

Dioxobis(Carboxylato)Chromium(VI) and Oxo(Carboxylato)Chromium(III): Reactions of CrO₃ with Carboxylic Acid Anhydrides

Ramesh Kapoor*, Ramneek Sharma, and Pratibha Kapoor

Department of Chemistry, Panjab University, Chandigarh-160014, India

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Dioxobis(carboxylato)chromium(VI), Chromium(VI) Oxide, Carboxylic Acid Anhydrides, IR Spectra

Reactions of carboxylic acid anhydrides [(RCO)₂O where R = CH₃, C₂H₅, *n*-C₃H₇ and CHCl₂] with excess of chromium(VI) oxide at low temperatures yield chromyl carboxylates, CrO₂(OOCR)₂. These compounds are non-conducting in polar organic solvents. IR spectra suggest the presence of both unidentate and bidentate carboxylato groups and discrete Cr=O units. The ¹H NMR spectra show the presence of only one type of carboxylato group.

Reactions of carboxylic acid anhydrides with CrO₃ in equimolar ratio yield reduced chromium(III) compounds of the type CrO(OOCR) at room temperature. Their millimolar solutions in C₆H₅NO₂, CH₃NO₂ and CH₃CN are non-conducting. IR spectra, magnetic susceptibility and some other properties have been investigated. Both types of compounds are polymeric in nature having covalent structures.

Introduction

In an earlier communication, we reported the preparation of anhydrous chromium(III) carboxylates by utilizing the reactions of CrO₃ with excess carboxylic acid anhydrides at about 100 °C [1]. We now report the preparation of some new CrO₂(OOCR)₂ and CrO(OOCR) compounds by the reactions of CrO₃ and carboxylic acid anhydrides [(RCO)₂O where R = CH₃, C₂H₅, *n*-C₃H₇ and CHCl₂] under different reaction conditions. Krauss [2] had reported the preparation of CrO₂(OOCCH₃)₂ by using similar reaction conditions, but had not investigated the nature of this compound. Preparation and characterization of a few more chromyl compounds, CrO₂X₂ (X = CF₃COO⁻, ClCF₂COO⁻, CF₃CF₂CF₂COO⁻ and ⁻OSO₂CF₃) has also been reported in the literature [3, 4].

Experimental

CrO₃ (BDH, LR) was dried at 110 °C *in vacuo* for 4 to 6 h. The carboxylic acid anhydrides were prepared by the reaction of sodium salt of carboxylic acid [5] with the corresponding acyl chloride [6]. The anhydrides were distilled over P₄O₁₀ before use.

(a) Preparation of CrO₂(OOCR)₂ compounds

CrO₃ (5.0 g, 0.05 mol) was stirred with a solution of acetic anhydride (2.0 g, 0.02 mol) in CCl₄ for 5 h in the absence of light and moisture and the tempera-

ture of the reactants was maintained below 0 °C. The dark red solution was filtered to remove unreacted CrO₃ and the filtrate was evacuated to remove CCl₄. The dark oily liquid was washed with fresh CCl₄ and pumpedried to a constant weight. Reactions of CrO₃ with other anhydrides were carried out under similar conditions.

(b) Preparation of CrO(OOCR) compounds

CrO₃ (5.0 g, 0.05 mol) and an equimolar amount of acetic anhydride (5.1 g, 0.05 mol) was stirred in CCl₄ for 4–6 h at room temperature in the absence of light and moisture. The solution was filtered and on evacuation yielded a sticky mass. It was washed with CCl₄ and finally dried under vacuum. Reactions with other carboxylic acid anhydrides were carried out under similar conditions.

All other experimental details were the same as have been mentioned in the earlier paper [1].

Results and Discussion

The analytical results along with some of the physical properties are summarized in Table I. The composition of the product depends upon the stoichiometry of the reactants [CrO₃:(RCO)₂O] and the temperature of the reaction. If carboxylic acid anhydride is used in large excess and the reaction is carried out at high temperature, then the product obtained is chromium(III) carboxylate [1]. However, when CrO₃ is taken in large excess and the temperature of the reactants is maintained below 0 °C, the product corresponds to chromyl carboxylate,

* Reprint requests to Dr. R. Kapoor.
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Table I. Analytical results and some physical properties.

