

G. Cainelli G. Cardillo

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# **Chromium Oxidations in Organic Chemistry**



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# Chromium Oxidations in Organic Chemistry

With 2 Figures and 93 Tables



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# Reactivity and Structure Concepts in Organic Chemistry

Volume 19

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## Preface

Chromium oxidation, well known and widely explored in organic chemistry since the very beginning of this science, is a topic of current interest for the organic chemist as evidenced by the continuous development of new techniques and procedures reported in the literature. Chromium oxidation is a simple process which can be easily performed in the laboratory and scaled up in industry as well. Although almost every oxidizable organic functional group may undergo chromium oxidation, the most important fields of application are the oxidation of alcohols, allylic and benzylic oxidation, oxidative degradation and oxidation of some organometallic compounds. A high degree of selectivity is often possible by choosing the most suitable reagent among those several ones now available.

This book takes account of the various functional groups that undergo oxidation and the entire literature up to 1982. It has been written in the hope to help the synthetic organic chemist in his experimental work. For this purpose a number of tables comprising yields and references have been included; detailed descriptions of typical procedures are meant to show the experimental conditions and the scope of the reactions.

We wish to thank Dr. Mario Orena for his valuable scientific and technical assistance and Prof. Bruno Camerino, who read the entire manuscript and corrected many of the errors.

Bologna, February 1984

Gianfranco Cainelli  
Giuliana Cardillo

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# Reactivity and Structure

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# I. Introduction

A great variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizable organic functional group [1]. In spite of this wide spectrum of action the reagents constitute useful tools for organic synthesis since the oxidation can often be controlled to give largely just one single product. Chromic acid is the most popular reagent of this type used in organic chemistry for well over a century. In the last two decades, however, a number of new chromium(VI) containing reagents together with special reaction conditions have been developed to improve the selectivity of oxidation and to deal with complex, highly sensitive compounds.

## 1. The Oxidation States of Chromium

As a typical transition element, chromium has the ground state electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ . The element exists in all oxidation states from  $2^-$  to  $6^+$ ; the highest state ( $6^+$ ) corresponds to the sum of the 3d and 4s electrons as with titanium and vanadium. The most common and stable oxidation state are  $2^+$ ,  $3^+$ , and  $6^+$ . The  $2^-$ ,  $1^-$ , 0, and  $1^+$  states are formal oxidation states held by chromium compounds such as carbonyl nitrosyls and organometallic complexes.

The lowest oxidation states are strongly reducing. For example, chromium(II) — the first oxidation state known in aqueous solution, — is widely used to perform reductions both in organic, as well as in inorganic chemistry. The most stable oxidation state is  $3^+$ . The oxidation states  $4^+$  and  $5^+$  are relatively rare. Only few compounds of chromium(IV) and chromium(V) have been isolated and they appear to be unstable in water as they rapidly disproportionate to chromium(III) and chromium(VI) compounds. Chromium(IV) and chromium(V) species are, however, important in chromium(VI) induced oxidations, since they always occur as transient intermediates. In its highest oxidation state ( $6^+$ ) chromium forms compounds which, with the exception of  $\text{CrF}_6$ , are all oxo compounds and are all strong oxidizing reagents.

## 2. The Chemistry of Chromium(VI)

One of the most important chromium(VI) derivatives is chromium trioxide. It may be obtained as an orange-red, highly poisonous precipitate on adding

## I. Introduction

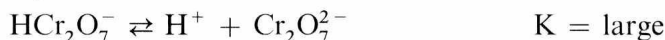
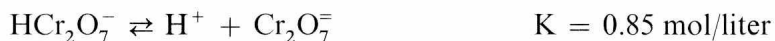
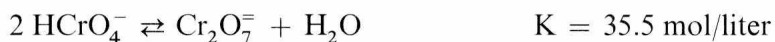
sulphuric acid to aqueous solutions of sodium or potassium dichromates, or on evaporating the water from a reaction mixture of sodium dichromate dihydrate and concentrated sulphuric acid. The structure of chromium trioxide has been determined by X-ray analysis [2] to be a linear polymer of chromium and oxygen atoms with two additional oxygen atoms linked to each chromium atom. Chromium trioxide dissolves in water with accompanying depolymerization:



The so formed chromic acid is a fairly strong acid [3].



