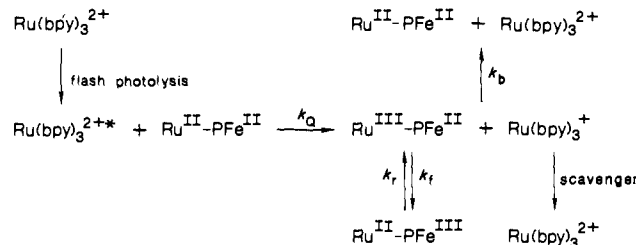


Figure 1. (a) Change in optical density of the heme absorption at 556 nm following flash photolysis of a 0.1 M, pH 7 phosphate solution containing $a_5\text{Ru}^{\text{II}}(48)\text{MbFe}^{\text{II}}$ ($5\ \mu\text{M}$), $\text{Ru}(\text{bpy})_3^{2+}$ ($65\ \mu\text{M}$), $\text{Ni}^{\text{II}}\text{Me}_6\text{ane}$ ($5\ \text{mM}$), and RBr ($20\ \text{mM}$); $25\ ^\circ\text{C}$. (b) First-order plot of the experimental data (\bullet). The line is a least-squares fit for these points.

Scheme I



to intramolecular ET: $a_5\text{Ru}^{\text{III}}(48)\text{MbFe}^{\text{II}} \rightarrow a_5\text{Ru}^{\text{II}}(48)\text{MbFe}^{\text{III}}$. This oxidation of the Fe^{II} -heme follows first-order kinetics for at least three half-lives with an observed rate constant of $0.058\ \text{s}^{-1}$. The kinetics were found to be independent of protein concentration ($5\text{--}50\ \mu\text{M}$), thereby establishing that bimolecular ET processes are not significant.

The rate of Fe^{II} to Ru^{III} ET for $a_5\text{Ru}(48)\text{MbFe}$ ($k_{\text{obsd}} = 0.058 \pm 0.004\ \text{s}^{-1}$) is within experimental error of that previously determined for the reverse ET ($k_{\text{obsd}} = 0.060 \pm 0.004\ \text{s}^{-1}$).² Kinetic analysis⁷ of a reversible unimolecular process yields an observed first-order rate constant that is equal to the sum of the forward (k_f) and reverse (k_r) rates:

$$a_5\text{Ru}^{\text{III}}(48)\text{MbFe}^{\text{II}} \xrightleftharpoons[k_r]{k_f} a_5\text{Ru}^{\text{II}}(48)\text{MbFe}^{\text{III}}; \quad k_{\text{obsd}} = k_f + k_r$$

Our finding that the observed rate constant is independent of the initial $[\text{Ru}^{\text{III}}\text{-PFe}^{\text{II}}]:[\text{Ru}^{\text{II}}\text{-PFe}^{\text{III}}]$ ratio demonstrates unequivocally that long-range ET in $a_5\text{Ru}(48)\text{MbFe}$ is reversible.

We have also employed the new methodology to measure the long-range ET rate in myoglobin modified at histidine-48 with $a_4\text{pyRu}$ (py = pyridine). This derivative of myoglobin was prepared and characterized by procedures analogous to those employed for $a_5\text{Ru}(48)\text{MbFe}$.^{2,8} The overall driving force for Fe^{II} to Ru^{III} ET in $a_4\text{pyRu}^{\text{III}}(48)\text{MbFe}^{\text{II}}$ is 220 mV larger than in $a_5\text{Ru}^{\text{III}}(48)\text{MbFe}^{\text{II}}$. The general features of the kinetics are similar

to those previously discussed for the $a_5\text{Ru}$ -modified protein except that the overall reaction is considerably faster. The measured Fe^{II} to Ru^{III} long-range ET rate of $2.5\ \text{s}^{-1}$ indicates that $\text{Ru}(48)\text{MbFe}$ follows Marcus theory with a reorganization energy (λ)⁹ similar to those reported for related protein^{10,11} and steroid-spacer¹² ET reactions. In terms of the Hoffman-Ratner treatment of gated ET reactions,¹³ our findings are of particular relevance because they show that the rates of long-range ET in ruthenium-modified myoglobins are not controlled by conformational interconversions.¹⁴

Acknowledgment. We thank Brian Hoffman, Walther Ellis, and Andy Axup for helpful discussions. This research was supported by National Science Foundation Grant CHE85-18793. C.M.L. acknowledges postdoctoral fellowship support from the NIH.

