

[Lithium *tert*-Butylperoxide]₁₂: Crystal Structure of an Aggregated Oxenoid

Gernot Boche,* Konrad Möbus, Klaus Harms, John C. W. Lohrenz, and Michael Marsch

Abstract: The X-ray crystal structure of the dodecameric lithium *tert*-butylperoxide [2]₁₂ is the first of an alkali or alkaline earth peroxide. It shows the lithium ion bridging the two oxygen atoms of the peroxide unit and a slight lengthening of the O–O bond, in agreement with quantum-chemical calculations. A calculation for the model reaction of MeLi with LiOOH to give MeOLi and LiOH reveals the importance of Li bridging the O–O bond in

the transition state of this reaction, as similarly discussed for many oxidation reactions of (transition-) metal peroxides. Preliminary theoretical studies of the O–O

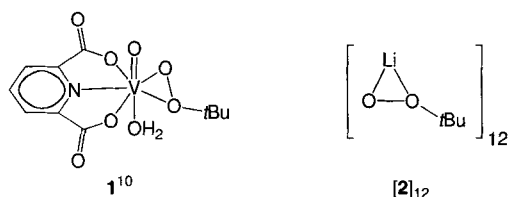
bond length (and thus of the oxenoid character) as a function of the aggregation of 2 disclose that increasing aggregation leads to stabilization of the charge at the anionic oxygen atom and thus to a reduction of the O–O bond length (oxenoid character). Related considerations of the effect of aggregation should also be valid for other lithium (organometallic) compounds and their structure and reactivity as well as other properties.

Keywords

aggregates · lithium compounds · oxenoids · peroxides · structure elucidation

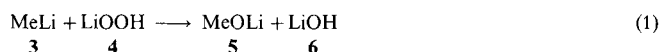
Introduction

Peroxide complexes of (transition-) metal compounds play an important role in (enantioselective) oxidation reactions.^[1] The Sharpless epoxidation^[2] and the transformation of sulfides into sulfoxides^[3] are well-known examples for titanium species. The importance of a molybdenum peroxide in oxidation reactions catalyzed by molybdenum peroxo complexes has recently been outlined.^[4] Other recent reports deal with acylperoxo–Fe^{III} porphyrin complexes,^[5] an alkylperoxo–Fe^{III}^[6] and a hydroperoxide–Fe^{III} intermediate.^[7] In many cases an η^2 -coordination of the ROO ligand to the metal is discussed, at least for the transition state of the oxidation reaction.^[1–4, 8] However, although several structures of η^1 -peroxide metal complexes have been published^[9] there are only two reports on the structure of an η^2 -complex (1).^[10] No solid-state structure has yet been reported for an alkali or alkaline earth metal peroxide.^[9]



In the context of our investigations of metalated (lithiated) hydroperoxides, their oxenoid character, and their reactions

with nucleophiles such as organometallic compounds,^[11] we report here the X-ray crystal structure determination of lithium *tert*-butylperoxide (2), which crystallizes as an η^2 -Li-bridged dodecamer [2]₁₂. We also performed a theoretical investigation of the model oxidation reaction of methylolithium MeLi (3) with lithium hydroperoxide LiOOH (4) to give lithium methyllate LiOCH₃ (5) and lithium hydroxide LiOH (6) [Eq. (1)] in order to gain an insight into the importance of lithium bridging the



two oxygen atoms of 4, as well as into other details of the transition state of this type of facile oxidation reaction of organometallic compounds.

Other model calculations, motivated by the only slight elongation of the O–O bond in [2]₁₂, indicate the importance of aggregation in the structure of an oxenoid like 2. It has long been known that the rate of reaction of an organolithium compound with an electrophile depends strongly on the aggregation state. Thus, McGarrity et al. reported in 1985 that dimeric *n*-butyllithium reacted 10 times faster with benzaldehyde than did the corresponding tetramer.^[12] Streitwieser et al. noticed recently the influence of the aggregation on the UV/Vis absorption spectra of Li enolates: the monomer absorbs at longer wavelengths than the aggregated species.^[13a] And Klumpp et al. reported lately^[13b] that even the chemoselectivity of an organolithium compound is a function of its aggregation. An understanding of the influence of aggregation on all sorts of ground- and transition-state properties of organometallic species is therefore of some importance. Our theoretical investigations of the influence of aggregation on the O–O bond lengths, and thus on the oxenoid character of lithium peroxides, give an explanation for that particular case that may be of more general significance.

