Tetrahedron Letters Vol. 21, pp 3861 - 3864 0040-4039/80/1001-3861$02.00/0

ACTIVATION OF DIMETHYL ETHER WITH TRANSITION METAL ATOMS

W. E. Billups,* Mark M. Konarski, Robert H. Hauge, and John L. Margrave
Department of Chemistry, Rice University, Houston, Texas 77001

Summary: The cocondensation of iron or manganese atoms with dimethyl ether at -196°C leads to organometallic products which upon hydrolysis at 25°C yield a mixture of mainly alkenes and alkanes.

There is considerable interest currently in the conversion of small, abundantly available molecules into useful petrochemicals. One process that has attracted interest is the conversion of methanol or dimethyl ether into a mixture of aliphatic and aromatic hydrocarbons.[1] We found recently that cocondensation of either calcium, barium, or strontium atoms with dimethyl ether gives products which upon hydrolysis yield a mixture of mainly low molecular weight alkynes, alkenes, and alkanes.[2] We have now investigated the reactions of some transition metal atoms with dimethyl ether and report some of these results here.

The cocondensation of either manganese or iron atoms with an excess of dimethyl ether (~ 100:1) at -196°C led to black powders after the matrices were warmed to room temperature and the unreacted ether removed *in vacuo*. No volatile products other than the ether were detected during the cocondensation process or as the matrix was warmed to room temperature.[3] When the cocondensation product was hydrolyzed, a complex mixture of products shown to be mainly alkenes and alkanes was produced. These results differ quite dramatically from the reactions of group 2 metals where the major products were alkynes.[2] The products and yields of typical hydrolysis experiments are presented in Table I. Hydrolysis of the cocondensation adducts in D_2O gives mono-, di- and trideuterated products, emphasizing the extensive carbon-metal bond formation that has occurred during the cocondensation process.

Table I. Products and Yields from the Hydrolysis of the Cocondensation Products of Manganese and Iron Atoms with Dimethyl Ether.

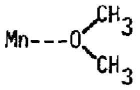
Product	Percent Composition[a] (Yield)[b]	
	Manganese	Iron
Methane	20.2 (0.060)	1.7 (0.022)
Ethylene	1.2 (0.004)	0.8 (0.010)
Ethane	13.7 (0.040)	1.2 (0.016)
Propene	2.4 (0.007)	1.9 (0.025)
Propane	9.9 (0.029)	4.8 (0.063)
Dimethyl Ether	4.4 (0.013)	4.1 (0.054)
Isobutane	1.6 (0.005)	2.7 (0.035)
1-Butene	2.7 (0.008)	4.3 (0.056)
n-Butane	9.3 (0.027)	18.1 (0.237)
2-Pentene	trace	-
1-Pentene	2.8 (0.008)	4.8 (0.063)
n-Pentane	4.7 (0.014)	8.2 (0.107)
1-Hexene	16.6 (0.049)	1.7 (0.023)
Benzene	2.1 (0.006)	-
C_7H_{16}	3.3 (0.010)	6.2 (0.081)
Toluene	0.7 (0.002)	-
n-Heptane	1.3 (0.004)	20.2 (0.265)
n-Octane	0.7 (0.002)	-
Unidentified	2.4 (0.007)	3.5 (0.046)

[a] Percent composition was obtained from gc-mass spectrometric analysis using a 4 ft x 1/8 in. nickel column packed with 5% QF-1 on 80/100 Poropak QS. The values presented are the average of three runs.

[b] Yields are presented as moles of product per mole of metal vaporized.

An X-ray powder diffraction pattern of the products obtained from iron atoms and the ether (before hydrolysis) showed Fe_3O_4 as a major species, whereas the adduct of manganese and dimethyl ether was found to contain MnO.

Evidence for intermediates that are probably formed at an early stage of the cocondensation reactions comes from a matrix study. Thus, cocondensation of manganese atoms with dimethyl ether in an argon matrix at 12°K yields an infrared spectrum with product bands at 1083.9 and 887.7 cm^{-1}. These appear as perturbations of the symmetric and antisymmetric stretching modes of the carbon-oxygen bond in dimethyl ether and can be assigned to a complex of structure **1**.



1

No further reaction was observed as the matrix was warmed to 30°K, suggesting that reactions leading to the products under investigation here occur as the matrix is warmed to room temperature. It is interesting, however, that photolysis of the complex with a 100 W mercury lamp at 12°K induces insertion of the metal into the carbon-oxygen bond to yield **2**. Species **2** exhibits

$$CH_3OMnCH_3$$

2

prominent bands at 512.2 and 567.6 cm^{-1} assigned to the metal-carbon stretch and the symmetric methyl band, respectively.[4]

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation (Grants C-490 and C-109) for support of this work.

References and Notes

1. S. L. Meisel, J. P. McCullough, C. H. Lechthaler, and P. B. Weisz, *Chemtech*, **6**, 86 (1976); C. D. Chang and A. J. Silvestri, *J. Catal.*, **47**, 249 (1977); E. G. Derouane, J. B. Nagy, P. Dejaifve, J. H. C. van Hooff, B. P. Spekman, J. C. Vedrine, and C. Naccache, *J. Catal.*, **53**, 40 (1978); W. Zatorski and S. Krzyzanowski, *Acta Phys. Chem.*, **24**, 347 (1978); see also: D. E. Pearson, *Chem. Commun.*, 397 (1974); L. Kim, M. M. Wald, and S. G. Brandenberger, *J. Org. Chem.*, **43**, 3432 (1978); S. Kikkawa, Y. Shimizu and S. Higuchi, *Chemistry Lett.*, 849 (1979).
2. W. E. Billups, M. M. Konarski, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, **102**, 3649 (1980); *J. Organometal. Chem.*, in press.
3. Neither methane nor hydrogen would have been trapped.
4. These values compare with ν_{M-C} = 500.7 cm^{-1} and ν_{CH_3} = 550.3 cm^{-1} for the species $HMnCH_3$ obtained from photolysis of manganese atoms in a methane matrix (submitted for publication). The absence of ν_{M-O} is consistent with spectral data from $HMnOCH_3$ (unpublished observation) indicating that it lies in the far infrared region.

(Received in USA 7 July 1980)