The tetrahydrofuran layer was separated and evaporated *in vacuo* to an oil. This oil was fractionally distilled, dissolved in abs. ether and dried over sodium hydroxide pellets. The pure hydrazine was obtained by fractionally distilling this ether solution.

N-Nitrosomethylaniline was reduced to 1-methyl-1-phenylhydrazine[5] in 77% yield which is an oil boiling at 106–109° (13 mm.).

N-Nitrosopiperidine was reduced to N,N-pentamethylene-hydrazine[6] in 75% yield. It is an oil boiling at 146–148° (730 mm.).

N-Nitrosodicyclohexylamine was reduced to 1,1-dicyclohexylhydrazine in 48% yield. It is a white crystalline solid boiling at 95–98° (4 mm.) which sublimes above 162°. The hydrochloride forms white flaky crystals from ether, m.p. 238–240° (cor.). The methiodide forms small white plates from abs. ether, m.p. 250–252° (cor.). *Anal.* Calcd. for hydrochloride $C_{12}H_{25}N_2Cl$: Cl, 15.23. Found: Cl, 14.94. *Anal.* Calcd. for methiodide $C_{13}H_{27}N_2I$: I, 37.51. Found: I, 37.06.

Skita and Rolfes[7] attempted to prepare 1,1-dicyclohexylhydrazine by reducing N-nitrosodicyclohexylamine with zinc and hydrochloric acid and obtained dicyclohexylamine. When they used zinc in absolute alcohol with acetic acid no hydrazine could be isolated.

The 1,1-dicyclohexylhydrazine has a nauseating and irritating odor beyond that produced by high molecular weight amines. This compound in lethal doses in white mice produces convulsions characteristic of central nervous system stimulation. The LD_{50} dose in mice by the intraperitoneal route is 77 mg./kg.

(5) W. W. Hartman and L. V. Roll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943. p. 418.

(6) Knorr, *Ann.*, **221**, 299 (1883).

(7) Skita and Rolfes, *Ber.*, **53**, 1251 (1920).

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Preparation of Telluric Acid

BY H. J. HORNER AND GUY WILLIAM LEONARD, JR.

Several methods for the preparation of telluric acid have been reported in the literature and are listed by Gilbertson.[1] These methods either give an impure product or require large excesses of oxidizing agent and special preparation of the tellurium. The preparation as developed by Mathers and co-workers[2] is the most widely used. However, purification of the crude telluric acid thus obtained required repeated recrystallizations from concentrated nitric acid solutions.

Hydrogen peroxide is the ideal oxidizing agent, but when it is used alone or in the presence of an acid, a very large excess of peroxide is needed. In basic solutions the oxidation of tellurium dioxide by a slight excess of hydrogen peroxide proceeds nicely to completion. By using ammonia solutions, the by-products are readily separated from the telluric acid.

Experimental

The commercial grade tellurium dioxide (approximately 76% pure) was found to contain impurities which vigorously catalyzed the decomposition of hydrogen peroxide. The tellurium dioxide was purified by dissolving it in 5 *N* sodium hydroxide. After filtering, the tellurium dioxide was reprecipitated by adding 10 *N* nitric acid to the filtrate until the solution was acid to phenolphthalein. The supernatant

(1) L. I. Gilbertson, THIS JOURNAL, **55**, 1460 (1933).

(2) F. C. Mathers, C. M. Rice, H. Broderick and R. Torney, *Inorganic Syntheses*, **3**, 145 (1950).

liquid was then decanted and the precipitate washed five times with distilled water. The purified material was dried for 24 hours at 110°. This method produced a compound of about 98% purity. Subsequent repetition of the above procedure made no appreciable change in the purity, because of coprecipitation of sodium salts.

Preliminary determinations revealed no apparent reaction between pure tellurium dioxide and 30% hydrogen peroxide. However, in the presence of dilute ammonia solution some oxidation occurred with the formation of a gum which prevented further reaction. Nevertheless the reactions occurring in concentrated ammonium hydroxide produced a white crystalline precipitate of an ammonium tellurate which did not interfere with the oxidation of the tellurium dioxide.