(9) Assuming that $k = A \exp(-(\Delta G^\circ + \lambda)^2/4\lambda RT)$ and that λ and A remain constant, the ET rate constant at the higher driving force is $k_1 = k_2 \exp[-((\Delta G_1^\circ + \lambda)^2 - (\Delta G_2^\circ + \lambda)^2)/4\lambda RT]$, where $\Delta G_1^\circ = -240\ \text{mV}$, $\Delta G_2^\circ = -20\ \text{mV}$, and $k_2 = 0.04\ \text{s}^{-1}$. For λ values between 1 and 2 eV, k_1 is predicted to be $\sim 2\ \text{s}^{-1}$.

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Novel Synthesis of a Polyketone via Radical Ring-Opening Polymerization of 2,2-Diphenyl-4-methylene-1,3-dioxolane

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Received January 26, 1987

Although the ionic ring-opening polymerization has been widely investigated, few papers have reported on the free radical ring-opening polymerization. Recent examples of the free radical ring-opening polymerization involve the vinylcyclopropanes,¹ unsaturated spiro orthocarbonates,² unsaturated spiro ortho esters,³ 2-phenyl-3-vinylloxylanes,⁴ cyclic ketene acetals such as 2-methylene-1,3-dioxolane,⁵ and 2-methylene-4-phenyl-1,3-dioxolane.⁶ In the course of researching the radical ring-opening polymerization of 2-substituted-4-methylene-1,3-dioxolanes, it was found that a polyketone was obtained in good yield by the polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane (**1**) accompanying the quantitative elimination of benzophenone without any side reactions. Although some ways of synthesizing a polyketone, such as the copolymerization of ethylene with carbon monoxide under high pressure,⁷ the oxidation of poly(vinyl alcohol),⁸ the cationic polymerization of a ketene or diketene,⁹ and

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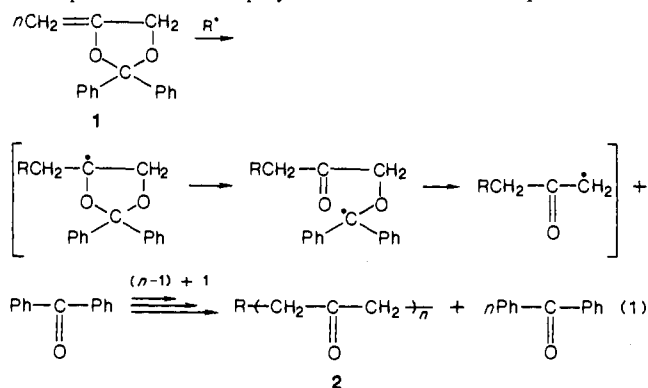
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the radical ring-opening polymerization of unsaturated cyclic ethers or diketene,¹⁰ have been reported; any of such obtained polymers contains undetermined structural units or no more than ketone moieties partially. We now report a novel synthesis of polyketone via the radical ring-opening polymerization of **1** accompanying the quantitative elimination of benzophenone.

Monomer **1**¹¹ was synthesized by the acetal formation as follows: benzophenone was allowed to react with 3-chloro-1,2-propanediol in benzene in the presence of *p*-toluenesulfonic acid (*p*-TsOH) with azeotropic removal of water for 6 h. The obtained chloro compound, 2,2-diphenyl-4-(chloromethyl)-1,3-dioxolane¹² was dehydrochlorinated with sodium methoxide in *N,N*-dimethylformamide (DMF) for 3 h at 50 °C. The polymerization of **1** was carried out at 120 °C in chlorobenzene in the presence of di-*tert*-butyl peroxide (DTBP) (3 mol %) as an initiator.¹³ Since the reaction mixture solidified as the polymerization proceeded, the polymerization of **1** almost stopped after about 7 h. The detection of benzophenone from the soluble part in methylene chloride after the purification indicated that **1** was polymerized with the elimination of benzophenone. All the IR spectra of thus obtained polymers (**2a** (time, 0.5 h), **2b** (2 h), **2c** (4 h), **2d** (7 h), **2e** (11 h), **2f** (16 h)) showed absorption at 1693 cm⁻¹ assigned to C=O group. All the ¹H NMR spectra showed only one signal at 2.62 ppm corresponding to methylene protons, and the ¹³C NMR spectrum of polymer **2f** showed two signals at 206.84 and 35.37 ppm corresponding to the carbonyl carbon and the methylene carbon, respectively. To our notice, neither aromatic proton nor aromatic carbon was found in all the spectra. Moreover, the found value of elemental analysis of polymer **2f** agreed with the calculated value for (C₃H₄O)_n. These spectral data and the result of the elemental analysis indicated that **1** underwent the ring-opening reaction accompanying the quantitative elimination of benzophenone to form polyketone **2** as shown in eq 1.



