Detailed powder diffraction data for $Fe(Fe_xAs_{2-x})$, $CoAs_3$, $CoAs_2$, and β-$NiAs_2$ have been submitted to the X-ray Powder Data File.

We are indebted to Miss Theresa Clarke for assistance in obtaining Debye–Scherrer patterns, and to Mr. D. S. Russell for analysis of reactants and alloys.

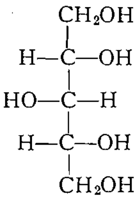
1. Heyding, R. D. and Calvert, L. D. Can. J. Chem. **35**, 449 (1957).
2. Heyding, R. D. and Calvert, L. D. Can. J. Chem. **35**, 1205 (1957).
3. Holmes, R. J. Science, **96**, 90 (1942).
4. Holmes, R. J. Bull. Geol. Soc. Am. **58**, 299 (1947).
5. Kochnev, M. I. J. Appl. Chem. (U.S.S.R.), **35**, 595 (1950).
6. Buerger, M. J. Z. Krist. **82**, 165 (1932).
7. Peacock, M. A. Proc. Roy. Soc. Can. **38**, 155 (1944).
8. Oftedal, I. Z. Krist. **66**, 517 (1928).
9. de Jong, W. F. Physica, **6**, 325 (1926).
10. Peacock, M. A. and Dadson, A. S. Am. Mineralogist, **25**, 561 (1940).
11. Kaiman, S. Univ. of Toronto Studies, Geol. Ser. **51**, 49 (1946).
12. Peacock, M. A. and Michener, C. E. Univ. of Toronto Studies, Geol. Ser. **42**, 95 (1939).
13. Thompson, R. M. X-ray Powder Data File, Card 9-8.

Received October 22, 1959.
Division of Applied Chemistry,
National Research Council,
Ottawa, Canada.

THE PENTITOL PENTANITRATES*

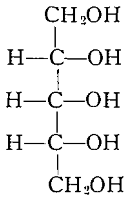
I. G. Wright and L. D. Hayward

In connection with a study of the selective denitration of polynitrate esters (1, 2, 3) we have prepared and characterized the crystalline, fully nitrated derivatives of the three isomeric pentitols, xylitol (I), ribitol (adonitol) (II), and L-(−)-arabinitol (III). The only previous references to the pentitol nitrates in the literature dated from the end of the last century and described xylitol pentanitrate (4) and the pentanitrate of D-(+)-arabinitol (IV) (5) as explosive, non-crystallizable sirups.



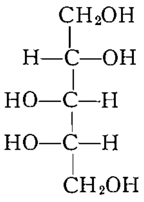
$$\begin{array}{c} CH_2OH \\ | \\ H{-}C{-}OH \\ | \\ HO{-}C{-}H \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

I



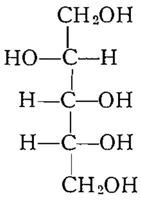
$$\begin{array}{c} CH_2OH \\ | \\ H{-}C{-}OH \\ | \\ H{-}C{-}OH \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

II



$$\begin{array}{c} CH_2OH \\ | \\ H{-}C{-}OH \\ | \\ HO{-}C{-}H \\ | \\ HO{-}C{-}H \\ | \\ CH_2OH \end{array}$$

III



$$\begin{array}{c} CH_2OH \\ | \\ HO{-}C{-}H \\ | \\ H{-}C{-}OH \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

IV

In the present work the stable, crystalline form of xylitol (I) was synthesized in 62% yield by the sodium borohydride reduction of D-xylose and was further identified through conversion to the known penta-*O*-acetyl derivative (6). The other two pentitols (II and III) were commercially available in crystalline form.†

Direct nitration of the pure pentitols in a mixture of fuming nitric acid and acetic anhydride at 0° C (7) gave the crystalline pentanitrate esters in excellent yield (Table I).

**Presented in part at the Symposium on the Chemistry, Technology, and Pharmacology of Nitric Acid Esters, 132nd meeting, American Chemical Society, New York, September 8–13, 1957.*
†Nutritional Biochemicals Corporation, Cleveland 28, Ohio.

Can. J. Chem. Vol. 38 (1960)

The structure and configuration of these high-explosive compounds were established through their nitrogen contents (Table I) and infrared spectra and by nearly quantitative conversion to the parent alcohols on catalytic hydrogenation (Table II).

TABLE I

The pentitol pentanitrates

Pentanitrate	Yield (%)	m.p. (° C)	Nitrogen content (%)[a]
Ribitol	90.2	33.5–34.0	18.2[b]
Xylitol	95.6	37–40	17.8[c]
L-(−)-Arabinitol	97.5	26.5–27.5	18.0[c]

[a] Theoretical value = 18.6%.
[b] Modified semimicro Kjeldahl method (10).
[c] Ultramicro procedure based on the Kjeldahl method and involving Nesslerization of the distilled ammonia (11, 12).

