methyl phosphate does not readily permit an explanation for the presumed configurational error to be ascertained.[25]

The result described in this communication and that recently described by Eckstein and Stec and their collaborators[12] constitute the third example of an enzyme-catalyzed phosphoryl transfer reaction whose stereochemical course is unaffected by sulfur substitution. This example is the first for a hydrolysis reaction, the previous two being for a kinase reaction (glycerol kinase)[3,4] and for a nucleotidyl transfer reaction (adenylate cyclase).[5,6]

Acknowledgment. We are grateful to Professors Fritz Eckstein and Jeremy Knowles for their encouragement and useful discussions. The high-field NMR spectra essential to this research were obtained with the generous cooperation and advice of Professor Philip Bolton. This research was supported by a grant from the National Institutes of Health (GM-22350).

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[25] Upon completion of the research described in this communication, we informed Dr. Lowe of our results. His reply, which was received after this manuscript had been completed, indicated that the configuration of the oxygen chiral methyl phosphate,[9] 5'-AMP,[7] and glucose 6-phosphate[7] all have the S_P rather than the R_P configuration as originally published. This error was explained by incorrect assignments of the geometries of the precursor hydrobenzoin cyclic triesters.

$(C_5Me_5)_2UCl\cdot THF$ Oxidative-Addition Reactions. 2. A Kinetic and Mechanistic Study

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In a recent communication,[1] we described $(C_5Me_5)_2UCl\cdot THF$, **1**, oxidative addition of alkyl halides, reactions which proceed according to the generalized stoichiometry of eq 1. These reactions, the first organoactinide oxidative additions to be described, were observed to proceed at rates unprecedented in organotransition-metal chemistry. Herein we report a kinetic and mechanistic study of these one-electron, U(III) to U(IV), oxidative additions.[2] This study is aimed primarily at understanding and quantifying this enhanced organoactinide reactivity. The results obtained (1) provide evidence for a halogen atom-abstraction $(S_{H}2)$[3c] oxidative-addition[3,4] mechanism, (2) include a wide range of RX relative rates, many of which were previously unavailable from studies of less reactive prototype transition-metal atom abstractors such as Co(II)[3g] or Cr(II)[3h], (3) quantify the exceptionally high reactivity of $(C_5Me_5)_2UCl$ as 10^4 and 10^7 faster than Co(II) coenzyme $B_{12(r)}$ and $[Cr(II)(en)_2]^{2+}$, respectively, and (4) demonstrate and quantify the key role of coordinative unsaturation[5] in achieving these high actinide oxidative-addition rates.

Evidence for radical intermediates in these reactions was obtained[1] from the addition of cyclopropylcarbinyl chloride to $(C_5Me_5)_2UCl\cdot THF$ in room temperature benzene to yield a significant amount of the ring opened product, $(C_5Me_5)_2UCl(\text{—}CH_2CH_2CH{=}CH_2)$. The formation of dimers, olefins, and alkanes [R–R, R(–H), and R(H), respectively, eq 1] from the

$$(a + 2b)(C_5Me_5)_2UCl\cdot THF + (a + b)RCl \xrightarrow{\text{benzene}} (a + b)(C_5Me_5)_2UCl_2 + b(C_5Me_5)_2UCl(R) + a[R\text{–}R, RH, R(\text{–}H)] + (a + 2b)THF \tag{1}$$

corresponding RCl is also consistent with a R· intermediate as are the relative RX rates observed for benzyl ~ tertiary > secondary > primary > neopentyl (vide infra).

The complete rate law, including the surprising and dramatic dependence upon added THF, was determined by monitoring the loss of $[U(III)]_T$,[6] λ_{max} 740 nm, at 0.0 °C for *n*-butyl and neopentyl chlorides. An overall second-order dependence, first order each in $[U(III)]_T$ and [RX], was established from the appropriate kinetic plots, which were linear over 80–90% reaction for the accessible ca. 4-fold, $1.5\text{–}6.0 \times 10^{-3}$ M, range of starting $[(C_5Me_5)_2UCl\cdot THF]$ and from the independence of the observed second-order rate constant, k_2(obsd), over a 5-fold, $0.97\text{–}5.0 \times 10^{-3}$ M alkyl chloride concentration range. The observed rate constants are: $k_2(\text{obsd}) = 17 \pm 3\ M^{-1}\ s^{-1}$ for *n*-BuCl at 0.0 °C, $k_2(\text{obsd}) = 31 \pm 3\ M^{-1}\ s^{-1}$ for *n*-BuCl at 22.0 °C, and $k_2(\text{obsd}) = 2.8 \pm 1.0\ M^{-1}\ s^{-1}$ for neopentyl chloride at 0.0 °C. The [THF] dependence of the 22.0 °C *n*-BuCl oxidative-addition rate law was established from the smooth, concave dependence of k_2(obsd) on [THF] added to the benzene/$(C_5Me_5)_2UCl\cdot THF$ solution; $k_2(\text{obsd}) = 31\ M^{-1}\ s^{-1}$ at 0:100 (v/v) THF/benzene decreasing to a near limiting $k_2(\text{obsd}) = 0.088\ M^{-1}\ s^{-1}$ at 40:60 (v/v) THF/

