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Preliminary communication

ACTIVATION OF DIMETHYL ETHER WITH BARIUM AND STRONTIUM ATOMS

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Summary

Organometallic compounds are produced when barium and strontium atoms are cocondensed with dimethyl ether at –196°C; hydrolysis of the cocondensation products from both reactions yields mainly C_1—C_8 alkanes, alkenes, and alkynes.

We found recently that the cocondensation of calcium atoms with dialkyl ethers leads to organocalcium compounds which upon hydrolysis yield a mixture of low molecular weight alkanes, alkenes and alkynes [1]. We have now investigated the reactions of other Group II metals with dimethyl ether and report some of these results.

The codeposition [2] of barium atoms or strontium atoms with a large excess (100/1) of dimethyl ether at –196°C results in the formation of organometallic compounds. Hydrolysis of the cocondensation products yields a mixture of mostly hydrocarbons which were identified by GC-mass spectroscopy. The products from typical experiments are listed in Table 1. Data from the studies with calcium [1] are also included for comparison. Hydrolysis in D_2O leads to extensive deuteration as illustrated in Table 2 for the hydrolysis of the barium atom-dimethyl ether cocondensation products. If one assumes that D_2O would label each carbon—metal bond, then it follows that extensive metallation of the organic material has occurred during the cocondensation process or during workup of the matrix.

Although we have no information regarding the structure of these cocondensation adducts, the high deuterium content of the alkynes (Table 2) suggest carbide-like species. The high carbon/hydrogen ratio of the products suggests that hydrogen is lost during the cocondensation process. Hydrogen was not produced during hydrolysis. We are unable to account for the minor differences in product composition from the various metals (Table 2), although the "missing" products, mainly C_2 and C_3 alcohols, would have been detected by GC-mass spectrometric analysis.

TABLE 1

PRODUCTS FROM THE HYDROLYSIS OF THE COCONDENSATION PRODUCTS OF GROUP II ATOMS AND DIMETHYL ETHER

Product	Percent composition[a] (yield)[b]		
	Barium	Strontium	Calcium
Methane	trace	1.4 (0.007)	1.0 (0.001)
Methanol	1.8 (0.007)	6.0 (0.029)	trace
Acetylene	30.6 (0.117)	24.0 (0.115)	16.0 (0.043)
Ethylene	1.4 (0.005)	16.2 (0.077)	20.1 (0.052)
Ethane	2.6 (0.01)	5.5 (0.026)	2.3 (0.006)
Propyne	2.9 (0.011)	0.9 (0.004)	0.8 (0.002)
Propene	trace	trace	1.5 (0.004)
Propane	trace	1.9 (0.009)	trace
1-butene	10.0 (0.038)	—	11.9 (0.031)
2-butene	30.6 (0.117)	18.9 (0.09)	20.1 (0.052)
Butane	2.9 (0.011)	—	—
Butanols	2.9 (0.011)	—	12.8 (0.033)
Pentane	—	7.0 (0.033)	—
C_6H_{10}	1.4 (0.005)	—	3.5 (0.009)
C_6H_{12}	6.0 (0.023)	3.0 (1.4)	16.2 (0.042)
C_6H_{14}	—	4.0 (1.9)	—
C_8H_{14}	—	1.5 (0.007)	2.7 (0.007)
C_8H_{18}	1.5 (0.006)	1.0 (0.005)	—

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

TABLE 2

PRODUCTS FROM THE HYDROLYSIS OF THE COCONDENSATION PRODUCT OF BARIUM ATOMS AND DIMETHYL ETHER IN D_2O

Product	Composition[a]	Deuterated products
Methane	<1	CH_3D
Methanol	1.9	CH_3DO
Acetylene	27.0	C_2HD, C_2D_2
Ethylene	1.5	C_2H_3D, $C_2H_2D_2$
Ethane	2.8	C_2H_5D
Propyne	3.1	$C_3H_2D_2$, C_3HD_3
Propene	<1	C_3H_5D, $C_3H_4D_2$
Propane	<1	C_3H_7D
1-butene	10.8	C_4H_7D, $C_4H_6D_2$
2-butenes	38.5	C_4H_7D, $C_4H_6D_2$
Butanols	4.2	C_4H_9DO
C_6H_{10}	1.5	$C_6H_{11}D$
C_6H_{12}	6.5	$C_6H_{11}D$
C_8H_{18}	1.6	$C_8H_{17}D$

[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.

Magnesium atoms do not react upon cocondensation with dimethyl ether. The Group I metals, lithium and potassium, also failed to react with dimethyl ether.

The activation of inert bonds with metal atoms also has been reported recently by others. Davis and Klabunde [3] observed the low temperature cleavage of alkanes by small clusters of nickel atoms. Hydrolysis of these products yielded a mixture of hydrocarbons, although no products with molecular weights higher than the starting alkane were observed. More recently, Skell and his co-workers [4] found that zirconium atoms activate carbon—carbon and carbon—hydrogen bonds in isoalkanes*.

The oxygen group of the ether probably serves as an activating point for the reactions under investigation here. A subsequent step would be the oxidative insertion of the metal atom into the carbon—oxygen bond of the ether yielding CH_3OMCH_3. It is quite obvious, however, that extensive insertion of the metal into carbon—carbon (or carbon—hydrogen) bonds must also be invoked to account for the products obtained from the hydrolysis experiments. Matrix isolation experiments to delineate these steps are in progress.

Finally, it is of interest that the conversion of dimethyl ether to a mixture of aliphatic and aromatic hydrocarbons in the C_4—C_{10} range (gasoline) is under active investigation [5]. Adaptation of the chemistry under investigation in this study to a catalytic process for the conversion of dimethyl ether to petrochemical raw materials would also be of considerable interest. Studies of this type as well as elucidation of the structures of the cocondensation products are under way.

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References

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*Spectroscopic evidence for the insertion of iron and diiron into methane has also been reported [4b].