Photochemical Reaction of Cr(VI) Oxyanions with Reducing Agents in the Aqueous Solution

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Masako SASAKI, Kenichi HONDA
and Shin-ichi KIKUCHI

The Institute of Industrial Science, The University of Tokyo
Roppongi, Minato-ku, Tokyo, Japan

Abstract

For the purpose of contributing to the basic study of photochemical process, photochemical reaction of Cr(VI) oxysalts such as dichromate and chromate compound with reducing agents, polyvinyl alcohol and several alkyl alcohols in the aqueous solution was investigated.

In the dilute aqueous solution of these Cr(VI) oxysalts, the photoactive species is acid chromate ion, HCrO$_4$– and chromate ion, CrO$_4^{2–}$, has no photosensitivity. The two charge transfer bands of acid chromate ion; $\lambda_{max}$ 350 and 440 m$m\mu$, give rise to the photoreduction reaction of Cr(VI) to Cr(III). The quantum yields of reduction of Cr(VI) to Cr(III) at 365 m$m\mu$ are smaller than 0.5 in these experimental conditions.

It is confirmed by spectrophotometry that the photoreduction products of Cr(VI) is Cr(III) complex ion in in the aqueous solution. During the photoreduction of Cr(VI) the reducing agents are oxidized and 3 mol of oxidized form of reducing agent is produced for 2 mol of Cr(VI).

By spectrometric and electron spin resonance method at $-196^\circ$C, it is observed that during the photoreduction process of Cr(VI) to Cr(III), it exists an intermediate valence state of chromium (Cr(V) or Cr(IV)).

§ 1. Introduction

Dichromate and chromate compounds have been commonly used, since almost the past century, to harden photochemically water soluble colloids$^1$, of which gelatin and polyvinyl alcohol were perhaps the most popular components. This water soluble colloids have some advantages, such as low cost and simple handling. Moreover, quite recently this system begins to be appreciated as a reliable phase holographic recording material$^2$.

Although the photochemically hardening process of dichromated colloid has been investigated by many workers$^3$ since its appearance, the chemistry and mechanism of reaction have not yet been satisfactorily explained.

The purpose of this work is to contribute to the photomechanical process and some previous studies on the photochemical reactions of dichromate and chromate (Cr(VI) oxyanions) with reducing agents such as polyvinyl alcohol and ethanol etc. in the aqueous solution were discussed by the authors$^4$,$^5$.

In this study, the change of electronic absorption spectra and pH values of their solution during irradiation, the photoreduction rates and its quantum yields were measured. The oxidation products of reducing agents, the reduction products of Cr(VI) oxyanions, and the dependence of the reaction of Cr(VI) oxyanions on the irradiation wave-length were also examined. An intermediate valence state of photoreduction from Cr(VI) to Cr(III) was detected by ESR spectrum and the absorption spectrum at $-196^\circ$C. The photo-
chemical reactions were studied by the changes of spectra between 300 and 700 m\(\mu\), in which region reducing agents have no absorption bands.

§ 2. Experimental

Materials for the preparation of all solutions were of reagent grade. The photochemical reactions were generally carried out in acetic acid-sodium acetate buffer solution with 1% polyvinyl alcohol or ethanol (50% V/V), and the sample contained in a quartz cell (4×1×1 cm\(^3\)) or a Pyrex glass cell (5×5×2 cm\(^3\)), was irradiated with a 270 W high-pressure mercury lamp at room temperature. The electronic absorption spectra and pH values were recorded on a Shimazu spectrometer Model MPS-50 and a Toaemps pH meter Model HM-5 A respectively. The detection of intermediate of photoreduction was investigated at —196°C under irradiation of a 500 W Xe-lamp. ESR spectrum (X-band) was recorded as the first derivative of absorption band by a Nihondenshi Model JES-3 BS-X and the sample, contained in a quartz tube (\(\phi=5\) mm), was cooled at —196°C during the measurements. Several glass filters such as UV-D2, VY-42, VV-40, VY-43 (Toshiba) and CS-7-83 (Corning) were used in some cases, and a heat-cut filter IRQ-80 (Toshiba) usually to eliminate the wave-length of less than 300 m\(\mu\) and of infrared.

