J. Am. Chem. Soc. **1986**, *108*, 1027–1032

downward distillation. A solution of ethyl *N*-nitroso-*N*-ethyl-*1,1*-d_2-carbamate (2 g, 13 mmol) in 20 mL of ether was added over 5 min. Fresh portions of ether were added until the distillate came over colorless. The orange solution of diazoethane-*1*-*d* in ether was cooled to −80 °C and transferred to a pressure bottle containing a large excess of allene (50 mL) at −80 °C. After a few hours at room temperature, the color disappeared and the reaction mixture was worked up as described previously;[31] 0.55 g (42% yield based on carbamate); ^{1}H NMR ($CDCl_3$) δ 1.49 (t, 3 H), 4.88 (half AB q, $J = 21$ Hz, 1 H), 5.04 (m, 1 H), 5.12 (m, 1 H), 5.02 (half AB q, $J = 21$ Hz, 1 H), 99% isotopic purity.

3-Methyl-4-methylene-*d*$_2$-1-pyrazoline-*5,5*-*d*$_2$ (13) was prepared as described previously[31] by the 1,3-dipolar addition of diazoethane[30] to allene-d_4:[26] ^{1}H NMR ($CDCl_3$) δ 1.51 (d, 3 H), 4.82 (q, 1 H), 99 ± 1% isotopic purity.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support for this research. We thank the University of Alberta Mass Spectrometry Laboratory and the NMR Facility for the spectra they measured.

Registry No. 2, 55503-95-2; **3**, 67301-35-3; **4**, 55503-94-1; **11**, 99810-34-1; **12**, 99810-35-2; **13**, 99810-36-3; **14**, 99810-37-4; **15**, 99810-38-5; **16**, 99810-39-6; **17**, 99810-40-9; **18**, 83846-54-2; *exo*-**19**, 99810-41-0; *endo*-**19**, 99810-58-9; *exo*-**20**, 99810-42-1; *endo*-**20**, 99810-59-0; **20** (unlabeled derivative), 99810-60-3; **21**, 99810-43-2; **21** (1,3-diol), 99810-61-4; **22**, 99810-44-3; **22** (3-oxo derivative), 98069-71-7; **23**, 99810-45-4; **24**, 99810-46-5; **24**-d_2, 99810-64-7; **25**, 99810-47-6; **26**, 99810-48-7; **27**, 99810-49-8; **28**, 99810-50-1; **28** (unlabeled derivative), 62872-93-9; **29**, 99810-51-2; **30**, 99810-52-3; **31**, 99810-53-4; **32**, 99810-54-5; **33**, 99829-05-7; **33** (unlabeled derivative), 99810-69-2; **34**, 99810-55-6; **34** (unlabeled derivative), 99829-06-8; **35**, 99810-56-7; **36**, 99810-57-8; $Me_2C{=}CHCO_2Me$, 924-50-5; $ClCO_2Me$, 79-22-1; $Ph_3P{=}CH_2$, 3487-44-3; $MeC({=}N_2)Me$, 2684-60-8; $D_2C{=}C{=}CD_2$, 1482-85-5; MeCHO, 75-07-0; $MeCH(OH)C({=}CH_2)CD_2OH$, 99810-65-8; $MeCH(OH)C({=}CH_2)CH_2OH$, 99810-66-9; $ClCH_2O(CH_2)_2OMe$, 3970-21-6; 2-$O_2NC_6H_4SeCN$, 51694-22-5; $MeCD_2NHCO_2Et$, 99810-70-5; MeCN, 75-05-8; $ClCO_2Et$, 541-41-3; $EtO_2CN(CD_2Me)NO$, 99810-71-6; $H_2C{=}C{=}CH_2$, 463-49-0; $N_2{=}CH_2Me$, 1117-96-0; $EtO_2C(NH_2)_2CO_2Et$, 4114-28-7; cyclopentadiene, 542-92-7; 1,2-dicarbethoxy-4-isopropylidenepyrazolidine-*5,5*-d_2, 99810-62-5; 4-isopropylidenepyrazolidine-*5,5*-d_2 hydrochloride, 99810-63-6; 5-carbomethoxy-2-norbornene, 6203-08-3; norbornenyl β-hydroxymethoxyethoxymethyl ether-β,β-d_2, 99810-67-0; norbornenyl β-hydroxymethoxyethoxymethyl ether, 99810-68-1; 1-methyl-2-methylenecyclopropane-d_2, 99829-07-9; ethylenecyclopropane-d_2, 99829-08-0; 1,1-dimethyl-2-ethylidenecyclopropane-d_2, 99829-09-1; isopropylenecyclopropane-d_2, 99829-10-4; 1,1-dimethyl-2-(methylene-d_2)cyclopropane, 99810-72-7; 1-methyl-2-(methylene-d_2)cyclopropane, 67399-01-3.

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Dioxetane Radical Cations in Solution. An ESR and Cyclic Voltammetry Study

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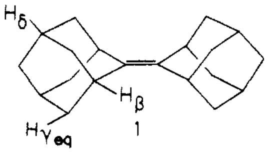
Abstract: The radical cation formed upon electrochemical oxidation either of adamantylideneadamantane **1** in an O_2-saturated solution or of the corresponding dioxetane **2** is shown by ESR spectroscopy to be $\mathbf{2}^+$. This radical cation is relatively long-lived in CH_2Cl_2:CF_3CO_2H:$(CF_3CO)_2O$ solvent mixtures at low temperatures. The resolved hyperfine splittings are 0.325 mT (4 H) and 0.075 mT (6 H). Using deuterated derivatives, the larger splitting has been assigned to two pairs of γ_{eq}-protons and the smaller one to the two remaining pairs of γ_{eq}-protons and one pair of β-protons, with each β-proton situated in a different adamantylidene moiety of $\mathbf{2}^+$ (the notation β and γ_{eq} refers to the structure of **1**). These data are consistent with a C_2 conformation of $\mathbf{2}^+$ which is twisted at the dioxetane ring and does not enantiomerize on the hyperfine time scale at −110 °C. Dioxetane radical cations $\mathbf{11}^+$ and $\mathbf{13}^+$ generated from isopropylideneadamantane **10** and 3-pentylideneadamantane **12**, respectively, have also been studied under similar conditions by ESR spectroscopy. Their hyperfine data give no evidence of twisting at the dioxetane rings and provide a further example for the sensitivity of the long-range splittings to orientation of bonds relative to the spin-bearing orbital. Cyclic voltammograms indicate that the $E°'$ value for **2** is 0.66 V anodic of **1** at −78 °C, so that electron transfer from **1** to $\mathbf{2}^+$ is exothermic by 15 kcal/mol.