TABLE II

Hydrogenation products of the pentitol pentanitrates

Pentanitrate	Ribitol	Xylitol	L-(−)-Arabinitol
% Yield	97.5	95.5	97.5
M.p., ° C	99–101	92–94[a]	101–103
Mixed m.p., ° C	99–102	92.0–94.5	101–103
Reported m.p., ° C	102	93.0–94.5	102
Reference	(9)	(8)	(9)

[a] Stable modification.

The infrared spectra of the pentanitrates of ribitol and xylitol in nujol mull and the spectrum of L-arabinitol pentanitrate as a liquid film showed closely similar peaks near 1650, 1265, and 750 cm^{-1}. The very strong peaks at 1650 and 1265 cm^{-1} were characteristic of covalent nitrate groups (14) and this was probably also true of the medium-to-weak peak near 750 cm^{-1} which has also been observed in a series of other nitrate esters in this laboratory (15). No peaks occurred in the frequency ranges for hydroxyl and carbonyl stretching in saturated acyclic compounds. A strong peak at 2910 cm^{-1} in the spectrum of L-arabinitol pentanitrate was attributed to the methylene group and was not observed in the other spectra since they were compensated with nujol.

The three pentitol pentanitrates reacted with dry pyridine at 20–24° C in much the same manner as D-mannitol hexanitrate (1, 2). The xylitol derivative evolved more gas and the pyridine solution became darker in color than with the arabinitol and ribitol compounds. Partially nitrated sirups were recovered in good yield from the pyridine solutions on dilution with water. The nitrogen contents, solubility, and infrared spectra of these products indicated that they were probably partially nitrated anhydropentitols. Further study of their constitution is in progress.

EXPERIMENTAL

Xylitol

A solution of D-xylose (66.0 g, m.p. 145–6° C, $[\alpha]_D^{22.5}$ +18.9±0.2°) in 400 ml of water was cooled in an ice bath, and a solution of 16.5 g of sodium borohydride in 100 ml of water was added dropwise. The temperature of the mixture rose to 45° C during the addition, the rate of evolution of hydrogen slowly decreased, and the solution became alkaline (pH 9). After the mixture had been standing for 1.5 hours at room temperature reduction was complete as shown by Fehling's test. Excess borohydride was destroyed with 6 *N* acetic acid and the solution was deionized and concentrated to a sirup under reduced pressure. The sirupy xylitol was freed of boric acid by repeated evaporations with methanol and crystallized after seeding with a sample obtained through the courtesy of Dr. M. L. Wolfrom, Ohio State University. After recrystallization from ethanol the xylitol (41.3 g, 61.5%) melted correctly at 93.0–94.5° C (8).

Acetylation of 3.8 g of the xylitol with acetic anhydride and sodium acetate yielded 3.7 g of pure xylitol pentaacetate melting at 62.0–63.5° C after recrystallization from methanol (6).

Nitration of the Pentitols

A suspension of the pentitol (1.0 g) in acetic anhydride (4 ml) was cooled in an ice–salt bath and a cooled solution of fuming nitric acid (5 ml) in acetic anhydride (5 ml) was added slowly with stirring. After 1 hour the reaction mixture was allowed to warm to room temperature during 30 minutes by which time all of the pentitol had dissolved. The mixture was then poured into ice water and the colorless, semisolid product was separated and dried *in vacuo* at 0° C for several days. The pentitol pentanitrate was recrystallized from five parts of dry toluene at about −40° C and was recovered on a glass funnel jacketed with melting chlorobenzene (m.p. −45° C) and fitted with a drying tube. Yields and melting points of the pentitol pentanitrates are shown in Table I together with the nitrogen analyses. The nitrates detonated under the hammer and were not decomposed after they were stored in a desiccator at 0–5° C for 3 years.

Hydrogenation of the Pentitol Pentanitrates

The pentitol pentanitrate (0.5 g) was dissolved in 95% ethanol (100 ml) and hydrogenated over palladium-on-charcoal catalyst (0.5–1.0 g) as previously described (1, 13). The yields, melting points, and mixed melting points of the recovered pentitols are shown in Table II.

The Action of Pyridine on the Pentitol Pentanitrates

The pentitol pentanitrate (100 mg) dissolved readily at 20° C in pyridine (6.2 ml) freshly distilled from barium oxide (b.p. 114.5–116.0° C). Within 2 minutes the initially colorless solution became yellow and evolved a colorless gas while the temperature increased to 24° C. After 6 hours at 20° C the solution was warmed to 50° C for 30 minutes which caused no apparent change in color or rate of gas evolution. The reaction mixture was then diluted with water (8 ml) and extracted with ether. Evaporation of the washed and dried ether extract yielded 50 to 65 mg of a colorless, viscous sirup.

