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Dimethyldioxirane and Acetone Are Not in Equilibrium

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The potential transfer of an oxygen atom from dioxiranes to a ketonic carbonyl group is disproved by appropriate D- and ^{13}C-labelling. As shown by ^{13}C NMR spectroscopy bis(trideuteriomethyl)dioxirane and [carbonyl-^{13}C]acetone are not in equilibrium with [D$_6$]acetone and [3-^{13}C]dimethyldioxirane.

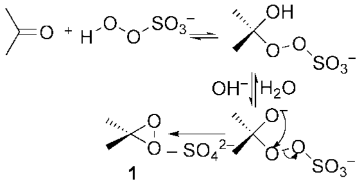
Introduction

Derivatives of dioxirane progressed during the last decades from laboratory curiosities to potent reagents for oxygen transfer to π-bonds, lone-pair electrons at heteroatoms and σ-bonds.[1–4] The structural identity of the oxygen-transferring species as dioxiranes was established by spectroscopic methods including ^{1}H, ^{13}C and ^{17}O NMR analysis.[5–8] The sterically hindered dimesityldioxirane could even be isolated in the crystalline state and structurally characterized by X-ray crystallography.[9] In contrast to the well-established and synthetically widely used epoxidation of olefinic double bonds by dioxiranes, the analogous oxygen transfer to a carbonyl π-bond with formation of a new dioxirane is unknown.

The problem of oxygen transfer between dioxiranes and ketones was briefly discussed by Murray in a fundamental review on the chemistry of dioxiranes.[1] Some arguments were summarized speaking against the uptake of an oxygen atom from dioxiranes by ketones; however, no final conclusion was drawn. In this communication the possible oxygen transfer between dimethyldioxirane and acetone, which would establish a degenerated equilibrium between both species, is investigated by means of D- and ^{13}C-labelling.

Results and Discussions

Solutions of dimethyldioxirane (**1**) in acetone are readily prepared by reaction of acetone with caroate (peroxymonosulfate) in water at pH = 7–8 (Scheme 1) followed by distillation under slightly reduced pressure (ca. 125 mbar).[2] Dilution of the acetone solution of **1** with water and extraction with tetrachloromethane results in a higher concentration of the reagent.[2] This procedure furnishes solutions of **1** in CCl$_4$/acetone (ca. 2:1, v/v) in concentrations ≥ 0.15 mol·L^{-1}.



Scheme 1. Generation of dimethyldioxirane (**1**).

In Figure 1 (a) the ^{13}C NMR spectrum of **1** prepared as described above is displayed. In good agreement with previous measurements in acetone, the ^{13}C resonances for the ring carbon atom and the methyl groups are found at δ = 101.3 (102,[7] 102.25,[5] 102.3[8]) ppm and 22.7 (22.5,[7] 22.68,[5] 22.69[8]) ppm. The signal for the quaternary carbon atom is significantly shifted to higher field (ca 1 ppm) when acetone is largely replaced by tetrachloromethane as solvent. This may be attributed to a smaller degree of solvation of the highly dipolar **1**[1] in tetrachloromethane resulting in a chemical shift closer to the value of δ = 99.2 ppm predicted by the IGLO approach for the isolated molecule at 0 K.[8] The ^{13}C NMR spectrum of bis(trideuteriomethyl)dioxirane (D$_6$-**1**) prepared analogously[10] is given in Figure 1 (b). The chemical shift of the ring carbon atom is slightly moved to δ = 101 ppm, whereas the value for the deuterated methyl groups exerts a stronger isotopic effect and is found as a septuplet at δ = 22.0 ppm ($^{1}J_{\mathrm{C,D}}$ = 19.3 Hz). To ensure that the chemical shifts of the quaternary carbon atoms in **1** and D$_6$-**1** are clearly resolved when both species are present in solution a 100:1 mixture of [D$_6$]acetone and [carbonyl-^{13}C]acetone (99 % ^{13}C) was subjected to the usual procedure for dimethyldioxirane generation. The ^{13}C NMR spectrum of the resulting mixture of the dimethyldioxirane isotopomers D$_6$-**1** and ^{13}C-**1** is presented in Figure 1 (c). The spectrum demonstrates that the signals for the ring carbon atom in D$_6$-**1** (δ = 101.0 ppm) and ^{13}C-**1** (δ = 101.3 ppm) can be identified without doubt when both iso-