In his review of the radical aspects of photooxygenation, Bartlett[1] reported an unpublished observation with M. J. Shapiro that $(p\text{-}BrC_6H_4)_3N^+$ converts adamantylideneadamantane **1** and $^3O_2$ to dioxetane **2**, pointing out the similarity of this reaction to the formation of endoperoxides from dienes, as described by Barton and co-workers.[2] He suggested[1] that both reactions proceed through the organic radical cation. In the same year, Haynes and co-workers,[3] as well as Tang and co-workers,[4] also argued for the intermediacy of diene radical cations in the conversion of dienes to endoperoxides. Later on, Nelsen and Akaba[5] reported the catalytic conversion of **1** to **2** by $(p\text{-}BrC_6H_4)_3N^+$, a reaction similar to those observed previously for the dienes.[2-4] Simultaneously, with Clennan and co-workers,[6] these authors[5] found that elec-



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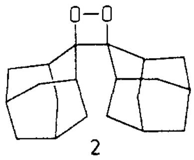

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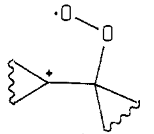
Table I. Cyclic Voltammetry for **1** and **2**[a]

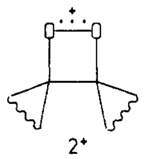
compd	atm[b]	temp, °C	scan rate, V/s	first wave,[c] V	second wave,[c] V
1	N_2	22	0.05	$E°'$ 1.62[.06]	E_p^{ox} 2.25
1	N_2	22	0.50	$E°'$ 1.62[.06]	E_p^{ox} 2.30
1	N_2	−78	0.05	$E°'$ 1.59[.07]	E_p^{ox} 2.31
1	N_2	−78	0.50	$E°'$ 1.59[.10]	E_p^{ox} 2.38
1	O_2	22	0.05	E_p^{ox} 1.56	E_p^{ox} 2.19
1	O_2	22	0.50	E_p^{ox} 1.61	E_p^{ox} 2.26
1	O_2	−78	0.05	E_p^{ox} 1.55	$E°'$ 2.25 [0.14]
1	O_2	−78	0.50	E_p^{ox} 1.60	$E°'$ 2.27 [0.26]
2	O_2	−78	0.20		$E°'$ 2.25 [0.15]
2	O_2	−78	2.0		$E°'$ 2.27 [0.22]

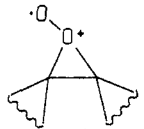
[a] 20:1:1 $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ containing 0.1 M n-Bu_4NBF_4. Pt electrode, reported vs. sce. [b] Solution saturated with the gas specified. [c] $E°'$ values given are $(E_p^{ox} + E_p^{red})/2$; numbers in brackets are $E_p^{ox} - E_p^{red}$.

trochemically generated radical cation $\mathbf{1}^+$ reacts rapidly enough with $^3O_2$ to show decreased oxidation current by cyclic voltammetry, whereby an $\overleftarrow{E}C\overrightarrow{E}$ CV wave[7] is observed. In addition, Ando and co-workers[8] studied the electrochemically catalyzed formation of dioxetane from **1** and some other olefins. The stereochemistry of this reaction, which proceeds via olefin radical cations and involves an addition of $^3O_2$, was compared to that of the reactions of olefins with $^1O_2$ and of olefin radical cations with superoxide.

Observation of $\overleftarrow{E}C\overrightarrow{E}$ electrochemistry shows that $\mathbf{1}^+$ reacts with $^3O_2$ to give a more powerful oxidant than $\mathbf{1}^+$, but it does not indicate the structure of the oxidant. Addition of O_2 to $\mathbf{1}^+$ could occur by formation of two C–O bonds, each between one C and one O atom, thus producing the dioxetane radical cation $\mathbf{2}^+$.


3^+


2^+


4^+

Alternatively, only one O atom might be bonded to either one or two C atoms so that the resulting species would be the peroxy cation $\mathbf{3}^+$ or the perepoxide radical cation $\mathbf{4}^+$, respectively.

In the present work, using a combination of cyclic voltammetry and ESR spectroscopy, we demonstrate that it is the dioxetane radical cation $\mathbf{2}^+$ which builds up in solution at a sufficiently high oxidation potential.

Results and Discussion

Cyclic Voltammetry. As previously reported,[9] the cyclic voltammogram of **1** under a N_2 atmosphere shows two oxidation waves. The first of them, for $\mathbf{1},\mathbf{1}^+$ electron transfer, is reversible, while the second one at a higher potential is totally irreversible. With the solvent methylene chloride (0.5 V/s scan rate), the E_p^{ox} value for the second wave was 0.34 V positive of the $E°'$ value for the first one. The second wave remains irreversible in the presence of acid, but it moves anodically relative to the reversible first-oxidation wave, a finding which suggests that a proton loss is coupled with removal of the second electron. The acid solvent employed was a 20:1:1 mixture (per volume) of $CH_2Cl_2:CF_3CO_2H:(CF_3CO)_2O$; its use allows a scan out to ca. 2.8 V vs. sce, before a substantial oxidation current is observed in a blank. However, we have now found that **1** is unstable in this solvent mixture if n-Bu_4NClO_4 serves for the supporting electrolyte as was the case in the previous work.[5,9] After standing for 4 h, the intensity of the peak current for the $\mathbf{1},\mathbf{1}^+$ oxidation wave dropped to half of its initial value, presumably by a reaction of **1** with $HClO_4$. A similar sensitivity of **1** to acid has also been noted by Akaba et al.[10] In the present work, the decay of **1** was avoided by replacing n-Bu_4NClO_4 by n-Bu_4NBF_4 as the supporting electrolyte and by using freshly prepared solutions after a minimum standing time.

