

topological representation of a closed system, any two points will thus be connectable by a series of lines, *i.e.*, a chain.<sup>4</sup> Such a topological representation is said to be connected. Conversely, connected topological representations represent closed stereochemical systems of permutational isomers. Since nondifferentiable reactions generate identical topological representations, nondifferentiability implies identical closure properties. For example, if  $p_0$  generates a closed stereochemical system and  $p_0'$  is not differentiable from  $p_0$  in a chiral environment, then  $p_0'$  also generates a closed stereochemical system.

Brocas' kinetic treatment of permutational isomerization reactions<sup>15</sup> is based on topological representations. One can easily show that if two reactions generate the same topological representation, their eigenvectors (as defined by Brocas) must be the same.

The concepts developed in this paper are thus seen to be useful for the description and solution of many problems in dynamic stereochemistry.

**Acknowledgments.** I am deeply indebted to Dr. Bertram Frenz for his help in revising the manuscript for publication.

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## On the Mechanism of Reduction of Cobalt(III) and Ruthenium(III) Hexaammine Complexes by Several Aliphatic Radicals

H. Cohen and D. Meyerstein\*

*Contribution from the Nuclear Research Centre—Negev, Beer-Sheva, Israel. Received July 26, 1971*

**Abstract:** The specific rates of reaction of several aliphatic radicals with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  were determined. Radicals on the  $\alpha$  carbon relative to OH or  $\text{NH}_2$  groups were shown to be stronger reducing agents than radicals on the  $\alpha$  carbon to a carboxylic or an amide group. The reactivity of the radicals  $\dot{\text{C}}\text{H}_2\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ ,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{OHCOO}^-$ , and  $\text{CH}_3\text{CO}\dot{\text{C}}(\text{O}^-)\text{CH}_3$ , toward  $\text{Ru}(\text{NH}_3)_6^{3+}$  increases along this series, whereas the reversed order of reactivities is found for the reactions with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Cu}_{\text{aq}}^{2+}$ . This order is different from the order of reactivities toward nitrobenzene and 2,3-butanedione where the reactivity increases along the series  $\text{CH}_3\dot{\text{C}}\text{OHCO}_2^-$ ,  $\dot{\text{C}}\text{H}_2\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ , and  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ . The latter order is identical with that of increasing  $\text{p}K$  of the OH group. The results are interpreted as suggesting that the contribution of  $\pi$  character to the orbital containing the unpaired electron in the radical significantly affects the specific rates of reactions. The implication of the results in radiobiology is discussed.

It has been suggested that aliphatic radicals, usually produced by hydrogen abstraction reactions, are relatively strong reducing agents.<sup>1-4</sup> Such radicals have been shown to reduce different organic compounds<sup>1-3</sup> and metal cations<sup>4,5</sup> both in organic and aqueous media. It has been shown that the specific rate of reduction depends on the structure of the radicals. Radicals  $\alpha$  to a hydroxylic or amino group being relatively strong reducing agents whereas radicals  $\alpha$  to a carboxylic group were shown to be less reactive. It has been suggested that many of these reduction reactions take place *via* an outer-sphere electron-transfer mechanism.<sup>6</sup>

Organic compounds are often used<sup>7</sup> as hydroxyl radical scavengers when reactions of  $e_{\text{aq}}^-$  or hydrogen atoms are studied in radiation chemistry.<sup>7</sup> However, relatively little is known on the chemical properties of

the radicals formed. This is believed to be of major importance in radiobiological systems, where most of the secondary intermediates are expected to be aliphatic radicals.

The reduction of cobalt(III) and ruthenium(III) hexaammine complexes proceeds always *via* the outer-sphere mechanism.<sup>8</sup> The only exception to this rule, suggested in the literature, is for the reduction of  $\text{Co}(\text{NH}_3)_6^{3+}$  by OH radicals, which was suggested to proceed *via* hydrogen abstraction from the ammine groups.<sup>9</sup> It will be shown that this mechanism does not apply for the radical reactions described in this study. We have decided to measure the specific rates of reduction of the latter complexes by several aliphatic radicals, with the hope of achieving a better understanding of their properties as outer-sphere reducing agents.

