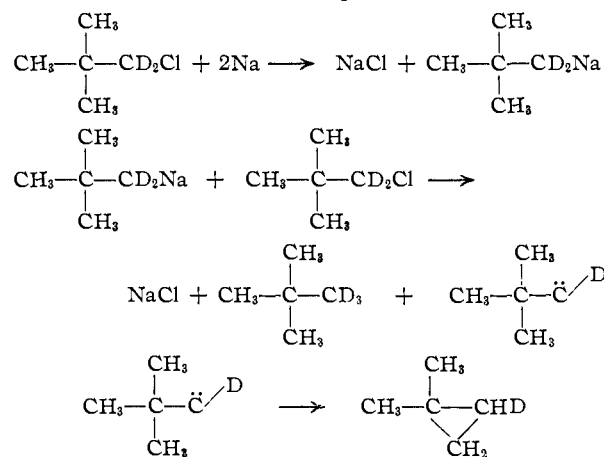


is not related to the above reaction, but represents conversion of neopentyl sodium or other intermediates, such as neopentyl radical, by reaction with moisture or the solvent.

A reasonable mechanism consonant with the close correspondence of yields of trideuterio-neopentane and monodeuterio-dimethylcyclopropane involves an  $\alpha$ -elimination step.



(7) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Office of Ordnance Research, Contract No. DA-36-061-ORD-607.

DEPARTMENT OF CHEMISTRY  
THE PENNSYLVANIA STATE UNIVERSITY  
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RECEIVED DECEMBER 16, 1960

PHILIP S. SKELL<sup>7</sup>  
A. PAUL KRAPCHO

#### THE ENTROPIES OF ASSOCIATION OF IONS

Sir:

It is the opinion of some workers that the entropy changes accompanying the association of ions in aqueous solution,  $\Delta S$ , are reasonably well understood<sup>1</sup> The changes usually are related to physical properties of the ions taking part or to their entropies of hydration,  $\Delta S_{\text{hyd}}$ . George,<sup>2</sup> in an analysis of a large number of data, recognized two types of behavior:

(1) For many ion pairs having one ion in common,  $\Delta S^0$  conformed to the empirical equation  $\Delta S^0 = -\Delta S_{\text{hyd}} + C$ , where  $C$  was a constant for each common ion. It was suggested that in these cases there was a loss of water of hydration and possible complex formation.

(2) Reactions for which  $\Delta S^0$  was independent of  $\Delta S_{\text{hyd}}$ . This was attributed to the formation of true ion pairs and was illustrated by data for

(1) R. J. P. Williams, *Ann. Reports Chem. Soc.*, **56**, 87 (1959).  
(2) J. H. B. George, *J. Am. Chem. Soc.*, **81**, 5530 (1959).

bivalent metal sulfates. Unfortunately, George used the figures of Singh<sup>3</sup> for calcium, strontium, barium and lead sulfates and these are not association entropies at all but refer to entropy changes,  $\Delta S^1$ , for the reaction  $\text{MSO}_4(\text{solid}) \rightleftharpoons \text{M}^{2+} + \text{SO}_4^{2-}$ . Indeed it would be difficult to recognize ion association in solutions of salts as sparingly soluble as barium sulfate. Where comparison is possible, for calcium sulfate,  $\Delta S^1 = 26.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  whereas  $\Delta S^0 = 16.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .<sup>4</sup> Furthermore,  $-\Delta S_{\text{hyd}}(\text{Mg}^{2+})$  used by George,  $71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , differs from the calculated value  $63.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .<sup>5</sup>

More data now are available for bivalent metal sulfates and these are given in the table together with  $\Delta S_{\text{hyd}}(\text{M}^{2+})$  and calculated values of  $\Delta S_{\text{hyd}}(\text{MSO}_4)$ .

TABLE I  
ENTROPIES OF ASSOCIATION AND OF HYDRATION

Reaction	$\Delta S^0$ (cal./deg. mole)	$-\Delta S_{\text{hyd}}$ ( $\text{M}^{2+}$ ) (cal./deg. mole)	$-\Delta S_{\text{hyd}}$ ( $\text{MSO}_4$ ) (cal./deg. mole)	Ref.
$\text{Mg}^{2+} + \text{SO}_4^{2-}$	26.2	63.7	66	6
$\text{Ca}^{2+} + \text{SO}_4^{2-}$	16.1	50.2	62.5	4
$\text{Mn}^{2+} + \text{SO}_4^{2-}$	22.6	61.5	63	7
$\text{Co}^{2+} + \text{SO}_4^{2-}$	16.6	65	71	7
$\text{Ni}^{2+} + \text{SO}_4^{2-}$	21.7	66.5	67	7
$\text{Zn}^{2+} + \text{SO}_4^{2-}$	24.4	64	67	6

It is apparent immediately that  $\Delta S^0$  is not independent of  $\Delta S_{\text{hyd}}(\text{M}^{2+})$  and the second class of behavior suggested by George<sup>2</sup> cannot be substantiated.

