The degree of fragmentation of metallocomplexes with cleavage of the metal—ligand bond

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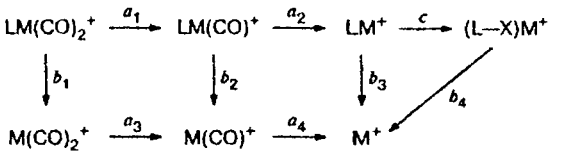
A new method for estimating the degree of fragmentation of metallocomplexes under electron impact with cleavage of the metal—ligand bond was suggested. The method is based on mass spectrometric data. Using a representative selection of 67 organometallic compounds of different classes such as metal carbonyls, metallocenes, and cymantrene and bensenechrometricarbonyl derivatives, a correlation between the degree of fragmentation and the dissociation energy of metal—ligand bonds was developed. The correlation is evidence that the parameter can be used for quantitative estimation of the reactivity of metallocomplexes in the gas phase.

Key words: metallocomplexes, mass spectrometry, degree of fragmentation, bond energy.

The elimination of ligands is the main direction of fragmentation of the majority of metallocomplexes of the $LM(CO)_n$ type under electron impact action. The intensities of the $LM(CO)_x^+$ and $M(CO)_x^+$ ions (x = 0—n) that formed are determined by the dissociation energies of the corresponding bonds.[1] Therefore, mass spectra are often used to estimate the relative stability of metal—ligand bonds. Several methods of estimation are known. For example, the ratio of intensities of peaks of $[L'Mn^+]/[LMn^+]$ ions in the mass spectra of $L'Mn(CO)_2L$ complexes characterizes the stability of the L'—Mn bond relative to that of the L—Mn bond.[2] The $[M-NMe_3]/\{[M-NMe_3] + [M-CO]\}$ value characterizes the change in the M—CO bond stability in the $(Me_3N)_3EM(CO)_5$ and $(Me_3N)_3EM(CO)_4E(NMe_3)_3$ complexes with different transition metals (M = Cr, Mo, and W) and elements (E = P, As, Sb, and Bi).[3,4] For the CpMn(X)(Y)(Z) complexes, a correlation between the total intensity of peaks of ions containing the CpMn, XMn, YMn, or ZMn fragments and dissociation energies of the corresponding bonds has been established.[5,6] All the correlations indicated above are appropriate for the qualitative or, in the best case, semiquantitative estimation of tendencies in the change in metal—ligand bond stability for a narrow range of related compounds and cannot be used for comparison of complexes of different classes.[7,8] In this work, we describe a general method for the calculation of the degree of fragmentation of different metallocomplexes fragmented under the electron impact action with cleavage of the metal—ligand bond.

The scheme of fragmentation of the $LM(CO)_2$ complex is presented below (Scheme 1).

Scheme 1



where a_1—a_4 is the fraction of ions fragmented with the elimination of the CO group; b_1—b_4 is the fraction of ions fragmented with the elimination of the L ligand; and c is the fraction of LM ions fragmented with the elimination of the X fragment.

According to this scheme, we can write the following system of equations for the intensities of ion peaks normalized to the total ionic current:

$$[LM(CO)_2] = 1 - a_1 - b_1,$$

$$[LMCO] = a_1 - a_2 - b_2,$$

$$[LM] = a_2 - b_3 - c,$$

$$[(L—X)\,M] = c - b_4,$$

$$[M(CO)_2] = b_1 - a_3,$$

$$[M(CO)] = a_3 + b_2 - a_4,$$

$$[M] = a_4 + b_3 + b_4.$$

Hence the following expressions can be written for the total fractions of the eliminated carbonyl groups and ligand L

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$$\Sigma a_i = 2 - 2[LM(CO)_2] + [LMCO] + 2[M(CO)_2] + [M(CO)], \quad (1)$$

$$\Sigma b_i = 1 - [LM(CO)_2] + [LMCO] + [LM] + [(L{-}X)M]. \quad (2)$$

Let us introduce the concept of the degree of fragmentation of a molecule with cleavage of the given metal—ligand bond as the ratio of the total fraction of the eliminated ligands to the number of these ligands in the starting molecule. For the example considered, we obtain two values: degree of decarbonylation $\alpha(CO) = \Sigma a_i/2$ and degree of elimination of the L ligand $\alpha(L) = \Sigma b_i/1$.

In the general case, for the L_nMX_m complex, the degree of fragmentation with cleavage of M—L and

Table 1. Average values of energies of metal—ligand bond cleavage (D_L/eV) and degree of fragmentation with the corresponding bond cleavage ($\alpha(L)$)