### Experimental Section

**Materials.** All solutions were prepared from triple distilled water. Cobalt(III) hexaammine perchlorate was precipitated with perchloric acid from a solution of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , supplied by K & K. The precipitate was purified by two recrystallizations from water. Ruthenium hexaammine chloride from Johnson,

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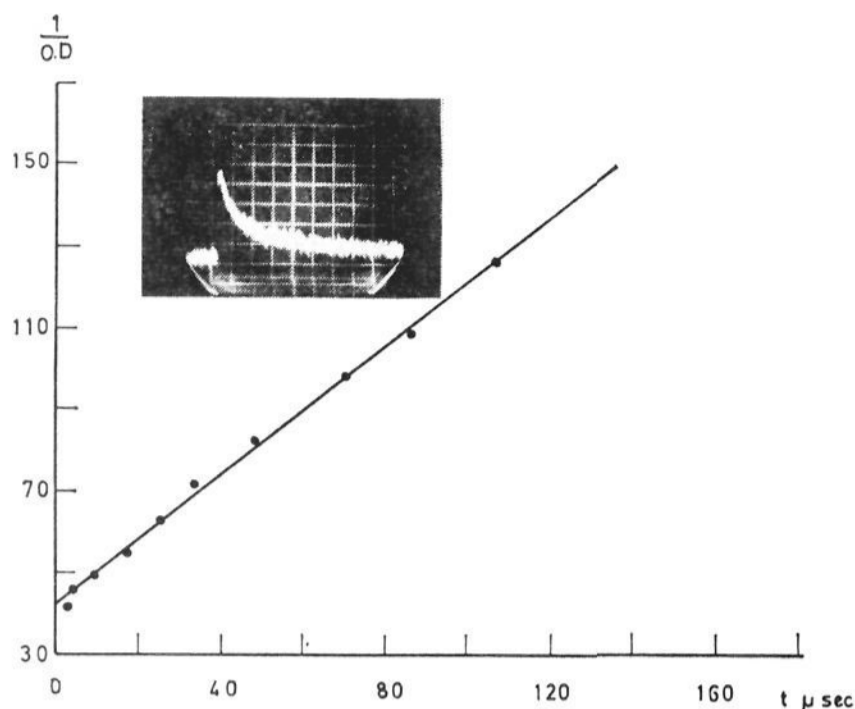


Figure 1. Second-order disappearance plot for the  $(\text{CH}_3)_2\text{COH}$  radical: solution composition,  $1 \times 10^{-2} M$  2-propanol, pH 6.0,  $\text{N}_2\text{O}$  saturated; pulse intensity,  $6 \times 10^{19} \text{ eV l}^{-1}$ ; insert, oscilloscope trace showing the disappearance of the radical; total light intensity, 0.800 V; abscissa,  $50 \mu\text{sec/div}$ ; ordinate, 0.020 V/div, measured at  $\lambda = 320 \text{ nm}$ .

Matthey and Co. was used after two further recrystallizations from dilute hydrochloric acid.

Nitrous oxide was purified from oxygen by bubbling through three washing bottles containing basic pyrogallol and then through two washing bottles containing triple distilled water.

**Procedure.** The procedure of preparation of samples for the pulse radiolytic experiments has been identical with that described earlier in detail.<sup>10,11</sup> The pulse radiolytic experiments were carried out using 0.2–1.5- $\mu\text{sec}$ , 5-MeV, 200-mA pulses from the electron linear accelerator at the Hebrew University of Jerusalem. The dose per pulse has been  $1\text{--}6 \times 10^{19} \text{ eV l}^{-1}$ . The irradiation cell was 4 cm long, the analyzing light travelling three times through the cell. The experimental setup in Jerusalem and the method used for evaluating the results have been described elsewhere in detail.<sup>12</sup> All experiments were carried out at room temperature,  $25 \pm 2^\circ$ .

The kinetics of disappearance of the organic radicals were followed at different wavelengths. The wavelength in each case was chosen so that the difference in the absorption coefficient of the radicals and the products would be as big as possible. No measurements could be carried out below 300 nm due to light absorption by the solutions.

The dose delivered by the linear accelerator was determined by the modified Fricke dosimeter for high-dose rates.<sup>13</sup>

The yield of  $\text{Co}^{2+}$  was determined by the method described by Katakis and Allen.<sup>9</sup>

## Results

Solutions saturated with  $\text{N}_2\text{O}$  and containing  $1 \times 10^{-2} M$  of different organic compounds at several pH's have been irradiated. The kinetics of disappearance of the radicals formed was followed. It was found for all the radicals studied that the mechanism of their disappearance obeyed a second-order rate law (e.g., Figure 1). The specific rates observed were in good agreement with those reported in the literature for these radicals.<sup>1,2,14–18</sup>

