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.

(6) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

(7) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras and S. Bril, *J. Chem. Phys.*, **32**, 1482 (1960).

(8) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *J. Am. Chem. Soc.*, **77**, 3951 (1955).

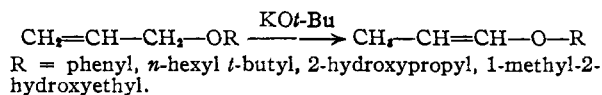DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 14, 1961

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.

$$CH_2=CH—CH_2—OR \xrightarrow{KOt-Bu} CH_3—CH=CH—O—R$$

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 × 10³ 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

(1) W. H. Snyder, unpublished results.

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

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 10⁹ 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.* 10⁵ 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.
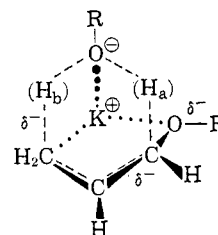
The α-hydrogen (Hₐ) is labilized by attraction to the alkoxide oxygen. By movement of a proton only, the complex with the hydrogen at the position Hᵦ results. The dotted lines represent simple electrostatic bonds, the dashed lines those with partial covalent character in the transition complex.

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.

(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.

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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.

(4) N. Sutin, *Nature*, **186**, in press (1961).