lief[4] that a similar situation obtains in other metal carbonyl hydrides. For example, recent infrared[6] and Raman[7,8] spectra of the $HFe(CO)_4^-$ ion show bands at 1897, 1937 and 1768, 1835, 1895 cm.$^{-1}$, respectively. Since only three C–O stretching frequencies are expected for such an ion with C_{3v} symmetry, there is a good possibility that one of these four frequencies belongs to the Fe-H stretching mode.

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SOLVENT EFFECTS IN THE BASE-CATALYZED ISOMERIZATION OF ALLYL TO PROPENYL ETHERS

Sir:

In the course of investigating the prototropic rearrangement of allyl ethers to their propenyl analog employing potassium *t*-butoxide as catalyst we have discovered some interesting effects of solvent on the rate of isomerization.

$$CH_2{=}CH{-}CH_2{-}OR \xrightarrow{KO\text{-}t\text{-}Bu} CH_3{-}CH{=}CH{-}O{-}R$$

R = phenyl, *n*-hexyl *t*-butyl, 2-hydroxypropyl, 1-methyl-2-hydroxyethyl.

In 1,2-dimethoxyethane 0.66 *M* in potassium *t*-butoxide, 0.68 *M* allyl phenyl ether required about 160 min. for 50% rearrangement to occur at 25°. On the other hand, in dimethyl sulfoxide 0.05 *M* in potassium *t*-butoxide the pseudo-first order half-time was only about 1.5 min. at the same temperature. Taking account of the difference in base concentration the rate is 1.4×10^3 faster in dimethyl sulfoxide.

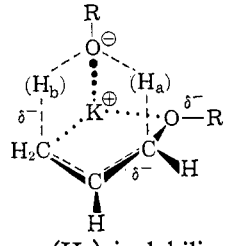
By gas phase chromatography, the phenyl propenyl ether formed in dimethoxyethane was found to be 97% *cis*-isomer, 99% *cis* in dimethyl sulfoxide. This is considerably in excess of the equilibrium concentration of about 65% *cis*.[1] The yield was also virtually quantitative, titrating over 99% propenyl ether by hydroxylamine hydrochloride.[2]

With allyl *n*-hexyl ether there is a very large decrease in rate upon addition of *tert*-butyl alcohol to the system. For instance, in dimethoxyethane 1.72 *M* in ether and potassium *t*-butoxide at 80° the pseudo-first order half-time is about 60 min. In the same solvent 1.6 *M* in the ether, 1.5 *M* in potassium *t*-butoxide but also 2.2 *M* in *t*-butyl alcohol, the pseudo-first order half-time is estimated to be about 15,000 min. at the same temperature. It should be emphasized that this latter half-time is not a true value for homogeneous solution since a white precipitate of *tert*-butyl alcohol potassium *t*-butoxide complex settles out of solution upon addition of the *tert*-butyl alcohol. This complex is still incompletely soluble at 80°. The decrease in rate probably is effected both by the insolubility of the catalyst as well as by hydrogen-bonding of the alcohol to the base.

These kinetic results were obtained by following the increase in intensity of the strong 5.98 μ band of the propenyl ether in the infrared.

Cram, Rickborn and Knox have noted increases as large as factor of 10^9 in the rate of deuterium exchange and the rate of racemization of asymmetrically trisubstituted methanes upon going from methanol to *tert*-butyl alcohol to dimethyl sulfoxide.[3] This compares to the factor of *ca.* 10^5 which we have observed on going from mixed dimethoxyethane–*tert*-butyl alcohol to dimethyl sulfoxide.

In order to explain the high degree of *cis*-stereospecificity of the rearrangement, and from examination of models, the structure shown seems a likely representation of two intermediate states for the rearrangement.



The α-hydrogen (H_a) is labilized by attraction to the alkoxide oxygen. By movement of a proton only, the complex with the hydrogen at the position H_b results. The dotted lines represent simple electrostatic bonds, the dashed lines those with partial covalent character in the transition complex.

We expect that a study of the deuterium exchange in *t*-butyl alcohol, dimethoxyethane, and dimethyl sulfoxide will shed further light on the mechanism of the rearrangement.

(1) W. H. Snyder, unpublished results.

(2) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. (France)*, 121 (1950).

(3) D. J. Cram, Bruce Rickborn, and Graham R. Knox, communication to THIS JOURNAL, not yet published. We are indebted to Professor Cram for sending us a copy of this communication prior to its appearance in print.

DEPARTMENT OF CHEMISTRY CHARLES C. PRICE
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THE RATE OF OXIDATION OF CYTOCHROME c BY FERRICYANIDE IONS[1]

Sir:

Four of the bonds of the octahedrally coördinated iron atoms in ferrohemoglobin and cytochrome c are to the nitrogen atoms of the pyrrole rings of protoporphyrin. The fifth bond is directly to the protein, probably through a nitrogen atom of the imidazole group of histidine.[2,3] The molecules differ, however, in the nature of the sixth group attached to the iron atoms. This sixth group is a water molecule in hemoglobin and another histidine residue in cytochrome c.[2,3] The rate of oxidation of the first heme group in ferrohemoglobin by ferricyanide ions is relatively slow.[4]

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Theorell and A. Akeson, *J. Am. Chem. Soc.*, **63**, 1084 (1941).