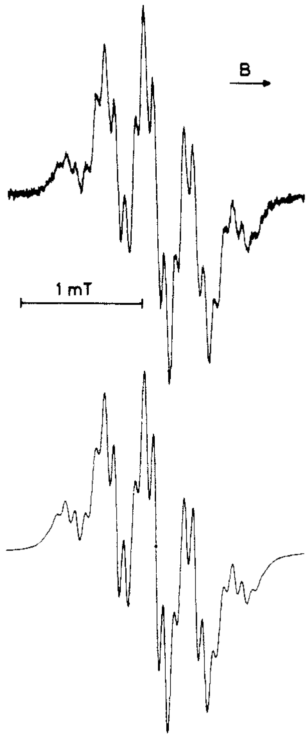


Figure 1. ESR spectrum of X^+ (top) and its computer simulation (bottom). Starting material, adamantylideneadamantane **1**. Experimental conditions: solvent mixture, 10:1:1 (per volume) of $CH_2Cl_2:CF_3CO_2H:(CF_3CO)_2O$, saturated with O_2; counterion, $CF_3CO_2^-$; temp, −110 °C; calculated derivative curve, hyperfine pattern [4L, 6S] (see text); line shape, Lorentzian; line width, 0.06 mT.

When the 20:1:1 solvent mixture is saturated with O_2, an $\overleftarrow{E}C\overrightarrow{E}$ wave appears near the first $\mathbf{1},\mathbf{1}^+$ oxidation wave, while the second wave occurs at a potential close to that observed for **1** under N_2 (Table I). At room temperature, this second wave is still totally irreversible, but in contrast to its behavior in the former experiment under N_2, it exhibits some reversibility below −30 °C. At −78 °C, the wave appears chemically reversible, although the large peak-to-peak separation indicates a slow electron transfer.

A similar behavior to that observed for the second wave of **1** with O_2, i.e., irreversibility at room temperature but chemical reversibility at low temperatures, is also exhibited upon oxidation of the dioxetane **2** in the 20:1:1 solvent mixture (Table I).[11] This finding strongly suggests that the same radical cation is formed in both cases. The electrochemical data require that the cation in question converts into **2** upon an uptake of an electron. We shall denote it as X^+ where X^+ might be $\mathbf{2}^+$, $\mathbf{3}^+$, or $\mathbf{4}^+$. Since X^+ is long-lived at low temperature, we expect that it can be characterized by ESR spectroscopy. As will be shown below, this expectation is borne out by experiment.

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(11) Large peak-to-peak separation, due to a slow electron transfer, has also been found for five-and six-membered ring dialkyl peroxides which yield long-lived radical cations at room temperature.[22]

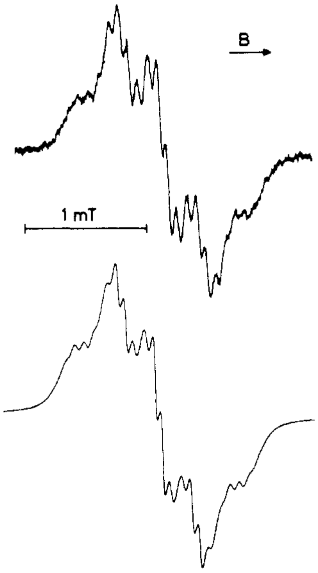
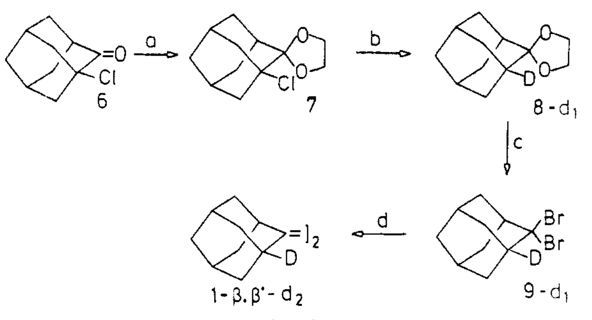


Figure 2. ESR spectrum of X-d_1^+ (top) and its computer simulation (bottom). Starting material **1**-γ_{eq}-d_1. Experimental conditions as for the spectrum in Figure 1. Calculated derivative curve: hyperfine pattern 45:45:10, [3*L*, 6*S*, 1*L*′]:[4*L*, 5*S*, 1*S*′]:[4*L*, 6*S*] (see text); line shape, Lorentzian; line width, 0.06 mT.

ESR Spectra. Figure 1 shows the ESR spectrum of X$^+$ observed upon electrochemical oxidation of **1** in a 10:1:1 mixture (per volume) of CH_2Cl_2:CF_3CO_2H:$(CF_3CO)_2O$, saturated with O_2, at −110 °C. The cylindrical electrolytic cell contained a gold helical anode and a platinum wire cathode along the axis.[12] Except for saturation with O_2 and a higher oxidation potential, the conditions were thus the same as for the generation of **1**$^+$ from **1** in a previous ESR study.[13] The spectrum of X$^+$ is also observed in an O_2-free 10:1:1 solvent mixture with the dioxetane **2** as the starting material. The *g* factor of X$^+$ is 2.0099 ± 0.0002, and as demonstrated by a computer simulation (Figure 1), its hyperfine pattern is perfectly reproduced with the use of the coupling constants of 0.325 ± 0.005 mT for four protons and 0.075 ± 0.005 mT for six protons. These two resolved hyperfine splittings will be referred to as *L* (larger) and *S* (smaller), respectively. The hyperfine pattern of X$^+$ is thus described by [4*L*, 6*S*], with only 10 out of 28 protons exhibiting observable coupling constants. It is essential to note that the occurrence of a 6*S* splitting rules out C_{2v} symmetry which requires four equivalent protons in every set. The hyperfine pattern [4*L*, 6*S*] must be interpreted as [2 × 2*L*, 3 × 2*S*]; i.e., it arises from five pairs of equivalent protons, thus being consistent with C_2 or C_s symmetry. The finding that some of these pairs (two and three, respectively) have apparently the same coupling constants is due to the limits of experimental resolution.