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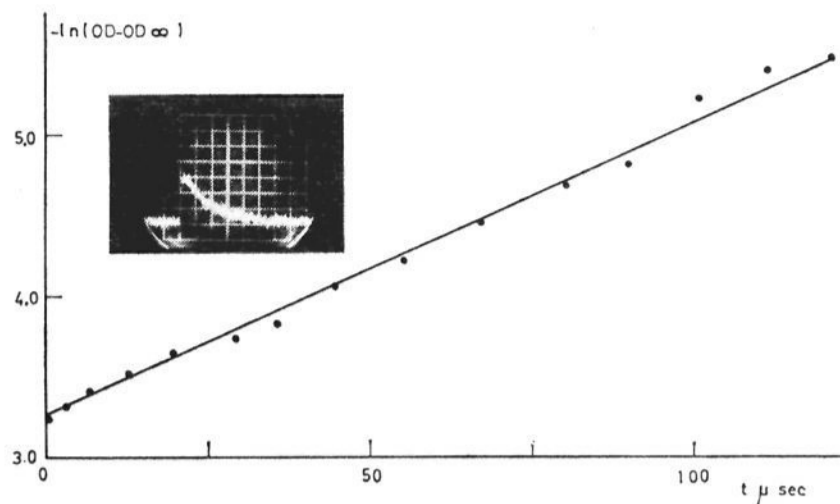


Figure 2. Pseudo-first-order disappearance plot for the  $(\text{CH}_3)_2\text{COH}$  radical in the presence of  $\text{Co}(\text{NH}_3)_6^{3+}$ : solution composition,  $1 \times 10^{-2} M$  2-propanol,  $9 \times 10^{-4} M$   $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ , pH 6.0,  $\text{N}_2\text{O}$  saturated; pulse intensity,  $6 \times 10^{19} \text{ eV l}^{-1}$ ; insert, oscilloscope trace showing the disappearance of the radical; total light intensity, 0.800 V; abscissa,  $20 \mu\text{sec/div}$ ; ordinate, 0.020 V/div, measured at  $\lambda = 300 \text{ nm}$ .

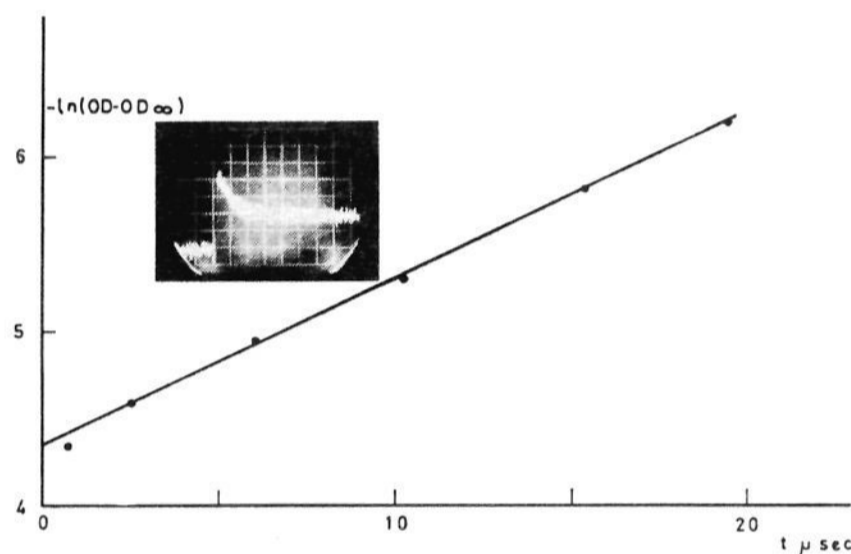


Figure 3. Pseudo-first-order disappearance plot for the  $(\text{CH}_3)_2\text{COH}$  radical in the presence of  $\text{Ru}(\text{NH}_3)_6^{3+}$ : solution composition,  $1 \times 10^{-2} M$  2-propanol,  $1 \times 10^{-4} M$   $\text{Ru}(\text{NH}_3)_6(\text{ClO}_4)_3$ , pH 6.0,  $\text{N}_2\text{O}$  saturated; pulse intensity,  $9 \times 10^{19} \text{ eV l}^{-1}$ ; insert, oscilloscope trace showing the disappearance of the radical; total light intensity, 0.800 V; abscissa,  $10 \mu\text{sec/div}$ ; ordinate, 0.010 V/div, measured at  $\lambda = 350 \text{ nm}$ .

