

sugar and the base would be sufficient. In the case of an ionic base such as tetramethylammonium benzoate the functions of base and electrolyte are combined and a simple second-order process results.

Implicit in the foregoing attempts to interpret the kinetics of these reactions is an assumption that ionic products or intermediates are difficult to form in inert solvents unless all charge transfers are balanced within the active complex itself. However, this conclusion is based only on reactions involving the cleavage of a carbon-oxygen bond in the solvents pyridine and nitromethane. The electrolyte effects are particularly marked in these cases but may in fact be merely an extreme example of a much more general phenomenon. For example, in the reaction of chloroacetate with thiosulfate ions in very dilute aqueous solution Kappana<sup>7</sup> observed a slight specific ion catalysis in addition to the normal salt effect. The order of catalytic activity was  $K^+ > NH_4^+ > Na^+ > Li^+ >$  and  $Cl^- > NO_3^- > SO_4^{2-}$  or the opposite of that found in the present work. Since the reaction is a nucleophilic substitution carried out in dilute aqueous solution

(7) A. N. Kappana, *J. Ind. Chem. Soc.*, **5**, 293 (1928).

the electrolyte effect cannot be accounted for in the same way as was done for the mutarotation reaction. In other studies on the same reaction Ciapetta and Tomlinson<sup>8</sup> observed marked specific ion catalysis in propanol-water solution, especially with polyvalent cations; they suggested that the powerful catalytic activity of the  $La^{+3}$  ion was due to the clustering around it of the reactant ions. Scattered through the literature<sup>9</sup> are other examples of what appear to be specific ion effects but in most cases they are small and cannot be distinguished from normal salt effects. However, if these specific ion effects are in fact fairly general with respect to both solvent and reaction type, then they are probably of a physical rather than chemical nature and the above attempt to assign the ions a specific function within the active complex is not justified.

OTTAWA, CANADA

(8) F. G. Ciapetta and H. M. Tomlinson, *J. Phys. Colloid Chem.*, **55**, 429 (1951).

(9) R. C. Anderson, G. W. Watt, *et al.*, *THIS JOURNAL*, **66**, 376 (1944); **67**, 2269 (1945); L. F. Audrieth, L. D. Scott and O. F. Hill, *ibid.*, **64**, 2498 (1942); F. A. Long, W. F. McDevit and F. B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813, 829 (1951); R. M. Schramm, W. Klapproth and F. H. Westheimer, *ibid.*, **55**, 843 (1951); L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).

## NOTES

### Formation of $Ce_2O_3 \cdot 2ZrO_2$ in the System $BaCl_2$ - $CeCl_3$ - $BaZrO_3$ <sup>1</sup>

By J. J. CASEY, LEWIS KATZ AND WILLIAM C. ORR

RECEIVED DECEMBER 13, 1954

The work reported in this paper has evolved from a study of ion distributions in solid-melt systems at high temperatures (about 1000°) in which the system principally studied has been  $BaCl_2$ - $CeCl_3$ - $BaZrO_3$ . Radiotracer experiments in which cerium ranged in concentration from 10<sup>-13</sup> to 18.7 atom % of the cerium-zirconium content showed that essentially none of the cerium remained in the molten phase. At low cerium content (Ce:Zr atom ratio = 0.01 to 0.053) some of the barium ions in barium zirconium oxide are replaced by cerium(III) ions. As the cerium content of the system is increased the principal reaction becomes one resulting in the formation of the phase  $Ce_2O_3 \cdot 2ZrO_2$ . This is rapidly oxidized in air at elevated temperatures to  $CeO_2 \cdot ZrO_2$ .

Because recent interest in the solid solutions of zirconia with other metal oxides has been wide-

spread,<sup>2-11</sup> arising in part from the desirability of obtaining systems in which the polymorphic inversion of zirconia from the high temperature tetragonal to the low temperature monoclinic form is suppressed, it was felt that the reaction described above merited further study.

#### Experimental

**Materials.**—Barium zirconium oxide was prepared by the solid state reaction of reagent grade zirconia and barium carbonate at 1300°. Barium carbonate was present in slight excess, and the excess barium oxide was leached from the product with acetic acid.

Cerium(III) chloride solution was prepared by reduction of cerium(IV) sulfate with hydrochloric acid in water solution. Cerium(III) hydroxide was precipitated, washed and redissolved in hydrochloric acid as many times as were necessary to remove all traces of sulfate ion.

(2) A. Dietzel and H. Tober, *Ber. deut. keram. Ges.*, **30**, No. 4, 71 (1953).

