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Kinetic Study of the Reaction of Aquochromium(II) Ions with Benzyl Radicals in Aqueous Solutions: Thermodynamics of the Chromium-Carbon Bond

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Flash-photolytic determinations based on both the photohomolysis of $CrCH_2Ph^{2+}$ (product ratio) and on the photodecomposition of $(PhCH_2)_2CO$ in the presence of Cr^{2+} (kinetic spectrophotometry) yielded a consistent value for k_{Cr}, the second-order rate constant for the reaction $Cr^{2+} + PhCH_2\cdot \rightarrow CrCH_2Ph^{2+}$, $k_{Cr} = (8.5 \pm 0.6) \times 10^7\ M^{-1}\ s^{-1}$ (23 ± 2 °C, 0–2 M CH_3CN in H_2O, 0.05 M $HClO_4$ at $\mu = 0.10$ M). This value, together with literature values or estimates for other quantities, affords $\Delta G° = -59.9$ kJ mol^{-1} ($\Delta G_{Cr}{}^{*} = 27.8$, $\Delta G_{-1}{}^{*} = 87.7$), $\Delta H° = -123 \pm 10$ kJ mol^{-1} ($\Delta H_{-1}{}^{*} = 133 \pm 3$), and $\Delta S° = -211 \pm 34$ J mol^{-1} K^{-1} ($\Delta S_{Cr}{}^{*} = -60 \pm 35$).

Introduction

Benzylpentaaquochromium(2+) ion was one of the first organochromium cations known.[1,2] Like other members of the homologous series $(H_2O)_5CrR^{2+}$, it results from the reaction between hydrated chromium(2+) ions and the free radical, eq 1. Unlike many others,[3] however, its formation rate is unknown, perhaps owing to the difficulty of generating benzyl radicals pulse radiolytically.

$$Cr(H_2O)_6{}^{2+} + PhCH_2\cdot \xrightarrow{k_{Cr}} (H_2O)_5CrCH_2Ph^{2+} + H_2O \qquad (1)$$

Data for this particular complex are needed (a) to resolve the kinetics and thermodynamics of free-radical reactions of $CrCH_2Ph^{2+}$,[4,5] (b) to complete the kinetic and thermodynamic characterization of benzylcobalamin[6] and other benzylcobalt (macrocycle) complexes,[7] and (c) to analyze reactions in which a benzyl group is transferred from one metal to another such as the reversible bimolecular reaction[8]

$$Cr(H_2O)_6{}^{2+} + PhCH_2Co(dmgH)_2OH_2 \rightleftarrows (H_2O)_5CrCH_2Ph^{2+} + (H_2O)_2Co^{II}(dmgH)_2 \qquad (2)$$

Two new and independent flash-photolytic methods have been developed. They permit determinations of the kinetics of formation of $(H_2O)_5CrCH_2Ph^{2+}$ and may have applicability to related systems.

Results and Interpretation

Photolysis of $(H_2O)_5CrCH_2Ph^{2+}$. UV irradiation results in Cr^{2+} and free benzyl radicals (reverse of eq 1),[9] which will either re-form $CrCH_2Ph^{2+}$ (eq 1) or dimerize (eq 3). The

$$2PhCH_2\cdot \xrightarrow{k_d} PhCH_2CH_2Ph \qquad (3)$$

extent of each depends upon the instantaneous concentrations of free radical and Cr^{2+} as well as the rate constants. The experiment consists of the measurement of the "recovery" of $CrCH_2Ph^{2+}$, $\Delta[CrCH_2Ph^{2+}]_\infty$, as a function of $[Cr^{2+}]_0$ ($(2.6–200) \times 10^{-5}$ M, by direct addition) and $[PhCH_2\cdot]_0$ (6–18 μM, by variation of $[CrCH_2Ph^{2+}]_0$ and the flash energy). The rate constant for radical dimerization is known independently,[11-14] $2k_d = 2.7 \times 10^9\ M^{-1}\ s^{-1}$, and thus the value of k_{Cr} can be obtained.

