in which it is only partially soluble. Colorless crystals of **2** or **3** were obtained by leaving the hot filtrates to cool on the bench. Yield of crystalline material (first batches) 26% and 27%, respectively; m.p. 180°C (decomp) and 175°C (decomp), respectively. Satisfactory C,H,Mg,N,Na analyses were obtained for both compounds.

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[3] Crystal data: General: All measurements were made at 123 K on a Rigaku AFC7S diffractometer by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), scan method ω. Intensities were corrected for Lp effects only. Structures were solved by direct methods[13] and refined on F using full-matrix least-squares.[14] Details given for **2** with **3** in parentheses. $C_{61}H_{114}Mg_2N_6Na_4$ ($C_{60}H_{112}Mg_2Na_4$): $0.7 \times 0.4 \times 0.4$ ($0.4 \times 0.15 \times 0.12$) mm^3, monoclinic, $P2_1/n$, $a = 15.277(2)$ (15.206(2)), $b = 8.213(2)$ (8.175(3)), $c = 25.541(6)$ (25.524(3)) Å, $\beta = 94.277(14)$ (93.855(10))°, $V = 3195(1)$ (3165(1)) Å^3, $\rho_{calcd} = 1.11$ (1.11) g cm^{-3}, $\mu = 0.105$ (0.106) mm^{-1}, $2\theta_{max} = 55$ (45)°; 8128 (4674) data measured, 7844 (4490) unique, $R_m = 0.021$ (0.039). H atoms were placed in calculated positions and all other atoms were treated anisotropically. $R = 0.0441$ (0.0623), $R_w = 0.0550$ (0.0655), GOF = 1.66 (1.40) based on 4770 (2899) observations with $I > 2\sigma(I)$, max/min residual electron density = 0.66/−0.31 (0.34/−0.28). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102591 and CCDC-102592. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A New and Simple Route to Alkali Metal Oxometalates**

Dieter Trinschek and Martin Jansen*

Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday

The alkali metal oxides are the strongest oxide bases available; the basicity increases from Li_2O to Cs_2O. Accordingly these exhibit pronounced reactivity in solid-state reactions to give ternary oxides. In particular, systematic research by Hoppe et al. has revealed that the cations in such ternary alkali metal oxometalates exhibit an extraordinarily wide variety of valence, structural chemistry, and physical properties. Insulators as well as ionic or metallic conductors, maximum (e.g. K_2FeO_4,[1] $K_6Co_2O_7$[2]) or minimum oxidation states (K_3FeO_2,[3] Cs_3AuO[4]), unusually low (K_2NiO_2[5]) or high (Na_3NO_4[6]) coordination numbers, and last but not least special coordination geometries (Na_4FeO_3,[7] $KCoO_2$[8]) are found in this class of compounds. However, the synthesis of these materials can be a rather tedious and difficult task. In particular, for the heavier alkali metals the procedure includes preparation and purification of the metals, their oxidation with molecular oxygen to oxides, peroxides, or hyperoxides with a well-defined composition. All preparative work including weighing and homogenizing the starting components must be performed under strictly inert conditions. Additional problems arise from the fact that the commonly used crucibles are attacked by the alkali metal oxides more or less severely. Finally, the reaction parameters must be chosen very carefully. In this paper we present a considerably simplified and generally applicable new route to multinary alkali metal oxometalates, which circumvents most of the difficulties noted above. The approach is based on the reaction of sodium azide with sodium nitrite or sodium nitrate, first described by Zintl and Baumbach[9] [Eq. (1) and (2)]:

$$3\,NaN_3 + NaNO_2 \longrightarrow 2\,Na_2O + 5\,N_2 \tag{1}$$

$$5\,NaN_3 + NaNO_3 \longrightarrow 3\,Na_2O + 8\,N_2 \tag{2}$$

This particular method has not been generally accepted for the preparation of sodium oxide itself, because the components often react in an unforeseeable way, with a tendency to explode, which agrees with our own experiences. However, the reaction always proceeds in a controlled manner, if the starting materials already contain the particular oxide for the synthesis of the alkali metal oxometalate thus diluting the azide/nitrate mixture, and if the reaction is conducted in a closed container. Under these conditions the evolving N_2 can

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moderate the reaction by increasing the nitrogen partial pressure.

The cylindrical reaction container (Figure 1) is equipped with squeeze seals. While the body is made of 9S29 K steel, the inlay consists of special metals according to the requirements of the chemical system under study (Cu, Au, Pt, Ni, Fe in most cases).[*] Although squeeze seals, which are less efficient than self-sealing systems (Bridgman seals), withstand the internal pressure to a certain degree, they let the nitrogen formed during the reaction escape safely.

