Resonance capture of electrons by cyclopentadienyltricarbonylmanganese and -rhenium derivatives

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Negative ion mass spectra of cyclopentadienyltricarbonylmanganese and -rhenium derivatives $RC_5H_4M(CO)_3$ (R = H, CN, COOH, COMe, COOMe, CH_2OH, CHO; M = Mn, Re) were studied. The subsequent detachment of carbonyl groups is the main process of the fragmentation of these compounds under the conditions of the resonance capture of electrons. On going from the rhenium complexes to manganese derivatives, the maxima of the yields of the ions $[M-nCO]^-$ (n = 1—3) shift to the lower energy region indicating that the stability of the Re—CO bond is higher than that of Mn—CO. The average lifetimes of the molecular negative ions relative to the autodetachment of an electron (τ_a) and to dissociation (τ_d) were measured. It was found that electron-accepting substituents increase the τ_a value and decrease τ_d.

Key words: negative ion mass spectrometry, resonance capture of electrons, cyclopentadienyltricarbonylrhenium and -manganese derivatives.

We have previously studied the formation of negative ions (NI) during the resonance capture of electrons by molecules of some cymantrene,[1] benzenechromiumtricarbonyl,[2,3] and π-allylirontricarbonyl halide[4] derivatives. In this report, we present the results of the comparative study of the behavior of several derivatives of cyclopentadienyltricarbonylmanganese (CTM) $RC_5H_4Mn(CO)_3$ (**1a—h**) (R = H (**a**), CN (**b**), CHO (**c**), COMe (**d**), CH_2OH (**e**), COOMe (**f**), $CH(Me)NH_2$ (**g**), n-C_5H_{11} (**h**), 1,3-CHO,$(NMe_2)C_5H_4Mn(CO)_3$ (**1i**), $Me_5C_5Mn(CO)_3$ (**1j**)), and cyclopentadienyltricarbonylrhenium (CTR) $RC_5H_4Re(CO)_3$ (**2a—f**) (R = H (**a**), CN (**b**), CHO (**c**), COMe (**d**), CH_2OH (**e**), COOH (**f**)) under the conditions of resonance capture.

Experimental

Mass spectra and effective yield curves were recorded on an MI-1201 instrument re-equipped to register NI during the resonance capture of electrons.[5] The electron energy scale was calibrated by the maximum of the effective yield of the ions $C_6H_5^-$ from C_6H_6 and SF_6^- from SF_6. The average lifetimes of molecular NI relative to the autodetachment of electrons were determined from the ratio of ions to neutral particles that appeared due to the autodetachment of electrons in the monitored ion beam.[6] The average lifetimes of molecular NI relative to dissociation were determined from the ratio of intensities (surface areas) of the peaks of the parent, daughter, and metastable ions.[7]

Results and Discussion

The NI mass spectra of the compounds studied are presented in Tables 1 and 2. The intensities of the peaks of the ions are presented as the maxima of the effective yield curves (EYC) in per cents of the peak that is maximum in intensity, and the energy of the electrons in the EYC maximum is given in parentheses. The formation of molecular NI is characteristic only of complexes containing electron-withdrawing substituents (R = CN, CHO, COMe, COOH, and COOMe). Their intensity is substantially higher in the spectra of CTR derivatives, because the electron affinity of the Re atom (0.15 eV) is higher than that of the Mn atom (−0.97 eV).

