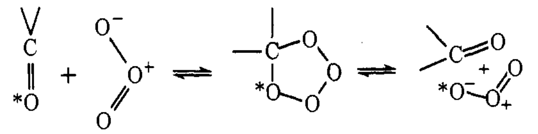
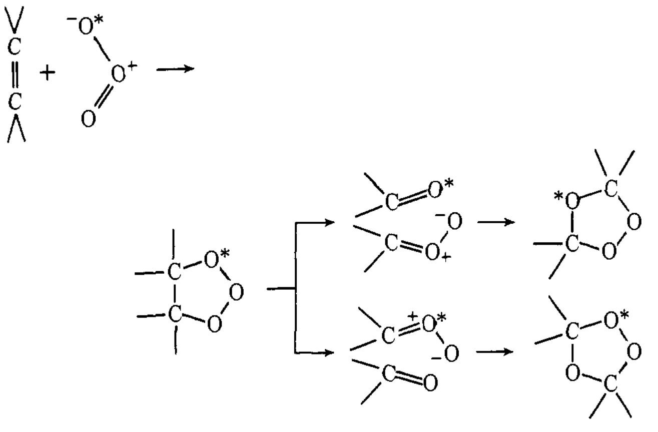


Such a reaction does not yield new products and was thus not observed before. However, in the process, the regenerated ozone might have exchanged one of its oxygens with the aldehyde and, if the aldehyde contained an ^{18}O, then this label could have been incorporated in the ozone. If we assume that this is a fast reaction, then the ozone could carry the ^{18}O to any position of the final ozonide and Story's finding of ^{18}O in the peroxide bridge would not require a new mechanism.



In order to determine this possibility we prepared some ^{18}O enriched isobutyraldehyde by mixing 0.088 g of the pure aldehyde with 0.5 g of about 40% enriched water (from Bio Rad Laboratories). The mixture was left at room temperature for 2 days and then refrigerated at 2° for about a month. The aldehyde layer was dissolved in an excess of spectrophotometric grade heptane solvent (Aldrich) and an aliquot was injected into a combined gas chromatograph mass spectrometer. The GC peak corresponding to the pure aldehyde was separated and analyzed by the mass spectrometer. From the relative heights of the peaks at mass 72 and 74, we calculated a 41% ^{18}O enrichment of the aldehyde.

Additional pure solvent was cooled in a Dry Ice-acetone bath and was saturated with ozone using a Welsback T-816 ozonator until the characteristic blue color of ozone developed. We then mixed approximately equal amounts of the isobutyraldehyde solution and the ozone solution and analyzed a sample in the GC mass spectrometer. Approximately 1 min had passed between the mixing and the injection into the GC. During this time the mixture was kept in the Dry Ice-acetone bath. The aldehyde was again separated in the GC and analyzed by the mass spectrometer. We now found an ^{18}O enrichment of only 27%, indicating that the aldehyde had lost 34% of its original label. A control experiment was performed after the mixture was left for 5 min at room temperature. This time the ^{18}O enrichment of the aldehyde was found to be only 17%. Thus the aldehyde had lost 59% of its original label which probably corresponds to 100% exchange with the minute amount of ozone that was present. A blank experiment, without ozone, did not yield any marked modification of the spectra.

Our experiment thus confirmed our hypothesis and showed that the loss of label by the aldehyde is much faster than the degradation of the aldehyde by ozone. Depending thus on the experimental conditions under which the ozonolysis of an olefin is made in presence of excess labeled aldehyde, one may thus obtain variable amounts of label in the peroxide bridge, without having to invoke a separate mechanism. It is obviously difficult to assess whether the reaction presented above can compete effectively with the direct reaction of ozone with alkenes. Furthermore, the maximum value of ^{18}O incorporation in the peroxide bridge is only 50%. Thus it remains to be seen whether our discovery explains all or only part of the observed isotopic distribution in ozonides.

The measurements were made using a Dupont 21-490B GC mass spectrometer interfaced with a Dupont 21-094 data system. The injection chamber was at 210°, the GC column at 78°, and the deflection chamber was at 190°. Heater no. 2 kept the GC line at 240° while heater no. 3 kept the jet separator at 250°. The flow rate was 24 μg/sec.