The effect of added  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  at different concentrations, in the range of  $5 \times 10^{-5}\text{--}1 \times 10^{-3} M$ , on the mechanism of disappearance of the organic radicals was studied. It was found that for most of the radicals the rate law of the disappearance reaction changed from second order to pseudo first order (Figures 2 and 3). All the kinetic plots were analyzed for first- and second-order disappearance, and pseudo-first-order rates were calculated when a good first-order decay plot was obtained for at least 2 half-lives. A correction for the disappearance reaction of the organic radical in the absence of the complexes was included when needed. For every rate constant at least ten kinetic traces were analyzed which were obtained by pulse radiolyzing ten sample solutions, prepared by using at least two different stock solutions to dilute to several different concentrations. In all the cases where a reaction with ruthenium(III) was measured a finite absorption, after the reaction ended, remained (see in Figure 3). This absorption is attributed

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Table I. Specific Rates of Reduction of Several Oxidants by Some Aliphatic Radicals<sup>a</sup>

Radical	pK of the radical	pH	$k_{R+Co(NH_3)_6^{3+}}$ , $M^{-1} sec^{-1}$	$k_{R+Ru(NH_3)_6^{3+}}$ , $M^{-1} sec^{-1}$	$k_{R+Cu_{aq}^{2+}}$ , $M^{-1} sec^{-1}$	$k_{R+C_6H_5NO_2}$ , $M^{-1} sec^{-1}$	$k_{R+CH_3COC(=O)CH_3}$ , $M^{-1} sec^{-1}$
$\dot{C}O_2^-$	<2.4	4.8 ± 0.1	$4.0 \times 10^7$	$2.0 \times 10^9$ <sup>f</sup>			
$\dot{C}H_2OH$	10.7	5-6	$1.4 \times 10^8$	$4.1 \times 10^7$	$1.1 \times 10^8$	$6.0 \times 10^7$ <sup>d</sup>	$6.5 \times 10^7$
$\dot{C}H_2O^-$		12 ± 0.1	$9.0 \times 10^9$			<10 <sup>7</sup> <sup>b</sup>	$1.1 \times 10^8$ <sup>c</sup>
$\dot{C}H_3CHOH$	11.6	5-6	$5.2 \times 10^7$	$5.5 \times 10^8$ <sup>f</sup>	$7.4 \times 10^7$	$2.7 \times 10^9$ <sup>b</sup>	
$\dot{C}H_3CHO^-$		12 ± 0.1	$8.5 \times 10^9$			$2.4 \times 10^8$ <sup>d,f</sup>	$5.6 \times 10^8$ <sup>c</sup>
$(\dot{C}H_3)_2\dot{C}OH$	12.2	5-6	$1.3 \times 10^7$	$9.2 \times 10^8$	$4.5 \times 10^7$	$3.3 \times 10^8$ <sup>b</sup>	
$(\dot{C}H_3)_2\dot{C}O^-$		12 ± 0.1	$5.0 \times 10^9$			$3.1 \times 10^9$ <sup>b</sup>	$6.0 \times 10^8$
$\dot{C}H_3\dot{C}(OH)CO_2^-$	9.8	6.0 ± 0.2	$7.0 \times 10^6$	$2.5 \times 10^9$		$1.6 \times 10^9$ <sup>b</sup>	$8.6 \times 10^8$ <sup>c</sup>
$\dot{C}H_3\dot{C}(O^-)CO_2^-$		12 ± 0.1	$2.4 \times 10^{10}$			$6.5 \times 10^7$ <sup>d,f</sup>	$2.8 \times 10^7$
$\dot{C}H_3CO\dot{C}(OH)CH_3^{\circ}$	4.4	1.2 ± 0.1	< $2.0 \times 10^5$	< $3.8 \times 10^6$			
$\dot{C}H_3CO\dot{C}(O^-)CH_3^{\circ}$		5.5 ± 0.2	< $1.8 \times 10^5$	$2.0 \times 10^9$			
$H_3^+\dot{N}CHCO_2^-$ <sup>d</sup>		5.7 ± 0.1	< $1.2 \times 10^7$	$4.0 \times 10^8$			
$\dot{C}H_2COOH$	4.5	2.5 ± 0.1	< $1.0 \times 10^7$	< $3.0 \times 10^7$			
$\dot{C}H_2COO^-$		7.3 ± 0.1	< $3.2 \times 10^6$	< $1.0 \times 10^7$			
$\dot{C}H(CO_2H)_2$	5.7	2.5 ± 0.1	< $8.0 \times 10^6$	< $1.1 \times 10^8$			
$\dot{C}ONH_2^{\circ}$		6.2 ± 0.1	< $3.6 \times 10^7$	< $7.0 \times 10^7$			
$\dot{C}H_3^{\circ}$							
HCON<		6.0 ± 0.1	< $1.0 \times 10^7$	< $3.0 \times 10^7$			
$\dot{C}H_2$							

