Journal of Organometallic Chemistry, 66 (1974) 149—153

REACTION OF LOW VALENT TRANSITION METAL COMPLEXES AND THEIR PHOSPHINE DERIVATIVES WITH KARL FISCHER REAGENT*

I. BOSNYÁK-ILCSIK, S. PAPP**, L. BENCZE and G. PÁLYI***
Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprém (Hungary)

(Received June 25th, 1973)

Summary

The Karl Fischer reagent reacts with many low valent transition metal complexes to bring about oxidation of the metal. The reaction can be used for the oxidimetric determination of these complexes in solution and must be taken into account when P^{III} ligands are determined in low valent metal complexes.

Introduction

It has been shown recently [1] that phosphorus(III) compounds can be determined selectively in the presence of phosphorus(V) derivatives, using the Karl Fischer reagent [2] as oxidizing agent. Hayton and Smith [1] also showed that R_3PH^+ compounds react with Karl Fischer reagent while R_4P^+ compounds are unreactive. They found that R_3P and R_3PH^+ ligands could be determined even in Co^{II}, Ni^{II} and U^{IV} complexes.

Since this method is simple and rapid, as well as selective for P^{III} in the presence of P^V, it seems to be of great importance in the analysis of transition metal organic and inorganic complexes containing phosphine ligands. Nevertheless the oxidizing action of Karl Fischer reagent suggests the possibility that in lower valent transition metal complexes the metal atom(s) might also be oxidized. The individual components of Karl Fischer reagent (pyridine, SO_2, I_2) are well known [3] to react with low valent transition metal complexes, but one could not reasonably predict how the reagent mixture would behave. The first results of an examination of such reactions are reported below.

(Continued on p. 153)

---

*A preliminary account of this work was presented at the VIIth West Hungarian Analytical Conference, Sept. 1971. Györ., A VII. Dunántúli Anal. Konf. Elöadásainak Kivonatos Gyüjteménye (Ed.: G. Várnai) Györ. 1971, p.74.

**Department of General and Inorganic Chemistry, Veszprem University of Chemical Engineering, Veszprem, Hungary.

***Author to whom correspondence should be addressed.

TABLE 1

COMPARISON OF THE MEASURED AND CALCULATED KARL FISCHER PERCENTAGES

Metal	Oxidation number	Compound	Basis of calculation		KF %	KF %
			No. of P^{III} ligands	Assumed oxidation of the metal or other reaction	calculated	found[a]
Fe	0	$Fe(CO)_5$		$Fe^0 \rightarrow Fe^{II}$	9.03	
				$Fe^0 \rightarrow Fe^{III}$	13.54	8.7 ± 0.5
	0	$Fe_3(CO)_{12}$		$Fe^0 \rightarrow Fe^{II}$	10.70	
				$Fe^0 \rightarrow Fe^{III}$	16.05	11.8 ± 0.9
	II	$Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$		$3H_2O$	16.53	
				$Fe^{II} \rightarrow Fe^{III}$	19.28	17.1 ± 0.6
	II	$Na_3[Fe(CN)_5(PPh_3)] \cdot 3H_2O$	1	$3H_2O$	12.58	
			1	$Fe^{II} \rightarrow Fe^{III}$	14.15	11.9 ± 0.5
	II	$(C_5H_5)_2Fe$		$Fe^{II} \rightarrow Fe^{III}$	4.83	0.0 ± 0.3
Co	−I	$[Co(CO)_4]^-$		$Co^{-I} \rightarrow Co^{II}$	15.76	
				$Co^{-I} \rightarrow Co^{III}$	21.03	15.5 ± 0.4
	0	$Co_2(CO)_8$[b]		$Co^0 \rightarrow Co^{II}$	9.42	
				$Co^0 \rightarrow Co^{III}$	14.12	9.3 ± 0.4
	0	$Co_4(CO)_{12}$		$Co^0 \rightarrow Co^{II}$	12.59	
				$Co^0 \rightarrow Co^{III}$	18.87	12.5 ± 0.4
	−I or 0	$Hg[Co(CO)_4]_2$		$Co^{-I} \rightarrow Co^{II}$	9.93	
				$Co^0 \rightarrow Co^{II}$	6.63	6.2 ± 0.3
	−I or 0	$Hg[Co(CO)_3(PPh_3)]_2$	1	$Co^{-I} \rightarrow Co^{II}$	8.89	
			1	$Co^0 \rightarrow Co^{II}$	7.11	6.7 ± 0.3
	−I or 0	$Co_3(CO)_9CY$ (Y=Cl, Br, I, Ph, i-Pr)		$Co^{-I} \rightarrow Co^{II}$[c]	14.23	For all Y
				$Co^0 \rightarrow Co^{II}$[c]	9.49	0.0 ± 0.3
Ni	0	$Ni(CO)_4$		$Ni^0 \rightarrow Ni^I$	5.26	
				$Ni^0 \rightarrow Ni^{II}$	10.52	10.1 ± 0.5

