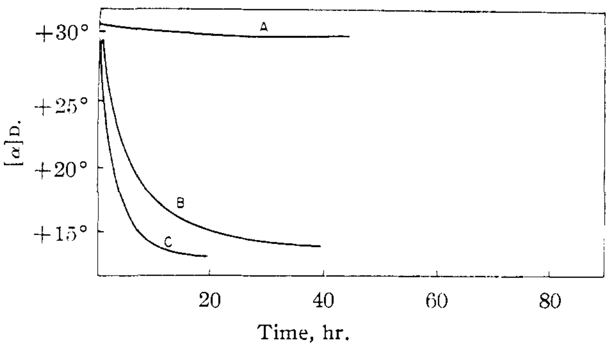

Fig. 5.—Hydrolytic mutarotation of D-gluconamide at 25° ($c$ 3); A, 0.008 $N$ HCl; B, water; C, 0.008 $N$ NaOH.

## Experimental

**Aldonamides.**—These were prepared from the lactones by reaction with liquid ammonia followed by solvent evaporation[9] or by reaction with concentrated ammonium hydroxide (sp. gr. 0.880) with subsequent precipitation by ethanol.[17] They were purified by recrystallization from di-*O*-methyl-1,2-ethanediol (Methyl Cellosolve) as recommended by Hockett.[11] The constants determined were: D-galactonamide, m.p. 170–171° dec., $[\alpha]^{25}D$ + 30.6°; D-gluconamide, m.p. 142–143°, $[\alpha]^{25}D$ +31.4°; L-mannonamide, m.p. 170–171° dec., $[\alpha]^{25}D$ +13.8°; D-ribonamide, m.p. 136–137°, $[\alpha]^{25}D$ +17°. The rotations were determined in aqueous solution ($c$ 3, $c$ 1 for L-mannonamide) and were extrapolated to initial time where required.

**Identification of Ammonium D-Gluconate as a Hydrolytic Product of D-Gluconamide.**—D-Gluconamide (1.500 g.) was dissolved in water and the volume adjusted to 50.00 ml. The solution was transferred to a 4-dm. glass polarimeter tube and the rotation followed until it became constant (+30.7 → +13.8°, 80 hr.). The solution was removed from the polarimeter tube and evaporated to dryness under reduced pressure. Recrystallization of the crystalline residue from 95% ethanol gave a quantitative yield of a white crystalline solid, m.p. 153–154°, $[\alpha]^{25}D$ +11.8° ($c$ 3, water). Comparison of this compound with authentic ammonium D-gluconate, $[\alpha]^{25}D$ +11.2° ($c$ 3, water), by melting point, melting point on admixture, and X-ray powder diffraction pattern showed them to be identical; X-ray powder diffraction data[18]: 8.92m, 5.10s(3,3), 4.88m, 4.66m, 4.44s(3,3), 3.85s(1,1), 3.34s(1,1), 3.21m, 3.11m, 2.91m, 2.56w, 2.51w, 2.43w, 2.30w.

**Mutarotation Data.**—The mutarotations were determined in 4-dm. or 6-dm. glass polarimeter tubes, unless otherwise noted. The data obtained are recorded in Figs. 1–5. The smooth curves shown were established by many points accurately determined by polarimetry; the complete data are on record.[19] The $p$H values of the solutions dropped during the rotation change.

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[17] J. W. W. Morgan and M. L. Wolfrom, This Journal, **78**, 1897 (1956).

[18] Interplanar spacings, Å., λ 1.5418 Å., and relative intensities, estimated visually: s, strong; m, medium; w, weak; first three strongest lines noted, (1) strongest, (1,1) about equal.

[19] R. B. Bennett, M. Sc. Thesis (M. L. Wolfrom, preceptor), The Ohio State University, 1955.