(3) D. Singh, *J. Sci. Research Benares Hindu Univ.*, **6**, 131 (1955).

(4) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(5) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(6) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3706 (1958).

(7) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3934 (1959).

DEPARTMENT OF CHEMISTRY  
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GEORGE H. NANCOLLAS  
RECEIVED DECEMBER 15, 1960

#### RARE EARTH STANNATES, $\text{R}_2\text{Sn}_2\text{O}_7$

Sir:

Polycrystalline stannates of general formula  $\text{R}_2\text{Sn}_2\text{O}_7$ , isostructural with pyrochlore, where  $\text{R} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Lu}$ , have been prepared by solid state reaction from intimate mixtures of  $\text{R}_2\text{O}_3$  and  $\text{SnO}_2$ . The details of preparation are the same as given in a recent publication.<sup>1</sup>  $\text{Tb}_2\text{O}_3$  was prepared by heating the commercial oxide mixture in hydrogen at  $680^\circ$  for 2 hours and cooling to room temperature in hydrogen.

X-Ray diffraction investigations were made on powder samples with filtered copper radiation using both film and Geiger diffractometer techniques. Experimental lattice constants, determined as before,<sup>1</sup> are compared with calculated lattice constants in Table I. The latter were obtained from linear equations<sup>1</sup> using the rare earth radii of Templeton and Dauben.<sup>2</sup> All of the lanthanide stannates now have been prepared

(1) C. G. Whinfrey, D. W. Eckart and A. Tauber, *J. Am. Chem. Soc.*, **82**, 2695 (1960).

(2) D. H. Templeton and C. H. Dauben, *ibid.*, **76**, 5237 (1954).

with the exception of the cerium and promethium compounds. The good agreement between experimental and calculated lattice constant sustains the earlier observation of a linear relationship between end-member stannates.

TABLE I

Compound	Lattice constant Exptl.	Å. Calcd.	Calcd. density	Beige color of compound
Tb <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	10.428 ± 0.005	10.430	7.815	Light
Dy <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	10.389 ± .006	10.401	7.988	Dark
Ho <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	10.374 ± .004	10.374	8.080	Light
Tm <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	10.330 ± .003	10.326	8.281	Very light
Lu <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	10.294 ± .004	10.286	8.515	Very light

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RECEIVED DECEMBER 10, 1960

### HYDRIDO COMPLEXES OF IRIDIUM

Sir:

While investigating routes to the lower oxidation states of some transition metals, we have obtained a series of compounds which appear to be hydrido complexes of iridium,  $[\text{IrH}_n\text{X}_{3-n}\text{L}_3]$  ( $n = 1, 2$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{As}$  or  $\text{Ph}_3\text{Sb}$ ). The compounds are prepared simply by heating an iridium salt and ligand with an alcohol (or aqueous alcohol), the mono-hydrido complexes readily being formed also at 25°. The latter are apparently related to those described recently<sup>1,2</sup> since the commencement of the present studies. The new complexes are air-stable, diamagnetic and non-electrolytes, and some of their other properties are summarized in the table.

TABLE I

Compound	Color	M.p., °C. (dec. in vac.)	Infrared spectrum in 2000 cm. <sup>-1</sup> region
$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$	Yellow	256	2200 Deuteride 1580 <sup>a</sup>
$[\text{IrHCl}_2(\text{Ph}_3\text{As})_3]$	Yellow	240	2170
$[\text{IrHCl}_2(\text{Ph}_3\text{Sb})_3]$	Yellow- orange	201	2100
$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]^b$	White	250	2215, 2110 Deuteride 1584, <sup>a</sup> 1515 <sup>a</sup>
$[\text{IrH}_2\text{Br}(\text{Ph}_3\text{P})_3]^b$	White	242	2240, 2090

<sup>a</sup>  $\nu_{\text{Ir-H}}/\nu_{\text{Ir-D}} = 1.39$  to 1.40; calcd., 1.41. <sup>b</sup> Light sensitive.

