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REACTION OF CHROMOCENE WITH CARBOXYLIC ACIDS AND SOME DERIVATIVES OF ACETIC ACID

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Summary

Crystalline chromocene reacts at 40°C with an excess of formic acid to give $Cr(O_2CH)_3 \cdot HCOOH$, cyclopentadiene and hydrogen. Aliphatic carboxylic acids $C_nH_{2n+1}COOH$ ($n = 2$–4) give nearly diamagnetic chromium(II) carboxylates and cyclopentadiene. Acetic anhydride gives chromium(II) acetate, and acetamide and *N*-ethylacetamide give diamagnetic compounds of the type $Cr(NRCOCH_3)_2$ ($R =$ H, C_2H_5) with elimination of cyclopentadiene.

Introduction

The products of the reactions of chromocene with inorganic acids depends on the conditions and the reactions can result in the elimination of one or both cyclopentadienyl rings and in the oxidation of chromium(II) to chromium(III) [1–4]. Organic acids studied include trimethylacetic acid [5,6] in benzene, benzoic acid in toluene, and anthracene-9-carboxylic acid in 1,2-dimethoxyethane [5], the products were the dinuclear complexes $Cr_2(O_2CR)_4 \cdot 2RCOOH$, or, in the case of dimethoxyethane, $Cr_2(O_2CR)_4 \cdot DME$. The reaction of chromocene with trifluoroacetic acid can also lead to elimination of one or both rings, depending on the conditions, in a redox process [7–9]. We describe below the reactions of chromocene with aliphatic carboxylic acids C_1–C_4 in completion of our study of reactions of chromocene with compounds containing the hydroxyl group [10–13], and also report on the reactions with acetic anhydride, acetamide, and *N*-ethylacetamide.

Results and discussion

Chromocene reacts with formic acid to form the blue solid $CrC_4H_5O_8$, cyclopentadiene, and hydrogen. The temperature dependence of the reciprocal of the corrected molar magnetic susceptibility indicates that the solid is antiferromagnetic, the value of the Weiss constant being 57 K. The calculated value of the magnetic

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TABLE 1

MAGNETIC MOMENTS OF THE REACTION PRODUCTS

	$\mu_{-180°C}$(BM)	$\mu_{20°C}$(BM)
$Cr(O_2CH)_3 \cdot HCOOH$		3.87 [a]
$Cr(OC_2CH_3)_2 \cdot CH_3COOH$	0.47	0.66
$Cr(O_2CCH_3)_2$	0.52	0.60
$Cr(O_2CC_2H_5)_2$	0.31	0.45
$Cr(O_2CC_3H_7)_2$	0.21	0.31
$Cr(NHCOCH_3)_2$	[b]	0.07
$Cr[N(C_2H_5)COCH_3]_2$	[b]	0.13

[a] Calculated from the Curie–Weiss equation. [b] $\chi_M^{kor} < 0$.

moment (Table 1) corresponds to the spin contribution of three unpaired electrons (d^3) of chromium(III) atoms. The IR spectrum indicated that no cyclopentadienyl rings were present in the solid. A band at 3350 cm^{-1} showed the presence of an OH group. The bands found in the C=O stretching vibrations region could be assigned to C=O groups of formic acid and formate. All the data correspond to a compound with the composition $Cr(HCOO)_3 \cdot HCOOH$. The reaction can therefore be represented by equation 1.

$$Cr(C_5H_5)_2 + 4\ HCOOH \rightarrow Cr(O_2CH)_3 \cdot HCOOH + 2\ C_5H_6 + 1/2\ H_2 \qquad (1)$$

Reactions of chromocene with acetic acid, propanoic acid and butanoic acid give solid products and cyclopentadiene only. In view of the absence of hydrogen in the products we conclude that the reactions are not of the redox type. Heating of the solid $CrC_6H_{10}O_6$, obtained by the reaction of chromocene with acetic acid and isolated at 60°C, gave a dark orange solid $CrC_4H_6O_4$ with elimination of CH_3COOH. Thus, all the final solid products of the reactions of chromocene with the three acids are chromium(II) carboxylates. The observed magnetic moments show these compounds to be almost diamagnetic (Table 1). Chromium(II) carboxylates were prepared previously by interaction of chromium(II) chloride and sodium carboxylate [14,15] and the values of their magnetic moments were found to be 0.50–0.73 BM. The diamagnetism of these dimeric solvates [16–18] and polymeric unsolvated chromium(II) acetate [19] was explained in terms of an overlap of *d*-orbitals of chromium atoms. All the observations indicate that the reactions of chromocene with aliphatic carboxylic acids have the form shown in eq. 2

$$Cr(C_5H_5)_2 + 2\ RCOOH \rightarrow Cr(O_2CR)_2 + 2\ C_5H_6$$

$$(R = CH_3, C_2H_5, C_3H_7) \qquad (2)$$

The stability of these carboxylates in air decreases with increasing length of their carbon chain.

