band maximum optical density by drawing each carbonyl absorption as a symmetric band.

The results of a set of experiments for carbon tetrachloride are given in Table I, while those for chloroform are in Table II. Values of

$$\alpha_{(\mathrm{HOAc})_2} = \frac{1}{C_{(\mathrm{HOAc})_2}\,l} \log \frac{I_0}{I}$$

where obtained from the intensities using the 0.034 mm. cell by extrapolation to high concentration and by correcting for the small amount of monomer present on the basis of an approximate equilibrium constant. A value for $\alpha_{(\mathrm{HOAc})}$ was then obtained from the results for the more dilute solutions from $\log I_0/I$ for the monomer and the monomer concentration as obtained from the stoichiometry.

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE REACTION $2\mathrm{HOAc} \rightleftarrows (\mathrm{HOAc})_2$ IN CARBON TETRACHLORIDE

Cell length, mm.	M_{HOAc}	$\left(\log \frac{I_0}{I}\right)_{(\mathrm{HOAc})_2}$	$\left(\log \frac{I_0}{I}\right)_{\mathrm{HOAc}}$	$C_{(\mathrm{HOAc})_2}$	C_{HOAc}	K, mole^{-1} l.
0.034	0.170	0.422	...	0.081	......	..
	.100	.250	...	.050	......	..
	.050	.128	0.01	.025	0.005	1000
0.250	.050	.814	.068	.0211	.0044	1090
	.025	.434	.047	.0113	.0030	1250
	.010	.160	.026	.0041	.0017	1420
1.10	.010	.690	.112	.0041	.0017	1420
	.005	.328	.072	.00190	.00105	1720
	.0025	.168	.050	.0099	.00074	1810
20.6	.00056	.442	.324	.000139	.000253	2170
	.00028	.180	.208	.000057	.000163	2150
	.000112	.054	.103	.0000170	.000080	2650

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE REACTION $2\mathrm{HOAc} \rightleftarrows (\mathrm{HOAc})_2$ IN CHLOROFORM

Cell length, mm.	M_{HOAc}	$\left(\log \frac{I_0}{I}\right)_{(\mathrm{HOAc})_2}$	$\left(\log \frac{I_0}{I}\right)_{\mathrm{HOAc}}$	$C_{(\mathrm{HOAc})_2}$	C_{HOAc}	K, mole^{-1} l.
0.034	0.349	0.820	(0.073)	0.147	(0.040)	(90)
	.174	.370	(.036)	.066	(.020)	(160)
0.095	.070	.428	.074	.0275	.0147	130
	.035	.204	(.050)	.0131	.010	130
1.00	.01395	.614	.309	.00374	.00583	110
	.00698	.267	.192	.00163	.00362	120
	.00279	.078	.098	.000475	.00185	140
20.4	.000558	.178	.493	.000053	.000455	260
	.000186	.040	.182	.000012	.000168	420

The equilibrium constants for CCl_4 solutions are satisfactorily constant, changing by about a factor of two for concentrations differing by a factor of about 500. This difference is greater than can be accounted for by errors in solution concentrations or determinations of optical densities or cell thicknesses.

All values are lower than the results of Harris and Hobbs[1] who give, for the dimerization equilibrium, the values 5,550 and 3,200 for concentrations in the ranges of about 0.003–0.07 *M* and 0.00025–0.0025 *M*, respectively. The latter constant is considered more reliable and it appears from the present results that the dependence of the equilibrium constant on concentration is the reverse of that indicated by the less reliable value of Harris and Hobbs.

The equilibrium constants in chloroform are likewise satisfactorily constant except at high dilutions and this deviation, as previously suggested, can be attributed to interaction with impurities in the chloroform.

The principal chloroform association with acetic acid occurs through hydrogen bonding to the monomer carbonyl. If all of the interaction is attributed to this and the dimer is considered unaffected in the chloroform, one calculates for the reaction

$$\mathrm{HOAc} + \mathrm{HCCl_3} \rightleftharpoons \mathrm{HOAc{\cdot}HCCl_3}$$

the equilibrium constant of about 0.2, representing a lower limit, which can be compared with association constants of alcohols of about 1.5 as reported by Coggeshall and Saier[2] or with that for the association of chloroform with triethylamine of 0.36 determined by Barrow and Yerger.[3]

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[2] N. D. Coggeshall and E. L. Saier, THIS JOURNAL, **73**, 5414 (1951).

[3] G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5247 (1954).