§ 3. Results and Discussions

3.1 The Absorption Spectra of Dichromate in the Aqueous Solution

In dilute aqueous solution, dichromat is present in several ionic states such as Cr\(_2\)O\(_7^{2-}\), HCrO\(_4^-\) and CrO\(_4^{3-}\) and these states depend on the pH of the solution.

These Cr(VI) oxyanions are in the following equilibrium\(^{4) - 8}\):  
\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^- \quad (1)
\]
\[
\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{3-} \quad (2)
\]

The pH dependence of the absorption spectra of dichromate in the aqueous solution was measured in the pH range from 1.3 to 14.0. Fig. 1 shows three typical curves; curve 1 is at pH 3.5, curve 2 at 6.0 and curve 3 at pH 8.3. The absorption spectra at pH<5 are similar to curve 1, at pH>8 to curve 3 and at the pH values between 5 and 8 the changes of the curves depend on pH. The relation of the molecular extinction coefficient at 370 m\(\mu\) (\(\varepsilon_{370}\)) to the pH values is shown in Fig. 2.

The equilibrium constant for the equation (2) was obtained from Fig. 2 and it can be

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Fig. 1. The pH dependence of the absorption spectra of Cr(VI) oxyanions in the aqueous solution.
shown that in dilute aqueous solution the main species at pH < 5 (curve 1) is HCrO$_4$-, at pH > 8 is CrO$_4^{2-}$. At pH values between 5 and 8, main species are in the form of HCrO$_4^-$ and CrO$_4^{2-}$ with a certain mole ratio.

3.2 The Photochemical Reaction of Cr(VI) Oxyanions in the Aqueous Solution

3.2.1 The Spectrum Change during Irradiation

The pH value of dilute aqueous solution of dichromate is about 6 and this solution shows no spectrum change with irradiation of light. On the other hand, when reducing agents such as polyvinyl alcohol or some other alcohols are added into the solution, the change in the spectrum is observed with irradiation. Fig. 3 shows the change in the spectrum with irradiation. In this case, polyvinyl alcohol was used as reducing agent.

During irradiation, the shift of the absorption band of $\lambda_{\text{max}}$ of 350 m$\mu$ to longer wavelength is observed at the initial stage and afterwards the absorbance at $\lambda_{\text{max}}$ 350 and 440 m$\mu$ decrease slowly. This phenomenon suggests that Cr(VI) is consumed very slowly during the photochemical reaction.

3.2.2 The pH Change during Irradiation

The shift of absorption maximum which is observed at the initial stage of the photochemical reaction, suggests the occurrence of pH change of the solution. As was expected, Fig. 4 (curve 1) shows the increase of the pH value of the solution with irradiation. In dark, pH of the solution remains unchanged (curve 2).

3.2.3 The pH Dependence of Photochemical Reaction

As mentioned before, the ionic form of Cr(VI) oxyanions changes with pH of the solution. During irradiation, pH value of the solution changes towards alkaline side and...
its rate becomes lower with higher pH value of the solution. Hence, it can be said that the photochemical reaction depends on pH value of the solution. From this standpoint, the photoreduction rates were measured at various pH.

The reaction rate was determined by measuring the degree of Cr(VI) consumption which showed directly the quantity of reduced Cr(VI). Fig. 5 shows the photoreduction curves where the absorption of Cr(VI) decreased with time of irradiation at pH 3.5, 6.3 and 7.9. In these reactions, the dark reaction was negligible. At pH 3.5 the rate

\[
\text{rate} = \text{Cr(VI)}_{\text{consumption}}
\]

showing the relationship between pH and the reaction rate.
of photoreduction of Cr(VI) is remarkably higher than those at other pH values. The rate at pH 6.3 is smaller than at pH 3.5, and at 7.9 no reduction takes place. It is confirmed that in dilute aqueous dichromate solution, photoactive species is HCrO$_4^-$ and CrO$_4^{2-}$ has no sensitivity to the irradiation.

