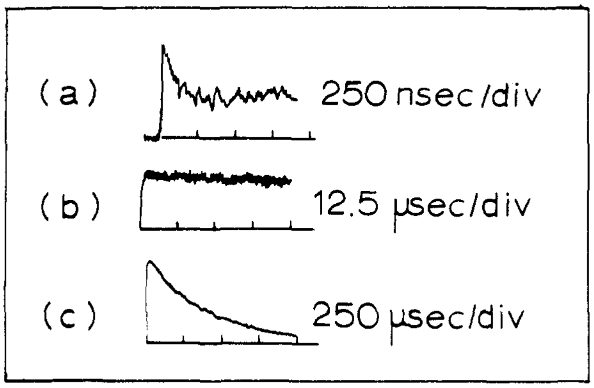


Figure 1. Luminescence intensity against time for $Cr(acac)_3$ at 77°K. Excitation wavelength is 593 nm; observation wavelength is 785 nm. Intensity units are arbitrary. RC time constants: (a) 25 nsec; (b) 500 nsec; (c) 5 μsec.

width of the monochromator and the improved red response of the photomultiplier employed. These results confirm that we have indeed observed the well-characterized phosphorescence of $Cr(acac)_3$.

There is no evidence for a maximum in luminescence intensity *vs.* time records. As shown in Figure 1b, on the time scale for which a maximum was previously reported, only a luminescence decay is observed with a lifetime of the phosphorescence decay within experimental error. At the fastest sweep rate used, Figure 1a, a rapid decay is observed, presumably due to scattered light from the laser, but no increase in luminescence intensity is observed. This requires that the ^2E_g state, from which phosphorescence occurs, is populated with a rate constant of 10^7 sec^{-1} or greater.

Our result implies that the intersystem crossing process is facile and that the lifetime of the $^4T_{2g}$ state is relatively short if crossing to a lower energy ^2E_g state is possible. It does not exclude a primary role for the $^4T_{2g}$ state in subsequent photochemistry since back thermal intersystem crossing from the ^2E_g to the $^4T_{2g}$ state could be equally facile.[8]

Acknowledgments. This work was supported in part by a grant from the National Science Foundation to J. T. Y. and by a grant from the Petroleum Research Fund, administered by the American Chemical Society, to J. K. B.

---

(8) G. B. Porter, S. N. Chem, H. C. Schläfer, and H. Gausmann, *Theor. Chim. Acta*, 20, 81 (1971).

(9) (a) Fellow of the Alfred P. Sloan Foundation, 1972–1974. (b) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

James T. Yardley,*[9a] James K. Beattie[9b]
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received September 8, 1972

Substitution Reactions of 1,1′-Dimethoxyuranocene and 1,1′-Bis(uranocyl)trimethylammonium Iodide with Organolithium Reagents[1]

Sir:

Uranocene, di-π-cyclooctatetraeneuranium, appears to be an f-orbital aromatic system homologous to the d-transition metallocenes;[2–4] however, the only reactions observed thus far with this new system are those at uranium[3] and at substituent groups.[5] We now report the first clear-cut reaction on the ligand rings.

1,1′-Dimethoxyuranocene[6] was prepared from methoxycyclooctatetraene[7] by conversion to the dianion and treatment with UCl_4 in THF. Structure assignment follows from analytical and spectral data;[8] for example, the visible spectrum shows four bands at λ_{max} nm (ε) 634 (860), 657 (540), 686 (460), and 698 (100), with the expected bathochromic shift[5] relative to uranocene. Furthermore, in common with the parent compound[3] and all other substituted uranocenes[5] studied, controlled air oxidation liberates the ligand rings in high yield. Stirring the dimethoxy compound with excess *n*-butyllithium in cyclohexane for 3 days at room temperature gives conversion to 1,1′-dibutyluranocene[5] in 70% yield. Similarly, *tert*-butyllithium gives 64% of 1,1′-di-*tert*-butyluranocene which was characterized by its mass spectrum (parent peak *m/e* 558) and visible absorption at λ_{max} nm (ε) 624 (1420), 652 (385), 671 (260), and 684 (125). The yields given are isolated yields of purified product. Phenyllithium, methyllithium, and lithium amide gave only unreacted starting material even after reaction periods of 7 days.

