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REACTIONS OF INTERMEDIATE OXIDATION STATES OF CHROMIUM: THE INDUCED OXIDATION OF ADIPIC ACID

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Chromic acid oxidation of a large number of organic compounds seems to proceed by the scheme[1,2]:

$$\mathrm{Cr(VI)} + \mathrm{S} \longrightarrow \mathrm{Cr(IV)} + \mathrm{P}$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)}$$

$$2\mathrm{Cr(V)} + 2\mathrm{S} \longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{P}$$

Hence, what we call "oxidation with chromic acid" is, in fact, an oxidation by Cr(V) to an extent of 67%. The reactivity of chromium (V) is therefore of prime interest.*

Chromium (V) must resemble chromium (VI) in many of its properties. Obviously, in all reactions in which a single oxidation product is produced, both valence states of chromium must react in a similar way, even though details of the mechanisms might be different. Furthermore, even the relative reactivities, or selectivities, of Cr(VI) and Cr(V) for closely related substrates do not differ appreciably[2,4]. For example,

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* An alternative scheme including the reactions of both Cr(V) and Cr(IV) with the organic substrate has also been considered. However, our recent results[3] have led us to question the reactivity of chromium (IV) towards organic compounds. The ensuing discussion has therefore been simplified by considering only Cr(V) responsible for the induced oxidation.

Wiberg and Richardson[2] have shown that the rate of oxidation of p-chlorobenzaldehyde relative to benzaldehyde is 1.38 for chromium (VI), and 1.20 for chromium (V).

However, a few instances are known in which the selectivities of chromium (VI) and chromium (V) are completely different. This leads to the effect known as induced oxidation[5,6], which is best exemplified by the facile oxidation of the otherwise unreactive iodide ion in the presence of ferrous ions:

$$\mathrm{Cr(VI)} + \mathrm{I^-} \longrightarrow \text{very slow reaction}$$

$$\mathrm{Cr(VI)} + \mathrm{Fe^{2+}} \xrightarrow{\text{fast}} \mathrm{Cr(V)} + \mathrm{Fe^{3+}}$$

$$\mathrm{Cr(V)} + \mathrm{I^-} \xrightarrow{\text{v. fast}} \mathrm{Cr(III)} + \mathrm{IO^-}$$

All except one of the systems in which the relative reactivity of chromium (VI) and chromium (V) is so drastically changed as to lead to induced oxidation consists of pairs in which one or both of the components are inorganic ions. The only purely organic example is the oxidation of indigo induced by oxalic acid[7]. In this communication we wish to report the first example of an induced oxidation involving two simple organic compounds.

The oxidation of cyclohexanone by chromic acid yields as the main product adipic acid, which is always accompanied by smaller amounts of both glutaric and succinic acids[8]. The simplest way in which the formation of the lower dicarboxylic acids could be explained is by further oxidation of adipic acid. However, adipic acid is very unreactive towards oxidation by chromic acid. Snethlage[9] found the oxidation of adipic acid by chromic acid in aqueous sulfuric acid too slow to be measured even at 100° at sulfuric acid concentrations lower than 50%. From our previous measurements in 99% acetic acid[10,11] one can estimate that cyclohexanone is at least 10,000 times more reactive towards chromic acid than adipic acid. Hence, no detectable degradation of adipic acid by chromic acid can be expected in the presence of even a small amount of cyclohexanone. Therefore only induced oxidation could be responsible for the formation of the lower dicarboxylic acids if adipic acid was to be considered as the precursor.

To prove that the lower dicarboxylic acids were indeed formed by induced oxidation of adipic acid in which cyclohexanone acted as the inductor, the oxidation of another ketone in the presence of adipic acid was investigated. 3-Methyl-2-butanone, a ketone reacting with chromium (VI) 1.58 times faster than cyclohexanone but unable to yield dicarboxylic acids as oxidation products, was selected as a suitable inductor.

The oxidation was carried out in 1.0 M perchloric acid at 50° with the initial concentrations: 3-methyl-2-butanone 1.5 M, adipic acid 0.137 M, chromic acid 0.75 M. The dicarboxylic acids present in the final reaction mixture were collected and analyzed in the form of the dimethylesters by gas-liquid chromatography in a way described elsewhere[8]. The presence of the products of induced oxidation was immediately apparent from the chromatogram. On quantitative evaluation, it was found that the mixture contained 2.3% glutaric acid, 3.5% succinic acid, and 94.2% adipic acid.

Having thus demonstrated the existence of induced oxidation in this case, it is of interest to estimate the relative reactivity of chromium (V) towards the two competing organic compounds, the ketone and the acid. By analogy with the oxidation of cyclohexanone[8], it can be assumed that methylbutanone is oxidized to acetone and acetic acid via the reactive hydroxyketone intermediate.* Basing the stoichiometry of the reaction on this assumption, the concentration of 3-methyl-2-butanone at the end of the reaction should be about 0.9 M, or more than six times higher than that of adipic acid. The average ratio of the inductor (ketone) to the substrate (adipic acid) is thus about nine. From this concentration ratio and from the amount of available chromic acid one can

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*The relative rate of 3-hydroxy-3-methyl-2-butanone to 3-methylbutanone under the reaction conditions used in this experiment is 14.3.

estimate that about 7% of the adipic acid should undergo oxidation. This estimate is based on the assumption that chromium (VI) does not react with adipic acid at all and that chromium (V), on the other hand, is completely non-selective and reacts with adipic acid and with the ketone in the ratios of their respective concentrations. The results given above show that actually about 6% of adipic acid underwent a degradation reaction; this figure is in surprisingly good agreement with the predicted value. Hence, although the reactivity of the ketone towards Cr(VI) is more than 15,000 times higher than that of adipic acid, both compounds are about equally reactive towards chromium (V).

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