THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTION

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Received February 9, 1961

The photochemistry of evacuated potassium iodide solutions at 2537 Å was investigated. The dependence of the initial quantum yields on pH, iodide ion concentration and light intensity was investigated. The nature of the residual pH independent yield at pH > 3 is discussed. The pH dependence of the initial quantum yields could be represented by a linear dependence on the square root of H⁺ ion concentration. It is shown that this is in agreement with a mechanism based on the theory of diffusion controlled scavenging. In H₂O solution an electron scavenger for a species (electrons or H atoms) formed in the photochemical cycle and yield H atoms in the bulk of the solution. The reactivity of H atoms photochemically produced in solution was investigated, and evidence for a pH dependent oxidation mechanism of I⁻ by H atoms is presented, which may involve the H⁺aq ion as the actual oxidizing agent.

Introduction

In the ultraviolet region aqueous solutions of iodide show an intense absorption band centered by a high oscillator strength \( f = 0.25 \). This band has been classified as a charge transfer spectrum. For the alkali halides in aqueous solutions the absorption band is typical of the anion and no spectroscopic evidence for ion pair formation has been found. The nature of the excited state has been a matter of controversy.

As has been well known for a long time aerated aqueous iodide solutions liberate free iodine on illumination. More recently the same was shown to occur in deaerated solution. The photochemical wavelength threshold was shown to coincide with the absorption band onset. Farkas and Farkas showed that the quantum yield was pH dependent, a conclusion supported by Franck and Plattman, who suggest a competition between the decay of the excited state and its interaction with H₂O⁺ ion as the reason for the pH dependence. On the other hand Rigg and Weiss conclude that the pH dependence arises out of the competition in bulk between the reaction of H + I and H₂⁺ formation by the reaction between H + H⁺. The two theories thus differ in their interpretation of radical formation and the relatively low quantum yield.

Recently the system has been investigated in the whole pH region in the presence of HClO₄ and by flash photolysis technique, where the existence of the I⁻ ion as intermediate was demonstrated.

The purpose of the present work was to investigate the mechanism of primary radical formation

5. (a) R. L. Plattman and J. Franck, Z. Physik, 138, 411 (1954);

in this system, and the possible specific role of the HO₂⁻ ion in this process. Another aspect of this work is the investigation of the chemistry of radicals photochemically produced. It was postulated by Weiss that H atoms in aqueous solutions may act as an oxidizing agent through the intermediate formation of H₂⁺. The occurrence of such oxidation reactions is now well established. Using H atoms externally generated it was shown that in the case of the I⁻ ion the results are consistent with the view that the actual oxidant is the H₂⁺ ion. Further independent investigation of this problem appeared desirable in the case of the photochemistry of I⁻.

Experimental

Light Source.—The light source was a low pressure mercury lamp operated at 1000 W, drawn from a step up transformer fed from stabilized mains. The current through the lamp (20–150 ma.) was varied by means of a Variac in the primary circuit of the lamp transformer. The output of the lamp was monitored by an I.P. 21 photomultiplier tube connected to a Photovolt instrument. About 90% of the light output is at 2537 Å.

The radiation was filtered through a 5 cm. quartz cell containing KI-1 aqueous solution permitting the isolation of the strong Hg 2537 Å line.

Actinometry was carried out by means of the uranyl oxalate actinometer. The chemical change was linear in light intensity as determined by the monitoring photocell. As a check a ferri oxalate actinometer was used. In a typical experiment we obtained for the light intensity, \( J \) (curran oxalate) \( J = 6.32 \times 10^{-7} \) einstein \( l^{-1} \) \( sec^{-1} \). \( J \) (ferri oxalate) \( J = 6.20 \times 10^{-7} \) einstein \( l^{-1} \) \( sec^{-1} \). Agreement between the results was satisfactory.

Reaction Cell.—The reaction cell was adapted from a 4 cm. quartz absorption cell with flat optical windows of 3 cm. optical length for light absorption at 2537 Å and 4 cm. optical length for spectrophotometry. It was connected to a vacuum system through a valve. The cell orientation relative to the light source was held fixed during all experiments. In this cell 13 cc. of solution was used for each irradiation. Another cell was employed for gasometric analysis, consisting of quartz cylindrical cell with flat optical windows as base, and 5 cm. optical length holding 60 cc. of solution.