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Observations on the Rare Earths. LXIII.[1] The Preparation of Anhydrous Rare Earth Metal Nitrates

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The literature records no general procedure for the preparation of anhydrous rare earth metal nitrates. It is true that reaction of fused ammonium nitrate with lanthanum oxide yields the anhydrous nitrate,[2] but with neodymium only the compound $Nd(NO_3)_3{\cdot}NH_4NO_3$ could be obtained under comparable conditions, and attempts to remove excess ammonium nitrate by thermal decomposition gave a basic neodymium nitrate.[2] All attempts at dehydration of hydrated nitrates have yielded basic products.

Reaction of liquid dinitrogen(IV) oxide with metal carbonates or oxides to yield anhydrous nitrates was probably first noted by Oswald,[3] who obtained sodium nitrate in this fashion. Subsequent studies[4–9] have shown the method to be a general one, the reactions proceeding most readily in closed containers at elevated temperatures and resultant high nitrogen(IV) oxide pressures.[8,9] Even under the most drastic conditions reported (87°, 14.5 atm.),[8,9] a number of instances of slow

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[1] For the preceding communication in this series, see T. Moeller and P. A. Zimmerman, THIS JOURNAL, **75**, 3940 (1953).

[2] L. F. Audrieth, E. E. Jukkola and R. E. Meints with B. S. Hopkins, *ibid.*, **53**, 1805 (1931).

[3] M. Oswald, *Ann. chim.*, [9] **1**, 32 (1914).

[4] E. Briner, J. B. Lugrin and R. Monnier, *Helv. Chim. Acta*, **13**, 64 (1930).

[5] G. Boh, *Ann. chim.*, [11] **20**, 421 (1945).

[6] C. C. Addison, J. Lewis and R. Thompson, *J. Chem. Soc.*, 2829, 2838 (1951).

[7] C. C. Addison and J. Lewis, *ibid.*, 2833 (1951); 1319 (1953).

[8] G. Gibson and J. J. Katz, THIS JOURNAL, **73**, 5436 (1951).

[9] J. R. Ferraro and G. Gibson, *ibid.*, **75**, 5747 (1953).

reaction or lack of reaction have been found. It seems reasonable to ascribe reactions with metal oxides to an ionic behavior of dinitrogen(IV) oxide as $NO^+NO_3^-$ and to formulate these as acid–base reactions as[7,8,10]

$$M^{+2}O^{-2} + 2NO^+NO_3^- \longrightarrow M^{+2}(NO_3)_2^- + N_2O_3$$

The present study involves an extension of a modification of the technique of Gibson[8,9] to reactions of rare earth metal oxides with liquid dinitrogen(IV) oxide and the resulting quantitative preparation of anhydrous nitrates of these elements.

Experimental

Materials Used.—Rare earth metal oxides were from the stocks at the University of Illinois, and each contained no more than spectroscopic traces of other rare earth elements as impurities. With the exception of praseodymium(III) oxide, each sample was ignited at 960° just prior to being used. Praseodymium(III) oxide was prepared by reducing the black compound Pr_6O_{11} with aqueous hydrazine[11] and after washing was dried with alcohol and ether and then over nitrobenzene in an Abderhalden drying pistol. Nitrogen(IV) oxide was obtained from a commercial cylinder and was condensed into the apparatus as required.

Apparatus and Procedure.—The essential details of the apparatus are indicated in Fig. 1. The cylinder of nitrogen(IV) oxide is connected to a drying tower A packed with phosphorus(V) oxide. This tower is joined to a storage vessel B through a 6 mm. vacuum stopcock. Attached to B is a 6 mm. glass manifold, with a connecting safety mercury monometer at C, trap and McLeod gage at D, and a dividing vacuum stopcock. The reaction vessel F is a stainless steel bomb of 150-ml. capacity.[12] A trap G and attachment to a high vacuum pump at H complete the system.

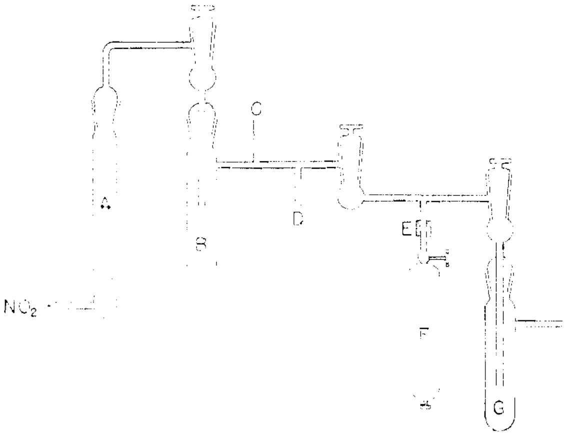

Fig. 1.—Apparatus for preparation of anhydrous rare earth metal nitrates.