Compound	Colour	Molar conductance* (ohm ⁻¹ cm ² mole ⁻¹)	Magnetic moment (BM)	Molecular weight	Analytical data**				
					Cr [%]	Cl [%]	C [%]	H [%]	N [%]
CrO ₂ (OOCCH ₃) ₂ (1)	red	13.1 ^a	—	436	25.4 (25.7)	—	23.60 (23.76)	3.04 (2.97)	—
CrO ₂ (OOCC ₂ H ₅) ₂ (2)	brownish-red	7.7 ^a	—	—	22.2 (22.6)	—	31.02 (31.30)	4.26 (4.35)	—
CrO ₂ (OOCC ₃ H ₇) ₂ (3)	greenish-yellow	10.6 ^a	—	—	19.8 (20.1)	—	36.62 (37.20)	5.40 (5.42)	—
CrO ₂ (OOCCHCl ₂) ₂ (4)	-do-	0.4 ^b	—	—	15.4 (15.3)	42.2 (41.8)	13.92 (14.12)	1.46 (0.59)	—
CrO(OOCCH ₃) (5)	brown	14.7 ^a	2.20	—	40.5 (40.9)	—	18.62 (18.90)	2.56 (2.36)	—
CrO(OOCC ₂ H ₅) (6)	-do-	7.6 ^a	2.51	—	36.3 (36.9)	—	26.31 (25.53)	3.89 (3.54)	—
CrO(OOCC ₃ H ₇) (7)	-do-	11.1 ^a	2.57	—	32.9 (33.5)	—	30.53 (30.96)	5.43 (4.51)	—
CrO(OOCCHCl ₂) (8)	-do-	6.3 ^a	2.97	—	26.1 (26.5)	37.1 (36.2)	12.62 (12.24)	1.22 (0.51)	—
CrO(OOCCH ₃)·NC ₅ H ₅ (9)	-do-	—	—	—	25.5 (25.2)	—	39.01 (40.78)	4.17 (3.88)	6.54 (6.79)
CrO(OOCC ₂ H ₅)·NC ₅ H ₅ (10)	-do-	8.7 ^c	—	426	22.4 (23.6)	—	43.20 (43.64)	4.82 (4.54)	6.40 (6.36)
CrO(OOCC ₃ H ₇)·NC ₅ H ₅ (11)	-do-	8.0 ^c	—	490	21.2 (22.2)	—	45.62 (46.15)	5.01 (5.13)	5.26 (5.98)
CrO(OOCCHCl ₂)·NC ₅ H ₅ (12)	-do-	7.0 ^c	2.77	270	18.2 (18.9)	24.6 (25.8)	30.08 (30.54)	2.28 (2.18)	5.01 (5.09)

* Required values for 1:1 electrolytes in CH₃CN^a, C₆H₅NO₂^b and CH₃NO₂^c are in the ranges: 120–160, 20–30 and 75–95 ohm⁻¹cm²mole⁻¹; ** required values are given in parentheses.

CrO₂(OOOCR)₂. Finally, when the reactants are taken in equimolar ratio and the reaction is carried out at room temperature, the analysis of the product corresponds to a chromium(III) compound, CrO(OOCR) (Table I).

The CrO₂(OOOCR)₂ [where R = CH₃, C₂H₅, *n*-C₃H₇ and CHCl₂] compounds are oily liquids. They have been found to be highly hygroscopic and react violently with water giving yellowish-green solutions. They are slowly reduced to a mixture containing CrO(OOCR) and Cr(OOCR)₃ on keeping at room temperature over a period of few days. They are soluble in polar organic solvents and their millimolar solutions in CH₃CN and C₆H₅NO₂ are non-conducting [7]. Molecular weight of CrO₂(OOCCH₃)₂ in nitrobenzene has been determined by freezing point method and is 436 which suggests its dimeric nature. These solutions are, however, unstable and a precipitate separates out on standing.