Columbus 10, Ohio

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[Contribution from the Department of Chemistry of The Ohio State University]

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

By M. L. Wolfrom, Alan Chaney and P. McWain

Received September 23, 1957

The presence of α-hydroxynitriles among the reduced pressure ignition products of cellulose nitrate has been established. The absence of other non-gaseous nitrogenous substances has been demonstrated. The previously reported yield data for carbonyl compounds has been shown to be slightly low as the result of α-hydroxynitrile formation which occurred under the prevailing acidic conditions before the earlier analyses were carried out. Determination of the yield of carbon monoxide under the ignition conditions employed indicates an over-all carbon recovery (all identified products) from cellulose nitrate of 88%; unidentified carbonyl compounds presumably account for the remainder. Acetic acid (and possibly ethanol) are the only ignition products found which can be ascribed to traces of the residual ethyl acetate casting solvent in the cellulose nitrate sheets; cellulose nitrate is the sole precursor of all of the other substances identified. Reignition, at 200 mm. pressure, of the solid oxycellulose nitrate of a low degree of polymerization, obtained by the ignition of cellulose nitrate at 2 mm. pressure, afforded formaldehyde, glyoxal and formic acid in amounts closely agreeing with those predictable as arising from a cellulose nitrate of like nitrogen (9.5%) content. These results are employed to interpret further the nature of cellulose nitrate ignition.

The previous communications in this series have described the ignition of cellulose nitrate under reduced pressure. At the lowest pressures investigated, a white fragmented oxycellulose nitrate was isolated in good yield.[3] The yield of this material decreased rapidly with increasing pressure and the easily condensable product was collected as a red-orange liquid. After dilution of this liquid with water, the amounts of the major organic components (formic acid, glyoxal, formaldehyde and hydrogen cyanide )were determined.[2] Of these components, hydrogen cyanide is the product concerning which the least has been reported and whose formation is least explicable by the postulated[2] reaction sequences. Suggestions were made[2] concerning the role of the fragmented oxycellulose nitrate in the formation of the small organic molecules from cellulose nitrate. Further evidence concerning these matters has been obtained and is reported herein.

## Experimental

**Apparatus for the Ignition of Cellulose Nitrate.**—The ignition apparatus previously described[3] for the preparation of the solid fragmented oxycellulose nitrate was modified by the attachment of a 50/30 standard glass semi-ball inner-joint at the large end of the combustion tube and the rubber

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[1] This work was performed under contracts DA-33-019-ord-2025 (Aberdeen Proving Ground) and DA-33-019-ord-2042 (Office of Ordnance Research) between the U. S. Army Ordnance Corps (technical supervising agency, Ballistic Research Laboratories of Aberdeen Proving Ground) and The Ohio State University Research Foundation (Projects 675 and 679). Preliminary communication: *Abstracts Papers Am. Chem. Soc.*, **132**, 16D (1957).

[2] Previous communication: 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, This Journal, **78**, 4695 (1956).

[3] 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).

stopper was replaced by an arrangement similar to that already described[2] except that a 50/30 standard glass semi-ball outer-joint replaced the 34/45 standard taper glass joint. Furthermore, a glass tube, 29 mm. o.d. by 27 cm., was inserted within the ignition tube itself. This apparatus was used for the preparation of the solid cellulose nitrate ignition product.

The apparatus employed for those ignitions in which the desired product was the liquid mixture was identical with that already described.[2]

**Ignition and Isolation of Products.**—The cellulose nitrate samples employed and their preparation have been described previously.[2,3] The conversion of the cellulose nitrate (12.5 g.) to the solid ignition product was carried out at 2 mm. in the manner previously reported[3] except that after each ignition the above-described glass tube, inserted in the ignition tube, was replaced by a clean tube. Thus, a number of tubes were obtained which had the solid ignition product adhering to the inner surface. The product was removed from the tubes by washing with methanol. The methanolic solution was filtered and added slowly to water. The precipitate (5 g.) which was formed was recovered by filtration, redissolved in methanol (60 ml.) and the solution treated with activated carbon (Darco G60) at reflux for 5 min. After cooling slightly, the solution was filtered through a bed of diatomaceous earth (Super-Cel, Johns-Manville) and the filtrate was added dropwise under mechanical stirring to 500 ml. of water. After 24 hr., the precipitate was coagulated by the addition of several drops of saturated sodium chloride solution and collected on a sintered-glass funnel. The precipitate was washed with water until the washings became chloride-free and was then air-dried on the filter to produce a hard cake which could be broken into small flat pieces weighing about 0.5 g. each. These pieces were dried further under reduced pressure over sodium hydroxide and phosphorus pentoxide.

