flections are only accidentally indexable on the basis of the large face centered cubic cell and do not in fact belong to the pattern of $Ce_2O_3 \cdot 2ZrO_2$.

Attempts were made to vary the composition of the phase but these were unsuccessful, as indicated by the constancy of the lattice parameter. It therefore appears likely that the phase represents a preferred structure. This is in harmony with the results of Trombe and Foex[11] on the zirconia-lanthanum oxide system. These authors found a preferred structure at the composition represented by $La_2O_3 \cdot 2ZrO_2$, for which they reported a lattice parameter of 5.39 Å. In the present work, a sample of $La_2O_3 \cdot 2ZrO_2$ was prepared by the same method as was used for $Ce_2O_3 \cdot 2ZrO_2$, and a lattice parameter of 10.8022 ± 0.0005 Å. was found. The doubling of the cell edge was again made necessary because of the presence of a few very weak lines.

It is interesting that the oxidized phase ($CeO_2 \cdot ZrO_2$) was produced at a temperature at which Duwez and Odell[6] found instability for those solid solutions with less than 90 mole % cerium(IV) oxide, their preparations having been carried out at 2000° with subsequent aging at lower temperatures. The results described here do not contradict theirs, for extended stability studies at high temperatures were not carried out. The results do indicate the interesting fact that a cubic solid solution of the composition $CeO_2 \cdot ZrO_2$ was prepared indirectly at 1000°, whereas the work of Duwez and Odell indicates that it could not have been prepared directly from the oxides at this temperature.

The tetragonal and monoclinic phases underwent no detectable contraction on oxidation, and it was, therefore, concluded that these phases contained little cerium. Both phases may be explained as being ZrO_2 which has only incompletely reverted from its high temperature tetragonal modification to its room temperature monoclinic form. The lattice parameters calculated for the tetragonal phase are $a = 5.08 \pm 0.01$ and $c = 5.19 \pm 0.01$ Å. Accepted values[6] for tetragonal ZrO_2 are $a = 5.084$ and $c = 5.170$ Å. The data for the monoclinic phase were not adequate for lattice parameter calculations.

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The Association of Some Diaryl-2-thienylmethyls

BY TING LI CHU AND THEODORE J. WEISMANN

The association of triarylmethyls in solution has been studied extensively by magnetic, spectrophotometric and oxygen absorption methods. However, their heterocyclic analogs, in which one or more aryl groups of a triarylmethyl are replaced by heterocyclic groups, have received only scanty

attention. Minnis[1] first reported the reaction between diphenyl-2-thienylchloromethane with molecular silver in benzene solution and claimed that the red color developed was due to the formation of the diphenyl-2-thienylmethyl free radical. In view of the lack of quantitative equilibrium data concerning this radical and its dimer, we have determined its magnetic susceptibility at room temperature by the Gouy method. The apparatus used, including a discussion of the calibration of the sample tube, has already been described.[2]

The reduction of diphenyl-2-thienylchloromethane was carried out on the vacuum bench by a method similar to that used by Lewis, Lipkin and Magel[3] for the preparation of the triarylmethyls. A weighed amount of diphenyl-2-thienylchloromethane, prepared by the method of Minnis[1] and dried thoroughly under vacuum, m.p. 81°, was introduced into the reduction vessel and the latter attached to the vacuum line. A measured volume of benzene and a trace of triethylamine, both dried over sodium–potassium alloy, were distilled into the reduction vessel; the halide dissolved readily forming a colorless solution. Silver amalgam was introduced into the vessel by a vacuum dumper and the vessel sealed-off under vacuum. On shaking the solution with silver amalgam, it gradually turned red. After sufficient shaking, the solution was filtered through a fritted glass disc into the calibrated sample tube which was connected to the side arm of the reduction vessel, and the sample tube sealed off. The apparent change in weight of the sample on application of the magnetic field, Δw, was measured immediately after the preparation as a precaution against decomposition. Corrections for the diamagnetic contributions to the measured susceptibility were approximated by admitting air to the solution and repeating the measurement of Δw. However, the color of the solution did not change in air nor was there any measurable change in Δw, indicating that the reaction product formed upon the reduction of diphenyl-2-thienylchloromethane with silver amalgam was diamagnetic. The solution, after magnetic measurements, was allowed to stand overnight; a light pink precipitate separated and was recrystallized to yield white crystals of m.p. 114°. This compound was shown to be 1,1,2,2-tetraphenyl-1,2-di-2-thienylethane from its chemical behavior and elementary analysis.[4] Thus the reduction of diphenyl-2-thienylchloromethane gave the stable diamagnetic hexasubstituted ethane.

