Oxidation of Substituted Alkyl Radicals by $IrCl_6^{2-}$, $Fe(CN)_6^{3-}$, and MnO_4^- in Aqueous Solution. Electron Transfer versus Chlorine Transfer from $IrCl_6^{2-}$ [1]

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Abstract: Alkyl radicals substituted at C_α by alkyl, carboxyl, hydroxyl, alkoxyl, and chlorine react in aqueous solutions with $Ir^{IV}Cl_6^{2-}$ to yield Ir(III) species. In the case of substitution by hydroxyl and alkoxyl, the rate constants are in the diffusion-controlled range ($(4–6) \times 10^9$ M^{-1} s^{-1}) and the reaction proceeds by electron transfer. In the case of ethyl, methyl, carboxymethyl, and chloromethyl radicals the rate constants range from 3.1×10^9 for ethyl to 2.8×10^7 M^{-1} s^{-1} for trichloromethyl and the reaction proceeds by chlorine transfer from $IrCl_6^{2-}$ to the alkyl radical. With isopropyl and *tert*-butyl radicals the reaction proceeds by both electron and chlorine transfer. Alkyl radicals also react with $Fe(CN)_6^{3-}$. The rate constants increase strongly with increasing alkylation at C_α from 5×10^6 for methyl to 3.6×10^9 M^{-1} s^{-1} for *tert*-butyl, indicating that the transition state for the reaction is highly polar. Rate constants for reaction of MnO_4^- with alkyl radicals are of the order 10^9 M^{-1} s^{-1}.

Organic radicals have been oxidized in aqueous solutions by a variety of inorganic[2-7] and organic[8-10] oxidants. By using this method, it is frequently possible to convert the radicals quantitatively into nonradical products such that radical–radical reactions are eliminated. In most cases this results in a drastically simplified product composition.

Obviously, the choice of the oxidant for a particular radical depends on the redox properties of the radical. α-Hydroxyalkyl radicals have long been known to be strong one-electron donors.[8,11] A similar behavior has been shown for α-alkoxyalkyl[11,12] and also for certain cyclohexadienyl[6,7,9-11,13] radicals. However, alkyl radicals unsubstituted at the α position have not been looked upon as typical reductants, although alkyl radicals have been shown to react with oxidants such as Cu^{2+} or $Fe(CN)_6^{3-}$.[3,4] The present study was undertaken to investigate specifically the effect of substitution at C_α of alkyl radicals on the rates of their redox reactions. Hexachloroiridate(IV) was used because of its ability to oxidize alkyl radicals in nonaqueous media.[14] Hexacyanoferrate(III) and permanganate were additionally investigated in order to obtain kinetic data for comparison.

Experimental Section

Sodium hexachloroiridate(IV) was obtained from Alfa Products. Its purity was $\geq 98\%$, based on its absorption in water at 490 nm. Diethyl and diisopropyl sulfoxide were prepared by oxidation of the corresponding sulfides with liquid N_2O_4 as the oxidant.[15] After vacuum fractional distillation, their purity was $\geq 99\%$, based on GC. Di-*tert*-butyl sulfoxide was prepared by oxidation of the sulfide with aqueous H_2O_2.[16] After recrystallization from chloroform, the purity was $\geq 98\%$, based on GC and IR.

For the pulse radiolysis experiments, solutions were prepared with use of reagent-grade water from a Millipore Milli-Q system. The solutions were saturated with N_2O (in order to convert e_{aq}^- into OH) or with N_2 and irradiated with 5-ns pulses from an Arco LP-7 linear accelerator with dose rates of 300–500 rads per pulse which produce initial radical concentrations of ~ 2 μM. The computer-controlled pulse radiolysis apparatus[17] was used for data acquisition. The concentration of substrate was generally between 1 and 100 mM. At least three different concentrations of oxidant ranging from 20 μM to 2 mM were used to determine the second-order rate constants presented in the tables. The yields of reduced oxidants were measured with reference to a N_2O-saturated 0.1 M formate or dioxane solution containing 0.5 mM oxidant for which $G(-\text{oxidant}) = G(OH) + G(H) = 6.6$.

Chloroalkanes, alkenes, and alkanes were removed from the ^{60}Co γ-irradiated aqueous solutions (dose rates of 0.5–1 krad g^{-1} min^{-1}) by bubbling them out into an evacuated container.[18] A known fraction was then analyzed by GC (flame ionization detection) using a 140-m glass

capillary column coated with SF 96 at 0 °C and hydrogen as the carrier gas.