Analysis.—Hydrogen was determined by a microgasometric method. The pressure was determined by a McLeod gauge.

Iodine was determined by its absorption as I⁻. The spectrophotometric light source was an ordinary 6V 3A tungsten hot wire bulb, with a cut off filter above 400 ma.

An empirical calibration was carried out by introducing a
known amount of I₂ in aqueous iodide solutions, into the reaction cell, and measuring optical densities by means of the IP 21 photomultiplier and the Photovolt instrument. It was found that the optical density was independent of iodide ion concentration above $10^{-4} \text{ M}$ and a linear dependence of $D$ on the iodide concentration up to $1.2 \times 10^{-3}$ mole liter$^{-1}$ was found with an apparent molar absorption coefficient 

$$\epsilon = 9 \times 10^3 \text{mole}^{-1} \text{liter cm}^{-1}$$. At lower $I^-$ concentrations a similar procedure was employed. The lower limit of iodine detected is about $2 \times 10^{-2}$ mole liter$^{-1}$ and the upper limit was $2.5 \times 10^{-4}$ mole liter$^{-1}$. This technique enabled an accurate determination of initial reaction yields.

Materials.—All chemicals used were of Analar grade. Solutions were prepared in triply distilled water (ordinary distillation followed by distillation from alkaline permanganate and phosphoric acid). Control experiments were carried out using water purified by irradiation with 200 kv. X-rays and decomposition of the H₂O₂ thus formed by irradiation with the 2537 Å, line of a low pressure Hg lamp. These experiments yielded the same results as obtained in triply distilled water.

Procedure.—A known amount of freshly prepared neutral potassium iodide solution or solid KI was introduced into the reaction vessel and the acid or buffer were added from a separate container, after evaporation, to avoid thermal oxidation. No thermal oxidation could be detected. Erratic results were obtained in solutions containing initial iodine concentration higher than $5 \times 10^{-4}$ M causing a decrease of the initial yield. This effect was most important at high pH and low $I^-$ concentration. The pH below 3.5 was adjusted by HSO₃⁻ and above pH 3.5 by K₂HPO₄-Na₂HPO₄ buffer ($10^{-3}$ M). The pH was determined at the end of each run.

The contents of the reaction cell were stirred continuously by a Teflon coated magnetic stirrer. For experiments on deoxygenated solutions the reaction cell was connected to the vacuum system for 20 seconds every five minutes until, after approximately 3.5 hours, its equilibrium vapor pressure was $1-2 \times 10^{-5}$ mm. The small reaction cell was kept in a thermostatted brass compartment in which water was circulated. Experiments were carried out at $25 \pm 0.2^\circ$.

At suitable intervals after the beginning of irradiation a mechanical shutter separating the cell and the lamp was closed and the amount of free iodine determined. Hydrogen was determined at the end of each run in the large irradiation vessel. These iodine and hydrogen determinations were in satisfactory agreement of about 10%.

Results and Discussion

Dependence of Initial Yields on pH and Light Intensity.—An initial quantum yield $\gamma_i$ was obtained from the expression

$$\gamma_i = \frac{1}{F} \int \frac{d[I]}{dt} \, dt$$

where $F$ is the light intensity. The dependence of $\gamma_i$ in evacuated solutions on pH, iodide ion concentration and light intensity was investigated.

Figure 1 presents the dependence of the yield of I₂ at constant light intensity on irradiation time. The initial slopes could be determined and hence $\gamma_i$ was approximately evaluated.

The pH dependence of $\gamma_i$ is shown in Fig. 2. Above pH 3.5 a residual pH independent quantum yield is observed. This is consistent with recent observations. The pronounced dependence of $\gamma_i$ in acid solutions is in qualitative agreement with previous investigations.

The initial quantum yield is independent of light intensity. This observation was confirmed with reasonable accuracy for a low pH region (pH 0.8). These data are presented in Fig. 3, and are consistent with other recent results.

