attempt to find a solvent which would preserve the Zr^{+4} species prior to complexing. A series of solutions was prepared with varying amounts of 2-nitroso-1-naphthol and zirconium in each for a continuous variation study. An equal volume of 2 M $HClO_4$ was then added to each to make the total $HClO_4$ concentration 1 M in each solution. Although immediately after preparation the maximum optical density seemed to be in the neighborhood of a one-to-one complex, after 66 hours a shift to a one-to-four ratio occurred as shown in Fig. 5.

A similar investigation was conducted using ethanol in place of the dioxane but the complex remained one-to-one upon the subsequent addition of $HClO_4$.

Since the optical density of the 2-nitroso-1-naphthol at the wave length of 560 mμ was found to be negligible (0.006) instability constants were calculated from a number of points on the 560 mμ curve in Fig. 5 where the dye was present in excess. A modification of Anderson's method[8] was used which gives the equation

$$\frac{(a_1 - x)(b_1 - 4x)^4}{x} = \frac{(a_2 - x)(b_2 - 4x)^4}{x}$$

where x is the concentration of the one-to-four complex, a_1 and b_1 the concentrations of zirconium-(IV) and 2-nitroso-1-naphthol in the one-to-four mixture having the same optical density as the sample containing concentrations of a_2 of zirconium-(IV) and b_2 of 2-nitroso-1-naphthol. The results of the calculations give an average pK value of 11.7 ± 0.2 for a concentration range of 1.2 to 3.0 $\times$ 10^{-4} M in $ZrCl_4$ and 2.70 to 2.88 M for 2-nitroso-1-naphthol.

The solutions are stable for slightly more than 66 hours but a slow decomposition of the dye sets in after about 85 hours.

NEW ORLEANS 18, LOUISIANA

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Action of Lithium Aluminum Hydride on Nitrate and Nitrite Esters

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A number of organic nitrate and nitrite esters have been shown to react with lithium aluminum hydride in ether solution to give, after hydrolysis, essentially quantitative yields of the parent alcohol. The other products were nitrous oxide, ammonia and hydrogen. Nitrites produced relatively more nitrous oxide and less ammonia than nitrates. Cellulose nitrates of various degrees of nitration were completely denitrated in tetrahydrofuran. Viscosity measurements indicated extensive degradation of the polymer had occurred.

In continuation of this Laboratory's search for a satisfactory method of denitrating nitrocellulose, we have investigated the reactions of lithium aluminum hydride in ether solution with a number of nitrate and nitrite esters. This report will be concerned with the over-all reactions of primary and secondary esters as well as the results obtained with nitrocellulose.

Kuhn[1] has recently reported that n-hexyl nitrate and n-hexyl nitrite react with hydrazine in the presence of a palladium or platinum catalyst to give nitrous oxide, nitrogen, water and high yields of the parent alcohol. Nitrogen is apparently the product of oxidation of the hydrazine and nitrous oxide the result of reduction of the ester. Thus, the ester produces a single nitrogen-containing material.

For purposes of this discussion the over-all reaction of nitrate and nitrite esters with lithium aluminum hydride will be divided into (1) the reaction step, and (2) the hydrolysis step. We have found the products of the first step to be nitrous oxide and hydrogen. The products of the second step are ammonia, hydrogen and the parent alcohol. Nitrites produce relatively more nitrous oxide and less ammonia than nitrates. The yields of alcohols in all cases are excellent. The results shown in Table I for n-hexyl nitrate and 2-octyl nitrite are typical of the various nitrates and nitrites studied, respectively.

TABLE I

REACTIONS OF NITRATES AND NITRITES WITH LITHIUM ALUMINUM HYDRIDE

Reactant	Moles hydride per mole reactant group	Moles gas per mole reactant group (reaction step)	N_2O in gas, % (reaction step)	Original N that forms NH_3, %
n-Hexyl nitrate	3.3	4.0–4.1	1–1.5	84–85
2-Octyl nitrite	1.8	2.6	3–4	56–60

An original aim was to determine the stoichiometric amounts of hydride required per mole of reactant ester. Using the Gilman–Schulze color test[2] data were obtained indicating that two moles of hydride react per mole of nitrate and one mole of hydride reacts per mole of nitrite. However, only modest yields of the alcohols were obtained, with considerable amounts of esters recovered unreacted. From these and other observations it was concluded that these reactions were not stoichiometric and that hydride was being effectively removed from solution. Amundsen and Nelson[3] have recently questioned the suitability of the Gilman–Schulze test for following the course of reduction of nitriles since different results were obtained with two nitriles that react similarly with hydride.

In a series of runs in which the ratio of hydride to reactant ester was varied for a number of nitrates and nitrites the minimum amounts of hydride re-

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(1) L. P. Kuhn, THIS JOURNAL, **73**, 1510 (1951).

