Characterization of Matrix-Isolated Cyclopropen-3-yl by EPR Spectroscopy[1]

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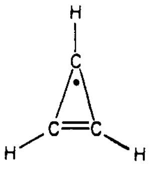
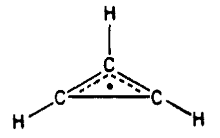
The simplest member of the series of fully conjugated cyclic radicals with the general formula $C_{2n+1}H_{2n+1}$ (n = 1, 2, 3, ...), cyclopropen-3-yl (**1**), has been the subject of much attention by theorists[2] but has not yet been characterized by any spectroscopic method although its presence has been inferred from voltammetric measurements.[3] Several alkyl-substituted derivatives have been detected by ESR[4] and optical spectroscopy[5] showing interesting structural and dynamic properties but attempts to obtain spectra of the parent compound have so far met with failure.[2d,4b,6]

Theoretical work, of which the MO calculations by Chipman and Miller are the most comprehensive,[2i] predicts an ethylenic structure of C_s symmetry (**1a**) as the lowest energy form. The hydrogen atom at the apex of the isoceles triangle is bent substantially out of the ring plane. The allylic structure (**1b**), which satisfies the Jahn–Teller theorem as well as **1a**, is predicted to be ~5 kcal/mol higher in energy. For any structure with less than D_{3h} symmetry the problem of pseudorotation comes into play, raising the question of the barrier height separating the three degenerate minima on the potential surface. Theoretical predictions for this barrier are 3-4 kcal/mol.[2]



1a



1b

In this paper we wish to report the EPR spectrum of **1** as observed in matrix isolation between 20 and 140 K confirming structure **1a** as the lowest energy form. A 10^{-2} molar solution of 3-chlorocyclopropene, carefully purified by GLC, in 11 M aqueous lithium chloride was quickly frozen inside a suprasil EPR tube at 77 K. The sample was then irradiated with γ-rays (1 Mrad) from a cobalt-60 source and transferred to a precooled EPR variable-temperature insert. A typical spectrum obtained is shown in Figure 1A, showing a clean doublet with some structure in each line and centered at g = 2.0030 ± 0.0003. Inspection of the spectrum immediately reveals the presence of a single proton with a large hyperfine (hf) coupling constant. Any additional proton hf splittings must be small and are contained within the line width. This is consistent with structure **1a** and rules out **1b** which requires two protons to carry a larger hf coupling than the third. A more quantitative evaluation requires a simulation which in its most sophisticated form contains 12 unknown parameters for a molecule with the symmetry of **1a**. The data clearly do not warrant this. Instead we have chosen two approximate simulations. The first assumes an isotropic g with a one-proton anisotropic hf-coupling tensor (A_3).[7] The remaining two proton hf couplings are absorbed by an adjustable line width. This four-parameter fit is shown in Figure 1B and the parameters are listed in Table I, column B, broken down into isotropic (a_3) and anisotropic (B_{nn}) components.

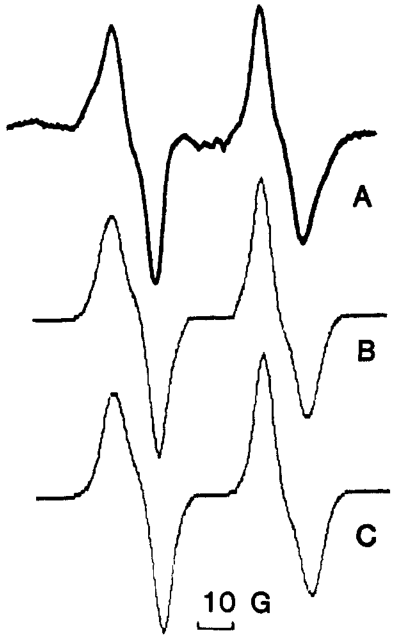


Figure 1. (A) Experimental X-band spectrum of γ-irradiated 3-chlorocyclopropene at 20 K. Field increase from left to right. (B) Simulation including only A_3 hf interaction. (C) Simulation including A_3 and $a_{1,2}$. Values are listed in the table.