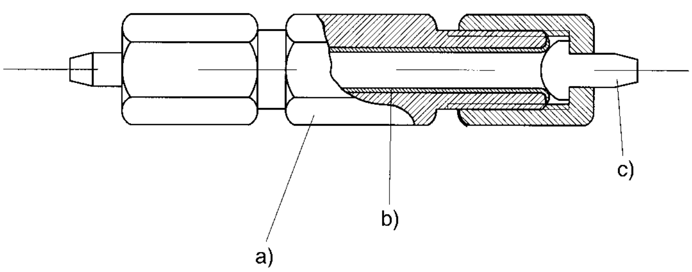

Figure 1. Construction of the crucible for the experiments. a) crucible (steel); b) inlay (e.g.) copper; c) stopper (e.g. copper).

The process steps are always the same, independent of the particular system under investigation. The weighed mixture of starting materials consisting of the alkali metal azide, alkali metal nitrite, or alkali metal nitrate, and a selected binary oxide as the reaction partner are thoroughly mixed and homogenized. This is normally achieved by wet grinding (acetone, ethanol) in a planet-ball-mill. After removal of the solvent the starting mixture is dried and then put into the crucible, which is sealed after having replaced the air with nitrogen or argon. The temperature schedule applied has to be optimized for each system. However, it has proved to be advantageous to keep the heating rate low (2 – 5 $K h^{-1}$) at the decomposition temperature (ranging from 300 to 350 °C) of the particular alkali metal azide.

The main advantage of the presented synthesis route is the simplification of the preparative work and the wide variety of systems that can be tackled. In addition to acid – base reactions without oxidation or reduction, it is also possible to perform redox reactions with simultaneous reduction or oxidation of the countercation. The examples ([Eq. (3) – (5)]: see also Table 1) show that only the azide/nitrate or azide/nitrite ratio needs to be varied to obtain the desired result.

$$9\,NaN_3 + 3\,NaNO_2 + 2\,ZnO \longrightarrow 2\,Na_6ZnO_4 + 15\,N_2 \text{ (neutral)} \tag{3}$$

$$8\,NaN_3 + 4\,NaNO_2 + Co_3O_4 \longrightarrow 3\,Na_4CoO_4 + 14\,N_2 \text{ (oxidizing)} \tag{4}$$

$$2\,NaN_3 + 4\,CuO \longrightarrow 2\,NaCu_2O_2 + 3\,N_2 \text{ (reducing)} \tag{5}$$

Table 1. Examples of reactions for the preparation of alkali metal oxometalates and alkali metal orthonitrates.