[*] Prof. Dr. G. Boche, Dipl.-Chem. K. Möbus, Dr. K. Harms, Dr. J. C. W. Lohrenz, M. Marsch
Fachbereich Chemie der Philipps-Universität Marburg
D-35032 Marburg (Germany)
Fax: Int. code + (6421) 28-8917
e-mail: boche@ps1515.chemie.uni-marburg.de

Results and Discussion

The crystal structure of lithium *tert*-butylperoxide [2]₁₂: Figure 1 shows the dodecameric aggregate [2]₁₂ with its polar nucleus of 12 lithium and 24 oxygen atoms and the hydrophobic shell resulting from the 12 *tert*-butyl groups. The details of the structure are better understood from Figure 2 with the asymmetric

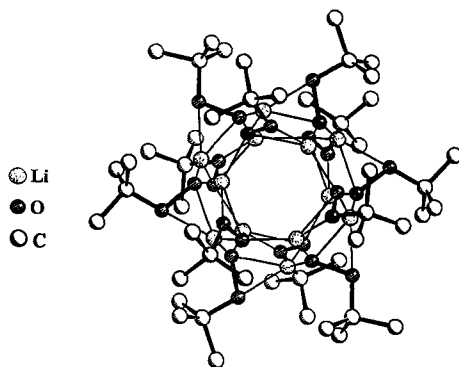


Fig. 1. Crystal structure of [LiOOtBu]₁₂ [2]₁₂ (hydrogen atoms have been omitted for clarity).

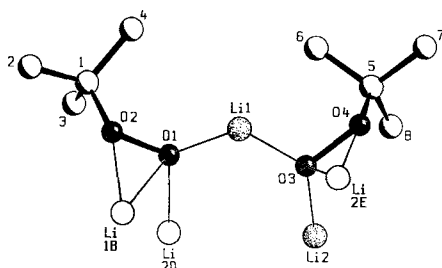
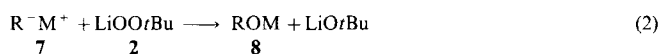


Fig. 2. Asymmetric unit of [2]₁₂ with the bonds to the Li⁺ neighbors. Significant bond lengths [pm]: O1–O2 147.5(3), O2–Li1B 190.9(5), O1–Li1B 210.9(5), O1–Li2D 190.2(5), O1–Li1 185.2(5), O3–O4 147.7(3), O4–Li2E 199.3(5), O3–Li2E 196.1(5), O3–Li1 191.3(5), O3–Li2 186.9(5).

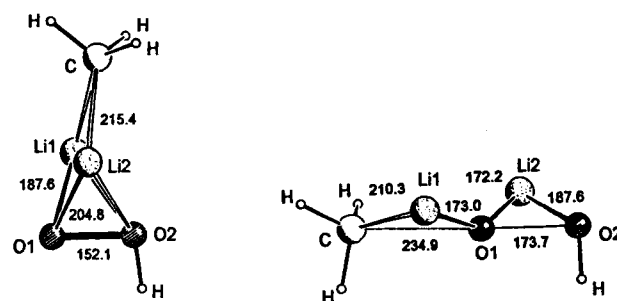
unit of [2]₁₂—two LiOOtBu molecules—and their next Li⁺ neighbors. Both O–O bonds of the asymmetric unit (O1–O2 and O3–O4, respectively) are bridged by lithium cations (Li1B and Li2E, respectively). In the case of Li1B the bond to the anionic oxygen atom O1 is longer than to O2 (210.9(5) and 190.9(5) pm, respectively). This contrasts with Li2E, which has a shorter bond to the anionic O3 than to O4 (196.1(5) and (199.3(5) pm, respectively). It is important for the discussion of the influence of aggregation on the structure of the oxenoid 2 that in the dodecamer [2]₁₂ each anionic oxygen atom is additionally bonded to two further lithium cations besides the bridging ones: O1 to Li1 (185.2(5) pm) and to Li2D (190.2(5) pm), and O3 to Li1 (191.3(5) pm) and to Li2 (186.9(5) pm). The bond lengths O1–O2 and O3–O4 (147.5(3) and 147.7(3) pm, respectively) are essentially identical. They are only slightly longer than the mean value of the O–O bond lengths in 12 crystals containing HO–OH (145.3 pm)^[9] and in 29 crystals with HO–OR (146.5 pm).^[9, 14] The O–O bond lengths in [2]₁₂ are of special interest in the context of the aggregation effects discussed later (see below).

