The interaction of zinc alkyls with dioxygen has received continuous interest for over 150 years, and common wisdom states that the oxygenation reactions of homoleptic zine alkyls are uncontrollably fast. Moreover, significant uncertainties concerning both the composition of the products and mechanistic considerations have persisted. In pioneering studies, Frankland contended in 1849 that controlled oxygenation of ZnEt₂ affords Zn(OEt)₂,[1] and in 1864 Butlerov[2] and Lissenko[3] independently argued for the formation of the partly oxygenated species Zn(Et)OEt. In 1890 Demuth and Meyer postulated the formation of the alkylperoxide Zn(Et)OEt from the insertion of an O₂ molecule into the Zn–C bond.[4] These pioneering interpretations have since been the subject of considerable debate,[5] however, most of the later studies considered the oxygenation reaction as proceeding with oxidation of both Zn–C bonds and the formation of compounds formulated as Zn(OOR)₂, Zn(OR)OOR, and Zn(OR)₂.[5c–f] Only very recently our group demonstrated convicingly that the controlled oxygenation of ZnMe₂ leads to the formation of partially oxygenated species in high yields,[6] and we structurally characterized the first examples of zinc alkylperoxides that were derived from the reaction of O₂ with monoaalkylzinc chelate complexes.[6,7] The latter results have come in contradiction to the commonly accepted mechanism, which assumes a radical-chain process (Scheme 1).[8]

Apart from fundamental interest in the interaction of zinc alkyls with dioxygen, many practical applications have been found in both organic and materials chemistry which involve the oxygenation process. For example, the seminal studies of Chaudret and co-workers demonstrated that controlled oxygenation of the ZnR₂ precursor in THF in the presence of an amine ligand and moisture affords in one step crystalline ZnO nanoparticles of controlled size and shape.[9,10] The importance of zinc alkylperoxide complexes is also readily apparent from their continued use as reagents in organic synthesis. For decades, the reaction of organozinc complexes (particularly Zn(R)X compounds in the presence of ether solvents) with O₂ has been used to prepare hydroperoxides or alcohols, depending on the reaction conditions.[11] Furthermore, the alkylperoxide species Zn(R)OOR, prepared in situ by treating ZnR₂ with molecular oxygen, was reported as an efficient epoxidizing reagent for enones,[12] and the modified systems that were supported by auxiliary ligands enabled to conduct the epoxidation stereoselectively[13] and regioselectively.[7,14] Contemporaneously, there has also been increased interest in various radical additions initiated by the ZnR₂/O₂ system, in which an alkyl radical, as it has been commonly assumed, is generated through the reaction of dialkylzinc with dioxygen and acts as the chain carrier.[15] In spite of many contributions in this area, there is no answer to the question of how the oxygenated products participate in the radical reactions. Pertinent to the subject of our studies is also the fact that in the latter reactions, organic substrates usually bear electron-donor sites that are capable of forming Lewis acid–base adducts with ZnR₂, and essentially adducts of the type [ZnR₂(L)]⁺ are actually involved in the reaction with dioxygen.

To obtain a deeper understanding of the factors that control reactions involving the ZnR₂/O₂ system, detailed information about the structure and properties of the organo-zinc intermediates is undoubtedly needed. However, it is perhaps astonishing that the reported systematic studies on the mechanistic aspects concerning the oxygenation of homoleptic zinc alkyls essentially end in the late 1960s.[5] As part of the ongoing exploration of the fundamental question as to whether well-defined zinc peroxides/alkoxides can be synthesized by the selective oxygenation of dialkylzinc complexes, we have conducted several control experiments to probe for factors that influence the reactivity and selectivity in the reaction of ZnBu₂ with dioxygen in the presence of donor ligands.

