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Supported Sulfide and Sulfur Oxy-Acid Salts. Involvement of Alumina-Induced Cannizzaro Reaction in the Reported Reduction of Aldehydes by Na<sub>2</sub>S/Alumina

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> 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 inorganicsolid-supported reagents for organic synthesis,<sup>1)</sup> we investigated the use of supported sodium sulfide and sodium salts of common sulfur oxy-acids; <u>i.e.</u> 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.<sup>2)</sup> Their standard reduction potentials, between  $E^{O}$ = -1.12 to -0.5 V,<sup>3)</sup> suggested the possibile use of the supported salts for selective reduction. Na<sub>2</sub>S·9H<sub>2</sub>O on alumina has been reported for a convenient synthesis of organic sulfides<sup>4)</sup> and, more recently, as a selective reductant for conversion of nitrobenzaldehydes to nitrobenzyl alcohols.<sup>5)</sup> 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 <sup>1</sup>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 <u>et al.</u>,<sup>5)</sup> 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 <u>in</u> <u>situ</u>, salt +  $Al_2O_3$ , mixed reagents (C) all gave similar results. It was noted that the type (A) reagent preparation<sup>5)</sup> only impregnated about half of the  $Na_2S$  used (<u>ca. 0.5 mmol/g effective loading</u>), and type (B) reagents loaded with a 'monolayer' salt coverage<sup>6)</sup> 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

Ru No	n RCHO • R	R support <sup>b</sup> )	Reagent salt	type <sup>a</sup> ,c)	Solvent	T OC	RCH <sub>2</sub> OH % GLC or <sup>1</sup> H NMR
1	C <sub>6</sub> H <sub>5</sub> -	Al <sub>2</sub> O <sub>2</sub> -acidic	Na <sub>2</sub> S	А	C <sub>6</sub> H <sub>12</sub>	80	32 <sup>d</sup> )
2	0,12	Al <sub>2</sub> O <sub>2</sub> -acidic	1	В	"12	85	26
3		$Al_2O_2$ -neutral	"	В		85	32
4	н	2,3	Na <sub>2</sub> SO <sub>2</sub>	В	**	85	38
5		п	NapSpOp	С	"	60	48
6		11	223	в	"	60	19
7	"	11	none	-		60	44
8	$4 - NO_2C_6H_4 -$	Al <sub>2</sub> O <sub>2</sub> -acidic	Na <sub>2</sub> S	А	"	80	<sub>38</sub> e)
9	204	$Al_{2}O_{2}$ -neutral	2	В		80	41
10		2,,3	Na <sub>2</sub> S <sub>2</sub> O <sub>2</sub>	В	"	80	50
11		11	11 2 3	В	MeCN	80	50
12	4-MeOC <sub>c</sub> H <sub>4</sub> -	"		В	$C_{6}H_{12}$	80	50
13	II 0 4	11	н	В	MeCN	80	-
14	PhCH(CH <sub>2</sub> )-	"	11	В	$C_{6}H_{12}$	80	50
15	" 3'		"	В	MeCN	80	-

Table 1. Reaction<sup>a)</sup> of RCHO with Alumina-Supported Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>SO<sub>3</sub>

a) See text.
b) Merck grade 1.
c) (A) prepared as Ref. 5; (B) and (C) 1 mmol/g.
d) with <u>ca</u>. 30% benzoic acid.
e) with <u>ca</u>. 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-2phenylethanal 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.<sup>7)</sup> Our results indicate that inorganic-solid-supported Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or Na<sub>2</sub>SO<sub>3</sub> do not have increased or altered specificity for reduction. The reported selectivity in the reducing ability of Na<sub>2</sub>S-alumina<sup>5)</sup> thus results from the support rather than the salt.

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