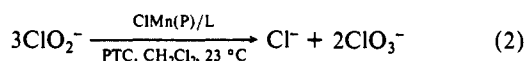


Table I. Observed Rates of Hydroxylation^a and Epoxidation with Oxochloride Anions Catalyzed by Mn(TMP)Cl/4-*tert*-Butylpyridine

substrate	initial turnover freq, min ⁻¹		
	LiOCl	NaClO ₂	NaClO ₃
cyclohexane	0.04	18	none
cycloalkene	230 ^b	49 ^c	none ^c

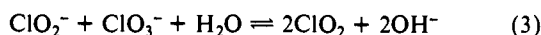
^a Reference 13. ^b Reference 5c; using cyclooctene and an imidazole ligand. ^c Cyclohexene.

solution of CIMn(P) and phase-transfer catalyst (PTC) to each of these, in the absence of hydrocarbon substrate, only the chlorite solution decomposes. It disproportionates irreversibly to chlorite and chlorate (eq 2).²³ The catalyzed decomposition of chlorite



in the presence of 1 equiv of chlorate reveals that the latter inhibits both the chlorite disproportionation and hydrocarbon hydroxylation.²⁵ Inner-sphere atom transfer between the oxochloride anions, even with very favorable thermodynamics, is known to be extremely slow in basic solution.²⁶ Transition-metal catalysis of such oxygen atom transfers has not previously been observed.

In aqueous solution, chlorine dioxide (ClO₂) should exist in equilibrium with a mixture of chlorite and chlorate, but the uncatalyzed rate of equilibration is very slow (eq 3).²⁷ We have



observed that a solution of ClO₂ in CCl₄²⁸ shows a very low activity for heptane hydroxylation and instead rapidly bleaches the manganese porphyrin catalyst. As ClO₂ reacts rapidly with DBMPH, an excess of the latter can act as a stabilizer against porphyrin bleaching by ClO₂. DBMPH has no effect on the rate or distribution of products in the hydrocarbon hydroxylation by chlorite; it is clear that ClO₂ is not the active oxidant under these conditions.

The regioselectivity of heptane oxidation does not distinguish chlorite from other manganese-based oxidants.^{31,8a} Both favor ω - 1 functionalization when hindered porphyrins (TMP or TDCPP) are used, as is also observed in P-450.³² Likewise, the oxidations of adamantane and 2-methylpentane yield product distributions with a similar regioselectivity³⁴ to that observed with

(23) The sum of hypochlorite, chlorite, and chlorate was determined by iodometric titration of the bromine formed upon treatment of acidified samples with bromide.²⁴ The sum of hypochlorite and chlorite, in the presence of chlorate, was assayed by simple iodometric titration without bromide treatment. Under standard reaction conditions,¹³ the initial rate of disproportionation is about 180 min⁻¹, over 10 times the rate of hydroxylation, thus requiring a significant excess of oxidant for hydrocarbon oxidation by chlorite.

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(25) It is thus advantageous¹³ to remove semicontinuously and add a new aqueous chlorite layer during the course of a hydroxylation to avoid developing a high concentration of chlorate in the aqueous layer. The origin of this inhibition may be a phase-transfer effect.

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(27) Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330.

(28) Chlorine dioxide was prepared via the method of Taube²⁹ and analyzed via its characteristic UV absorption at ca. 360 nm (ε = 1250 M cm⁻¹).³⁰

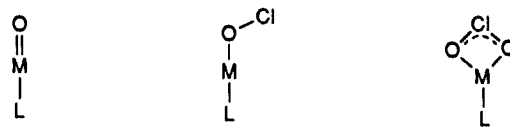
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(31) In chlorite hydroxylation of heptane catalyzed by the hindered porphyrins CIMn(P), P = TDCPP and TMP, the relative reactivities per hydrogen at carbons 1:2:3:4 were 3:54:24:19; in contrast, for the flat porphyrins P = TF₂PP and TPP, this ratio was 1:37:32:30.¹³ These may be compared to ratios observed in cytochrome P-450 hydroxylation³² and free-radical chlorination³³ of heptane 9:74:11:6 and 11:31:29:29, respectively.

