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Enhanced Basicity of Ag_2O by Coordination to Soft Anions

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In Ag_2O-mediated benzylation, the addition of a catalytic amount of KI can greatly improve reactivity. This is usually attributed to the formation of a more reactive iodo-substituted electrophile. However, our studies show this to be due to the enhanced basicity of Ag_2O through coordination of soft iodide anions to the silver atom, and show KI to be an initiator. A catalytic amount of Ag_2O and NaBr can catalyze transesterification reactions, indicating the enhanced basicity of Ag_2O by bromide. We believe that this is a general effect for metal oxides and soft anions, applicable to a wider range of organic reaction systems.

It is well known that many organic reactions are strongly catalyzed by bases. The bases are usually amines, anions, and metallic oxides, chosen as catalysts according to their nucleophili city and basicity. Silver oxide (Ag_2O) is a very weak metallic oxide base that is not generally used as a base catalyst. It is more often used as a Lewis acid to donate empty orbital to electron-rich atoms.[1] Use of Ag_2O as a Lewis acid to activate halides has long been employed in organic synthesis for the creation of reactive cationic organic/inorganic species.[2] Selective protections play an important role in organic synthesis strategies, especially in carbohydrate chemistry.[3] Thus, many methods have been developed to obtain regioselective benzylation[4] or esterification[5] of carbohydrates. Ag_2O-mediated selective protections are appealing owing to their efficiency and their environmental benefits.[2d–i] Ag_2O has also been used as an indispensable additive in organotin catalyzed glycosylation[6] and organoboron catalyzed benzylation.[4b] The addition of iodide salts has often been used to improve the reactivities of alkylation/acylation reactions. The improved reactivity was often attributed to the formation of a more reactive electrophile RI through the substitution of iodide for the less reactive electrophile RX (X stands for Cl or Br).[2e,f,7] Thus, a catalytic amount of potassium iodide (KI) was also added in Ag_2O-mediated selective acylation,[2d,e] benzylation[2h,i] or sulfonylation.[2f,g] However, we recently demonstrated that the improved reactivity for iodide promoted organotin-mediated carbohydrate benzylation was due to coordination of iodide to tin atom.[4a] In this study, we showed that the improved reactivity of Ag_2O-mediated benzylation by KI was due to the enhanced basicity of Ag_2O through the coordination of iodide to silver, and KI was an initiator (Figure 1). Although Ag_2O was initially used as a Lewis acid, donating empty orbitals to halides (X^-), and thus catalyzing the leaving of the halide groups, the resulting AgX led to the formation of AgO^-, which is a strong base and capable of deprotonation of the OH group. This principle was further supported by X-ray diffraction (XRD) data, theoretical calculations, and experiments on transesterification reactions. To the best of our knowledge, this is the first demonstration of a weak metallic oxide base with soft anions being employed as a strong base to catalyze organic reactions.

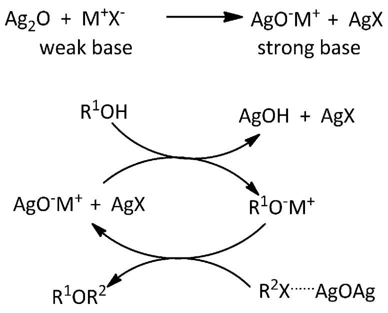

Figure 1. Halide promoted Ag_2O-mediated protection of hydroxyl group due to enhanced basicity of Ag_2O by coordination to soft anions. X stands for Cl, Br and I. M stands for K, Na and TBA.

