Journal of Organometallic Chemistry, 76 (1974) 89—93

IONIZATION AND APPEARANCE POTENTIALS OF COBALT CARBONYL COMPLEXES

O. GAMBINO, G.A. VAGLIO, R.P. FERRARI and M. VALLE

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

(Received February 19th, 1974)

Summary

The ionization potentials of the compounds $Co_2(CO)_6C_2H_2$, $Co_2(CO)_6C_2(CH_3)_2$, $Co_2(CO)_6C_2(CF_3)_2$, $Co_2(CO)_6C_2(CH_2Cl)_2$ and $Co_2(CO)_6C_2CH_3C_6H_5$ have been determined by electron impact measurements and found to show a good correlation with the Taft σ^* constants of the substituent groups on the ligand. The average ionic dissociation energies of the Co—CO bonds are mainly dependent on the π acceptor ability of the ligand, and exhibit the sequence $(CF_3)_2 < H_2 < (CH_3)_2$. Suggestions concerning the Co—ligand bond strengths are discussed in connection with the relative kinetic reactivities of such compounds in exchange and carbonyl group substitution reactions.

Introduction

Carbon monoxide isotopic exchange [1] and substitution reactions [2] have not enabled us to obtain any direct evidence on the relative strength of metal—CO bonds in $Co_2(CO)_6C_2RR'$ complexes, the kinetic results having tended to rule out the simple breakdown of a Co—CO bond as rate determining step.

In this paper we report the ionization potentials and the dissociation bond energies for ions arising from $Co_2(CO)_6C_2H_2$, $Co_2(CO)_6C_2(CH_3)_2$, $Co_2(CO)_6C_2(CF_3)_2$, $Co_2(CO)_6C_2(CH_2Cl)_2$ and $Co_2(CO)_6C_2CH_3C_6H_5$. The fragmentation patterns of the first four compounds have been reported previously [3]. The mass spectrum of $Co_2(CO)_6C_2CH_3C_6H_5$ is briefly discussed below. The correlation between ionization potentials and Taft σ^* constants of R and R' groups and the effects of the ligand on the Co—CO bond energies are considered with the object of obtaining supporting evidence for the mechanism proposed for the replacement of carbonyl groups in $Co_2(CO)_6C_2RR'$ complexes.

Results and discussion

The mass spectrum of $Co_2(CO)_6C_2CH_3C_6H_5$, given in Table 1, shows the usual elimination of the carbonyl groups, followed by loss of the cobalt atoms in two successive steps to give $C_9H_8^{\cdot+}$ and $C_9H_7^+$. The corresponding metastable transitions are present.

The ionization potentials of the $Co_2(CO)_6C_2RR'$ compounds (Table 2) are very close to the ionization potential of cobalt, viz. 7.86 eV [9]. This is in agreement with the usually accepted hypothesis that the removed electron comes from an orbital having a high degree of metallic character.

Figure 1 shows the plot of ionization potentials of the $Co_2(CO)_6C_2RR'$ vs. the Taft $\sigma^*_R + \sigma^*_{R'}$ constants of the substituent groups. The ionization potentials of alkynes do not exhibit a similar correlation; literature values for C_2H_2 (11.41 eV) [10], $CH_3C{\equiv}CH$ (10.36 eV) [10], $CH_3C{\equiv}CCH_3$ (9.19 eV) [11], $C_2H_5C{\equiv}CH$ (10.18 eV) [10], and $C_6H_5C{\equiv}CH$ (8.82 eV) [10], when taken together with the values of 10.48 eV for $ClCH_2C_2CH_2Cl$ and 10.64 for $BrCH_2C_2H$ indicate that the inductive effect is not the only factor affecting the energy of the highest occupied molecular orbital, when substituents other than alkyl groups are present. The coordinated ligands behave in a different way and the electron withdrawing power of the R + R' groups appears to be the main factor influencing the loss of the least firmly bound electron in the complexes.

