CHEMISTRY LETTERS, pp. 1315-1316, 1987.

Supported Sulfide and Sulfur Oxy-Acid Salts. Involvement of Alumina-Induced Cannizzaro Reaction in the Reported Reduction of Aldehydes by Na_2S/Alumina

Takashi ANDO,* James H. CLARK,+ David G. CORK, and Takahide KIMURA

Department of Chemistry, Shiga University of Medical Science, Otsu, Shiga 520-21
+ Department of Chemistry, University of York, York YO1 5DD, U.K.

Cannizzaro type oxidation-reduction of aromatic and aliphatic aldehydes, promoted by alumina, was observed during study of inorganic-solid-supported sodium sulfide and sulfur oxy-acid salts.

As part of our continuing program of development and application of inorganic-solid-supported reagents for organic synthesis,[1] we investigated the use of supported sodium sulfide and sodium salts of common sulfur oxy-acids; *i.e.* sulfite, dithionite, and thiosulfate. Although these salts have been fairly well studied for organic synthesis, they have generally been employed in phase transfer conditions for reduction.[2] Their standard reduction potentials, between E^o= -1.12 to -0.5 V,[3] suggested the possibile use of the supported salts for selective reduction. $Na_2S \cdot 9H_2O$ on alumina has been reported for a convenient synthesis of organic sulfides[4] and, more recently, as a selective reductant for conversion of nitrobenzaldehydes to nitrobenzyl alcohols.[5] We now wish to report that the latter reduction occurs primarily due to an alumina-promoted oxidation-reduction.

The attempted reductions of aldehydes using several 'impregnated' or '*in situ* mixed' Al_2O_3-supported sulfide and sulfur oxy-acid salts are summarized in Table 1. Typically the reagent (2-3 equiv.) was efficiently mixed with the aldehyde (1 mmol) in 5 ml of solvent in a screw-capped test tube. After 20-24 h the products were analyzed by GLC and/or ^{1}H NMR. In the former case MeCN, ether and a little MeOH was added and thoroughly shaken with the reaction mixture to facilitate removal of the organic products from the solid reagent. For analysis by NMR the reaction solvent and several ether and MeCN washings of the solid reagent were collected and evaporated. The yields of alcohols were never above 50%, and when alumina was replaced by silica, Florisil, K10 clay or molecular sieves the reduction was negligible.

The impregnated Na_2S-Al_2O_3 reagent (A) of Hojo *et al.*,[5] prepared by mixing acidic Al_2O_3 with aq Na_2S followed by filtration; the impregnated reagents (B) prepared by slow evaporation of an aq solution of the salt onto alumina; and *in situ*, salt + Al_2O_3, mixed reagents (C) all gave similar results. It was noted that the type (A) reagent preparation[5] only impregnated about half of the Na_2S used (*ca.* 0.5 mmol/g effective loading), and type (B) reagents loaded with a 'monolayer' salt coverage[6] or higher gave poor results (no reduction at 3 mmol/g) compared to lower loaded (<1 mmol/g) ones. These observations, and more importantly the

Table 1. Reaction[a] of RCHO with Alumina-Supported Na_2S, $Na_2S_2O_3$, and Na_2SO_3

Run No.	RCHO R	Reagent support[b]	salt	type[a,c]	Solvent	T °C	RCH_2OH % GLC or ^1H NMR
1	C_6H_5-	Al_2O_3-acidic	Na_2S	A	C_6H_{12}	80	32[d]
2	"	Al_2O_3-acidic	"	B	"	85	26
3	"	Al_2O_3-neutral	"	B	"	85	32
4	"	"	Na_2SO_3	B	"	85	38
5	"	"	$Na_2S_2O_3$	C	"	60	48
6	"	"	"	B	"	60	19
7	"	"	none	-	"	60	44
8	4-$NO_2C_6H_4$-	Al_2O_3-acidic	Na_2S	A	"	80	38[e]
9	"	Al_2O_3-neutral	"	B	"	80	41
10	"	"	$Na_2S_2O_3$	B	"	80	50
11	"	"	"	B	MeCN	80	50
12	4-$MeOC_6H_4$-	"	"	B	C_6H_{12}	80	50
13	"	"	"	B	MeCN	80	-
14	PhCH(CH_3)-	"	"	B	C_6H_{12}	80	50
15	"	"	"	B	MeCN	80	-

a) See text. b) Merck grade 1. c) (A) prepared as Ref. 5; (B) and (C) 1 mmol/g.
d) with ca. 30% benzoic acid. e) with ca. 34% 4-nitrobenzoic acid.

reduction with a sample of alumina, water-washed and dried as the impregnated reagents (run 7, Table 1), lead us to believe that the surface of water-treated alumina efficiently promotes a Cannizzaro type oxidation-reduction of aldehydes.

Although only the alcohol products were recovered in the reaction solvent and by washing the reagents with organic solvents, carboxylic acids were recovered from the supported reagents after addition of a little concd HCl. The reaction is clearly induced at the alumina surface since replacement of cyclohexane with a dipolar solvent, acetonitrile, completely prevented the reaction of 2-methyl-2-phenylethanal and 4-methoxybenzaldehyde (runs 12-15). However, the same change of solvent failed to prevent the oxidation-reduction of 4-nitrobenzaldehyde, which presumably adsorbs to the alumina surface, via its nitro group, equally well in both solvents (runs 10/11).

Chromatography on activated alumina was once reported to cause a similar oxidation-reduction of an aliphatic aldehyde.[7] Our results indicate that inorganic-solid-supported Na_2S, $Na_2S_2O_3$ or Na_2SO_3 do not have increased or altered specificity for reduction. The reported selectivity in the reducing ability of Na_2S-alumina[5] thus results from the support rather than the salt.

We wish to acknowledge a J.S.P.S.-Royal Society research fellowship to DGC.

References

1) T. Ando, J. H. Clark, D. G. Cork, M. Fujita, and T. Kimura, J. Org. Chem., 52, 681 (1987). 2) D. Landini, L. Milesi, M. L. Quadri, and F. Rolla, J. Org. Chem., 49, 152 (1984). 3) "Handbook of Chemistry and Physics," 67th ed, ed by R. C. Weast, Chemical Rubber Co., Ohio (1986), p. D-151. 4) B. Czech, S. Quici, and S. L. Regen, J. Chem. Soc., Chem. Commun., 1980, 113. 5) Y. Kamitori, M. Hojo, R. Masuda, and M. Yamamoto, Chem. Lett., 1985, 253. 6) ca. 2 mmol/g, also see Ref. 1. 7) F. A. Lamb, P. N. Cote, B. Slutsky, and B. M. Vittimberga, J. Org. Chem., 39, 2796 (1974).

(Received April 9, 1987)