Under the conditions of the resonance capture of electrons, the main fragmentation process of all compounds studied (except **2e**) is the subsequent detachment of the carbonyl groups (the corresponding metastable peaks are observed in the mass spectra of several CTM derivatives) to form the ions $RC_5H_4M(CO)_n^-$ (n = 0—2) in several resonance regions (see Tables 1 and 2). The simultaneous detachment of two CO groups is also possible, which can be seen by the presence of the corresponding metastable peak in the spectrum of **1i** (see Table 1). The peaks of the $RC_5H_4M(CO)_2^-$ ions with a 17-electron valence shell have the highest (as a rule, maximum) intensity. On going from the Re complexes to the Mn derivatives, the maxima of the yield of $[M-nCO]^-$ ions (n = 1—3) shift to the region of lower

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Table 1. Intensities of the peaks of ions (I (%)) in the maxima of the effective yield curves in the mass spectra of the resonance capture of electrons of CTM derivatives

Ion	**1a**, H	**1b**, CN	**1c**, CHO	**1d**[a], COMe	**1e**, CH_2OH	**1f**[b], COOMe	**1g**, $CH(Me)NH_2$	**1h**, C_5H_{11}	**1i**[c], CHO,NMe_2	**1j**, Me_5
M				0.5 (0.0)		2.0 (0.0)			0.2 (0.0)	
M−CO	100.0 (0.3)	100.0 (0.3)	100.0 (0.3)	100.0 (0.3)	100.0 (0.3)	100.0 (0.3)	100.5 (0.5)	100.0 (0.8)	100.0 (0.3)	100.0 (0.9)
	11.0 (1.4)	68 (0.8)						24.0 (2.4)		27.0 (2.5)
M−2CO			<0.1 (0.3)							
	2.0 (2.9)	13 (2.3)	2.5 (2.6)	1.0 (2.5)	0.3 (3.2)	0.6 (2.6)	14.0 (2.6)	7.6 (2.7)	0.7 (2.4)	0.2 (3.1)
M−3CO	0.5 (3.8)	11.2 (2.9)	1.1 (3.3)	0.9 (3.0)	0.2 (3.7)	1.1 (3.1)		8.8 (3.3)	2.5 (2.6)	0.9 (3.7)
M−H							4.8 (6.8)	1.9 (6.3)		3.1 (6.9)
M−H−CO								4.6 (6.8)		0.6 (7.4)
M−H−2CO								2.4 (7.0)		
M−H−3CO								1.6 (8.0)		
M−R							1.5 (4.8)			
							0.7 (6.8)			
M−R−CO							0.4 (7.0)			
M−R−2CO							0.2 (7.5)			
L	<0.1 (3.4)	9.8 (3.9)	1.0 (4.7)	0.2 (4.7)		0.3 (4.2)	0.2 (4.5)	1.8 (4.8)	1.5 (3.9)	
	0.1 (5.4)	4.9 (6.2)	0.6 (7.3)	0.1 (7.4)		0.3 (5.0)	0.1 (6.8)	3.0 (6.5)		
	<0.1 (6.9)					0.1 (7.4)				
	<0.1 (8.4)									
R		0.1 (7.4)								
		0.2 (9.5)								
M→M−CO			0.5 (0.0)	0.2 (0.0)		0.7 (0.0)				
M−CO→M−2CO	<0.1 (2.2)	0.4 (0.3)	0.1 (0.3)	0.1 (0.3)		0.1 (0.3)			<0.1 (2.1)	
		0.3 (0.7)	0.1 (2.1)	0.1 (2.3)		0.1 (2.4)				
		0.4 (1.8)								
M−2CO→M−3CO		0.1 (2.7)	<0.1 (2.7)	<0.1 (2.7)		0.0 (3.0)			<0.1 (2.5)	
		<0.1 (3.4)	<0.1 (3.6)	<0.1 (3.4)		0.0 (3.5)				
M−CO→M−3CO									<0.1 (2.5)	

Note. The values of the resonance maxima (eV) are presented in parentheses. Other ions: $[M-NH_2]^-$, 0.2 (6.8); $[M-Me-NH_2]^-$, 1.5 (2.3); $[M-Me-NH_2-CO]^-$, 3.5 (2.8); $[M-Me-NH_2-2CO]^-$, 2.7 (3.0).

[a] τ_a = 129; τ_d = 14; [b] τ_a = 114, τ_d = 20; [c] τ_a = 148.