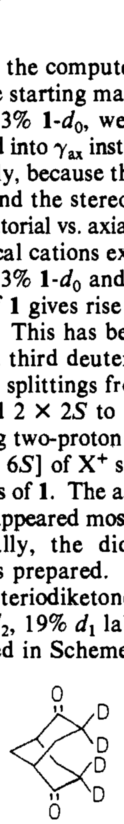
The ESR spectrum of X$^+$ (Figure 1) remains unchanged when the electrochemical oxidation in an O_2-saturated 10:1:1 solvent mixture is carried out on dideuterioadamantylideneadamantane *1*-δ,δ'-d_2, available from the previous work.[13] None of the four δ-protons of **1** is thus responsible for either splitting, *L* or *S*. By contrast, the [4*L*, 6*S*] pattern of X$^+$ is modified when the same procedure is applied to the monodeuterio derivative **1**-γ_{eq}-d_1, also prepared previously.[13] The pertinent ESR spectrum of X-d_1^+, presented in Figure 2, can be fitted by using a 50:50 mixture of hyperfine patterns [3*L*, 6*S*, 1*L*′]:[4*L*, 5*S*, 1*S*′], where $L' = 0.1535L = 0.050$ mT and $S' = 0.1535S = 0.012$ mT are deuteron splittings. Consequently, all eight γ_{eq}-protons of **1** must give rise to observable coupling constants, 2 × 2*L* and 2 × 2*S*. The agreement between the experimental and calculated spectra is significantly improved if ca. 10% of apparently undeuterated material (**1**-d_0) is accounted for, i.e., if a 45:45:10 mixing of [3*L*, 6*S*, 1*L*′]:[4*L*, 5*S*, 1*S*′]:[4*L*, 6*S*] is taken as a basis for the computer simulation (Figure 2). Since a MS analysis of the starting material gave **1**-γ-d_1, where $\gamma = \gamma_{eq} + \gamma_{ax}$, and only 3% **1**-$d_0$, we suppose that ca. 7% of deuterium was incorporated into γ_{ax} instead of γ_{eq} positions. Such a distribution is not unlikely, because the preparation of **1**-γ_{eq}-d_1 proceeds via a γ-radical and the stereochemistry is determined by the selectivity of an equatorial vs. axial deuterium transfer from *n*-Bu_3SnD. The 10% radical cations exhibiting the pattern [4*L*, 6*S*] might thus be due to 3% **1**-d_0 and ca. 7% **1**-γ_{ax}-d_1, if none of the eight γ_{ax}-protons of **1** gives rise to a resolved splitting in the ESR spectrum of X$^+$. This has been proven to be actually the case by the study of a third deuterated derivative.

Scheme I



^{a}$(HOCH_2)_2$, TsOH (51%). ^{b}Na^0, *t*-BuOD, THF (93%). ^{c}PBr_5 (88%). ^{d} Mg^0, Et_2O (83%).

The absence of resolved splittings from the δ-protons and the assignment of 2 × 2*L* and 2 × 2*S* to four pairs of γ_{eq}-protons requires that the remaining two-proton coupling constant, 2*S*, in the hyperfine pattern [4*L*, 6*S*] of X$^+$ should belong to a pair of either β- or γ_{ax}- or ϵ-protons of **1**. The assignment of this coupling constant to two β-protons appeared most reasonable, and in order to verify it experimentally, the dideuterioadamantylideneadamantane **1**-β,β'-d_2 was prepared. After having found that conversion of the tetradeuteriodiketone **5**-d_4 to adamantanone-β,β-d_2 yielded only 81% d_2, 19% d_1 labeled adamantanone, we followed the route depicted in Scheme I.



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This route started from 1-chloro-2-adamantanone (6) which was prepared by the method of Hiršl-Starčević and Majerski.[14] It proceeded via the ketal **7**, its conversion to **8**-d_1[15] (analysis by MS: 98% **8**-d_1 and 2% **8**-d_0), dibromination to **9**-d_1, and coupling to **1**-β,β'-d_2.[16] The final product contained one deuterium in each adamantylidene moiety (analysis by MS: 96% **1**-β,β'-d_2 and 4% **1**-β-d_1).

Electrochemical oxidation of **1**-β,β'-d_2 in an O_2-free 10:1:1 solvent mixture of $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ yields the radical cation **1**-β,β'-d_2^+, the ESR spectrum of which justifies our previous assignment of the coupling constant of 0.058 mT to four equivalent β-protons in **1**$^+$.[13] When the oxidation of **1**-β,β'-d_2 is performed in an O_2-saturated solution and at a higher potential, it leads to the dideuterated radical cation X-d_2^+, exhibiting the ESR spectrum shown in Figure 3. This spectrum is fitted by a computer simulation (Figure 3) which makes use of a 50:25:25 mixture of [4*L*, 5*S*, 1*S*′]:[4*L*, 4*S*, 2*S*′]:[4*L*, 6*S*], where $S' = 0.1535S = 0.012$ mT stands again for a deuteron splitting. Such a hyperfine pattern is consistent with two out of four β-protons having the coupling constant *S*.

The resulting assignments of the resolved hyperfine splittings for X$^+$ are thus as follows: 0.325 mT (*L*) to two pairs of γ_{eq}-

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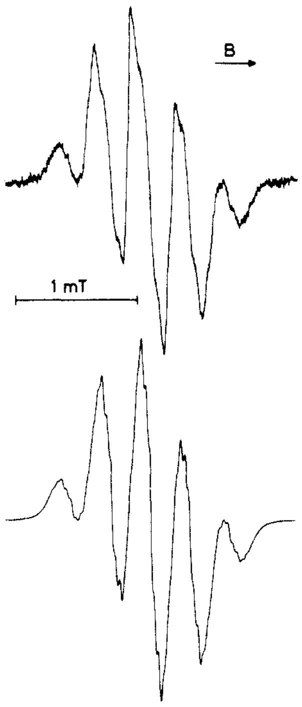


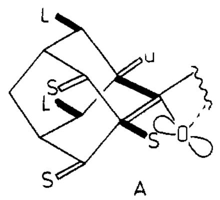
Figure 3. ESR spectrum of X-d_2^+ (top) and its computer simulation (bottom). Starting material: **1**-β,β'-d_2. Experimental conditions as for the spectrum in Figure 1. Calculated derivative curve: hyperfine pattern 50:25:25, [4*L*, 5*S*, 1*S'*];[4*L*, 4*S*, 2*S'*]:[4*L*, 6*S*] (see text); line shape, Lorentzian; line width, 0.05 mT.

protons and 0.075 mT (*S*) to two remaining pairs of γ_{eq}-protons and to one pair of β-protons, whereby each of the two β-protons must be situated in a different adamantylidene moiety. The splittings from the second pair of β-protons, the 4 pairs of γ_{ax}-protons, the 2 pairs of δ-protons, and the 2 pairs of ϵ-protons are too small to be resolved, a nonsurprising result, in view of the complexity of the hyperfine interaction with as many as 14 pairs of protons.