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Reversible Intramolecular Electron Transfer in an Oxidized Nickel Porphyrin

Sir:

The occurrence of metalloporphyrin π-cation radicals in nature prompted us to speculate[1] that the redox chemistry of the cytochromes might proceed via an intermediate iron porphyrin π-cation radical, viz.,

$$\mathrm{Fe^{II}cyt} \longrightarrow \underset{\mathbf{1}}{[\mathrm{Fe^{II}cyt}]^{\cdot +}} \rightleftharpoons \underset{\mathbf{2}}{[\mathrm{Fe^{III}cyt}]^{+}}$$

The species **1** containing a hole in a porphyrin π orbital needs to be in equilibrium with the isoelectronic ferric species to account for the equilibrium properties of the

$$[\mathrm{Ni^{II}TPP}]^{\cdot +},\ \mathrm{ClO_4^-} \underset{\Delta}{\overset{-\Delta}{\rightleftharpoons}} [\mathrm{Ni^{III}TPP}]^{+},\ \mathrm{ClO_4^-}$$

electron transfer process. Although unusual, examples in which transition metal complexes of macrocycles related to porphyrins undergo irreversible internal electron transfer analogous to that mentioned above are known. Thus reduced cobalt tetradehydrocorrins[2] or tetraazaanulenes[3] evidence electron transfer from metal to ligand orbitals.

Similarly, Wolberg and Manassen[4,5] reported EPR evidence for formation of a Ni(III) species when tetraphenylporphinatonickel(II) (NiTPP) was electrochemically oxi-

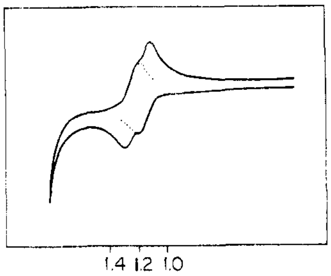

Figure 1. Cyclic voltammogram of $\mathrm{Ni^{II}TPP}$ in methylene dichloride containing tetrapropylammonium perchlorate. The voltage was measured against Ag|AgCl.

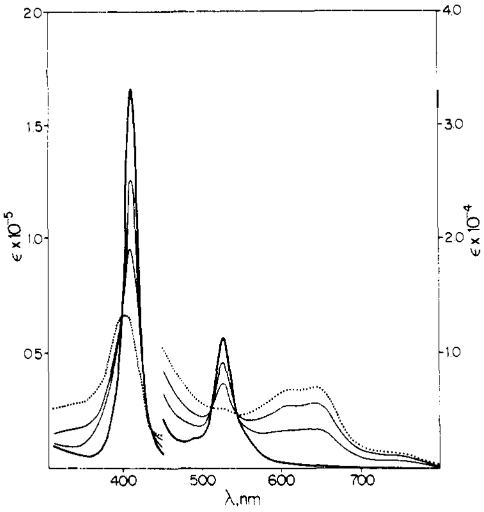

Figure 2. Changes in electronic absorption spectrum of $\mathrm{Ni^{II}TPP}$ during electrolysis at 1.24 V: $\mathrm{Ni^{II}TPP}$ (—), $[\mathrm{Ni^{II}TPP}]^{\cdot+}$ (· · ·).

dized in benzonitrile at the first polarographic wave. Within minutes $[\mathrm{Ni^{III}TPP}]^{+}$ decayed yielding, apparently, a cation radical of the divalent nickel complex, $[\mathrm{Ni^{II}TPP}]^{\cdot+}$. In contrast we had reported[6] that $[\mathrm{Ni^{II}TPP}]^{\cdot+}$, with methylene dichloride as solvent, was the only product of oxidation at the first wave. In a reexamination of this system it is now possible to establish evidence for *reversible* electron transfer between $[\mathrm{Ni^{II}TPP}]^{\cdot+}$ and $[\mathrm{Ni^{III}TPP}]^{+}$, analogous to that suggested for **1** $\rightleftharpoons$ **2** in the cytochromes.

In CH_2Cl_2 containing tetrapropylammonium perchlorate, $\mathrm{Ni^{II}TPP}$ displayed two, overlapping but reversible, cyclic voltammetry curves at 1.20 and 1.29 V vs. Ag|AgCl (Figure 1). Controlled potential electrolysis at 1.24 V proceeded to completion and coulometry established that 1.0 ± 0.1 electrons molecule^{-1} were removed. Simultaneous optical monitoring of the electronic absorption spectrum (Figure 2) with observation of isosbestics and complete recovery of $\mathrm{Ni^{II}TPP}$ upon electroreduction indicated that the oxidized product was stable. The electronic absorption spectrum[7,8] and magnetic circular dichroism spectrum of the product were characteristic of a porphyrin π-cation radical as was the EPR spectrum at 300 K with $g = 2.0041$ and a peak-to-peak width of 48.2 G.