The irradiated aqueous solutions were also analyzed for alcohols by GC. Samples (4 μL) of the aqueous solutions, containing 0.01–0.1 mM of an internal standard (e.g., 1-propanol), were injected directly into a modified[19] Varian 1400 instrument with flame ionization detection. The split ratio was 1:20. A 100-m glass capillary column coated with Carbowax 1500 was used at 95 °C. The carrier gas was N_2. Retention times were of the order of 10–15 min. The detection limit corresponded to 2–5 μM aliphatic alcohol.

The identity of the reduced Ir species (a mixture of $Ir^{III}Cl_6^{3-}$ and $Ir^{III}Cl_5(H_2O)^{2-}$) was determined spectrophotometrically. The visible spectrum was recorded after γ irradiation with doses sufficient to bleach the 490-nm peak of $IrCl_6^{2-}$ by $\geq 95\%$. With use of concentrated perchloric acid, the pH was then adjusted to 0–1 and the solution was oxidized with chlorine. After removal of the excess chlorine, the spectrum was again recorded and analyzed with respect to the $IrCl_6^{2-}/IrCl_5(H_2O)^-$ composition using published spectral data.[20]

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2266 from the Notre Dame Radiation Laboratory.

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(15) Addison, C. C.; Sheldon, J. C. *J. Chem. Soc.* **1956**, 2705.

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Table I. Rate Constants[a] for the Reaction of Substituted Alkyl Radicals with IrCl$_6^{2-}$, Fe(CN)$_6^{3-}$, and MnO$_4^-$

radical	produced by eq no.	k, M^{-1} s^{-1}		
		IrCl$_6^{2-}$	Fe(CN)$_6^{3-}$	MnO$_4^-$
ĊH$_3$	3, 5	1.15×10^9	$(5 \pm 1) \times 10^6$	1.05×10^9
ĊH$_2$CH$_3$	3, 5	3.1×10^9	5.0×10^7	$\sim 2 \times 10^9$
ĊH(CH$_3$)$_2$	3, 5	3.6×10^9	1.25×10^9	
Ċ(CH$_3$)$_3$	3, 4	3.8×10^9	3.6×10^9	
ĊH$_2$Cl	5	$\sim 1 \times 10^9$	$<5 \times 10^5$	$\sim 1 \times 10^9$
ĊHCl$_2$	5	$\sim 5 \times 10^8$	$<5 \times 10^5$	$\sim 1 \times 10^9$
ĊCl$_3$	5	2.8×10^7		4×10^8
ĊH$_2$CH$_2$Cl	5	$\sim 1 \times 10^9$		
ĊH$_2$CH$_2$OH	c	$\sim 2 \times 10^9$	$\sim 5 \times 10^7$ [b]	
ĊH$_2$C(CH$_3$)$_2$OH	4	1.2×10^9		
ĊH$_2$OH	4	6.0×10^9	4.0×10^9 [b]	
CH$_3$ĊHOH	4	4.5×10^9	5.3×10^9 [b]	
(CH$_3$)$_2$ĊOH	4	4.7×10^9	4.7×10^9 [b]	
ĊH$_2$OCH$_3$	4	6.5×10^9	4.3×10^9	
CH$_3$ĊHOCH$_2$CH$_3$	4	5.7×10^9	4.0×10^9	
(CH$_3$)$_2$ĊOCH(CH$_3$)$_2$	4	3.6×10^9	3.6×10^9	
ĊHCH$_2$OCH$_2$CH$_2$O	4	5.4×10^9		6.5×10^9
ĊH$_2$CO$_2$H	4	1.4×10^9	2×10^6	
ĊH$_2$CO$_2^-$	4	4.2×10^8		
HO$_2$CĊHCH$_2$CO$_2$H	4	4.6×10^8		
$^-$O$_2$CĊHCH$_2$CO$_2^-$	4	1.1×10^8		
HO$_2$CĊHOH	4	2.3×10^9	1.0×10^8	
$^-$O$_2$CĊHOH	4	2×10^9	5.0×10^8 [b]	
$^-$O$_2$CĊHO$^-$	4	1.8×10^9	7.5×10^8	
ĊO$_2^-$	4	1.7×10^9	1.1×10^9 [b]	
ĊH$_2$CHO	d	1.7×10^9		
C$_6$H$_5$O·	e	$\sim 4 \times 10^9$		
(benzene-OH adduct structure)	f	2.7×10^9 [g]	1.8×10^7 [h]	

[a] Measured at 22 ± 2 °C. Accurate to $\pm \leqslant 10\%$ except where noted by $\sim$, where the accuracy is $\pm \leqslant 20\%$. The pH was 4–6, except where ionizable radicals were studied. In these cases the pH was adjusted to give the species shown. [b] From ref 3. [c] By OH addition to ethylene. [d] From reaction of OH with 2-chloroethanol followed by elimination of HCl. [e] From reaction of OH with phenol at pH 11.3. [f] By OH addition to benzene. [g] From Selvarajan, N.; Raghavan, N. V. *J. Phys. Chem.* **1980**, *84*, 2548. [h] From ref 6.