Re	0	$Rh_4(CO)_{12}$		$Rh^0 \rightarrow Rh^I$	4.81	
				$Rh^0 \rightarrow Rh^{II}$	9.61	
				$Rh^0 \rightarrow Rh^{III}$	14.42	13.6 ± 0.8
	I	$Rh_2(CH_3CH_2COO)_2(CO)_3(PPh_3)$	1		2.57	
			1	$Rh^I \rightarrow Rh^{III}$	7.72	7.6 ± 0.4
	I	$Rh(CH_3CH_2COO)(CO)(PPh_3)_2$	2		4.93	
			2	$Rh^I \rightarrow Rh^{III}$	7.39	6.8 ± 0.5
	I	$RhCl(PPh_3)_3$	3		5.83	
			3	$Rh^I \rightarrow Rh^{III}$	7.77	7.4 ± 0.4
Cr	0	$Cr(CO)_6$		$Cr^0 \rightarrow Cr^I$	4.08	
				$Cr^0 \rightarrow Cr^{II}$	8.16	0.0 ± 0.3
Mo	0	$Mo(CO)_6$		$Mo^0 \rightarrow Mo^I$	3.40	
				$Mo^0 \rightarrow Mo^{II}$	6.81	0.0 ± 0.3
	II	$MoCl_2(CO)_3(PPh_3)_2$	2		4.64	
			2	$Mo^{II} \rightarrow Mo^{IV}$	6.95	
			2	$Mo^{II} \rightarrow Mo^{VI}$	9.27	4.6 ± 0.4[d]
W	0	$W(CO)_6$		$W^0 \rightarrow W^I$	2.55	
				$W^0 \rightarrow W^{II}$	5.11	0.0 ± 0.3
	II	$WCl_2(CO)_3(PPh_3)_2$	2		4.16	
			2	$W^{II} \rightarrow W^{IV}$	6.25	
			2	$W^{II} \rightarrow W^{VI}$	8.33	4.3 ± 0.5[d]
	IV	$WCl_4(Ph_2PCH_2CH_2PPh_2)$	2		4.96	
			2	$W^{IV} \rightarrow W^{VI}$	7.44	5.1 ± 0.22
	IV	$WCl_4(C_5H_5N)_2$		$W^{IV} \rightarrow W^{VI}$	4.44	0.0 ± 0.2

---

[a] Standard deviation given for five measurements. [b] Titrant in toluene solution. [c] For Y = I. [d] The reaction of the complex with the titrant occurred very slowly (1-4 h), and thus reproducibility was rather poor.

Experimental

The Karl Fischer reagent was either prepared from its components or used as supplied by Reanal (Budapest). Transition metal complexes were prepared according to published procedures [3 - 10]. The purity of the complexes was checked by elemental and thermogravimetric analyses as well as by IR spectroscopy.

The titrations were performed using a Labor (Budapest) Type 5354 automatic titrator with biamperometric end point detection.

Results and discussion

Low valent transition metal complexes with or without phosphine ligands were titrated against the Karl Fischer reagent. The results are summarized in Table 1.

From comparison of the experimental Karl Fischer percentages (KF%) [1] with those calculated assuming various reasonable changes in the oxidation number of the transition metal atom and taking into account the reaction of the titrant with eventual P^{III} ligands, the following conclusions can be drawn.