Infrared spectra of the compounds have been recorded in Table II. The C—O stretching region is

quite complex which may be attributed to the dual nature of bonding of the carboxylato group in these compounds. The bands at *ca.* 1710 and between 1210 to 1270 cm⁻¹ may be interpreted as belonging to C=O and C—O stretching modes of unidentate carboxylato group [8]. The bands at *ca.* 1600 and 1550 cm⁻¹ may be assigned to $\nu_a(\text{COO}^-)$ stretching mode for bidentate carboxylato group [8, 9]. The presence of more than one band suggests the unsymmetrical nature of carboxylato groups in these compounds. The absorption band between 940–980 cm⁻¹ is assigned to the asymmetric and symmetric stretching modes of the CrO₂ group [3, 4]. Other carboxylato group bands have been assigned by comparison to the spectra of sodium carboxylates [10, 11]. Bands below 500 cm⁻¹ which cannot be assigned to internal vibrations of carboxylato group may be assigned to the deformation mode of Cr—O group by analogy to the spectra of CrO₂Cl₂ and CrO₂F₂ [12]. It may be inferred from the infrared data that these compounds contain both a unidentate

Tab. II. Infrared spectral bands (cm⁻¹) and their assignments for compounds **1** to **12***.

Assignments	1	2	3	4	5	6	7	8	9	10	11	12
C = O str.	1710 s	1705 s	1705 s	1730 s	—	—	—	—	—	—	—	—
COO asym. str. + 8a**	1610 m, 1600 m	1605 s, 1600 m	1605 s, 1600 m	1660 m, 1600 s,	1600 s,	1600 s,	1600 s,	1680 s,	1615 s,	1615 s,	1610 s,	1650 s,
COO sym. str.	1565 m	1555 sb	1545 mb	1610 w	1535 m	1525 m	1535 m	1585 s	1605 s	1610 s	1605 s	1585 s
CH ₂ sym. bend def.	1420 m	1405 s	1415 m	1415 s	1415 s	1415 m	1415 m	1415 s	1410 m	1410 m	1410 m	1405 s
−CH ₂ COO (adj to COO)	—	1455 w, sh	1460 m	—	—	1460 w	1455 w	—	—	1455 w	1440 m	—
CH ₃ bend def.	—	1420 w	1440 m	—	—	1440 sh	1440 sh	—	—	1440 m	—	—
−CH ₂ wagging	1460 w, 1370 m	1380 sh,	—	1450 m,	1375 w	—	—	1455 sh,	1372 s	1370 w	—	—
	1420 m,	1330 sh		1440 m,				1345 w				
	1330 s			1340 w								
	—	1300 m	1310 m,	—	—	1300 m	1310 m,	—	—	1300 s	1305 s	—
			1280 m				1255 w,					
							1200 w					
C−O str.	1240 s	1230 m	1215 m	1270 m	—	—	—	—	—	—	—	—
CH bend	—	—	—	1200 mb	—	—	—	1225 s	—	—	—	1240 s
CH ₃ rock	1045 m, 1075 s,	1010 m	1050 w,	—	1040 m,	1075 s,	1090 m,	—	1045 s	1045 s	1040 s	—
	1010 m	1010 m	1040 w,		1025 w	1005 m	1065 m,					
			1010 w				1000 w					
1**	—	—	—	—	—	—	—	—	1015 s	1015 s	1005 s	1020 s
(Cr = O) mode	955 s	970 s	940 s	980 s	970 s,	960 s,	965 s,	965 s	940 s	940 s	930 s	980 s,
					950 s	940 s	940 s					955 s
C−C skeletal	900 m	950 s	1090 s	910 mb	940 m	880 mb	890 m	930 w	950 m	965 m	940 s	—
CH ₂ rock	—	810 m	780 m	—	—	810 w,	750 sh	—	—	780 s,	780 s,	730 s
						785 m				760 s	755 s	
CCl ₂ asym. str.	—	—	—	820 s	—	—	—	825 s	—	—	—	840 m
CCl ₂ sym. str.	—	—	—	780 m	—	—	—	785 m	—	—	—	790 m
CCOO in-plane bend	715 w	755 mb	755 sh	720 m	720 m	720 m	710 m	720 m	720 sh	715 m	715 m	725 m
COO def.	740 w,	640 s	650 s	730 m	650 s	640 m	720 m	740 w	670 s	640 w	645 s	640 s
	670 m											
CH or COO out of plane	605 w	570 sh	620 w	670 m	620 w	620 w	630 w	650 w,	—	—	—	—
								620 w				
6a**	—	—	—	—	—	—	—	—	640 s	630 s	635 s	630 s
16b**	—	—	—	—	—	—	—	—	415 m	415 m	425 sh	415 sh
(Cr−O) modes	540 m,	535 s,	460 m,	520 w,	425 s,	440 s,	450 m,	460 m,	400 s,	355 w,	440 s,	355 m
	390 m	295 m	350 sh	445 sh	395 s,	410 s,	440 m,	355 m,	380 w,	300 s,	380 w,	305 s
					330 m	340 w	380 w	325 w	305 s	300 s	305 s	