Results and Discussion

Radiolysis of water is a convenient way of producing known concentrations of radicals. The primary radicals

$$H_2O \rightsquigarrow e_{aq}^-, OH, H \qquad (1)$$
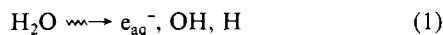
are formed with yields of 2.7 (e$_{aq}^-$), 2.8 (OH), and 0.6 (H) molecules per 100 eV of absorbed energy. The primary radicals can easily be converted to yield the desired secondary radicals. Commonly, N$_2$O is used to convert e$_{aq}^-$ into OH radicals

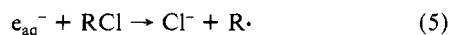$$N_2O + e_{aq}^- + H_2O \rightarrow N_2 + OH^- + OH \qquad (2)$$
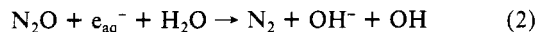
In this study, alkyl radicals were produced by three different methods: Addition of OH radicals to dialkyl sulfoxides followed by fragmentation of the adduct to yield sulfinic acids and alkyl radicals,[21]

$$OH + R_2SO \rightarrow RSO_2^- + H^+ + R· \qquad (3)$$
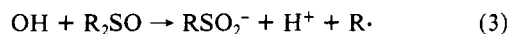
H abstraction by OH and H from aliphatics,

$$OH + RH \rightarrow H_2O + R· \qquad (4)$$
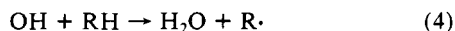
and reaction of e$_{aq}^-$ with chloroalkanes

$$e_{aq}^- + RCl \rightarrow Cl^- + R· \qquad (5)$$

1. Optical Pulse Radiolysis Studies. The reaction of the alkyl radicals with IrCl$_6^{2-}$ was investigated by monitoring the absorption of IrCl$_6^{2-}$ at 490 nm. The reaction of R· with IrCl$_6^{2-}$ resulted in a bleaching of the IrCl$_6^{2-}$ absorption. The decrease in the IrCl$_6^{2-}$ concentration (at initial concentrations of ≥ 0.1 mM) occurred with half-lives ≤ 10 μs and the amount of IrCl$_6^{2-}$ removed within 100 μs was equal to the concentrations of alkyl radicals produced,

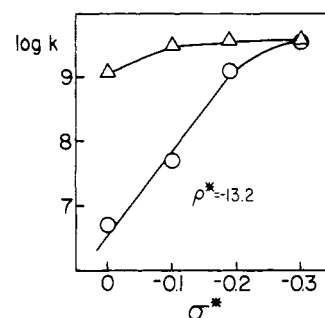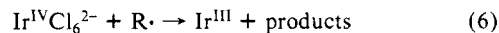**Figure 1.** Taft plots for the reactions of ĊH$_n$(CH$_3$)$_{3-n}$ with IrCl$_6^{2-}$ (triangles) and Fe(CN)$_6^{3-}$ (circles). For the latter reaction, $\rho^* = -13.2$. k is in units of M^{-1} s^{-1}.

as determined by, e.g., conductance measurements.[21] The results are explained by conversion of Ir(IV)Cl$_6^{2-}$ into Ir(III) species, which do not absorb at 490 nm,[20] cf. eq 6.

$$Ir^{IV}Cl_6^{2-} + R· \rightarrow Ir^{III} + products \qquad (6)$$

The rate constants obtained for reaction 6 are listed in Table I. With the alkyl radicals not substituted by OR at C$_\alpha$, the rate constants increase up to the diffusion-controlled limit with increasing degree of alkylation at C$_\alpha$. This is also shown in Figure 1, which contains a Taft plot of the kinetic data for the series methyl through *tert*-butyl radical. The increase runs parallel with the increase in electron-donating power of the radicals or the stability of the corresponding positive ions in this series as measured, e.g., by the ionization potential[22] of the radicals. If steric

(20) Chang, J. C.; Garner, C. S. *Inorg. Chem.* **1965**, *4*, 209.