The data analysis is complicated because this represents competition between a pseudo-first-order and a second-order reaction. This and other complications were allowed for as described in the Experimental Section. The data are displayed in Figure 1, which depicts the decline in $\Delta[CrCH_2Ph^{2+}]_\infty$ with increasing $[R\cdot]_0$ and decreasing $[Cr^{2+}]_0$, normalized to permit the inclusion of all points on a single scale. The curve drawn through the data corresponds to the "best fit" value of $k_{Cr} = (8.5 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$.

Photolysis of Dibenzyl Ketone: Direct Kinetic Determination of k_{Cr}. The UV photolysis of this ketone is an efficient source of benzyl radicals, yielding $2PhCH_2\cdot + CO$ (eq 4 and 5).[15]

$$(PhCH_2)_2CO \xrightarrow{h\nu} [(PhCH_2)_2CO]^* \rightarrow PhCH_2\cdot + PhCH_2\dot{C}O \qquad (4)$$

$$PhCH_2\dot{C}O \rightarrow PhCH_2\cdot + CO \qquad (5)$$

When carried out in the presence of Cr^{2+}, this scheme yields $CrCH_2Ph^{2+}$ (and in fact it provides a convenient and practical new synthetic route). Because the photolysis is efficient and rapid, it can be made the basis for the direct flash-photolytic determination of k_{Cr}, as described in the Experimental Section.

The value of k_{obsd} is directly proportional to the average concentration of Cr^{2+}, as shown in Figure 2. A least-squares analysis yields an intercept of essentially zero, $(0.6 \pm 1.9) \times 10^3\ s^{-1}$, and a slope, $k_{Cr} = (8.5 \pm 0.8) \times 10^7\ M^{-1}\ s^{-1}$ (23 ± 2 °C with 2 M CH_3CN).

Discussion

The rate constants reported for the reactions of $Cr(H_2O)_6{}^{2+}$ with carbon-centered free radicals span a relatively narrow range, from $3.4 \times 10^7\ M^{-1}\ s^{-1}$ for $\cdot CH(CH_3)OC_2H_5$ to 1.6×10^8 for $\cdot CH_2OH$.[3] The value for $PhCH_2\cdot$, $k_{Cr} = 8.5 \times 10^7\ M^{-1}\ s^{-1}$, is in no sense exceptional. The values of k_{Cr} are the same by the two independent methods, and the addition of 2 M CH_3CN in the second (to increase the solubility of the ketone) was without detectable effect.

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(9) Photolysis of $(H_2O)_5CrR^{2+}$ complexes, although alluded to on occasion (e.g.: Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779) has not to our knowledge been studied systematically. Our experience is that the benzyl complex is considerably more photolabile than the alkyls. In the cases reported, UV photolysis leads largely and perhaps entirely to homolytic cleavage, even in alkyls, whereas irradiation of the 400-nm maximum typical[10] of the latter does not.

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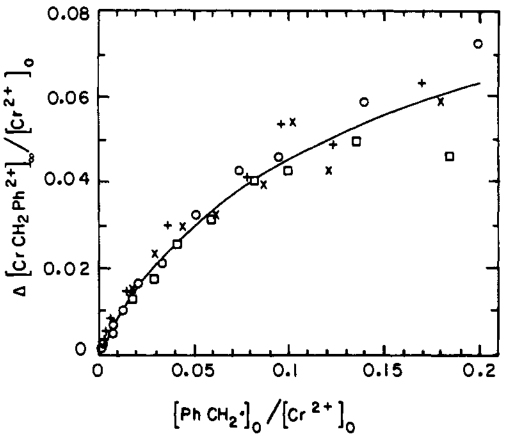

Figure 1. Increased yield of $CrCH_2Ph^{2+}$ as a function of the initial concentration of $PhCH_2\cdot$. Four series with varying ranges of $[PhCH_2\cdot]_0$ were normalized by division of both axes by $[Cr^{2+}]_0$. Data refer to experiments having the following approximate values of $[PhCH_2\cdot]_0$: 6 μM (□); 11 μM (×); 15 μM (○); 18 μM (+). The solid line is the curve calculated from eq 6 for $k_{Cr} = 8.5 \times 10^7$ M^{-1} s^{-1}.