<sup>a</sup> All the solutions contained  $1 \times 10^{-2} M$  of the organic solute, those which were at a pH higher than 3 were saturated with  $N_2O$ , and those which were at a pH lower than 3 were saturated with Ar. Unless otherwise mentioned the standard deviation in the rate constants is ±15%. pK values were taken from ref 3 and 15-17. <sup>b</sup> Values taken from ref 1. <sup>c</sup> Values taken from ref 2. <sup>d</sup> The concentration of the organic solute was  $1 \times 10^{-1} M$ . <sup>e</sup> The solution contained  $1 \times 10^{-3} M$  2,3-butanedione and  $1 \times 10^{-2} M$  2-propanol which reacted with H, OH radicals to yield  $(\dot{C}H_3)_2\dot{C}OH$  which attacked the 2,3-butanedione to yield the desired radicals. <sup>f</sup> The standard deviation in the rate constants is ±30%. <sup>g</sup> Suggested by ref 18.

to the Ru(II) hexaammine complex which is known to absorb in the spectral range used.<sup>19</sup> (The formation of  $Ru(NH_3)_6^{2+}$  as a stable product of the reaction  $\dot{C}H_2OH + Ru(NH_3)_6^{3+}$  has already been reported).<sup>20</sup>

The results are summarized in Table I. Two main factors contributed to the relative large error limit of some results (Table I). (a) In some of the reactions with  $Ru(NH_3)_6^{3+}$  the difference between the molar absorption coefficient of the radicals and the  $Ru(NH_3)_6^{2+}$  was small. (b) For the relatively slow reactions the correction due to the second-order disappearance of the radicals was quite large (up to 50%).

The yields of  $Co^{2+}$  after four and eight pulses were delivered to the solutions were measured. It was found that for solutions saturated with  $N_2O$  and containing  $1 \times 10^{-2} M$  methanol, ethanol, 2-propanol, lactate, and formate at pH 6.0 and  $9 \times 10^{-4} M$   $[Co(NH_3)_6]-(ClO_4)_3$ ,  $G(Co^{2+}) = 6.0 \pm 0.5$ . For the solutions containing glycine as the organic solute  $G(Co^{2+}) = 4.0 \pm 0.5$  was determined. The yield was not measured in solutions containing acetate, malonate, formamide, and dimethylformamide as the radicals formed from these solutes did not react with  $Co(NH_3)_6^{3+}$  (see Table I).

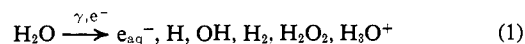
The difference in the order of reactivities of the radicals  $\dot{C}H_2OH$ ,  $\dot{C}H_3\dot{C}HOH$ ,  $(\dot{C}H_3)_2\dot{C}OH$ , and  $\dot{C}H_3\dot{C}OHCO_2^-$  toward  $Ru(NH_3)_6^{3+}$  and  $Co(NH_3)_6^{3+}$  was attributed to the difference in the electronic configuration of the complexes (see Discussion). In order to verify these assumptions the specific rates of reaction of the radicals  $\dot{C}H_2OH$ ,  $\dot{C}H_3\dot{C}HOH$ , and  $(\dot{C}H_3)_2\dot{C}OH$  with  $Cu_{aq}^{2+}$  were determined. The results are summarized in Table I. The specific rates of reaction of several radicals with 2,3-butanedione and nitrobenzene

were also measured. These results are summarized in Table I.

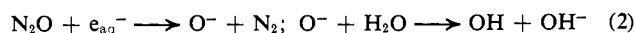
The results indicate that the radicals formed from the alcohols are very strong reducing agents (see below). We have tried, therefore, to measure the specific rates of reaction of the radical  $\dot{C}H_3\dot{C}HOH$  with  $NO_3^-$ ,  $NO_2^-$ ,  $BrO_3^-$ , and  $IO_3^-$  at pH 6. It was found that all these reactions are slower than  $5 \times 10^6 M^{-1} sec^{-1}$ . On the other hand, the specific rates of reaction of the radical  $\dot{C}H_3\dot{C}HO^-$  with  $BrO_3^-$  and  $IO_3^-$  at pH  $11.8 \pm 0.1$  were determined as  $3.0 \pm 0.5 \times 10^7 M^{-1} sec^{-1}$  and  $7.5 \pm 0.2 \times 10^8 M^{-1} sec^{-1}$ , respectively.

## Discussion

The radiolysis of water may be described by



the yields of the products in neutral solutions being:<sup>7</sup>  $G_{e_{aq}^-} = 2.6$ ,  $G_{OH} = 2.65$ ,  $G_H = 0.6$ ,  $G_{H_2O_2} = 0.75$ , and  $G_{H_2} = 0.45$  ("G value" is defined as the number of molecules of product formed by the absorption of 100 eV by the sample). The hydrated electron reacts with  $N_2O$  according to



the specific rate of reaction 2 being<sup>21</sup>  $k_2 = 5.6 \times 10^9 M^{-1} sec^{-1}$ . In neutral solutions saturated with  $N_2O$ ,  $2 \times 10^{-2} M$ , the yield of OH is therefore increased to  $G(OH) = G_{OH} + G_{e_{aq}^-} = 5.25$ . (A somewhat higher yield is plausible due to the effect of  $N_2O$  on  $G_{H_2}$ .<sup>22</sup>)