Procedure.—A ten-gram sample of tellurium dioxide, purified and oven-dried, was placed in a 250-ml. erlenmeyer flask fitted with a rubber stopper. To the flask was added a mixed solution of 10 ml. of 30% hydrogen peroxide and 75 ml. of concentrated ammonium hydroxide. After the pressure generated by the initial reaction had subsided the flask was stoppered and set aside. During this period, the flask was frequently shaken. After 24 hours, the mixture was heated on a steam-bath until the vapors were free of ammonia, and the volume of solution had been reduced to 45 ml. Next, 10 ml. of concentrated nitric acid was added to the above solution. During the addition of the nitric acid, the ammonium tellurate dissolved. After 24 hours the supernatant liquid was removed from the crystals of telluric acid which had formed, and the liquid was further concentrated to 20 ml. Another 10 ml. of concentrated nitric acid was added and after an additional 24 hours the crops of crystals were combined. Further purification was accomplished by one recrystallization from distilled water. This method produces telluric acid of 99.99% purity and in yields of 75–80%. The telluric acid was analyzed by the method of Gooch and Howland.[3] The flame test and Nessler reagent showed that the telluric acid was not contaminated with either sodium or ammonium ions.

(3) F. A. Gooch and J. Howland, *Am. J. Sci.*, [3] **48**, 375 (1894).

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The Effect of Fluorine on Praseodymium Trifluoride

BY THEODORE P. PERROS AND CHARLES R. NAESER

Since it has been shown that cerium tetrafluoride could be prepared quantitatively from cerous fluoride with fluorine at 500°,[1] it was thought to be of interest to determine what effect elemental fluorine would have on praseodymium trifluoride at this and other temperatures. Klemm[2] fluorinated praseodymium trichloride and obtained a mixture of the chloride and fluoride.

Experimental

Fluorine was prepared by the apparatus described by Von H. von Wartenberg.[1] A graphite anode was used. The rate of production of fluorine was about 35 ml. per minute.

A combustion boat was made from a fluorite cupel since most other substances which might be used for a boat are reacted upon by fluorine at temperatures above 500°.

A nickel tube 1/8″ in thickness, 7/8″ inside diameter and 14″ in length was used to house the combustion boat. The reaction tube was heated to the desired temperatures in an electric combustion furnace. The joints between the apparatus and the reaction tube were sealed with plaster of Paris. Before each run the system was dried by air.

Praseodymium trifluoride was prepared by the addition of hydrofluoric acid to a solution of the trichloride which had been warmed to 80°. The precipitate was filtered and

(1) Von H. von Wartenberg, *Z. anorg. allgem. Chem.*, **244**, 337 (1940).

(2) Klemm and Henkel, *ibid.*, **220**, 180 (1934).

washed with absolute alcohol. The precipitate was dried in an oven at 110°. Analysis indicated that the salt contained only a small amount of water (2–3%). About 0.7 g. of sample was used in each of the runs.

Table I contains a summary of the runs which were made.

TABLE I

	Temperature of reaction tube, °C.	Duration in hours of fluorination period
1	Room temperature	4.5
	Room temperature	7.5
2	300	4
	300	7
3	500	3
	500	8
4	625	3.75
	625	7.5
5	700	4
	700	7.5
6	800	4
	800	7.5

After each run, the sample was tested with hydriodic acid to determine whether any oxidation had occurred. In each instance, the results were negative. This confirms the work of Klemm.[2]

In the preliminary stages of this investigation when a platinum combustion boat was used, praseodymium(III) fluoplatinate was one of the products formed at temperatures above 500°. Detailed information on this and other fluoplatinates will be the subject of a paper now in preparation.