The Nature of the Absorption Act and Primary Products.—There is good agreement between the experimental spectroscopic results and their recent theoretical interpretations regarding the nature of the primary absorption act. Both the theory of Smith and Symons and that of Stein and Treinin agree in that they postulate as did Platzman and Franck a symmetrical excited state in which the electron is not bound to a single solvent molecule but rather is bound in the field formed by the oriented water molecules of the solvent medium. In spite of detailed differences, concerning the structure of the excited level, both groups recently have concluded that in the excited state the electron probably is confined to the first hydration layer of water molecules.

The restrictions imposed by the Franck-Condon principle on the optical electron transfer process have to be considered. The life time of the spherically symmetrical excited state of the iodide ion, is of the order of the relaxation time of the solvent molecules. After a period of $10^{-13}$ to $10^{-14}$ sec. an iodine atom and an electron are formed. There is no experimentally observed fluorescence in aqueous iodide solutions. The life time of an

Fig. 1.—Photo-oxidation yields of iodide solutions at constant light intensity, $I = 0.15$ M, $J = 9.7 \times 10^{-1}$ einstein liter$^{-1}$ sec.$^{-1}$: Curve 1, 0.74 M H₂SO₄; 2, pH 0.65; 3, pH 0.90; 4, pH 1.10; 5, pH 1.36; 6, pH 1.78; 7, pH 2.2; 8, pH 2.6.

Fig. 2.—The pH dependence of the initial quantum yields.
excited state required before fluorescent radiative transition to the ground state occurs is of the order of \(10^{-8}\) sec. or longer. Therefore in systems like that of aqueous iodide after \(10^{-10}\) to see.

The Residual Yield.—Independent evidence derived from the investigation of the chemistry of hydrogen atoms in iodide solutions indicates that at pH above 3 no oxidation reaction of I\(^-\) ion by H atoms occurs. Thus in this pH region the possible reactions of the radicals in bulk will be hydrogen atom recombination

\[
2H \rightarrow H_2
\]

and iodine formation by the mechanism proposed by Grossweiner and Matheson

\[
\begin{align*}
1 + I^- & \rightarrow I_2 \\
2I_2 & \rightarrow I^- + I^- \\
I^- + I^- + I^- & \rightarrow 2I
\end{align*}
\]

These back reactions are possible

\[
\begin{align*}
H + I & \rightarrow H^+ + I^- \\
H + I_2 & \rightarrow H^+ + 2I^- \\
I^- & \rightarrow I^-
\end{align*}
\]

As these experiments were carried out at relatively high [I\(^-\)] concentration, it is reasonable to assume that every iodine atom introduced into the bulk is converted into the I\(^-\) ion. This assumption is consistent with the results of Grossweiner and Matheson. Including reactions 2,3,4 and 8 in the kinetic scheme the steady-state treatment for the intermediates I, I\(^-\) and H readily leads to

\[
\frac{d[Y]}{dt}_0 = \frac{k_{a\beta}}{2k_4 + k_6(k_3/k_4)^{1/2}}
\]

where \(\alpha\) is the quantum yield for the introduction of radicals into the bulk.

The relation between the experimental residual yield \(y_{1r}\) and \(\alpha\) will be considered for two limiting cases

\[
\begin{align*}
(\alpha) & \quad k_3 = k_4 = k_5 \\
(\beta) & \quad k_3 = k_4 \gg k_5
\end{align*}
\]

As both reactions 2 and 4 are diffusion controlled, these are the relevant cases. Thus \(\alpha\) is of the order of \(2\gamma_r^+ = 3\gamma_r^-\).

In Fig. 4 the photochemical curves at various I\(^-\) concentrations at pH 5.5 are presented. From the initial slopes the residual yield is obtained \(\gamma_r^+ = 0.03 \pm 0.005\). The initial residual yield is independent of I\(^-\) concentration.

Graphical Evaluation of Initial Yields.—In the photochemical system the iodine yield versus time curves (Fig. 1) are departing from linearity indicating an efficient back reaction. This effect causes a considerable inaccuracy in the estimation of the initial quantum yields. This difficulty is mainly manifested at high pH and low I\(^-\) concentrations.