Chromocene reacts with acetic anhydride to form a solid $CrC_4H_6O_4$, cyclopentadiene, methane, ethane and an unidentified volatile compound. No formation of hydrogen was noticed. The solid was found to be nearly diamagnetic (Table 1), its IR spectrum was almost identical with that of the product of the reaction of chromocene and acetic acid and with that of chromium(II) acetate [20]. X-ray powder diffractograms showed that the solid obtained from chromocene and acetic anhydride was identical with that from chromocene and acetic acid. (The intensities of the diffraction peaks of the product from the anhydride was low and so some weak peaks were not observed.) The only solid product of the reaction of chromocene with acetic anhydride is chromium(II) acetate.

The reaction of chromocene with acetamide gives a diamagnetic solid $CrC_4H_8N_2O_2$ with elimination of cyclopentadiene. The IR spectrum of this solid shows the presence of an NH group (a sharp band at 3362 cm^{-1} instead of two broad bands of the NH_2 group in acetamide at 3350 and 3180 cm^{-1}). The most intense C=O stretching band is shifted from 1672 cm^{-1} in acetamide to 1580 cm^{-1}. Two sharp bands at 691 and 663 cm^{-1} are found instead of the intense broad band at 700 cm^{-1} (NH_2 wag), and the sharp band at 580 cm^{-1} (OCN) has been replaced by two bands at 600 and 560 cm^{-1}. The spectrum showed that no cyclopentadienyl rings were present. The results indicate that the solid product is $Cr(CH_3CONH)_2$, formed in the process shown in eq. 3

$$Cr(C_5H_5)_2 + 2\,CH_3CONH_2 \rightarrow Cr(NHCOCH_3)_2 + 2\,C_5H_6 \qquad (3)$$

The reaction of chromocene with *N*-ethylacetamide takes the same course, the only products being $Cr(CH_3CONC_2H_5)_2$ and cyclopentadiene. The following changes were found in the IR spectrum of the obtained solid compared with that of *N*-ethylacetamide: the strong band at 3283 cm^{-1} (NH stretch.) disappeared, the most intense band (C=O stretch) shifted from 1651 to 1575 cm^{-1}, the strong band at 1550 cm^{-1} (CNH def.) disappeared, and the band at 1292 cm^{-1} (CN stretch) shifted to 1277 cm^{-1}.

$Cr(NHCOCH_3)_2$ and $Cr[N(C_2H_5)COCH_3]_2$ are diamagnetic (Table 1) and we assume that their structures are analogous to that of polymeric chromium(II) acetate [19].

Experimental

Chromocene was prepared by the reaction of sodium cyclopentadienide with chromium(II) chloride as described previously [21]. Liquid reactants were dried, refluxed in purified argon [13], and distilled in vacuum. Their purities were checked by GLC. Acetamide was sublimed in vacuum and resublimed in the reaction apparatus. The reactions were carried out in a sealed evacuated glass apparatus fitted with extensions permitting magnetic measurements, isolation of samples for chemical, GLC on X-ray diffraction analyses, and measurement of the IR spectrum. In all cases the molar ratio of crystalline chromocene to the other reactant was between 1/10 and 1/20.

The magnetic susceptibility was measured in the range 90–300 K using a variable temperature Gouy balance (Newport Instruments, England). The observed magnetic molar susceptibilities were corrected for diamagnetism using Pascal constants. Magnetic moments calculated by use of the Curie (or Curie–Weiss) equation from the observed susceptibilities are given in Table 1. The IR spectra were measured with Specord IR 75 spectrometer (Carl Zeiss, Jena, GDR) on Nujol mulls in the spectral range 4000–400 cm^{-1}. The powder data were obtained with an HZG-4 X-ray diffractometer (VEB Freiburg Präzisionsmechanik, GDR) using Cu-K_α radiation with discrimination of the K_β radiation by Ni filter. Volatile components of the product mixture were identified by GLC [10].