The ignition of these pieces of the fragmented oxycellulose nitrate was accomplished by placing them in a cone-shaped spiral formed from the ignition wire in the combustion apparatus. The ignition of the solid product was similar in appearance to that observed for cellulose nitrate sheets. Otherwise, the ignitions designed to produce the liquid mixture of products were performed exactly as described earlier.[2] In some of the work the liquid ignition products obtained in the cold traps and the ignition tube[2] were maintained as separate fractions for analysis.

**Analysis for the Organic Components of the Ignition Products.**—The analyses for formaldehyde, total carbonyl and formic acid were made as reported previously.[2] However, the isolation of formic acid from the water solution of the liquid mixture of products was changed. Steam distillation of aliquots (10 ml.) was employed in preference to distillation to dryness under reduced pressure. Since the resulting volume of solution to be employed (200 ml.) was greater, the concentration of the mercuric chloride solution added was increased such that the final concentration of the mercuric chloride precipitation mixture was identical to that previously described.[2]

For the purposes of the present work, the glyoxal assay of Hatcher, Holden and Toole[4] was employed with some modification. Thus, 10-ml. aliquots of the aqueous solution of the liquid mixture of products (*p*H 2.0–2.5) were titrated potentiometrically to *p*H 7.0 with 0.1 *N* sodium hydroxide. After the addition of 10 ml. of neutral 3% hydrogen peroxide, the further consumption of base was followed at *p*H 7.0 for 40 min. The consumption of base was normally 90% complete in 20 min. and the consumption after 40 min. was negligible.

Analytical methods for cyanide ion have been reported previously,[2] and in part of the current investigation an identical procedure was employed (exceptions are specifically noted). However, a consideration of the problem suggested that more information might be gained by other methods. Thus, aliquots of the aqueous mixture of ignition products were neutralized potentiometrically to *p*H 7.2 with 6 *N* sodium hydroxide and the resulting solution frozen and the water removed by lyophilization at ice-bath temperature. The semi-solid residue was subjected to a sealed tube modification of the Kjeldahl nitrogen analysis.[5] These results indicated the presence of 0.20 mmole of nitrogen per mmole[6] of cellulose nitrate (12.6% N) ignited at 200 mm. pressure.

Since this value was considerably greater than could have been due to cyanide ion alone, recourse was made to the colorimetric method and aeration apparatus developed by Bruce, Howard and Hanzal[7] for the analysis of cyanide and α-hydroxynitriles in plasma or serum. Our calibration curve was identical in every respect to theirs. Analyses on aliquots of the liquid reaction products, after dilution some 5000-fold to obtain concentrations in the proper range for this method, indicated the presence therein of total cyanide and α-hydroxynitrile equivalent to 0.19 mmole per mmole[6] of cellulose nitrate (12.6% N, solvent free) assuming[7] a 10% correction factor. If the combustion products were dissolved as rapidly as possible in 0.1 *N* sodium hydroxide (not as reported previously[2]), no cyanide ion could be detected after acidification and the value for α-hydroxynitrile increased, 0.30 mmole per mmole[6] of cellulose nitrate (12.6% N, solvent free) ignited at 200 mm., being detectable by the colorimetric method. The magnitude of this value decreased slowly with time after the products were dissolved in base. The amounts of α-hydroxynitrile formed are essentially independent of ignition pressure as shown in Fig. 1.

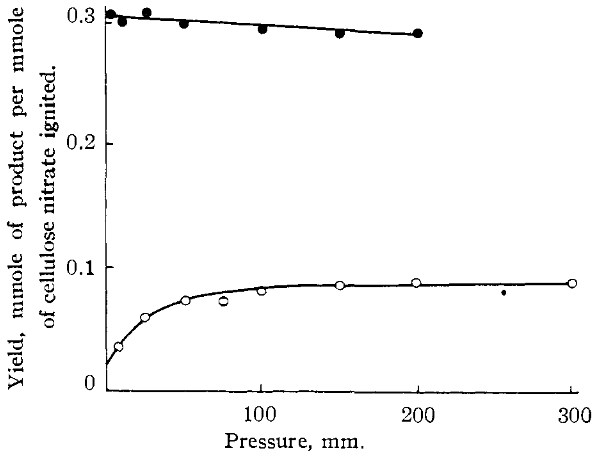

Fig. 1.—Pressure dependency for the formation of cyanide ion (○) and total (ionic and combined) cyanide (●) from the ignition of 12.6% N cellulose nitrate.