N,N-Dimethylaminocyclooctatetraene[9] was converted to the corresponding uranocene derivative.[8] Reaction with methyl iodide in THF for 24 hr gave the bistrimethylammonium iodide, $U(C_8H_7NMe_3{}^+I^-)_2$, as an insoluble crystalline material that was characterized by elemental analysis, and by the infrared spectrum which is similar to those of known uranocene derivatives. This compound also reacts readily with either *n*-butyllithium or *tert*-butyllithium to give the corresponding 1,1′-dialkyluranocene in 59 and 67% yields, respectively. However, the ammonium salt also reacts with phenyllithium to give 45% of 1,1′-diphenyluranocene[5] and with methyllithium to give 52% of 1,1′-dimethyluranocene.

The most reasonable reaction mechanism appears to involve a carbanion chain sequence initiated by metalation of the substituted uranocene at the position adjacent to the heterosubstituent and involving as an intermediate a uranium complex of cyclooctatrienyne.

This mechanism accounts for the sensitivity of the reaction to the effective basicity of the alkyllithium. Cyclooctatrienyne is a well-established intermediate in reactions of bromocyclooctatetraene with strong bases.[10] Direct nucleophilic substitution at the ligand

---

(1) This research was supported in part by National Science Foundation Grant No. GP-31803.

(2) A. Streitwieser, Jr., and U. Muller-Westerhoff, *J. Amer. Chem. Soc.*, 90, 7364 (1968).

(3) A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *ibid.*, submitted for publication.

(4) A. Streitwieser, Jr., in "Topics in Non-benzenoid Aromatic Compounds," T. Nozoe, Ed., in press.

(5) A. Streitwieser, Jr., and C. A. Harmon, *Inorg. Chem.*, submitted for publication.

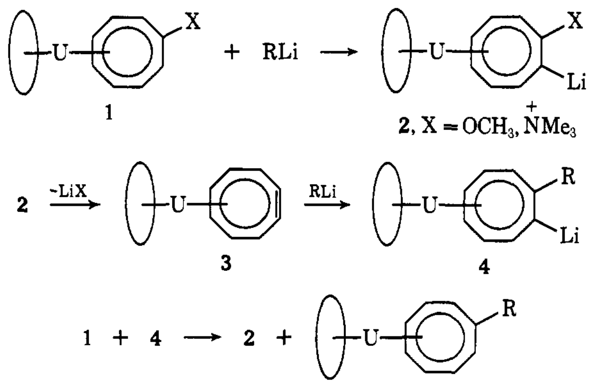
(6) Di-π-(methoxycyclooctatetraene)uranium; the trivial nomenclature follows in a natural way from the trivial name of "uranocene" assigned to the parent structure. Since di-π-cyclopentadienylactinide sandwich complexes have never been prepared and appear to be unlikely as aromatic organometallic compounds, the use of the actinocene nomenclature for di-π-cyclooctatetraeneactinides should occasion no ambiguity.

(7) J. Gasteiger, G. Gream, R. Huisgen, W. Konz, and U. Schnegg, *Chem. Ber.*, 104, 2412 (1971).

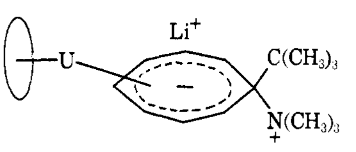
(8) To be reported in detail in a subsequent paper.

(9) C. A. Harmon and A. Streitwieser, Jr., *J. Org. Chem.*, in press.

(10) A. Krebs, *Angew. Chem.*, 77, 966 (1965); S. Ozawa, Ph.D. Dissertation, University of California, Berkeley, 1966.



ring appears to be a less probable mechanism; in particular, the intermediate or transition state involved in the facile reaction of the trimethylammonium salt with *tert*-butyllithium **5** would appear to be highly strained.



5

Although other mechanisms can be written that involve **3**, such as direct reaction with RLi, the carbanion chain mechanism is supported by stoichiometry. Only a 1.1:1 molar ratio of RLi to ligand is required to effect >95% conversion to product. Furthermore, analogy is available in the apparent involvement of a "ferrocyne" intermediate in some reactions of chloroferrocene with bases.[11]

These reactions add to the growing chemistry of organoactinide compounds.[12] They provide important chemical evidence of the strength and covalency of the metal–ligand bond in uranocene compounds and promise to provide a useful new route to other uranocene derivatives.

(11) J. W. Hoffman, L. H. Keith, and R. L. Asbury, *J. Org. Chem.*, **36**, 1600 (1965).

(12) R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev.*, **7**, 1 (1971).