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[1] Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.*, in press. These reactions were discovered during our investigation of uranium–transition-metal heterobimetallic complexes. We thank Professor Tobin Marks and his research group for the exchange of unpublished information on $[(C_5Me_5)_2UCl_2]^-\cdot Na^+$, a Na(Hg) reduction product of $(C_5Me_5)_2UCl_2$.

[2] (a) References to the oxidative-addition reaction prior to 1977 are summarized in: Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515. (b) Tsou, T. T.; Kochi, J. K. *Ibid.* **1979**, *101*, 6319. (c) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434. (d) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838. (e) Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1980**, 1448. (f) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1980**, *19*, 571. (g) Harrod, J. F.; Hamer, G.; Yorke, W. *J. Am. Chem. Soc.* **1979**, *101*, 3987. (h) Drago, R. S.; Nozari, M. S.; Klinger, R. J.; Chamberlain, C. S. *Inorg. Chem.* **1979**, *18*, 1254. (i) Mureinik, R. J.; Weitzberg, M.; Blum, J. *Ibid.* **1979**, *18*, 915. (j) Burke, N. E.; Singhal, A.; Hintz, M. J.; Ley, J. A.; Hui, H.; Smith, L. R.; Blake, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 74. (k) Klabunde, K. J.; Roberts, J. S. *J. Organomet. Chem.* **1977**, *137*, 113. (l) Otsuka, S.; Ataka, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1118. (m) Ohtani, Y.; Fujimoto, M.; Yamagishi, A. *Ibid.* **1977**, *50*, 1453. (n) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501 (o) Collman, J. P.; MacLaury, M. R. *Ibid.* **1974**, *96*, 3019. (p) Pearson, R. G.; Figdore, P. E. *Ibid.* **1980**, *102*, 1734. (q) Labinger, J. A.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3230. (r) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Ibid.* **1980**, *19*, 3236.

[3] (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 7. (b) Poutsma, M. L. "Free Radicals"; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. II, Chapter 14. (c) Ingold, K. U.; Roberts, B. P. "Free-Radical Substitution Reactions"; Wiley-Interscience, New York, 1971. (d) Schneider, P. W.; Phelan, P. F.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 77. (e) Halpern, J.; Maher, J. P. *Ibid.* **1965**, *87*, 5361. (f) Kwiatek, J.; Seyler, J. K. *J. Organomet. Chem.* **1965**, *3*, 421. (g) Blaser, H. U.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 1684. (h) Kochi, J. K.; Powers, J. W. *Ibid.* **1970**, *92*, 137.

[4] It is of interst to compare U to Ti, Zr, and Hf oxidative additions, given the recently established[5] similarities between organoactinide and group 4B chemistry. Evidence for an atom-abstraction pathway by Zr(III) has appeared[4a] although only a few studies of Ti, Zr, or Hf oxidative additions are available.[4a–f] (a) Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660. The reported rate for *n*-BuBr reacting with Cp_2ZrL_2 (26 °C, PhH, 12-fold excess $L = PPh_2Me$) of $540\ M^{-1}\ s^{-1}$ has been corrected to $0.054\ M^{-1}\ s^{-1}$. Williams, G. M.; Gell, K. I.; Schwartz, J. *Ibid.* **1980**, *102*, 7619. (b) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. (c) Dormond, A.; Kolavudh, T.; Tirouflet, J.; *C. R. Hebd. Seances Acad. Sci., Ser. C* **1976**, *282*, 551. (d) Dormond, A.; Kolavndh, T.; Tirouflet, J. *J. Organomet. Chem.* **1979**, *165*, 319. Coutts, R. S. P.; Wailes, P. C. *J. Organomet. Chem.* **1974**, *73*, C5. (f) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1972**, 790.