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topomers coexist. The ^{13}C resonances of the geminal methyl groups in D$_6$-**1** and ^{13}C-**1** appear expectedly as septuplet at δ = 22.0 ppm and as doublet at δ = 22.7 ppm ($^1J_{C,C}$ = 46.2 Hz). Due to a concentration ratio of [^{13}C-**1**]/[D$_6$-**1**] = 10^{-2}, the doublet for the unlabelled methyl groups in ^{13}C-**1** can only be seen after prolonged accumulation [inset in Figure 1 (c)].

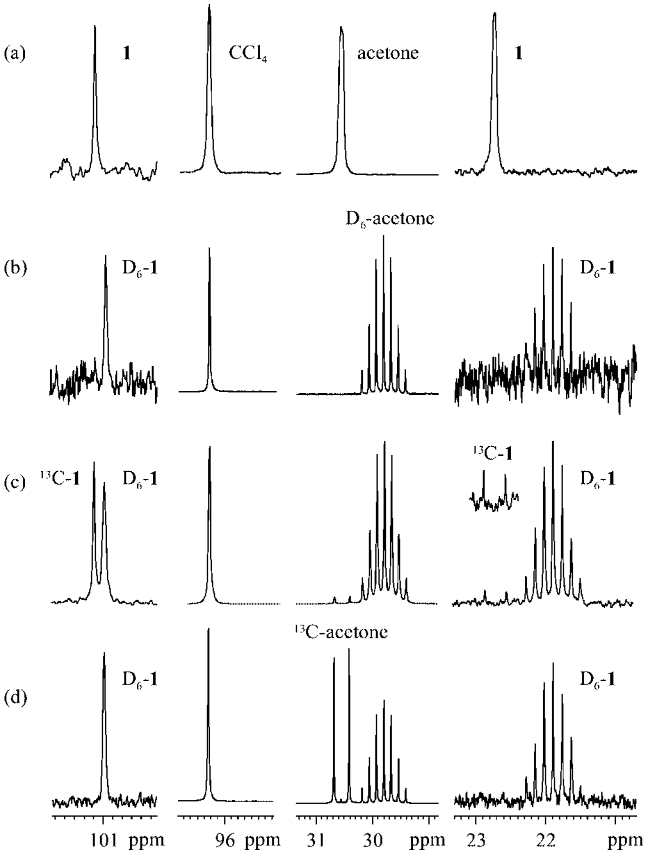
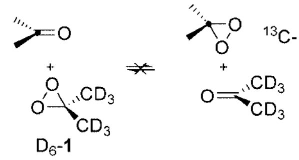


Figure 1. ^{13}C NMR spectroscopic data of solutions of dimethyldioxirane (**1**) (a), bis(trideuteriomethyl)dioxirane (D$_6$-**1**) (b), a 100:1 mixture of D$_6$-**1** and [3-^{13}C]dimethyldioxirane (^{13}C-**1**) (c), and a mixture of 550 µL of D$_6$-**1** (ca. 0.2 mol·L^{-1}) and 50 µL of [carbonyl-^{13}C]acetone (d) in CCl$_4$. The solvent CCl$_4$ is used as internal reference (δ = 96.3 ppm). The ^{13}C signals of the carbonyl group in acetone, [D$_6$]acetone and [carbonyl-^{13}C]acetone are not shown.