Although the Ag_2O-mediated method led to good selectivities for acetylation, benzoylation, and sulfonylation of 2,3-diols in 4,6-*O*-benzylidene gluco- and galactopyranosides,[2f] good selectivities for benzylation have only been reported for non-carbohydrate substrates.[2h,i] To investigate why this has been the case, methyl 4,6-*O*-benzylidene-α-glucoside **1** was tested using Ag_2O-mediated benzylation, where 1.1 equiv. of Ag_2O and 1.5 equiv. of benzyl bromide (BnBr) were employed with acetonitrile (MeCN) as a solvent. When other methods have been used, the 2-OH of **1** has usually been regioselectively benzylated.[3c,4a] Although our results have shown that the Ag_2O-mediated method to be less successful for the regioselective benzylation of glucoside **1**. By analysis of the unreacted starting material, we discovered the reason why a catalytic amount of potassium iodide (KI) could greatly improve Ag_2O-mediated benzylation (Table 1). Without the addition of KI (entry **1** in Table 1), the reaction proceeded very slowly. With the addition of 0.1 equiv. of KI (entry **2** in Table 1), the reaction proceeded rapidly, and 30% and 8% of the starting material **1** remained after 4 h and 8 h, respectively. The rapid reaction also occurred in less polar solvent dichloromethane (entry **3** in Table 1). If the improved reactivity with the addition of KI was

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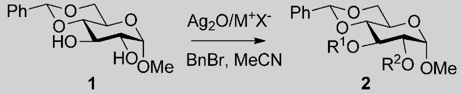
Table 1. Recorded unreacted starting material at various conditions for Ag_2O-mediated benzylation of glucoside **1**.[a]



1 **2**

a) R^1 = H, R^2 = Bn; b) R^1 = Bn, R^2 = H; c) R^1 = Bn, R^2 = Bn

Entry	Various conditions	Reaction time [h]	Unreacted substrate [%][b]
1	Only Ag_2O	1	100
		4	95
2	With KI	4	30
		8	8
3	DCM as solvent	1	48
		4	27
4	With KBr	1	88
		4	59
5	With NaI	1	75
		4	44
6	With TBAI	1	28
		4	22
7	With KF	1	94
		4	92
8	With TBAB	1	41
		4	26
9	With TBACl	1	43
		4	32
10	With TBAF	1	91
		4	84
11	With Na_2S	1	87
		4	76
12	With NaOH	1	49
		4	28

[a] Reagents and conditions: substrates (50 mg), Ag_2O (1.1 equiv.), BnBr (1.5 equiv.), M^+X^- (0.1 equiv.), RT. [b] NMR yield.

due to the formation of more reactive BnI from BnBr, the addition of 0.1 equiv. of KBr would be ineffective. However, when KBr was tested (entry **4** in Table 1), the reaction remained highly reactive, with 88% and 59% of unreacted **1** in 1 h and 4 h respectively, thus excluding the proposal that the improved reactivity is due to the formation of more reactive BnI (also see Figure **S1**). When sodium or tetrabutylammonium (TBA) cations were used instead of the potassium cation, the reaction remained highly reactive (entry **5**, **6** in Table 1), indicating that the cation does not play dominating role on the reactivity. It was recently found that the acetylation of hydroxyl groups with acetic anhydride can be activated by the formation of H-bonds between the hydroxyl groups and anions.[5a,b] Thus, we firstly hypothesized that the activated benzylation by KI was due to the formation of H-bonds between the hydroxyl groups and iodide. If this was the case, the anions that can form stronger H-bond with hydroxyl group should have higher activation ability for benzylation, and the activation order would be $F^- > Cl^- > Br^- > I^-$. However the addition of KF proved inefficient (entry **7** in Table 1). Considering about the better solubility of tetrabutylammonium salts in acetonitrile, in further experiments, 0.1 equiv. of tetrabutylammonium salts of Br, Cl and F were used in the benzylations (entries **8**–**10** in Table 1) to compare their activation ability with that of TBAI. These experiments indicated an exactly opposite activation ability order: $I^- > Br^- > Cl^- > F^-$. The remained glucoside **1** in one hour were 28, 41, 43, and 91% and in four hours were 22, 26, 32, and 84%, respectively, for TBAI, TBABr, TBACl, and TBAF. The same activation order was obtained when BnCl was used instead of BnBr (Table **S1**).