The hyperfine data for X^+ are fully compatible with those expected for the dioxetane radical cation $\mathbf{2}^+$ in a twisted conformation of C_2 symmetry which has been found for the neutral dioxetane **2** by an X-ray crystallographic structure analysis.[18] The twisting at the dioxetane ring in **2** relieves the serious steric hindrance arising from two pairs of γ_{ax}-protons in the eclipsed form of C_{2v} symmetry. This form presumably represents an intermediate between two equivalent twisted conformations and it lies energetically high enough to freeze $\mathbf{2}^+$ on the hyperfine time scale at −110 °C. The alternating line-width effect expected as the twisted forms interconvert more rapidly was not observed below −80 °C, and decomposition of $\mathbf{2}^+$ precluded going to higher temperatures.

The structure $\mathbf{3}^+$ of the peroxide radical cation, with two nonequivalent adamantylidene moieties, is excluded by the finding that each of the two equivalent β-protons having the coupling constant of 0.075 mT (*S*) is situated in a different moiety. An equilibration between two structures $\mathbf{3}^+$ would lead to equivalence of the two moieties if it were fast enough on the hyperfine time scale at a temperature as low as −110 °C. However, such an equilibration, which is unlikely to occur under the conditions of our experiment, would manifest itself in δ-proton coupling constants exceeding by far those observed for X^+. Also, the structure $\mathbf{4}^+$ of the perepoxide radical cation seems incompatible with the experimental data for X^+, since separation of the γ_{eq}-protons by five bonds from the radical center precludes hyperfine splittings of 0.325 mT.

Attributing the ESR spectrum of X^+ to the dioxetane radical cation $\mathbf{2}^+$ in a twisted C_2 conformation, we are confronted with the problem of assigning the resolved 2 × 2*L* and 2 × 2*S* splittings to four specific pairs of γ_{eq}-protons and the 2*S* splitting to one of the two pairs of β-protons. In this respect, it is important to note that on twisting the dioxetane ring in $\mathbf{2}^+$, half of the C_α–C_β and C_γ–H_{eq} bonds in each adamantylidene moiety become almost parallel to the 2p axis of the spin-bearing AO at the O atom. Such an arrangement is demonstrated by the structure A of $\mathbf{2}^+$.

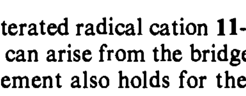


A

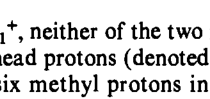
L = large (0.325 mT)
S = small (0.075 mT)
u = unresolved

In A, the bonds aligned with the 2p axis are filled in black, whereas their nonaligned counterparts are unfilled. Since the spin population is expected to be transferred from the oxygen 2p AO to the hydrogen 1s AO's through the "filled-in" bonds, we proposed that the 2 × 2*L* splittings (0.325 mT) should be assigned to the two pairs of γ_{eq}-protons at such C_γ–$H_{\gamma_{eq}}$ bonds, leaving the 2 × *S* splittings (0.075 mT) for the two pairs of γ_{eq}-protons at the "unfilled" C_γ–$H_{\gamma_{eq}}$ bonds. Analogously, the resolved 2*S* splitting, due to β-protons, is assigned to the pair of protons at the "filled-in" C_β–H_β bonds; i.e., the splitting from the other pair of β-protons at the "unfilled" C_β–H_β is assumed to be too small to be resolved. An experimental test of these assignments requires the synthesis of specifically double-labeled deuterioderivatives of **1** as the starting material; such a synthesis can hardly be carried out at present.

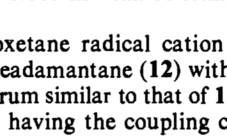
In addition to $\mathbf{2}^+$, we have studied the ESR spectra of the radical cations obtained from O_2 adducts of monoolefins in which one adamantylidene moiety is replaced by an alkylidene group. Electrochemical oxidation of isopropylideneadamantane **10** in an O_2-saturated 20:1:1 mixture of CH_2Cl_2:CF_3CO_2H:$(CF_3CO)_2O$, at −90 °C, yields the same radical cation as an analogous oxidation of the dioxetane **11**[17] in an O_2-free solution. The ESR spectrum, attributed to $\mathbf{11}^+$, exhibits two hyperfine splittings of 0.285 ± 0.005 and 0.085 ± 0.005 mT, each for two protons ($g = 2.0092 \pm 0.0002$). Since an identical spectrum was observed for the monodeuterated radical cation **11**-d_1^+, neither of the two resolved splittings can arise from the bridgehead protons (denoted β in **1**). This statement also holds for the six methyl protons in $\mathbf{11}^+$, as proven by the ESR spectrum of **11**-d_6^+. From the substantial narrowing of lines on going from $\mathbf{11}^+$ to **11**-d_6^+, a coupling constant of 0.025 ± 0.005 mT can be estimated for the six methyl protons in $\mathbf{11}^+$.



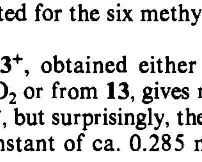
11-d_6



11-d_1



10



11

The dioxetane radical cation $\mathbf{13}^+$, obtained either from 3-pentylideneadamantane (**12**) with O_2 or from **13**, gives rise to an ESR spectrum similar to that of $\mathbf{11}^+$, but surprisingly, the number of protons having the coupling constant of ca. 0.285 mT is increased from two to three.