(*i*) The transition metal is oxidized by the reagent if the oxidation state is *below* Fe^{II}, Co^{II}, Ni^{II} and Rh^{III}, (i.e. in complexes containing these valence states the transition metal is not oxidized). No oxidation was detected with W^{II}, W^{IV} and Mo^{II} compounds.

(*ii*) Some M^0 or $M^{\pm 1}$ complexes of exceptional stability such as $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ and $Co_3(CO)_9CX$ (X = Cl, Br, I, i-Pr) did not react.

(*iii*) With all the complexes containing phosphorus(III) ligands, the measured KF% values were in accord with KF% values calculated on the basis of consumption of the reagent by these ligands and by the metal.

(*iv*) No reaction was detected between the Karl Fischer reagent and the following ligands: CO, CN^-, π-(C_5H_5), NH_3, C_5H_5N, Cl^-, I^-.

(*v*) Results obtained with $Hg[Co(CO)_4]_2$ and its phsophine derivative provide the first chemical evidence for the covalent Co^0—Hg^0—Co^0 metal—metal bonding in these compounds, which was postulated previously on the basis of IR ν(C—O) spectra [11] and confirmed by other spectroscopic [12,14, 15] and diffraction [13] methods.

(*vi*) The above results indicate that the use of the Karl Fischer reagent as an oxidizing agent provides a convenient possibility for determination of the concentration of low valent transition metal complexes (e.g. solutions of $Co_2(CO)_8$, $[Co(CO)_4]^-$, $Rh_4(CO)_{12}$).The method, in contrast to the generally used oxidation—complexometric titration procedure, is rather specific for the low valent species in the presence of higher valent impurities.

(*vii*) The method of Hayton and Smith for the determination of P^{III} compounds can be used for P^{III} ligands of low valent transition metal complexes provided great care is taken in the evaluation of the results, and the possible oxidation of the transition metal is taken into account.

Acknowledgement

The authors acknowledge the encouragement of this work by Prof. L.

Markó (Veszprem) and the valuable advice of Prof. B.C. Smith (London, Canada), as well as the kind collaboration in the preparative and experimental work of Drs. A. Vizi-Orosz, G. Csontos and Miss Á. Bodor (Veszprém).

References

1 B. Hayton and B.C. Smith, J. Inorg. Nucl. Chem., 31 (1969) 1369.
2 K. Fischer, Angew. Chem., 48 (1935) 394.
3 E.g. G. Bor, A fém-karbonilok és származékaik kémiájá (Chemistry of metal carbonyls and their derivatives), Akadémiai Kiadó, Budapest, 1966; F. Calderazzo, R. Ercoli and G. Natta in I. Wender and P. Pino, eds., Metal Carbonyls. Organic Syntheses Via Metal Carbonyls, Vol. 1, Interscience, New York, 1968, p.1.
4 P. Szabó, L. Markó and G. Bor, Chem. Techn., 13 (1961) 549.
5 B. Heil, C. Sc. Thesis, Veszprém, 1969.
6 G. Csontos, B. Heil and L. Markó, J. Organometal. Chem., 37 (1972) 183.
7 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
8 W. Hieber, Z. Anorg. Allg. Chem., 204 (1932) 165.
9 (a) D.J. Kenney, T.P. Flynu and J. Gallini, J. Inorg. Nucl. Chem., 20 (1961) 75; (b) R. Nast and K.W. Kroger, Z. Anorg. Allg. Chem., 341 (1965) 189.
10 L. Bencze, J. Organometal. Chem., 37 (1972) C37.
11 G. Bor and L. Markó, Spectrochim. Acta, 16 (1960) 1105; G. Bor, Inorg. Chim. Acta, 3 (1969) 196.
12 H. Stammreich, K. Kwai, O. Sala and P. Krumholz, J. Chem. Phys., 35 (1961) 2175.
13 G.M. Sheldrick and R.N.F. Simpson, J. Chem. Soc. A, (1968) 1005;
R.F. Bryan and A.R. Manning, Chem. Commun., (1968) 1316.
14 J.M. Burlitch and A. Ferrari, Inorg. Chem., 9 (1970) 563.
15 R.J. Ziegler, J.M. Burlitch, S.E. Hayes and W.R. Risen, Inorg. Chem., 11 (1972) 702.