(2) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3740 (1948).

(3) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 243 (1951).

quired for complete reaction were found to be 3.3 moles per mole of nitrate and 1.8 moles per mole of nitrite. These values were determined from a plot of moles of reaction step gas evolved per mole of ester *versus* moles of hydride per mole of ester. There was no significant variation among the various nitrates and nitrites studied.

The total volume of reaction step gases was also a criterion of the extent of reaction. As shown in Table I, 4.0 moles of gas were obtained per mole of nitrate and 2.6 moles of gas per mole of nitrite. Nitrogen was shown to be absent in both steps of the process by analyses of the gases produced in runs where atmospheric nitrogen had been completely flushed from the system with hydrogen prior to beginning the reaction. In order to determine the amount of nitrous oxide produced separate samples of the gas were taken for infrared and combustion analyses. The presence of ammonia, and the absence of hydrazine, in the hydrolysis step gases was demonstrated by comparison of the infrared spectra of the gas and of its sulfate salt (prepared by the absorption of the gas in concentrated sulfuric acid) with authentic samples. Ammonia was measured quantitatively by absorption in standard hydrochloric acid. The nitrogen balance thus obtained was low for both nitrates and nitrites because of the solubility of nitrous oxide in the reaction solution. The possibility that ammonia arose from reduction of nitrous oxide was eliminated by the demonstration that nitrous oxide would not react with hydride under the conditions of our experiments.

Experimental

Materials.—Lithium aluminum hydride was obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Commercial anhydrous diethyl ether was used. Stock solutions (800–1000 ml.) in ether were prepared and dispensed from an all glass, buret-equipped reservoir. To assay the solution, known volumes were run into filter flasks under an atmosphere of dry nitrogen. The flasks were transferred to a desiccator and the ether removed. They were then placed in an ice-bath and fitted through a stopper to the delivery tube of a buret. The side-arm was connected to an inverted graduate containing water. Hydrogen, liberated by the careful addition of water from the buret, was measured. The solutions assayed from 0.032 to 0.046 g. of hydride per ml. and maintained their strength for at least nine days.

Nitrate esters were prepared using a mixture of nitric acid, acetic anhydride and acetic acid. Nitrites were prepared using sodium nitrite and sulfuric acid.[4] Identifications of esters and parent alcohols were made by infrared spectra, refractive indices and nitrogen analyses (du Pont nitrometer).[5]

The denitration reaction was carried out with *cis*-cyclohexane-1,2-diol dinitrate (b.p. 106–108° at 1 mm., $n^{27}\text{D}$ 1.4758, d^{25}_{4} 1.324; lit. values, none), *trans*-cyclohexane-1,2-diol dinitrate (b.p. 92–93° at 1 mm., $n^{27}\text{D}$ 1.4732, d^{24}_{4} 1.315; lit. values, none), *n*-hexyl nitrate (b.p. 46° at 1 mm., $n^{24.5}\text{D}$ 1.4180, $n^{26.5}\text{D}$ 1.4169, $n^{32}\text{D}$ 1.4142, $d^{24.5}_{4}$ 0.9745; lit. values, none. Calcd. for $C_6H_{13}O_3N$: N, 9.52. Found: N, 9.26[6]), cyclohexyl nitrate (b.p. 37° at 1.5 mm., $n^{24}\text{D}$ 1.4530, d^{24}_{4} 1.0908, lit. b.p. 70–72° at 12 mm., d^{18}_{18} 1.104[7]), 2-octyl nitrate (b.p. 48° at 1 mm., $n^{27}\text{D}$ 1.4222; lit. values, b.p. 76° at 10 mm., $n^{20}\text{D}$ 1.4250[8]), *n*-hexyl nitrite (b.p. 50° at 48 mm., $n^{23}\text{D}$ 1.3977; lit. values, b.p. 52° at 44 mm., *n*(?) 1.4018[9]), cyclohexyl nitrite (b.p. 41° at 20 mm., $n^{24}\text{D}$ 1.4326; lit. values, b.p. 31° at 10 mm., $n^{18}\text{D}$ 1.4372[10]), 2-octyl nitrite (b.p. 63° at 20 mm., $n^{24}\text{D}$ 1.4068; lit. values, b.p. 50–51° at 9 mm., $n^{20}\text{D}$ 1.4082).[8] All boiling points are uncorrected. As a further test of purity the infrared absorption spectrum of each ester was examined for the absence of the hydroxyl band, thus assuring complete esterification. The nitrites were used promptly after preparation to avoid decomposition.

Nitration.—The method is described below in the preparation of *cis*-cyclohexane-1,2-diol dinitrate.

