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Short Communication

THERMAL BEHAVIOUR OF BENZENESULFENAMIDES AND OF THEIR CHROMIUM CARBONYL COMPLEXES

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Abstract

Benzenesulfenamides with the formula R–S–N–(R′)$_2$ (R=C_6H_5 and R'=NC_4H_8O, C_7H_7 and C_6H_{11}) and their chromium carbonyl complexes were studied by means of TG and mass spectrometric methods. The thermal behaviour of the compounds the stabilities of free sulfenamides are lower than those observed for the corresponding chromium carbonyl complexes. Combined thermogravimetry – mass spectrometry results suggest that the fragmentation mechanism of the carbonyl complexes involves cleavage of the Cr–S and Cr–CO bonds while that of sulfenamide depends mainly on the dissociation rates of the NR_2 groups.

Keywords: chromium carbonyl complexes, sulfenamide complexes, thermal analysis

Introduction

Although chromium carbonyl complexes with S–N compounds in which the metal-ligand bond occurs *via* the sulphur atom are relatively rare [1, 2], some systematic studies on the coordinating properties of such kind of compounds have lead to the synthesis of a series of metal complexes bonded *via* the sulfur atom [3–7].

Notwithstanding the lone pair of electrons on the sulfur atom, the nucleophilicity of benzenesulfenamides is rather low, probably due to the partial double bond character of the S–N linkage [4, 5]. These compounds are, how-

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ever, capable of acting as weak π-acceptor ligands. Their π-acceptor capacity, arising probably from the presence of free d-orbitals on the sulfur atom, is indeed enough for leading to the formation of the carbonyl complexes *via* this atom. The synthesis and crystal structure of the pentacarbonyl-(N,N-dicyclohexyl-benzenesulfenamide)chromium(0) complex described recently [7] have confirmed such kind of coordination.

In this paper, the thermal behaviour and mass spectral fragmentation of the following series of N,N-sulfenamides(I–III), as well as those of their pentacarbonyl chromium complexes(IV–VI), are reported,

$C_6H_5SNR_2$ (I - III)

$(CO)_5CrS(C_6H_5)NR_2$ (IV - VI)

I, IV NR_2 = morpholine
II, V NR_2 = dicyclohexylamine
III, VI NR_2 = dibenzylamine

Experimental

The sulfenamides were prepared according to literature procedures [6]. Chromium carbonyl complexes were synthesized as previously reported [3, 6] from $Cr(CO)_6$ and the corresponding ligand by photochemical substitution.

The thermal stability was investigated using a Netzsch thermal balance. Thermogravimetric (TG) and absolute pressure measurements were made in ceramic crucibles at heating rates of 5 K min^{-1}, by continuously recording the

Table 1 Thermal stabilites of sulfenamides of the type $R^1SNR^2R^3$ and of their carbonyl complexes

Sulfenamides			
R^1	R^2, R^3	T/K	References
2-Acetamidoethyl	2-Benzothiazolyl, H	428	10
2-Acetamidoethyl	Morpholine	413	10
2-Acetamidoethyl	o-Phthaloyl	428	10
n-Butyl	Piperidine	413	10
t-Butyl	Ethyl, Ethyl	373	10
Phenyl	Morpholine	313	Present work
Phenyl	Dicyclohexyl	313	Present work
Phenyl	Dibenzyl	313	Present work
Complexes			
$Cr(CO)_5S(C_6H_5)NC_4H_8O$		333	Present work
$Cr(CO)_5S(C_6H_5)N(C_6H_{11})_2$		339	Present work
$Cr(CO)_5S(C_6H_5)N(CH_2C_6H_5)_2$		331	Present work

mass loss rates. Vapour species evolved during the decomposition of the compounds were identified by using a quadrupole mass spectrometer (Extranuclear Laboratoires, Pittsburgh). Mass spectra were taken in the range 310–570 K with an ionizing electron energy of 70 eV.

Results and discussion

All the compounds described in this work have TG curves pointing to the same decomposition pattern. They decompose in a continuous manner without any breaks along their thermolysis curves which could be assigned to the formation of some stable intermediates.

The observed decomposition temperatures are reported in Table 1. With respect to the decomposition of free sulfenamides begin around 313 K, while the complexes decompose at higher temperatures, namely at about 330 K. Comparing with the decomposition temperatures of other derivatives (Table 1), the thermal stabilities of the benzenesulfenamides I–III appear to be relatively low, probably due to the influence of the phenyl group on the S–N bond.

Mass spectroscopic analyses of the decomposition products of the studied compounds are reported in Table 1. Comparison of the spectra of the free sulfenamides with those of the respective complexes shows that under these conditions i.e. at temperatures above the decomposition points of the products, the organic pyrolysis products are in general the same.

The fragmentation of free sulfenamide is rather complex, particularly due to the presence of many strong ions derived from the organic groups *R* and *R'*. Although the peaks corresponding to R'_2N generally have low intensities, the fragments characteristic of the respective amines [8] are always clearly observed. The presence of the ion $C_6H_5S^+$ ($m/z=109$) points to processes characterized by the cleavage of nitrogen–sulfur bonds.