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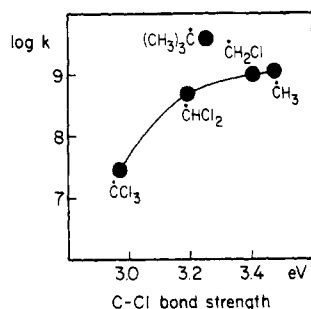
Figure 2. A plot of log k (in units of M^{-1} s^{-1}) for reaction of $\dot{C}H_nCl_{3-n}$ with $IrCl_6^{2-}$ vs. the C–Cl bond strength of Cl–CH_nCl_{3-n}. The bond strengths are from ref 23. $(CH_3)_3\dot{C}$ is shown for comparison.
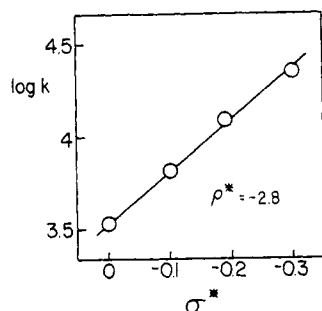
Figure 3. Taft plot for the reduction of $IrCl_6^{2-}$ by ionized alkylsulfinic acids $CH_n(CH_3)_{3-n}SO_2^-$. ρ^* = –2.8.

Table II. Rate Constants for the Reduction of $IrCl_6^{2-}$ by Alkylsulfinic Acid Anions RSO_2^- [a]

R	k, M^{-1} s^{-1}	R	k, M^{-1} s^{-1}
CH_3	3.4×10^3	$(CH_3)_2CH$	1.2×10^4
CH_3CH_2	6.4×10^3	$(CH_3)_3C$	2.2×10^4

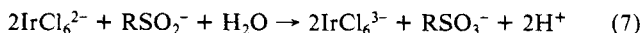[a] Measured at 22 + 2 °C and pH 4–6. Accurate to $\pm \leqslant 10\%$.

factors were important, the reverse trend would be observed. Substitution with an alkyl group whose Taft σ^* constant is positive (e.g., as with $\dot{C}H_2CH_2OH$ and $\dot{C}H_2CH_2Cl$) does not lead to an increase in the rate constant for reaction with $IrCl_6^{2-}$. This again is evidence that the electron-donating power of the alkyl radical is important, i.e., that polar structures in the transition state for the reduction of $IrCl_6^{2-}$ are involved. If H is replaced by Cl in CH_3, the rate constants decrease drastically (Table I and Figure 2).

The influence of charge on the rate constants can be seen with the radicals carrying carboxyl groups: the rate constants decrease upon ionization. The small electronic factor (CO_2^- is less electron withdrawing than CO_2H) is obviously counteracted by the effect of electrostatic repulsion between the reaction partners.

All radicals substituted at C_α by OH or OR react with diffusion-controlled rates. Therefore, unlike the case of the simple alkyl radicals, the increase in the electron-donating abilities in the series $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$[11] and $CH_3O\dot{C}H_2$, $CH_3\dot{C}HOC_2H_5$, $(CH_3)_2\dot{C}OCH(CH_3)_2$[12] does not show up in the rate constants for reaction with $IrCl_6^{2-}$.

When the radicals R were produced via eq 3, there was a further decrease in the concentration of $IrCl_6^{2-}$ that occurred on the millisecond to second time scale. The rate of this decrease increased linearly with increasing $IrCl_6^{2-}$ concentration and the amount of $IrCl_6^{2-}$ removed by this slow reaction was twice that removed in reaction 6. The slow reaction was absent when the alkyl radicals were produced via eq 4 or 5. The slow process is suggested to involve reduction of $IrCl_6^{2-}$ by the sulfinic acids formed in reaction 3, cf. eq 7. The rate constants measured for

$$2IrCl_6^{2-} + RSO_2^- + H_2O \rightarrow 2IrCl_6^{3-} + RSO_3^- + 2H^+ \qquad (7)$$

(23) Tarama, K. In "Handbook of Organic Structural Analysis", Yukawa, Y., Ed.; W. A. Benjamin: New York, 1965; p 537.

Table III. Yields[a] of Products from the Reaction of Alkyl Radicals R· with $IrCl_6^{2-}$

R·	RCl/R·	R(-H)/ R·	ROH/R·	RH/R·	(R-R)/R·
CH_3	$\geqslant 0.92$		<0.05	0.02	0.02
CH_3CH_2	0.94	0.06	<0.05	$\leqslant 0.01$	$\leqslant 0.01$
$(CH_3)_2CH$	0.53	0.37	<0.10	$\leqslant 0.01$	$\leqslant 0.01$
$(CH_3)_3C$	0.23^b	0.37	0.40^c	$\leqslant 0.01$	$\leqslant 0.01$

[a] The yields are expressed as fractions per unit of R· formed in the initiation reaction (eq 3). The concentration of the sulfoxides was 0.01–0.1 M; [$IrCl_6^{2-}$] was 0.5 mM. Radiation chemical doses were chosen such that $\leqslant 15\%$ of the initially present $IrCl_6^{2-}$ was depleted. The error in the yields is $\leqslant \pm 5\%$. [b] This value is obtained as the difference between full yield and the yield of H^+ (77%), as measured by conductivity. [c] This value is obtained as the difference between the yield of H^+ and that of 2-methyl-propene (37%).

reaction 7 are listed in Table II. It is obvious that the rate constants increase strongly with increasing electron-donating power of the alkyl substituent (cf. Figure 3).

