

REACTIONS OF CHROMOCENE WITH DIOLS AND SOME THEIR DERIVATIVES

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Chromocene reacts with diols having OH groups at 1,3 position or at a greater distance to give chromium(II) diolates. Only the chromium(II) diolates obtained from reactions with 1,2-diols give the chromium(III) diolates with excess of the reagent. Alkylation of one of these hydroxyl groups, however, prevents the oxidation-reduction course. The reaction of chromocene with 2-chloroethanol gives chromium(II) 2-chloroethanolate in the first step, chromium(III) 2-chloroethanolate being the final reaction product.

Reaction of chromocene with hydroxy compounds (as that with other compounds containing active hydrogen atom) involves elimination of cyclopentadiene rings. Solid products of the reaction of chromocene with aliphatic alcohols are chromium(II) alcoholates¹, chromium(III) amino alcoholate is formed with 2-aminoethanol², with 2-(N,N-diethylamino)ethanol, however, the reaction gives the corresponding chromium(II) amino alcoholate. Acetylacetone³ reacts with chromocene to give chromium(II) acetylacetonate which, further, gives chromium(III) acetylacetonate in excess acetylacetone. Also the reaction of chromocene with hydroxyl groups of silica⁴, which represents the basis of preparation of the catalyst for ethylene polymerization, is accompanied by elimination of one or both the rings. However, the fundamental requirement made on an active polymerization centre is preservation of the chromium atoms at the +II oxidation state. Investigation of interaction of chromocene with diols and their derivatives should contribute to elucidation of reaction course of chromocene with hydroxy compounds from the point of view of effects of the presence of another functional group at the aliphatic chain on the oxidation state of chromium in the solid reaction products.

EXPERIMENTAL

Preparations

Chromocene was prepared and purified by the procedures described elsewhere¹, the diols and their derivatives were purified and dried by repeated distillation or vacuum sublimation. The reactions of chromocene with diols were carried out in evacuated ampoules with sealed extensions allowing

removal of excess diol by distillation or sublimation and preparation of the sample for magnetic measurements and analyses. Fine crystalline chromocene (0.01 mol) reacted with liquid diols (0.2 mol) at room temperature, the solid diols reacted in melt.

Analyses

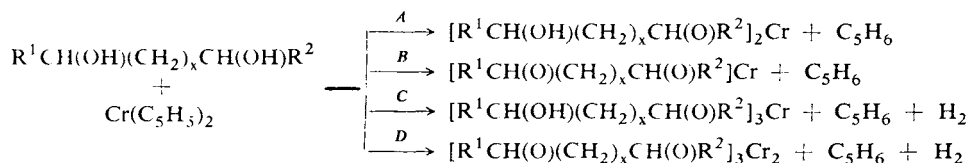
Chromium content in the solid products was determined (after their decomposition by melting with alkaline-oxidation mixture) spectrophotometrically (CrO_4^{2-} , $\lambda = 400 \text{ nm}$). Carbon and hydrogen content was determined by classical combustion analysis. The analyses of products are given in Table I. For separation and identification of the gaseous products we used a Fractovap GV 200 gas chromatograph with flame ionisation detector and a Chrom IV apparatus with a heat conductivity sensor¹. The presence of hydroxyl groups in the products was proved by the IR spectra measured in Nujol with the use of a Specord IR 75 apparatus.

Magnetic Measurements

The oxidation state of chromium in the solid reaction products was determined from the magnetic moments calculated from the Curie-Weiss equation on the basis of the measured temperature dependence of molar magnetic susceptibility. The magnetic susceptibility was measured within the temperature interval from 90 to 300 K using a Variable Temperature Gouy Balance (Newport Instruments, England)¹. The found values of molar magnetic susceptibilities were corrected with respect to diamagnetism.

RESULTS AND DISCUSSION

Liquid diols react with fine crystalline chromocene at room temperature already, the reaction with solid diols does not proceed until in their melt. The lowest temperature at which the solid reaction products were isolated was given by the temperature at which the excess diol was removed by distillation or sublimation. All the solid products were insoluble in usual polar and non-polar solvents, hence the products could not be separated in the cases of formation of mixtures. The reaction course of chromocene with diols can be represented by Scheme 1.



