 65 to 69°) afforded only two definitive bands. These bands were identical chromatographically with known formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazones.

Estimation of Elemental Carbon Produced by the Ignition of Cellulose Nitrate.—A 10.0-g. sample of 12.6% N cellulose nitrate was ignited in the usual manner. The water-insoluble products were collected and dried at 1 mm. over phosphoric anhydride; yield 201 mg. This mixture was extracted with warm acetone. The acetone extracts were concentrated and dried under reduced pressure over phosphoric anhydride; yield 132 mg. of unchanged cellulose nitrate. The water- and acetone-insoluble fraction was extracted with aqua regia, washed with water and dried. The residue (55 mg.) was elemental carbon; 2.1% of the carbon introduced as cellulose nitrate.

Interference of Vicinal Dicarbonyl Compounds with the Glyoxal Analysis.—Solutions of a number of carbonyl compounds in water were prepared with known concentrations of about 0.05 *M*. Aliquots, 20 ml., of these solutions were adjusted to *p*H 7 (Beckman model H) with 0.05 *N* sodium hydroxide. After the addition of 10 ml. of 3% hydrogen peroxide, the uptake of base (0.05 *N*) required to maintain *p*H 7 was measured. DL-Glycerose, glycolic acid, glycolaldehyde, dihydroxyacetone, formaldehyde and acetaldehyde consumed negligible amounts (less than 0.5 ml.) during 60 min. In contrast, methylglyoxal, pyruvic acid and 2,3-butanedione consumed about two equivalents of base per mole in 60 min. Since methylglyoxal is formed in all the nitrate ignitions studied to date, the recorded[3] glyoxal yields determined by peroxide oxidation are more correctly cited as vicinal dicarbonyl in spite of the low proportion (less than 5%) of interfering substances.[15]

COLUMBUS 10, OHIO

---

(24) J. H. Ross, *Anal. Chem.*, **25**, 1288 (1953).

(25) Interplanar spacing, Å., CuKα radiation.

(26) Visually estimated relative intensity; s, strong; m, medium; w, weak.