In the case of di-*tert*-butyl sulfoxide as a source of *tert*-butyl radicals (eq 3), an additional depletion of $IrCl_6^{2-}$ was observed on the 100 μs time scale. The rate constant for reduction of $IrCl_6^{2-}$ by this process, which accounts for 22% of the total depletion of $IrCl_6^{2-}$ prior to the occurrence of reaction 7, was determined to be 5×10^7 M^{-1} s^{-1}. It is suggested that radical I, formed by H abstraction by OH from *tert*-butyl sulfoxide, is responsible for this intermediate bleaching of $IrCl_6^{2-}$, as shown in reaction 8.

$$Ir^{IV}Cl_6^{2-} + (CH_3)_3CS(O)C(CH_3)_2\dot{C}H_2 \rightarrow Ir^{III} + products$$
$$I$$
$$(8)$$
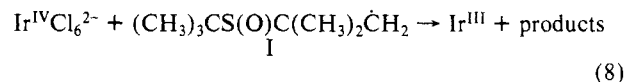
On the basis of conductivity data, the yield per OH of radical I has been determined to be 0.21,[21] which is in excellent agreement with the 0.22 yield found using the optical method.

2. Product Analysis Studies. Reaction of OH (produced by γ radiolysis of N_2O-saturated aqueous solutions) with dimethyl, diethyl, and diisopropyl sulfoxide in the presence of $IrCl_6^{2-}$ leads to the production of methyl, ethyl, and isopropyl chloride, respectively (Table III). In the case of dimethyl and diethyl sulfoxide essentially 1 equiv of alkyl chloride is produced per alkyl radical R· formed.

The reaction between methyl and ethyl radical and $IrCl_6^{2-}$ therefore proceeds by chlorine transfer (reductive dechlorination of chloroiridate) as shown in eq 9 for methyl radical. In the case of ethyl radical there is a 6% contribution due to production of ethylene.

$$\dot{C}H_3 + IrCl_6^{2-} + H_2O \rightarrow CH_3Cl + IrCl_5(H_2O)^{2-} \qquad (9)$$
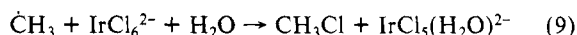
Equation 9 is in agreement with the bleaching of the $IrCl_6^{2-}$ absorption at 490 nm and with the conductance experiments (section 3) which show the absence of H^+ production. $IrCl_5(H_2O)^{2-}$, the inorganic product of reaction 9, has a very low extinction at 490 nm. The quantitative production of $IrCl_5(H_2O)^{2-}$ on reaction with $\dot{C}H_3$ or $CH_3\dot{C}H_2$ was shown by γ-radiolysis experiments in which $\geq 95\%$ of the initially present $IrCl_6^{2-}$ was removed by reaction 9. The $IrCl_5(H_2O)^{2-}$ formed was then oxidized by Cl_2 to yield $IrCl_5(H_2O)^-$, which has a characteristic absorption spectrum with a maximum at 450 nm. On the basis of the known extinction coefficient[20] of $IrCl_5(H_2O)^-$ at 450 nm, it is concluded that $\dot{C}H_3$ and $CH_3\dot{C}H_2$ react by $\geq 95\%$ via eq 9. When this procedure was used, it could be shown that the radicals $\dot{C}H_2C(CH_3)_2OH$, $\dot{C}H_2CO_2H$, $\dot{C}H_2Cl$, and $\dot{C}HCl_2$ react also quantitatively by chorine transfer. With $\dot{C}H_2C(CH_3)_2OH$, this conclusion can also be drawn from the results of the conductance experiments, which showed the absence of H^+ production (see section 3).

When $\dot{C}H(CH_3)_2$ was produced by reaction 3 and reacted with $IrCl_6^{2-}$, 2-chloropropane was formed, as shown by GC analysis of the aqueous solutions. However, the yield of 2-chloropropane was only 54% of that of $\dot{C}H(CH_3)_2$ produced in eq 3. The re-

