970 Russian Chemical Bulletin, International Edition, Vol. 50, No. 6, pp. 970—973, June, 2001

Reactivity of benzenetricarbonylchromium derivatives under conditions of dissociative ionization in the gas phase

Yu. S. Nekrasov,★ Yu. N. Sukharev, E. E. Tepfer, D. V. Zverev, and S. O. Yakushin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yusnekr@ineos.ac.ru

The reactivity of benzenetricarbonylchromium derivatives under conditions of their fragmentation by electron impact was studied. The generalized structural and mass spectral characteristics formed on the basis of the information theory, molecular graph theory, and theory of absolute reaction rates were used to establish correlations between some of these characteristics.

Key words: mass spectrometry, reactivity, complexes of transition metals, derivatives of benzenetricarbonylchromium, correlation equations, information indices.

We have previously[1—7] proposed two methods for quantitative estimation of the reactivity of molecules under the conditions of their fragmentation by electron impact using the generalized (integral) characteristics of the mass spectra. The first of them is based on the calculation of experimental and information mass spectral indices, which are formed taking into account all ions appeared in the dissociative ionization of molecules[1,2] and, as shown for several classes of organometal compounds, correlate with structural and/or electron parameters of the compounds under study.[3—6] The second characteristics of the reactivity is the degree of fragmentation of a molecule *via* a specific direction. It takes into account all array of ions appeared in the studied decomposition process (for example, decarbonylation of metal carbonyl complexes) and correlates with the mean dissociation energies of the corresponding bonds.[7]

In this work, we used these methods to study the reactivity of more than 40 benzenetricarbonylchromium derivatives $RC_6H_5Cr(CO)_3$ (Table 1).

The following mass spectral and structural characteristics were used.

1. Stability of a molecule to electron impact (W), which is equal to the ratio of the intensity of the molecular ion peak (I_{M^+}) to the total intensity of all ion peaks in the mass spectrum (ΣI_i). The value of this dimensionless characteristic can vary from 0 to 1 and is the fraction of nondecomposed molecular ions formed during the ionization of the studied compound.

$$W = I_{M^+}/\Sigma I_i. \tag{1}$$

2. Weighted mean mass of all ions composing the mass spectrum

$$m^+ = \Sigma m_i P_i, \tag{2}$$

where m_i and P_i are the mass and probability of the appearance of a specific ion ($P_i = I_i/\Sigma I_i$). The m^+ value cannot exceed the molecular weight of the studied substance.

3. Degree of fragmentation of complexes with the elimination of the carbonyl (α_{CO}) and arene (α_{Ar}) ligands is the fraction of eliminated ligands during dissociative ionization.[7] The value of this dimensionless characteristic, which can vary from 0 to 1, is calculated taking into account the probability of formation of all ions containing this ligand.

$$\alpha_{CO} = [3 - \Sigma nP_{ArCr(CO)_n} - \Sigma nP_{Cr(CO)_n}]/3 \quad (n = 1—3) \tag{3}$$

$$\alpha_{Ar} = 1 - \Sigma P_{ArCr(CO)_n} \quad (n = 0—3) \tag{4}$$

4. Information indices of the element composition of the starting molecule (H_M) and weighted mean element compositions of charged (H_z) and neutral fragments (H_n) formed during dissociative ionization.

The total material balance of the fragmentation of the $C_XH_YO_ZCr_K$ molecule under electron impact can be presented as follows:

$$C_XH_YO_ZCr_K{}^+ \longrightarrow C_xH_yO_zCr_k{}^+ + C_{X-x}H_{Y-y}O_{Z-z}Cr_{K-k}.$$

The number of atoms of the jth element (L_j) in the weighted mean composition of charged fragments is calculated by the formula

$$L_j = \sum_{i=1}^{k} n_{ji} P_i\,, \tag{5}$$

where n_{ji} is the number of atoms of the jth sort in the ith ion, P_i is the probability of the appearance of the ith ion, and k is the number of ions in the mass spectrum. The information indices of element composi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 930—932, June, 2001.