Table 2 Mass spectra of a sulfenamide and its chromium carbonyl complexes at temperatures above the descomposition point*

	Compounds						
Ionic species**	*m/z*	I	II	III	IV	V	VI
$C_6H_5SNCH_2C_6H_5$	215	–	–	4	–	–	–
$C_6H_5SNC_6H_{11}$	207	–	1	–	–	–	–
$(C_6H_{11})_2N$	181	–	2	–	–	–	–
$C_6H_5SNC_3H_6$	165	–	8	–	–	–	–
$C_6H_5SNCH_3$	138	–	12	4	–	5	–
C_6H_5SNCH	136	20	–	–	3	–	–
$(CO)_3Cr$	136	–	–	–	5	5	2
$C_6H_5SNH_2$	125	–	12	–	–	–	–

Table 2 Continued

	Compounds						
Ionic species**	*m/z*	I	II	III	IV	V	VI
C_6H_5SN	123	6	–	–	2	–	–
$C_7H_7NCH_3$	120	–	–	–	–	–	19
C_7H_7NCH	118	–	–	–	–	–	14
C_6H_5S	109	59	12	13	10	12	5
$(CO)_2Cr$	108	–	–	–	6	79	5
$C_6H_5CH_2N$	106	–	–	–	–	–	17
C_6H_5CHN	105	–	–	9	–	–	–
$C_6H_{11}N$	98	–	31	–	–	1	–
$C_6H_5CH_2$	92	–	–	–	–		100
C_6H_5CH	91	–	–	100	–	–	–
$C_4H_8ONH_2$	86	10	–	–	29	–	–
C_6H_{11}	83	–	30	–	–	–	–
C_6H_9	81	–	–	–	–	24	–
$(CO)Cr$	80	–	–	–	9	100	15
C_6H_5	77	3	5	5	–	12	31
C_6H_9	69	10	10	–	–	–	–
C_6H_8	68	–	–	–	–	12	–
C_5H_5	65	25	8	17	10	–	95
C_5H_4	64	–	–	–	–	14	–
C_4H_7	55	–	100	–	–	–	–
C_3H_6N	56	100	–	–	53	–	–
Cr	52	–	–	–	19	100	15
C_4H_3	51	–	–	–	–	–	29
C_3H_6	42	17	–	–	7	–	–
C_3H_5	41	–	–	–	–	–	12
C_3H_4	40	–	64	98	–	16	–
C_3H_3	39	–	–	–	–	–	29
S	32	–	–	33	–	–	–
CO	28	–	–	–	100	90	8
CHO	28	57	–	–	–	–	–

*The temperatures of the spectra are follows: I:349 K; II:327 K; III: 320 K; IV: 342 K; V: 341 K, VI: 353K.

**Unless otherwise indicated, all ions are singly charged.

In general, considerable difficulties were experienced in obtaining mass spectra of the carbonyl complexes; even at low temperature, electron impact often causes rapid decomposition of the $Cr(CO)_5$ fragment. However, sufficient information was obtained to understand the fragmentation of these complexes as that shown in Table 2. Moreover, information about the thermal decomposition mechanism of the complexes can be supplemented by comparing the mass spectra of the pyrolysed species with those of the unpyrolysed ones.

The main features of the mass spectra under these two sets of conditions are summarized in Table 3.

At high temperature, sulfur-containing fragments are in general scarce, the thione species $C_6H_5S^+$ [8] being the most important. Fragments $C_6H_5{-}S{-}NCH_n$ $n=1, 2, 3$ [9] involving C–N and C–C bond cleavages, can also be detected in the high temperature spectra.

At temperatures lower than the decomposition point, a series of fragments characteristic of chromium carbonyl sulfur complexes [6] can be observed. Under these conditions, where the temperatures exceed the respective

Table 3 Mass spectrum at temperatures below and above the decomposition point[a] for the complex $Cr(CO)_5(C_6H_5\text{-}SN(C_6H_{11}))_2$

Fragment	Intensity[b]		
	m/z	Ib	Ia
$Cr(CO)_5(R{-}SNR_2)$	481	1.5	–
$Cr(CO)(R{-}S{-}NR_2)$	369	0.6	–
$Cr(R{-}S{-}NR_2)$	341	4.7	–
$R{-}S{-}NR_2$	289	31.2	–
$Cr(CO)_4$	164	13.3	–
$C_6H_5{-}S{-}N{-}CH_3$	138	–	5
$Cr(CO)_3$	136	9.5	5
C_6H_5SH	110	12	–
C_6H_5S	109	10	12
$Cr(CO)_2$	108	–	79
$C_6H_{11}N$	98	24.8	1
C_6H_{11}	83	25.4	–
$Cr(CO)$	80	3.3	100
C_6H_5	77	4.4	12
C_5H_8	68	3.2	12
C_3H_5N	56	14.1	–
CO	28	100	90

a. Decomposition temperature, 339 K

b. Intensity of mass spectrum at 320 K(Ib) and at 353 K(Ia) decomposition points of the free sulfenamides, the latter are, however, detected by the spectra, in agreement with the stabilization effect of the carbonyl chromium coordination deduced from thermal stability measurements described above. This effect contrast with the effect of the coordination on the sulfenamides S–N bond which, as evidenced by IR [6] and X-ray diffraction analysis [7], became weaker after interaction with the metal. This fact indicates that the decomposition mechanism of sulfenamides is mainly governed by the dissociation rate of the NR_2 groups into the R^+ ions which, as mentioned above, are always well represented in the mass spectra of these compounds.

The most probable mechanism for the thermal decomposition of chromium carbonyl complexes thus involves cleavage of the Cr–S and Cr–CO bonds followed by the classical fragmentation pattern of the sulfenamides [10].

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