27
3/21/79

ORNL/TM-6736

MASTER

**Synthesis of Aliphatic Nitrate Esters
by Reaction of Metal Nitrates
with Phosphate Esters**

W. H. Baldwin
Walter E. Clark
W. B. Howerton

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, contractors, subcontractors, or their employees, makes any warranty, express or implied, nor assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, nor represents that its use by such third party would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION

SYNTHESIS OF ALIPHATIC NITRATE ESTERS BY REACTION OF METAL
NITRATES WITH PHOSPHATE ESTERS

W. H. Baldwin*
Walter E. Clark
W. B. Howerton

*Retired.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Date Published: March, 1979

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. CRITERIA	2
3. EXPERIMENTAL METHODS AND RESULTS	3
4. RECOMMENDED PROCEDURE FOR PREPARATION OF PURE <u>n</u> -BUTYL NITRATE	4
5. REFERENCES	6

SYNTHESIS OF ALIPHATIC NITRATE ESTERS BY REACTION OF METAL
NITRATES WITH PHOSPHATE ESTERS

W. H. Baldwin*
Walter E. Clark
W. B. Howerton

ABSTRACT

A safe and simple method of synthesizing short-chain alkyl nitrates is described. This method, which should be of general utility, was found to be useful in preparing compounds for studies to determine the fate of organic materials in nuclear fuel reprocessing operations.

Nitrate esters of short-chain alkyl alcohols can be conveniently obtained by distilling mixtures of the appropriate trialkyl phosphate with metallic nitrate salts. Runaway reactions are avoided by using only those metal nitrates that initially undergo an endothermic reaction with the trialkyl phosphate. The nitrates of lithium, iron(III), and uranium, among others, meet this criterion; lithium nitrate was found to be the most convenient. The purity of the product is more dependent on the temperature used and the purity of the nitrate salt than on the specific metal present in the salt.

Details of the synthesis of n-butyl nitrate are given as an example of the method.

1. INTRODUCTION

Methods described in the literature for the synthesis of organic nitrates include (1) nitration of the appropriate alcohol with nitrate-free azeotropic HNO_3 ,¹ $\text{HNO}_3\text{-H}_2\text{SO}_4$ nitrating acid,² nitrosyl sulfuric acid,³ N_2O_5 ,⁴ or O_2NBF_4 ;⁵ (2) nitrolysis of the corresponding halide, especially the iodide;⁶ and (3) treatment of the corresponding iodide with silver nitrate.⁷ In cases where conditions must be kept especially mild, the reaction between the appropriate chloroformate ester and silver nitrate has been employed.⁸ Butyl nitrate has been observed to be

*Retired.

formed by the dealkylation of tributyl phosphate by $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$,⁹ although this specific reaction apparently has not been used as a synthetic method. General methods of preparation and reactions of aliphatic nitrate esters have been reviewed by Smith,¹⁰ Urbanski,¹¹ Boschan et al.,¹² and Connon.⁴

The use of nitrating acid can be difficult to control in the synthesis of any ester except possibly methyl nitrate. Some of the other methods yield a mixture of products which tend to complicate the separation of the pure nitrate ester. Therefore, we selected the reaction of an inorganic nitrate salt with an appropriate ester, in particular the trialkyl phosphate ester, as an outstandingly safe and convenient method for preparing gram amounts of the pure nitrate ester. The purpose of this report is to describe our method and to present details of the synthesis of n-butyl nitrate as an example of its use.

2. CRITERIA

Direct esterification with $\text{HNO}_3\text{-H}_2\text{SO}_4$ is quite satisfactory for synthesizing methyl nitrate;² thus no other preparation method is needed. However, the reaction for the higher homologs becomes difficult to control, and yields and purities are likely to be low even if explosions are avoided. Vogel has reported that propyl and butyl nitrates can be prepared by distillation from a mixture of the appropriate alcohol and azeotropic nitric acid, followed by fractionation of the distillate to separate the alcohol from the nitrate that is formed.¹ Unfortunately, poor yields (i.e., only about 20%) were obtained in our experiments with this method.

Our first criterion for a satisfactory method of preparing organic nitrates was that violent reaction should be impossible. We therefore considered the use of only those inorganic nitrates which first undergo an endothermic reaction with the phosphate ester. This includes, among others, the nitrates of lithium, iron(III), zinc, uranium, aluminum, thorium, and zirconium but eliminates sodium nitrate which, upon heating, enters directly into an exothermic reaction with the phosphate ester.¹³ A second criterion was that rearrangement of the organic chain be minimized.

3. EXPERIMENTAL METHODS AND RESULTS

Methyl, ethyl, n-butyl, and isobutyl nitrates were prepared from the corresponding trialkyl phosphates. n-Tributyl phosphate (TBP) was used in a series of experiments designed to compare the effects of different salts and conditions on chain rearrangement and yields. In general, the amount of degradation or rearrangement observed was found to be more dependent on the temperature of the reaction and the purity of the salt than on the metal present in the salt. Thus crude $\text{UO}_2(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ at 165°C yielded a complex product mixture which contained considerably less than 50% n-butyl nitrate.