C. A. Harmon, A. Streitwieser, Jr.*
Department of Chemistry, University of California
Berkeley, California 94720

Received September 9, 1972

Cysteine-Catalyzed Hydrogen Isotope Exchange at the 5 Position of Uridylic Acid

Sir:

Recent reports from several laboratories have shown that some sulfur-containing agents such as 2-mercaptoethylamine,[1] bisulfite,[2,3] and glutathione[4] are effective in catalyzing the hydrogen isotope exchange of pyrimidine nucleosides at the 5 position. This type of study is of considerable interest because such a method is potentially useful for labeling nucleic acids. The chemically induced hydrogen isotope exchange of uridine has also received attention as a model for enzymic alkylation of uracil derivatives, since thymidylate synthetase is known to catalyze the hydrogen isotope exchange as well as methylation.[5] We wish to report that cysteine is a very efficient catalyst for the hydrogen isotope exchange of uridine 5′-phosphate at position 5, and that it exerts the catalytic effect by a cooperative function of the SH and amino groups.

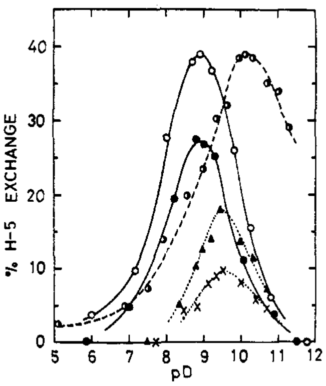


Figure 1. pD profile of the hydrogen–deuterium exchange at position 5 of uridine 5′-phosphate and of 3-methyluridine. Incubation was at 37° for 24 hr. Each D_2O solution (1 ml) contained 100 mg of disodium uridine 5′-phosphate or 80 mg of 3-methyluridine. pD was adjusted by the addition of NaOD or DCl, and no pD change was detected during the incubation. Exchanges of uridine 5′-phosphate: (○) cysteine (0.5 *M*); (●) 2-mercaptoethylamine (0.5 *M*); (×) 2-mercaptoethanol (1.2 *M*); (▲) 2-mercaptoethanol (1.2 *M*) + trimethylamine (1 *M*). Exchange of 3-methyluridine: (◑) cysteine (0.5 *M*).

Incubation of uridine 5′-phosphate in D_2O solution containing 1.0 *M* L-cysteine at 37° and pD 8.8 resulted in 100% hydrogen–deuterium exchange at the 5 position after 7 days, while no significant change was detected in the absence of cysteine under the same conditions. The extent of the exchange was determined by nmr as detailed elsewhere[3] utilizing the change in shape of the proton signal at the 6 position.[1] The pD dependence of the exchange catalyzed either by cysteine, 2-mercaptoethylamine, or 2-mercaptoethanol is presented in Figure 1. The cysteine-catalyzed exchange of uridine 5′-phosphate at pD 9.0 and 37° proceeded by pseudo-first-order kinetics. The apparent rate constants at various concentrations of cysteine were: concentration of cysteine/rate constant (hr^{-1}), 0.25 *M*/0.819 $\times 10^{-2}$; 0.5 *M*/2.29 $\times 10^{-2}$; 0.75 *M*/3.98 $\times 10^{-2}$; 1.0 *M*/6.05 $\times 10^{-2}$. The method of cysteine catalysis, which can be carried out in nearly neutral solutions, appears to be more effective compared with other known methods.[6-11] Thus, most of the reported procedures for the exchange involve reactions at higher temperatures, and the bisulfite–amine method which can be done at 37° is still less efficient than the cysteine catalysis when compared at an equal reagent concentration.

3-Methyluridine also underwent the hydrogen-deu-

(1) S. L. Heller, *Biochem. Biophys. Res. Commun.*, **32**, 998 (1968).

(2) K. Kai, Y. Wataya, and H. Hayatsu, *J. Amer. Chem. Soc.*, **93**, 2089 (1971).

(3) Y. Wataya and H. Hayatsu, *Biochemistry*, **11**, 3583 (1972).

(4) T. I. Kalman, *ibid.*, **10**, 2567 (1971).

(5) M. I. S. Lomax and G. R. Greenberg, *J. Biol. Chem.*, **242**, 1302 (1967).

(6) R. M. Fink, *Arch. Biochem. Biophys.*, **107**, 493 (1964).

(7) R. W. Chambers, *J. Amer. Chem. Soc.*, **90**, 2192 (1968).

(8) R. J. Cushley, S. R. Lipsky, and J. J. Fox, *Tetrahedron Lett.*, 5393 (1968).

(9) D. V. Santi and C. F. Brewer, *J. Amer. Chem. Soc.*, **90**, 6236 (1968).

(10) D. V. Santi, C. F. Brewer, and D. Farber, *J. Heterocycl. Chem.*, **7**, 903 (1970).

(11) W. J. Wechter, *Collect. Czech. Chem. Commun.*, **35**, 2003 (1970).