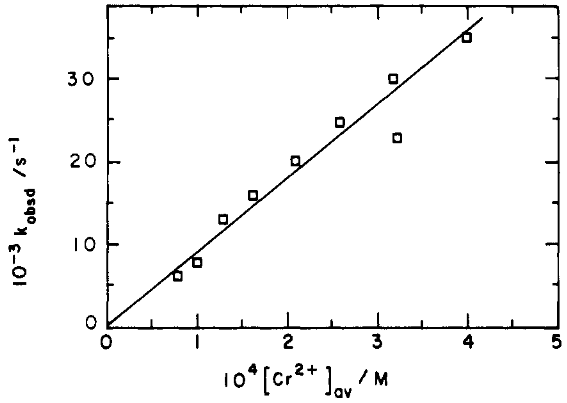

Figure 2. Pseudo-first-order rate constant variation with the average concentration of Cr^{2+} in flash-photolytic experiments utilizing dibenzyl ketone. The rate constants were evaluated from the later stages of the kinetic curves where the rate of reaction of $PhCH_2\cdot$ with Cr^{2+} is much greater than that of free-radical dimerization and where $[Cr^{2+}]$ is nearly constant.

With the value of k_{Cr} known, certain additional quantities can be calculated. The homolytic equilibrium[16] of eq 1 is reversible. The direct determination[5] of the rate of homolysis of $(H_2O)_5CrCH_2Ph^{2+}$ gave k_{-1} (2.63 ± 0.21) × 10^{-3} s^{-1} (25 °C). The equilibrium constant for reaction 1 is $K_1 = k_{Cr}/k_{-1}$ = (3.3 ± 0.4) × 10^{10} M^{-1}. The standard free energy change of the reaction is thus $\Delta G_1^\circ = -59.9$ kJ mol^{-1} ($\Delta G_{Cr}^{*} = 27.8$, $\Delta G_{-1}^{*} = 87.7$ kJ mol^{-1}).

Further thermodynamic values depend on estimates. The temperature dependence of k_{Cr} has not been measured, but it is likely to be quite small, corresponding to ΔH_{Cr}^{*} in the range 0–20 kJ mol^{-1}; in what follows we take $\Delta H_{Cr}^{*} = 10 \pm 10$ kJ mol^{-1}. Combined with $\Delta H_{-1}^{*} = 133 \pm 3$ kJ mol^{-1}, and $\Delta S_{-1}^{*} = 153 \pm 11$ J mol^{-1} K^{-1}, this value yields $\Delta H_1^\circ = -123 \pm 13$ kJ mol^{-1}, $\Delta S_1^\circ = -211 \pm 34$ J mol^{-1} K^{-1}, and $\Delta S_{Cr}^{*} = -60 \pm 35$ J mol^{-1} K^{-1}. None of the values is remarkable. The bond enthalpy of the chromium–carbon bond, represented by $-\Delta H_1^\circ$, is typical of values for other metal–carbon bonds.[16,17] The kinetic lability of $CrCH_2Ph^{2+}$ toward homolysis is promoted by a favorable entropy term, $T\Delta S_{-1}^{*} = 45$ kJ mol^{-1} at 25 °C, offsetting the large value of ΔH_{-1}^{*}. The large positive value of ΔS_{-1}^{*} arises here, as for other CrR^{2+} complexes,[16,18] from the dissociative character of the homolysis process (bond breaking, largely uncompensated for by any bond making), as well as from the disordering of the solvent by the release into it of the benzyl radical, a group poorly solvated by water.