### 3.2.4 The dependence of Photoreduction on the Irradiation Wave-length

As described in the previous section, the photoactive species in the present reaction system is HCrO$_4^-$ which has two absorption bands of $\lambda_{\text{max}}$ 350 and 440 $\mu$m in the region between 300 and 700 $\mu$m. Although it is well known that the photoreduction occurs at the absorption band of $\lambda_{\text{max}}$ 350 $\mu$m, the photoreduction at 440 $\mu$m is not yet well investigated.

Symons and collaborators concluded that these two absorption bands of HCrO$_4^-$ were the charge transfer bands brought about by the degeneracy of symmetry of CrO$_4^{2-}$. If this conclusion is valid, the photochemical reaction will be expected to occur by irradiation of both absorption bands. Using a high pressure Kreft type mercury lamp as light source with a wave-length selection glass filter and the sample contained $[\text{Cr}_2\text{O}_7^{2-}]=2 \times 10^{-4}$ mol/l (acetate buffer solution-1% PVA, pH=3.50), experiments of photoreduction were carried out and the results are given in Fig. 6.

It is confirmed that these two absorption bands give rise to the photoreduction from Cr(VI) to Cr(III). However, the efficiency of longer wave-length, 440 $\mu$m is slightly higher than that of 365 $\mu$m, the difference of efficiencies is not very important, considering that the absorption at 440 $\mu$m is not complete absorption.

![Diagram of CT bands of HCrO$_4^-$](image)


<table>
<thead>
<tr>
<th>Wavelength ($\AA$)</th>
<th>No. of incident photons (Relative value)</th>
<th>Molar extinction coefficient</th>
<th>Ratio of absorbed photons (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>1.82</td>
<td>1380</td>
<td>8.67</td>
</tr>
<tr>
<td>4358</td>
<td>1.26</td>
<td>230</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate const. of the photoreduction ($k$) at 25$^\circ$C</th>
<th>$k/N_0$ (Relative value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>14.97 X $10^{-5}$ min$^{-1}$</td>
</tr>
<tr>
<td>4358</td>
<td>2.99 X $10^{-8}$ min$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 6. The wave-length dependence of the photoreduction.
3.2.5 The Photoreduction Rate of Cr(VI) in the Aqueous Solution

The photochemical reaction of Cr(VI) oxyanions with reducing agents is essentially the photoreduction of Cr(VI) to Cr(III)\(^4\). The rate of typical photoreduction is given in Fig. 7. The photoreduction rate is of first order in relation to the concentration of Cr(VI).

In this case, assuming that Lambert-Beer's law is applicable, the following equation can be obtained:

\[
\frac{dc}{dt} = KI_l[1 - \exp(-\varepsilon_sc_l)], \tag{3}
\]

where
- \(\varepsilon_s\): absorption coefficient of HCrO\(_4^{-}\) at \(\lambda m\mu\)
- (The photolytic products of Cr(VI) have no absorption at \(\lambda m\mu\))
- \(I_l\): intensity of incident light
- \(l\): length of the optical path
- \(K\): constant
- \(c\): initial concentration of HCrO\(_4^{-}\)

Here, in the case of Fig. 7, \(\varepsilon_sc_l \ll 1\). Then, the equation (3) can be simply written as follows:

\[
- \frac{dc}{dt} = KI_l\varepsilon_sc_l. \tag{4}
\]

Therefore, in view of the above equation, it seems to be correct that the photoreduction rate is of first order in relation to the concentration of Cr(VI). According to equation (4), it must be considered that the photoreduction rate depends on the intensity of light, the kind and the concentration of reducing agents and volume of reaction cell etc.

3.2.6 The Dependence of the Kind of Reducing Agents on the Rate of Photoreduction

The reaction rate was measured using various alcohols as reducing agents and the results are shown in Fig. 8. In case that reducing agents is alkyl alcohol, the reaction rate is higher with longer alkyl chain. That is to say, alcohol which has higher electron donating ability, in otherwords, lower ionization potential has higher reducing power. However, in the case that an alcohol of lower ionization potential has unsaturated or side chain, the reaction rate becomes lower. The photoreduction scheme is suggested to be different depending on the type of alcohols. Therefore, the reducing power of the agent can not explained completely by ionization potential. Although the structure of reducing agent should be considered, ionization potential of the reducing agents can be regarded as one of the measures of oxidizability of reducing agents of similar structure.
3.2.7 The Effect of Oxygen on the Photoreduction Rate

The photoreduction of Cr(VI) oxyanions has a possibility of generation of oxygen\(^{(10,11)}\), but the actual formation of oxygen has not been observed. If oxygen is formed during the photochemical reaction, the reduction rate will be affected by the concentration of oxygen in the solution.

