chloride (5 mL) were refluxed for 1 h in a 50-mL, round-bottomed flask. After removal of the thionyl chloride on a rotoevaporator, absolute methanol (25 mL) was added, and the resulting mixture was allowed to stand overnight. The methanol was removed on a rotoevaporator, and the resulting yellow solid was recrystallized from hexane to give 0.53 g (67%) of light yellow crystals, mp 68–70 °C. The proton NMR spectrum of this compound was consistent with that expected for the methyl ester.

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Communications

Oxygen-17 and Carbon-13 Identification of the Dimethyldioxirane Intermediate Arising in the Reaction of Potassium Caroate with Acetone

Summary: Starting with ^{17}O-labeled or 2-^{13}C-labeled acetone, ^{17}O and ^{13}C NMR evidence could be gathered which supports the dioxirane structure for the peroxide intermediate isolated from reaction solutions containing potassium caroate and acetone.

Sir: During the last decade we have collected kinetic, ^{18}O-labeling, and stereochemical data that stringently suggest dioxiranes—i.e., the smallest ring peroxide species containing carbon—are generated in the reaction of potassium peroxymonosulfate (caroate) with ketones.[1-3] Recently, the case for the existence of dioxiranes in the condensed phase was completed by Murray and Jeyaraman by showing that a number of low-molecular-weight dialkyldioxiranes can actually be isolated from buffered (pH 7, $NaHCO_3$) aqueous solutions containing caroate and the parent ketone.[4] Indeed, in the elegant procedure devised by these authors, room temperature distillation in a flow of inert gas allows one to remove from the reaction solution some of the dioxirane intermediate that builds up in a stationary concentration during the early stages of the reaction between the inorganic peroxide and the ketone (e.g., Scheme I).[4] Along with observations concerning reactivity, the spectroscopic evidence presented is convincing for the dioxirane structure.[4] Dimethyldioxirane solutions are observed to yield acetone diperoxide **3**,[4] and this even in the absence of Lewis acid catalysts (although much more slowly). Also in view of the debated dioxirane **1**–carbonyl oxide **2** dichotomy,[3,4,6-9] we have sought ^{17}O NMR confirmation of the structure of the peroxide intermediate generated as in Scheme I.

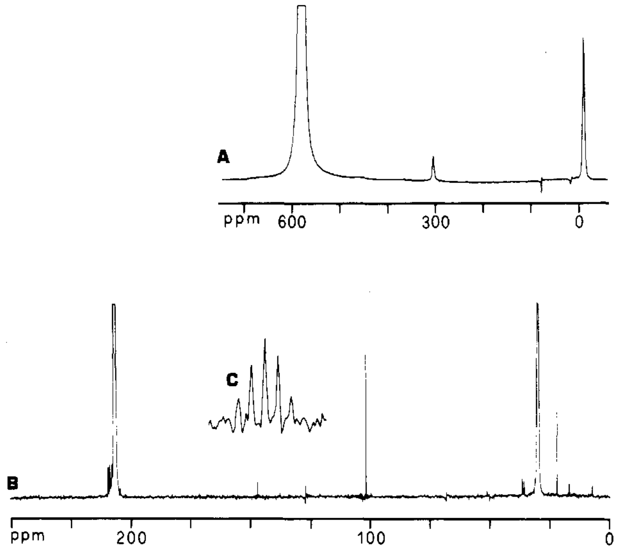

Figure 1. (A) ^{17}O NMR spectrum of ca. 0.06 M dimethyldioxirane (**1**; ^{17}O labeled) in acetone, at 4 °C (27.12 MHz, recorded over ca. 16 h, 570 000 scans, no sensitivity enhancement applied to FID before FT); (B) ^{1}H decoupled ^{13}C NMR spectrum of endocyclic carbon-labeled (ca. 5% ^{13}C) 0.06 M dimethyldioxirane in acetone, at 4 °C (50.03 MHz, 4040 scans, digital resolution 0.39 Hz/point, 0.16-s sensitivity enhancement); (C) insert (50-Hz sweep width, 5103-Hz sweep offset, 37 380 scans) shows the ^{1}H-coupled spectrum portion relative to the ^{13}C resonance at 102 ppm.

The difficulties routinely encountered in the detection of ^{17}O NMR resonances of peroxide oxygens in natural abundance are well understood.[10-13] In particular, as we

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(5) The procedure and apparatus described by Murray and Jeyaraman (ref 4a) were used with only minor modifications: alternative to the addition of solid caroate, we found it also suitable to add a cold satured aqueous solution of $KHSO_5$ (containing ca. 10^{-3} M $EDTANa_2$, to cut down uncatalyzed peroxide decomposition) to the reaction flask containing water, acetone, and $NaHCO_3$ (or $KHCO_3$); argon instead of helium was used to remove dimethyldioxirane (and acetone) from the reaction solution, and a three-way distillation receiver was connected to a dry ice/$CHCl_3$-cooled condenser to allow collection of fractions.