maining product found was propene with a relative yield of 37%. In the case of *tert*-butyl radical 2-methylpropene was found with a yield of 37%. *tert*-Butyl alcohol is also among the reaction products. However, the concentration of *tert*-butyl alcohol could not be measured quantitatively, due to thermal decomposition of di-*tert*-butyl sulfoxide in the GC injection block. One of the expected products of the reaction of IrCl$_6^{2-}$ with *tert*-butyl radical is *tert*-butyl chloride. Again, this cannot be determined quantitatively, due to its rapid hydrolysis. It is also difficult to determine accurately the degree of dechlorination of IrCl$_6^{2-}$ by $\dot{C}H(CH_3)_2$ and $\dot{C}(CH_3)_3$ using the optical spectroscopic method. This is because the sulfinic acids produced by reaction of OH via eq 3 react with IrCl$_6^{2-}$ by electron transfer to yield IrCl$_6^{3-}$ (reaction 7). As a result, the ratio IrCl$_6^{3-}$/IrCl$_5$(H$_2$O)$^{2-}$ is changed in favor of IrCl$_6^{3-}$. Because of overlapping spectra of IrCl$_6^{2-}$ and IrCl$_5$-(H$_2$O)$^-$ (obtained after oxidation with Cl$_2$), the determination of a small (additional) contribution of either component is liable to a large error. More reliable numbers for the fraction of dechlorination of IrCl$_6^{2-}$ by *tert*-butyl and isopropyl radical are therefore obtained from the conductance experiments (see section 3). These values are also reported in Table III.

In contrast to the alkyl-, carboxyl-, or chloro-substituted alkyl radicals described above, alkyl radicals substituted at C$_\alpha$ by OR (R = H or alkyl) all react with IrCl$_6^{2-}$ by electron transfer and not by chlorine exchange. This is shown by the fact that, after reaction with the radicals >$\dot{C}$OR, IrCl$_6^{2-}$ can be fully regenerated by oxidation with Cl$_2$. Electron transfer as the mechanism of reaction between IrCl$_6^{2-}$ and >$\dot{C}$OR is also deducible from the results of the conductance experiments which show the production of one H$^+$ per reacting IrCl$_6^{2-}$ (see section 3). For α-hydroxyalkyl radicals, the reaction may thus be formulated as:

$$>\dot{C}OH + IrCl_6^{2-} \rightarrow >C=O + IrCl_6^{3-} + H^+ \qquad (10)$$
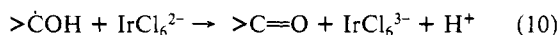
With α-alkoxyalkyl radicals a carbocation is expected to be formed, which reacts with water[12] to yield an acetal and H$^+$. E.g., for the radical from dioxane

 (11)
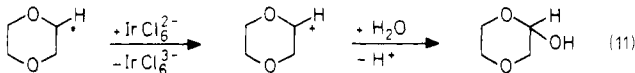
Finally, from the spectroscopic product analysis data relating to hydroxycarboxylic acids it is concluded that alkyl radicals substituted at C$_\alpha$ by both OH and CO$_2$H (or CO$_2^-$) undergo electron and not chlorine transfer; i.e., the influence of the OH group predominates over that of CO$_2$H.

3. Conductometric Pulse Radiolysis Studies.

The reactions of $\dot{C}H_2OH$, $\underline{\dot{C}HCH_2OCH_2CH_2O}$, $\dot{C}H_2C(CH_3)_2OH$, $\dot{C}H_3$, CH$_3\dot{C}H_2$, (CH$_3$)$_2\dot{C}H$, and (CH$_3$)$_3\dot{C}$ with IrCl$_6^{2-}$ were investigated at pH 3–5, using the fast response conductivity apparatus described.[24] With $\dot{C}H_2OH$ and $\underline{\dot{C}HCH_2OCH_2CH_2O}$ there was an increase of conductance after initiation of the reaction. This increase is essentially due to the production of H$^+$. Based on the equivalent conductances of H$^+$, IrCl$_6^{2-}$, and IrCl$_6^{3-}$, one H$^+$ was formed per IrCl$_6^{2-}$ removed. The rate of production of H$^+$ was identical with that measured optically for the depletion of IrCl$_6^{2-}$. In contrast, $\dot{C}H_3$, CH$_3\dot{C}H_2$, and $\dot{C}H_2C(CH_3)_2OH$ did not produce H$^+$ on reaction with IrCl$_6^{2-}$ (the yield of H$^+$ was ≤5% of that generated by reaction of $\dot{C}H_2OH$). However, with (CH$_3$)$_2\dot{C}H$ and (CH$_3$)$_3\dot{C}$, production of H$^+$ was observed with a rate identical with that measured optically for the (fast) depletion of IrCl$_6^{2-}$ (half-lives ≤5 μs).