Fig. 9 shows that in the deaerated solution, the rate constant is higher than in the oxygen saturated solution. The rate constant of photoreduction changes with the concentration of oxygen in the solution. In the reaction condition described in Fig. 8, the order of magnitude of rate constant is at N\(_2\) saturation \(k=0.261\, \text{min}^{-1}\), at air saturation \(k=0.165\, \text{min}^{-1}\) and at O\(_2\) saturation \(k=0.090\, \text{min}^{-1}\).

Then, it is confirmed that oxygen present in the solution decreases the reduction rate. Although the direct detection of the formation of oxygen during irradiation was tried by oxygen electrode of membrane type (Toadempa Model OE-211, its minimum
sensitivity is 0.2 ppm) the existence of oxygen was not observed.

However, the fact that oxygen lowers the reduction rate may be explained by the re-oxidation of intermediate species, or the deactivation of excited states of Cr(VI) oxyanions or the direct oxidation of reducing agents. Intermediate species will be described in the section 3.5.

On the other hand, as oxygen electrode can detect only oxygen in molecular state, the possibility of formation of atomic oxygen by photochemical reaction still remains.

3.3 The Photoreduction Product of Cr(VI) Oxyanions in the Aqueous Solution

Although it was expected that photoreduction products of Cr(VI) oxyanions was Cr(III) compound\(^{13}\), clear assignment has not yet been given. Fig. 10 shows the absorption spectrum of a final product of photoreduction after sufficient irradiation where reducing agent is ethanol. The final product of photoreduction has two absorption bands in visible region. This absorption spectrum similar to that of Cr(III) complexes seems to be Cr(III).

On the other hand, an empirical equation between the first \((\nu_1)\) and the second \((\nu_2)\) absorption bands of Cr(III) complexes in visible region was given by Tsuchida\(^{14}\) and Kuroya\(^{15}\) as expressed below.

\[
\nu_2 - \nu_1 = 21 \times 10^{13} \text{ sec}^{-1} \tag{5}
\]

\[
\nu_2 = (1.189 \times \nu_1 + 13.31) \times 10^{13} \text{ sec}^{-1} \tag{6}
\]

where

\[
\begin{align*}
\nu_2 & : \quad ^1T_{1g}(F) \leftrightarrow ^4A_{2g}(F) \\
\nu_1 & : \quad ^1T_{2g}(F) \leftrightarrow ^4A_{2g}(F).
\end{align*}
\]

If the photoreduction product is Cr(III) complexes, its two absorption bands will satisfy this relation.

The observed values and those calculated from the equation of some of Cr(III) complexes and the photoreduction products are summarized in Table 1. The observed absorption bands of photoreduction product satisfy the relation. The experiments using X-band ESR spectrum in the aqueous solution or in EPA solution (ethyl ether: isopentane: ethanol = 5:5:2) at \(-196^\circ \text{C}\), were carried out to examine the photoreduction product.

The ESR spectrum (Fig. 11) shows very broad line and the spectrum agrees with O'Reilly's\(^{16}\) observation of Cr(III) ion in chromia-alumina catalyst. Therefore, from the absorption spectrum and ESR spectrum, the photoreduction product of Cr(VI) oxyanion is confirmed to be Cr(III) compound.