Experimental Section

Materials. Solutions of $(H_2O)_5CrCH_2Ph^{2+}$ were prepared by the reaction of benzyl bromide and an acidic solution of $Cr(ClO_4)_2$ in aqueous acetone.[2,4] The product was purified by chromatography on an ice–water jacketed column of Sephadex G-25 ion-exchange resin, from which it was rinsed free of acetone and eluted with dilute perchloric acid. The manipulations and reactions of $CrCH_2Ph^{2+}$ were carried out under Cr^{2+}-scrubbed nitrogen. The UV–visible spectrum of the complex agreed with literature values;[2,4] the maximum at λ 356 nm (ε 2.21 × 10^3 M^{-1} cm^{-1}) was used to determine $[CrCH_2Ph^{2+}]$. In measurements made using the flash-photolysis detection system, chemical filters[19] ($CuSO_4$ or I_2 solutions) were often used to prevent photolysis of the complex by the analyzing light. Absorbance measurements were often made slightly off the maximum, at 364 nm (ε 2.09 × 10^3 M^{-1} cm^{-1}), where the higher sensitivity of our apparatus enhances the accuracy.

Dibenzyl ketone (Eastman Organic Chemicals) was recrystallized from pentane. Other materials were reagent grade chemicals used as purchased. Solutions were maintained at 0.05 M perchloric acid and (by addition of lithium perchlorate) 0.10 M ionic strength. Measurements were made at ambient (23 ± 2 °C) temperature. The solutions used for dibenzyl ketone photolysis also contained 2 M acetonitrile to increase its solubility.

Flash Photolysis of $(H_2O)_5CrCH_2Ph^{2+}$. Solutions that contained the desired initial concentrations of $CrCH_2Ph^{2+}$ ((0.39–1.0) × 10^{-4} M) and Cr^{2+} ((0–2) × 10^{-3} M) were prepared anaerobically in a cylindrical quartz spectrophotometer cell of 2- or 5-cm path length. The cell was then placed in the flash photolysis apparatus, a Xenon Corp. Model 710 unit equipped with fast-extinguishing Xenon flash lamps, and given a single, high-intensity pulse of 60–130 J. The solution transmittance at 356 or 364 nm was recorded on a Nicolet digitizing oscilloscope immediately before and after the photolysis. Blank experiments, some with $[Cr^{2+}]_0 = 0$ and others with high $[Cr^{2+}]$, were interspersed between other measurements. Values from the one blank afforded a value of $[PhCH_2\cdot]_0$ under a given set of conditions, as described subsequently; those from the other were used to demonstrate (by extrapolation) that net decomposition of $CrCH_2Ph^{2+}$ does not occur when $[Cr^{2+}]$ is sufficiently high.

The photolytically produced benzyl radicals either recombine with Cr^{2+} (eq 1, k_{Cr}) or form dibenzyl (eq 3, $2k_d$). Solution of the differential rate equations yields the expression[20] (6) for $\Delta[CrCH_2Ph^{2+}]_\infty$,

$$\Delta[\mathrm{CrCH_2Ph^{2+}}]_\infty = \frac{k_{Cr}[\mathrm{Cr^{2+}}]_{av}}{2k_d} \ln \left\{ 1 + \frac{2k_d[\mathrm{PhCH_2\cdot}]_0}{k_{Cr}[\mathrm{Cr^{2+}}]_{av}} \right\} \quad (6)$$