Table 2. Intensities of the peaks of ions (I (%)) in the maxima of the effective yield curves in the mass spectra of the resonance capture of electrons of CTR derivatives

Ion	**2a**, H	**2b**, CN	**2c**, CHO	**2d**, COMe	**2e**, CH_2OH	**2f**, COOH
M		79.0 (0.0)	100.0 (0.0)	100.0 (0.0)		100.0 (0.0)
M−CO	100.0 (1.7)	100.0 (1.1)	2.5 (1.1)	25.0 (1.5)		75.0 (1.3)
	25.0 (4.0)	13.0 (3.5)	0.1 (2.9)	33.0 (3.6)		
M−2CO	0.7 (5.7)	45.0 (4.3)	5.4 (3.5	3.3 (4.4)		0.6 (3.6)
M−3CO	1.4 (9.2)	8.0 (6.2)	0.1 (5.7)	0.1 (4.5)		
M−H					0.4 (8.0)	18.0 (1.0)
M−2H					100.0 (0.4)	
M−R				9.3 (4.4)	2.7 (4.1)	6.9 (4.1)
					2.9 (6.1)	19.0 (6.6)
	0.4 (9.0)				2.2 (8.8)	5.2 (8.5)
M−R−CO	6.5 (9.3)			0.8 (5.0)	1.6 (7.2)	19.0 (6.8)
M−R−2CO	4.5 (9.8)				1.4 (9.2)	8.0 (8.6)
M−OH					0.5 (6.3)	0.2 (1.7)
					0.5 (8.3)	

Note. The values of the resonance maxima (eV) are presented in parentheses. For compounds **2b**—**2d** and **2f**, τ_a = 42, 39, 37, and 29, respectively.

energies because the Re—CO bond is stronger than the Mn—CO bond.[8] The same can be said about the $M-C_5H_4R$ bond. Its cleavage to form $RC_5H_4^-$ ions is characteristic only of the Mn complexes, while all fragmentation processes of the CTR derivatives (decarbonylation, elimination of the substituent R or its fragments) occur with retention of the $Re-C_5H_4R$ bond (see Tables 1 and 2).

Along with the central M atom, the nature of the substituent R exerts a substantial effect on the spectra of the resonance capture of electrons of the compounds studied. In particular, for monosubstituted CTM, as well as for benzenechromiumtricarbonyl derivatives,[2] the tendency for the values of the maxima of the yield of the $[M-CO]^-$ ions formed in the second resonance region (1—3 eV) to increase is observed as the electron-donating properties of substituents increase, which testifies that the strength of the M—CO bond increases in this series (see Table 1). The specific structural features of the complexes are manifested to the greatest extent in the fragmentation of the substituent in the cyclopentadienyl ring. For example, the CTM derivatives with alkyl substituents (**1g,h,j**) undergo dehydrogenation to form a series of $[M-H-nCO]^-$ (n = 0—3) ions (see Table 1), and the carboxyl derivative of CTR is characteristic of the detachment of the hydroxy group (see Table 2). The hydroxymethyl derivative of CTR **2e** occupies a special place. Its behavior under the conditions of the resonance capture of electrons differs qualitatively from the behavior of the other compounds studied, including the corresponding analog of CTM **1e**. Unlike the majority of metal carbonyl derivatives,[1—4] this complex does not undergo decarbonylation, and the main process of its fragmentation is the elimination of the H_2 molecule to form the ion $[M-2H]^-$ in the first resonance region (0.4 eV). A few other directions of decomposition (elimination of the H atom, OH and CH_2OH groups) are realized to a small extent and at considerably higher energies of electrons (see Table 2). It is difficult to explain this fact unambiguously. It can only be assumed that the $[M-2H]^-$ ion has the structure of the molecular NI of formyl-CTR, which, according to the mass spectrum of **2c**, is very stable and can be easily formed from formyl-CTR by the capture of thermal electrons. This supposition can be indirectly tested by comparing the spectra of the resonance capture of electrons of the corresponding CTM derivatives **1c** and **1e**: formyl-CTM **1c** does not form molecular NI and hydroxymethyl-CTM **1e** is not characterized by the elimination of a H atom.