The transition state of the reaction of MeLi with LiOOH—model reaction (1): Lithiated hydroperoxides like 2 are excellent electrophiles towards all sorts of organometallic nucleophiles

R[–]M⁺ 7; this means that they are important oxidants for the transformation of 7 into alkoxides 8 [Eq. (2)].^[11, 15]



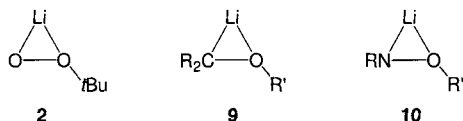
According to stereochemical studies the nucleophiles R[–]M⁺ 7 retain their stereochemistry at the anionic carbon atom, at least in the cases of R[–]M⁺ = cyclopropyllithium^[16] and vinylolithium.^[17] We have confirmed these observations with cyclopropyl Grignard reagents and cuprates,^[18] and with vinyl Grignards.^[19] These results suggest an S_N2-type reaction of 7 with 2 rather than an electron-transfer–recombination sequence. The σ_{O–O} bond in LiOOH 4, which is weakened compared with the one in HOOH, and the rather low-lying σ*_{O–O} orbital in 4^[11a] are in accord with a one-step mechanism for the oxenoid reaction (2). MP2(fc)/6-31G(d) calculations do indeed lead to a favorable S_N-type transition state of the model reaction (1) of MeLi (3) with LiOOH (4) to give MeOLi (5) and LiOH (6). As shown in Scheme 1, MeLi and LiOOH first form



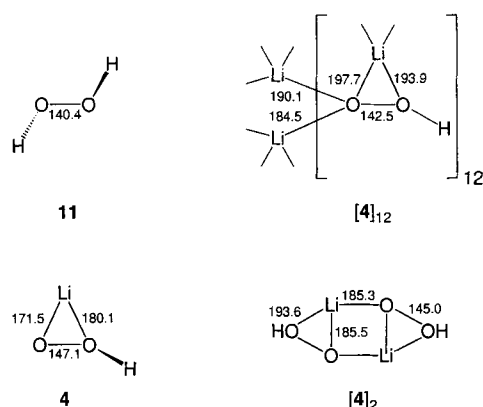
Scheme 1. The reaction of CH₃Li (3) with LiOOH (4) gives the complex CH₃Li·LiOOH (3·4) and, via the transition state [3·4][‡], the product complex CH₃OLi·LiOH (5·6). Left: 3·4, –55.2 kcal mol^{–1}; right, [3·4][‡], –16.6 kcal mol^{–1}; energy relative to CH₃Li + LiOOH (3 + 4), MP2(fc)/6-31G(d), bond lengths in pm.