The specific rates of reaction of the hydroxyl radical with all the organic solutes studied range between  $5 \times$

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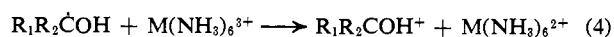
$10^7$  and  $6 \times 10^9 M^{-1} \text{sec}^{-1}$ ,<sup>21</sup> and their rates of reaction with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  (measured by competition with  $\text{CNS}^-$ ) are slower than  $2 \times 10^8 M^{-1} \text{sec}^{-1}$ .<sup>23</sup> Also the specific rates of reaction of hydrogen atoms with the organic solutes, with the exception of acetate and malonate,<sup>21</sup> are higher than the corresponding rates of reaction with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$ .<sup>24</sup> Therefore, under the conditions used in this study, all the primary radicals formed by the pulse react with the organic solutes yielding secondary radicals. In order to obtain the radicals  $\text{CH}_3\text{CO}\dot{\text{C}}(\text{O}^-)\text{CH}_3$  and  $\text{CH}_3\text{CO}\dot{\text{C}}\text{OHCH}_3$ ,  $\text{N}_2\text{O}$  saturated solutions containing  $1 \times 10^{-2} M$  2-propanol and  $1 \times 10^{-3} M$   $\text{CH}_3\text{COCOCH}_3$  were used. Under these conditions both OH and H radicals react with the 2-propanol yielding the radical  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  which in turn reduces the 2,3-butanedione yielding the desired radical (depending on pH). The structure of these radicals as well as their spectra are known.<sup>1,2,15-19</sup> In this study we have measured the specific rates of reaction of these radicals with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  by following the effect of the complexes on the mechanism of disappearance of the organic radicals.

The results clearly indicate that the radicals  $\alpha$  to an OH or  $\text{NH}_2$  group as well as  $\dot{\text{C}}\text{O}_2^-$  reduce the  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  complexes. This is concluded from the following observations. (a) These radicals react with the complexes, as shown by the effect of the complexes on their rate of disappearance, the most reasonable reaction being a redox reaction. (b) The formation of  $\text{Co}^{2+}$  with a yield identical with the radical yield was observed. (c) The formation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  was observed. (d) The formation of  $\text{CH}_2\text{O}$  as the product of the reaction  $\dot{\text{C}}\text{H}_2\text{OH} + \text{Co}(\text{NH}_3)_6^{3+}$  has been reported.<sup>4</sup>

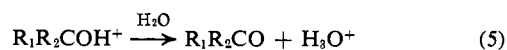
As the reduction of these complexes proceeds always *via* the outer-sphere mechanism, the reactions occurring might be written as



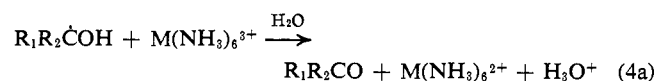
and



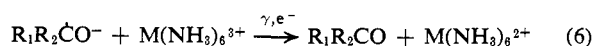
followed by



No evidence for the formation of  $\text{R}_1\text{R}_2\text{COH}^+$  as an intermediate exists and it is more plausible that the reaction occurring is



We cannot rule out the possibility that  $\text{R}_1\text{R}_2\text{COH}^+$  is formed as an intermediate and that due to its short lifetime no distinct adsorptivity could be detected under our experimental conditions. The observation that the basic form of these radicals is more reactive even after correcting for the electrostatic effects is explained by the fact that in the reaction



no bond breaking, the O-H bond, is required prior to the electron-transfer reaction.

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An alternative mechanism of reduction of these complexes by radicals might involve hydrogen atom abstraction from the  $\text{NH}_3$  groups. This mechanism might be ruled out due to the following reasons. (a) The products of the reaction  $\dot{\text{C}}\text{H}_2\text{OH} + \text{Co}(\text{NH}_3)_6^{3+}$  according to this mechanism would be  $\text{CH}_3\text{OH} + \text{Co}^{2+}$  and not  $\text{CH}_2\text{O} + \text{Co}^{2+}$  as observed.<sup>4</sup> (b) This mechanism has been suggested for the reactions of OH radicals,<sup>9</sup> which are much stronger H abstracting reagents than the radicals studied in this work, and even for them this reaction is slower than those observed in this study.<sup>23</sup> Furthermore, H atoms which are strong hydrogen-abstracting reagents, forming the radicals studied in this work, do react with  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  with a specific rate of  $1.8 \times 10^8 M^{-1} \text{sec}^{-1}$ <sup>24</sup> *via* a mechanism involving no hydrogen abstraction.