In addition to the standard parameters of mass spectra of the resonance capture of electrons (intensities of peaks of ions and values of maxima of EYC), we also measured the average lifetimes of the molecular NI relative to the autodetachment of an electron (τ_a/ms). In the case of the two CTM derivatives, whose spectra contain metastable peaks corresponding to decarbonylation of the molecular ion, their lifetimes relative to dissociation (τ_d) were also measured.

The regression analysis of the values of τ_a (see Table 2) and of the σ_p constants of substituents for four CTR derivatives showed that they form a linear dependence according to the equation $\tau_a = 21.71 + 32.05\,\sigma_p$ ($n = 4$, $r = 0.939$), *i.e.*, the electron-withdrawing substituents enhance the stability of the molecular NI relative to the autodetachment of an electron. The similar tendency is characteristic of the two CTM derivatives **1d** and **1f**, whose spectra contain molecular NI. It can be seen from the data in Table 1 that the τ_a value increases on going from **1f** (R = COOMe, σ_p = 0.436) to **1d** (R = COMe, σ_p = 0.502). By contrast, τ_d decreases as σ_p increases, *i.e.*, electron-withdrawing substituents destabilize NI relative to dissociation, which agrees with the aforementioned tendency for weakening of the M—CO bond on going from electron-donating to electron-withdrawing substituents.

Thus, the presence of molecular NI in mass spectra of the resonance capture of electrons depends on two competitive factors: their stability relative to the autodetachment of an electron (which depends on the electron affinity and the number of vibrational degrees of freedom of the studied molecule) and the lifetime relative to dissociation (which is determined by the strength of the chemical bonds). Therefore, CTM derivatives containing both strong electron-withdrawing (**1b,c**) and electron-donating (**1e,g,h,j**) substituents do not form long-lived (in the mass spectral time scale of 1—10 ms) molecular ions. However, the introduction of a dimethylamino group into the formylcymantrene molecule (**1i**) results in the appearance of the peak of the molecular NI in its mass spectrum.

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References

1. Yu. S. Nekrasov, V. K. Mavrodiev, V. F. Sizoi, and V. I. Khvostenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1299 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 1157 (Engl. Transl.)].
2. Yu. S. Nekrasov, V. I. Khvostenko, I. I. Furley, N. I. Vasyukova, V. K. Mavrodiev, A. Sh. Sultanov, and G. A. Tolstikov, *J. Organomet. Chem.*, 1981, **212**, 373.
3. Yu. S. Nekrasov, V. I. Khvostenko, I. I. Furley, N. I. Vasyukova, and G. A. Tolstikov, *J. Organomet. Chem.*, 1981, **212**, 369.
4. Yu. S. Nekrasov, V. K. Mavrodiev, V. A. Mazunov, V. I. Khvostenko, N. P. Avakyan, and I. I. Kritskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1428 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1308 (Engl. Transl.)].
5. V. A. Mazunov and V. I. Khvostenko, *Prib. Tekhn. Eksp.* [*Experimental Equipment and Technique*], 1969, 224 (in Russian).
6. V. I. Khvostenko, I. I. Furlei, V. A. Mazunov, and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 680 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22** (Engl. Transl.)].
7. I. I. Furlei, V. K. Mavrodiev, E. E. Shul'ts, R. V. Kunakova, U. M. Dzhemilev, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2477 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2291 (Engl. Transl.)].
8. N. A. Nesmeyanov, B. V. Lokshin, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 1049 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1969, **11** (Engl. Transl.)].
9. K. Meier and J. Seibl, *Int. J. Mass Spectrom. Ion Phys.*, 1974, 99.

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