a complex 3·4, which is 55.2 kcal mol^{–1} more stable than the reactants 3 and 4. The O–O bond in 3·4 is doubly bridged by lithium and has essentially the same bond length as the O–O bond in the noncomplexed LiOOH 4 (152.1 and 151.8 pm, respectively). As the transition state [3·4][‡] is reached (Scheme 1), important changes occur: the anionic methyl group migrates into the O–O bond axis of LiOOH, corresponding to nucleophilic substitution at the electrophilic oxenoid oxygen atom O1. This leads to a lengthening of the O–O bond in [3·4][‡] to 173.7 pm. It is also evident from the structure of [3·4][‡] that the methyl group is “conducted” to O1 by means of Li1, and that Li2 bridges O1 and O2 finally to form the leaving group LiOH (6)—a kind of metal-assisted ionization. The transition state [3·4][‡] is 16.6 kcal mol^{–1} more stable than the reactants 3 and 4, while the complex of the reaction products 5·6 is 160.0 kcal mol^{–1} more favorable than 3 and 4. It should be mentioned that LiOOH (4) has also served in other cases as a model for quantum-chemical investigations of oxidation reactions with metal–peroxide complexes.^[20] Bach and Schlegel,^[20b] for example, investigated the reaction of 4 with NH₃, while the SH₂ reaction was studied by Jørgensen.^[20c] suffice to say that likewise an S_N2-type transition state was found for these oxenoid reactions with 4.

The influence of aggregation on the structure of lithium *tert*-butylperoxide (2): What structure is to be expected for an oxenoid like lithium *tert*-butylperoxide, which is as strong an electrophile as the related carbenoids **9** and nitrenoids **10**?^[11]



What is the influence of the aggregation on the O–O bond lengths in different aggregates $[2]_x$, O–O bonds that should be elongated compared with the one in the hydroperoxide HOO-*t*Bu, as is the case with the C–O bond in **9**^[21] and the N–O bond in **10**?^[22] Quantum-chemical calculations with HOOH (**11**) as a model for hydroperoxides, LiOOH (**4**) as a model for monomeric lithiated hydroperoxides, $[4]_{12}$ for a dodecamer, and $[4]_2$ for a dimeric aggregate provided a first insight (Scheme 2). For



Scheme 2. HF/6-31+G(d)5D structures of **4**, $[4]_{12}$, $[4]_2$, and **11**; bond lengths in pm.

these calculations we chose the comparatively low theoretical level HF/6-31+G(d)5D in order to be able to include also the dodecamer $[4]_{12}$ in our investigations. The structure of $[4]_{12}$ shows the bridging of the oxygen atoms with lithium and the contact of the anionic oxygen atoms to two further lithium cations, exactly as observed in the solid-state structure of $[2]_{12}$ (Figs. 1 and 2). The O–O bond in the model $[4]_{12}$ is only slightly elongated to 142.5 pm compared with that of HOOH (**11**) (140.4 pm). A similar result has been found experimentally for $[2]_{12}$ (147.5(3) and 147.7(3) pm) compared with HOOH in crystals (mean value 145.3 pm). In the monomer model LiOOH (**4**), however, the O–O bond is much longer (147.1 pm) (Scheme 2), as expected for an oxenoid.^[11a] This suggests that the additional stabilization of the negative charge at the anionic oxygen atoms of $[4]_{12}$ ($[2]_{12}$) by the lithium cations of two further LiOOH (LiOO*t*Bu) molecules is responsible for the difference. The calculated O–O bond length in the η^2 -bridged dimeric $[\text{LiOOH}]_2$ $[4]_2$ with one further Li⁺ at the anionic oxygen atoms is in agreement with this suggestion: it is shorter (145.0 pm) than in the monomer **4** (147.1 pm), however, longer than in $[4]_{12}$ (142.5 pm).^[23–25] One can conclude from these theoretical studies that the O–O bond length in a monomeric lithium peroxide should be distinctly longer than the O–O bond in $[2]_{12}$ —which still has to be shown experimentally. A similar aggregation effect might be responsible for the above-mentioned difference between the UV absorption of a monomeric enolate and that of its higher aggregates, which absorb at shorter wavelengths than the monomer.^[13a]

