latter may be readily converted to the former. Conformational analysis of the *trans*-glycol requires the arrangement: 2-phenyl (e), 2-hydroxyl (p), 1-hydroxyl (p) while in the *cis*-glycol the following arrangement obtains: 2-phenyl (e), 2-hydroxyl (p), 1-hydroxyl (e). It is implied in the work of Beckett, Pitzer and Spitzer[3] that the energy difference in similar systems between 2(p), (e) and (p), 2(e) is of the order of 1 kcal./mole. It has, indeed, been shown that the molar heat of combustion in the case of the *cis*-glycol is 1563.1 kcal. and that of the *trans*-glycol, 1564 kcal.[4]

A novel method has recently been employed by Woodward for the synthesis of *cis*-glycols[5] based upon Winstein's work on neighboring group effects.[6] The method involves the *trans* addition of iodine to a double bond followed by attack by silver acetate to give the *trans*-iodoacetoxy compound. The presence of water in the acetic acid used as solvent leads to the formation of the *cis*-glycol monoacetate. Finally, saponification leads to the *cis*-glycol.

When applied to 1-(2,3-dimethoxyphenyl)-cyclohexene, this method led to the same glycol obtained by the standard hydroxylation procedures. That the stable conformation in this case is, indeed, the *cis*-glycol was shown by the preparation of an acetonide using anhydrous copper sulfate as catalyst. Acetonide formation proceeds at a slow rate because one of the hydroxyl groups is tertiary, but is practically complete within 96 hours. Although cases of *trans*-glycols forming acetonides are known when mineral acid is used as catalyst[7] due to prior rearrangement to the *cis*-glycol, no such cases have been reported when copper sulfate is used as catalyst.

Experimental

***cis*-2-(2,3-Dimethoxyphenyl)-cyclohexane-1,2-diol.**—1-(2,3-Dimethoxyphenyl)-cyclohexene (4.77 g.) was dissolved in analytical glacial acetic acid (100 ml.) in a three-necked flask equipped with stirrer, reflux condenser and thermometer. Silver acetate (8.22 g.) was added followed by finely powdered iodine (5.85 g.) in small portions to the vigorously stirred reaction mixture over a period of 30 minutes at room temperature. During this time the temperature rose from 26 to 33°. When all the iodine had been absorbed, as indicated by the color of the mixture, aqueous acetic acid (9.85 ml. prepared by dilution of 2.0 ml. of water up to 50 ml. with glacial acetic acid) was added and the reaction mixture was heated in a boiling water-bath with vigorous stirring for 3 hours. After cooling, sodium chloride (20 g.) was added, the mixture was stirred for 30 minutes more and the insoluble precipitate was removed by filtration. The precipitate was washed with hot benzene and the combined filtrate was evaporated under reduced pressure. The residue was treated with methanol, filtered to remove a small amount of insoluble material, and to the filtrate was added a solution of potassium hydroxide (2 g.) in methanol (10 ml.). After hydrolysis had proceeded overnight, the methanol was removed under reduced pressure, water was added and the mixture was extracted with ether. Removal of the solvent and trituration of the residue with methylcyclohexane yielded 3.2 g. (56%) of *cis*-2-(2,3-dimethoxyphenyl)-cyclohexane-1,2-diol, m.p. 104–105°, identical with the product described by Bergmann, *et al.*[2]

2-(2,3-Dimethoxyphenyl)-cyclohexane-1,2-diol Acetonide.—The glycol (2 g.) was dissolved in acetone (200 ml., distilled from anhydrous potassium carbonate) and was shaken mechanically with anhydrous copper sulfate (10 g.) for 96 hours. After filtration and evaporation of the solvent under reduced pressure, the residue was dissolved in chloroform and chromatographed over alumina. The acetonide (2.1 g.) passed through the column readily and any glycol still present remained in the column. The analytical sample of the oily acetonide was prepared by heating the material in a high vacuum at 70° for 24 hours.

Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.10; H, 8.16.

In the infrared spectrum, the hydroxyl band present in the glycol at 2.86 μ, was completely absent. A strong band at 9.68 μ and a band of medium intensity at 11.35 μ were present.[8]

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[3] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[4] P. E. Verkade, *et al.*, *Ann.*, **467**, 217 (1928).

[5] We are indebted to Dr. R. B. Woodward for making this information available to us and for kindly assenting to its disclosure prior to his own publication of the details of the method.

[6] *Cf.* S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2787 (1942).

[7] *Cf.* A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 981 (1940); *C. A.*, **35**, 3603 (1941).