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[6] Between 1.25×10^{-3} and 6.1×10^{-3} M in benzene at 25 °C, Beer's law is obeyed by $(C_5Me_5)_2UCl\cdot THF$ with ϵ (apparent, 740 nm) $3.09 \pm 0.08 \times 10^2\ M^{-1}\ cm^{-1}$. Evidence given in the text shows that there exists, however, a THF dissociative equilibria with $K_{eq} = 1.4 \times 10^{-2}$ M, $(C_5Me_5)_2UCl\cdot THF \rightleftharpoons (C_5Me_5)_2UCl + THF$, so that at 1.25×10^{-3} M, 92% of the U(III) is in the THF free form while at 6.1×10^{-3} M, 75% has dissociated a THF. Beer's law is obeyed in this concentration range since the two U(III) forms have very similar visible spectra.

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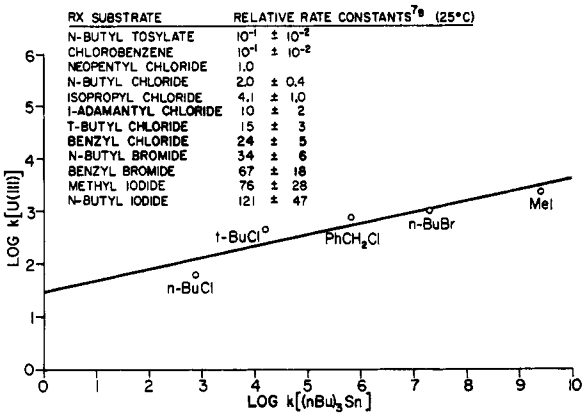


RX SUBSTRATE	RELATIVE RATE CONSTANTS[7b] (25°C)
N-BUTYL TOSYLATE	$10^{-1} \pm 10^{-2}$
CHLOROBENZENE	$10^{-1} \pm 10^{-2}$
NEOPENTYL CHLORIDE	1.0
N-BUTYL CHLORIDE	2.0 ± 0.4
ISOPROPYL CHLORIDE	4.1 ± 1.0
I-ADAMANTYL CHLORIDE	10 ± 2
T-BUTYL CHLORIDE	15 ± 3
BENZYL CHLORIDE	24 ± 5
N-BUTYL BROMIDE	34 ± 6
BENZYL BROMIDE	67 ± 18
METHYL IODIDE	76 ± 28
N-BUTYL IODIDE	121 ± 47

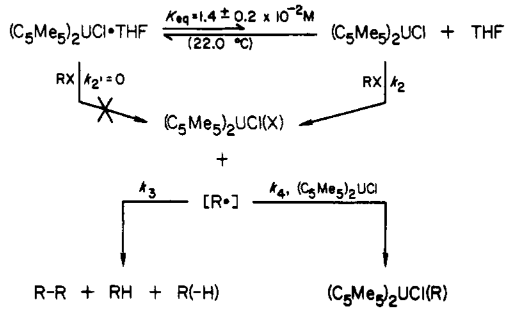
Figure 1.

benzene. The observed [THF] dependence is characteristic of a prior equilibrium, $(C_5Me_5)_2UCl{\cdot}THF \rightleftharpoons (C_5Me_5)_2UCl + THF$, where $K_{eq} \ll 1$ and where the relative reactivity is $(C_5Me_5)_2UCl \gg (C_5Me_5)_2UCl{\cdot}THF$. Derivation of the necessary kinetic equation[7] followed by the appropriate plot of the data shows that $1/k_2$(obsd) vs. [THF] is linear with the slope = 2.1 ± 0.2 s and intercept = 0.031 ± 0.003 M s. The full rate law is consistent with the prior equilibrium and rate-determining step of Scheme I with[7a] $K_{eq} = 1.4 \pm 0.2 \times 10^{-2}$ M, $k_2 = 21 \pm 2$ M^{-1} s^{-1}, and $k_{2'} = 0$ for *n*-BuCl at 22.0 °C. The small K_{eq} for THF dissociation reflects the high oxygen affinity[5] of organoactinide reagents, and $k_2' = 0$ (within experimental error) suggests that coordinative unsaturation and the availability of an inner sphere process is a requirement for these facile oxidative-addition reactions.