"Almost" anhydrous nitric acid was prepared by distilling *in vacuo* fuming nitric acid (density 1.5) with twice its weight of concentrated sulfuric acid.[11]

In a three-necked flask equipped with a mercury sealed stirrer, thermometer and dropping funnel were placed 19 ml. (0.33 mole) of acetic acid and 19 ml. (0.2 mole) of acetic anhydride. The mixture was maintained at 0° as 16.8 ml. (0.4 mole) of "almost" anhydrous nitric acid was added. The dropping funnel was replaced with a small erlenmeyer flask containing 11.6 g. (0.1 mole) of *cis*-cyclohexane-1,2-diol (m.p. 97–98°, lit. 98°[12]) which was fitted to the neck of the reaction vessel through a section of large rubber tubing. The solution was stirred at 0° during the course of the addition (30 minutes), and for an additional 45 minutes. It was poured into ice-water and the yellow ester layer separated. The aqueous layer was extracted with several portions of ether, the ether extracts combined, washed with several portions of 5% sodium carbonate solution and then with water. The *p*H of the ether extract was 4.5–5. Excessive washing with base reduced yields considerably. The ester was dried over sodium sulfate and distilled *in vacuo* (b.p. 106–108° at 1 mm., $n^{27}\text{D}$ 1.4758, d^{25}_{4} 1.324; lit. values, none); yield 15 g. This material was a colorless liquid with a musty, rather fragrant odor.

Anal. Calcd. for $C_6H_{10}O_6N_2$: N, 13.58. Found: N, 13.39, 13.49.

The preparation of *trans*-cyclohexane-1,2-diol dinitrate was carried out in a similar manner from *trans*-cyclohexane-1,2-diol (m.p. 101.5–103°, lit. 103.5–104°)[13]; yield 14.8 g., 71.8%, colorless, fragrant liquid, $n^{27}\text{D}$ 1.4732, b.p. 92–93° (1 mm.), d^{24}_{4} 1.315.

Anal. Calcd. for $C_6H_{10}O_6N_2$: N, 13.58. Found: N, 13.36, 13.42.

A check on configuration of the two nitrates was obtained by electrolytic reduction[14] of each ester to the parent diol, which, in turn, was identified by infrared spectra and derivatization to the respective dibenzoate (m.p. *cis*-cyclohexane-1,2-diol dibenzoate 62.6–63.6°; lit., same. *trans*-Cyclohexane-1,2-diol dibenzoate 92–93°, lit. 93–93.5°[15]).

Denitration.—The procedure given below for the reaction of *n*-hexyl nitrate illustrates the method.

Under a nitrogen atmosphere in a carefully dried 500-ml. three-necked flask was placed 284 ml. (0.33 mole) of a stock solution of lithium aluminum hydride in ether. The flask was equipped with a condenser, a mercury sealed stirrer and a dropping funnel containing 14.7 g. (0.10 mole) of *n*-hexyl nitrate (b.p. 46° at 1 mm., $n^{24.5}\text{D}$ 1.4180). All openings were protected from atmospheric moisture by calcium chloride–soda lime tubes. The evolved gases were led successively from the top of the condenser through vapor condensing Dry Ice–acetone traps (to stop the ether), and a bubble counter to indicate the rate of evolution of gas. They were then collected over water in a pair of 1-liter graduates. The apparatus permitted the diversion of the stream of gas from a full graduate to an empty one. The nitrate was added dropwise with stirring at a rate sufficient to maintain refluxing (1–1.5 hours). The formation of an amorphous pre-

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(4) W. A. Noyes, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 108.

(5) P. J. Elving and W. R. McElroy, *Ind. Eng. Chem., Anal. Ed.*, **14**, 84 (1942).

(6) M. J. Taras, *ibid.*, **22**, 1020 (1950).

(7) F. Fichter and A. Petrovitch, *Helv. Chim. Acta*, **24**, 253 (1941).

(8) N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffland, THIS JOURNAL, **69**, 307 (1947).

(9) L. Henry, *Rec. trav. chim.*, **24**, 357 (1905).

(10) L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 285 (1936).

(11) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 280.

(12) M. F. Clark and L. N. Owen, *J. Chem. Soc.*, 318 (1949), Method ii.

(13) J. B. Brown, H. B. Henbest and E. R. H. Jones, *ibid.*, 3639 (1950).

(14) Performed by Dr. Frederick Kaufman of the Ballistic Research Laboratories.

(15) P. E. Verkade, J. Coops, Jr., A. Verkade-Sandbergen and Chr. J. Maan, *Ann.*, **477**, 279 (1930).