[8] For the position of the ether bands in the infrared *spectra* of acetonides, see R. B. Woodward, *et al.*, THIS JOURNAL, **74**, 4241 (1952).

Reaction of Some Metallic Oxides with Liquid Dinitrogen Tetroxide. Oxides of the First and Second Periodic Groups and Lead[1]

BY JOHN R. FERRARO AND GEORGE GIBSON

RECEIVED JUNE 25, 1953

This is the first of a planned series of studies being undertaken at this Laboratory on the reaction of liquid dinitrogen tetroxide with various oxides. Other workers have studied reactions of the oxides CaO,[2] CuO and Cu_2O,[3,4] PbO,[4] HgO[4] and ZnO,[5] with gaseous or liquid N_2O_3 or N_2O_4. The oxides studied in this series are listed in Table I.

Experimental

Materials.—Pb_3O_4, PbO_2, BaO_2, BaO (71% $Ba(OH)_2$), Cu_2O, HgO, Hg_2O and $Hg(NO_3)_2$ were reagent grade chemicals. PbO, ZnO, PbO and MgO were prepared by the thermal decomposition of the respective carbonates and CaO and SrO from their oxalates. Ag_2O and CuO were prepared by precipitation from solution with NaOH, followed by drying to the oxide. N_2O_4 (cylinder) was dried before use by passing through a P_2O_5 drying tower.

Analyses.—Dinitrogen tetroxide content (as NO_2) in the reaction products was determined by cerate oxidation, as previously described.[6] Copper and mercury determinations were done by standard electrolytic procedures. Calcium, cadmium, lead, zinc and magnesium were determined gravimetrically by ignition of the reaction product to the oxide. Water analyses were done by the standard Karl Fischer procedure.

Apparatus and Procedure.—The apparatus and experimental procedure have been described elsewhere.[6] The reactants were heated to 87° at 14.5 atm. NO_2 pressure except for $Ca(OH)_2$, HgO, Hg_2O and $Hg(NO_3)_2$ which reacted completely at 25° and 1.1 atm. NO_2 pressure. All transfers or operations on the products were carried out in a dry-box.

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[1] Presented in part at the 122nd Meeting of the American Chemical Society, September, 1952.

[2] M. Ostwald, *Ann. chim.*, (IX) 1, 32 (1914); J. R. Partington and F. A. Williams, *J. Chem. Soc.*, **125**, 947 (1924); E. Briner, J. P. Lugrin and R. Monnier, *Helv. Chim. Acta*, **13**, 64 (1930).

[3] E. Divers and T. Shimidzu, *J. Chem. Soc.*, *Trans.*, **47**, 630 (1885); J. R. Park and J. R. Partington, *J. Chem. Soc.*, **125**, 72 (1924); J. R. Partington, *ibid.*, **125**, 663 (1924).

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

[5] C. C. Addison, J. Lewis and R. Thompson, *J. Chem. Soc.*, 2829, 2838 (1951); C. C. Addison and J. Lewis, *ibid.*, 2833 (1951).

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

TABLE I

REACTION OF OXIDES WITH LIQUID N_2O_4

Oxide	Reaction time, hr.	Oxide reacted, %	NO_2 in product, %	Metal(II) cation in product, %
PbO	7	84	Nil[a]	
Pb_3O_4	9	86[b]	Nil	
PbO_2	7	97	Nil	
Ag_2O	11	100	2.06	
ZnO	6.5	100	37.84[c]	19.14[c]
CdO	7	80	1.61	
MgO	6.5	90	26.84[c]	11.96[c]
CaO	6	50	0.81	
$Ca(OH)_2$[d]	350 days[e]	100	Nil	
SrO	14.5	0	0.22	
BaO_2	8	25	.13	
BaO[f]	14.5	99	.24	
CuO	14.5	85	31.94[c]	22.95[c]
Cu_2O	7.5	100	32.03	22.43
HgO	400 days[e]	100	19.53	47.95
Hg_2O	16 days[e]	100	16.87	

[a] Nil = 0.1% or less by weight of NO_2. [b] Residual oxide Pb_3O_4 by X-ray diffraction pattern. [c] Corrected for unreacted oxide in product. [d] $Ca(NO_3)_2 \cdot H_2O$ isolated: Found: H_2O, 9.52. Theory: H_2O, 9.88. [e] Time (in days), indicates the time the oxide remained in contact with N_2O_4 prior to analysis rather than the time for actual reaction. Observable reaction occurred in these cases in from 4 to 48 hours. [f] 71% $Ba(OH)_2$.