Compound	Reaction	Conditions T[°C]/t[h]
Na_2ZnO_2[12]	$3\,NaN_3 + NaNO_2 + 2\,ZnO \rightarrow 2\,Na_2ZnO_2 + 5\,N_2$	390/20
t-$Na_2Zn_2O_3$[13]	$3\,NaN_3 + NaNO_2 + 4\,ZnO \rightarrow 2\,Na_2Zn_2O_3 + 5\,N_2$	650/50[a]
$Na_{10}Zn_4O_9$[14]	$15\,NaN_3 + 5\,NaNO_2 + 8\,ZnO \rightarrow 2\,Na_{10}Zn_4O_9 + 25\,N_2$	500/50
Na_4SiO_4[15]	$3\,NaN_3 + NaNO_2 + SiO_2 \rightarrow Na_4SiO_4 + 5\,N_2$	500/50
Na_4TiO_4[16]	$3\,NaN_3 + NaNO_2 + TiO_2 \rightarrow Na_4TiO_4 + 5\,N_2$	450/50
$NaTiO_2$[17]	$NaN_3 + TiO_2 \rightarrow NaTiO_2 + 3/2\,N_2$	900/18
Na_5InO_4[18]	$15\,NaN_3 + 5\,NaNO_2 + 2\,In_2O_3 \rightarrow 4\,Na_5InO_4 + 25\,N_2$	475/50
$NaCuO$[19]	$2\,NaN_3 + 2\,CuO \rightarrow 2\,NaCuO + 3\,N_2$	550/80
$NaCu_2O_2$[20]	$2\,NaN_3 + 4\,CuO \rightarrow 2\,NaCu_2O_2 + 3\,N_2$	625/50
Na_4CoO_4[21]	$8\,NaN_3 + 4\,NaNO_2 + Co_3O_4 \rightarrow 3\,Na_4CoO_4 + 14\,N_2$	550/20
Na_3NO_3[10]	$4\,NaN_3 + 2\,NaNO_3 \rightarrow 2\,Na_3NO_3 + 6\,N_2$	400/24
K_3NO_3[11]	$4\,KN_3 + 2\,KNO_3 \rightarrow 2\,K_3NO_3 + 6\,N_2$	420/24
$KCuO$[22]	$KNO_2 + 3\,KN_3 + 2\,Cu_2O \rightarrow 4\,KCuO + 5\,N_2$	460/48
$NaNiO_2$[23]	$NaN_3 + NaNO_2 + 2\,NiO \rightarrow 2\,NaNiO_2 + 2\,N_2$	650/10[b]
$CsCuO$[24]	$2\,CsN_3 + 2\,CuO \rightarrow 2\,CsCuO + 3/2\,N_2$	400/24
Cs_2ZnO_2[25]	$5\,CsN_3 + CsNO_3 + 3\,ZnO \rightarrow 3\,Cs_2ZnO_2 + 8\,N_2$	410/24
Cs_2NiO_2[5]	$5\,CsN_3 + CsNO_3 + 3\,NiO \rightarrow 3\,Cs_2NiO_2 + 8\,N_2$	420/50
Rb_2NiO_2[5]	$5\,RbN_3 + RbNO_3 + 3\,NiO \rightarrow 3\,Rb_2NiO_2 + 8\,N_2$	420/48
$RbCuO$[26]	$2\,RbN_3 + 2\,CuO \rightarrow 2\,RbCuO + 3/2\,N_2$	450/50
Li_2NiO_2[27]	$5\,LiN_3 + LiNO_3 + 3\,NiO \rightarrow 3\,Li_2NiO_2 + 8\,N_2$	450/50
$LiCuO$[22]	$2\,LiN_3 + 2\,CuO \rightarrow 2\,LiCuO + 3/2\,N_2$	450/50
$LiTiO_2$[28]	$LiN_3 + TiO_2 \rightarrow LiTiO_2 + 3/2\,N_2$	820/5[b]
$LiTi_2O_4$[29]	$LiN_3 + 2\,TiO_2 \rightarrow LiTi_2O_4 + 3/2\,N_2$	820/5[b]

[a] Sample was quenched. [b] Reaction time in days.

In most cases, the novel synthesis route yields the same ternary oxides of the alkali metals as those obtained from the direct reaction of the alkali metal oxides. However, in some cases the products are different. For instance, Na_3NO_4 has not been available by the azide/nitrate route so far. Evidently, the oxide basicity of the alkali metal oxides is not fully reached. On the other hand, this method presents a way to obtain new sodium zincates that could not be synthesized by the traditional route in spite of intensive efforts. The reason might be that the starting materials are more efficiently homogenized, and that the in situ generated alkali metal oxide is highly reactive. How elegantly this azide/nitrate route works becomes evident when using it for the preparation of the alkali metal orthonitrates:[10, 11] the only preparative step is to mix the appropriate amounts of the alkali metal nitrites, which are easily available and stable in air, with the respective azides and to start the reaction. Batches of several grams of starting materials yield very pure products.

In conclusion, the new synthesis route for the preparation of ternary alkali metal oxometalates presented herein combines several favorable aspects: general applicability for different chemical systems, the starting materials are easy to handle, and, finally, the alkali metal oxide is generated in situ in a highly reactive form.

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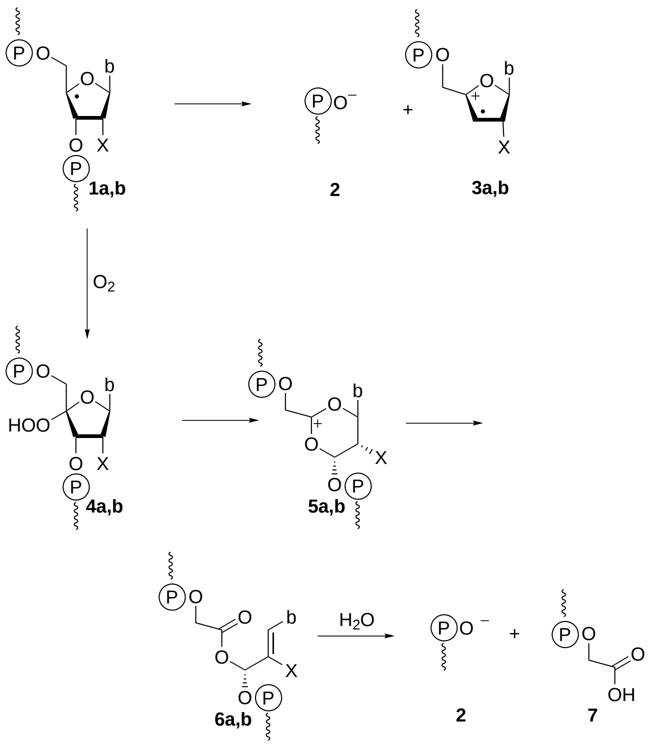
Differences Between 4′-RNA and 4′-DNA Radicals during Anaerobic and Aerobic Strand Cleavage[**]