Efforts to use this method and apparatus on more concentrated solutions (0.05 *M* formaldehyde and 0.02 *M* sodium cyanide) failed even when the aeration time was increased 10-fold. However, excess cyanide ion (0.05 *M* sodium cyanide and 0.04 *M* formaldehyde) could be collected quantitatively in only slightly increased aeration times. This finding provided a method which permitted analysis for hydrogen cyanide in our mixture of reaction products in a manner that avoided all of the difficulties which often arose in the previous method.[2] Thus, an aliquot (10 ml.) of the aqueous mixture of ignition products was acidified with 5 ml. of 20% trichloroacetic acid and aerated into a receiving tube containing 5 ml. of 0.1 *N* sodium hydroxide. The contents of the receiving tube, after a 1-hr. aeration period, were analyzed for cyanide employing titration with silver nitrate (0.0200 *N*) in the presence of ammonia and potassium iodide.[8] In this process formaldehyde was shown to be only slightly volatile and did not interfere. The amounts of hydrogen cyanide detectable by this method decreased as the mixture of ignition products aged. No cyanide ion could be detected after 72 hr. if the mixture of products was diluted as previously[2] described; however,

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

(5) Analyses by Galbraith Microanalytical Laboratory, Knoxville, Tenn.

(6) The millimoles of cellulose nitrate were calculated by division of the grams decomposed by the sum of the millimolecuar 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).

(7) R. B. Bruce, J. W. Howard and R. F. Hanzal, *Anal. Chem.*, **27**, 1346 (1955).

(8) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 188.

if greater dilutions (2–4-fold) were employed, cyanide ion could still be detected after 96 hr.

The results obtained for the ignition products of cellulose nitrate by the above methods are recorded in Tables I–IV. All values in the tables are the average of at least two determinations which agreed to within 2% or better, except that some of the cyanide values were single analyses because of the large volume of solution necessary in the precipitation method.[2]

TABLE I

EFFECT OF TIME ON THE AQUEOUS SOLUTIONS OF THE LIQUID MIXTURE OF CELLULOSE NITRATE IGNITION PRODUCTS[a]

| Product | Yield, mmole/mmole ignited[b] | | |
|---|---|---|---|
| | Current work | | Previous work[e] |
| | Fresh[c] | Aged[d] | |
| Formic acid | 0.470 | 0.468 | 0.426 |
| Glyoxal | .200 | .180 | .176 |
| Formaldehyde | .326 | .284 | .297 |
| Cyanide (ion) | .074[f] | .006[f] | .085[g] |
| Total acid | .546 | .609 | .... |
| Volatile acid | .501 | .561 | .... |
| Total free carbonyl | .849 | .780 | .... |

[a] Cellulose nitrate, 12.6% N, cast from ethyl acetate solution and ignited at 200 mm. pressure. [b] See footnote 6. [c] Duplicate analyses initiated within 2 hr. after completion of ignition. [d] Duplicate analyses begun 72 hr. (storage at room temperature) after ignition. [e] See ref. 2. [f] Aeration analysis method. [g] In the previous work only this analysis would qualify as analysis of fresh material by the definition in footnote *c*.

TABLE II

EFFECT OF TIME ON THE AQUEOUS SOLUTIONS OF THE LIQUID MIXTURE OF CELLULOSE NITRATE[a] IGNITION PRODUCTS FROM VARIOUS PARTS OF THE COMBUSTION SYSTEM

| Product[e] | Yield, mmole/mmole ignited[b] | | | | | |
|---|---|---|---|---|---|---|
| | Fresh[c] | | | Aged[d] | | |
| | Traps[f] | Ignition tube[g] | Sum[h] | Traps[f] | Ignition tube[g] | Sum |
| Glyoxal | 0.019 | 0.166 | 0.185 | 0.018 | 0.166 | 0.184 |
| Formaldehyde | .186 | .145 | .331 | .150 | .143 | .293 |
| Formic acid | .236 | .181 | .417 | .237 | .179 | .416 |
| Cyanide (ion) | .067 | None | .067 | .009 | None | .009 |
| Total acid | .299 | 0.211 | .510 | .305 | 0.218 | .523 |

