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PHASE TRANSITION IN SOLID $MnRe(CO)_{10}$

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Summary

X-ray diffraction measurements show that solid $MnRe(CO)_{10}$ exhibits a reversible structural change at 343 ± 1 K. The transition enthalpy is determined by differential calorimetry $\Delta H_{343} = 3.23 \pm 0.05$ kcal mol^{-1}. Values of thermodynamic functions relative to the transition are compared with those of the symmetrical compounds $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. In the temperature range 298 to 458-473 K, $PPh_3(CO)_4M—M(CO)_4PPh_3$ (M = Mn or Re) undergoes no phase transition.

Introduction

Two early X-ray and DTA studies on $Mn_2(CO)_{10}$ [1] and $Re_2(CO)_{10}$ [2] have revealed for these metal carbonyls a reversible phase transition in the solid state when heated at 341 K and 361 K respectively, under nitrogen. In contrast, bis(η-cyclopentadienyltricarbonylmolybdenum) undergoes no phase transition in the temperature range 298 to 423 K [1]. By drop-calorimetry, measurements [3] on these two compounds allowed us to obtain the transition enthalpies and entropies, and the thermal capacity increments at constant pressure from 300 to 360 K ($Mn_2(CO)_{10}$) and from 300 to 400 K ($Re_2(CO)_{10}$). In previous publications [1,2] it has been suggested that the observed transition could be due to intramolecular change from a staggered D_{4d} to an eclipsed D_{4h} configuration. In the present work, we extend these studies to the dissymmetrical compound $MnRe(CO)_{10}$ and we compare the results obtained with those for the symmetrical compounds. The experimental techniques were X-ray diffraction (Debye—Scherrer pattern) and differential calorimetry.

Experimental

$MnRe(CO)_{10}$ was synthesized from $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Alfa Inorganics) according to the following known reaction [4-8]:

$NaMn(CO)_5 + BrRe(CO)_5 \rightarrow NaBr + MnRe(CO)_{10}$

Twice sublimed $MnRe(CO)_{10}$ was checked by IR spectroscopy [5,7,8] and microanalysis (calcd.: C, 23.02; Mn, 10.55; Re, 35.72; found: C, 23.21; Mn, 10.63; Re, 34.81%). It has also been carefully verified that no mixture of unreacted nor reoxidized $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ is obtained [4,6]; polarographic (D.C. and pulse polarography) reduction of $MnRe(CO)_{10}$ in dimethylformamide (0.1 *M* tetraethylammonium perchlorate as supporting electrolyte) exhibited one single wave, at $U_{1/2} = -1.38$ V/SCE, whereas in the same conditions $Mn_2(CO)_{10}$ is reduced at $U_{1/2} = -1.03$ V/SCE and $Re_2(CO)_{10}$ at $U_{1/2} = -1.66$ V/SCE. Like the electrochemical reduction of the symmetrical compounds [9] the electrochemical reduction of $MnRe(CO)_{10}$ leads to $[M(CO)_5]^-$ anions according to the following electrochemical reaction:

$MnRe(CO)_{10} + 2\,e \rightarrow [Mn(CO)_5]^- + [Re(CO)_5]^-$

However, these electrochemical reductions being irreversible, the intermediate value of $U_{1/2}$ $MnRe(CO)_{10}$ cannot be used as an argument to confirm or to invalidate the previous mass spectrometric results [10], and the relevant theoretical arguments [11] on the relative bond dissociation energies of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$. The polarographic results are here only useful to show that the compound obtained in the synthesis is not a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. On the other hand, we examined the $[M(CO)_4PPh_3]_2$ (M = Mn, Re). $[Mn(CO)_4PPh_3]_2$ was prepared by photochemically-initiated reaction [12], and checked by IR spectroscopy [12,13], m.p., microanalysis (calcd.: C, 61.53; H, 3.49; found: C, 61.65; H, 3.52%) and pulse polarography ($U_{1/2} = -1.27$ V/SCE). $[Re(CO)_4PPh_3]_2$ was obtained from $Re_2(CO)_{10}$ and triphenylphosphine on refluxing in boiling xylene under experimental conditions described earlier [14]. Microanalysis gave: calcd.: C, 47.1; H, 2.7; found: C, 47.2; H, 2.8%. The IR spectra were in good agreement with those published [14-16] and pulse polarography gave only one reduction wave at $U_{1/2} = -1.9$ V/SCE.