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A: metal oxo B: metal hypochlorite C: metal chlorite

Figure 1. Possible structures present in metalloporphyrin-catalyzed "shunt" reagent oxidations.

manganese porphyrins and a series of alternative "shunt" oxidants.⁷ Active-site steric constraints appear to control the regioselectivity.

In conclusion, we report herein the discovery of both chlorite disproportionation and hydrocarbon oxidation catalyzed by manganese(III) porphyrins in the presence of an axial base (4-*tert*-butylpyridine). The observed oxidations are metal centered and yield, via parallel pathways, products of both two-electron (alcohol) and four-electron (ketone) oxidation. As evidenced by its relative reactivity for epoxidation and hydroxylation, its longevity (yields >10³ based on metalloporphyrin), its insensitivity to free-radical scavengers that inhibit hypochlorite, and its parallel formation of two- and four-electron-oxidation products, the identity of the chlorite oxidant is fundamentally different from that formed by hypochlorite and other shunt reagents in combination with manganese porphyrins. A metal-oxo species or a hypochlorite complex (A and B, Figure 1) is implicated as the active oxidant in the latter cases. Unique reactivity may, therefore, be proposed for a chlorite complex (C, Figure 1), including the ability to deliver the four-electron-oxidation capacity of chlorite to appropriate substrates. Note that such a process would not require a formal redox change at the metal.

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(34) Adamantane shows a relative reactivity per tertiary:secondary hydrogen of 88:12 while the relative reactivity per tertiary:secondary:primary hydrogen for oxidation of 2-methylpentane is 114:28:1. The regioselectivity of P-450 for 2-methylpentane is 150:25:1.^{32b}

[3 + 2 + 2] Cycloaddition Reactions between Formaldehyde O-Oxide and Keto Aldehydes: A New Method for the Synthesis of Polycyclic Peroxides

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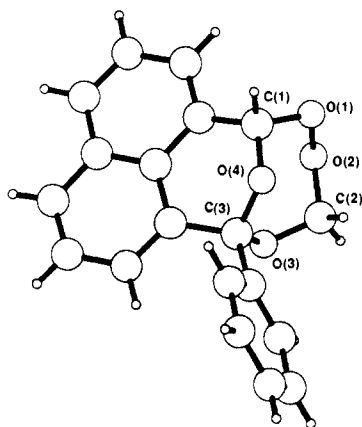
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[3 + 2] cycloaddition reactions between carbonyl oxides, generated in situ by ozonolysis of olefins, and carbonyl compounds to give ozonides (1,2,4-trioxolanes) are well established.¹ Recently, it has been found that carbonyl oxides readily undergo cycloaddition reactions with alkenes,² imines,³ and nitrones⁴ af-

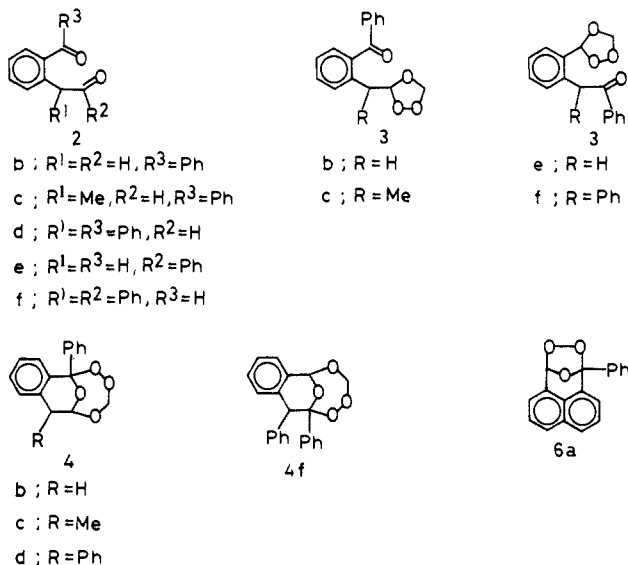
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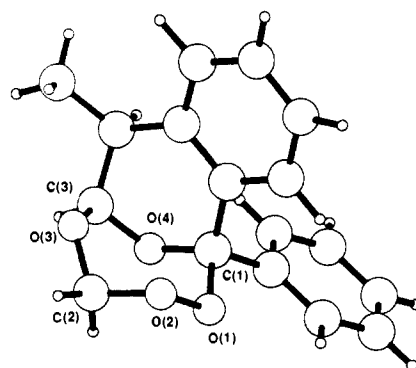
Figure 1. Crystal structure of cycloadduct **5a**.

forming the corresponding 1,2-dioxolanes, 1,2,4-dioxazolidines, and 1,2,4,5-trioxazinanes, respectively. We now report the first examples of polycyclic peroxides, containing the comparatively rare 1,2,4,6-tetroxepane system,⁵ formally derived from [3 + 2 + 2] cycloadditions between formaldehyde *O*-oxide and keto aldehydes.