the increase (or recovery) in $[CrCH_2Ph^{2+}]$ from immediately after the flash until the end of the reaction. The value of $[Cr^{2+}]_{av}$ is only slightly different from the added concentration of Cr^{2+}, since the additional quantity formed by the flash, and then in part consumed by recombination, is usually much smaller than the added concentration. The quantity $[PhCH_2\cdot]_0$ is the initial concentration of the free radical at the (hypothetical) instant where the flash has extinguished but before any reaction of the radical has occurred. The value of $[PhCH_2\cdot]_0$ is approximated by the concentration of $CrCH_2Ph^{2+}$ lost in the blank experiments without added Cr^{2+}; in practice two offsetting corrections, both fortunately relatively small (each <10% of the total concentration), were needed. The first corrects for the amount of recombination that occurs between the newly formed Cr^{2+} and the radical, even when Cr^{2+} is not added. Estimates were made iteratively, as further fitting to eq 6 refined the value of k_{Cr}. The second corrects in an approximate manner for the amount of both reactions that occur during the flash, a period of some 40 μs, the more so at higher $[Cr^{2+}]$ and $[PhCH_2\cdot]_0$. The intensity–time profile of the flash, determined experimentally, was analyzed by graphical integration

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of small segments to estimate instantaneous rates of free-radical production during the flash. This analysis was coupled with solutions[20] of the differential rate laws for $-d[PhCH_2\cdot]/dt$ and $d[CrCH_2Ph^{2+}]/dt$ to calculate the "initial" value of $[PhCH_2\cdot]$ at the time taken as $t = 0$ in eq 6. This too was done iteratively, the calculation being reported for refined values of k_{Cr}. Although not a rigorous solution to the problem, it is adequate for the case at hand since quite minor adjustments in $[PhCH_2\cdot]_0$ resulted.

The determination of k_{Cr} itself was made on the basis of eq 6, comparing observed and calculated values of $\Delta[CrCH_2Ph^{2+}]_\infty$ in numerous experiments at various $[Cr^{2+}]_{av}$ and $[PhCH_2]_0$. The success of the procedure is illustrated by the comparison shown in Figure 1. The "best fit" value cited for k_{Cr} and an assessment of its precision were found by visual matching.

Kinetic Spectrophotometry Using Dibenzyl Ketone. The ketone, characterized by an absorption maximum at 295 nm (ϵ 220 M^{-1} cm^{-1}), undergoes photolysis according to eq 4 and 5.[15] Under the conditions used (0.5 mM $(PhCH_2)_2CO$ in 2 M aqueous acetonitrile, 0.05 M $HClO_4$ at ionic strength 0.10 M with $(0.8–4.0) \times 10^{-4}$ M Cr^{2+}), $[PhCH_2\cdot]_0$ is estimated to be ca. 6×10^{-5} M. The reaction rate was followed by monitoring the progress of the reaction at 364 nm where $CrCH_2Ph^{2+}$ is the only high-absorbing species present. The evaluation of k_{Cr} from the rate law $d[CrCH_2Ph^{2+}]/dt = k_{Cr}[Cr^{2+}][PhCH_2\cdot]$ is, however, not simply a matter of a pseudo-first-order analysis because dimerization of the organic radical also defines $[PhCH_2\cdot]$ at any time during the run. The "kinetic observable" thus obeys parallel pseudo-first-order and second-order rate equations, the analysis of which over the entire course of a reaction is complicated in the present instance by the large uncertainty in $[PhCH_2\cdot]_0$[21] and by the accessible range of $[Cr^{2+}]$. Thus, a modified procedure was adopted. Sufficiently late in the progress of any run, the condition $[Cr^{2+}]_t >> [PhCH_2\cdot]_t$ will eventually prevail; consequently, the rate of the second-order dimerization reaction will become much smaller than that of the pseudo-first-order component. In practice, only absorbance–time values in the very last segment (with only 2–10% of reaction remaining, depending on the conditions in each run) were used in the kinetic analysis. This subset of the data, analyzed according to standard pseudo-first-order kinetics, yielded a value of k_{obsd} that varied linearly with $[Cr^{2+}]$. (The latter was, of course, essentially the value of $[Cr^{2+}]$ near the end of the run.) The use of the amplification features of the digitizing oscilloscope was important in acquiring the kinetic data.