* sb = strong and broad; s = strong; mb = medium and broad; m = medium; w = weak; sh shoulder;

** bands due to pyridine ring.

and a bidentate carboxylate group. The ¹H NMR spectrum of CrO₂(OOCCH₃)₂ at 90 MHz shows only a single peak at τ , 7.62 ppm [8]. A plausible explanation may be a rapid exchange which results in a single line.

Oxo(carboxylato)chromium(III) compounds are stable, non-hygroscopic and do not melt up to 200 °C. The inability of these compounds to oxidize KI to I₂ in acidic media suggests that chromium in these compounds has been reduced to trivalent state. These compounds have slight solubility in polar organic solvents such as nitrobenzene, nitromethane and acetonitrile. Their millimolar solutions in these solvents are non-conducting. The compounds are paramagnetic and show magnetic moments between

2.20 to 2.97 BM at room temperature (Table I). These values are much below the spin-only value of 3.88 BM observed for Cr^{III} complexes [13] and thus suggest a polymeric structure with significant Cr—Cr antiferromagnetic interaction [14] probably through bridging carboxylato groups. The dimeric acetate, Cr₂O₂(OOCCH₃)₂ has been mentioned in the literature and was obtained by heating Cr₂O(OH)(OOCCH₃)₃ at 400 °C [15].

The infrared spectra of these complexes have been recorded in Table II. The bands at *ca.* 1600 and 1525 cm⁻¹ have been assigned to $\nu_a(\text{COO}^-)$ stretching mode. The $\nu_s(\text{COO}^-)$ stretching mode has been assigned to a band at *ca.* 1415 cm⁻¹. Other pertinent bands have also been assigned. The UV-visible

spectra of solutions of these compounds in methanol have been recorded. The presence of three bands at *ca.* 17,000 (${}^4T_{2g}(F) \leftarrow {}^4A_{2g}$), 27,500 (${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$) and 47,500 (${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$) suggest that chromium in these compounds is six coordinate [16].

Compounds **5** to **8** react with pyridine to give 1:1 addition compounds **9** to **12**. These compounds also behave as non-electrolytes (Table I). Molecular weights of CrO(OOCC₂H₅)·NC₅H₅ and CrO(OOCC₃H₇)·NC₅H₅ as determined by freezing point method in nitrobenzene are in agreement with their dimeric formulations (Table I). However, the molecular weight of CrO(OOCCHCl₂)·NC₅H₅ corresponds to its monomeric formulation. IR spectra of

these complexes are quite complex as a result of the overlapping of vibrational bands of carboxylato group and pyridine [17, 18]. The **8a** mode of pyridine cannot be distinguished clearly due to its overlapping with the $\nu_a(\text{COO}^-)$ stretching mode of the carboxylato group which also occurs in the same region (Table II). However, the **1** mode which occurs at 991 cm⁻¹ in pyridine can be distinctly assigned to a band at *ca.* 1020 cm⁻¹. Other significant changes involve shift to higher frequencies in amine ring vibrations of free pyridine at 601 and 403 to *ca.* 630 and 415 cm⁻¹ in these complexes. These changes suggest coordination of nitrogen atom of pyridine to Cr atom.

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