Complex	Subset *1*				Complex	Subset *2*			
	L	D_L	$\alpha(L)$	Ref.		L	D_L	$\alpha(L)$	Ref.
$Ni(CO)_4$	CO	1.63	0.63	9, 10, 12, 19	$Mn(CO)_5Br$	Br	3.55	0.60	16
$Fe(CO)_5$	CO	1.43	0.74	9, 10, 12, 19	$Mn(CO)_5H$	H	3.18	0.67	17
$Cr(CO)_6$	CO	1.10	0.82	9—11, 13, 18	$Mn(CO)_5SiMe_3$	CO	0.82	0.91	17
$Mo(CO)_6$	CO	1.70	0.65	9—11, 13, 18	$Mn(CO)_5SiMe_3$	$SiMe_3$	5.90	0.27	17
$W(CO)_6$	CO	2.07	0.62	9—11, 13, 18	$CpCo(CO)_2$	CO	1.70	0.82	21
$V(CO)_6$	CO	1.33	0.76	9	$CpCo(CO)_2$	Cp	5.10	0.30	21
$Cr(CO)_5CS$	CO	0.90	0.73	13	$CpV(CO)_4$	CO	1.50	0.85	21
$Mo(CO)_5CS$	CO	1.39	0.64	13	$CpV(CO)_4$	Cp	5.20	0.29	21
$W(CO)_5CS$	CO	1.84	0.58	13	$CpMn(CS)(NO)I$	Cp	5.20	0.37	6
$W(CO)_5CS$	CS	3.82	0.13	13	$CpMn(CS)(NO)I$	NO	1.38	0.87	6
$Cr(CO)_5C(Me)OMe$	CO	0.95	0.81	14	$Cp'Mn(CS)(NO)I$	Cp	5.59	0.23	6
$Cr(CO)_5PPh_3$	CO	0.35	0.92	15	$Cp'Mn(CS)(NO)I$	NO	1.54	0.82	6
$Mn(CO)_5Br$	CO	1.06	0.82	16	$Cp'Mn(CO)_3$	CO	1.12	0.88	24
$Re(CO)_5Cl$	CO	2.02	0.53	16	$Cp'Mn(CO)_3$	Cp	5.12	0.28	24
$Re(CO)_5Cl$	Cl	3.83	0.26	16	$Cp'Mn(CO)_2CS$	CS	3.05	0.58	24
$Mn(CO)_5H$	CO	1.06	0.78	17	$CpMn(CO)_2SOMe$	CO	0.28	1.00	22
$CpMn(CO)_3$	CO	0.95	0.83	20—22, 24	$Cp'Mn(CO)(CS)PPh_3$	CS	1.82	0.83	5
$CpMn(CO)_3$	Cp	3.44	0.32	20—22, 24	$Cp'Mn(CO)(CS)AsPh_3$	CO	0.86	0.95	5
$CpMn(CO)_2CS$	CO	0.74	0.81	24	$Cp'Mn(CO)(CS)AsPh_3$	$AsPh_3$	5.44	0.33	5
$CpMn(CO)_2CS$	Cp	4.28	0.08	24	$Cp'Mn(CO)(CS)SbPh_3$	CO	0.69	0.96	5
$CpMn(CO)_2CS$	CS	3.00	0.49	24	$Cp'Mn(CO)(CS)SbPh_3$	CS	1.53	0.88	5
$CpMn(CS)(NO)I$	CS	2.32	0.60	6	$Cp'Mn(CO)_2PPh_3$	CO	1.00	0.89	5
$Cp'Mn(CS)(NO)I$	CS	2.40	0.50	6	$Cp'Mn(CO)_2AsPh_3$	CO	1.03	0.94	5
$Cp'Mn(CO)_2CS$	CO	0.72	0.87	24	$Cp'Mn(CO)_2AsPh_3$	$AsPh_3$	6.29	0.16	5
$Cp'Mn(CO)_2CS$	Cp'	4.02	0.20	24	$Cp'Mn(CO)_2SbPh_3$	$SbPh_3$	6.13	0.28	5
$Cp'Mn(CO)(CS)PPh_3$	CO	0.79	0.88	5	$C_6H_8Fe(CO)_3$	CO	1.30	0.94	23
$Cp'Mn(CO)_2SbPh_3$	CO	1.01	0.85	5	$HPhCr(CO)_3$	CO	0.98	0.87	20, 30
$CpMn(CO)_2C_5H_8$	CO	0.41	0.88	22	$HPhCr(CO)_3$	Ar	2.90	0.68	20, 30
$CpMn(CO)_2C_5H_8$	C_5H_8	0.82	0.87	22	$MePhCr(CO)_3$	CO	1.12	0.90	30
$CpMn(CO)_2C_4H_8$	CO	0.41	0.95	22	$ClPhCr(CO)_3$	CO	1.03	0.92	30
$CpMn(CO)_2C_7H_8$	CO	0.33	0.88	22	$MeOPhCr(CO)_3$	CO	1.05	0.91	30
$CpMn(CO)_2C_7H_{10}$	CO	0.31	0.87	22	$MeOPhCr(CO)_3$	Ar	2.75	0.69	30
$CpMn(CO)_2C_7H_{12}$	CO	0.43	0.87	22	$MeO_2CPhCr(CO)_3$	CO	0.99	0.93	30
$CpMn(CO)_2C_8H_{14}$	CO	0.44	0.89	22	$H_2NPhCr(CO)_3$	CO	1.15	0.93	30
$CpMn(CO)_2MA$	CO	0.35	0.92	22	Cp_3Sm	Cp	4.07	0.47	28, 33
$CpMn(CO)_2P(Pr^i)_3$	CO	0.63	0.88	22	Cp_3Tm	Cp	4.50	0.43	28, 29
$CpMn(CO)_2NHMe_2$	CO	0.44	0.78	22	Cp_3Ho	Cp	4.63	0.39	28, 29
$CpMn(CO)_2CNC_6H_{11}$	CO	0.41	0.86	22	Cp_3Dy	Cp	4.70	0.40	28
$C_6H_8Fe(CO)_3$	C_6H_8	4.67	0.12	23	Cp_3Gd	Cp	4.73	0.35	28
Cp_3Yb	Cp	3.20	0.50	28, 29, 33	Cp_3Tb	Cp	4.80	0.33	28
Cp_2Mg	Cp	3.13	0.46	26, 33	Cp_3Pr	Cp	4.98	0.41	28, 29
Cp_2Mn	Cp	3.14	0.50	26, 27	Cp_3Er	Cp	5.00	0.36	28
Cp_2V	Cp	3.75	0.32	26, 27	Cp_3Nd	Cp	5.08	0.40	28, 33
Cp_2Fe	Cp	4.08	0.25	25—27, 33	Cp_3Lu	Cp	5.12	0.33	28, 29
Cp_2Co	Cp	4.23	0.28	26, 27, 33					
Cp_2Ru	Cp	4.44	0.15	25, 26					
Cp_2Ni	Cp	3.45	0.34	25—27, 33					

