Evidence of a Crystalline Phase Transition of Decacarbonyldirhenium

By **P. Lemoine, M. Gross,*** and **J. Boissier,** Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide et Département Science des Matériaux, E.N.S.C.S., Université Louis Pasteur, Strasbourg, France

The thermal behaviour of decacarbonyldirhenium has been investigated. A reversible crystalline phase transition appears at 92 °C in all atmospheres studied: nitrogen, air, argon, and oxygen. A Debye–Scherrer *X*-ray diffraction diagram of the new crystalline phase is submitted, and an interpretation of the transition is suggested.

Two studies dealt with the thermal properties of decacarbonyldirhenium.[1,2] According to Ginzburg[1] the differential thermal analysis curve, most probably drawn in an inert atmosphere, shows two breaks, the first at *ca.* 91 °C and the second at *ca.* 158 °C. The low-temperature transition (90·2—91·8 °C) could not be related to any transformation, whereas the high-temperature transition (155—161 °C) was identified as fusion of decacarbonyldirhenium. Segel and Anderson[2] investigated the quadrupolar coupling of the two rhenium isotopes, ^{185}Re and ^{187}Re, in decacarbonyldirhenium as a function of temperature and stated the existence of a solid-state phase transition at 92 °C, but no interpretation was suggested. We have now used thermogravimetric analysis, d.t.a., and *X*-ray powder data.

EXPERIMENTAL

Decacarbonyldirhenium was a resublimed Alfa Inorganics product. Its purity was checked by i.r. spectroscopy.[3-5]

RESULTS

Differential Thermal Analysis.—When an inert atmosphere (nitrogen or argon) is used, the d.t.a. curve shows breaks at 92 °C, where the transformation takes place without any observable loss of weight, and at 170 ± 10 °C. The weight-loss curve shows a slow loss of weight from 100 °C on, increasing with temperature. We agree[1] that the second peak is due to fusion. Both peaks are endothermic. Our object was only to investigate the transformation at *ca.* 92 °C, so we drew d.t.a. curves up to 100 °C, using alumina as a reference compound, and at 100 °C we reversed the heating programme to drop to ambient temperature (20 °C). We then noticed at *ca.* 60 °C an exothermic peak. An *X*-ray diffraction analysis at 25 °C shows that heated and then cooled decacarbonyldirhenium has the same structure as at the beginning of the experiment, so the transformation is reversible.

X-*Ray Diffraction.*—We tried to discover whether the endothermic transformation at 92 °C corresponds to a change in the crystalline structure of decacarbonyldirhenium by recording the *X*-ray diffraction diagram of the product at various temperatures (Plate) on a Guinier–Lenne–Nonius camera. Part 1 of the diffraction exposure shows the diffraction diagram of decacarbonyldirhenium at ambient temperature before heating. Part 2 was recorded over 30 h on heating the specimen from ambient temperature to 90 °C. In this part the film was moving at a speed of 5 mm h^{-1}. The instantaneous height of the diagram is 3 mm corresponding to the width of the opening for the diffracted *X*-rays. Part 3 corresponds to the highest temperature reached, 95 °C, the film remaining motionless. Part 4 represents the Debye–Scherrer diagram of the specimen cooled to ambient temperature, and Part 5 shows the diagram of the aluminium leaves used as support, without any decacarbonyldirhenium.

Interplanar spacing of decacarbonyldirhenium for various temperatures (Fe-K_α radiation; 1 degree of angle = 4 mm)

20 °C					75 °C		From 20 °C to 75 °C	95 °C	
d/Å	*I*	*h*	*k*	*l*	*d*/Å	*I*	Δ*d*/Å	*d*/Å	*I*
7·14	s	0	0	2	7·17	s	+0·03		
7·05	s	2	0	0	7·05	s	0		
6·36	vs	1	1	0	6·39	vs	+0·03	6·84	vs
5·88	vs	2	0	$\bar{2}$	5·90	vs	+0·02	5·94	vs
5·06	vs	2	1	$\bar{1}$	5·10	vs	+0·04	4·19	m
4·45	m	2	0	2	4·45	m	0	3·58	vw
3·92	w	3	1	0	3·94	w	+0·02	3·51	vw
3·82	m	3	1	$\bar{2}$	3·84	m	+0·02		
3·61	m	2	0	$\bar{4}$	3·63	m	+0·02		
3·57	m	0	2	0	3·60	m	+0·03		
3·52	m	4	0	0	3·52	m	0		
3·40	w	1	2	$\bar{1}$	3·43	w	+0·03		
3·26	vw	4	1	$\bar{1}$	3·27	vw	+0·01		
3·19	m	2	2	0	3·21	m	+0·02		
3·15	m	3	1	2	3·16	m	+0·01		
3·05	m	2	2	$\bar{2}$	3·07	m	+0·02		
3·00	s	4	1	$\bar{3}$	3·02	s	+0·02		
2·96	vw	4	0	$\bar{4}$	2·98	vw	+0·02		
2·94	w	4	1	1	2·95	w	+0·01		
2·88	m	3	2	$\bar{1}$	2·90	m	+0·02		
2·86	m	4	0	2	2·87	m	+0·01		
2·78	vw	2	2	2	2·80	vw	+0·02		
2·71	w	1	2	3	2·74	w	+0·03		
2·70	w	3	2	1	2·70	w	0		
2·62	w	5	1	0	2·62	w	0		
2·53	w	{4 {0	2 2	$\bar{2}$ 4	2·56	w	+0·03		
(2·50)					2·51	w	+0·01		
2·44	m	{4 {6	1 0	$\bar{5}$ $\bar{2}$	2·44	m	0		
2·38	s	{0 {4	0 1	6 3	2·39	s	+0·01		
2·28	m				2·30	m	+0·02		
2·27	vw				2·29	vw	+0·02		
2·25	w	(2	3	$\bar{1}$)	2·28	w	+0·03		
2·23	w	(4	2	2)	2·24	w	+0·01		
2·15	w				2·16	w	+0·01		
2·04	m				2·05	m	+0·01		