In the spectrum of **13**-d_4^+, with **12**-d_4 as the starting material, the splitting from the third proton is no longer observable. Thus, it is (only) one of the four methylene protons in the two ethyl substituents which exhibits a relatively strong hyperfine interaction. This finding indicates that the rotation of the ethyl groups is frozen on the hyperfine time scale at −90 °C, rendering the four meth-

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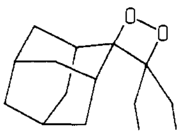
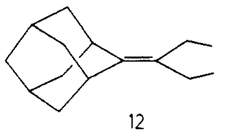
[17] Nelsen, S. F.; Kapp, D. L.; Teasley, M. F. *J. Org. Chem.* **1984**, *49*, 579.

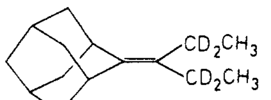
[18] Numan, H.; Wieringa, J. H.; Wynberg, H.; Hess, J.; Vos, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591.



13



12



12 -d4

ylene protons nonequivalent in the preferred conformation. The hyperfine splittings from such protons (γ to O atom) must be very sensitive to the orientation of the bonds relative to the 2p axis at the O atom, because the (estimated) coupling constant of the corresponding six protons in the free-rotating methyl groups of **11**$^+$ (0.025 mT) is lower than that observed for one methylene proton in **13**$^+$ (0.285 mT) by an order of magnitude.

The hyperfine data and g factors for the dioxetane radical cations **2**$^+$, **11**$^+$, and **13**$^+$ are summarized in Table II. A feature common to **11**$^+$ and **13**$^+$ is the presence of two coupling constants of 0.285 and 0.085 mT, both undoubtedly due to pairs of protons in the adamantylidene moiety. Since the findings for **11**-$d_1$$^+$ rule out the assignment to β-protons, those giving rise to the two coupling constants could, in principle, be γ_{eq}-, γ_{ax}-, δ-, and ϵ-protons. Guided by their similarity to the hyperfine data for **2**$^+$ (0.285 vs. 0.325 mT and 0.085 vs. 0.075 mT), it is tempting to assign both values to pairs of γ_{eq}-protons. Such an assignment is, however, by no means secured, since the bonds in the adamantylidene moieties of **11**$^+$ and **13**$^+$ may have an orientation different from that of the corresponding bonds in **2**$^+$ relative to the spin-bearing oxygen 2p AO. There is no evidence that the radical cations **11**$^+$ and **13**$^+$, which lack the steric strain present in **2**$^+$, are twisted at their dioxetane rings under the conditions of our ESR experiment. In particular, the finding that the adamantylidene protons in both radical cations are pairwise equivalent argues against such a twist.

Conclusions

The radical cation X$^+$, obtained by oxidation of either adamantylideneadamantane **1** + O_2 or its dioxetane **2** is **2**$^+$ in a conformation twisted at the dioxetane ring. Similarly, one expects that the oxidized tetraalkyldioxetanes generally exist in solution as the dioxetane radical cations. It is noteworthy that semiempirical calculations, both open-shell MINDO/3 and MNDO, predict the radical cation of the parent ethene perepoxide to be over 30 kcal/mol higher in energy than the corresponding dioxetane radical cation.[19]

The radical cation **2**$^+$ is the probable precursor of **2** in its chain formation from **1**$^+$ and O_2.[17] The electron transfer from **1** to **2**$^+$ is exothermic by 15 kcal/mol (0.66 V, as indicated by the $E^{\circ\prime}$ values at −78 °C), thus providing a strong driving force for the overall conversion of **1** to **2**. The short and long lifetimes of **2**$^+$ at room and low temperatures, respectively, are consistent with the low chain length for oxidative conversion of **1** to **2** at +25 °C and the large increase in such length at −78 °C.[17]

Experimental Section

1-Chloroadamantanone Ethylene Ketal (7). A solution of 1.5 g of 1-chloroadamantanone (8.1 mmol), 1.5 mL of ethylene glycol, and a crystal of *p*-toluenesulfonic acid in 50 mL of benzene was heated at reflux until no more water was removed by azeotropic distillation. The solution was cooled and diluted with diethyl ether. The organic solution was washed with saturated bicarbonate solution, washed with brine, and then dried with $MgSO_4$. The solvents were removed under reduced pressure, and the resultant oil was distilled (120 °C, 0.1 mmHg). The crude ketal was purified by chromatography (5% ethyl acetate/hexane on silica gel) and sublimation to yield 950 mg of white solid (51%), mp 35–36 °C: ^1H NMR ($CDCl_3$) δ 4.2–3.9 (m, 4 H), 2.47 (br s, 1 H), 2.40 (br s, 1 H), 2.0 (m, 7 H), 1.6 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 110.7, 73.4, 66.1, 45.3, 40.3, 35.3, 33.9, 30.6.

Table II. Proton Coupling Constants (in mT), Assignments, and g Factors for the Dioxetane Radical Cations **2**$^+$, **11**$^+$, and **13**$^+$

				g
2$^+$	0.325; 4 H ($2 \times 2H_{\gamma eq}$)	0.075; 6 H ($2 \times 2H_{\gamma eq}$; $2H_{\beta}$[a])		2.0099
11$^+$	0.285; 2 H ($2H_{\gamma eq}$[c])	0.085; 2 H ($2H_{\gamma eq}$[c])	0.025;[b] 6 H ($6H_{methyl}$)	2.0092
13$^+$	0.285; 3 H ($2H_{\gamma eq}$;[c] $1H_{methylene}$)	0.085; 2 H ($2H_{\gamma eq}$[c])		2.0093

[a] Each H_β in different adamantylidene moiety. [b] Estimate of the unresolved splitting (see text). [c] Assignment not secured.