For halide anions, the softness follows the order: $I^- > Br^- > Cl^- > F^-$, the order seen above for activation ability. Thus, the hard–soft acid–base (HSAB) principle may provide an explanation as to how KI activated the Ag_2O-mediated protections. For Ag_2O, oxide anion is a hard base, and Ag^+ is a soft acid. Thus, when Ag_2O encounters a soft base such as Br^- or I^-, the soft Ag^+ preferentially coordinates to the soft base Br^- or I^-, leading to the formation of AgO^- (Figure 1). AgO^-, a much stronger base than Ag_2O, deprotonates the hydroxyl group, then followed by benzylation with BnBr to regenerate AgO^- and AgBr and restart the cycle. Consequently, a softer anion would be an initiator and show higher activation ability in these reactions. As can be seen (entry **11** in Table 1), the soft sulfur anion also appeared activation ability for the reaction. Without consideration of the essential reason (HSAB principle), the positive effect of catalytic amount of halides (X) could be simply explained by the precipitation of AgX, with the formation of basic species AgO^-. The relative solubility of AgX in acetonitrile follows the order: AgI > AgBr > AgCl > AgF, the order seen above for activation ability. The basicity in the reaction simply depends on the amount of halides and remains unchanged until Ag_2O is depleted. Without the addition of halides, there is no AgO^- formed, thus the benzylation showing low reactivity. According to this mechanism, we hypothesized that the addition of a catalytic amount of hydroxyl anion should also trigger the activation process. As can be seen (entry **12** in Table 1), the addition of 0.1 equiv. of NaOH proved efficient. The conversion of Ag_2O to AgI and hydroxide in aqueous iodide solution on open-circuit potential has been reported.[8] The enhanced basicity can also be confirmed by the measurement of pH values (Figure **S2**, **S3**). The results indicate that Ag_2O (6 mg) or TBABr (8 mg) alone in water (1 mL) appears roughly 6–7 of pH value, whereas the mixture of Ag_2O (6 mg) with TBABr (8 mg) in water appears roughly 13–14 of pH value. Powder X-ray diffraction (XRD) data indicated the formation of AgBr after Ag_2O and KBr were mixed thoroughly (Figure **S4**). It was reported that AgOK were obtained as colorless, tetragonal single crystals under very harsh condition.[9] Density functional theory (DFT) calculations for four reactions of Ag_2O with KX (X = F, Cl, Br, or I) further support the proposed principle on the enhanced basicity of Ag_2O by coordination to soft halides.

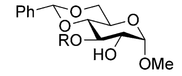
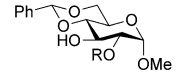
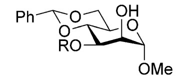
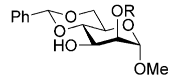
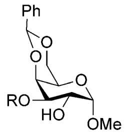
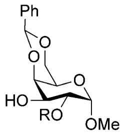
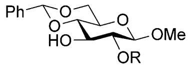
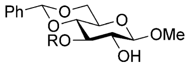
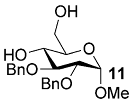
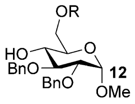
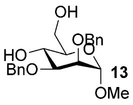
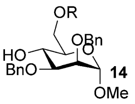
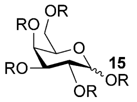
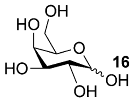
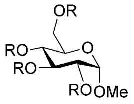
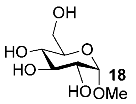
The relative electronic energies in gas phase (ΔE_{gas}) and solvation-corrected relative electronic energies (ΔE_{sol}) of the four reactions [Eqs. (1–4)] were given. It is seen that both ΔE_{sol} and ΔE_{gas} decrease in the order F > Cl > Br > I, indicating that the stability of AgX follows the order AgF < AgCl < AgBr < AgI, consistent with the HSAB principle that Ag^+ as a soft acid forms a stronger bond with softer bases such as I^-. Moreover, according to the stability of AgX, the ability to generate AgOK from the reaction of Ag_2O with KX is in the order KF < KCl < KBr < KI. In other words, a great quantity of AgOK is generated when Ag_2O meets with KI, while little AgOK even without