SCHEME 1

If both the hydroxyl groups are on adjacent carbon atoms (compounds *I*, *II*), then the reactions taking place at room temperature lead predominantly to products type *A* and *B*, since in gaseous products only slight amount of hydrogen could be found (the blue reaction products were not isolated). This type of reaction is significant up to 75°C which is documented by magnetic moments of the solid reaction product

TABLE I
Composition of the products

Compound Diol of derivative	$t, ^\circ\text{C}$	Solid products				Gaseous products
		type ^a (M_r)	calculated/found			
			% Cr	% C	% H	
<i>I</i> 1,2-Ethanediol	—	<i>A</i> (174·12)	29·87	27·60	5·79	
	—	<i>B</i> (112·05)	46·41	21·44	3·60	
	—	<i>C</i> (235·18)	22·11	30·64	6·43	
	—	<i>D</i> (284·15)	36·60	25·36	4·26	
	70	—	32·38	27·65	5·92	} $\text{C}_5\text{H}_6, \text{H}_2$
150	—	37·14	24·33	4·38		
<i>II</i> 1,2-Propanediol	—	<i>A</i> (202·17)	25·72	35·65	6·97	
	—	<i>B</i> (126·08)	41·24	28·58	4·80	
	—	<i>C</i> (277·26)	18·75	38·99	7·63	
	—	<i>D</i> (326·24)	31·82	33·14	5·56	
	75	—	26·29	36·37	7·30	} $\text{C}_5\text{H}_6, \text{H}_2$
150	—	30·35	34·73	5·48		
<i>III</i> 1,3-Butanediol	—	<i>A</i> (230·23)	22·59	41·74	7·88	
	—	<i>B</i> (140·11)	37·12	34·30	5·76	
	80	—	31·11	37·42	6·65	} C_5H_6
150	—	35·10	35·35	6·11		
<i>IV</i> 1,4-Butanediol	—	<i>A</i> (230·23)	22·59	41·74	7·88	
	—	<i>B</i> (140·11)	37·12	34·30	5·76	
	130	—	30·71	37·65	6·69	} C_5H_6
	190	—	36·88	34·06	5·85	
<i>V</i> 2,2-Dimethyl- -1,3-propanediol	—	<i>A</i> (258·28)	20·13	46·50	8·58	
	—	<i>B</i> (154·13)	33·73	38·96	6·54	
<i>VI</i> 1,6-Hexanediol	130	—	27·47	42·41	7·38	C_5H_6
	—	<i>B</i> (168·16)	30·92	42·85	7·19	
<i>VII</i> 2-Butyne-1,4-diol	130	—	30·57	40·26	7·28	C_5H_6
	—	<i>C</i> (136·12)	16·92	46·91	4·92	
<i>VIII</i> 2-Ethoxyethanol	130	—	16·92	47·10	4·79	$\text{C}_5\text{H}_6, \text{H}_2$
	—	(R^3O) ₂ Cr ^b (230·23)	22·58	41·74	7·88	
<i>IX</i> 2,2'-Oxybisethanol	35	—	22·28	41·51	8·05	C_5H_6
	—	<i>B</i> (156·11)	33·30	30·78	5·17	
<i>X</i> 2-Chloroethanol	160	—	33·12	30·57	5·18	C_5H_6
	—	(R^4O) ₂ Cr ^c (211·01)	24·64	22·77	3·82	
	—	(R^4O) ₃ Cr ^c (290·52)	17·90	24·81	4·16	
	15	—	24·43	23·05	3·59	C_5H_6
	20	—	17·65	24·72	4·33	$\text{C}_5\text{H}_6, \text{H}_2$

^a *A, B, C, D* see Scheme 1, $\text{R}^1 \text{R}^2 = \text{H, alkyl}$; ^b $\text{R}^3 = \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2$; ^c $\text{R}^4 = \text{ClCH}_2\text{CH}_2$.

(Table II). At 150°C, however, the oxidation-reduction course of the reactions is decisive, magnetic moments of the solid products approach the theoretical value for three unpaired electrons belonging to chromium atoms in +III oxidation state, the reaction products being stable in air. The hydroxyl groups were proved by a broad band whose maximum was found within the interval 3 360–3 260 cm⁻¹ for the products *A*, *C*. This band was absent in the products type *B*, pure product *D* was not isolated.

The 1,3 position at an aliphatic chain secures, even at 150°C, that the two hydroxyl groups will behave as in monohydroxy compounds, *i.e.* chromium(II) alcoholates are formed (compound *III*). The same reaction was also observed with the diols having the two hydroxyl groups separated by a longer saturated chain (*IV*, *V*, *VI*).

The oxidation of chromium(II) to Cr(III) was observed with saturated aliphatic diols at higher temperatures in such case only when the two hydroxyl groups were located at adjacent carbon atoms (*I*, *II*). For the reactions taking place without a change of oxidation state of chromium we could calculate molar ratio of the products type *A* and *B* (*III*–*VI*). In all the cases the products type *A* were predominant at lower temperatures, whereas at higher temperatures the both hydroxyl groups reacted to 70–100% extent (type *B*).