Table 1. Structural and mass spectral indices of $RPhCr(CO)_3$

R	Na	M_m	m^+	P_{Cr}	W	H_{MS}	α_{Ar}	α_{CO}	H_M	H_z	H_n	$(H_z + H_n)/H_M$
H	19	214	90	0.64	0.12	1.54	0.66	0.86	1.68	1.76	1.48	1.93
F	19	232	81	0.68	0.07	1.65	0.72	0.90	1.89	2.07	1.66	1.98
Cl	19	249	86	0.70	0.06	1.48	0.73	0.91	1.89	2.03	1.67	1.96
I	19	340	114	0.63	0.07	2.11	0.69	0.87	1.89	1.99	1.69	1.95
NH_2	21	229	82	0.72	0.05	1.39	0.73	0.93	1.87	1.93	1.69	1.94
Me	22	228	88	0.68	0.09	1.38	0.70	0.90	1.64	1.69	1.47	1.93
$CH=CH_2$	23	240	97	0.63	0.09	1.52	0.64	0.91	1.62	1.63	1.47	1.91
CH_2OH	23	244	91	0.55	0.06	1.79	0.55	0.94	1.69	1.80	1.51	1.96
OMe	23	244	93	0.66	0.07	1.70	0.68	0.91	1.69	1.80	1.51	1.96
Et	25	242	93	0.66	0.06	1.44	0.67	0.92	1.60	1.60	1.46	1.91
COOMe	25	272	102	0.60	0.06	2.01	0.61	0.93	1.70	1.81	1.53	1.97
cyclo-C_3H_5	26	254	96	0.61	0.03	1.72	0.63	0.95	1.59	1.55	1.46	1.90
NMe_2	27	257	107	0.58	0.06	1.73	0.61	0.90	1.76	1.74	1.63	1.92
$(CH_2OH)_2$	27	274	107	0.53	0.04	2.07	0.59	0.95	1.69	1.74	1.54	1.95
Me_3	28	256	91	0.71	0.05	1.31	0.71	0.94	1.56	1.57	1.44	1.92
Pr	28	256	121	0.48	0.08	1.81	0.48	0.91	1.56	1.45	1.49	1.87
C_3H_6Br	28	335	160	0.36	0.06	2.32	0.38	0.93	1.74	1.66	1.64	1.89
cyclo-C_4H_7	29	268	121	0.50	0.07	1.93	0.51	0.91	1.55	1.47	1.46	1.89
CMe_2OH	29	272	90	0.73	0.00	1.29	0.73	0.93	1.62	1.62	1.49	1.92
Ph	29	290	131	0.51	0.07	1.79	0.53	0.90	1.53	1.47	1.43	1.90
C_6H_4Br	29	369	81	0.76	0.01	1.20	0.90	0.93	1.69	1.92	1.53	2.04
cyclo-C_4H_7OH	30	284	165	0.24	0.08	3.18	0.33	0.92	1.60	1.46	1.56	1.89
PhO	30	306	111	0.68	0.04	1.27	0.68	0.94	1.58	1.64	1.45	1.96
CMe_3	31	270	135	0.41	0.08	1.91	0.41	0.91	1.53	1.39	1.48	1.88
Me_4	31	270	103	0.65	0.05	1.40	0.66	0.94	1.53	1.48	1.43	1.90
$C_6H_4NH_2$	31	305	156	0.43	0.09	1.95	0.43	0.87	1.68	1.61	1.59	1.90
PhCO	31	318	116	0.66	0.00	1.14	0.66	0.98	1.56	1.58	1.44	1.93
CH_2Ph	32	304	157	0.40	0.07	1.48	0.41	0.92	1.51	1.36	1.46	1.87
C_6H_4COOH	32	334	140	0.38	0.06	2.72	0.45	0.90	1.60	1.69	1.46	1.97
$(C_2H_4OH)_2$	33	302	113	0.45	0.01	2.50	0.45	0.98	1.62	1.57	1.52	1.91
$PhCH=CH$	33	316	155	0.46	0.06	1.64	0.47	0.91	1.49	1.39	1.43	1.89
C_6H_4COMe	34	332	87	0.76	0.01	1.15	0.84	0.96	1.54	1.72	1.41	2.03
PhC_2H_4	35	318	187	0.24	0.06	1.53	0.24	0.94	1.49	1.29	1.49	1.87
C_6H_4NHAc	36	347	98	0.70	0.00	1.36	0.75	0.98	1.68	1.77	1.56	1.98
cyclo-$C_6H_4CHC_6H_4$	38	376	197	0.43	0.05	1.58	0.43	0.92	1.41	1.29	1.37	1.89
p-$CMeOHC_6H_4$	39	348	184	0.32	0.08	2.68	0.32	0.90	1.51	1.42	1.49	1.92
cyclo-C_6H_4CHPh	40	378	172	0.51	0.05	1.54	0.52	0.94	1.42	1.32	1.37	1.90
$C_6H_4SnPh_2$	52	563	278	0.32	0.04	2.44	0.34	0.95	1.48	1.40	1.43	1.92
Br	19	293	99	0.68	0.05	1.62	0.75	0.93	1.89	1.99	1.68	1.94
trans-C_5H_7Cl	30	315	150	0.42	0.07	2.29	0.42	0.92	1.70	1.56	1.65	1.88
cis-C_5H_7Cl	30	315	154	0.32	0.08	2.21	0.32	0.92	1.70	1.54	1.67	1.88