The reduction of diphenyl-2-thienylchloromethane was also carried out in a dilute solution and its absorption spectrum in the visible region measured on a Beckman spectrophotometer. This spectrum appeared to be almost identical with that of the red diphenyl-2-thienylmethyl cation solution prepared by dissolving the halide in phosphorus oxychloride. Apparently, the diphenyl-2-thienylmethyl cation was formed during the reduction of the halide with silver amalgam. It is very

(1) W. Minnis, THIS JOURNAL, 51, 2143 (1929).
(2) T. L. Chu and S. C. Yu, ibid., 76, 3367 (1954).
(3) G. N. Lewis, D. Lipkin and T. T. Magel, ibid., 66, 1579 (1944).
(4) Calcd. for $C_{34}H_{26}S_2$: C, 81.89; H, 5.25; S, 12.86. Found: C, 82.13; H, 5.41; S, 12.53.

unlikely that ionic dissociation of the ethane would take place in a solvent of low dielectric constant such as benzene. However, diphenyl-2-thienyl-chloromethane appears to be much less stable than triphenylchloromethane. Probably, the ionic dissociation of diphenyl-2-thienylchloromethane is catalyzed by the presence of silver amalgam. Minnis apparently was misled by the ease of formation of this cation and arrived at the erratic conclusion that diphenyl-2-thienylmethyl was responsible for the red color of the solution.

In the present investigation, phenyl-α-naphthyl-2-thienylchloromethane also was synthesized. Its reduction with silver amalgam in benzene also gave a red solution which was diamagnetic; white crystals of 1,2-diphenyl-1,2-di-α-naphthyl-1,2-di-2-thienylethane, m.p. 140°, were isolated from this solution in almost quantitative yield.

As a conclusion, no evidence of paramagnetism was found during the reduction of diphenyl-2-thienylchloromethane or phenyl-α-naphthyl-2-thienylchloromethane with silver amalgam in benzene solution. The diamagnetic hexasubstituted ethanes which were isolated showed no tendency to dissociate in solution.

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Aluminum Suboxide Formed in Reaction of Aluminum with Alumina

BY C. NORMAN COCHRAN

The existence of an aluminum suboxide has been proposed by many early workers.[1] More recently the volatility of alumina in the presence of aluminum was attributed by Zintl and co-workers[2,3] to the formation of gaseous AlO. Grube, Schneider Esch and Flad[4] determined from the distillate composition that silicon reacted with alumina at 1800° to form Al_2O along with SiO. Brewer and Searcy[5] reasoned that gaseous Al_2O is formed when alumina is heated with a reducing agent whereas gaseous AlO and atomic oxygen are the principal products when alumina is heated alone. The bands in the blue and green regions of the spectrum from an aluminum discharge in air were ascribed to AlO by Mulliken.[6] Baur and Brunner[7] ascribed a lowering of the melting point of alumina mixed with aluminum to Al_8O_9. Beletskii and Rapoport[8]

(1) Gmelin, "Handbuch der anorganischen Chemie, Aluminum," Teil B. Berlin, 1934, p. 4.

(2) E. Zintl. W. Krings and W. Brauning, German Patent 742,330 (October 14, 1943).

(3) E. Zintl, W. Morawietz and E. Gastinger, Z. anorg. Chem., 245, 8 (1940).

(4) G. Grube, A. Schneider, U. Esch and M. Flad, ibid., 260, 120 (1949).

(5) L. Brewer and A. W. Searcy, THIS JOURNAL, 73, 5308 (1951).

(6) R. S. Mulliken, Phys. Rev., 26, 561 (1925).