Evidence for an Ir-H bond is obtained from infrared spectra: deuteration indicates that the sharp bands observed in the 2000 cm.<sup>-1</sup> region are associated with hydrogen vibrations, and their frequency suggests that they derive from  $\nu_{\text{Ir-H}}$ , by analogy with other hydrido complexes of transition metals.<sup>1,2,3</sup>

$[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$  is best prepared (95% yield) from  $(\text{NH}_4)_2\text{IrCl}_6$  and triphenylphosphine (6 moles) in aqueous 2-methoxyethanol at 100°. (Anal. Calcd. for  $\text{IrCl}_2\text{P}_3\text{C}_{64}\text{H}_{46}$ : Ir, 18.3; Cl, 6.7; P, 8.8; C, 61.7; H, 4.4. Found: Ir, 18.5; Cl, 6.5; P, 9.0; C, 61.2; H, 4.3.) The other mono-

(1) J. Chatt and B. L. Shaw, *Chem. and Ind.*, 931 (1960).

(2) J. Lewis, R. S. Nyholm and G. K. N. Reddy, *ibid.*, 1386 (1960).

(3) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960), and references quoted therein.

hydrido complexes given in the table were obtained under similar conditions or from aqueous ethanol or 2-ethoxyethanol. In these solvents at 25°,  $[\text{IrHX}_2\text{L}_3]$  begins to precipitate after a few hours, a yield of 80% being obtained after several days or weeks. Halogen acid also has been detected in these reactions (hydride/acid  $\cong 1/1$ ; cf. ref. 2).

Under more vigorous conditions, by heating  $(\text{NH}_4)_2\text{IrCl}_6$  and triphenylphosphine (10-16 moles) in ethylene glycol to 190°,  $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$  is formed in 87% yield. (Anal. Calcd. for  $\text{IrClP}_3\text{C}_{64}\text{H}_{47}$ : Ir, 18.9; Cl, 3.5; P, 9.1; C, 63.8; H, 4.7; mol. wt., 1017. Found: Ir, 18.6; Cl, 3.3; P, 9.0; C, 64.3; H, 4.8; mol. wt. in  $\text{CHCl}_3$ , 997.) The corresponding bromide is obtained under identical conditions. (Anal. Calcd. for  $\text{IrBrP}_3\text{C}_{64}\text{H}_{47}$ : Ir, 18.1; Br, 7.5; P, 8.8; C, 61.1; H, 4.5; mol. wt., 1061. Found: Ir, 18.6; Br, 7.6; P, 8.7; C, 61.4; H, 4.4; mol. wt. in  $\text{CHCl}_3$ , 1158.) These compounds represent the first dihydrido complexes of iridium, and probably of any metal synthesized under these simple conditions. The dideuterio complex was prepared by refluxing a suspension of  $[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$  in  $\text{C}_2\text{H}_5\text{OD}$  for 10 days.

$[\text{IrH}_2\text{Cl}(\text{Ph}_3\text{P})_3]$  reacts slowly with HCl (in ether) to give  $[\text{IrHCl}_2(\text{Ph}_3\text{P})_3]$ , but the latter is remarkably resistant to acid at 30°. With excess chlorine (in  $\text{CHCl}_3$ ), the dihydride is oxidized to  $[\text{IrCl}_4(\text{Ph}_3\text{P})_2]$ . Other isomers of each of the hydrides have been found and are being studied.

Experiments are continuing to investigate the role of the solvent in some of these unusual reactions and to examine the reactions and structures of the products. Dr. R. G. Hayter, to whom the author is indebted for valuable suggestions and discussions, has carried out further reductions of some of these compounds with  $\text{LiAlH}_4$  and  $\text{LiAlD}_4$ , and these will be reported later.

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I. VASKA

RECEIVED DECEMBER 12, 1960

### 17 $\alpha$ ,21-ISOPROPYLIDENEDIOXY STEROIDS

Sir:

This communication describes the preparation and use of a new protective group for the labile dihydroxyacetone side chain of the corticosteroids. It has been found that cyclic ketal formation occurs readily between the 17 $\alpha$ ,21-diol grouping of the cortical side chain and 2,2-dimethoxypropane in an acid catalyzed exchange reaction to give 17 $\alpha$ ,21-isopropylidenedioxypregnanes in good yields. A solution of 2 g. of prednisolone in 4 ml. of dimethylformamide and 15 ml. of 2,2-dimethoxypropane with 10 mg. of *p*-toluenesulfonic acid was heated for 6 hours to give 1.1 g. of 17 $\alpha$ ,21-isopropylidenedioxy-1,4-pregnadiene-3,20-dione-11 $\beta$ -ol (I),<sup>1</sup> m.p. 243-247°,  $[\alpha]_D +106^\circ$ . Other corticoid derivatives prepared had these constants: 17 $\alpha$ ,21-iso-

(1) Satisfactory analyses have been obtained for all new compounds herein described. Ultraviolet absorption spectra are in 95% ethanol. Rotations are in chloroform and melting points are uncorrected. The isopropylidenedioxy derivatives display a characteristic infrared absorption band at 7.25 $\mu$  (chloroform).