(3) J. Pierrey, *Ann. Chim.*, [12] **4**, 133 (1949).

(4) H. v. Wartenburg and W. Gurr, *Z. anorg. allgem. Chem.*, **196**, 374 (1931).

(5) A. Gambey and G. Chaudron, 14me Congr. chim. ind. Paris Oct., 1934, 5 pp.

(6) P. Duwez and F. Odell, *J. Am. Cer. Soc.*, **33**, 274 (1950).

(7) R. Schenck and H. Roters, *Z. anorg. allgem. Chem.*, **211**, 65 (1933).

(8) G. Braver and H. Gradinger, *Naturwiss.*, **38**, 559 (1951).

(9) P. Duwez, H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, **98**, 356 (1951).

(10) F. Hund, *Z. Elektrochem.*, **55**, 363 (1951).

(11) P. Trombe and M. Foex, *Compt. rend.*, **233**, 254 (1951).

(1) Based upon a dissertation submitted by J. J. Casey to the Graduate School of the University of Connecticut in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was carried out under Contract No. AT(30-1)-1154 between the Atomic Energy Commission and the University of Connecticut.

**Procedure.**—To prepare mixtures containing any desired ratio of cerium to zirconium the following method was used. The desired amount of barium chloride (usually about 2.9 g.) was weighed into a porcelain crucible and the appropriate volume of a standard solution of cerium(III) chloride was added. The mixture was kept in an atmosphere of dry hydrogen chloride during evaporation and dehydration at 125–130°. It was vacuum dried for one hour at the elevated temperature and cooled under vacuum. The barium zirconium oxide (usually about 0.300 g.) was added, and the thoroughly mixed sample was transferred to a covered platinum test-tube which was then sealed under vacuum in a fused silica capsule.

The capsule was placed in a furnace at 1000°, and reaction was allowed to take place for a minimum of 18 hours. The sample was then removed from the furnace and reached room temperature within one-half hour. The product was removed from the test-tube and finely ground in a cool agate mortar. It was then leached free of barium chloride with cold water. The residue was freed of water by washing several times with acetone and was dried in a vacuum desiccator. X-Ray data were obtained for the residues so prepared and also for residues that were oxidized for several hours at 1000°.

X-Ray powder photographs were taken with Picker cameras of radius 35 and 107 mm. and copper K- $\alpha$  radiation. The films for the calculations were from the large camera and were corrected for shrinkage.

### Results

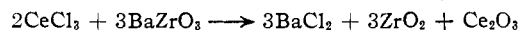
With increasing value of the ratio Ce:Zr, gradual disappearance of the cubic perovskite pattern of barium zirconium oxide was noted. At the same time there appeared new lines which could be attributed to the sum of patterns from a face-centered cubic phase, a tetragonal phase, and a monoclinic phase. Table I shows this gradual change.

TABLE I

VARIATION IN X-RAY PATTERNS WITH INCREASING CERIUM CONTENT

Atom ratio Ce:Zr	BaZrO <sub>3</sub>	F. C. C.	Tetrag.	Mono.
0.026	vs	None	None	None
.064	vs	vvw	None	vvw
.122	vs	m	vw	vw
.202	s	m	w	w
.430	m	s	w	w
.501	w	s	w	m
.636	vw	vs	w <sup>+</sup>	m
.667	None	vs	w <sup>+</sup>	m

Only after the Ce:Zr atom ratio had surpassed 0.667 was any Ce(III) ion found in the solidified molten phase. This fact, and the X-ray data, indicated that the reaction was essentially



but that the oxide products were present in more than one phase. Further support for the postulated reaction was obtained from tracer experiments using radiobarium. These showed that residues from runs in which the Ce:Zr atom ratio was 0.667 contained less than 1.4% Ba.

Lattice parameters for the face-centered cubic phase were calculated from the X-ray data for several of the residues obtained from samples of different Ce:Zr ratios. They were the same within the limits of experimental error. The lattice parameter was originally determined to be about 5.35 Å., but the presence of certain weak lines required a doubling of the cell edge, which was calculated to be

10.699 Å. with an estimated error of  $\pm 0.005$  Å. The low precision was the result of the very diffuse character of the lines in the back reflection region, where there was no resolution into doublets, even in the case of annealed samples. The lines from a typical residue indexable on a face-centered cell are presented in Table II.