A weighed quantity (*ca.* 2 g.) of dried rare earth metal oxide is placed in the bomb through the hole in the bottom, which is then closed. The bomb is connected to the glass manifold by wrapping a strip of aluminum foil tightly around the glass–metal junction, covering with unvulcanized rubber tape, and coating with glyptal resin. The result is a gas-tight, easily broken seal. The system is evacuated (*ca.* 0.02 mm.) and the stopcock dividing the manifold closed. About 30 ml. of dinitrogen(IV) oxide (*ca.* 15-fold excess) is condensed into vessel B, using a liquid nitrogen bath. The system is isolated by closing the two end stopcocks, and the dinitrogen(IV) oxide is condensed into the bomb by surrounding the bomb with liquid nitrogen and vessel B with water at *ca.* 40°. The valve on the bomb is closed, and the seal at E is cut. The tube at the top of the bomb is closed with a stainless steel cap, and the bomb and its contents are heated in an oven at 150° for 24 hours. During this time, the internal pressure probably reaches *ca.* 80 atm.

After being cooled to room temperature, the bomb is connected to a series of magnesium perchlorate towers and an aspirator, and the nitrogen oxides are bled off. The bomb is then evacuated by pumping for several hours, using an acetone–solid carbon dioxide trap, and dry air is admitted. The bomb is opened in a dry-box and the contents transferred to a weighed container. This is heated in an Abderhalden pistol at 137° (using xylene) to constant weight and sealed. The yield is determined from (1) increase in weight during reaction and (2) analyses of the product for nitrate and rare earth metal content. Completion of reaction is judged by complete solubility of product in water.

Analysis.—Weighed samples of the anhydrous nitrates were dissolved in water. Aliquots were analyzed for rare earth metal contents by evaporating to dryness, igniting and weighing as oxides and for nitrate contents by the gravimetric nitron procedure.[13] Absence of nitrite (and probably nitrogen(IV) oxide of solvation) was established by negative diphenylamine test.

Results and Discussion

As indicated by the data in Table I, reaction of rare earth metal oxides with liquid dinitrogen(IV) oxide is a satisfactory procedure for preparing the anhydrous nitrates. Although intermediates containing nitrogen(IV) oxide of solvation were undoubtedly formed, these materials decomposed to the nitrates under the conditions specified and were not characterized. Yields obtained were quantitative, but at heating temperatures below 140° they were materially reduced. It seems probable that yield of anhydrous nitrate in this type of reaction depends markedly upon temperature and that by the use of more drastic conditions some of the yields reported by Gibson[8,9] might be improved.

TABLE I

REACTIONS OF RARE EARTH METAL OXIDES WITH LIQUID DINITROGEN(IV) OXIDE

				Analyses, %			
				Nitrate		R. E. metal	
Oxide	Product	Color	Yield, %	Calcd.	Found	Calcd.	Found
La_2O_3	$La(NO_3)$	White	100	57.26	56.67	42.75	42.99
Pr_2O_3	$Pr(NO_3)_3$	Green	100	56.91	56.91	43.10	43.13
Nd_2O_3	$Nd(NO_3)_3$	Violet	100	56.32	56.32	43.69	43.65
Sm_2O_3	$Sm(NO_3)$	Cream	100	55.28	55.72	44.70	44.92
Gd_2O_3	$Gd(NO_3)_3$	White	100	54.25	54.31	45.76	45.85
Y_2O_3	$Y(NO_3)_3$	White	100	67.67	66.49	32.35	32.76

The anhydrous nitrates obtained are voluminous powders, with colors comparable to those of the chlorides, which dissolve rapidly and completely by highly exothermic processes in water, ethanol or anhydrous ethylenediamine to give clear solutions. Absorption bands in ethanol solutions due to rare earth metal ions are identical with those observed in aqueous solution.[14,15]

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(10) C. C. Addison and R. Thompson, *J. Chem. Soc.*, S 211 (1949).

(11) R. Gher, Bachelor's Dissertation, University of Illinois (1948).

(12) Style No. HD 300, Hoke Incorporated, Englewood, New Jersey. Rated at 122 atm. and provided with a valve at one end and a threaded stainless steel plug at the other.

(13) M. Busch, *Ber.*, **38**, 861 (1905).

(14) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(15) T. Moeller and F. A. J. Moss, THIS JOURNAL, **73**, 3149 (1951).