The experimental device to study the temperature dependence of X-ray diffraction patterns has already been described [1,2,17]. To obtain quantitative thermal data, a differential M.C.B. calorimeter [18] was used. The calorimetric cell was filled under pure argon free from oxygen. The results have been obtained with 0.384 g of $MnRe(CO)_{10}$ (M.W. = 521.2 g). All thermal studies (X-ray diffraction and calorimetry) were carried out under inert atmosphere (nitrogen or argon).

Results

X-ray diffraction patterns

On heating $MnRe(CO)_{10}$ under controlled inert atmosphere (N_2) Debye—Scherrer X-ray diffraction patterns exhibit a structural change at 343 ± 1 K.

TABLE 1

DEBYE—SCHERRER X-RAY DIFFRACTION PATTERN OF $MnRe(CO)_{10}$

Patterns obtained at ambient temperature 298 K and after reversible structural change ($T > 343$ K).

$MnRe(CO)_{10}$					$Mn_2(CO)_{10}$		$Re_2(CO)_{10}$	
298 K			$T > 343$ K		298 K		298 K	
d (Å)	*I*	*hkl*	*d* (Å)	*I*	*d* (Å)	*hkl*	*d* (Å)	*hkl*
7.12	100	002	6.81	100	7.08	002	7.14	002
7.01	30	200	5.87	60	6.82	200	7.05	200
6.35	100	110	5.33	10	6.28	110	6.36	110
5.80	80	$20\bar{2}$	4.15	10	5.72	$20\bar{2}$	5.88	$20\bar{2}$
5.05	90	$21\bar{1}$ $11\bar{2}$			5.00	$11\bar{2}$	5.06	$21\bar{1}$
4.38	30	202			4.37	202	4.45	202
3.76	40	310			3.82	310	3.92	310
3.56	40	020			3.54	020	3.57	020

The new pattern obtained above 343 K seems to correspond to a more symmetrical structure, such as in $Mn_2(CO)_{10}$ [1] and $Re_2(CO)_{10}$ [2], with less diffraction lines than the low temperature one. After heating at 348 K, followed by cooling to 298 K, the initial low temperature pattern reappears: the structural change is therefore reversible. Table 1 gives the measured inter-reticular lengths respectively at ambient temperature (298 K) and after the structural change ($T > 343$ K). The relative intensities of the diffraction lines are given.

The inter-reticular planes are indexed by analogy with the lines of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ obtained on the same pattern. $[M(CO)_4PPh_3]_2$ exhibits no structural change in the temperature range studied (see below).

Differential calorimetry

The experimental values of the transition enthalpies for $MnRe(CO)_{10}$ are:

Series 1: $\Delta H_{343} = 3.23$ (kcal mol^{-1})
Series 2: $\Delta H_{343} = 3.22$ (kcal mol^{-1})
Series 3: $\Delta H_{343} = 3.23$ (kcal mol^{-1})

Discussion

The comparative results on $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ are listed in Table 2.

TABLE 2

COMPARISON BETWEEN THERMODYNAMIC TRANSITION FUNCTIONS OF $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ AND $MnRe(CO)_{10}$

	$Mn_2(CO)_{10}$	$Re_2(CO)_{10}$	$MnRe(CO)_{10}$
Temperature (K)	341 ± 1	371 ± 1	343 ± 1
Enthalpy (kcal mol^{-1})	3.5 ± 0.1	3.8 ± 0.1	3.23 ± 0.05
Entropy [a] (cal K^{-1} mol^{-1})	10.3 ± 0.5	10.4 ± 0.5	9.4 ± 0.3

[a] Assuming the transition to be entirely isothermal.