[a] Cellulose nitrate, 13.2% N, cast from ethyl acetate solution and ignited at 200 mm. pressure. [b] See footnote 6. [c] Analyses begun in duplicate within 2 hr. after completion of the ignition. [d] Analyses begun 72 hr. (storage at room temperature) after ignition. [e] See Experimental part for analytical methods. [f] Cooled by a mixture of acetone and solid carbon dioxide. [g] Cooled with tap water (about 15°). [h] Experiments in which the ignition tube was cooled with ethanol at −60° afforded essentially the same totals; thus: glyoxal, 0.190; formaldehyde, 0.338; and cyanide, 0.065. The distribution of the products between various parts of the system was shifted considerably under these conditions, greater quantities being found in the ignition tube.

In an attempt to obtain a carbon balance for the cellulose nitrate ignition, small amounts (0.20 g.) of cellulose nitrate were ignited in a closed system (4 liters capacity) at 200 mm. under nitrogen. The gaseous products were swept with nitrogen through two traps cooled by solid carbon dioxide and acetone, three gas-washing bottles containing 0.1 *N* sodium hydroxide, a tube containing cupric oxide at 680°, and finally through three more sodium hydroxide bottles. The contents of the gas-washing bottles were subsequently analyzed for carbonate.[9] It was thus demonstrated that 1.36 mmoles of carbon dioxide and 2.36 mmoles of carbon monoxide were produced for each mmole[6] of cellulose nitrate (12.6% N, solvent-free) ignited.

TABLE III

EFFECT OF THE FILM CASTING SOLVENT ON THE YIELD OF CELLULOSE NITRATE IGNITION PRODUCTS[a]

| Product | Yield, mmole/mmole ignited[b] | | |
|---|---|---|---|
| | Ethyl acetate | Acetone[c] | No solvent[d] |
| Formic acid | 0.417 | 0.427 | 0.436 |
| Glyoxal | .185 | .173 | .190 |
| Formaldehyde[e] | .330 | .361 | .337 |
| Cyanide (ion)[e,f] | .065 | .063 | .066 |
| Total acid | .523 | .539 | .458 |

[a] Cellulose nitrate, 12.6% N, ignited at 200 mm. pressure. [b] See footnote 6. [c] Distribution between traps and ignition chamber similar to that in Table II. [d] These films were prepared by drying sheets, cast from ethyl acetate, to constant weight (150 hr.) at 65° under reduced pressure (0.05 mm.) over phosphorus pentoxide; weight loss about 4%. [e] These analyses were on fresh material, see Table I; the others were made within 24–72 hr. [f] Similar results were obtained for 13.2% N cellulose nitrate; yields unaffected by casting solvent.

TABLE IV

PRODUCTS OBTAINED ON IGNITION (AT 200 MM.) OF THE FRAGMENTED OXYCELLULOSE NITRATE[a]

| Product | Yield, mmole/mmole ignited[b] | | |
|---|---|---|---|
| | Oxycellulose nitrate[c] | | Cellulose nitrate |
| | 9.4% N[d] | 9.6% N[e] | 9.5% N[f] |
| Formic acid | 0.55 | 0.49 | 0.63 |
| Glyoxal | .25 | .24 | .24 |
| Formaldehyde | .34 | .32 | .36 |
| Cyanide (ion) | .02 | .03 | .. |
| Total acid | .56 | .49 | .. |

[a] See ref. 3. [b] Calculation of these values depends on the assumption that the repeating unit of the oxycellulose nitrate possesses an average molecular weight not significantly different from that of cellulose nitrate of the same nitrogen content. This assumption being made, the calculations follow the method cited in footnote 6. For comparison, these analyses (except those for cyanide ion) were on aged solutions, see Table I. [c] These products (unpurified) exhibited a very weak paramagnetic resonance absorption. [d] Prepared from 12.6% N cellulose nitrate. [e] Prepared from 13.2% N cellulose nitrate. [f] Theoretical values, arising from the extrapolation of the data of ref. 2, Fig. 4, to a degree of substitution of 1.62 (9.5% N).