* All mass spectral indices were calculated from the mass spectra reduced to the monoisotopic composition using the AELITA program.[8]

tions containing l elements are calculated using the Shannon formula

$$H_i = -\sum_{j=1}^{l}(n_{ji}/N)\log_2(n_{ji}/N), \qquad (6)$$

where n_{ji} and N are the number of atoms of the jth sort in the ith ion and the total number of atoms in the ith molecular formula. They are expressed in information units (bits) and are the quantitative measure of complexity of the element composition of the corresponding molecule.

5. Information index of mass spectrum (H_{MS}). From the point of view of the information theory, the mass spectrum is the distribution of probabilities of formation of ions of each sort (P_i). Substituting the values of these probabilities into the Shannon formula, we obtain the amplitude information index H_{MS}, which, as other mass spectral indices presented above, is the integral characteristics of the reactivity of the studied molecule under the conditions of its fragmentation by electron impact[6]:

$$H_{MS} = -\Sigma p_i \log_2 P_i. \qquad (7)$$

The indices, molecular weights (M_m), and the number of atoms in the molecule (N_a) are presented in Table 1.

Table 2. Parameters of the linear regression $Y = a + bX$

Equation	X	Y	b	a	S_b	S_a	S_Y	r	n
1	M_m	m^+	0.612	−53.93	0.042	12.44	15.37	0.931	35
2	W	α_{CO}	−0.983	0.984	0.063	0.004	0.009	0.938	35
3	P_{Cr}	α_{Ar}	1.060	−0.014	0.025	0.014	0.022	0.989	39
4a	Na	α_{Ar}	−0.020	1.115	0.002	0.043	0.046	0.937	26
4b	Na	α_{Ar}	−0.016	1.158	0.001	0.023	0.014	0.996	7
5a	H_{MC}	α_{Ar}	−0.329	1.161	0.018	0.031	0.034	0.973	25
5b	H_{MC}	α_{Ar}	−0.277	1.192	0.024	0.052	0.043	0.971	10
6	H_{M}	H_z	1.591	−0.963	0.080	0.131	0.062	0.960	35
7	H_{M}	H_n	0.616	0.504	0.042	0.068	0.032	0.932	35
8	H_{M}	$H_z + H_n$	2.167	−0.402	0.057	0.094	0.045	0.987	39

Note. S_b, S_a, and S_Y are the standard errors for the regression coefficients a, b, and Y, respectively; r is the correlation coefficient; and n is the number of points.

The linear correlations between some indices were established (Table 2) using the regression analysis (performed by the EXCEL program package) of these data.

The weighted mean mass m^+ depends linearly on the molecular weight (see Table 2, Eq. (1)). Since the m^+ value can easily be calculated from the mass spectrum, this correlation can be used for the estimation (with an accuracy of ~5%) of the molecular weight of benzenetricarbonylchromium derivatives nonstable to electron impact, whose mass spectra do not contain a peak of the molecular ion (among 41 compounds studied in this work, we met two such cases).

The correlation between the W and α_{CO} values (see Table 2, Eq. (2)) indicates that the stability of the molecular ions of the benzenetricarbonylchromium derivatives is completely determined by the low-energy elimination of the carbonyl groups. This follows from the values of regression coefficients a and b, which are equal to unity within an error. This implies that, in the limiting case where $W = 0$, the degree of carbonylation is equal to 1, *i.e.*, all carbonyl ligands are completely eliminated.

Another correlation between the mass spectral characteristics concerns P_{Cr} and α_{Ar} (see Table 2, Eq. (3)). The regression coefficients a and b are equal to 0 and 1, respectively, within an error. It follows from this that the Cr^+ ions are formed almost exclusively by the fragmentation of the ArCr^+ ions and only to an insignificant extent due to $\mathrm{Cr(CO)}_n{}^+$ decomposition.