Table I[a]

	A (theory[2i])[b]	B	C
a_3	32.9	34.1	34.1
B_{xx}	-9.0	-11.1	-11.1
B_{yy}	-2.3	-2.6	-2.6
B_{zz}	11.3	13.7	13.7
$a_{1,2}$	-5.2	0.0	|2.5|
LW		5.0	2.5

[a] All values in gauss. [b] The B_{nn} tensor has been diagonalized, corresponding to a rotation by 47° around the x-axis of the coordinate system of ref 2i. This points B_{zz} essentially along the C–H bond of C-3.

The spacing of the components of the doublet determines a_3 quite unambiguously while the line shapes, particularly the inflection point, yield a fairly unique set of the principal components of the B tensor. The second simulation (Figure 1C) includes an isotropic hf coupling ($a_{1,2}$) for the two ethylenic protons in **1a** and a different line width. The values used are listed in Table I, column C, and must be regarded as a suggestion for the magnitude of $a_{1,2}$ that can be supported by the width of the line. Since no anisotropic components are included for these hf couplings, the value has a large uncertainty.

On the basis of these results we are confident that the carrier of the spectrum is the cyclopropenyl radical. This conclusion is supported by control experiments which showed that spectrum 1A is obtained only from solutions containing unhydrolyzed chlorocyclopropene.[8] Most important is the close agreement of the isotropic and anisotropic hf interactions observed with those

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(7) Close inspection of the spectrum reveals a small difference between the low- and high-field lines. This is probably due to a small anisotropy of the g factor. The line shape best reproduced by the simulation is the high-field line.

(8) Hydrolysis in H_2O and D_2O resulted only in a decrease of the observed signal.

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predicted by Chipman and Miller (Table I, Column A). The large value of a_3 is similar to that observed for the corresponding protons in 1,2-dimethylcyclopropen-3-yl[4b] and is characteristic for a σ radical. This requires that the hydrogen is substantially bent out of the ring plane, probably by 40-50°.

Our present work does not enable us to determine the dynamics of pseudorotation in **1a** because the matrix softens at 140 K and the spectrum disappears. However, there are no substantial changes on heating from 20 to 140 K, putting a lower limit of 3 kcal/mol on the height of the barrier if we assume the preexponential factor to be $10^{12.5}$–10^{13}.

In summary, we believe we have generated and trapped the elusive cyclopropen-3-yl radical and have determined its symmetry and gross structure. Perhaps the most remarkable outcome of this work is the almost quantitative agreement of the observed EPR spectrum with the predicted one, demonstrating the power of modern ab initio MO methods!

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Registry No. 1, 19469-08-0; 3-chlorocyclopropene, 17336-56-0.

On the Mechanism of Olefin Epoxidation by Oxo-Iron Porphyrins. Direct Observation of an Intermediate

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Interest in the elucidation of biological strategies for the metabolism of oxygen has focused sustained attention on the mechanism of cytochrome P-450[1] and the development of synthetic metalloporphyrin models[2] for these processes. That an oxo-iron intermediate is produced in the enzymic cycle is now generally accepted.[3] Rate saturation and competitive inhibition for iron and manganese porphyrin systems have been interpreted by Collman et al. to indicate the formation of a stable intermediate during the epoxidation of olefins.[2m,n] The preparation and characterization of an oxo-iron(IV) porphyrin radical species, **1**, in our laboratories[4] which is kinetically competent to oxidize hydrocarbons has now allowed the examination of the oxygen-transfer step. We describe here the direct observation of an intermediate olefin-iron porphyrin complex and its subsequent evolution to the product epoxide.