Harald Strittmatter, Adrian Dussy, Urs Schwitter, and Bernd Giese[*]

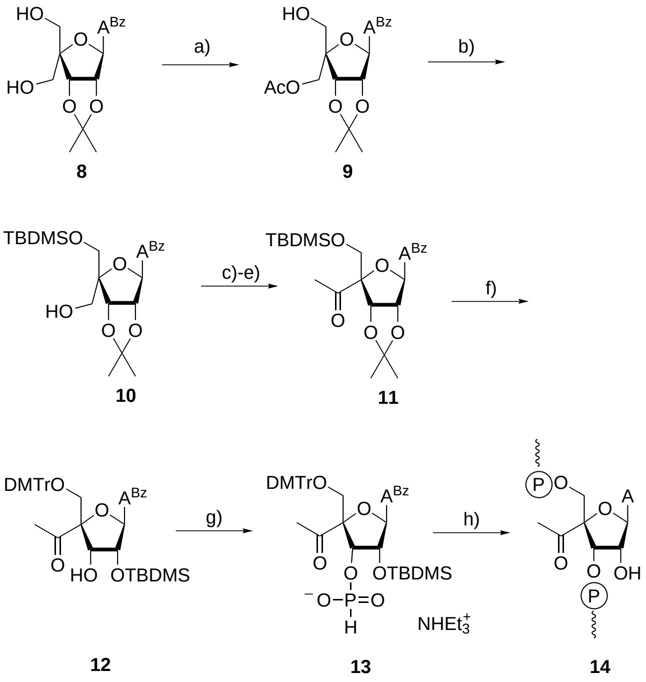
The mechanism of DNA strand cleavage by 4′-DNA radicals has been elucidated to a large extent in recent years.[1] Under anaerobic conditions a spontaneous strand cleavage takes place whereby a heterolytic C,O bond scission at C3′ leads to the 5′-phosphate **2** as the stable cleavage product (Scheme 1). In the presence of O_2 the 4′-DNA radical **1a** is converted first into hydroperoxide **4a**, then to cation **5a**, which after β-elimination (**5a**→**6a**) and subsequent hydrolysis leads to the stable cleavage products 5′-phosphate **2** and 3′-phosphoglycolate **7**.

The mechanism of the corresponding RNA cleavage, however, has been hardly investigated. Nevertheless, studies by Hecht[2] have shown that bleomycin, which generates 4′-nucleotide radicals, cleaves RNA slower than DNA. Since bleomycin binds better to t-RNA[3] than to DNA, the difference in cleavage efficiency might be explained by a difference in the reactivity of the 4′-oligonucleotide radical **1a** relative to **1b**. In order to prove this we have synthesized oligonucleotide **14** in which one ribonucleotide carries an acetyl group at position C4′ (Scheme 2). In analogy to the



a: X = H; **b**: X = OH

Scheme 1. Nucleotide strand cleavage by 4′-radicals under anaerobic and aerobic conditions. b = nucleobase. wavy line = nucleotide strand.



Scheme 2. Synthesis of 4′-acetylated RNA. a) MeC(OMe)$_3$, camphorsulfonic acid, 20 °C; HOAc, 0 °C, 42 %; in the second diastereomer (formed in 41 % yield) the acetyl group was cleaved off to reform nucleoside **8**; b) TBDMSCl, imidazole, 40 °C; NaOMe, 20 °C, 5 min, 72 %; c) Dess-Martin periodinane, 80 %; d) MeMgCl, 93 %; e) Dess-Martin periodinane, 85 %; f) CF$_3$CO$_2$H; TBDMSCl; CF$_3$CO$_2$H; DMTrCl; 68 %; g) PCl$_3$, 1,2,4-triazole; Me$_3$NH$^+$HCO$_3^-$; 78 %; h) DNA synthesizer. A^{BZ} = benzyladenine, DMTr = 4,4′-dimethoxytrityl, dT = 2′-deoxyribosylthymine, TBDMS = *tert*-butyldimethylsilyl.

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