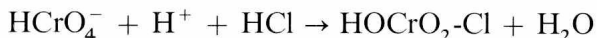
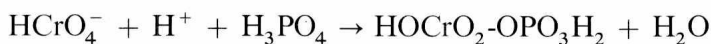
In dilute aqueous solution it largely exists as  $\text{HCrO}_4^-$ . In more concentrated solutions ( $>0.05 \text{ M}$ ) it exclusively dehydrates to the dichromate anion and its protonated forms [4]:



At high concentrations polychromates may be formed. The equilibria are pH dependent. Above pH 8 only  $\text{CrO}_4^{2-}$  ions exist. As the pH is lowered, the equilibria shift; between pH 2–6,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are at an equilibrium. The equilibria are labile, and by adding cations which form insoluble chromates, only chromates — i.e. no dichromates — are precipitated. Moreover, the above reported equilibria depend on the nature of the acid used. It appears that there is a direct involvement of the mineral acid which furnishes the protons [4]:



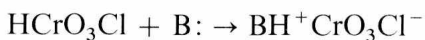
Thus the following species are formed in the protonation of  $\text{HCrO}_4^-$  by the various mineral acids:



It has also been suggested that chromium(VI) dissolved in acetic acid solutions may exist in the form of an acetylchromate ion [5]:



Complex formation between chromic acid and an anion results in a change in the dissociation constant; the more electron-withdrawing the anion, the larger the dissociation constant appears to be thus the order of increasing effect on the constant for the three above reported species is  $\text{H}_3\text{PO}_4 < \text{HCl} < \text{H}_2\text{SO}_4$  [6]. Several salts  $\text{M}(\text{CrO}_3\text{X})$  have been described ( $\text{X}$  = halogen,  $\text{M}$  = alkali metal or ammonium). For example potassium chlorochromate can be prepared as orange crystals simply by dissolving potassium bichromate in hot 6 M hydrochloric acid. By adding an organic heterocyclic base to the aqueous solution of chlorochromic acid the corresponding salts may be obtained as colored crystalline solids:

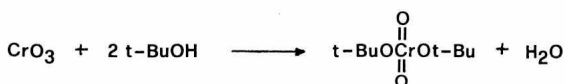
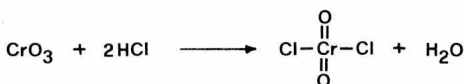
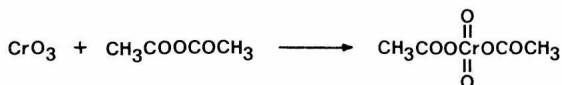


$\text{B:}$  = heterocyclic base

Pyridinium chlorochromate and bipyridinium chlorochromate which represent useful oxidizing reagents, are examples of this kind of compounds:



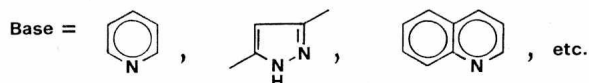
Chromium trioxide reacts under depolymerization with acetic anhydride, hydrogen chloride, and tert-butyl alcohol, to give the corresponding di-substituted products: chromyl acetate, chromyl chloride, and di-tert-butyl chromate, which are soluble in many organic solvents and constitute valuable oxidizing reagents in organic chemistry:



Another type of chromium(VI) compound arises from the Lewis acid properties displayed by chromium trioxide. Chromium trioxide indeed forms many adducts with organic heterocyclic bases of the general formula  $\text{CrO}_3 \cdot$

## I. Introduction

· 2Base, in which the base may be, e.g. either pyridine, dimethylpyrazole, picolines, or quinolines:



Some of these adducts, for example the chromium trioxide-(pyridine)<sub>2</sub> adduct, which is easily obtained by simply mixing the components at room temperature, represent useful reagents for the oxidation of organic compounds under mild conditions.