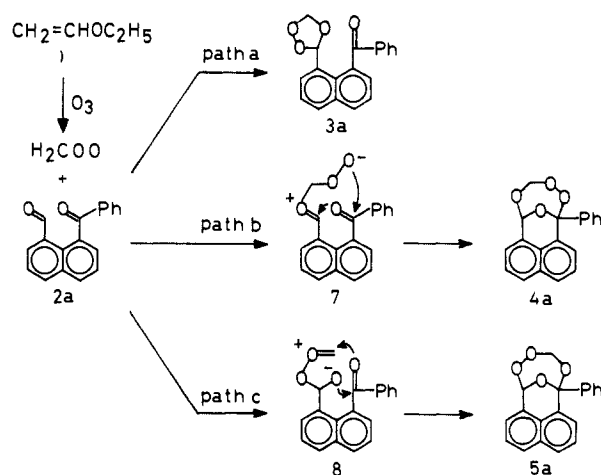
A solution of ethyl vinyl ether (**1**) (3 mmol) and 1-benzoyl-8-formylnaphthalene (**2a**) (1 mmol) in methylene chloride (20 mL) was ozonized (3 mmol of ozone) at $-70\text{ }^{\circ}\text{C}$. Rapid column chromatography (silica gel; elution with benzene-hexane, 1:1 v/v, and then with benzene) of the crude product mixture afforded phenylacenaphthylene ozonide (**6a**) (1%), two isomeric adducts **4a** (3%) and **5a** (6%), the normal [3 + 2] cycloadduct **3a** (21%), and recovered keto aldehyde **2a** (47%). Since isomers **4a** and



5a could not be readily distinguished by conventional spectroscopic techniques⁶ (see also supplementary material), the structure of **5a** was determined unambiguously by X-ray crystallography. The crystal structure of **5a** (Figure 1) shows clearly that the molecule contains a central 1,2,4,6-tetroxepane ring in which the terminal

Figure 2. Crystal structure of cycloadduct *endo-4c*.

Scheme I



oxygen of the formaldehyde *O*-oxide has become bonded to the original carbonyl carbon of the formyl group in **2a**.

The mechanism outlined in Scheme I accounts for the formation of the observed peroxidic products. Ozonolysis of the vinyl ether **1** yields selectively formaldehyde *O*-oxide,²⁻⁴ which is considered more likely to attack the less sterically hindered formyl group of **2a**. A normal [3 + 2] cycloaddition process would provide the ozonide **3a** directly (path a). The formation of adducts **4a** and **5a** indicates that [3 + 2 + 2] cycloaddition processes must also be operative. Although concerted [3 + 2 + 2] cycloaddition reactions would be disallowed by orbital symmetry, the stepwise mechanism⁷ shown in paths b and c in Scheme I is consistent with the structures of **4a** and **5a**. Thus, partial capture of the formaldehyde *O*-oxide by the formyl group of **2a** would give the zwitterionic intermediates **7** and **8**, which on subsequent intramolecular cyclization with concomitant incorporation of the adjacent benzoyl group would yield **4a** (path b) and **5a** (path c), respectively.

Treatment of the ozonide **3a** with trifluoroacetic acid (1 equiv) in methylene chloride at $20\text{ }^{\circ}\text{C}$ for 2 h led to the formation of **4a** (25%) and **5a** (16%), together with keto aldehyde **2a** (20%). It is notable that the ratio of **4a** to **5a** in the acid-catalyzed rearrangement is significantly different from that in the ozonolysis experiment, suggesting that **4a** and **5a** are not secondary ozonolysis products resulting from adventitious acid-catalyzed rearrangement of the ozonide **3a**.