CONTRIBUTION FROM THE
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Kinetics and Some Hydrogen Isotope Effects of the Reaction of Diphenyldiazomethane with Acetic Acid in Ethanol[1]

BY JOHN D. ROBERTS AND CLARE M. REGAN

As part of other investigations,[2,3] we have had occasion to study the kinetics and hydrogen isotope effects of the reaction of diphenyldiazomethane with acetic acid in ethanol using the techniques previously developed for other carboxylic acids.[2–5] As might be expected, the reaction of acetic acid with diphenyldiazomethane is very similar to that with benzoic acid in that it is accurately first order in acid as well as diazo compound and shows similar salt and medium effects (cf. Table I). All of the data are consistent with the hypothesis that acetic acid and benzoic acid react with diphenyldiazomethane by similar mechanisms involving rate-determining proton transfers from undissociated acid to diazo compound. Indeed, the only very striking difference between the behaviors of the

(1) Supported in part by the program of research of the United States Atomic Energy Commission.

(2) J. D. Roberts and C. M. Regan, *Anal. Chem.*, **24**, 360 (1952).

(3) J. D. Roberts, W. Watanabe and R. E. McMahon, THIS JOURNAL, **73**, 760 (1951).

(4) (a) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts and W. Watanabe, *ibid.*, **72**, 4869 (1950).

(5) J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, **74**, 3679 (1952).

two acids is that a considerably higher fraction of benzhydryl acetate (87%) is formed with acetic acid than benzhydryl benzoate (55%) with benzoic acid[3] (Table II). This difference is likely to be due to steric hindrance since acetic acid with its small methyl group should be more reactive in a direct reaction[3] with diphenyldiazomethane than benzoic acid.

TABLE I

RATES OF REACTION OF DIPHENYLDIAZOMETHANE WITH ACETIC ACID IN ABSOLUTE ETHANOL AT 30.0°

Acetic acid, mole/l.	Diphenyl- diazo- methane, mole/l.	Salt, mole/l.	k_2, (moles/l.)$^{-1}$ min.$^{-1}$
0.0341	0.00218	....	0.562
.0683	.00328	....	.556
.1472	.00547	....	.578
.1472	.00547	0.033 LiClO$_4$	.624
.1472	.00547	.067 LiClO$_4$	.645
.1472	.00547	.100 LiClO$_4$	.692
.1472	.00547	.033 NaOAc	.523[a]
.1472	.00547	.067 NaOAc	.493[a]
.1472	.00547	.100 NaOAc	.462[a]
.1542[b]	.00526	....	2.12
.1542[c]	.00526	....	1.30
.1787[d]	.00947	....	0.166
.0953[e]	.00526	....	0.553
.0953[e,b]	.00526	....	2.12
.0953[e,c]	.00526	....	1.23
.1759[e,d]	.00947	....	0.151

[a] The same slowing of rate by carboxylate ion was observed with benzoic acid and admits of a similar explanation.[3] [b] Solvent was 82.5% ethanol–17.5% water (by volume). [c] Solvent was 82.5% ethanol–17.5% deuterium oxide (by volume), 38% calculated replacement of O–H groups by O–D groups. [d] Solvent was C$_2$H$_5$OD which was prepared as described previously.[5] [e] CD$_3$COOD used in place of CH$_3$COOH.

TABLE II

ACETIC ACID CONSUMPTION IN DIPHENYLDIAZOMETHANE REACTION AT 30.0° IN ABSOLUTE ETHANOL

Acetic acid, mole/l.	Diphenyldiazo- methane, mole/l.	Salt, mole/l.	Eq. acid consumed/ eq. of diphenyl- diazo- methane[a]
0.0440	.000915	....	0.88
.0440	.00915	....	.86
.0440	.00915	0.070 LiClO$_4$	.83
.0440	.00915	.070 LiClO$_4$	.82

[a] Determined by the procedure of ref. 3.

As part of our program of research on isotope effects,[3,5] several hydrogen isotope effects on the acetic acid–diphenyldiazomethane reaction were measured and are listed in Table I. Substitution of C$_2$H$_5$OD for ordinary ethanol as the solvent (with consequent replacement of O–H by O–D in the carboxyl group of the acetic acid) caused a very substantial decrease in the reaction rate (3.5-fold for acetic acid as compared with 3.6-fold for benzoic acid[5]) as expected for a rate-determining proton transfer. Similar replacement of 38% of the O–H bonds by O–D bonds in 82.5% ethanol–17.5% water brought about a 39% decrease in the reaction rate with acetic acid as compared with 38% with benzoic acid.[3] In a number of experiments