Further electrolysis of $[\mathrm{Ni^{II}TPP}]^{\cdot+}$ at 1.44 V with a removal of 0.95 electron molecule^{-1} yielded a solution whose optical spectrum (Figure 3) was that of the π-dication, $[\mathrm{Ni^{II}TPP}]^{2+}$ (incorrectly identified in ref 4 as the π-cation radical $[\mathrm{Ni^{III}TPP}]^{\cdot 2+}$. Proof of this assignment resulted from its reaction with methanol which gave the isoporphyrin[9] ($\lambda_{\max}{}^{\mathrm{CH_3OH}}$ 785 (ϵ 5800), 871 nm (ϵ 11,000)). At this stage the results were unexceptional and served only to confirm our earlier report and reinterpret Wolberg's and Manassen's observations.

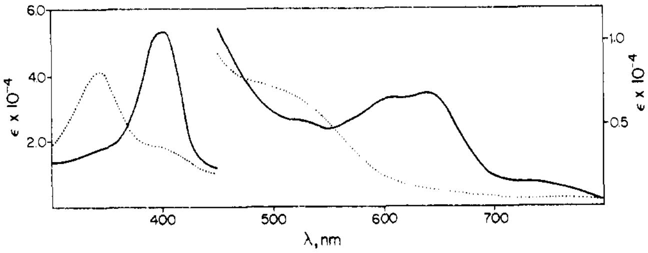

Figure 3. Electronic absorption spectrum of $[\mathrm{Ni^{II}TPP}]^{\cdot+}$ (—) and $[\mathrm{Ni^{II}TPP}]^{2+}$ (· · ·).

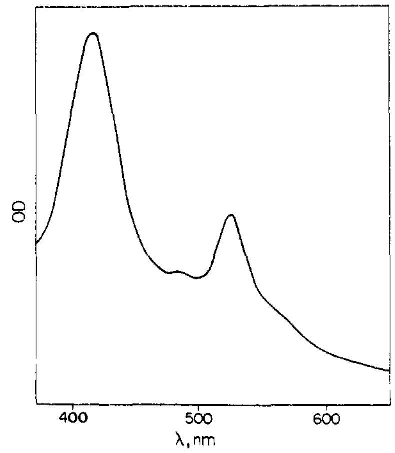

Figure 4. Electronic absorption spectrum of $[\mathrm{Ni^{III}TPP}]^{+}$ at 110 K in frozen CH_2Cl_2. Determined with the "opal glass method".[12]

However, upon cooling the CH_2Cl_2 solution of $[\mathrm{Ni^{II}TPP}]^{\cdot 2+}$ to 77 K, the green, room temperature solution turned to an orange-red solid. These optical absorption changes were paralleled by the behavior of the EPR spectra. At 77 K the free radical signal was replaced by an EPR spectrum with $g_{\perp} = 2.286$ and $g_{\parallel} = 2.086$. These values are characteristic of the low-spin d^7 Ni(III) complexes reported by Busch[10] and by Wolberg and Manassen. Additionally, the electronic absorption spectrum (Figure 4) at 110 K displayed the Soret (418 nm) and visible (526 nm) bands of a typical metalloporphyrin in which bonding ligand π orbitals are filled.

The reversible, temperature-dependent transformation can be described as

$$\mathrm{Fe^{II}cyt} \rightleftharpoons [\mathrm{Fe^{III}cyt}]^{+}$$

This intramolecular electron transfer thus establishes a precedent for the reversible electron route postulated in the cytochromes and encourages us to seek the same phenomenon in iron porphyrins.

Stability of the Ni(III) form at reduced temperature is anion and solvent sensitive and trivalent nickel is not observed with Br^- or PF_6^- nor in benzonitrile. It is plausible to envisage that axial coordination of ClO_4^- to $[\mathrm{Ni^{II}TPP}]^{\cdot+}$ is favored at low temperatures where solubility of the porphyrin ion is reduced. Such coordination is established[11] in crystalline $[\mathrm{ZnTPP}]^{\cdot+}$, ClO_4^-. Concomitant raising of the d^2_z orbital would favor $d^2_{xy}d^2_{xz}d^2_{yz}d^1_{z^2}$Ni(III).