Adamantanone-*1-d*-Ethylene Ketal (8-d_1). To a solution of 440 mg of 1-chloroadamantanone ethylene ketal (1.93 mmol) in 15 mL of dry THF was added 1.5 g of *tert*-butyl alcohol-*O-d* (Aldrich Chemical Co., 98% D, used as received). A piece of freshly cut sodium metal was added (0.23 g), and the mixture was heated to reflux overnight. The slurry was cooled to 0 °C, and the reaction mixture was quenched by the slow addition of 1.5 mL of D_2O. The mixture was poured into diethyl ether, and the organic solution was washed twice with water and once with saturated bicarbonate solution. The solution was dried with $MgSO_4$, and the solvents were removed to yield 350 mg of adamantanone-*1-d* ethylene ketal (93%, used without further purification): ^1H NMR ($CDCl_3$) δ 3.92 (s, 4 H), 1.98 (br s, 2 H), 1.90 (br s, 2 H), 1.73 (br s, 3 H), 1.65 (m, 6 H). Mass spectral analysis shows 98% d_1, 2% d_0.

2,2-Dibromoadamantane-*1-d*. A neat mixture of deuterioketal (330 mg, 1.7 mmol) and PBr_5 was heated to 80 °C for 3 h. The resultant red slurry was quenched by slow addition of 10 mL of water. The residues were partitioned between water and hexane, and the organic solution was washed with water and saturated bicarbonate. The hexane solution was dried with $MgSO_4$ and the solvents were removed under reduced pressure to yield 400 mg of pale-white solid (88%), which was used without further purification: ^1H NMR ($CDCl_3$) δ 2.65–2.50 (m, 5 H), 1.95–1.70 (m, 8 H).

Adamantylideneadamantane-*1,1′/3′-d*$_2$ (1-β,β'-d_2). To a slurry of Mg turnings (0.45 g) in 20 mL of refluxing diethyl ether was slowly added a solution of deuteriodibromide (420 mg, 1.4 mmol) and 1,2-dibromoethane (as initiator, 0.87 g) in 10 mL of diethyl ether. After addition, the solution was refluxed for 12 h. The reaction mixture was cooled to room temperature and quenched by the slow addition of 25 mL of water. The liquids were decanted from the resultant inorganic salts; the solids were washed with pentane and discarded. The combined organic layers were washed with water, saturated bicarbonate solution, and brine. The solution was dried with $MgSO_4$, and the solvents were removed under reduced pressure to yield 160 mg of crude olefin (83%). The powder was sublimed to yield white crystals, mp 162–172 °C. Mass spectral analysis shows 94% d_2, 6% d_1: ^1H NMR ($CDCl_3$) δ 2.90 (br s, 2 H), 1.95–1.60 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 133.1 (C_q), 39.7 (CH_2), 39.6 (CH_2), 37.5 (CH_2), 37.0 (CH/D), 28.7 (CH).

Isopropylideneadamantane-*1-d* (10-d_1). To a solution of adamantanone-*1-d* (50 mg, 0.33 mmol, obtained by hydrolysis of the deuterioketal with 2 N HCl in ethanol) in 8 mL of dry THF at −78 °C was added 4 mL of a 0.11 M solution of isopropyllithium in pentane. The resultant mixture was stirred 30 min at −78 °C and then warmed to room temperature. The reaction was quenched with 1 mL of H_2O. The reaction mixture was partitioned between water and diethyl ether, and the organic layer was washed with water, saturated bicarbonate solution, and brine. The solution was dried with $MgSO_4$, and the solvents were removed under reduced pressure. To the resultant white solid was added 10 mL of 85% H_3PO_4, and the slurry was warmed to 80 °C with stirring for 3 h. The mixture was cooled and poured onto ice. The reaction mixture was washed with pentane, which was backwashed with water and saturated bicarbonate. The solution was dried with $MgSO_4$, and the solvents were removed under reduced pressure to yield 40 mg (68% yield) of isopropylideneadamantane-*1-d*: ^1H NMR ($CDCl_3$) δ 2.88 (br s, 1 H), 2.0–1.6 (m, 12 H), 1.60 (s, 6 H).

Isopropylideneadamantane-*1′,1′,1′,3′,3′,3′-d*$_6$ (10-d_6). To a slurry of $TiCl_3$ (5.74 g, 37.2 mmol) in dimethoxyethane (60 mL) was added in portions 0.9 g of Li wire (freshly etched in methanol) with stirring under argon. The slurry was heated to reflux for 1 h and then cooled to room temperature. A solution of adamantanone (280 mg, 1.86 mmol) and acetone-d_6 (480 mg, 7.44 mmol) in 15 mL of dimethoxyethane was slowly added. The slurry was stirred at room temperature for 1.5 h and at reflux overnight. The slurry was cooled and diluted with pentane and dimethoxyethane. The mixture was twice filtered through Florisil, and the solvents were removed under reduced pressure. The resultant yellow semisolid was sublimed to give a mixture of the desired olefin, adamantylideneadamantane, and 2-adamantanol. The mixture was dissolved in 3 mL of CH_2Cl_2 and allowed to sit for 2 days at room temperature, at

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(19) Chen, C.-C.; Fox, M. A. *J. Comput. Chem.* **1983**, *4*, 488.

which time the adamantanol had precipitated. Evaporation of the mother liquor gives a clear semisolid, which is 80% desired olefin and 20% adamantylideneadamantane. The mixture of olefins was dissolved in 2 mL of methanol and cooled to −78 °C to afford crystals (20 mg) of isopropylideneadamantane-d_6, which was used without further purification.

3-Pentylideneadamantane (12). A solution of *tert*-butyllithium (2 mL, 1.9 M, 3.8 mmol) in pentane was added to 20 mL of diethyl ether at −43 °C. A solution of 2-iodoadamantane (460 mg, 1.75 mmol) in 9 mL of pentane was added, and the solution was stirred for 1 h. The solution was cooled to −78 °C, and 320 mg of 3-pentanone (3.8 mmol) was added dropwise via syringe. The solution was stirred 15 min at −78 °C and then slowly warmed to room temperature. The reaction mixture was washed with water and saturated bicarbonate solution and dried with $MgSO_4$. The solvents were removed by distillation under reduced pressure, and the crude alcohol was treated with 5 mL of 85% H_3PO_4 at room temperature for 18 h. The mixture was poured into ice and extracted with pentane. The pentane solution was washed with water and saturated bicarbonate and dried with $MgSO_4$. The solvents were removed under reduced pressure, and the crude olefin was Kugelrohr distilled to yield 200 mg (56%) of the desired 3-pentylideneadamantane: ^1H NMR ($CDCl_3$) δ 2.78 (br s, 2 H), 1.98 (q, 4 H), 1.9–1.6 (m, 12 H), 0.9 (t, 6 H).