![Fig. 10. The absorption spectrum of the photoreduction product (Cr(III) compound).](image-url)
Table 1. The absorption bands of the photoreduction products and of Cr(III) complexes.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>The first band $\nu_1$ ($\chi_1$)</th>
<th>The second band $\nu_2$ ($\chi_2$)</th>
<th>$\nu_2 - \nu_1$</th>
<th>$\nu_2 = 1.189 \times \nu_1 + 13.31^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA/Acetate buffer solution</td>
<td>51.7 (580)</td>
<td>71.4 (420)</td>
<td>19.7</td>
<td>73.8 (obs.)</td>
</tr>
<tr>
<td>EtOH/Acetate buffer solution</td>
<td>51.7 (580)</td>
<td>71.8 (418)</td>
<td>20.1</td>
<td>73.8 (obs.)</td>
</tr>
<tr>
<td>[Cr(OH)₆]³⁺</td>
<td>51.4 (584)</td>
<td>72.8 (412)</td>
<td>21.4</td>
<td>74.5 (obs.)</td>
</tr>
<tr>
<td>Cr(OH)₄⁺⁺</td>
<td>52.5 (572)</td>
<td>73.6 (408)</td>
<td>21.1</td>
<td>75.81 (ref. 54, 3)</td>
</tr>
<tr>
<td>Cr(O²⁻)⁺⁺</td>
<td>52.6 (571)</td>
<td>71.4 (420)</td>
<td>18.8</td>
<td>75.85 (ref. 6)</td>
</tr>
</tbody>
</table>

$\nu$: frequency ($\times 10^{14}$ sec⁻¹)  
$\lambda$: wave-length (mp)


3.4 Quantum Yields of the Photoreduction of Cr(VI) to Cr(III)

Quantum yields of the photoreduction of Cr(VI) to Cr(III) are given in Table 2. The measurement of light quanta was carried out by the ferrioxalate actinometry. In our experimental condition, the quantum yield obtained was smaller than 0.5. In addition, in the case of discussing the quantum yield of photoreduction of Cr(VI), it will be necessary to consider the environment of reaction, because the quantum yield of photoreduction depends on the kind of reducing agents and their concentrations.

The stoichiometry between reductant and oxidant was then investigated. From the results of a gas-chromatography (Ohkura-thermal conductivity type), the oxidation products of reducing agents such as ethanol and iso-propanol were detected as acetoaldehyde and acetone, respectively and these products were measured quantitatively. It is found that 3 mol of oxidized form of reducing agent was produced for the consumption of each 2 mol of Cr(VI) oxyanions (HCrO₄⁻).

3.5 An Intermediate Species of Photoreduction of Cr(VI) to Cr(III)

The photoreduction is obviously three electrons transfer process. Therefore, it is expected that in the photoreduction process of Cr(VI) to Cr(III), an intermediate valence...
state of chromium ion will be formed. For the detection of intermediate valence state, the absorption spectrum was investigated at $-196^\circ$C under irradiation.

The spectra of intermediate in EPA solution are shown in Fig. 12.

The similar spectrum is observed also in the aqueous solution. During irradiation, the absorption band having $\lambda_{\text{max}}$ 600–610 m$\mu$ appears with the decrease of Cr(VI). This new absorption band is different from that of the final photoreduction product concerning molar extinction coefficient and $\lambda_{\text{max}}$

\[
\text{intermediate \hspace{0.5cm} final product} \\
\{ \lambda_{\text{max}} = 610 \sim 620 \text{ m}\mu \quad \lambda_{\text{max}} = 580, \ 420 \text{ m}\mu \}.
\]

When the temperature increases from $-196^\circ$C to room temperature, the intermediate is reduced to Cr(III).

Life time of the intermediate is longer than 40 hrs at $-196^\circ$C. The decrease of the absorbance of intermediate begins at $-160^\circ$C and when the temperature reaches to $-140^\circ$C, its absorption spectrum disappear completely. The details on the intermediate valence state

![Fig. 12. Absorption spectra of blue intermediate ($-196^\circ$C).](image)

1. Before irradiation  
2. After 1 hr. of irradiation  
3. After 1.5 hr. of irradiation
of chromium will be reported elsewhere.

The blue intermediate has a possibility that it is alcoholic radical or hydrated electron. However, the similar absorption spectrum of the intermediate is observed with various kinds of alcohols. Even when polyvinyl alcohol is used as reducing agent, the blue species can also be observed. Here in Fig. 13, the spectrum of the blue species is compared with the spectrum of the photoreduction product (Cr(III) compound), that of an alcoholic radical and that of hydrated electron. These spectrum are different from one another.