(3) P. George and R. L. J. Lyster, Conference on Haemoglobin (1957), Publication 557, National Academy of Sciences—National Research Council, Washington, D. C., p. 33.

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One interpretation consistent with this result is that the water molecules coördinated to the iron atoms in hemoglobin tend to slow down its rate of oxidation to ferrihemoglobin.[4] In order to obtain additional information concerning the role of these coördinated water molecules we have studied the rate of oxidation of ferrocytochrome c by ferricyanide ions and compared this rate with that of the ferrohemoglobin–ferricyanide reaction.

Two sources of cytochrome c were used. Cytochrome c, prepared from fresh beef hearts according to the Keilin and Hartree procedure,[5] and horse heart cytochrome c, supplied by the California Corporation for Biochemical Research (Boehringer), were purified by chromatography on Amberlite XE-64 resin.[6,7] The preparations were reduced with hydrogen and palladium[8] and the ferrocytochrome estimated spectrophotometrically.[9]

The rate of the ferrocytochrome c–ferricyanide reaction was followed spectrophotometrically using the rapid flow apparatus which has been previously described.[10] The reaction was investigated at 25° in a phosphate buffer with a *p*H of 6.0 and an ionic strength of 0.10. Second order kinetics were observed. The specific rate constants obtained with the two preparations of cytochrome c were the same within the experimental error of the measurements. The mean of these measurements together with the rate constant of the ferrohemoglobin–ferricyanide reaction and the standard free energy changes of the reactions is presented in Table I.

TABLE I

OXIDATION OF FERROHEMOGLOBIN AND FERROCYTOCHROME c BY FERRICYANIDE IONS AT 25° IN A PHOSPHATE BUFFER WITH A *p*H OF 6.0 AND AN IONIC STRENGTH OF 0.10

Reaction[a]	ΔG^0, kcal. mole^{-1}	k, l. mole^{-1} sec.$^{-1}$
$Hb(H_2O)$–$Fe(CN)_6^{3-}$	−6.2[b]	$7.0 \pm 0.5 \times 10^4$[c]
Cyt. c–$Fe(CN)_6^{3-}$	−3.5[b]	$1.6 \pm 0.1 \times 10^7$

[a] $Hb(H_2O)$ is ferrohemoglobin; Cyt. c is ferrocytochrome c. [b] W. Mansfield Clark, "Oxidation-Reduction Potentials of Organic Systems," The Williams and Wilkins Company, Baltimore, Md., 1960, p. 455. [c] N. Sutin, *Nature*, 186, 000 (1961).

It is apparent from Table I that the oxidation of ferrocytochrome c byf erricyanide ions proceeds much more rapidly than the oxidation of ferrohemoglobin. This is contrary to what one might expect from considerations of the relative values of the standard free energy changes of the two reactions.[11]

In contrast to the position of the heme group in cytochrome c, which is buried in the interior of the protein, the heme groups in hemoglobin are situated on the surface of the molecule.[12,13] This makes it unlikely that the difference in the rates of the two reactions is due to a type of steric hindrance in which it is more difficult for a ferricyanide ion to approach close to a heme group in hemoglobin than to one in cytochrome c.

The above measurements are consistent with the suggestion that the relatively slow rate of the ferrohemoglobin–ferricyanide reaction might be due to the water molecules coördinated to the iron atoms in hemoglobin.[4] On the other hand, the conjugated groups coördinated to the iron atom in cytochrome c create an environment which is particularly suited to the rapid transport of electrons, such as is required in the respiratory chain.[14]

We wish to thank Dr. Lucile Smith for her helpful suggestions concerning the preparation of cytochrome c, Dr. Robert Smillie and co-workers in the Biology Department of this Laboratory for making some of their facilities available to us, and Mrs. Catherine Paul for assisting in the preparation and purification of the cytochrome c.

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BOOK REVIEWS

Nouveau Traité de Chimie Minérale. Tome XV. Uranium et Transuraniens. Premier Fascicule. Uranium. Edited by PAUL PASCAL, Membre de l'Institut. Masson et Cie., 120, Boulevard Saint-Germain, Paris 6, France. 1960. 1 + 734 pp. 17.5 × 26 cm. Price, broché, 115 NF.; cartonné toile, 127 NF.

The fifteenth volume of Pascal's Nouveau Traité describes uranium and the transuranium elements. Only uranium is covered in the first part. Actinium, thorium and protactinium are not treated as beginning an actinide series, but are discussed separately in volumes 7, 9 and 12, respectively.

The most striking feature of the volume on uranium is its sheer bulk. There are 725 pages devoted to this element, a larger number than are allotted to any other single element discussed in the eleven volumes which have appeared thus far. The metals of the sixth group, chromium, molybdenum and tungsten, for comparison, are allotted only 1012 pages altogether. This emphasis on uranium does not reflect its current commercial importance in the chemical world, of course, but rather is due to the great interest it commands as a possible energy source.

Following an introduction by M. Salesse, Chef du Département de Métallurgie du Commissariat à l'Énergie Atomique, there are eleven chapters which have been prepared by more than twenty authors. The first eight chapters cover such topics as isotopes, minerals, preparation and production from the ore, physical properties, mechanical properties, alloys and their use as nuclear fuels, and metallography. The last three chapters, which discuss chemical properties, analysis and aqueous corrosion of uranium and