ENERGY, GEOMETRY AND NMR CHEMICAL SHIFTS OF DIMETHYLDIOXIRANE

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Ab initio calculations suggest that dimethyldioxirane is more stable than dioxirane by 21 kcal/mol. The electronic structure and geometry of the former, however, provide no evidence for increased kinetic stability. Calculated ^{13}C NMR chemical shifts for the two compounds differ considerably from shifts published recently for dimethyldioxirane.

1. Introduction

Carbonyl oxide (1) and its cyclic isomer dioxirane (2) have attracted considerable interest as possible intermediates in the ozonolysis of alkenes, and in the oxidation of diazo compounds, carbenes, and ketones [1–3]. The high reactivity of both 1 and 2 has prevented their isolation and physical characterization for a long time. However, recent progress in synthesis and spectroscopic techniques has led to a variety of observations that provide considerable insight into the properties of 1 and 2. For example, the geometry of 2 has been determined by microwave methods [4][†]. In addition, derivatives of 1 and 2 have been investigated under matrix isolation conditions employing infrared and ultraviolet spectroscopy [6].

While these investigations had to be carried out at low temperatures to prevent chemical reactions, Murray and Jeyaraman (MJ) recently reported a simple method of preparing alkyl dioxiranes from peroxymonosulfate and ketones [7]. They recorded NMR, IR, and UV spectra for these compounds and described their chemical behaviour in some detail. Although these observations seem to support the existence of stable alkyl dioxiranes, it is nevertheless

[†] For early work on derivatives of 2 see ref. [5].

surprising that alkyl groups may stabilize 2 to such an extent that dioxiranes can be stored for several days [7]. Also, the NMR chemical shifts reported for dimethyldioxirane (3) are rather unusual for a cyclic peroxide [8]. In order to obtain independent information about the properties of alkyl dioxiranes, we have carried out extensive ab initio calculations on 3 which are part of a long-term effort aimed at a theoretical characterization of labile peroxides such as 1 and 2 [9–13]. In this work, we present energy (stability), geometry and NMR chemical shifts for 3 and discuss them with respect to the observations made for the peroxymonosulfate–acetone system [7].

2. Computational details

Geometry optimizations of 2 and 3 have been carried out at the RHF and MP2 [14] levels of theory employing the 4-31G [15] and 6-31G* [16] basis sets [†]. Previous investigations have shown that the geometries of cyclic peroxides are fairly well described at MP2/6-31G* level [9–12]. In the case of larger peroxides, HF/4-31G can be used since it

[†] A detailed discussion of the calculated geometry of 3 will be published later [17].

mimics MP2/6-31G* results due to a fortuitous cancellation of basis set and correlation errors [11]. ^{1}H, ^{13}C, and ^{17}O NMR chemical shifts have been determined by the recently developed IGLO (individual gauge for localized orbitals) method [18]. For this purpose, two Huzinaga basis sets [19] have been used, namely basis I: (7s3p/3s) contracted to [4111,21/21], and basis II: (9s5p1d/5s1p) contracted to [51111,2111,1/311,1], the exponents of the polarization functions being $\alpha_d(C) = \alpha_d(O) = 1.0$ and $\alpha_p(H) = 0.65$.
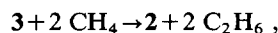
3. Results and discussion

In table 1 calculated geometries and energies of **2** and **3** are summarized. Table 2 contains theoretical ^{13}C chemical shifts for **1–3** and acetone.

The geometry of the dioxirane ring in **3** is similar to that in **2**. The CO bond length in **3** is slightly increased (≈ 1 pm) and the external ring angle widened by 1–2°. The preferred conformation of the methyl groups in **3** is identical with that found for propane. Of note is the relatively short CC bond in **3** (150 pm, table 1), which can be explained by assum-

ing sp^2–sp^5 hybridization for the ring carbon atom. The increase in s character of the hybrid orbitals responsible for bonding with the methyl groups leads to strengthening of the CC bond [22] $^{\sharp}$.