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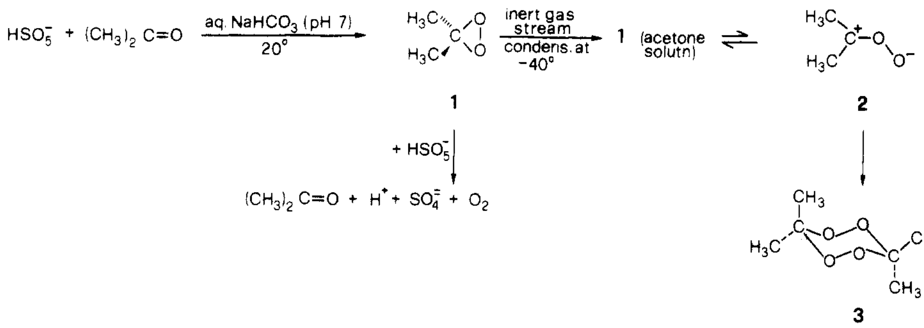
Scheme I



had to deal with dilute solutions of the peroxide, we deemed it essential to provide the O–O bond with significant ^{17}O enrichment.[12] This was done by a small-scale run of the reported procedure,[4a] using ^{17}O-labeled (10.4%) acetone.[14] We could then record ^{17}O NMR spectra of freshly prepared solutions of the intermediate; an example is shown in Figure 1. Notice that acetone solvent and residual water give rise to strong ^{17}O resonances appearing at 573 and −11 ppm, respectively;[15] along with these, a single absorption is present at δ 302 ($\Delta\nu_{1/2} \simeq$ 113 Hz). This resonance cannot be due to the dimer **3**, as we find that acetone diperoxide (in acetone, 4 °C) yields a single resonance at 263 ppm ($\Delta\nu_{1/2} \simeq$ 350 Hz). Since the currently available ^{17}O NMR techniques allow one to detect separate resonances for magnetically nonequivalent oxygens of the O–O bond in simple peroxides (e.g., *t*-BuOOH),[12,13] one is led to conclude that the peroxide intermediate has the dioxirane structure **1**. Indeed, in the temperature range from 0 to 25 °C, no significant change in chemical shift or line width of the given resonance occurs that could be ascribed to the onset of a dynamic process; thus, it is unlikely the single resonance observed is due to the rapid interconversion of two nonequivalent oxygens as in carbonyl oxide **2**.

Noteworthy, the ^{17}O chemical shift of dimethyldioxirane (λ_{max} 335 nm, $\epsilon \simeq 260$)[4a] is some 27–22 ppm downfield from that of simple four- or five-membered ring peroxides,[13] namely, dioxetanes ($\lambda_{max} \simeq$ 280 nm)[8d] and dioxolanes (λ_{max} < 220 nm). It would be tempting to link this phenomenon to a larger negative paramagnetic contribution to shielding on the basis of a Ramsey-type equation, relating chemical shifts to the reciprocal of ΔE for the lowest energy electronic transition.[16,17]

We found the labeling technique to be also useful in assessing the ^{13}C NMR identification of **1**.[18] In fact, while the CH_3 resonance reported for **1** (δ 22.7)[4a] appears quite consistent, the ring-carbon resonance given (δ 214.)[4a,19] seems too far downfield for an sp^3-carbon, even in a strained-ring state.[20] Thus, we employed acetone that was labeled with ^{13}C (ca. 5%) exclusively at the carbonyl carbon[21] to obtain solutions of dioxirane labeled at the endocyclic carbon by following the mentioned procedure (suitably scaled down to $^1/_3$).

The ^{13}C NMR spectrum is presented in Figure 1. Comparison with the analogous spectra of unlabeled dioxirane permits location unambiguously at 102. ppm for the ring carbon resonance. It is significant that the ^1H-coupled spectrum correctly yields, for this resonance, a septet with the proper intensity ratios and ^2J = 5.5 Hz (Figure 1). Other features of the ^1H-coupled spectrum also agree with the assigned structure **1**; namely, $\delta(CH_3)$ 22.5 (quartet of quartets, ^1J = 127.5 Hz and ^3J = 2.2 Hz). By way of comparison, for acetone diperoxide **3** in acetone, we find δ 20.5 and 22.3 (axial and equatorial CH_3;[22] two sets of quartets in the ^1H-coupled spectrum, ^1J = 129 Hz).

Thus, the spectroscopic evidence presented herein corroborates the dioxirane structure for the peroxide intermediate generated by the acetone/caroate system. Since it is now clear that, in the absence of effective nucleophiles, dioxiranes can have sufficient kinetic stability to be characterized or even isolated, new avenues appear to be open to investigate aspects of their reactivity other than peroxidic oxygen transfer.[3]

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Registry No. 1-^{17}O, 106114-68-5; 1-endocyclic ^{13}C, 106114-69-6; 3, 1073-91-2; H_2O-^{17}O, 13768-40-6; acetone-^{17}O, 74681-51-9; acetone, 67-64-1; potassium peroxymonosulfate, 37222-66-5.

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