## Discussion

Analyses have been reported[2] for glyoxal, formaldehyde, hydrogen cyanide and formic acid, the major easily condensable, organic products formed on the ignition of cellulose nitrate under suitably reduced pressure. However, no consideration was given to the known interaction of cyanide ion with aldehydes and ketones. It has now been demonstrated (Table I) that the cyanide ion, detectable immediately following ignition, disappears soon thereafter. Qualitative data indicate that the rate of disappearance is dependent on the dilution and *p*H employed, as expected from consideration of the rate equation for the cyanohydrin addition reaction.[10] Decreases in the amounts of formaldehyde, glyoxal and total carbonyl were found (Table I) that correspond closely to the decrease in cyanide ion. From a consideration of reaction rates and equilibrium values, glyoxal and formaldehyde may be expected to be the major reactants in this cyanohydrin addition, as observed, especially since about 75% of the total free carbonyl in the mixture is due to these substances. Consideration of the data in Table I shows that the analyses for car-

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(9) Reference 8, p. 152.

(10) W. J. Svirbely and J. F. Roth, THIS JOURNAL, **75**, 3106 (1953).

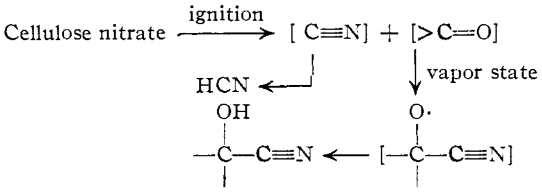
bonyl compounds, reported in the previous work,[2] were carried out after the cyanohydrin addition reactions had proceeded essentially to completion. This should not alter the discussion that was presented[2] on the mechanism of the ignition of cellulose nitrate.

Examination of Table II suggests further that the aging effects observed in this work primarily arise from the cyanohydrin condensation but other aging processes caused by the small amounts of nitrogen oxides and acids present[2] probably occur simultaneously and may be important over longer time intervals. The slow acid hydrolysis of ethyl acetate, which survived the ignition unaltered, may be responsible for the observed increases in acidity occurring during a 72-hr. aging period (Tables I and II). One general conclusion can be drawn from these observations, namely, all analyses should be made as soon as feasible if a close correspondence to the actual amounts of cyanide ion and carbonyl substances formed in the ignition is to be obtained.

Analyses for free cyanide ion and $\alpha$-hydroxynitrile, following the colorimetric method of Bruce, Howard and Hanzal,[7,11] indicated a total of 0.19 mmole per mmole[6] of cellulose nitrate ignited (12.6% N, 200 mm.) when the reaction products were collected in the described fashion.[2] On the same mixture of ignition products it was found that the total nitrogen was 0.20 mmole per mmole[6] of cellulose nitrate ignited. This agreement indicates that no other easily condensable nitrogenous substances are produced by these ignitions. When the ignition products were collected (without the standing period previously employed[2]) by washing the combustion apparatus with 0.1 *N* sodium hydroxide, the yields of $\alpha$-hydroxynitrile were those shown by Fig. 1. No cyanide ion was detectable under these conditions. The increased amount of nitrile found probably was due to the partial loss of gaseous hydrogen cyanide during the standing period in the procedure previously employed[2] to allow the escape of the volatile nitrogen oxides.

This discovery of $\alpha$-hydroxynitriles among the ignition products from cellulose nitrate suggests an alternative fate to those presented earlier[3] for the formaldehyde believed to arise primarily[3,12] from C6 of the anhydro-D-glucose units. However, since all of the carbonyl compounds encountered[2] in the mixture of ignition products would be expected to be reactive toward cyanide ion, no definite proportion can be ascribed to formaldehyde.