Conclusion

The first X-ray crystal structure determination of an alkali or alkaline earth peroxide, $[2]_{12}$, shows that the two oxygen atoms are bridged by lithium and that there is only a slight elongation of the O–O bonds compared with the O–O bonds of HOOH and HOOR (2.3 and 1.1 pm, respectively). Quantum-chemical investigations of the structures of HOOH (**11**), and of LiOOH (**4**), $[\text{LiOOH}]_2$ ($[4]_2$), and $[\text{LiOOH}]_{12}$ ($[4]_{12}$) as models for different aggregates of lithium peroxides, indicate that the aggregation is of critical importance for the O–O bond lengths in these species: the shortest O–O bond length is calculated for $[4]_{12}$ (142.5 pm), while it is longer in $[4]_2$ (145.0 pm) and **4** (147.1 pm). This indicates that the slight elongation of the O–O bond in $[2]_{12}$ is a result of the additional stabilization of the negative charge at the anionic oxygen atom by the lithiums of two other lithium peroxides **2**, which corresponds to the results of the X-ray crystal structure of $[2]_{12}$. In $[4]_2$ the anionic oxygen atom is bonded to one more lithium cation, while in **4** it is only in contact with the bridging one. Model calculations of the reaction of LiOOH (**4**) with MeLi (**3**) to give MeOLi (**5**) and LiOH (**6**) are in agreement with an S_N2 -type transition state for this important oxidation reaction of an organometallic species R^-M^+ (**7**) with lithium peroxides like **2**. The stereochemistry of such oxenoid reactions corresponds to an S_N2 mechanism, which apparently is more favorable than a two-step electron-transfer–recombination sequence.

Experimental Procedure

Preparation of crystals of LiOO*t*Bu $[2]_{12}$: Diisopropylamine (350 mg, 3.46 mmol) in 3 mL tetrahydrofuran was deprotonated with *n*-butyllithium (3.2 mmol, 2.0 mL of a 1.6 M solution in hexane) to give lithium diisopropylamide. *tert*-Butylhydroperoxide (288 mg, 3.2 mmol) was added to this solution, which then was kept at -30°C . After 3 d crystals suitable for an X-ray crystal structure determination were formed. Yield: 120 mg (42%).

X-ray single crystal data collection and structure analysis of $[2]_{12}$ $[(C_3H_7)_4Li_2O_4]_6$, $M = 1152.60$: Rhombohedral, space group $R\bar{3}$, $a = b = 2079.9(1)$, $c = 1450.1(1)$ pm, $V = 5423.7(5) \times 10^{-30} \text{ m}^3$, $Z = 3$, $\rho_{\text{calc}} = 1.057 \text{ Mg m}^{-3}$, $\mu(\text{CuK}\alpha) = 0.649 \text{ mm}^{-1}$. The data were collected on an Enraf–Nonius CAD4 diffractometer with graphite monochromated $\text{CuK}\alpha$ radiation, $T = 218(2) \text{ K}$, 873 measured reflections ($3.9 < \theta < 55^\circ$), 867 unique ($R_{\text{int}} = 0.053$). Structure solution by direct methods (SHELXTL-PLUS), refinement on F^2 with all unique reflections (SHELXL-93). The non-hydrogen atoms were refined anisotropically, the hydrogens on calculated positions with fixed isotropic temperature factors. The parameters of the weighting scheme were calculated by the program as 0.0623, 8.1397; the extinction parameter was 0.00031(9). Refinement converged to $wR2$ ($R1$ for 810 reflections with $I > 2\sigma(I)$) was 0.045, the goodness of fit (on F^2) was 1.115, 134 refined parameters. All calculations were performed on a Micro-VAX II and a DEC 3000-300X [26–30].

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- [24] If the anionic O atom of LiOOH **4** is coordinated to LiOH and to Li^+ ($4\cdot\text{LiOH}\cdot\text{Li}^+$) an O–O bond length of 143.2 pm is calculated. MP2/6-31G(d) calculations of the O–O bond lengths lead to the following results: [**4**]₂ 151.5 pm and [**4**·LiOH·Li⁺] 150.3 pm. Thus, the O–O bond lengths in these aggregates are similarly shorter than in the monomer **4** (151.8 pm); however, the shortening is less pronounced than in the HF/6-31 + G(d)5D calculations.
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