Chromium(VI) derivatives behave as strong oxidizing reagents. Table 1 is a summary of the standard ( $E^\circ$ ) and formal ( $E^{\circ'}$ ) potentials of a number of half reactions of the chromium(VI) system.

**Table 1.** Standard and Formal Potentials of Some Chromium Redox Systems

System	$E^{\circ a}(\text{V})$	$E^{\circ'}$	Medium	Ref.
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}$	$2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} + 1.33$	+1.00	1 F HCl	7, 9
		+1.08	3 F HCl	9
		+1.08	0.5 F $\text{H}_2\text{SO}_4$	9
		+1.15	4 F $\text{H}_2\text{SO}_4$	9
		+1.02	1 F $\text{HClO}_4$	9
$\text{Cr}_2\text{O}_7^{2-} + 6 \text{H}^+ + 6 \text{e}$	$2 \text{CrO}_2^- + 3 \text{H}_2\text{O} + 0.80$			8
$\text{CrO}_4^{2-} + 8 \text{H}^+ + 3 \text{e}$	$\text{Cr}^{3+} + 4 \text{H}_2\text{O} + 1.48$			8
$\text{CrO}_4^{2-} + 4 \text{H}^+ + 3 \text{e}$	$\text{CrO}_2^- + 2 \text{H}_2\text{O} + 0.94$			8
$\text{CrO}_4^{2-} + 2 \text{H}^+ + 3 \text{e}$	$\text{CrO}_3^- + \text{H}_2\text{O} + 0.36$			8
$\text{H}_2\text{CrO}_4 + 6 \text{H}^+ + 3 \text{e}$	$\text{Cr}^{3+} + 4 \text{H}_2\text{O} + 1.33$			8
$\text{HCrO}_4^- + 7 \text{H}^+ + 3 \text{e}$	$\text{Cr}^{3+} + 4 \text{H}_2\text{O} + 1.35$			8

The formal potential varies with the ionic strength and types of ions present in solution. A comparison between the formal and the standard potential for the chromium(VI) system in water shows the importance of the complex formation with inorganic ligands, acid-base equilibria, and activity coefficients.

The conversion of Cr(VI) to the stable Cr(III) species involves a 3-electron change which has only a low probability of occurring in a single step. This implies the formation of chromium in intermediate oxidation states [Cr(V) and Cr(IV)] in practically every oxidation reaction. The oxidation power of Cr(VI) is influenced by the structure of the reagent, the nature of the reaction medium, and its pH. Thus, alkaline  $\text{CrO}_4^{2-}$  has a reduced oxidizing power, while strong acids enhance the oxidizing power of Cr(VI). It has been establish-



ed that the dichromate anion is a weaker oxidizing agent than the chromate anion. Moreover, although the anhydride  $\text{CrO}_3$  and the chloride  $\text{CrO}_2\text{Cl}_2$  are both powerful oxidizers, the chlorochromate anion  $\text{CrO}_3\text{Cl}^-$  is much less active than the  $\text{CrO}_3\text{OH}^-$  anion. The electrode potentials of chromium trioxide in some donor solvents has been determined electrochemically by means of a platinum electrode. Table 2 reports the results obtained.

It appears that electron donors like hexamethyl-phosphotriamide and dimethylsulphoxide strongly reduce the electrode potential probably as a result of complex formation.