The RX alkyl, structure-reactivity and halogen dependence was determined at 25 °C in benzene for 12 total RX, including X = I, Br, Cl, OTs, by pairwise competition experiments, monitoring the loss of RX in the ^1H NMR spectra. The results and the propagated error bars are tabulated in Figure 1 along with a log/log plot comparing the U(III) rates to those for one of the better studied organometallic atom abstractors,[8] $Bu_3Sn\cdot$. The relative RCl rates of benzyl ~ tertiary > secondary > primary > neopentyl and *n*-BuI > *n*-BuBr > *n*-BuCl are consistent with rate-determining formation of an R· intermediate with carbon–halogen bond cleavage in the transition state. The linear log/log correlation with the $Bu_3Sn\cdot$ data lends credence to both sets of data and suggests a similar rate-determining step for both the U(III) and $R_3Sn\cdot$ reagents.

An atom-abstraction mechanism (Scheme I) is consistent with all of our observations.[9]

Scheme I. Atom-Abstraction Mechanism of $(C_5Me)_2UCl$ Oxidative Addition of Alkyl Halides (Benzene)



To summarize, the results presented herein (1) provide evidence for an atom-abstraction RX oxidative-addition mechanism to $(C_5Me_5)_2UCl$; (2) quantify the reactivity of $(C_5Me_5)_2UCl$ in benzene as 10^4–10^7 faster than any known[10] isolable, transition-metal systems reacting by halogen atom abstraction, as only 42 times slower than the transient intermediate $Bu_3Sn\cdot$ in the case of alkyl chlorides, and as even 4.0 times faster than the S_N2 reagent[2a] $Fe(CO)_4{}^{2-}$; (3) quantify the relative rates of $(C_5Me_5)_2UCl/(C_5Me_5)_2UCl{\cdot}THF$ as 20:0 and suggest that this difference reflects primarily the difference in the degree of coordinative unsaturation[5,11] and thus the availability of an inner sphere pathway for the 7- and 8-coordinate U(III) species.

Further studies of organoactinide oxidative additions and the possible extension of this work to organolanthanides is currently under investigation.

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(7) (a) The k_2 (obsd) given in Scheme I and used in the text includes a statistical factor, $(a + 2b)/(a + b)$, introduced by the reaction stoichiometry (and equal to 1.55 and 1.08 for *n*-butyl and neopentyl chlorides, respectively), $k_2\,(\text{obsd}) = (a + 2b)/(a + b)\,[K_{eq}k_2/([\text{THF}] + K_{eq})]$, when $k_2' = 0$. A plot of $1/k_2$(obsd) vs. [THF] will be linear if $k_2' = 0$ and will have slope = $1/[(a + 2b)/(a + b)]K_{eq}k_2$ and intercept = $1/[(a + 2b)/(a + b)]k_2$. From the observed slope and intercept, the values $K_{eq} = 1.4 \pm 0.2 \times 10^{-2}$ M and $k_2 = 21 \pm 2$ M^{-1} s^{-1} were obtained. (b) The relative rates in Figure 1 are relative $k_2\,(\text{obsd})/[(2a + b)/(a + b)]$, i.e., they do not include the statistical factor from the stoichiometry[7a] since the disappearance of RX was monitored, $-d[RX]/dt = k_2(\text{obsd})/[(a + 2b)/(a + b)][U(III)]_T[RX]$.

(8) (a) Sakura; H. "Free Radicals"; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. II, p 771. (b) See also ref 3b.