If the alkyl radicals are produced via eq 3, this reaction provides an internal calibration for any subsequent reaction that leads to conductivity changes. An example for this is given in Figure 4, which shows the changes in conductance that result from the reaction of OH with di-*tert*-butyl sulfoxide in the presence of IrCl$_6^{2-}$. The initial steep rise (half-life 13 ns) is due to reaction 3, which accounts for ~55% of the total conductance increase measured at 18 μs after initiation of the reaction. The subsequent

(24) Janata, E. *Radiat. Phys. Chem.* **1982**, *19*, 17.
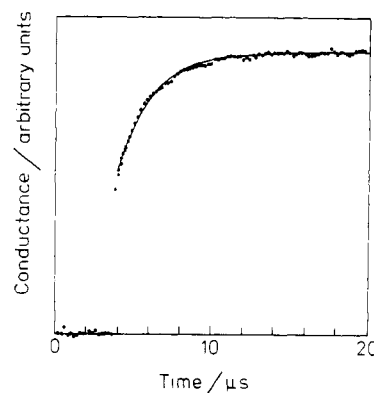
Figure 4. Conductance changes resulting from the reaction of OH with 0.01 M di-*tert*-butyl sulfoxide in the presence of 0.11 mM IrCl$_6^{2-}$ at pH 4.0. The solid line is from a computer fit of the experimental points assuming a pseudo-first-order process giving rise to the conductance change.

rise (half-life 1.6 μs) is due to reaction of *tert*-butyl radical with IrCl$_6^{2-}$. A quantitative analysis of this reaction[25] showed that 77% of the *tert*-butyl radicals react by producing H$^+$. In the case of isopropyl radical the corresponding number is 50%.

The combined results of the conductance and of the product analysis experiments (section 2) are summarized in eq 12. In the case of methyl and ethyl radical, the reaction proceeds by ≥95% via path A, i.e., via chlorine transfer (inner-sphere electron transfer). In the case of isopropyl and *tert*-butyl there is a 50 and 77% contribution, respectively, of outer-sphere electron transfer (path B), and the resulting cation[26] decays by deprotonation (path C) or by reaction with water (path D). In the case of isopropyl there is a ≥4:1 preference for deprotonation over reaction with water, whereas with *tert*-butyl deprotonation and reaction with water occur with approximately equal probabilities (see Table III).[27]

 (12)
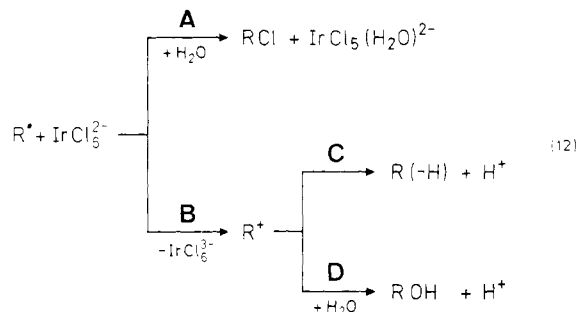
4. Mechanism of Reaction between Alkyl Radicals and IrCl$_6^{2-}$.

The reaction between simple alkyl radicals and IrCl$_6^{2-}$ has been previously observed in acetonitrile and acetic acid as solvents.[14] However, since the production of the alkyl radicals was rate determining, rate constants for their reaction with IrCl$_6^{2-}$ could not be measured. By product analysis studies it could be shown[14] that $\dot{C}H_3$ and CH$_3\dot{C}H_2$ reacted exclusively by chlorine transfer, whereas with (CH$_3$)$_2\dot{C}H$ and (CH$_3$)$_3\dot{C}$ there was an appreciable

(25) There is a ~10% contribution due to the reaction H + IrCl$_6^{2-}$ → H$^+$ + IrCl$_6^{3-}$.

(26) The cation may not be "free", but may exist as an ion pair with IrCl$_6^{3-}$.

(27) These results may be compared with the product distributions measured for the same carbocations produced by different methods. The (S$_N$1) hydrolysis of *tert*-butyl chloride or bromide yields ~17% isobutene and ~83% *tert*-butyl alcohol, i.e., the ratio C/D ~ 1:5. In the case of isopropyl, the carbocation was produced by reaction of nitrous acid with 2-propylamine in aqueous solution and C/D was found to be 1:2, using the GC technique described in the *Experimental* Section. These data show that the cations have a much greater tendency to undergo β deprotonation if produced via eq 12 than if generated by the classical reactions. This difference may result from ion pairing (cf ref 26), which disfavors the attack of water at the α carbon. The difference may also reflect differences in hydration resulting from the different carbocation precursors.

contribution of electron transfer. As shown in sections 2 and 3, in aqueous solution $\dot{C}H_3$, $CH_3\dot{C}H_2$, and other primary alkyl radicals react also by chlorine transfer. From the dependence of the reaction rate constants on structure in the series Me·, Et·, *i*-Pr·, *t*-Bu· (Figure 1) it is, however, evident that the transition state for the chlorine transfer reaction is of polar character. The rate constants increase with decreasing ionization potential[22] of the alkyl radical. If the C–Cl bond energies were important, the rate constants should *decrease* in going from Me· to *t*-Bu·, since the C–Cl bond energies decrease in this series.[23] In the case of *t*-Bu·, the transition state seems to be essentially ionic (percentage of electron transfer = 77).