Reaction	$\Delta E_{gas}/\Delta E_{sol}$ (kcal mol^{-1})	
$Ag_2O + KF \longrightarrow AgOK + AgF$	18.6/18.5	(1)
$Ag_2O + KCl \longrightarrow AgOK + AgCl$	9.6/14.7	(2)
$Ag_2O + KBr \longrightarrow AgOK + AgBr$	6.3/12.1	(3)
$Ag_2O + KI \longrightarrow AgOK + AgI$	1.0/8.7	(4)
	ΔE_{sol} (kcal mol^{-1})	
$Ag_2O + EtOH \longrightarrow AgO(H)Ag^+ + EtO^-$	2.7	(5)
$AgOK + EtOH \longrightarrow AgO(H)K^+ + EtO^-$	-15.2	(6)

Figure 2. The density functional theory (DFT) calculations were performed for the four reactions [Eqs. (1–4)] of Ag_2O with KX (X = F, Cl, Br, or I).

Table 2. Intramolecular and intermolecular acyl migration catalyzed by Ag_2O/NaBr.

$$R^1OH + R^2COOR^3 \xrightarrow{Ag_2O/X^-} R^3OH + R^2COOR^1$$

Entry	Substrate	Migrated product	NMR ratio
1[a]	 **3a**: R = Ac; **3b**: R = Bz	 **4a**: R = Ac; **4b**: R = Bz	**3a**:**4a** (37:63) **3b**:**4b** (17:83)
2[a]	 **5a**: R = Ac; **5b**: R = Bz	 **6a**: R = Ac; **6b**: R = Bz	**5a**:**6a** (31:69) **5b**:**6b** (50:50)
3[a]	 **7a**: R = Ac; **7b**: R = Bz	 **8a**: R = Ac; **8b**: R = Bz	**7a**:**8a** (68:32) **7b**:**8b** (56:44)
4[a]	 **9a**: R = Ac; **9b**: R = Bz	 **10a**: R = Ac; **10b**: R = Bz	**9a**:**10a** (35:65) **9b**:**10b** (16:84)
5	 **11**	 **12** **12a**: R = Ac; **12b**: R = Bz	**12a** (90%)[b] **12b** (85%)[c]
6	 **13**	 **14** **14a**: R = Ac; **14b**: R = Bz	**14a** (85%)[b] **14b** (80%)[c]
7[d]	 **15** **15a**: R = Ac; **15b**: R = Bz	 **16**	Quant.
8[d]	 **17a**: R = Ac; **17b**: R = Bz	 **18**	Quant.

Reaction conditions: [a] substrates (50 mg), acetonitrile (1 mL), Ag_2O (0.1 equiv.), NaBr (0.1 equiv.), RT–40 °C, 24 h.; [b] substrates (50 mg), Ag_2O (0.1 equiv.), NaBr (0.1 equiv.), EtOAc (1 mL), RT, 24 h.; [c] substrates (50 mg), Ag_2O (0.1 equiv.), NaBr (0.1 equiv.), MeOBz (0.2 mL), vacuum, 40 °C, 1 h. [d] substrates (100 mg), Ag_2O (0.1 equiv.), NaBr (0.1 equiv.), MeOH (1 mL), RT, 2–12 h.