Addition of urea to the reaction mixture practically eliminated all side products except n-butyl alcohol, which was present in a large percentage. When the $\text{UO}_2(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was recrystallized from water before use and the reaction temperature was lowered to 150°C , the product consisted of about 97% n-butyl nitrate and 3% n-butyl alcohol. With reagent-grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 165°C , the product contained less than 90% n-butyl nitrate; however, at 145°C , the same reaction mixture yielded n-butyl nitrate of greater than 99% purity (except for water). Yields were generally poor below 145°C , apparently because the nitration reaction is slow at such temperatures.

The presence of water of hydration in the reactant salt contributes an undesirable impurity, which necessitates an added fractional distillation step in the preparation. This can be avoided by using lithium nitrate that has been previously dehydrated by drying overnight at 100°C . If the anhydrous salt is transferred quickly to the reaction vessel, a negligible amount of water will be taken up. If desired, the reaction mixture can be dried further by subjecting it to a vacuum.

The reaction appears to be completely safe. No vigorous exothermic reactions were observed in the more than 50 preparations tried. Traces of brown fumes were noted only when the reaction flask was overheated in various attempts to improve the yield. Such attempts were self-defeating since they resulted in thermal decomposition of the phosphate ester.

The purity of each product was checked using a Model 7300 Packard gas-liquid chromatograph with a column of Carbowax 20 M on Chromosorb P.

4. RECOMMENDED PROCEDURE FOR PREPARATION OF PURE n-BUTYL NITRATE

Based on the results obtained in this study, the following procedure is recommended for the preparation of n-butyl nitrate.

The synthesis is carried out in a round-bottom flask equipped with a magnetic stirrer and a distillation head. The head discharges into a receiver that is connected through a second receiver, held at -80°C with dry ice--propanol, to an adjustable vacuum source (Fig. 1). The reaction mixture consists of anhydrous lithium nitrate and a 30% molar excess of dry, vacuum-distilled n-butyl phosphate. The excess is calculated on the basis of replacement of a single butyl group. The lithium nitrate should be transferred to the reaction flask as rapidly as possible to avoid hydration.

The stirred reaction mixture is heated in an oil bath at 150°C for about 5 hr under a vacuum of about 30 mm Hg. Yields of 50 to 60% can be obtained by heating for only 1.5 to 2 hr, but yields on the order of 90% or greater require longer periods. As the butyl nitrate distills off, the reaction mixture thickens and then solidifies rather suddenly to form a gelatinous mass. Prolonged heating under vacuum is necessary for recovery of the remainder of the butyl nitrate.

The first receiver contains n-butyl nitrate contaminated with TBP, while the n-butyl nitrate in the second receiver is essentially pure. After the reaction vessel has cooled, the pressure is lowered to about 3 mm and the n-butyl nitrate is distilled from the first receiver into the second, leaving the TBP behind. If the reactants are not thoroughly dried, any residual water will freeze out on the walls of the second receiver. The pure liquid product is poured off while this ice is still frozen.

Typical products examined by gas chromatography showed very pure n-butyl nitrate containing 0.02 to 0.05 vol % of TBP and sometimes a trace of n-butyl alcohol.

Fig. 1. Experimental arrangement for the preparation of pure alkyl nitrates.

5. REFERENCES

1. A. I. Vogel, J. Chem. Soc. 1948, 1847.
2. A. P. Black and F. H. Babers, in Org. Synth. 2, 412 (1950).
3. R. deKreuk, Rec. Trav. Chim. Pays-Bas 61, 820 (1942).
4. H. W. Connon, Eastman Org. Chem. Bull. 42(2), 5 pp. (1970).
5. G. Olah et al., Chem. Ber. 89, 2374 (1956); through Chem. Abstr. 51, 8001.
6. H. V. Svetlakov et al., J. Org. Chem. USSR 4(11), 1893 (1968).
7. E. Biron, Chem. Zentr. 1901(I), 366; through Beilstein.
8. R. Boschan, J. Am. Chem. Soc. 81, 3341 (1959).
9. A. J. Moffat and R. D. Thompson, J. Inorg. Nucl. Chem. 16, 365 (1961).
10. P. A. S. Smith, Open Chain Nitrogen Compounds, Vol. II, pp. 455-513, W. A. Benjamin, New York, 1966.
11. T. Urbanski, Chemistry and Technology of Explosives, Vols. I and II, Macmillan, New York, 1964 and 1965.
12. R. Boschan, R. Menow, and R. Van Dolah, Chem. Rev. 55, 485 (1955).
13. W. H. Baldwin, ORNL, unpublished work, 1959.

ORNL/TM-6736

INTERNAL DISTRIBUTION

1. B. M. Benjamin	23. V. F. Raaen
2. C. M. Blood	24. B. B. Spencer
3. J. M. Chandler	25. Martha Stewart
4-13. W. E. Clark	26. O. K. Tallent
14. C. J. Collins	27. R. G. Wymer
15. D. J. Crouse	28-29. Central Research Library
16. R. L. Fellows	30. Y-12 Technical Library -
17. R. T. Jubin	Document Reference Section
18. J. Q. Kirkman	31-35. Laboratory Records
19. M. H. Lloyd	36. Laboratory Records, R.C.
20. A. L. Lotts	37. ORNL Patent Section
21. J. C. Mailen	
22. A. P. Malinauskas	

EXTERNAL DISTRIBUTION

38. W. H. Baldwin, Erie, TN 37763
39. Office of Assistant Manager, Energy Research and Development,
DOE-ORO, P.O. Box E, Oak Ridge, Tenn. 37830
- 40-66. Technical Information Center, Oak Ridge, Tenn. 37830