The powder diagram of decacarbonyldirhenium at ambient temperature was used to assign indices, the cell constants being[6,7] $a_0 = 14{\cdot}70$, $b_0 = 7{\cdot}15$, $c_0 = 14{\cdot}91$ Å, $\beta = 106°$, and the space group $I^{2}_{a}(C^{6}_{2h})$ leading to an absence

---

[1] A. A. Ginzburg, *Zhur. priklad Khim.*, 1961, **34**, 2569.

[2] S. L. Segel and L. A. Anderson, *J. Chem. Phys.*, 1968, **49**, 1407.

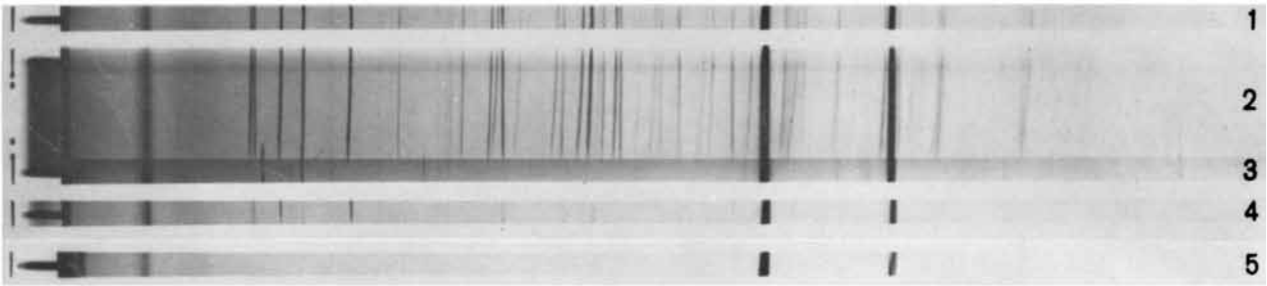
[3] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 2953.

[4] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1964, **3**, 1123.

[5] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 1329.

[6] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

[7] L.F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.

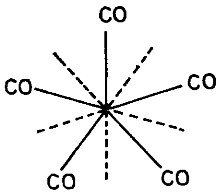

1
2
3
4
5

of hkl reflections when $h + k + l = 2n + 1$ and $h0l$ when $h = 2n + 1$. There is some doubt as to the indices to be given to the lines corresponding to $d_{hkl} < 2{\cdot}53$. Their rather weak intensity does not allow great precision.

From 92 °C upwards we get a new diagram of five lines, the interplanar spacings of which are given in the Table. A new structure appears, which was revealed by the thermal phenomenon and could be observed on the d.t.a. curves at 92 °C. Among the five new lines only one seems to be a prolongation of a line of the previous diagram: the strong line corresponding to plane $(20\bar{2})$ ($d_{hkl} = 5{\cdot}88$ Å at 20 °C). It might be the result of a coincidence. Finally, after cooling, the X-ray diagram is identical to that at the outset, which shows again the reversibility of the phenomenon.

DISCUSSION

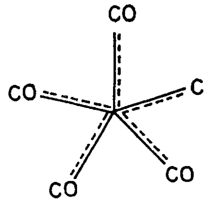
According to Dahl and Rundle[7] decacarbonyldirhenium and decacarbonyldimanganese are among the first polynuclear metal carbonyls known to be linked only by a direct metal–metal bond. Further, it has been established[6,7] that the five carbonyls linked to a metal atom are in a staggered position in relation to the five other carbonyls linked to the other metal atom [structure (I)]. It is possible that the signalled structure change is the result of a rotation round a metal–metal axis, to set the carbonyls in an opposed position (II). In such an assumption, the change from staggered to opposed form would bring about an increase of symmetry, and so reduce the number of lines on the new powder diagram. Some planes (*e.g.*, plane $20\bar{2}$) might not be affected by the change in structure.



staggered form

(I)

Temperature 20 °C



opposed form

(II)

Temperature >92 °C

We conclude that as temperature increases from 20 to 90 °C the crystalline structure of decacarbonyldirhenium changes gradually, the change being in certain interplanar spacings. A new structure appears at *ca.* 92 °C, which explains the presence of a reversible endothermic d.t.a. peak. The change in structure may be due to a transition from a staggered to an opposed form.

[1/2037 *Received, 7th February,* 1972]