Further ozonolyses of vinyl ether **1** were carried out in the presence of a series of keto aldehydes **2b-f**. New [3 + 2 + 2] cycloaddition products **4b-d** were isolated in yields of around 20% from the reactions involving keto aldehydes **2b-d**.⁸ X-ray crystallographic analysis of the major isomer of **4c**⁸ established

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(6) **3a**: an oil; ¹H NMR δ 4.92 (s, 1 H), 4.99 (s, 1 H), 6.58 (s, 1 H), 7.2–8.0 (m, 11 H); IR 1660, 1270 cm⁻¹. (C₁₉H₁₄O₄) C, H. **4a**: mp 141–143 °C; ¹H NMR δ 5.36 (d, *J* = 10 Hz, 1 H), 5.53 (d, *J* = 10 Hz, 1 H), 6.63 (s, 1 H), 7.01 (d, *J* = 7 Hz, 1 H), 7.2–8.1 (m, 10 H); ¹³C NMR δ 96.09 (1 C), 96.62 (1 C), 106.91 (1 C), 124.74–137.62 (16 C). (C₁₉H₁₄O₄) C, H. **5a**: mp 120 °C dec; ¹H NMR δ 5.35 (dd, *J* = 10.0 and 1.5 Hz, 1 H), 5.83 (d, *J* = 10.0 Hz, 1 H), 6.68 (d, *J* = 1.5 Hz, 1 H), 6.90 (d, *J* = 7.0 Hz, 1 H), 7.1–8.0 (m, 10 H); ¹³C NMR δ 96.71 (1 C), 101.17 (1 C), 103.88 (1 C), 123.88–140.09 (16 C). (C₁₉H₁₄O₄) C, H. **6a**: mp 130–131 °C; ¹H NMR δ 6.78 (s, 1 H), 7.1–7.9 (m, 11 H). (C₁₈H₁₂O₃) C, H.

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(8) Compounds **4b** (17%), **4c** (exo:endo = 33:63, 19%), and **4d** (exo:endo = 12:88, 25%).

that it was *endo-4c* (Figure 2), resulting exclusively from a mechanism analogous to that in path b (Scheme 1); no adducts derived from the alternative mode of addition [cf. path c (Scheme 1)] were observed. The normal [3 + 2] cycloadducts **3b,c** were also obtained in yields of 9% and 2%, respectively. Under similar conditions, keto aldehydes **2e,f** afforded the corresponding ozonides **3e** (39%) and **3f** (22%) as the major peroxidic products. Treatment of **3f** with trifluoroacetic acid at room temperature gave the rearrangement product **4f** (21%). Substantial quantities of the starting keto aldehydes **2b-f** were also recovered in each case.

Supplementary Material Available: Physical properties, including melting points and NMR, IR, and analytical data, of compounds **3a-c,e,f**, **4a,b**, *exo-* and *endo-4c,d*, **4f**, **5a**, and **6a** and crystal data, bond lengths and angles, fractional coordinates, and anisotropic vibration parameters for compounds *endo-4c* and **5a** (15 pages); listing of observed and calculated structure factors for compounds *endo-4c* and **5a** (21 pages). Ordering information is given on any current masthead page.

Production of Protonated Methanol Ions via "Intermolecular" Reactions within van der Waals Clusters of Dimethyl Ether

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Mass spectrometric studies of van der Waals clusters have proliferated during the last decade, and much has been learned concerning the formation and physical properties of many cluster systems.¹ The study of chemical reactions within clusters has also attracted considerable attention driven by the desire to create a conceptual bridge between the two seemingly disparate fields of gas-phase and condensed-phase chemistry.

Various groups have recently observed the generation of new cluster ions that are not observed in typical gas-phase bimolecular reactions (i.e., chemistry that can only occur within a cluster). These new processes include the generation of $(\text{NH}_3)_n\text{N}_2\text{H}_8^+$ ions from ammonia clusters,² $(\text{CH}_3\text{OCH}_3)_n\text{H}_3\text{O}^+$ ions from dimethyl ether clusters,³ $(\text{CH}_3\text{F})_n\text{CH}_3\text{CH}_3^+$ ions from methyl fluoride clusters,⁴ and most recently, $(\text{C}_2\text{H}_4\text{F}_2)_{n \geq 4}\text{H}^+$ from clusters of 1,1-difluoroethane.⁵ We feel this body of work has revealed a new class of chemical reactions within clusters and hope to employ these systems to further study the role played by ion solvation in the reaction dynamics within cluster ions. To that end, we have reinvestigated neat clusters of dimethyl ether (DME) and have observed a new cluster ion of the formula $(\text{DME})_n\text{CH}_3\text{OH}_2^+$.