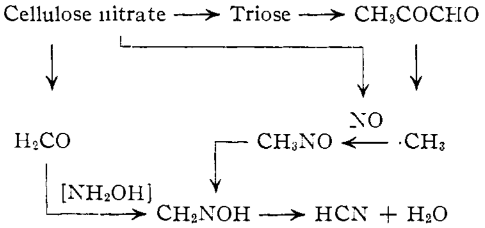
The lack of variation in the yield of triply-bound carbon–nitrogen with pressure (Fig. 1) is surprising in view of the pronounced variations reported[2] for the other organic ignition products of cellulose nitrate. This fact suggests that the cyano group is stable once formed and that its formation occurs early in the ignition process. Furthermore, its combination with carbonyl groups probably occurs to some extent while still in the vapor state for otherwise the experiments carried out at lower ambient temperatures would have been expected to afford more cyanide ion, which was not the case (Table II, footnote *h*),



Stable products could be formed by subsequent hydrogen abstraction processes.

Although the data in Table III were collected in an attempt to elucidate the role of the cellulose nitrate casting solvent, it is apparent that for the components investigated very little effect was observed. Total acid values were affected most and the results are as expected on the basis that no acetic acid is formed unless solvent is present in the cast sheets. These data also require that cellulose nitrate be the precursor of the other ignition products. It had been suggested in our previous work[2] and by others[13] that some or all of the hydrogen cyanide may arise from the interaction of the nitrogenous substances formed by the ignition of cellulose nitrate with residual solvent decomposition products. The data in Table III suggest that this hypothesis is erroneous and conclusive proof will be presented elsewhere.[12]

The formation of the cyano grouping during the ignition of cellulose nitrate is difficult to explain. Several mechanistic sequences may be visualized. Possibly formaldehyde and a partially reduced oxide of nitrogen combine to afford formaldehyde oxime which subsequently decomposes to hydrogen cyanide and water. Alternatively, methyl radicals may be generated by the decomposition of methylglyoxal (pyruvaldehyde, propanonal). The presence of a triose (identified as the phenylosazone) among the reduced pressure ignition products of cellulose nitrate has been established[2] and the facile transformation of both keto- and aldo-trioses to methylglyoxal under acidic or basic conditions has been demonstrated.[14] Thus, the sequences depicted may be responsible for the formation of the cyano grouping. At present no evidence to confirm or refute these speculations is available.



The solid product formed at low pressures and collected by the circumstance that it was ejected from the hot surface of the ignited cellulose nitrate,

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(11) These authors state the "$\alpha$-hydroxynitriles under alkaline conditions liberate hydrocyanic acid." It should be pointed out that the alkaline conditions merely catalyze this equilibrium reaction and that the real reason for the liberation of hydrocyanic acid under their conditions is strictly a consequence of the dilutions (*ca.* $10^{-5}$ *M*) employed as can be proved by consideration of the equilibrium constant data[10] available. This interpretation should not be construed as casting doubt on their experimental work which has been confirmed in the course of this investigation.

(12) F. Shafizadeh and M. L. Wolfrom, THIS JOURNAL, **80**, in press (1958).

(13) C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, **59**, 773 (1955).

(14) C. L. Bernier and W. L. Evans, THIS JOURNAL, **60**, 1381 (1938).

has been characterized[3] as an oxycellulose nitrate fragment of a very low degree of polymerization. At higher pressures the product is the liquid mixture[2] noted previously. It was a matter of interest to determine whether the solid reaction product could give rise to the liquid mixture. It has now been determined that the solid product, when put into suitable form, can be ignited and gives rise at 200 mm., to a mixture of products (Table IV) comparable in composition to that predictable as arising from a cellulose nitrate of like nitrogen (9.5%) content. The solid and liquid products accordingly represent intermediate and possibly consecutive stages in the ignition of cellulose nitrate. The solid product has undergone a profound degree of chain scission and in this process it has also been partially denitrated and oxidized. It is, however, still capable of forming an intermediate liquid mixture of low molecular weight products comparable to that obtained, under the same conditions, from a propellant type cellulose nitrate.