In the first step of our studies, a solution of ZnBu₂ in THF at −78°C was treated with an excess of molecular oxygen, and the reaction mixture was stirred for approximately one minute. Then, the excess O₂ was removed in vacuum, and a white crystalline solid deposited from the solution after several hours at −25°C. The spectroscopic data indicated that the interaction of the putative Lewis acid–base adduct [ZnBu₂(thf)] with O₂ led to the selective oxygenation of one Zn–C bond and the formation of the alkoxide compound [[ZnBu₂(O–Bu(thf))]₂] (Scheme 2). The IR spectrum of the resulting product did not show the characteristic O–O peroxidic stretching vibration for alkylperoxide moieties, and the 1H NMR spectrum consisted of single resonances for each group of protons. Thus, the oxidation of the first Zn–C bond in the presence of THF does not lead to an isolable alkylperoxide species. Nevertheless, this process offers a

Scheme 1.

initiation \[ \text{R} \]

propagation \[ \text{R}^* + \text{O}_2 \rightarrow \text{ROO}^* \]

\[ \text{M} - \text{R} + \text{ROO}^* \rightarrow \text{M-OOR} + \text{R}^* \]

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route for the selective formation of alkylzinc alkoxides. Repetition of the reaction at room temperature resulted in the formation of a complex mixture of inseparable products. The crystals of that were obtained directly by the procedure outlined above were found to be suitable for single-crystal X-ray diffraction analysis. The structure consists of a centrosymmetric dimer in which the two four-coordinate zinc centers are bridged by the tert-butoxide groups with the formation of a planar Zn$_2$O$_2$ core (Zn1–O1 1.982(1) Å, Zn1–O1’ 1.986 (1) Å, Figure 1). The coordination environment of the zinc atoms is completed by one tert-butyl group (Zn1–C5 2.016(2) Å) and one thf molecule (Zn1–O2 2.239(1) Å). To determine the effect of the strength of donor ligands on the oxygenation reaction, we conducted the analogous studies in the presence of 4-methylpyridine (py-Me). We expected that the application of py-Me as a strong N-donor ligand should decrease the reactivity of the Lewis acid–base adduct [ZnBu$_2$(μ-OOBu)(py-Me)]$_2$ as well as enhance the stability of the resulting oxygenated products. Indeed, when a solution of ZnBu$_2$ in THF with one or two equivalents of py-Me was exposed to an excess of molecular oxygen (1 atm) at −78°C, only traces of the oxygenation products were detected in the 1H NMR spectrum after two hours. However, when the reaction involving the 1:1 or 1:2 ZnBu$_2$/py-Me system was conducted at about −45°C for approximately 15 minutes, the tert-butyliperoxide compound [ZnBu$_2$(μ-OOBu)(py-Me)]$_2$ (2) was isolated in good yield as a colorless solid after work up. Apparently, the pyridine ligand stabilizes the tert-butyliperoxide species that results from the insertion of O$_2$ into one Zn–C bond. In the case of this ZnBu$_2$/py-Me system, the oxygenation reaction is easy to monitor as the reaction mixture is initially yellow and becomes colorless upon the formation of the tert-butyliperoxide compound. Strikingly, we did not observe any induction period or inhibition of the oxygenation reaction in the presence of 0.1 mol% TEMPO (2,2,6,6-tetramethylpiperidine N-oxide).

The 1H NMR spectrum of 2 indicated two chemically inequivalent tert-butyl groups and one py-Me molecule. The presence of the Zn–OOrBu linkage was confirmed by the IR spectrum, which exhibited a band of weak intensity at 868 cm$^{-1}$ that is attributable to the O–O peroxidic stretching vibration. The alkyliperoxide compound 2 is surprisingly stable in solution in a nitrogen atmosphere under ambient conditions. Prolonged exposure of the reaction mixture to dioxygen resulted in further oxygenation, albeit at a significantly slower rate than the first step. Presumably, the formation of relatively stable four-coordinate alkylzinc species inhibits the oxidation of the remaining Zn–C bonds.