Although the changes in geometry caused by methyl substitution of **2** are relatively small, its (thermodynamic) stability increases. This can be seen by considering the energy change for the isodesmic reaction ††

$$3 + 2\, CH_4 \rightarrow 2 + 2\, C_2H_6 ,$$

which is 21 kcal/mol (HF/4-31G: 20.3 kcal/mol; MP2/6-31G*: 21.4 kcal/mol). Relevant energy data for the compounds $(CH_3)_2CX_2$ with electronegative X (X = F, OR, Cl) [24] suggest that the major part of this stabilization is due to the electron donor character of the two methyl groups releasing electron density at the (positively charged) tetrasubstituted carbon atom. A smaller part of the isodesmic stabilization energy of **3** (about 2 kcal/mol per CC bond) stems from CC bond strengthening (vide infra) as

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$^{\sharp}$ For hybrid orbitals in three-membered rings, see ref. [23].

†† Energies of CH_4 and C_2H_6 are: −40.13977 and −79.11593 hartree (HF/4-31G); −40.33704 and −79.50397 hartree (MP2/6-31G*).

Table 1
Theoretical energies and geometries of dioxirane (**2**) and dimethyldioxirane (**3**) (see fig. 1)

Molecule	Parameter [a]	HF/4-31G	MP2/6-31G* [b]	Exp. [c]
2	energy	−188.31235	−189.10781	
	$R(OO)$	153.5	152.9	151.6
	$R(CO)$	141.0	139.8	138.8
	$R(CH)$	106.7	108.9	109.0
	∠HCH	117.6	116.6	117.3
3	energy	−266.29708	−267.47572	
	$R(OO)$	153.2	152.1	
	$R(CO)$	142.1	141.7	
	$R(CC)$	149.3	150.3	
	$R(CH_i)$	107.8	108.1*	
	$R(CH_o)$	108.2	108.5*	
	∠CCC	119.2	121.3	
	∠CCH$_i$	109.6	109.6*	
	∠CCH$_o$	110.2	110.2*	
	∠H$_o$CH$_o$	108.5	108.2*	

[a] Energies in hartree, distances in pm, angles in deg. The subscripts i and o denote inwardly directed ($\tau(H_iCCC) = 180°$) and outwardly directed CH bonds.

[b] Values for **2** are from ref. [9]. The geometry of **3** has been partially optimized at the MP2 level. Starred parameters have been obtained at the HF/6-31G* level [17].
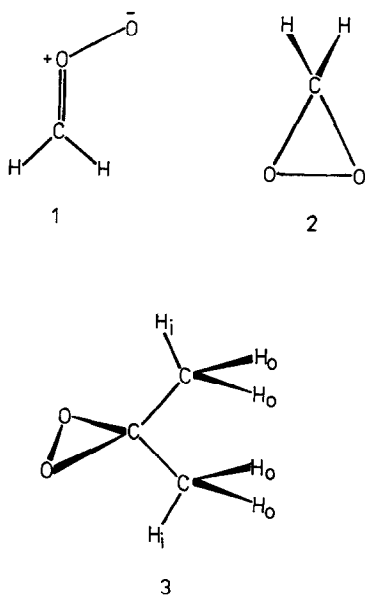
Fig. 1. The structures of 1, 2 and 3.

can be deduced from the isodesmic reaction energy of dimethylcyclopropane [25].

Although methyl or alkyl substitution of 2 leads to an increase in stability, calculated energies do not necessarily imply that 3 is also kinetically more stable than 2. The kinetic stability of 3 largely depends on the ease of O–O bond rupture and the subsequent decomposition or rearrangement of dioxirane [7]. According to the calculated O–O bond lengths of 2 and 3 (table 1) methyl substitution does not induce any significant O–O bond strengthening. Analysis of the electron density distribution in the O–O bonding

region reveals that both O–O bonds are relatively weak, probably because of ring strain and destabilizing lone-pair–lone-pair repulsions.

While the calculated energies and geometries provide only indirect evidence for the existence of 3 as a possibly long-lived intermediate in the peroxymonosulfate–acetone system, the theoretical NMR chemical shifts can be directly compared with the relevant data published by MJ [7]. Since ^{1}H chemical shifts[‡] depend more strongly than ^{13}C shifts on temperature, medium, and other external factors, we confine ourselves to discussing only the latter. As can be seen from the values obtained for acetone (table 2), calculated ^{13}C shifts are reliable within 10 ppm.