AgOK is generated when Ag_2O meets with KF due to the instability of AgF. The natural bond orbital (NBO) charges of O in both Ag_2O and AgOK were thus analyzed to compare the ability of each to remove a proton from an alcohol. The NBO charge of O in AgOK (−1.514) was more negative than that of O in Ag_2O (−1.309), showing the basicity of AgOK to be stronger than Ag_2O. Furthermore, by using ethanol (EtOH) as the model of alcohol, the solvation-corrected relative electronic energies, ΔE_{sol}, of the reaction of Ag_2O and AgOK with EtOH [Eqs. (5) and (6)] were calculated. The reaction of Ag_2O with EtOH is endothermic (2.7 kcal mol^{-1}) while the reaction of AgOK with EtOH is exothermic (15.2 kcal mol^{-1}), indicating that the anion EtO^- is more easily generated from the reaction of AgOK with EtOH, i.e., AgOK is a stronger base than Ag_2O and so can more easily remove the proton from EtOH, producing the anion EtO^-.

If our proposed principle is valid, the transesterification reaction would be able to be catalyzed by the mixture of Ag_2O with soft halides, such as bromide and iodide. However, Ag_2O or soft halides alone would not catalyze these reactions. Ag_2O-mediated acyl migration has been reported recently.[10] As the mechanism was unclear at that time, 1 equiv. of Ag_2O with the addition of 0.1 equiv. of TBAI was employed in the reaction. In our cases, only 0.1 equiv. of Ag_2O with the addition of 0.1 equiv. of NaBr was used. We firstly tested intramolecular acyl migration of substrates **3**, **5**, **7**, and **9** to corresponding compounds **4**, **6**, **8**, and **10** (entries **1**–**4** in Table 2). The results are in accordance with previous reports[10b] where 1 equiv. of Ag_2O and 0.1 equiv. of TBAI were employed. The acylation of carbohydrate diols **11** and **13** by EtOAc/MeOBz with the addition of 0.1 equiv. of NaBr and 0.1 equiv. of Ag_2O, leading to regioselectively mono-acylated products **12a**/**12b** and **14a**/**14b** in 90/85% and 85/80% isolation yields respectively (entries **5** and **6** in Table 2). The deprotection of acyl groups for penta-acetyl/benzoyl-galactose **15** and tetra-acetyl/benzoyl-glucoside **17** is also tested with Ag_2O/Br^- in methanol (entries **7** and **8** in Table 2), leading to deprotected products **16** and **18** in quantitative yields. All these intermolecular and intramolecular transesterification have been successfully catalyzed by the mixture of 0.1 equiv. of Ag_2O and 0.1 equiv. of soft halide. However, these reactions cannot proceed with whether 1 equiv. of Ag_2O or 1 equiv. of halide alone. Autocatalysis of reactions of alkyl halides with Ag_2O had been noticed as early as 1937.[11] It was further found that AgI/Ag_2O combinations accelerate transesterification reactions of inositol derivatives.[12] However, a large amounts of Ag_2O and AgI were used in those cases ($\geqslant$ 1 equiv.). We compared our method with AgI/Ag_2O method in the transesterification of ethyl benzoate in methanol. With 0.1 equiv. of Ag_2O and 0.1 equiv. of KI, the transesterification of ethyl benzoate was completed in 0.5 h. However, with 2 equiv.

of Ag_2O and 1 equiv. of AgI, the transesterification proceeded very slow, leading to only 9% conversion rate in 4 days. Though Ag_2O is insoluble in acetonitrile, the mixture turned into a clear solution with the addition of more than 3 equiv. of TBAI or TBABr and displayed very strong basicity (Figure **S5**). It may indicate the formation of AgO^- and $(AgX_2)^-$. Thus, the reaction catalyzed by AgO^- should be homogeneous catalysis. Through the investigation of the Ag_2O-route in the synthesis of Ag^I *N*-heterocyclic carbine complexes by DFT calculations, the advantage of Ag_2O was attributed to its stronger basicity.[13] However, we suggest that it should be also attributed to the strong basicity of AgO^- which is formed through coordination of iodide anion to Ag_2O.