Further confirmation of the polyketone structure was carried out by the chemical reaction of the obtained polymer with phenylhydrazine.¹⁴

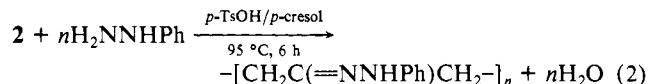
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(11) 2,2-Diphenyl-4-methylene-1,3-dioxolane (**1**): yield 59.4%; bp 82 °C (0.06 mmHg); mp 39.0–40.0 °C; IR (neat) 3063, 3032, 2886, 1686, 1068, 756 cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 7.93–7.13 (m, 10 H, Ar H's), 4.03–3.80, 4.70–4.30 (m, 4 H, C=CH₂, OCH₂).

(12) 2,2-Diphenyl-4-(chloromethyl)-1,3-dioxolane: yield 69.0%; bp 126 °C (0.07 mmHg); mp 42.0–43.0 °C; IR (neat) 3063, 3028, 2889, 1076, 1030, 752 cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 8.00–6.73 (m, 10 H, Ar H's), 4.60–3.13 (m, 5 H, CH₂Cl, OCH₂, OCH).

(13) Six sealed polymerization tubes (5 mL) containing **1** (2.00 g, 8.39 mmol), DTBP (36.8 mg, 0.252 mmol), and chlorobenzene (4.3 mL) were heated at 120 °C for 0.5, 2, 4, 7, 11, and 16 h, respectively. The resulting products were purified by dissolution in *p*-cresol, followed by precipitation in the mixture of methylene chloride and triethylamine (10:1). The precipitated materials were dried under reduced pressure at room temperature to give 0.035 g of **2a** (7.6%), 0.125 g of **2b** (26.9%), 0.246 g of **2c** (52.3%), 0.348 g of **2d** (75.5%), 0.365 g of **2e** (77.5%), and 0.371 g of **2f** (78.8%), respectively: [η] 0.63 dL/g at 30 °C in *m*-cresol; IR (KBr) 2912, 1693, 1408, 1331, 1055 cm⁻¹ (**2a–f**); ¹H NMR (Me₂SO-*d*₆, 140 °C, 100 MHz) δ 2.62 (s, 4 H, CH₂COCH₂) (**2a–f**); ¹³C NMR (Me₂SO-*d*₆, 140 °C, 25.00 MHz) δ 206.84 (CO), 35.37 (CH₂) (**2f**); Anal. Calcd. for (C₃H₄O)_n: C, 64.27; H, 7.19. Found: C, 64.64; H, 7.01 (**2f**).



In the IR spectrum of the reaction product, the absorption of C=O group disappeared completely but the new absorptions at 1601 cm⁻¹ assigned to C=N and the phenyl group were observed. These results strongly supported the structure of **2**.

Although the five-membered ring containing two oxygen atoms (dioxolane) has lower strain energy, that the reaction proceeded smoothly might be caused by the formation of a stable radical, diphenylmethyl radical, which cannot attack the olefin, and as a result the production of the ketone group (benzophenone). In other words, the predominant formation of a ketone group and diphenylmethyl radical is the driving force for the polymerization of **1**.

It is also expected that the ketone moieties can be easily incorporated into the backbone of vinyl polymers by a copolymerization method. In practice, it has been already found that the ketone moieties can be incorporated into the backbone of polystyrene. A report relating to the copolymerization of **1** with vinyl monomers will be presented subsequently.

(14) A solution of the polymer (24.3 mg) and phenylhydrazine (170 mg) in *p*-cresol (1.5 mL) was heated at 95 °C for 6 h in the presence of *p*-TsOH (0.075 g). After *p*-TsOH was destroyed by the addition of triethylamine (0.1 mL), the product was purified by precipitation in a mixture of ether and triethylamine (10:1). The precipitated polymer was dried under reduced pressure at room temperature to give 55.8 mg of polyimide (88.0%): IR (KBr) 2976, 2939, 1601, 1496, 1184, 694 cm⁻¹.

NMR Properties of the Complexes

trans-[M(η²-H₂)(H)(PEt₂CH₂CH₂PEt₂)₂]⁺, M = Fe, Ru, Os; Intramolecular Exchange of Atoms between η²-Dihydrogen and Hydride Ligands

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Received December 17, 1986

An important question arising from the recent discovery of several η²-dihydrogen complexes^{1–8} is under which conditions is the η²-dihydrogen coordination mode, M(η²-H₂), preferred over the classical, dihydride structure, M(H)₂?⁹

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