The initial yields were calculated on the basis of the assumption, to be discussed later, that at relatively low pH below 2.0 hydrogen atoms in the bulk act as oxidizing agents for I\(^-\) ions; or alternatively may reduce I\(^-\). Disregarding for the moment the actual oxidation and reduction mech-

\[
\begin{align*}
(22) & \quad J. Franck and F. Haber, Sitzungsber. Preuss. Akad. Wiss., 250 (1931).
\end{align*}
\]
PHOTOCHEMISTRY OF IODIDE ION IN AQUEOUS SOLUTION

The rate of formation of $I_2$ can be represented by

$$\frac{d[I_2]}{dt} = \frac{\alpha J}{2} \left( 1 - \frac{k_{ox}[I^-]}{k_{ox}[I^-] + k_t[I_2]} \right) = \frac{\alpha J k_{ox}[I^-]}{k_{ox}[I^-] + k_t[I_2]}$$

(II)

where $k_{ox}$ and $k_t$ are the composite rate constants for oxidation of $I^-$ and reduction of $I_2$ by $H$ atoms.

In the pH region below 2 it is assumed that the rate of introduction of radicals into the bulk is equal to the initial photo-oxidation yield.

Integration of equation II for the initial stages of the reaction experimentally investigated when $I^-$ can be considered as effectively constant, leads to the result

$$\frac{t}{[I_2]} = \frac{1}{\alpha d} + \frac{1}{2\alpha d} \frac{E_t}{k_{ox}[I^-]} [I_2]$$

(III)

The plots of $t/[I_2]$ versus $[I_2]$ are presented in Fig. 5 and 6 for various $H^+$ and $I^-$ concentrations. The plots are linear up to $[I_2] = 2 \times 10^{-8} \text{ M}$, in good agreement with equation III.

From the intercepts in Fig. 5 and 6 the initial photo-oxidation yields are obtained. The initial quantum yields at various pH obtained by this method are presented in Table I. These results are compared with the initial yields obtained directly from the initial slopes of the curves in Fig. 1. The results thus obtained by the extrapolation method are about 5-20% higher, although they show the same general pH dependence as the initial yields directly obtained. These results clearly indicate that in the low pH region the initial quantum yield is pH dependent.

**Table I**

<table>
<thead>
<tr>
<th>pH</th>
<th>Initial Quantum Yields for Photo-oxidation of Evacuated 0.15 M KI Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>From Fig. 1</td>
</tr>
<tr>
<td>0.9</td>
<td>0.226</td>
</tr>
<tr>
<td>1.1</td>
<td>0.200</td>
</tr>
<tr>
<td>1.36</td>
<td>0.107</td>
</tr>
<tr>
<td>1.78</td>
<td>0.130</td>
</tr>
</tbody>
</table>

The pH Dependence of $\gamma_1$.—The pH dependence of the initial quantum yield in the region below pH 3.5 may be due to either of the causes: (a) Interaction of the $H^+$ ion with the excited state of the iodide or with one of the species participating in the secondary recombination in the photochemical cage. These possible mechanisms will lead to a pH dependent rate of introduction of radicals into the bulk. (b) It was proposed by Rigg and Weiss that a scavenging reaction of $H$ atoms occurs

$$H + H^+ \leftrightarrow H_2^+$$

followed by

$$H_2^+ + I^- \rightarrow H_2 + I$$

(10)

These reactions are assumed to compete with the back reactions 7 and 8.

In this mechanism, no clear cut distinction between secondary cage recombination and bulk recombination was presented. However, the treatment is based on conventional steady-state ki-
The residual yield for the introduction of the radicals into the bulk is

$$\alpha' = \Gamma (1 - \beta')$$  \hspace{1cm} (VI)

where $\Gamma$ is the cross-section for primary photodissociation followed by the formation of radical pair in a solvent cage.

In the presence of a scavenger the probability of a radical to escape geminate recombination is\(^{26,23}\)

$$\int h(t) \left( 1 - e^{-\beta' \tau} \right) dt = \beta' - \int h(t) e^{-\beta' \tau} dt =$$

$$\beta' - \int_{\text{4s} / \beta'}^{\infty} \frac{dt}{t} e^{-\beta' \tau} dt =$$

$$2a \left( \pi k [S] \right)^{1/2} - \frac{S a t k \beta'}{2} [S] \quad \text{(VII)}$$

where $k$ is the long time bulk rate constant for the scavenging reaction,\(^{29}\) $[S]$ the scavenger concentration, and $a$ is a parameter defined by Noyes.\(^{25}\)