According to theory the C atom of 2 resonates at 83 ppm (basis II, table 2). On going from 2 to 3 this signal moves downfield by 10–15 ppm which is typical of methyl substitution [26]. At the same time, the signal from the methyl carbon atoms shifts 5–10 ppm upfield relative to the corresponding signal in acetone. The calculated ^{13}C chemical shift of the ring carbons of 2 and 3 is in line with shifts observed for carbon bonded to two oxygen atoms (see, e.g., $H_2C^*(OCH_3)_2$: 109.9 ppm; $(CH_3)_2C^*(OCH_3)_2$: 99.9 ppm; C2 in 1,3-dioxane: 94.8 ppm, and 1,3-dioxolane: 95.0 ppm [20]). The ^{13}C shift of 2 is almost identical with the experimental value for 1,2-dioxetane (76.14 ppm) reported by Adam and Baader [8]. The resonance signal observed by MJ [7] appears more than 100 ppm downfield, in a range that is typ-

‡ The calculated ^{1}H chemical shifts (basis II) of 3 are: 0.31 ppm (H_i) and 0.73 ppm (H_o). MJ report a value of 1.65 ppm [7].

Table 2
^{13}C NMR chemical shifts relative to TMS [a]

Molecule [b]	Carbon	Basis I	Basis II	Exp. [c]
acetone	CH_3	25.6	23.5	30.7
	CO	212.0	209.7	206.7
1	CH_2	247.8	227.0	
2	CH_2	76.5	82.6	
3	CH_3	16.3	17.0	22.72
	C	84.1	99.2	214.04

[a] Chemical shifts in ppm.
[b] Experimental geometries have been used for acetone: ref. [21] and 2: refs. [4,5]. Geometry of 1: MP2/6-31G*: ref. [9]. Geometry of 3: this work.
[c] Experimental values for acetone from ref. [20]. Shift values of 3: this work.

ical of the carbonyl C of acetone dissolved in a medium with a relatively large dielectric constant [27]. In the same region, about 20 ppm downfield, the ^{13}C chemical shift of **1** is expected to be seen (table 2). However, in view of the low thermodynamic and kinetic stability of **1** [9,10,13], the presence of alkyl carbonyl oxide in the reaction mixture investigated by MJ can be excluded.

The ^{13}C chemical shifts observed by MJ cannot belong to **3**. Experimental efforts should be aimed at investigating the ^{13}C NMR spectrum at 100 ppm and beyond 100 ppm in order to account for a downfield shift due to solvent effects. However, an unequivocal identification of **3** might be difficult since the ring carbons of acetone diperoxide resonate in the same region (102 ppm [7]). Alternatively, ^{17}O NMR shifts may be investigated. The calculated gas phase values relative to H_2O at 0 K are: 820 ppm (CO*, **1**), 770 ppm (OO*, **1**), 250 ppm (**2**), 330 ppm (**3**), and 680 ppm (acetone). As is well known [28], experimental ^{17}O shifts exhibit large gas-to-liquid and solvent shifts. In addition, they are strongly temperature dependent. This may lead to deviations of up to 100 ppm between theory and experiment. Nevertheless, theory does suggest that ^{17}O shifts should facilitate the identification of **3**.

In conclusion we stress that our results do not exclude the possibility that **3** is formed in the peroxymonosulfate–acetone system. The formation of **3** is likely in view of the increase in (thermodynamic) stability caused by dimethyl substitution of **2**. However, a low concentration of **3**, the solvent (acetone), and the presence of other peroxidic compounds in the reaction medium may affect the recording of the ^{13}C NMR spectrum of **3** [++]. The NMR spectroscopic identification of **3** should be assisted by the ab initio shift values presented in this work.

Acknowledgement

[++] Recent NMR spectroscopic measurements suggest that the ^{13}C signal at 214 ppm does not belong to **3** [29].

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