In conclusion, although Ag_2O itself is a weak base and is usually used as Lewis acid catalyst, its basicity can be greatly enhanced by the coordination of a soft halide anion to Ag^+. Thus, KI as an initiator activated Ag_2O-mediated protections were found to be due to the enhanced basicity of Ag_2O. The basicity depends on the initial additive amount of KI and remains unchanged until Ag_2O is depleted. We believe that this is a general effect for metal oxides and soft anions, applicable to a wider range of organic reaction systems. The catalyst will show the particular advantage in organic reactions related with substitution of a soft anion and requiring an unchanged basic condition.

Experimental Section

General preparation method for fresh Ag_2O: A stoichiometric amount of saturated sodium hydroxide solution was added dropwise to a silver nitrate aqueous solution (10 mL, 0.2 M) to form a large amount of precipitate. After being filtered, washed with deionized water for three times, washed with ethanol and dried at 40 °C, solid silver oxide was obtained as brown powder.

General Ag_2O-mediated benzylation: Carbohydrate substrates (50 mg) in dry acetonitrile (1 mL) were added silver oxide (1.1 equiv.), halide salts (0.1 equiv.), and benzyl bromide (1.5 equiv.). The mixtures were stirred at room temperature for 1–4 h. The conversion rates were calculated through the detection of product compositions by ^1H NMR analysis.

General Ag_2O-mediated acyl migration: Carbohydrate substrates (50 mg) in dry acetonitrile (1 mL) were added silver oxide (0.1 equiv.) and sodium bromide (0.1 equiv.). The mixtures were stirred at room temperature or 40 °C for 24 h. The product distributions were directly detected by ^1H NMR spectrum.

General Ag_2O-mediated intermolecular acyl migration: Condition A: carbohydrate substrates (50 mg) in dry ethyl acetate (1 mL) were added silver oxide (0.1 equiv.) and sodium bromide (0.1 equiv.). The mixtures were stirred at room temperature for 24 h. After being filtered, the filtrate was concentrated in vacuum. Purification of the residue by flash column chromatography (2:1 hexane-ethyl acetate) afforded the products. Condition B: carbohydrate substrates (50 mg) in dry methyl benzoate (1 mL) were added silver oxide (0.1 equiv.) and sodium bromide (0.1 equiv.). The mixtures were stirred at 40 °C under vacuum for 24 h. After being filtered, the filtrate was concentrated in vacuum. Purification of the residue by flash column chromatography (2:1 hexane-ethyl acetate) afforded the products.

General Ag_2O-mediated deacylation: Condition A: carbohydrate substrates (100 mg) in dry methanol (1 mL) were added silver oxide (0.1 equiv.) and sodium bromide (0.1 equiv.). The mixtures were stirred at room temperature for 2–12 h. After being filtered, the filtrate was concentrated in vacuum. Purification of the residue by flash column chromatography (2:1 methanol-ethyl acetate) afforded the products. Condition B: carbohydrate substrates (100 mg) in dry methanol (1 mL) were added silver oxide (0.1 equiv.) and bromide or chloride resin (85 mg). The mixtures were stirred at room temperature for 2–12 h. After being filtered, the filtrate was concentrated to afford the products.

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Keywords: base catalysis · coordination · hard-soft acid-base · silver

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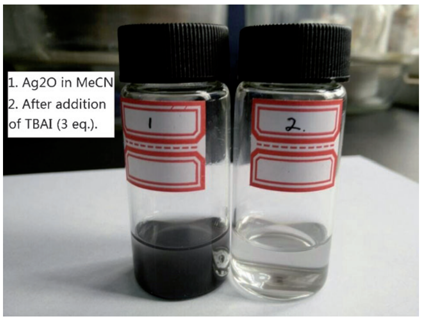
Enhanced Basicity of Ag_2O by Coordination to Soft Anions



All your base belongs to us: In Ag_2O-mediated benzylation, the addition of a catalytic amount of KI can greatly improve reactivity. Our studies show this to be attributable to the enhanced basicity of Ag_2O through coordination of soft iodide anions to the silver atom, and show KI to be an initiator. Thus, NaBr as an initiator combined with Ag_2O has been successfully used to catalyze transesterification reactions.