The nitrogen contents of the thoroughly dried products from ribitol, xylitol, and arabinitol pentanitrates were 15.0, 14.5, and 12.5% respectively. These products were insoluble in water, *n*-hexane, and carbon tetrachloride and readily soluble in ethyl acetate, ether, and acetone. The infrared spectra (potassium bromide windows) showed the presence of covalent nitrate groups (1635–1650 cm^{-1} and 1273–1287 cm^{-1} and 747–750 cm^{-1}) and no carbonyl groups. An hydroxyl stretching frequency (3420 cm^{-1}) appeared only in the spectrum of the product from L-arabinitol pentanitrate.

We thank Mr. I. G. Csizmadia for nitrogen analyses and the Defence Research Board of Canada for funds in support of this research.

1. Hayward, L. D. J. Am. Chem. Soc. **73**, 1974 (1951).
2. Brown, J. R. and Hayward, L. D. Can. J. Chem. **33**, 1735 (1955).
3. McKeown, G. G. and Hayward, L. D. Can. J. Chem. **33**, 1392 (1955).

4. Bertrand, G. Bull. soc. chim. (3), **5**, 740 (1891).
5. Vignon, L. and Gerin, F. Compt. rend. **133**, 641 (1901).
6. Wolfrom, M. L. and Kohn, E. J. J. Am. Chem. Soc. **64**, 1739 (1942).
7. Honeyman, J. and Morgan, J. W. W. J. Chem. Soc. 3660 (1955).
8. Carson, J. F., Waisbrot, S. W., and Jones, F. T. J. Am. Chem. Soc. **65**, 1777 (1943).
9. Lohmar, R. L. *In* The carbohydrates, chemistry, biochemistry, physiology. *Edited by* W. Pigman. Academic Press, Inc., New York. 1957. p. 243.
10. Brown, R. K. and Purves, C. B. Pulp Paper Mag. Can. **48**, No. 6, 100 (1947).
11. Tourtellotte, W. W., Parker, J. A., Alving, R. E., and DeJong, R. N. Anal. Chem. **30**, 1563 (1958).
12. Hawk, P. B., Oser, B. L., and Summerson, W. H. Practical physiological chemistry. 13th ed. McGraw-Hill Book Co., Inc., New York. 1954.
13. Hayward, L. D. and Purves, C. B. Can. J. Chem. **32**, 19 (1954).
14. Bellamy, L. J. The infrared spectra of complex molecules. 2nd ed. Methuen & Co. Ltd., London. 1958.
15. Hayward, L. D. To be published.

RECEIVED OCTOBER 23, 1959.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, B.C.

A TEST OF TRANSITION STATE THEORY

G. O. PRITCHARD,* H. O. PRITCHARD,† G. H. MILLER,* AND J. R. DACEY‡

The transition state theory of the radical combination reactions $CX_3 + CX_3 \rightarrow C_2X_6$ has not yet been satisfactorily formulated because the concept of the transition state itself in the reactions is so indeterminate. Nor is the situation made any easier by the lack of good data on the frequency factors of such combination reactions and of the reverse decompositions. It has, however, been assumed that whatever the transition state may be, there must be free rotation of the CX_3 groups about the incipient C—C bond (1). A further difficulty arises in the calculation of frequency factors because the major contribution to the entropy of activation is dependent on the unknown pressure of the free radicals, since there is a change in the number of species in these reactions (2). Recently, Pritchard and Dacey (3) have obtained a ratio of frequency factors for CX_3 radical combination reactions which can be used as a test of transition state theory because the uncertainties in the formulation of the respective transition states cancel out.

Pritchard and Dacey studied the competition of the three reactions

$$CH_3 + CH_3 \xrightarrow{k_{11}} C_2H_6$$
$$CH_3 + CF_3 \xrightarrow{k_{12}} CH_3CF_3$$
$$CF_3 + CF_3 \xrightarrow{k_{22}} C_2F_6$$

by photolyzing mixtures of CH_3COCH_3 and CF_3COCF_3, and found that the ratio $k_{12}/(k_{11}k_{22})^{\frac{1}{2}} = 0.52\pm0.06 \exp[(1070\pm100)/RT]$ at pressures where three body restrictions were absent.

Considering the scheme

$$\text{2 radicals} \xrightarrow{\Delta S^*} \text{transition state} \xleftarrow{\Delta S'} \text{ethane,}$$

---

*Chemistry Department, University of California at Santa Barbara, Goleta, California.
†Department of Chemistry, University of Manchester, Manchester 13, England.
‡Chemistry Department, Royal Military College of Canada, Kingston, Ontario.

Can. J. Chem. Vol. 38 (1960)