3-Pentanone-*2,2,4,4-d*$_4$. The tetradeuterioketone was prepared by the method of Saunder et al.[20] A mixture of 3-pentanone (17.2 g, 0.1 mol), D_2O (6 mL, 0.3 mol), and K_2CO_3 (50 mg) was heated to reflux for 24 h. The mixture was cooled, and the aqueous layer was removed by pipet. A solution of K_2CO_3 in 6 mL of D_2O was added, and the mixture was heated to reflux for another 24 h. This cycle was repeated 5 times. The ketone was dried with anhydrous K_2CO_3 and distilled to yield approximately 4 g of 3-pentanone-*2,2,4,4-d*$_4$ which was free of H contamination by ^1H NMR.

3-Pentylideneadamantane-*2′,2′,4′,4′-d*$_4$ (12-*d*$_4$). A solution of 2-lithioadamantane was prepared by the method of Wynberg.[21] A solution of *tert*-butyllithium (1.9 M, 4 mL, 7.6 mmol) was added to 40 mL of anhydrous diethyl at −78 °C. A solution of 2-iodoadamantane (905 mg, 3.5 mmol) in 20 mL pentane was added, and the solution was warmed to −45 °C for 1 h. The solution was cooled to −78 °C, and 3-pentanone-*2,2,4,4-d*$_4$ (480 mg, 5.3 mmol) was slowly added via syringe. The solution was stirred 30 min at −78 °C and then slowly warmed to room temperature. The reaction mixture was washed with a saturated bicarbonate solution and dried with $MgSO_4$. The solvents were removed under vacuum, and the crude product was distilled (80 °C, 0.1 mmHg) to give 600 mg (76% yield) of the desired alcohol: ^1H NMR ($CDCl_3$) δ 2.14 (br d, 2 H), 2.08 (br s, 2 H), 1.9–1.5 (m, 10 H), 0.80 (s, 6 H).

A slurry of 200 mg (0.44 mmol) of alcohol in 10 mL of 85% H_3PO_4 was heated to 70 °C for 3 h. The solution was cooled to room temperature and poured onto ice. The aqueous mixture was washed with pentane, which was backwashed with water and saturated bicarbonate solution. The organic solution was dried with $MgSO_4$, and the solvents were removed to give an oil, which was distilled to give 80 mg (43%) of the desired olefin-d_4: ^1H NMR ($CDCl_3$) δ 2.78 (br s, 2 H), 1.9–1.6 (m, 12 H), 0.90 (s, 6 H). Mass spectral analysis shows 97% d_4, 3% d_3.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and also to the Swiss National Science Foundation. D.L.K. thanks Amoco and Wisconsin Alumni Research Foundation for fellowships.

Registry No. 1, 30541-56-1; **1**-*β,β′-d*$_2$, 99810-90-9; **2**, 35544-39-9; **2**$^+$, 99829-61-5; **7**, 99810-87-4; **8**-d_1, 99810-88-5; **10**, 20441-18-3; **10**-d_1, 99810-93-2; **10**-d_6, 99810-94-3; **11**$^+$, 99810-84-1; **11**-d_6^+, 99810-97-6; **12**, 99810-86-3; **12**-d_4, 99810-95-4; **13**$^+$, 99810-85-2; **13**-d_4^+, 99810-98-7; 1-chloroadamantanone, 81315-72-2; 2,2-dibromoadamantane-*1-d*, 99810-89-6; adamantylideneadamantane-*1-d*, 99810-91-0; adamantanone-*1-d*, 99810-92-1; adamantanone, 700-58-3; acetone-d_6, 666-52-4; adamantylideneadamantane, 30541-56-1; 2-adamantanol, 700-57-2; 2-iodoadamantane, 18971-91-0; 3-pentanone, 96-22-0; 3-pentanone-*2,2,4,4-d*$_4$, 6400-97-1; 3-(adamant-2-yl)pentan-3-ol-*2,2,4,4-d*$_4$, 99810-96-5.

Supplementary Material Available: ESR spectra of **11**$^+$, **11**-d_6^+, **13**$^+$, and **13**-d_4^+ and their computer simulations (3 pages). See any current masthead for ordering information.

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Protonated Hydronium Dication, H_4O^{2+}. Hydrogen–Deuterium Exchange of $D_2H^{17}O^+$ in HF:SbF_5 and $DH_2{}^{17}O^+$ in DF:SbF_5 and Theoretical Calculations[1a]

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Abstract: Isotopic hydronium ions $D_2H^{17}O^+$ and $DH_2{}^{17}O^+$ in 1:1 (molar) HF:SbF_5/SO_2 and DF:SbF_5SO_2 solutions, respectively, at −15 °C undergo slow hydrogen–deuterium exchange as monitered by ^{17}O NMR spectroscopy. The rate of such exchange increases with the increase in the acidity of the fluoroantimonic acid medium (1:2 molar composition). The previously observed lack of exchange of isotopic hydronium ions in the somewhat weaker Magic Acid, FSO_3H:SbF_5, medium ($H_0 \approx -21.5$) suggests that in the stronger HF:SbF_5 medium ($H_0 \approx -25$ to -28), the exchange occurs through the intermediacy of protonated hydronium dication. Consequently, the structure and stability of protonated hydronium dication has been probed by ab initio theory. The T_d symmetry structure, **2**, was found to be the minimum energy structure at the HF/6.31G* level. Although **2** at the HF/6.31G* level is thermodynamically unstable (dissociation preferred by 59.2 kcal/mol), it seems to have significant kinetic stability (deprotonation barrier 39.4 kcal/mol).

The existence of protonated water, H_3O^+ (**1**, hydronium ion), was first postulated in 1907.[2] Its preeminent role in acid-catalyzed reactions was first realized from the acid–base theory of Brønsted and Lowry.[3] The evidence for the presence of hydronium ion

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