Our molecular beam apparatus consists of a Campargue-type beam source⁶ and has been described previously.⁷ The cluster beam is generated from neat DME (Linde, minimum purity⁸

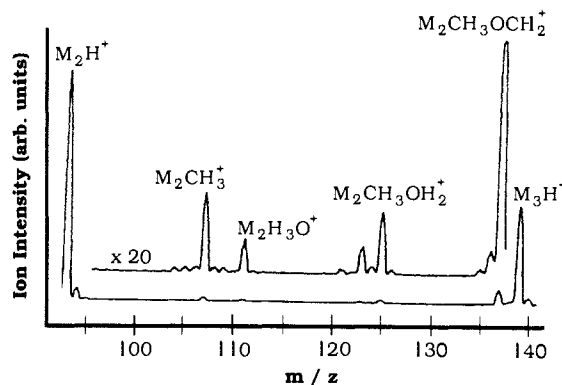


Figure 1. Raw mass spectrum of neat dimethyl ether clusters at 70 eV from 80 to 140 amu. Major ion peaks are identified by their empirical formulas ($M = (\text{CH}_3)_2\text{O}$).

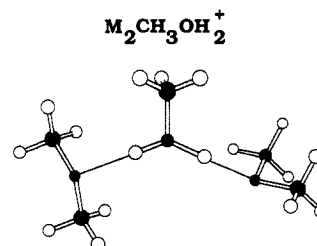
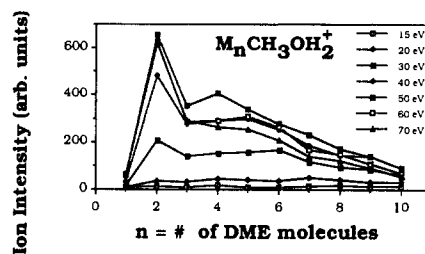


Figure 2. Top: Plot of $[(\text{CH}_3)_2\text{O}]_n\text{-CH}_3\text{OH}_2^+$ ion intensity as a function of n for a variety of electron energies (15–70 eV). Note prominent magic number for $n = 2$. Bottom: Proposed structure for the $((\text{CH}_3)_2\text{O})_2\text{-CH}_3\text{OH}_2^+$ cluster ion. This species is the most prevalent of all cluster ions in the series $[(\text{CH}_3)_2\text{O}]_n\text{-CH}_3\text{OH}_2^+$ and is believed to be a protonated methanol molecule with two DME molecules hydrogen bonded to it. The dark circles correspond to carbon atoms and the shaded circles to oxygen atoms, while the open circles are hydrogen atoms.

99.0%) expanded at 1.5 atm through a 250- μm orifice. The mass spectrometer is an Extrel C-50 instrument (200 W, $3/8$ -in-diameter rods, open-design ionizer) capable of unit mass resolution and uniform sensitivity up to $m/z = 1400$. The electron emission current for these experiments was kept at 0.65 mA. During beam operation, the pressure in the mass spectrometer chamber was kept below 5×10^{-7} Torr.

Figure 1 shows a typical 70-eV electron impact mass spectrum of DME clusters extending from the dimer to the trimer. In addition to the expected peaks, there are two additional peaks corresponding to the hydronium ion (which has been reported before³) and protonated methanol ions, both solvated by two DME molecules. This sequence of peaks is observed throughout the entire cluster mass spectrum to the limit of our sensitivity.

We have based our identification of the $(\text{DME})_n\text{CH}_3\text{OH}_2^+$ ions not only on mass assignment of that particular sequence of peaks but also on the observation of strong "magic" numbers in the DME cluster mass spectrum (i.e., cluster size values at which variations in an otherwise smoothly varying ion distribution occur). Magic numbers provide important clues as to the structure of the cluster ion and the identity of the central ionic moiety.⁹ The top of Figure

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