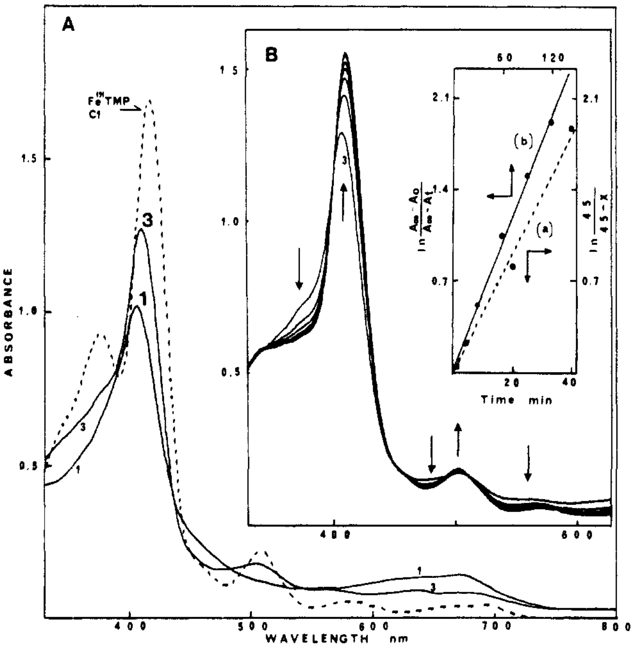

Figure 1. (A) (---) Based on yields of cyclooctene oxide (A^∞ = 45%) at −78 °C in 430 μL of CH_2Cl_2 containing Fe(TMP)Cl (3.9 × 10^{-3} mmol), mCPBA (4.3 × 10^{-3} mmol), and cyclooctene (3.1 × 10^{-2} mmol). (B) (—) Based on the spectral change from **3** to Fe^{III}TMP at 416 nm in CH_2Cl_2 at −43 °C.

Visible spectral changes after the addition of olefins to **1** *indicated that a stable intermediate was formed prior to epoxide production.* The oxidation of either Fe(TMP)Cl or Fe(TMP)OH (**2**) (TMP = 5,10,15,20-tetramesitylporphyrin) (1.63 × 10^{-5}M) in methylene chloride with 2.2. equiv of *m*-chloroperoxybenzoic acid (mCPBA) at −42 °C produced a visible spectrum characteristic of **1** (Figure 1A). The addition of 5 μL of cyclooctene caused a distinct color change, green to dark green, within a minute, and an altered visible spectrum (Figure 1A) of an intermediate species **3** appeared which decayed in a first-order fashion over 3 h to Fe^{III}(TMP) (Figures 1B and inset b; k = 2.8 × 10^{-4} s^{-1}). The EPR spectrum of this intermediate (**3**) formed at −78 °C with 1.1 equiv of mCPBA followed by 8 equiv of cyclooctene showed no evidence of iron(III) but **3** decomposed to Fe^{III}(TMP) upon warming to room temperature.

Quenching **3** with iodide after 24 s gave less than 2% cyclooctene oxide. Lengthening the time between olefin addition and the iodide quench caused a *first*-order increase in the epoxide yield over 5 h to a maximum of 45% at a rate similar to the appearance of iron(III) (k = 3.2 × 10^{-4} s^{-1}) (Figure 1B, inset a). However, the addition of 3 equiv of imidazole or 1% methanol to a preformed solution of **3** at −78 °C led to a 46% yield of cyclooctene oxide after only 3 min.

The rate of reaction of **1** *with substituted styrenes correlated with the Hammett* σ^+. Fe(TMP)OH (**2**) was oxidized in methylene chloride with 2.2 equiv of mCPBA at −50 °C to produce **1**. Upon the addition of 400–2000 equiv of styrene both the disappearance of **1** and the formation of **3** were monitored over at least 2 half-lives (40–200 s). Good pseudo-first-order kinetics were obtained for all substrates and no rate saturation was observed under these conditions. The observed rate constants correlated with σ^+ with a large negative ρ^+ (−1.9). The reaction of **1** with the same styrenes in the presence of 1% methanol led to the regeneration of Fe^{III}TMP with the identical Hammett correlation (x = *p*-OMe, *p*-Me, H, *p*-Cl).

The adduct **3** *formed from* **1** *and cyclooctene decomposed in the presence of methanol and styrene to produce only cyclooctene oxide.* A 1-mL solution of **1** formed at −78 °C from Fe^{III}(TMP)Cl (7.8 × 10^{-3} M) and 1.2 equiv of mCPBA in methylene chloride was allowed to react with 10 μL of cyclooctene for 5 min to product **3**. The addition of 10 μL of styrene led to the *slow* production of cyclooctene oxide (37%) and styrene oxide (17%)

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