TABLE 1

MASS SPECTRUM OF $Co_2(CO)_6C_2CH_3C_6H_5$ AT 75 eV

m/e	Ion	Intensity
402	$Co_2(CO)_6C_2CH_3C_6H_5^{\cdot+}$	6
374	$Co_2(CO)_5C_2CH_3C_6H_5^{\cdot+}$	26
346	$Co_2(CO)_4C_2CH_3C_6H_5^{\cdot+}$	16
318	$Co_2(CO)_3C_2CH_3C_6H_5^{\cdot+}$	17
290	$Co_2(CO)_2C_2CH_3C_6H_5^{\cdot+}$	29
262	$Co_2(CO)C_2CH_3C_6H_5^{\cdot+}$	66
234	$Co_2C_2CH_3C_6H_5^{\cdot+}$	35
219	$Co_2C_2C_6H_5^+$	2
203	$Co(CO)C_2CH_3C_6H_5^+$	5
175	$CoC_2CH_3C_6H_5^+$	96
174	$CoC_9H_7^{\cdot+}$	4
160	$CoC_2C_6H_5^{\cdot+}$	3
143	$Co(CO)_3^+$	4
118	$Co_2^{\cdot+}$	13
116	$C_9H_8^{\cdot+}$	100
115	$C_9H_7^+$	68
89	$C_7H_5^+$	12
59	Co^+	18
58	$C_9H_8^{2+}$	3
57.5	$C_9H_7^{\cdot 2+}$	4

TABLE 2

IONIZATION POTENTIALS AND BOND DISSOCIATION ENERGIES FOR $Co_2(CO)_6C_2RR'$ COMPOUNDS

Compound	IP (eV)	$\bar{D}_5$ (eV)	$\bar{D}_4$ (eV)	$\bar{D}_3$ (eV)	$\bar{D}_2$ (eV)	$\bar{D}_1$ (eV)	$\bar{D}_0$ (eV)	$\sigma^*_R + \sigma^*_{R'}$
$Co_2(CO)_6C_2(CH_3)_2$	7.80	0.82	0.94	1.06	1.14	1.21	1.30	0.00
$Co_2(CO)_6C_2H_2$	7.96	0.75	0.89	1.00	1.11	1.23	1.27	0.98
$Co_2(CO)_6C_2(CF_3)_2$	8.88	0.65	0.80	1.02	0.99	1.07	1.14	5.8
$Co_2(CO)_6C_2(CH_2Cl)_2$	8.3							2.10
$Co_2(CO)_6C_2CH_3C_6H_5$	7.85							0.60

Measurement of the ionization potential of $Co_2(CO)_6C_2(COOCH_3)_2$ ($\sigma^*_R + \sigma^*_{R'} = 4.00$) was unsuccessful because of the very low abundance of the molecular ion [3].

The appearance potentials of the $Co_2(CO)_nC_2RR'^{\cdot+}$ fragment ions (n varying from 5 to 0), where R = R' = CF_3, H, CH_3, were measured and the average Co—CO bond dissociation energies $\bar{D}_n$ in the ionic species calculated according to eqn. 1 [12]. Inspection of the values listed in Table 2 indicates that the

$$\bar{D}_n = (AP \text{ of } Co_2(CO)_nC_2RR'^{\cdot+} - IP \text{ of } Co_2(CO)_6C_2RR')/(6-n) \tag{1}$$

Co—CO bond strength in these compounds is little affected by the nature of R and R', so that the differences in the ionic $\bar{D}_n$ of some corresponding ions are close to experimental errors. This is true also for ions from $Co_2(CO)_6C_2(CH_3)_2$ and $Co_2(CO)_6C_2(CF_3)_2$, which are thought to exhibit the largest differences. However it is noteworthy that the $\bar{D}_n$ values for loss of the first two carbonyl groups increase in the sequence $CF_3 < H < CH_3$. The influence of the ligand on the loss of the other carbonyl groups appears to be smaller, but all the ions coming from $Co_2(CO)_6C_2(CF_3)_2$ show the lowest ionic $\bar{D}_n$. This result is in contrast with data for $ArCr(CO)_3$ compounds, for which the dissociation energies for the loss of the first and second carbonyl group exhibit opposite slopes vs. the Hammett functions of the substituents on the ligand [13].

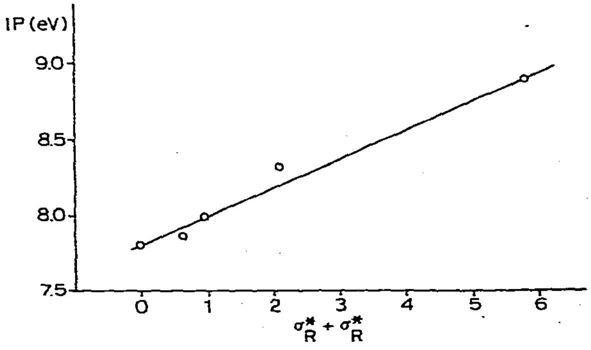

Fig. 1. Plot of the ionization potentials of $Co_2(CO)_6C_2RR'$ complexes against the sum ($\sigma^*_R + \sigma^*_{R'}$) of the Taft substituent constants for R and R'.