**Table 2.** Electrode Potentials of  $\text{CrO}_3$  in Some Donor Solvents [10]

Solvent	Electrode potential mV <sup>a</sup>
Acetonitrile	1632
Acetic acid	1533
Nitromethane	1470
Sulpholane	1467
Acetic anhydride	1361
Acetone	1095
Trimethylphosphate	1052
Propanediol-1,2-carbonate	1010
Water	875
Dimethylformamide	845
Dimethylsulphoxide	541
Pyridine	541
Hexamethylphosphoric triamide	406

<sup>a</sup> Electrode potentials mV, vs. SCE, using a Pt electrode, ere measured by pH meter in a solution of 100 mg  $\text{CrO}_3$  in 10 ml solvent at 25 °C.

### 3. Chromium(VI) as Oxidant in Organic Chemistry

The largest part of the chromium(VI) oxidations of organic compounds is performed under aqueous acidic conditions. Chromium trioxide and sodium or potassium bichromate are generally used as the chromium(VI) source, while aqueous sulphuric acid and acetic acid are the most frequently employed acids. Cosolvents like acetone (Jones reagent), benzene, methylene chloride, or ether (two phase system) are often added in order to deal with water insoluble organic compounds. This type of reagent has been used to oxidize almost every oxidizable organic compound ranging from alkanes to alcohols and aromatic compounds. Since the oxidation is strongly acid catalysed, the reaction rate is generally high. However, the low pH of the reaction medium and the presence of water, favoring hydrolytic reactions,

## I. Introduction

exclude the use of this class of reagents for the oxidation of molecules containing acid sensitive groups, among them the majority of usual protecting groups. Moreover, the oxidation of primary alcohols does not stop at the aldehyde under these conditions but leads, in general, to the corresponding acids.

The adducts of chromium trioxide with heterocyclic bases, for instance the chromium trioxide-pyridine complex (Sarett's reagent) and the salts of halochromic acids with heterocyclic bases (the most important of them being pyridinium chlorochromate) are all more or less soluble in a variety of organic solvents, especially methylene chloride and therefore may be used under anhydrous conditions. This class of reagents has been recently developed specifically for the oxidation of acid sensitive alcohols. Owing to the absence of water, aldehydes are generally obtained in high yield from primary alcohols. These reagents, being inert towards double bonds, have also been used for the allylic oxidation of alkenes. Moreover, they have been employed for the oxidation of a variety of other organic products as e.g. organoboron compounds. Some neutral or almost neutral chromium(VI) reagents have also been developed. Di-tert-butyl-chromate has been recommended for allylic oxidations, although the results are often poor. Solutions of tetraalkylammonium salts of chromic acid in benzene and chlorinated hydrocarbons, and of chromium trioxide in hexamethylphosphoric triamide have been recently used for the oxidation of alcohols under anhydrous, neutral conditions.

A class of chromium(VI) reagents, obtained by supporting chromium trioxide and chromic or halochromic acid on insoluble organic and inorganic polymeric matrixes has been recently described. These reagents oxidize alcohols in a great variety of organic solvents under anhydrous conditions. The insolubility of these reagents offers the advantage of reducing the work procedures to mere filtration.

Chromyl chloride has been widely employed, notably in the past, for the oxidation of arylalkanes and a variety of other hydrocarbons (Etard reaction). However, owing to the poor selectivity and the low yields, this reaction does not appear to be particularly useful for organic synthesis. More interesting are the recent applications of this reagent for oxidation of alkenes and enolethers.

## References of Chapter I

### 1. Cfr. for Reviews:

- (a) Wiberg, K. B.: Oxidation by chromic acid and chromyl compounds in: *Oxidation in Organic Chemistry, Part A*, p. 69. New York, Academic Press 1965
- (b) Bosche, H. G.: *Chrom-Verbindungen als Oxidationsmittel* in: *Houben-Weil Methoden der Org. Chemie*, Vol. 4/1b, Stuttgart, Thieme Verlag 1975
- (c) House, H. O.: Oxidation with chromium and manganese compounds, in: *Modern Synthetic Reactions*, (ed. Benjamin, W. A.), London, 1972