In reporting our results on the reduced pressure ignition of cellulose nitrate, it has been convenient to record yield variations with pressure. It is known that the temperature of the decomposition process, as measured by thermocouple probes,[13] changes with pressure with lower pressures being accompanied by lower temperatures. The removal of reactant gases under reduced pressure is a further consideration. Temperature changes may affect the rates of certain of the reaction processes to a greater extent than the others, producing alterations in the yields of the various products. As the pressure of the reaction system is reduced, the initially formed products, both solid and gaseous, may be expelled more rapidly from the hot reaction zone, preventing their further reaction. The rate of generation of oxygen radical sites and nitrogen dioxide by the homolytic cleavage of the nitrate ester groups is probably temperature-dependent. The subsequent interactions of these initial products would depend on temperature and pressure. The reactive oxygen radicals, once formed, could suffer various fates leading to stable products. They could abstract hydrogen atoms from other positions in the molecule; they could undergo rearrangement with either chain cleavage or the formation of small carbon fragments, as formaldehyde, formic acid or glyoxal; or they could fail to react. Some evidence for this last fate might be adduced from the observation (Table IV) of a very weak paramagnetic resonance absorption, indicative of the presence of radical sites, in samples of the solid fragmented oxycellulose nitrate (crude) isolated from the ignition of cellulose nitrate at 2 mm. pressure. However, a more probable explanation for this observation is that the solid simply absorbs gaseous nitric oxide and that it is the absorbed gas which is responsible for the indicative paramagnetic resonance absorption.[15] Postulated reaction sequences illustrative of other fates have been presented previously.[2,3]

With the determination that 1.36 mmoles of carbon dioxide and 2.36 mmoles of carbon monoxide are produced per mmole[6] of cellulose nitrate ignited, essentially all of the carbon introduced as cellulose nitrate has been found among the ignition products. Summation (Table V) for the products reported herein and elsewhere[2] gives a carbon recovery of 88% or about 5.3 of the six carbons present in the anhydro-D-glucose unit. The fate of the remaining 12% will probably be defined by research now being undertaken on the identity and yields of carbonyl substances other than glyoxal and formaldehyde (see Table I). A similar summation for nitrogen indicates that only about 74% of the amount introduced as cellulose nitrate has been recovered. It is believed that the unrecovered 26% is a combination of nitrogen, a known ignition product,[2] and nitric oxide, which latter probably was not completely retained by the condensing system employed[2] to obtain the analytical samples in the previous work.

Table V

Carbon and Nitrogen Yields from Cellulose Nitrate Ignition[a]

| Product | Mmoles/ mmole detected[b] | Mmoles/mmole present Carbon | Nitrogen |
|---|---|---|---|
| Formic acid | 0.47 | 0.47 | .. |
| Glyoxal | .20 | .40 | .. |
| Formaldehyde | .34 | .34 | .. |
| Carbon dioxide | 1.36 | 1.36 | .. |
| Carbon monoxide | 2.36 | 2.36 | .. |
| Nitric oxide | 1.01[c] | .. | 1.01 |
| Nitrous oxide | 0.25[c] | .. | 0.50 |
| Nitrogen dioxide[d] | .14[c] | .. | .14 |
| Cyanide (ionic) | .18[e] | 0.18 | .18 |
| $\alpha$-Hydroxynitrile | .12[f] | 0.24 | .12 |
| Summation | ... | 5.24 (88%) | 1.95 (74%[g]) |

[a] The ignitions were carried out under nitrogen at 200 mm. pressure. [b] Ignition of 12.6% N cellulose nitrate except as noted. [c] From cellulose nitrate containing 13.2% N; data from ref. 2. [d] May be an artifact due to admission of air. [e] This value represents the sum of the ionic cyanide actually found (0.07, Table I) and the difference (0.11) in $\alpha$-hydroxynitrile detected under different isolation conditions; see Discussion. [f] Difference between total combined (Fig. 1) and previous entry. [g] Calculated for an original nitrogen content of 13.2% (D. S. 2.65).

**Acknowledgment.**—Preliminary observations on the distribution of products in the parts of the combustion system were made by Messrs. E. E. Dickey and R. S. Bower. The authors wish to credit Mr. G. P. Arsenault of this Laboratory with the original observation of the effect of time on the organic components of the aqueous solution of the cellulose nitrate ignition products. The paramagnetic resonance absorption measurements were very kindly made by Dr. John P. O'Meara and Mr. Frank K. Truby of the Southwest Research Institute, San Antonio, Texas. Acknowledgment is made of the valued counsel of Dr. L. P. Kuhn of Aberdeen Proving Ground.

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