Single crystals of 2 suitable for an X-ray crystal structure determination were grown from THF at −25°C. As seen in Figure 2, the molecule adopts a dimeric aggregation in the solid state by bridging through the tert-butyliperoxide groups and the two four-coordinate zinc centers. The coordination environment of the zinc atoms is completed by one tert-butyl group and one py-Me ligand. The tert-butyliperoxide ligands are oriented in an eclipsed–staggered conformation. A similar tert-butyliperoxide geometry was found in the related indium and gallium complexes [M$_2$Bu$_2$(μ-OOBu)]$_2$ and such a geometry presumably minimizes repulsion between the lone

![Figure 1. Molecular structure of 1 with thermal ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity.](image1)

![Figure 2. Molecular structure of 2 with thermal ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity.](image2)
pairs of electrons on the oxygen atoms. The aromatic rings of the py-Me ligands are perpendicular with respect to the central ZnO ligands. The corresponding bond lengths Zn1–C5 (2.008(11) Å), Zn1–O1 (1.990(8) Å), and Zn1–O1’ (1.987(8) Å) and the Zn1-O1-Zn1’ angle (101.88(27)°) are similar to those found for 1. The O1–O2 bond length of 1.4289(11) Å is close to that found in other zinc alkylperoxides.[6,7]

The results not only highlight the marked tendency of zinc dialkyls to undergo oxidation of only one alkyl group under controlled conditions but also demonstrate that the identity of the donor ligand has a significant influence on the oxygenation process. The relatively strong Lewis base py-Me essentially inhibited the oxygenation of ZnBu2 at -78°C, whereas the reaction at slightly elevated temperature (ca. -45°C) resulted in the highly selective formation of the alkylzinc peroxide compound 2. In contrast, the thf-solvated species [ZnBu2(thf)] reacted rapidly with dioxygen even at -78°C to selectivity form the alkylzinc alkoxide 1. Our recent studies demonstrated that the attack of O2 on the three-coordinate metal center is the initial step in the oxygenation of the alkylzinc chelate complexes [[RZn(L,L’)]], (L,L’ = deprotonated amino alcohol).[8] Thus, the lower reactivity of the methylpyridine adduct(s) [ZnBu2(py-Me)] toward O2 at -78°C compared to that of the tetrahydrofuran adduct(s) [ZnBu2(thf)] may be understood in terms of the more hindered access of the oxygen molecule to the low-coordinate metal centers of the former species. Presumably, the dissociation of a ligand from the putative four-coordinate [ZnRL2(L)] complex is required prior to the effective attack of dioxygen (see A and B, Scheme 3).[18]

Furthermore, the selective formation of the partially oxygenated four-coordinate compounds 1 and 2 are perhaps unexpected in view of the high reactivity of previously reported zinc dialkyls toward dioxygen, though this result is consistent with our recent findings that four-coordinate alkylzinc species are inert toward further oxygenation.[8a] Another key observation is the stabilization of the resulting alkylperoxide Zn(alkyl)OOBu species by the nitrogen ligand.

The observed high selectivity is not consistent with the widely accepted mechanism involving a free-radical chain reaction that is initiated by an advantageous radical R* (Scheme 1). Moreover, our earlier studies demonstrated that the initial step in the oxygenation of the main-group-metal alkyls involves the attack of O2 on the metal center and that the approaching O2 molecule has strong geometric requirements.[9] These findings indicate that O2 must enter the first coordination sphere to oxidize alkylzinc complexes (B, Scheme 3), and one may view the primary step as involving the noncovalent activation of O2 by the metal center (C). This weak interaction changes the electronic structure of the dioxygen molecule and induces low-energy pathways. Accordingly, the coordination of dioxygen to the metal center is followed by electron transfer from the Zn–C bond to O2 to afford a solvent-caged radical pair D. At low temperature the postulated caged radical pair rearranges to generate selectively the alkylperoxide E (triplet-to-singlet surface crossing is required in order to transform D into E). However, at higher temperature the alkyl radical may diffuse away from the cage, which potentially constitutes the source of alkyl radical. This view finds support in the mentioned observation that the thf solvate of ZnBu2 reacted with O2 with the formation of a complex mixture of products at ambient temperature.