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Registry No. $(H_2O)_5CrCH_2Ph^{2+}$, 34788-74-4; $(PhCH_2)_2CO$, 102-04-5; $PhCH_2Br$, 100-39-0; $Cr(ClO_4)_2$, 13931-95-8; Cr^{2+}, 22541-79-3; $PhCH_2\cdot$, 2154-56-5.

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(21) The direct determination of $[PhCH_2\cdot]_0$ is complicated by the occurrence of reaction 1 during the flash. The formation of highly absorbing $(H_2O)_5CrCH_2Ph^{2+}$ causes the amount of 290-nm light available to $(PhCH_2)_2CO$ to decrease with time.

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Kinetics and Mechanism of the Complexation Reaction of Gallium(III) with Tropolone As Studied by a High-Pressure Stopped-Flow Technique. Evidence for a Dissociative-Interchange Mechanism

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The formation kinetics of the 1:1 gallium(III) complex with tropolone (HL) in acidic aqueous media has been studied spectrophotometrically at various temperatures and pressures by means of a stopped-flow technique. The rate law is expressed as $d[GaL^{2+}]/dt = (k_{Ga} + k_{GaOH}K_{GaOH}[H^+]^{-1})(1 + K_{H_2L}[H^+])^{-1}(1 + K_{GaOH}[H^+]^{-1})^{-1}[Ga^{3+}][HL]$, with $k_{Ga} = 38 \pm 1$ M^{-1} s^{-1}, $k_{GaOH} = (8.2 \pm 0.2) \times 10^3$ M^{-1} s^{-1}, and $K_{GaOH} = [GaOH^{2+}][H^+][Ga^{3+}]^{-1} = (1.3 \pm 0.1) \times 10^{-3}$ M at 25 °C and $I = 0.50$ M at atmospheric pressure. The activation parameters for the reaction of Ga^{3+} (k_{Ga} path) and the reaction of $GaOH^{2+}$ (k_{GaOH} path) are as follows: $\Delta H^*{}_{Ga} = 61 \pm 10$ kJ mol^{-1}, $\Delta S^*{}_{Ga} = -12 \pm 30$ J K^{-1} mol^{-1}, $\Delta V^*{}_{Ga} = 4.0 \pm 1.3$ cm^3 mol^{-1}; $\Delta H^*{}_{GaOH} = 29 \pm 11$ kJ mol^{-1}, $\Delta S^*{}_{GaOH} = -74 \pm 38$ J K^{-1} mol^{-1}, $\Delta V^*{}_{GaOH} = 2–4$ cm^3 mol^{-1}. Positive activation volumes for both the k_{Ga} and the k_{GaOH} paths point to a dissociative-interchange mechanism.

Introduction

The kinetic behavior of divalent metal ion M^{2+} in complexation reactions in aqueous solution has been mostly interpreted by a dissociative-interchange mechanism,[1] in which the overall formation rate constant k_M is given by $K_{os}k_M^{-H_2O}$ where K_{os} and $k_M^{-H_2O}$ refer to the formation constant of an outer-sphere complex and the water-exchange rate constant at M^{2+}, respectively. This mechanism has been shown to be valid also for complexation reactions involving multidentate ligands having no extra stabilization of an outer-sphere complex and no steric inhibition due to their bulkiness.[2] Merbach and his co-workers have reported the negative values of activation volume for the complexation[3] as well as the water exchange at $V(H_2O)_6^{2+}$.[4] On the basis of these findings they concluded an associative-interchange mechanism for the substitution on this cation.

For trivalent metal ions, on the other hand, the mechanism of complexation reactions is still somewhat in doubt except for chromium(III)[5] and iron(III).[6] This arises mainly from the limited number of ligands suitable for kinetic measurements and from the complicated hydrolysis reactions of the metal ions.[7] The complexation of Ga^{3+} has been claimed to

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