Solid $MnRe(CO)_{10}$ exhibits a reversible phase transition at 343 ± 1 K, a transition temperature very close to that of $Mn_2(CO)_{10}$. The transition enthalpy obtained by differential calorimetry is 3.23 ± 0.05 kcal mol^{-1}. The calculated transition entropy, assuming the process to be isothermal, is 9.4 ± 0.3 cal K^{-1} mol^{-1}. The transition enthalpy of the dissymmetrical compound is smaller than the transition enthalpies of the relevant symmetrical compounds. If one assumes that the transition is due to a change of molecular configuration from a staggered D_{4d} form (low temperature) to an eclipsed D_{4h} form (above the transition temperature) (see ref. 19), it is possible to explain this smaller value of ΔH_{343} by the fact that dissymetry allows easier libration in $MnRe(CO)_{10}$ than in $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$. The hypothesis on which the entropy calculations are based prevents us from offering detailed comment.

X-ray diffraction and differential calorimetry measurements on disubstituted similar metal—metal compounds like $PPh_3(CO)_4M—M(CO)_4PPh_3$ (M = Mn, Re) have not so far shown any structural change in the temperature range studied (298-458 K and 298-473 K respectively). In this case the absence of transition may be explained, at first sight, by steric effects due to the large size of the PPh_3 ligands.

Further studies are now in progress to extend these results to linear trimetallic compounds, especially $(CO)_nM—Hg—M(CO)_n$ (M = Mn, Re, Co).

References

1 M. Gross and P. Lemoine, Bull. Soc. Chim. Fr., (1972) 4461.
2 P. Lemoine, M. Gross and J. Boissier, J. Chem. Soc., Dalton Trans., (1972) 1626.
3 P. Lemoine, M. Gross, J. Bousquet, J.M. Letoffe and M. Diot, J. Chem. Thermodyn., in press.
4 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and I.S. Kolomnikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1963) 194.
5 A.N. Nesmeyanov, G.G. Dvoryantseva, Y.N. Sheinker, N.E. Kolobova and K.N. Anisimov, Dokl. Akad. Nauk SSSR, (1966) 169, 843.
6 S.A.R. Knox, R.J. Hoxmeier and H.D. Kaesz, Inorg. Chem., 10 (1971) 2636.
7 N. Flitcroft, D.K. Huggins and H.D. Kaesz, Inorg. Chem., 3 (1964) 1123.
8 H.C. Lewis Jr., and B.N. Storhoff, J. Organometal. Chem., 43 (1972) 1.
9 P. Lemoine, A. Giraudeau and M. Gross, Electrochim. Acta, in press.
10 H.J. Svec and G.A. Junk, J. Amer. Chem. Soc., 89 (1967) 2836.
11 I. Wender and P. Pino, Organic Synthesis via Metal Carbonyls, Vol. 1, Interscience, New York, 1968, p. 263.
12 A.G. Osborne and M.H.B. Stiddard, J. Chem. Soc., (1964) 634.
13 W. Hieber and W. Freyer, Chem. Ber., 92 (1959) 1765.
14 M. Freni, D. Giusto and P. Romiti, J. Inorg. Nucl. Chem., 29 (1967) 761.
15 P.W. Jolly and F.G.A. Stone, J. Chem. Soc., (1965) 5259.
16 F. Nyman, Chem. Ind. (London), (1965) 604.
17 P. Lemoine and M. Gross, J. Therm. Anal., 6 (1974) 159.
18 P. Barbert, C.E.A. Patent EN, 7 019 831, 29 may 1970.
19 F.A. Cotton, Bull. Soc. Chim. Fr., (1974) 2587.