In conclusion, the reported studies open the way for the preparative exploitation of reactions involving zinc dialkyls and dioxygen. Moreover, a plausible hypothesis concerning the mechanism of O2 activation by organometallic compounds has certainly been advanced. With more experimental results, it should then be possible to test and quantitatively improve the accuracy of the description of the proposed stepwise mechanism for the insertion of dioxygen into M–C bonds.

**Experimental Section**

1: A stirred solution of ZnBu2 (0.403 g, 2.25 mmol) in THF (5 mL) was cooled to -78°C. Under slightly reduced pressure an excess of dry dioxygen (1 atm) was introduced. After a minute the excess O2 was removed, and the system was purged with nitrogen by using a vacuum–nitrogen line. The reaction mixture was stored at -78°C, and white crystalline product deposited. Yield: 76%; 1H NMR (400 MHz, [D8]THF, 25°C, TMS): δ = 1.00 (s, 9H, C(CH3)3), 1.15 (s, 9H, OOC(CH2)3), 1.67 (m, 4H, CH2), 3.5 ppm (m, 4H, OCH2), IR (nujol): ν = 1465(s), 1389(s), 1377(s), 1368(s), 1360(s), 1241(s), 1175(s), 1075(m), 1023(m), 1009(m), 940(m), 932(m), 895(s), 808(m), 756(m), 535 cm-1 (s). Elementary analysis (%) calcd for C24H52O4Zn2: C 53.93, H 9.74; found: C 53.82, H 9.78.

2: 4-Methylpyridine (0.209 g, 2.25 mmol) was added to a solution of ZnBu2 (0.403 g, 2.25 mmol) in THF (4 mL) at ambient temperature. The resulting yellow solution was then cooled to -45°C, and an excess of dry dioxygen (1 atm) was introduced. The oxygenation was continued until the solution became colorless (ca. 15 min). The reaction mixture was cooled to -78°C, and the system was purged with nitrogen by using a vacuum–nitrogen line. The mixture was stored at -25°C, and white crystalline product deposited. Yield: 67%; 1H NMR (400 MHz, [D8]THF, 25°C, TMS): δ = 1.05 (s, 9H, C(CH3)3), 1.00 (s, major, 9H, C(CH3)3), 1.02 (s, major, 9H, OOC(CH2)3), 1.10 (m, 9H, OOC(CH2)3), 2.31 (s, 3H, py-CH), 7.20 (d, J(HH) = 5.6 Hz, 2H, py), 8.52 ppm (d, J(HH) = 5.6 Hz, 2H, py), the two observed inequivalent signals for the Bu group and the OOBu group in the relative ratio 1:8 for each group indicates the presence of geometrical isomers of 2: IR (nujol): ν = 1670(m), 1622(s), 1607(m), 1584(m), 1562(m), 1504(m), 1463(s), 1377(s), 1355(s), 1251(m), 1238(m), 1128(m), 1218(m), 1195(s), 1162(w), 1117(w), 1099(w), 1070(m), 1024(s), 1010(m), 979(w), 958(w), 938(w), 840(m), 771(m), 745(s), 693(m), 651(m), 594(w).
113.108(4), b


16. We note that during the course of our studies a publication reporting the synthesis and molecular structure of $[\text{ZnBu}_2(\mu-\text{OrBu})(\text{thf})]_2$, which was derived from the direct reaction between ZnBu$_2$ and iBuOH, appeared; see reference [10x].


18. It is reasonable to assume that the four-coordinate adducts $[\text{ZnBu}_2(\mu-py-Me)_2]$ and $[\text{ZnBu}_2(\mu-py-Me)(\text{thf})]$ are relatively stable at low temperature in contrast to the $[\text{ZnBu}_2(\text{thf})]_2$ adduct, which likely easily dissociates to the three-coordinate species $[\text{ZnBu}_2(\text{thf})]$ even at $\approx$78°C. For a discussion of the relative stability of zinc dialkyls with donor ligands, see: A. C. Jones, P. O’Brien, CVD of Compound Semiconductors, VCH, Weinheim, 1997, chap. 2.