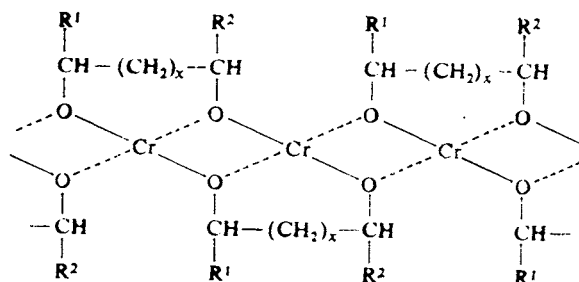
TABLE II
Properties of the solid products

Compound	<i>t</i> , °C	Colour	Type ^a , mol%	Magnetic moment	Weiss constant K
<i>I</i>	70	light blue	<i>A</i> + <i>B</i> + <i>C</i> + <i>D</i>	4.48	165
	150	greenish blue		4.18	121
<i>II</i>	75	light blue	<i>A</i> + <i>B</i> + <i>C</i> + <i>D</i>	4.01	168
	150			3.91	125
<i>III</i>	80	bluish violet	30% <i>A</i> , 70% <i>B</i>	5.49	482
	150		11% <i>A</i> , 89% <i>B</i>	5.35	435
<i>IV</i>	130	light violet	32% <i>A</i> , 68% <i>B</i>	5.07	330
	190		100% <i>B</i>	4.84	212
<i>V</i>	130	light blue	34% <i>A</i> , 66% <i>B</i>	4.97	393
<i>VI</i>	130	ochre	100% <i>B</i>	5.08	287
<i>VII</i>	130	light green	100% <i>C</i>	3.81	295
<i>VIII</i>	35	pink	100% (R ³ O) ₂ Cr	4.73	270
<i>IX</i>	160	light violet	100% <i>B</i>	5.09	269
<i>X</i>	15	pink	100% (R ⁴ O) ₂ Cr	4.79	276
	20	green	100% (R ⁴ O) ₃ Cr	3.67	238

^a See footnotes in Table I.

The reaction of chromocene with 2-butyne-1,4-diol (VII) at 130°C gave chromium(III) monoalcoholate as the only solid product. The presence of multiple bond in the chain between the hydroxyl groups has thus fundamental effect on the reaction course, since the interaction of chromocene with 1,4-butanediol had no redox character even at 190°C.

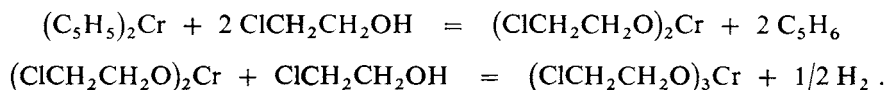
High values of the Weiss constants (Table II) for all the chromium(II) and chromium(III) alcoholates indicate extensive chaining of the individual paramagnetic centres by means of oxygen bridges. This idea is also supported by their insolubility in water and in usual organic solvents. Thus the formulae given in the reaction scheme represent only stoichiometric units from which polynuclear bridged structures are formed (Scheme 2).



SCHEME 2

Effect of another substituent in aliphatic monohydroxy compounds on the oxidation state of chromium in the products of their reactions with chromocene can also be followed in interactions of chromocene with some derivatives of diols. The reaction of chromocene with 2-ethoxyethanol gives chromium(II) 2-ethoxyethoxide ($C_2H_5 \cdot OCH_2CH_2O)_2Cr$ (VIII) as the only reaction product. Thus alkylation of one of the hydroxyl groups prevented the oxidation-reduction process characteristic for vicinal diols (I, II). Also the reaction with 2,2'-oxybisethanol (IX) had no redox character the two hydroxyl groups being separated by sufficiently long chain with inactive oxygen atom.

The reaction of chromocene with 2-chloroethanol proceeded in two steps. After 10 min at 15°C, pink-violet chromium(II) 2-chloroethoxide was isolated which, however, changed into green chromium(III) 2-chloroethoxide in excess 2-chloroethanol at 20°C. The two subsequent reactions can be expressed as follows:



Most probably, a similar two-step process also takes place in the reactions of chromocene with 1,2-diols which proceed as reduction-oxidation processes at higher temperatures.

The pink chromium(II) 2-chloroethanolate gave a grey-blue compound of the same composition after longer storage in vacuum or immediately on heating. The found magnetic moment again, indicates the chromium oxidation state + II which agrees with high sensitivity to the presence of oxygen. The Weiss constant is almost doubled which is probably due to a more perfect chaining of chromium atoms, and the coordination change is also supported by the colour change.

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