(7) E. Baur and R. Brunner. Z. Elektrochem., 40, 154 (1934).

(8) M. S. Beletskii and M. B. Rapoport, Doklady Akad. Nauk SSSR. 80, 751 (1951).

on heating a pelleted mixture of aluminum and alumina above 1800° under 1 mm. pressure obtained coarse crystals which were thought to be Al_2O. Using a high temperature X-ray technique Hoch and Johnston[9] reported solid Al_2O between 1100 and 1500°, solid Al_2O and AlO between 1500 and 1600° and solid AlO above 1600°.

Weight Loss Experiments.—About 0.3 g. of 99.99% aluminum in a tantalum carbide-lined tantalum boat was covered with a 1-g. loose fitting lid of pure sintered alumina, with no contact between the aluminum and alumina. The boats were held in a 12" long, 1" o.d. graphite tube centered in a 1.5" i.d. graphite susceptor heated by a 10" long induction coil. Overlapping tantalum sheets lined the inside of the graphite tube through the reaction zone. The susceptor was insulated from an outer Pyrex envelope by a $1/2$" thick layer of outgassed lampblack. The boats and contents were held at temperature for at least 15 minutes. Temperature readings with a Leeds and Northrup optical pyrometer sighted on the boat were corrected for window absorption but not for lack of black body conditions.

In four runs at 1700–1500° and with total pressures less

TABLE I

ALUMINA–ALUMINUM WEIGHT LOSS

Alumina-covered tantalum carbide boat containing aluminum, tantalum shielded graphite charge tube

°C.	Residual pressure, mm.	G. loss		Al:O atomic ratio	
		Al_2O_3	Al	Exp.	Calcd.[a]
1700	1	0.09	0.18	3.0	2.2
1690	1	.11	.19	2.8	2.2
1650	1	.08	.15	3.0	2.2
1500	1	.07	.13	3.1	2.3
1510	0.4	.12	.17	2.4	2.3
1700	10^b	.20	.24	2.2	2.2

[a] Aluminum at its vapor pressure reacting with alumina to form Al_2O, data of Brewer and Searcy. [b] Pressure of added argon.

than 1 mm. the weight losses corresponded to aluminum to oxygen atomic ratios of 2.8 to 3.1. To further increase the equilibrium between the aluminum vapor and the alumina, sintered alumina 100 to 250 mesh was heaped over the aluminum for the fifth and sixth of these runs. About three quarters of the alumina weight loss was from the powder over the aluminum, the balance was from the alumina lid. The atomic ratios for the volatile products in these runs approach Al_2O. The aluminum to oxygen atomic ratios for the volatile reduction products were calculated from Brewer and Searcy[5] for the equation

$$4Al(v) + Al_2O_3(s) \longrightarrow 3Al_2O(v)$$
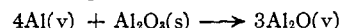
These are listed in the table for comparison with the experimental values.

Spectroscopic Investigations.—The emission spectra from aluminum arcs in nitrogen, argon and oxygen atmospheres were compared using a quartz prism Gaertner spectrograph. In the range from 2700 to 8700 Å. no extra bands were found in the oxygen atmosphere that had not been previously ascribed to AlO.

The absorption spectrum of the vapors from the alumina-aluminum reaction was investigated with a Cenco replica grating spectrograph, Catalog No. 87102, from 3400 to 7500 Å. and with a Model DU Beckman spectrophotometer from 2800 to 3400 Å. Charges consisted of two $3/8$" diameter pellets made from a mixture of calcined alumina and atomized aluminum. The pellets were heated at temperatures up to 2200° in tantalum carbide boats in the same induction heated system as used for the weight loss experiments. A continuum was projected through quartz windows at both ends of the 5 ft. long Pyrex envelope which enclosed the susceptor. Argon at 1 atmosphere pressure flowed slowly through the envelope during measurements.

The characteristic absorption lines of trace elements, aluminum vapor and aluminum hydride were noted. The spectrum of AlO was not noted nor any unidentified spectrum.

(9) M. Hoch and H. L. Johnston, THIS JOURNAL, 76, 2560 (1954).