TABLE II

LINES INDEXABLE ON F. C. C. CELL, UNOXIDIZED RESIDUE  
 $N = h^2 + k^2 + l^2$ ;  $d$  = interplanar spacing in ångström units;  $I$  = intensity;  $a$  = cell edge in ångström units

$N$	$d$	$I$	$a$	$N$	$d$	$I$	$a$
11	3.217	vvw	10.670	59	1.3894	w	10.672
12	3.078	vs	10.663	64	1.3363	w	10.690
16	2.665	s	10.660	67	1.3028	vvw	10.663
19	2.451	vw	10.684	76	1.2262	m	10.670
20	2.375	vvw	10.622	80	1.1955	iii	10.693
24	2.186	vvw	10.710	96	1.0914	m	10.694
27	2.054	vw	10.673	108	1.0281	m	10.684
32	1.8888	vs	10.685	128	0.9453	vvw	10.695
35	1.8022	vvw	10.662	132	.9320	vw	10.708
40	1.6949	vvw	10.720	140	.9037	m	10.693
44	1.6113	vs	10.688	144	.8913	m	10.696
48	1.5422	m	10.685	160	.8457	m	10.697
51	1.4978	vvw	10.696	172	.8160	iii	10.702
52	1.4790	vvw	10.665	176	.8043	iii	10.670
56	1.4237	w	10.654				

TABLE III

LINES INDEXABLE ON F. C. C. CELL, OXIDIZED RESIDUE

$N$	$d$	$I$	$a$	$N$	$d$	$I$	$a$
3	3.037	vs	5.260	24	1.0758	iii	5.270
4	2.630	s	5.260	27	1.0135	m	5.266
8	1.8631	vs	5.270	32	0.9319	m	5.272
11	1.5886	s	5.269	35	.8910	s	5.271
12	1.5210	m	5.269	36	.8787	m	5.272
16	1.3154	m	5.262	40	.8327	m	5.266
19	1.2093	s	5.271	43	.8036	m	5.267
20	1.1788	m	5.272	44	.7941	m	5.268

By comparison with the work of Duwez and Odell it was concluded that the face-centered cubic phase in the oxidized residue was a solid solution of cerium(IV) oxide and zirconium(IV) oxide of approximately 50 mole % composition. This means that the face-centered cubic phase in the unoxidized residue must have the approximate composition  $\text{Ce}_2\text{O}_3 \cdot 2\text{ZrO}_2$ . The X-ray data for this phase resemble quite closely those for  $\text{Cd}_2\text{Ta}_2\text{O}_7$ ,<sup>12</sup> which has the pyrochlore structure, and would indicate that  $\text{Ce}_2\text{O}_3 \cdot 2\text{ZrO}_2$  also has a structure of this type. In  $\text{Cd}_2\text{Ta}_2\text{O}_7$ , each cadmium ion is surrounded by eight oxygens at the corners of a distorted cube and each tantalum ion is surrounded by six oxygens at the corners of an octahedron. If the phase  $\text{Ce}_2\text{O}_3 \cdot 2\text{ZrO}_2$  does possess the pyrochlore structure, we should expect the smaller zirconium atoms to be the cations octahedrally coordinated by oxygens.

Two of the reflections listed in Table II ( $N = 20$  and  $N = 52$ ) are incompatible with the space group of pyrochlore,  $O_h^1\text{-Fd}3m$ , and a third reflection ( $N = 132$ ) is incompatible with the pyrochlore arrangement of atoms. However, it is highly probable that these three very weak re-

(12) A. Bystrom, *Arkiv. Kemi Min. Geol.*, **18A**, no. 21 (1945).

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<sup>11</sup> 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  $10.8022 \pm 0.0005$  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<sup>6</sup> 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<sup>6</sup> 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.

**Acknowledgment.**—The authors wish to acknowledge the very generous interest of Dr. Roland Ward and the many fruitful suggestions he made during the course of the investigation.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CONNECTICUT  
STORRS, CONNECTICUT

### The Association of Some Diaryl-2-thienylmethyls

BY TING LI CHU AND THEODORE J. WEISMANN

RECEIVED NOVEMBER 11, 1954

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<sup>1</sup> 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.<sup>2</sup>

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<sup>3</sup> for the preparation of the triarylmethyls. A weighed amount of diphenyl-2-thienylchloromethane, prepared by the method of Minnis<sup>1</sup> 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,  $\Delta w$ , 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  $\Delta w$ . However, the color of the solution did not change in air nor was there any measurable change in  $\Delta w$ , 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.<sup>4</sup> 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  $C_{24}H_{20}S_2$ : C, 81.89; H, 5.25; S, 12.86. Found: C, 82.13; H, 5.41; S, 12.53.