We have previously[9] established a linear plot of the logarithm of the ratio of intensities of the peaks of the ions $[\mathrm{Cr}^+]/[\mathrm{ArCr}^+]$ in the mass spectra of the benzenetricarbonylchromium derivatives and the number of vibrational degrees of freedom of the corresponding molecules ($3N_{\mathrm{a}} - 6$). A similar correlation exists between α_{Ar} and N_{a} (see Table 2, Eqs. (4a), (4b)).

According to the quasi-equilibrium theory of mass spectra, the degree of fragmentation of molecules under electron impact is affected, along with the number of vibrational degrees of freedom, by the activation energy of the reaction and the vibrational frequency of the cleaved bond,[10] which can differ in the series of compounds under study. Precisely this situation explains the existence of two linear correlations between α_{Ar} and N_{a} similarly to that observed for the correlation between $\ln([\mathrm{Cr}^+]/[\mathrm{ArCr}^+])$ and N_{a}.[9] At the same time, the existence of this correlation indicates that the number of atoms in the molecule is the main factor that affects the elimination of the arene ligand.

The α_{Ar} value also correlates linearly with the mass spectral index H_{MS} (see Table 2, Eqs. (5a), (5b)), *i.e.*, a change in the information content of mass spectra of the benzenetricarbonylchromium derivatives is determined by their fragmentation with the Ar—Cr bond cleavage. By contrast, the α_{CO} value, which characterizes another pathway of decomposition (with the elimination of carbonyl groups) is almost independent of the nature of the R substituent (see Table 1) and, hence, makes a constant contribution to a change in H_{MS}.

A linear correlation was also found between the information indices of element compositions of the starting molecule (H_{M}) and weighted mean element compositions of the charged (H_z) and neutral fragments (H_n) (see Table 2, Eqs. (6)—(8)). The ratio $(H_z + H_n)/H_{\mathrm{M}} = 1.93\pm0.04$ remains virtually unchanged for all compounds studied (see Table 2), *i.e.*, the total information content of the weighted mean element compositions of the neutral and charged products appeared during the fragmentation of the benzenetricarbonylchromium derivatives is doubled compared to the information content of the starting molecule. Eight derivatives $\mathrm{RPhCr(CO)_2PPh_3}$, which have the same value $(H_z + H_n)/H_{\mathrm{M}} = 1.94\pm0.01$, are also characterized by a similar regularity.

The results obtained indicate the adequate character of the proposed approach for the quantitative estimation of the reactivity of molecules under their dissociative ionization and establishment of the structure—reactivity correlations.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32814a) and INTAS (Grant 99-00478).

References

1. V. A. Skorobogatov, E. V. Konstantinova, Yu. S. Nekrasov, Yu. N. Sukharev, and E. E. Tepfer, *Commun. Math. Chem. (MATCH)*, 1991, 215.
2. Yu. N. Sukharev, Yu. S. Nekrasov, N. S. Molgachova, and E. E. Tepfer, *Org. Mass Spectrom.*, 1993, **28**, 1555.
3. Yu. S. Nekrasov, E. E. Tepfer, and Yu. N. Sukharev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 381 [*Russ. Chem. Bull.*, 1993, **42**, 343 (Engl. Transl.)].
4. Yu. S. Nekrasov, N. S. Molgacheva, Yu. N. Sukharev, E. E. Tepfer, and S. Yu. Nekrasov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2073 [*Russ. Chem. Bull.*, 1993, **42**, № 12 (Engl. Transl.)].
5. Yu. S. Nekrasov, E. E. Tepfer, Yu N. Sukharev, V. A. Skorobogatov, and E. V. Konstantinova, *Teoriya grafov i ee prilozheniya* [*Theory of Graphs and its Applications*], Novosibirsk, 1994, Issue 151, 88 (in Russian).
6. Yu. S. Nekrasov, Yu. N. Sukharev, E. E. Tepfer, and N. S. Molgacheva, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2683 [*Russ. Chem. Bull.*, 1996, **45**, 2542 (Engl. Transl.)].
7. Yu. S. Nekrasov, D. V. Zverev, and A. I. Belokon′, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1374 [*Russ. Chem. Bull.*, 1998, **47**, 1336 (Engl. Transl.)].
8. Yu. N. Sukharev and Yu. S. Nekrasov, *Org. Mass Spectrom.*, 1976, **11**, 1232.
9. Yu. S. Nekrasov and N. I. Vasyukova, *Org. Mass Spectrom.*, 1979, **14**, 422.
10. K. Levsen, *Fundamental Aspects of Organic Mass Spectrometry*, Verlag Chemie, New York, 1978.

Received October 10, 2000