The integration of $h(t)$ is valid according to this approximation only after a certain period corresponding to the formation of distinct chemical species and subsequent few diffusive displacements. This period is selected as the relaxation time of the solvent molecules $10^{-11}$ sec. Thus we set $4a^2/\beta'^2 = 10^{-11}$ sec. and as $\beta' \sim 1$ hence $4a^2/\beta'^2 = 10^{-11}$ sec. The theoretical expression for relatively low scavenger concentrations is thus given by

$$\alpha = \alpha_i + 2ak \left( \pi k [S] \right)^{1/2} \quad \text{(VIII)}$$

Fitting our experimental results into this scheme using the value of $W = 0.33$ obtained from Fig. 3 we obtain $k = 3 \times 10^8 \text{ M}^{-1} \text{ sec.}^{-1}$ as an upper limit, assuming $\Gamma = 1$.

The nature of the scavenging reaction will now be considered. A plausible mechanism for hydrogen atom scavenging by $H^+$ is that of $H_2^+$ formation according to reaction 9.\(^9\) However independent experimental work\(^{15}\) indicates that the rate constant of $H_2^+$ formation is relatively low, $k_9 \sim 10^8 \text{ M}^{-1} \text{ sec.}^{-1}$, a result which is much lower than the scavenging rate constant. Thus we are forced to conclude that $H_2^+$ formation is not involved in the scavenging reaction. The magnitude of the rate constant $k$ shows that the scavenging process involves electron transfer. However at present we cannot decide whether it is an $H$ atom or an electron which undergoes the random walk process in the photochemical cage and which interacts with $H^+$.

Thus the scavenging mechanisms may involve the charge transfer process

$$(I + H) + H^+ \rightarrow I + H^+ + H$$

Theoretical estimations\(^{29}\) indicate the efficiency of this reaction at relatively large separations.

Alternatively the scavenging reaction may involve thermal electron capture by the hydronium ion, which may be an efficient process. The possibility of specific reactions of thermalized electrons was considered in detail in radiation chemistry.\(^{28,31}\) Recently the question of the distinction between hydrogen atoms and related species was raised. Thus Barr and Allen\(^{25}\) postu-

lated the existence of two forms of H atoms in aqueous solutions. One of these probably is the thermalized electron.\(^3,4\)

**Dependence of \( \gamma \) on I\(^-\) Concentration.**—The experimental results presented in Fig. 6 indicate that the initial quantum yield is independent of initial iodide concentration in the concentration region \( 5 \times 10^{-4} \) to 0.15 M at low pH. These results were obtained under conditions of total light absorption which hold up to the lower I\(^-\) concentration employed. These results are in variance with previously reported experimental data\(^6\) and indicate that contrary to previous suggestions\(^8,11\), the iodide ion concentration does not affect the rate of introduction of radicals into the bulk.

**Radical Reactions in the Bulk.**—As a result of the scavenging reaction, or by diffusion away from original partners, hydrogen and iodide atoms are introduced into the bulk. At relatively low pH below 2.0 hydrogen atoms act as oxidizing agents for the iodide ion. Recently this fact was demonstrated by oxidation of the iodide ion by H atoms externally generated, and it was shown that the results are consistent with an oxidation mechanism involving H\(_2\)\(^+\) as the actual oxidizing species.\(^15\) In this low pH region the initial rate of introduction of H atoms into the bulk is equal to the initial photo-oxidation rate.

The nature of the oxidation reaction of I\(^-\) by atomic hydrogen in the photochemical system was investigated by considering the compound rate constants ratio \( k_r/k_{ox} \). This value was obtained from the ratio of slope to intercept from Figs. 5 and 6. The accuracy of the rate constants obtained is about 5%. These data are presented in Table II.