The decrease in $\overline{D}_n$ for $Co_2(CO)_nC_2RR'^{\cdot+}$ ions with the electron withdrawing power of the ligand does not depend on the number and symmetry of the remaining carbonyl groups, and is reasonably ascribed to a major contribution of the π component to the Co—CO bond. The ability of the ligand to withdraw charge from the metal leads to the electrons being less available for the back donation into the antibonding orbitals of the carbonyl groups. Similar ligand effects on the ionization potentials and bond energies have been reported for $L^1 L^2 Fe_2(CO)_6$ complexes [14].

The trends in the ionic bond energies have been shown to apply also to neutral bond energies in the case of monometal carbonyls, and this is assumed to hold for some dimetal carbonyls [12, 15—18]. We suggest that this concept can be extended to $Co_2(CO)_6C_2RR'$ compounds, and we can thus use the data collected in Table 2 to evaluate the relative Co—CO bond energies in the neutral molecules. These values then enable the variation in the $Co—C_2RR'$ bond energies (which could not be directly measured, because no loss of ligand from the molecular ion occurs) to be established. The lowering in the Co—CO bond energy with an increase in the electron withdrawing characteristics of R and R′ means that more electrons are available for back donation to the acetylenic ligand, so that the $Co—C_2RR'$ bond is strengthened. In contrast, other factors being equal, the rate constants for the substitution reactions decrease as the electron withdrawal of R and R′ groups is increased [1, 2]. Therefore it follows that the mass spectrometric data give further support to the kinetic mechanism suggested, which involves the loosening of the $Co—C_2RR'$ bond as rate determining step, as well as to the ligand displacement order in $Co_2(CO)_6C_2RR'$ compounds.

Experimental

All compounds were prepared by published methods [4—7].

An Hitachi RMU 6H single focussing mass spectrometer, equipped for automatic recording of ionization efficiency curves, was used for all measurements. The compounds were introduced through an all-glass molecular leak inlet at room temperature. Ionization and appearance potentials were determined by Warren's method [8], using a computer program. Xenon and argon were employed as standards. The reproducibilities for all measurements were within ± 0.05 eV, except for the ionization potential of $Co_2(CO)_6C_2(CH_2Cl)_2$, for which it was ± 0.1 eV.

References

1 G. Cetini, O. Gambino, P.L. Stanghellini and G.A. Vaglio, Inorg. Chem., 6 (1967) 1225.
2 G. Cetini, O. Gambino, P.L. Stanghellini and R. Rossetti, Accad. Naz. dei XL, 18 (1967) 18.
3 O. Gambino, G.A. Vaglio, R.P. Ferrari, M. Valle and G. Cetini, Org. Mass Spectrom., 6 (1972) 723.
4 H.W. Sternberg, H. Greenfield, R.A. Friedel, J. Wotiz, R. Markby and I. Wender, J. Amer. Chem. Soc., 76 (1954) 1457.
5 H. Greenfield, H.W. Sternberg, R.A. Friedel, J. Wotiz, R. Markby and I. Wender, J. Amer. Chem. Soc., 78 (1956) 120.
6 J.L. Boston, D.W.A. Sharp and G. Wilkinson, Chem. Ind. (London), (1960) 1137.
7 G. Cetini, O. Gambino, R. Rossetti and E. Sappa, J. Organometal. Chem., 8 (1967) 149.
8 J.W. Warren, Nature (London), 165 (1950) 810.
9 C.E. Moore, Atomic Energy Levels, Natl. Bur. Std. Circ. No. 467, U.S. Govt. Printing Office, Washington D.C., 1958.

10 R.W. Kiser, Introduction to Mass Spectrometry and Its Applications, Prentice-Hall, Englewood Cliffs, N.J., 1965, p. 308.
11 H. Bock and H. Seidl, J. Chem. Soc. B, (1968) 1158.
12 G.A. Junk, H.J. Svec and R.J. Angelici, J. Amer. Chem. Soc., 90 (1968) 5758.
13 J.R. Gilbert, W.P. Leach and J.R. Miller, J. Organometal. Chem., 49 (1973) 219.
14 G.A. Junk, F.J. Preston and H.J. Svec, J. Chem. Soc. A, (1970) 3171.
15 A. Foffani and S. Pignataro, Z. Phys. Chem. (Leipzig), 45 (1965) 79.
16 G.A. Junk and H.J. Svec, Z. Naturforsch. B, 23 (1968) 1.
17 D.R. Bidinosti and N.S. McIntyre, Can. J. Chem., 45 (1967) 641.
18 G.A. Junk and H.J. Svec, J. Chem. Soc. A, (1970) 2102.