Table II

Ester	Original alcohol			Product alcohol		
	B.p. or m.p., °C.	n^t_D	t, °C.	B.p. or m.p., °C.	n^t_D	t, °C.
cis-Cyclohexane-1,2-diol dinitrate	M. 97–98[a]	....	...	M. 98	....	..
trans-Cyclohexane-1,2-diol dinitrate	M. 101.5–103[b]	....	...	M. 102–103	....	..
n-Hexyl nitrate	157–158[c]	1.4158	26[d]	157	1.4160	25
n-Hexyl nitrite	157–158	1.4158	26	157–158	1.4159	26
Cyclohexyl nitrate	160–161[e]	1.4644	24[e]	160	1.4642	26
Cyclohexyl nitrite	160–161	1.4644	24	160	1.4640	25
2-Octyl nitrate	179[f]	1.4242	24[f]	179–180	1.4243	24
2-Octyl nitrite	179	1.4242	24	179	1.4244	25

[a] Ref. 12. [b] Ref. 13. [c] B.p. 157.0–157.8°.[16] [d] n^{25}_D 1.4161.[17] [e] B.p. 161.1°, n^{25}_D 1.46477.[19] [f] Ref. 17.

cipitate caused the solution to become progressively whiter as the reaction proceeded. Following the addition of the ester, the mixture was refluxed an additional half-hour. The volume of gases collected, essentially hydrogen, was 9010 ml. (4.0 moles of gas per mole of nitrate). The flask was cooled in an ice-bath and the complex and excess hydride decomposed by the dropwise addition of water. When reaction no longer occurred the contents of the flask were made acid with hydrochloric acid and the ether layer separated. The aqueous layer was extracted three times with ether and the combined ether extracts dried over sodium sulfate. After removal of the ether there was obtained 9.1 g. of *n*-hexyl alcohol (b.p. 157°, n^{25}_D 1.4160, lit. b.p. 157.0–157.8°,[16] n^{25}_D 1.4161[17]); yield 90%.

In order to permit thorough flushing of the system samples of gas were taken at intervals near completion of addition of the ester. These samples were analyzed for nitrous oxide by determining the extinction of the infrared band at 7.7 microns and comparing with a standard calibration plot of volume of nitrous oxide *vs.* extinction. The average amount of nitrous oxide was 1% (0.008 mole N). Similar samples were collected for combustion analyses in the Blacet–MacDonald–Leighton apparatus[18] and shown to contain 98% hydrogen and 1% nitrogen. The presence of the latter was due to residual air, because nitrogen was not found in runs where air had been completely flushed from the system with hydrogen prior to beginning the reaction.

The amount of ammonia produced was determined in a separate but similar run, as follows. After the addition of the ester was complete, the complex and hydride were destroyed in the usual way. The mixture was then warmed and stirred while a stream of nitrogen swept the ammonia into a flask containing excess standard acid. Precautions were taken to prevent the carrying over of any alkali. The procedure was continued until no more ammonia could be detected in the reaction vessel, 8 to 10 hours being required. The ammonia evolved, determined by back titration with standard base, was 0.084 mole. The N balance was thus 0.10 mole N input as opposed to 0.092 mole N output. The balance was short because of the solubility of the nitrous oxide in the ether solution.

Occasionally, for reasons unknown, the reaction of the nitrates with hydride would begin sluggishly and speed up only after periods of from one to four hours. In all other aspects these runs proved entirely satisfactory.

The reactions of nitrites were carried out in the same way with the exception that their greater reactivity precluded the need of external heating.

The yields of the product alcohols from the five nitrates and three nitrites studied ranged from 87 to 98%. The boiling points and refractive indices of the alcohols originally used in the preparation of the esters are compared in Table II with those of the product alcohols. It is quite likely that less than quantitative yields are due to the usual losses involved in isolation and purification.

Four nitrocellulose samples, ranging from 13.0–13.9% nitrogen, were subjected to the denitration reaction. Solutions of nitrocellulose in tetrahydrofuran were added dropwise to stock solutions of hydride (0.015–0.020 g. hydride per ml.) in the same solvent, and the mixture refluxed. On completion of the reaction the gelatinous material was shaken with several portions of saturated sodium potassium tartrate solution to remove the greater part of the lithium aluminate, and then washed several times with 2% hydrochloric acid until tests for lithium and aluminum were negative. Yields of the dried material were 90–95%. Complete denitration was obtained as evidenced by the absence of a nitrate absorption band in the infrared and by a negative diphenylaminesulfonic acid test.[20] Viscosity measurements in cuprammonium solution[21] revealed, however, that extensive degradation of the polymer had occurred.

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[16] S. C. J. Olivier, *Rec. trav. chim.*, **55**, 1034 (1936).

[17] L. M. Ellis, Jr., and E. E. Reed, This Journal, **54**, 1678 (1932).

[18] F. E. Blacet and G. D. MacDonald, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 334 (1934), and earlier papers.

[19] J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **34**, 718 (1937).

[20] F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Company, Inc., New York, N. Y., 1946, p. 244.

[21] Committee on the Viscosity of Cellulose, Division of Cellulose Chemistry, American Chemical Society, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 49 (1929).