**Table II**

<table>
<thead>
<tr>
<th>pH</th>
<th>( 1/1^+ ), M</th>
<th>( 1/H^+ ), M(^{-1} )</th>
<th>( 10^{-1} ) ( k_r/k_{ox} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>1.5 x 10(^{-1})</td>
<td>4.15</td>
<td>0.58</td>
</tr>
<tr>
<td>0.87</td>
<td>1.5 x 10(^{-2})</td>
<td>...</td>
<td>0.89</td>
</tr>
<tr>
<td>0.87</td>
<td>1.5 x 10(^{-2})</td>
<td>...</td>
<td>1.0</td>
</tr>
<tr>
<td>0.9</td>
<td>1.5 x 10(^{-3})</td>
<td>7.7</td>
<td>0.76</td>
</tr>
<tr>
<td>1.1</td>
<td>1.5 x 10(^{-3})</td>
<td>11.9</td>
<td>1.46</td>
</tr>
<tr>
<td>1.36</td>
<td>1.5 x 10(^{-3})</td>
<td>23.3</td>
<td>2.25</td>
</tr>
<tr>
<td>1.78</td>
<td>1.5 x 10(^{-3})</td>
<td>57.0</td>
<td>5.20</td>
</tr>
</tbody>
</table>

The ratio of the rate constants is found to be pH dependent. A plot of this ratio as a function of \( 1/[H^+] \) is a straight line, with a positive intercept. (Fig. 8). The experimental results can be fitted by the expression

\[
k_{ox} = 1.5 \times 10^3 + 900 \sqrt{[H^+]} \tag{IX}
\]

No dependence of \( k_r/k_{ox} \) on I\(^-\) could be detected up to \( 1.5 \times 10^{-1} \) M. For higher iodide concentrations the results were not accurate enough to establish this point.

Thus we obtain
\[
\frac{k_{z2}}{k_{z1}} = \frac{k_{z1} + k_{x2}(k_{x3}/k_{x2} + [I^-]) + k_{x2} k_{x2} [I_2]}{I^-}
\]

For relatively low \( I_2 \) concentrations the linear term in \( I_2 \) can be neglected. This is indicated from Figs. 5 and 6 where no deviations from linearity were observed.

The pH dependence of the ratio of the rate constants is consistent with the oxidation mechanism involving \( H_2^+ \). The oxidation mechanism involving abstraction of \( H \) atoms from the hydration layer requires that the ratio of the rate constants should not depend on \( pH \), while the triple collision mechanism\(^{36} \) requires that the intercept in Fig. 8 should be zero. Neither of these conditions is fulfilled.

It should be pointed out however that while the photochemical data indicate a \( pH \) dependent mechanism for the oxidation of \( I^- \) by \( H \) atoms, these results by themselves do not yield absolute evidence for the oxidation mechanism involving \( H_2^+ \). The main effect of \( H^+ \) ion on the photochemistry is due to the \( pH \) dependence of the rate of introduction of radicals into the bulk. The difficulties of the detection of the dependence of \( k_{z2}/k_{z1} \) on \( I^- \) ion concentration which probably cancels out due to opposite effects remain to be elucidated.


THE NATURE OF THE CHROMIUM(VI)—1,5-DIPHENYLCARBOHYDRAZIDE REACTION. II. THE CHROMIUM(II)—DIPHENYLCARBAZONE REACTION\(^{1,2} \)

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Received February 6, 1961

Chromium(II) reacts with diphenylcarbazone in aqueous solution to give an intense magenta color. A molar absorbancy index of \( 3.6 \times 10^4 \) (based on chromium(II) concentration) has been obtained at 546 nm. The absorption spectrum is very similar to that of the magenta product of the aqueous chromium(VI)—1,5-diphenylcarbohydrazide reaction. It is concluded that the same colored substance, a chromium complex, is formed in both reactions.

Introduction

In several previous investigations\(^3\)–\(^5\) it has been found that chromium(II) reacts with diphenylcarbazone (phenylazoformic acid—2-phenylhydrazide) in aqueous media to give an intense magenta color, similar to that arising from the aqueous chromium(VI)—1,5-diphenylcarbohydrazide reaction. Very recently, however, Babko and Getman\(^6\) have reported that chromium(II) does not react with diphenylcarbazone. They attribute the results of previous investigations to the use of chromous acetate. Since they have found that diphenylcarbazone in acetate acid has the same color whether chromium(II) is present or not, Babko and Getman conclude that the color observed by previous workers must have resulted from the side reaction of diphenylcarbazone with acetic acid.

Because of the doubt thrown on the existence of the chromium(II)—diphenylcarbazone reaction, which had seemed to be closely related to the chromium(VI)—1,5-diphenylcarbohydrazide reaction, we have made a detailed investigation of this and related systems.

1. This work was assisted by a research grant from the National Science Foundation.