Results and Discussion

The data in Table I are representative of several experiments for each of the listed oxides, prepared at low temperatures. Confirming previous observations,[4,6] the oxides prepared at higher temperatures were much less reactive.

The catalytic effect of water on oxide–liquid N_2O_4 reactions is illustrated by the data for $Ca(OH)_2$ and BaO (71% $Ba(OH)_2$).

The products were either the corresponding anhydrous nitrates or the NO_2 addition compounds of the following analytical composition: $Mg(NO_3)_2 \cdot NO_2$, $Zn(NO_3)_2 \cdot 2.6$ to $3.3\ NO_2$, $Cu(NO_3)_2 \cdot 2NO_2$ and $Hg(NO_3)_2 \cdot 2NO_2$. These addition compounds were decomposed to the anhydrous nitrates at 10^{-5} mm. and at temperatures ranging from 90 to 140°, depending upon the thermal stability of the particular compound. The preparation of $Mg(NO_3)_2$ was not particularly successful due, we believe, to a concurrent decomposition of the $Mg(NO_3)_2$.

Zinc oxide heated in the presence of liquid dinitrogen tetroxide gave as a product a light brown, viscous oil, which solidified completely to a light yellow, waxy solid in approximately eight hours. The same solid product was obtained with zinc oxide and liquid dinitrogen tetroxide at room temperature. We believe $Zn(NO_3)_2 \cdot 2.6$ to $3.3\ NO_2$ represents a mixture of $Zn(NO_3)_2 \cdot 2N_2O_4 + Zn(NO_3)_2$ isolated at 30° whereas Addison[5] obtained $Zn(NO_3)_2 \cdot 2N_2O_4$ at 15°. In this series of addition compounds, $Zn(NO_3)_2 \cdot 2N_2O_4$ is intermediate in thermal stability between $Cu(NO_3)_2 \cdot 2NO_2$ and $Hg(NO_3)_2 \cdot 2NO_2$.

The copper(I) oxide exhibited a rather unusual behavior toward liquid dinitrogen tetroxide. At room temperature there was no observable reaction other than a slight darkening of the oxide. At 87°, however, the solid product increased in bulk volume some tenfold over that of the original oxide, producing a jade green micro-crystalline solid. In all of these experiments a considerable excess of dinitrogen tetroxide liquid was present after reaction, but in the case of the copper(I) reaction, only about 0.5 ml. of the 20 to 30 mole excess was observed as free liquid. Apparently the reaction product has the ability to absorb a large quantity of the excess dinitrogen tetroxide present; however, no reduction in the bulk volume of the solid product was observed when the excess liquid dinitrogen tetroxide was pumped off. It is interesting to note that the reaction product of copper(II) oxide did not exhibit this property.

Mercury(I) and (II) oxides and anhydrous mercury(II) nitrate reacted with the liquid dinitrogen tetroxide to produce brown viscous oils which were immiscible in the solvent. The oily product could be frozen with liquid nitrogen to a yellow glass-like solid having a conchoidal fracture. The softening point of this material was slightly below the freezing point of liquid dinitrogen tetroxide. $Hg(NO_3)_2 \cdot 2NO_2$ remained as an oil at 25 to 30° in a nitrogen dioxide gas atmosphere of 750 mm., but lost NO_2 very rapidly below this pressure at 30°, yielding a pale yellow solid having a composition approximating $Hg(NO_3)_2 \cdot 0.7NO_2$. This latter product when heated gave mercury(II) nitrate. The reaction of anhydrous mercury(II) nitrate with liquid dinitrogen tetroxide was carried out for the purpose of confirming the composition of the oily product obtained for the oxides. $Hg(NO_3)_2 \cdot 2NO_2$ is the most unstable of these nitrogen dioxide-containing compounds investigated to date. $Hg(NO_3)_2 \cdot 2NO_2$ may be the same compound reported by Boh[4] as his unidentified product obtained from the reaction of mercury(II) oxide and dinitrogen trioxide.

Acknowledgments.—The authors wish to thank Messrs. M. Brodsky and I. Kalnin of the Chemistry Department for their assistance in preparing the X-ray patterns mentioned above; also the Argonne National Laboratory for the loan of the bomb tube apparatus used in this research.

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Divergent Electrophoretic Properties of Dissolved and Adsorbed Trypsin

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RECEIVED JULY 20, 1953

There is good experimental evidence that the electrophoretic mobilities of inert particles suspended in a protein solution (microscope method) are often not greatly different from the mobility of the dissolved protein, as determined by the moving boundary method under comparable conditions of *p*H, ionic strength, etc.[1] However, large differences have been noted with several proteolytic

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