It is not surprising that in aqueous solution the percentage of electron transfer between $IrCl_6^{2-}$ and *i*-Pr· or *t*-Bu· (50 and 77%) is more than that[14] in acetonitrile (15 and 50%) and comparable to that[14] in acetic acid (80% for *t*-Bu·). This is as expected on the basis of the greater ability of water to solvate ionic structures such as those involved in electron transfer.

The radicals substituted at C_α by oxygen react exclusively by electron transfer. This is suggested to result from the stabilization by electron-pair donation from oxygen of carbocationlike species in the electron-transfer transition state, as shown in eq 13.

$$Cl^{2-}{}_{5}Ir\!\!-\!\!Cl \overset{\delta-}{\frown} \cdot \overset{3+}{\underset{|}{C}}\overset{\frown}{\underset{\bar{O}}{}}\!\!-\!\!R \qquad (13)$$
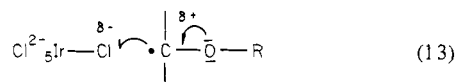
On the basis of the product analysis data, the reaction between the chlorinated methyl radicals and $IrCl_6^{2-}$ proceeds by chlorine transfer. As seen in Table I, the rate constants decrease in going from methyl to trichloromethyl. In this series the rate constants correlate with the bond strengths of the C–Cl bond formed (Figure 2), but not with the ionization potentials[22] of the radicals. This shows that the transition state is not polar. If polar structures did contribute, the rate constants should increase in the series methyl through trichloromethyl, since the ionization potentials decrease in this direction.

Figure 3 contains a Taft plot for the electron-transfer reduction of $IrCl_6^{2-}$ by the alkylsulfinic acids. The ρ^* value is -2.8, which may be compared with $\rho^* = -1.3$ for the pK_a values of the sulfinic acids[21] in aqueous solution. This shows that the electronic properties of the substituents influence the oxidation reaction by $IrCl_6^{2-}$ more than the proton dissociation reaction.

5. Reaction of Alkyl Radicals with $Fe(CN)_6^{3-}$ and MnO_4^-. Table I contains the rate constants for the reaction of alkyl radicals with $Fe(CN)_6^{3-}$ and MnO_4^-. The rate constants were obtained

by monitoring the bleaching of the ions at 420 and 545 nm, respectively. The rate constants for the bleaching of MnO_4^- are all close to the diffusion-controlled limit, i.e., MnO_4^- is an efficient oxidant for alkyl radicals. Some potentially interesting rate constants could not be measured since MnO_4^- reacted thermally with the compounds from which the radicals had to be produced.

The rate constants for reduction of $Fe(CN)_6^{3-}$ increase very strongly with decreasing ionization potential of the alkyl radical and they correlate with the Taft σ^* constants of the alkyl groups to give a large negative ρ^* $(=-13.2)$ (Figure 1). This strongly indicates that the transition state for the reaction has ionic character as in an electron-transfer mechanism. In the case of reaction of $\dot{C}H_3$ and $CH_3\dot{C}H_2$·, which were produced via eq 3 by γ radiolysis of aqueous solutions in the presence of 2 mM Fe-$(CN)_6^{3-}$, a search for CH_3CN or CH_3CH_2CN as reaction products was made and none was found $(G(RCN)/G(OH) \leq 0.05)$. If ligand transfer does not occur between $Fe(CN)_6^{3-}$ and $\dot{C}H_3$ or $CH_3\dot{C}H_2$·, it is even less likely for isopropyl and *tert*-butyl radicals.

The dependence of the rate constants on the ionization potentials of the alkyl radicals (or on the Taft σ^* values of the alkyl substituents) is much more pronounced with $Fe(CN)_6^{3-}$ than with $IrCl_6^{2-}$ (Figure 1). This is due to the fact that the latter (redox potential 0.87 V) is a more powerful oxidant than the former (redox potential 0.36 V). A similar dependence of reaction rate sensitivity to substitution on the redox potential of the oxidant has recently been found for the electron-transfer reaction between hydroxycyclohexadienyl radicals and quinones.[10]

The rate constants for reaction of α-alkoxyalkyl radicals with $Fe(CN)_6^{3-}$ are diffusion controlled and similar to those[3] of α-hydroxyalkyl radicals. The reaction probably proceeds by electron transfer, the carbocation involved being stabilized by conjugation with the adjacent oxygen.