Note. L is eliminaated ligand, Cp is C_5H_5, and Cp' is MeC_5H_4.

M—X bonds can be calculated from the following equations:

$$\alpha(L) = \{n - \Sigma(n - i)[L_{n-i}MX_{m-j}]\}/n, \quad (3)$$

$$\alpha(X) = \{m - \Sigma(m - j)[L_{n-i}MX_{m-j}]\}/m. \quad (4)$$

The α(L) values vary from 0 to 1 and are dimensionless, which allows them to be used for comparison of the degree of fragmentation of different complexes with elimination of any ligands. It is noteworthy that Scheme 1 for the calculation of α(L) does not take into account the possibility of formation of monocharged LM^+ ions from bicharged molecular ions. In addition, in the calculations of α(L) one should take into account ions of the (L—X)M type, which appear during the fragmentation of the ligand (see Scheme 1 and Eq. (2)).

To establish the information content of the suggested α(L) value as a parameter characterizing the reactivity of organometallic compounds under conditions of their electron impact fragmentation in the gas phase, we analyzed the published data on the stability of metal—ligand bonds. The average values of dissociation energies of metal—ligand bonds (D_L) taken from the literature and the values of the degree of fragmentation α(L) with the corresponding bond cleavage calculated from the mass spectra by Eq. (3) for 67 various metal complexes (metal carbonyls, metallocenes, and cymantrene and benzenechrometricarbonyl derivatives) are presented in Table 1. Regression analysis of these data shows that D_L and α(L) are related by a linear function, and the whole set of compounds studied can be divided into two subsets, each of which is characterized by its regression line (Fig. 1, Table 1). The correlation Eqs. (5) and (6) obtained are physically substantiated, since they contain free terms close to unity. This implies that in the limiting case where the bond dissociation energy is equal to zero, the degree of fragmentation is equal to unity by definition, *i.e.*, all ligands are completely eliminated.

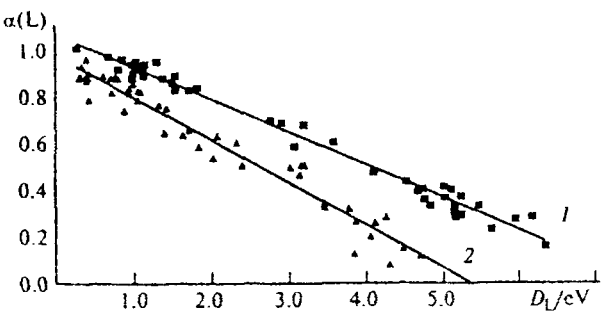

Fig. 1. Dependences of α(L) on D_L: *1* and *2* are regression lines for subsets.

$$\alpha(L) = 1.059(\pm 0.010) - 0.140(\pm 0.003) \cdot D_L; \quad r = 0.992, \; n = 44 \quad (5)$$

$$\alpha(L) = 0.971(\pm 0.014) - 0.182(\pm 0.006) \cdot D_L; \quad r = 0.978, \; n = 47 \quad (6)$$

According to the quasi-equilibrium theory of mass spectra, the electron impact-induced fragmentation of molecules is affected, along with the activation energy, by the frequency of the cleaved bond and the number of vibrational degrees of freedom of the decomposing ion.[1] This explains two linear relationships between D_L and α(L) for the representative selection of metallocomplexes containing different ligands and central metal atoms.

Thus, the established correlation between the degree of fragmentation and the stability of the cleaved bond indicates that the α(L) parameter can be used for quantitative estimation and comparison in the unified dimension scale of reactivity of different classes of metallocomplexes in processes of electron impact-induced cleavage of metal—ligand bonds.

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