To test the possible transfer of an oxygen atom from bis(trideuteriomethyl)dioxirane (D$_6$-**1**) to acetone (Scheme 2), 50 µL of [carbonyl-^{13}C]acetone was added to a ca. 0.2 M solution of D$_6$-**1** in tetrachloromethane/[D$_6$]acetone (550 µL) at 4 °C. The ^{13}C NMR spectrum of this mixture exhibits the ^{13}C resonances of D$_6$-**1**, [D$_6$]acetone and [^{13}C]acetone; however, the ^{13}C resonance for the labelled ring carbon atom of ^{13}C-**1** at δ = 101.3 ppm is absent [Figure 1 (d)]. Repeated measurements of the sample kept at 4 °C for 4 d[11] produced identical spectra as shown in Figure 1 (d). Finally, the sample was warmed up to room temperature, kept at this temperature for 10 h and measured again. Except for some decrease in the signal-to-noise ratio[11] which could be balanced by prolonged accumulation, no significant changes in the spectral appearance could be noted, in particular, the signal for the ^{13}C-enriched ring carbon atom of ^{13}C-**1** remained absent.



Scheme 2. Exclusion of oxygen transfer from bis(trideuteriomethyl) dioxirane (D$_6$-**1**) to [carbonyl-^{13}C]acetone (• = ^{13}C).

In conclusion, the NMR experiments presented above demonstrate that [carbonyl-^{13}C]acetone and bis(trideuteriomethyl)dioxirane (D$_6$-**1**) are not in equilibrium with [3-^{13}C]dimethyldioxirane (^{13}C-**1**) and [D$_6$]acetone.

Experimental Section

General: The ^{13}C NMR spectroscopic data were collected with a Bruker AMX 600 spectrometer by single pulse excitation with proton decoupling (flip angle 30°, delay time 5 s, acquisition time 852 ms) at a temperature of 4 °C. The number of scans varied between 512 (**1**) and 122880 (mixture of ^{13}C-**1** and D$_6$-**1**). Solutions of dimethyldioxirane (**1**) in CCl$_4$ containing some acetone were prepared as described in refs.[2,4]

Bis(trideuteriomethyl)dioxirane (D$_6$-1): Solutions of bis(trideuteriomethyl)dioxirane (D$_6$-**1**) in CCl$_4$ containing some [D$_6$]acetone were prepared in a microapparatus disigned for diazomethane generation from Diazald® (Aldrich). The flask was charged with [D$_6$]acetone (5 mL), $4\cdot10^{-4}$ M aqueous Na$_2$EDTA (6.6 mL) and sodium hydrogencarbonate (1.51 g, 17.97 mmol). To the well-stirred mixture Oxone® (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$, 3.13 g, 5.08 mmol) was added in 5 portions in intervals of 3 min at 5–10 °C. After the last addition, the Dewar flask of the microapparatus was filled with dry ice/acetone and the pressure slowly lowered to 125 mbar. A mixture of D$_6$-**1** and [D$_6$]acetone began to condense and was collected in a cooled (dry ice) receiver flask over ca. 40 min. The distillate (ca. 6 mL) was diluted with ice-cold water (10 mL) and extracted in 3 portions with precooled (–10 °C) CCl$_4$ (1.8 mL). The organic phase (ca. 2.5 mL) was dried with molecular sieves (4 Å) at –20 °C for 12 h. The titer was determined by reaction of an aliquot (0.5 mL) with excess thioanisole and electronic integration of the ^{1}H NMR signals of the CH$_3$ groups in the unreacted thioanisole, the sulfoxide and the sulfone. Typical concentrations of 0.15–0.2 mol·L^{-1} in CCl$_4$/[D$_6$]acetone (ca. 2:1, v/v) were obtained. The ratio of CCl$_4$/[D$_6$]acetone was roughly estimated by comparison of the corresponding NMR signal intensities with calibrating mixtures of the two solvents.

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[11] In order to show that the dimethyldioxirane solutions prepared as described are sufficiently persistent to enable NMR measurements over several days, the dependency of the concentration on time was measured. Starting with an initial concentration of 0.16 $mol\cdot L^{-1}$, the following values ($mol\cdot L^{-1}/d$) were found for storage at 4 °C: 0.16/1, 0.14/4, 0.11/7. At room temperature the concentration dropped from 0.16 to 0.14 $mol\cdot L^{-1}$ after 1 d.

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