The most interesting feature of the results is the fact that the order of reactivities of the radicals  $\dot{\text{C}}\text{H}_2\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ , and  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  toward  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  is reversed. The order of reactivities toward  $\text{Ru}(\text{NH}_3)_6^{3+}$  fits the order found for the reduction of nitrobenzene<sup>1</sup> and 2,3-butanedione.<sup>2</sup> Such a difference in the order of reactivities usually indicates a difference in the reaction mechanism. However, as discussed above, it seems highly unlikely that the reduction of either  $\text{Co}(\text{NH}_3)_6^{3+}$  or  $\text{Ru}(\text{NH}_3)_6^{3+}$  does not proceed *via* the outer-sphere mechanism. (For the reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  the formation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  as the stable product has been shown.<sup>20</sup>) The main difference between these complexes, regarding redox reactions, is that the added electron enters an  $e_g$  orbital in  $\text{Co}(\text{NH}_3)_6^{3+}$  and a  $t_{2g}$  orbital in  $\text{Ru}(\text{NH}_3)_6^{3+}$ . This difference has three kinetic effects. (a) In the case of the reduction of  $\text{Co}(\text{III})$  there is a spin multiplicity change from 1 to 4, which makes the reaction spin forbidden and, therefore, might slow down the reaction.<sup>25</sup> (b) The electrons added to the  $e_g$  orbital of the cobalt have an antibonding character thus causing a relative large increase in the cobalt-ligand bond length, during the reduction reaction. On the other hand, in reactions of  $\text{Ru}(\text{III})$  the added electron enters the  $t_{2g}$  orbital which has a nonbonding character and therefore causes little change in the metal-ligand bond length.<sup>25</sup> (c) The  $t_{2g}$  orbital due to its symmetry properties overlaps effectively with  $\pi$  orbitals on the ligand. On the other hand, the  $e_g$  orbital has a  $\sigma$  symmetry and, therefore, does not overlap well with  $\pi$  orbitals of the ligands.<sup>3</sup>

The first two effects may account for the difference in the specific rate of the self exchange between the di- and trivalent complexes of cobalt and ruthenium. These two effects cannot account for a different order of reactivities of a series of reductants toward these complexes.

In order to explain the effect of the different substituents on the reactivity of the  $\text{R}_1\text{R}_2\dot{\text{C}}\text{OH}$  radicals toward different oxidants, one has to analyze the different orders of reactivities observed. The order of reactivities toward  $\text{Co}(\text{NH}_3)_6^{3+}$  is  $\dot{\text{C}}\text{H}_2\text{OH} > \text{CH}_3\dot{\text{C}}\text{HOH} > (\text{CH}_3)_2\dot{\text{C}}\text{OH} > \text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2^- > \text{CH}_3\text{CO}\dot{\text{C}}(\text{O}^-)\text{CH}_3$ . The reversed order of reactivities is found for the reactions with  $\text{Ru}(\text{NH}_3)_6^{3+}$ . A third order of reactivities is found for the reactions with nitrobenzene and 2,3-butanedione where  $(\text{CH}_3)_2\dot{\text{C}}\text{OH} > \text{CH}_3\dot{\text{C}}\text{HOH} > \dot{\text{C}}\text{H}_2\text{OH} > \text{CH}_3\text{C}(\text{OH})\text{CO}_2^- > \text{CH}_3\text{CO}\dot{\text{C}}(\text{O}^-)\text{CH}_3$ . The

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latter order of reactivities is identical with the order of the change in the  $pK$ 's of the corresponding radicals.<sup>2,3,14,16</sup> It has been suggested that the latter order indicates that the reactivity is determined by the electron density on the oxygen atom.<sup>1,2</sup> It is clear from our results that the order of reactivities toward  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  is not determined by this factor.

Another factor which is being changed gradually along the series of radicals studied is the symmetry character of the orbital in which the unpaired electron is located. In a  $\text{CH}_3$  radical, which is planar, the electron is located in a nonbonding  $p$  orbital. In the  $\dot{\text{C}}\text{H}_2\text{OH}$  radical the probability of finding the unpaired electron on the oxygen atom is considerable and the radical is not planar.<sup>26</sup> The probability of finding the unpaired electron on the oxygen atom increases along the series  $\text{CH}_2\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ , and  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ ,<sup>3,27</sup> thus increasing the double bond character of the C–O bond. This means that the unpaired electron is located in an orbital, the  $\pi$  character of which increases along this series. It is reasonable to assume that the  $\pi$  character of the orbital in which the unpaired electron is located is even larger in the radicals  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2^-$  and  $\text{CH}_3\text{CO}\dot{\text{C}}(\text{O}^-)\text{CH}_3$  due to resonance stabilization. In the latter radical it is believed that both oxygen atoms are equivalent and, therefore, the unpaired electron is located in this case in a  $\pi$  orbital.