(9) (a) An alternate mechanism, common to reactions of this type,[3a] is the possibility of an outer sphere electron transfer,[9b–d] $(C_5Me_5)_2UCl + RX \rightleftharpoons (C_5Me_5)_2UCl^+\,RX^{-}\cdot$, with equilibrium constant K_{eq}, rather than inner sphere atom abstraction. Several lines of evidence argue effectively against the electron-transfer mechanism: (1) first and foremost is the requirement of coordinative unsaturation in the U(III) oxidative additions, a feature readily understood in terms of an inner sphere but not in terms of an outer sphere process; (2) a second line of evidence is that the electron transfer appears to be nearly 1.5 V uphill and thus too endergonic to be facile. The cyclic voltammogram of $(C_5Me_5)_2UCl_2$ in THF gave[1] a $E_{1/2}[U(IV)/U(III)] = -1.3$ V vs. SCE. Using this $E_{1/2}$ value as a negative limit for the U(IV)/U(III) couple of $(C_5Me_5)_2UCl$ and from the *Ep*[9e] of *n*-BuCl ~ −2.8 V (SCE) (which includes kinetic effects but is probably[9f] $Ep \geq E_{1/2}$), one can estimate $E_{total} \leq -2.8 + 1.3 = -1.5$ V and thus $K_{eq} \leq 10^{-25}$ (25 °C) for $(C_5Me_5)_2UCl + BuCl \rightleftharpoons (C_5Me_5)_2UCl^+ + BuCl^{-}\cdot$. Although there is an interesting problem with calculations of this type in that several "unfavorable"[9c,d] electron transfers have suprisingly facile rates, we know of no electron transfers apparently uphill by ca. 1.5 V that have rates near our k_2(*n*-BuCl, 25 °C) = 20 M^{-1} s^{-1}. In fact, even though it has a more negative $E_{1/2} = -1.67$ V (SCE) the radical anion of perylene, $Na^+C_{20}H_{12}{}^{-}\cdot$, reacts 586 times more slowly with *n*-BuBr, k_2 (obsd, 20 °C in THF)[9c] = $5.8 \pm 0.2 \times 10^{-1}$ M^{-1} s^{-1}; (3) a third line of evidence is derived from the relative RCl reactivities. When electron transfer takes place, one generally sees a correlation of log *k* with *Ep*[9c] and this is not what is observed from the following data: RX (relative rate, *Ep* (V, SCE) PhCl (10^{-1}–10^{-2}, −2.57)[9c], *n*-BuCl (2, −2.8)[9c], $(CH_3)_3CCl$ (15, −2.6)[9c], $PhCH_2Cl$ (24, −1.2).[9g] It is worth noting, however, that in addition to atom abstraction some alternate, slower pathway appears to exist since *n*-BuOTs does react with $(C_5Me_5)_2UCl{\cdot}THF$.[2p] (b) Bank, S.; Bank, J. F. *ACS Symp. Ser.* **1978**, *No. 69*, Chapter 21. (c) Bank, S.; Jucket, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7742. (d) Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 571. (e) Lambert, F. L.; Ingall, G. B. *Tetrahedron Lett.* **1974**, 3231. (f) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 707; see p 718. (g) Streitwieser, A., Jr.; Perrin, C. *J. Am. Chem. Soc.* **1964**, *86*, 4938. (h) Walling, C. *Ibid.* **1980**, *102*, 6854.

(10) (a) For example, k_2 ($PhCH_2Cl$, 25 °C, $Co(II)B_{12(s)}$ in $MeOH/H_2O$)[3g] = 1.0×10^{-2} M^{-1} s^{-1} while k_2($PhCH_2Cl$, 25 °C, $(C_5Me_5)_2UCl$ in benzene) = 2.4×10^2 M^{-1} s^{-1}; k_2 (*n*-BuBr, 25 °C, $Cr(III)en_2{}^{2+}$ in DMF/H_2O)[3h] = 1.4×10^{-4} M^{-1} s^{-1} while k_2 (*n*-BuBr, 25 °C, $(C_5Me_5)_2UCl$ in benzene) = 3.4×10^2 M^{-1} s^{-1}; k_2 (*n*-$C_5H_{11}Cl$, 25 °C, $Rh(I)[C_2DOBF_2]$ in THF)[2o] = 6×10^{-6} M^{-1} s^{-1} while k_2 (*n*-BuCl, 22 °C, $(C_5Me_5)_2UCl$ in benzene) = 20 M^{-1} s^{-1}. (b) An interesting and probably better comparison under consideration is the system[4] Cp_2MCl (M = Ti, Zr, Hf) + RX. Cp_2ZrCl, with its more negative ca. −1.8 V vs. SCE Zr(IV)/Zr(III) couple,[10c] could be even more reactive than $(C_5Me_5)_2UCl$. (c) El Murr, N.; Chalyard, A.; Tirouflet, J. *J. Chem. Soc., Chem. Commun.* **1980**, 446.

(11) A detailed study of the magnetic and other properties of $(C_5Me_5)_2UCl$, its THF adduct, and the RX reactions of other actinide and transition-metal[10b] systems will be required to completely settle this point.

Stereochemistry of an Enzymatic Baeyer-Villiger Reaction. Application of Deuterium NMR

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Enzymatic conversion of ketones to esters is known to be a common feature in the microbial degradation of a wide variety