Reaction of $Cr(C_5H_5)_2$ with HCOOH. This vigorous reaction was controlled by stepwise addition of HCOOH to the crystalline chromocene. A brown intermediate dissolved in an excess of HCOOH to form a blue solution from which a blue crystalline product was obtained. The excess of HCOOH was evaporated off in vacuum and the residual solid washed with heptane and dried in vacuum at 40°C. Found (w_i%): C, 21.02; H, 2.30; Cr, 22.56. $CrC_4H_5O_8$ calcd.: C, 20.61; H, 2.16; Cr, 22.30%. IR spectrum (ν, cm^{-1}) 473s, 646m, 697w, 726m, 800w, 846m, 1017w, 1126m, 1260w, 1519w-sh, 1560vs, 1640w-sh, 1726s, 3379m(b).

Reaction of chromocene with CH_3COOH, C_2H_5COOH and C_3H_7COOH. Exothermic reactions gave deep coloured solutions (blue, red violet, dark red) and crystalline precipitates. The solids were dried in vacuum at 60°C.

Reaction product with CH_3COOH. Found: C, 30.98; H, 4.25; Cr, 22.85. $CrC_6H_{10}O_6$ calcd.: C, 31.31; H, 4.39; Cr, 22.59%. IR spectrum (ν, cm^{-1}): 417vw, 440vw, 460m, 556w, 620m, 679s, 717w, 867m, 942w, 1020m, 1041m, 1280s, 1346m, 1520m, 1585vs, 1690vs, 1784w, 3380m.

Reaction product with C_2H_5COOH. Found: C, 36.54; H, 5.48; Cr, 26.32. $CrC_6H_{10}O_4$ calcd.: C, 36.37; H, 5.09; Cr, 26.24%. IR spectrum (ν, cm^{-1}): 420s, 597w, 660s, 697m, 750w, 809m, 889m, 1011w, 1076m, 1083sh, 1240m, 1297s, 1420s, 1515w, 1535sh, 1560vs.

Reaction product with C_3H_7COOH. Found: C, 42.90; H, 6.59; Cr, 22.85. $CrC_8H_{14}O_4$ calcd.: C, 42.44; H, 6.24; Cr, 22.97%. IR spectrum (ν, cm^{-1}): 440m, 460m, 654m, 730m, 802m, 874w, 998w, 1107w, 1215w, 1266m, 1320m, 1350w, 1423s, 1470vs.

Reaction product with CH_3COOH at 140°C. Found: C, 28.51; H, 3.49; Cr, 30.59. $CrC_4H_6O_4$ calcd.: C, 28.25; H, 3.55; Cr, 30.57%. IR spectrum (ν, cm^{-1}): 422s, 445w, 625m, 629m, 687vs, 694s, 945w, 1040m, 1053m, 1357s, 1567vs.

Reaction with $(CH_3CO)_2O$. The addition of $(CH_3CO)_2O$ to chromocene results in an exothermic reaction to give a red violet solution from which an orange brown solid was formed after 1 h. This solid was washed with acetic anhydride then with heptane, and dried in vacuum at 60°C. Found: C, 28.45; H, 3.66; Cr, 30.29. $CrC_4H_6O_4$ calcd.: C, 28.25; H, 3.55; Cr, 30.57%. IR spectrum (ν, cm^{-1}): 422m, 626m, 629w, 687vs, 694s, 943w, 1039m, 1053m, 1352s, 1420s, 1572vs.

Reaction of chromocene with CH_3CONH_2. This reaction was carried out in molten acetamide at 90°C, and the excess of acetamide was removed by sublimation at 120°C. The obtained ochre solid was extremely unstable in air. Found: C, 28.26; H, 4.80; N, 16.66; Cr, 30.90. $CrC_4H_8N_2O_2$ calcd.: C, 28.58; H, 5.01; N, 16.72; Cr, 30.93%. IR spectrum (ν, cm^{-1}): 560w, 600m, 663m, 691m, 734m, 932w, 1017w, 1041w, 1175s, 1207s, 1580vs, 3362m.

Reaction of chromocene with $CH_3CONHC_2H_5$. The yellow solid obtained by this reaction was washed with heptane and dried at 90°C. Found: C, 43.01; H, 7.40; N, 12.39; Cr, 23.40. $CrC_8H_{16}N_2O_2$ calcd.: C, 42.85; H, 7.19; N, 12.49; Cr, 23.19%. IR spectrum (ν, cm^{-1}): 463w, 602w, 620s, 785m, 825w, 935w, 1010w, 1060m, 1117s, 1277w, 1330s, 1345m, 1420s, 1575vs.

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