We are, therefore, tempted to speculate that the increase in reactivities along this series of radicals toward  $\text{Ru}(\text{NH}_3)_6^{3+}$  is due to a better overlap of the  $t_{2g}$  orbital of the complex with the electron in the  $\pi$  orbital on the radical. The ratio of the specific rates of reaction of the radicals  $\dot{\text{C}}\text{H}_2\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ , and  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  with  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{NH}_3)_6^{3+}$  is much smaller than that expected from the Marcus theory<sup>28,29</sup> assuming that both complexes are reduced *via* the same mechanism, though the reactions are not diffusion controlled. This indicates, according to this hypothesis, that the overlap of the unpaired electron in the radical is still better with the  $e_g$  orbital of the complex. This means that in these radicals the orbital in which the unpaired electron is located has a stronger  $\sigma$  than  $\pi$  character. This is reasonable as it is known that the electron spends most of its time near the carbon atom.<sup>3,26,27</sup> The above suggested speculation is based on the assumption that the symmetry requirements for the orbital in which the electron on the reductant is located in outer-sphere reactions are similar to those usually accepted for inner-sphere reactions.<sup>8</sup> In other words this means that also for these outer-sphere reactions, as for inner-sphere reductions, some kind of intermolecular axis can be defined.

If this hypothesis is correct, it is expected that the order of reactivities of these radicals toward other complexes in which the added electron enters an  $e_g$  orbital should be the same as that toward  $\text{Co}(\text{NH}_3)_6^{3+}$ .

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We have, therefore, measured the specific rates of reaction of the radicals  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ ,  $\text{CH}_3\dot{\text{C}}\text{HOH}$ , and  $\dot{\text{C}}\text{H}_2\text{OH}$  with  $\text{Cu}_{\text{aq}}^{2+}$ . It was found, Table I, that the order of reactivities in this case increases along this series, thus corroborating our speculation. It should be pointed out that it is commonly accepted that electron-withdrawing groups, *e.g.*,  $\text{CONH}_2$ , slow down the specific rates of reaction of organic radicals with  $\text{Cu}_{\text{aq}}^{2+}$ .<sup>6</sup> The order of reactivities found in this study is opposed to that expected according to this theory. We have no explanation other than the hypothesis suggested to the order of reactivities observed. It should be mentioned, however, that the mechanism of reduction of  $\text{Cu}_{\text{aq}}^{2+}$  has not been shown to be the outer-sphere mechanism. We would like to add that our results explain the discrepancy between the specific rates of reaction of  $\text{Cd}^+$  and  $\text{Zn}^+$  with  $\text{Cu}^{2+}$  by the pulse radiolytic and competition techniques.<sup>10,30</sup> In the latter case the reaction  $\text{CH}_3\dot{\text{C}}\text{HOH} + \text{Cu}_{\text{aq}}^{2+}$  was neglected.

When we started this study it was hoped that the results would enable an estimate of the redox potentials of the radicals studied, using the Marcus theory<sup>28,29</sup> in a procedure similar to that used for the calculation of the redox potentials of  $\text{Zn}^+$  and  $\text{Cd}^+$ .<sup>24</sup> From the results it is clear that a correct estimate of these redox potentials may be carried out only after deciding whether the reductions of  $\text{Co}(\text{NH}_3)_6^{3+}$  or  $\text{Ru}(\text{NH}_3)_6^{3+}$  follow the Marcus theory. It seems difficult to answer this question at this moment. Furthermore, meanwhile the polarographic half-wave potentials of some of these radicals have been reported.<sup>31</sup> From the latter results the redox potentials of the radicals can be very accurately estimated. However, no straightforward correlation between these values and those obtained from our results could be suggested. More experiments in this direction seem to be required before a full understanding of the mechanisms involved will be achieved.

It is expected that in an irradiated biological system a large part of the primary radicals will react with aliphatic compounds producing secondary radicals on positions  $\alpha$  to amino or hydroxy groups. If these secondary radicals are strong reducing agents as suggested from these results it is most reasonable to assume that they would reduce many of the transition metal complexes available in the system. As most of the transition metal cations in biological systems are bound to enzymes, this might explain the high specificity of the damage caused in radiobiological systems, at sites adjacent to transition metal cations.

**Acknowledgments.** The authors are indebted to Professor L. Zalkow and Dr. G. Navon for many helpful discussions. We wish also to express our thanks to Miss E. Wajcman for technical assistance and to the linac group at the Hebrew University of Jerusalem for their care in operating the linac and maintaining the electronic equipment.

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