Therefore, the blue intermediate is confirmed as the intermediate valence state (Cr(IV)) or Cr(V)) of chromium compound.

On the other hand, during irradiation, ESR signal can be observed in Cr(VI) oxyanions aqueous solution with reducing agents at $-196^\circ$C. These signal appears after the solid solution was coloured under irradiation. In Fig. 14 ESR spectrum shows two signals of $g=1.979$ and $g=2.003$ which have different temperature dependence. The signal of $g=2.003$ increases gradually with irradiation at $-196^\circ$C.

After irradiation, when the temperature rises to $-170^\circ$C, the signal shows the line narrowing and the increase of the intensity. When the temperature reaches to $-160^\circ$C, this signal exhausts. On the other hand, the signal of $g=1.979$ shows slightly different behavior from another. Although the $g$ value of the former is very similar to that of Cr(III) compound, these line widths are quite different.

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1: Before irradiation
2: After irradiation with 3650 Å light

Fig. 14. ESR spectra of solid solution of HCrO$_4^-$ EtOH-Acetate buffer solution (at $-196^\circ$C).
ent. That is to say, the signal of Cr(III) compound has a broader line. During the temperature increase from $-196^\circ C$ to $-170^\circ C$, the intensity and line width of the signal of $g=1.979$ does not change. But when the temperature rise to $-160^\circ C$, the intensity of the signal increases twice of the signal at $-170^\circ C$. It is hence suggested that some chemical reactions occur at about $-160^\circ C$. During the temperature rises from $-196^\circ C$ to room temperature, these signals disappear.

In addition, behavior of these signals is slightly different from absorption spectrum of the blue species. With irradiation the absorbance of blue species reaches rapidly to the saturation and when temperature increases from $-196^\circ C$ to $-140^\circ C$, absorbance diminishes. Therefore, it is very difficult to conclude that ESR signal and the absorption spectrum at $-196^\circ C$ come from same intermediate species. It is not so unreasonable to suppose that the signal of $g=1.979$ may be due to chromium (V) valence state, because similar signal was observed by Wiberg\(^{19}\).

Although the signal of $g=2.003$ has not been assigned, this signal may be due to alcoholic radical. On the ESR study, further examination and discussion are expected.

3.6 Mechanisms of Photoreduction Process

Here, the possible scheme of the photoreduction of Cr(VI) oxyanions with reducing agents will be described.

Possible schemes of the photoreduction from Cr(VI) to Cr(III) given by the authors are shown in Fig. 15. In the schemes, ethanol is used as reducing agent and the number of oxygen to chromium atom is provisionally given. Although initial step has not been observed, the photoreduction occurs by light absorption of Cr(VI) compound. On the second step, the intermediate species is produced. The Cr(V) compound which gives ESR signal must be produced by electron transfer between chromium (VI) and chromium (IV). It may be possible to expect the formation of an alcoholic radical in the photoreduction process, but this problem remains unsolved.

§ 4. Conclusion

Although several problems on the photochemical reaction process still remains uncertain, the following experimental results were obtained.

1. In the dilute aqueous solution of Cr(VI) oxyanions added with reducing agents, the photoactive species is acid chromate ion ($HCrO_4^-$) and chromate ion ($CrO_4^{2-}$) has no photosensitivity.

The two charge transfer bands of acid chromate ion give rise to the photoreduction reaction of Cr(VI) to Cr(III).

2. The photochemical reaction of acid chromate ion is a three electron reduction process of Cr(VI) to Cr(III) and Cr(III) compound forms complex ion in the aqueous solution.

On the other hand, during the photochemical reaction the reducing agents are oxidized and 3 mol of oxidized form of reducing agent is produced for 2 mol of Cr(VI).

3. The quantum yields of reduction of Cr(VI) to Cr(III) at 365 $\mu m$ are smaller than 0.5 in our experimental conditions.

4. By electronic absorption and ESR spectra at $-196^\circ C$ it is confirmed that during the photoreduction process of Cr(VI) to Cr(III) the intermediate valence state of chromium (Cr(IV) or Cr(V)) is produced.

References


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7) J. Y. Tong and E. L. King, *ibid.*, 75, 6180 (1953).