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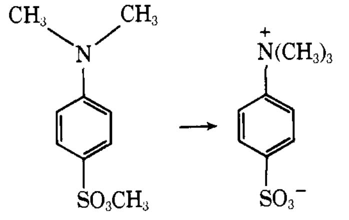
Enhancement of a Chemical Reaction Rate by Proper Orientation of Reacting Molecules in the Solid State

Sir:

Efforts to understand catalytic enhancement of chemical reaction rates have often been aided by attributing orienting and proximity-inducing properties to the catalysts.[1] Given the knowledge that proper orientation and proximity facilitate chemical reaction, chemists have looked to the crystalline state for situations in which particularly reaction-favorable molecular relationships might be found.[2] However, although many reports exist of topochemical control of product formation selectivity,[3] we have been unable to find an example in the literature (outside the polymerization area) of a solid-state accelerated thermal reaction. We now wish to report the identification of such a process, along with an X-ray diffraction study of the compound involved which shows that the molecules are nearly ideally oriented for reaction in the solid state.

We have reinvestigated the rearrangement of methyl *p*-dimethylaminobenzenesulfonate (I) to the *p*-trimethylammoniumbenzenesulfonate zwitterion (II).[4,5] At room temperature, compound I appears to be indefinitely stable in soluton, but (as reported by Kuhn and Ruelius[4]) it arranges with a half-life of about 7 days in the solid state. Isolation and NMR analysis of water-soluble II show it to be a demonstrably different chemical substance (and not simply a different crystalline modification of I[6]); consistent with this observation is the fact that we have been unable to reproduce the claimed reversion[6] of II to I in aqueous ethanol, but instead recover II unchanged after subjection to the reported[6] conditions.



I II

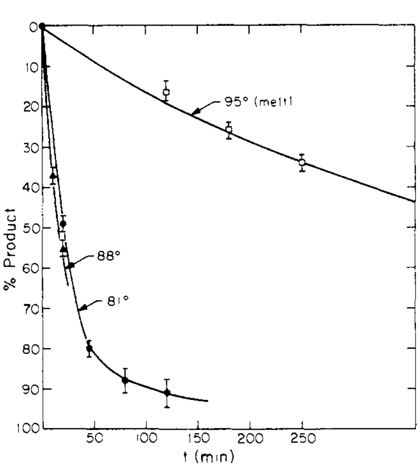


Figure 1. Time dependence of the per cent of product observed in the thermal conversion of methyl *p*-dimethylaminobenzenesulfonate (I) to *p*-trimethylammoniumbenzenesulfonate (II) at three different temperatures: ●, 81°, crystal; ▲, 88°, crystal; □, 95°, melt.

The rate of I → II rearrangement increases with temperature but, contrary to earlier statements,[4,5] *this is only true at temperatures below the melting point.* Higher temperatures, melting the material, introduce a sharp *decrease* in the rate of conversion. A simple plot of product concentration vs. time is shown in Figure 1;[7] based on these data it appears that the solid rearranges at least 25 times faster than the melt. Reaction of a roughly 50:50 mixture of I-d_0 and methyl-labeled I-d_9, and analysis of the product by field desorption mass spectrometry,[8] reveals extensive methyl scrambling in the product II, indicating that the reaction is inter- rather than intramolecular.

Both the intermolecularity and the rapid rate of this reaction are beautifully consistent with the single-crystal X-ray structure of I. Recrystallization of I from methanol gave monoclinic crystals. The data set used consisted of three subsets individually corrected for decay due to the solid state rearrangement, but collectively scaled together yielding 750 reflections whose intensities were greater than $3\sigma(I)$ ($3\sigma R = 0.098$). Lattice constants in the monoclinic space group $P2_1/c$ are $a = 8.942$ (2) Å, $b = 10.507$ (3) Å, $c = 11.232$ (2) Å and $\beta = 90.88$ (2)°; with four formula units per cell the calculated density is 1.43 g cm^{-3}. See paragraph at end of paper for supplementary material.

The bond distances and angles are all within acceptable values. The stacking of the molecules within one chain in the crystal, viewed perpendicular to the [101] plane, is shown in Figure 2. The molecules stack in alternating directions with the aromatic rings inclined 76° to each other and with each nitrogen atom in nearly perfect alignment with the sulfonate ester methyl group of the adjacent molecule. The C(9)· · ·N distance is 3.54 Å and the O(1)–C(9)· · ·N angle is 147°. The system therefore requires only minimal structural change to transfer the methyl group from the oxygen atom of one molecule to the nitrogen atom of the adjacent molecule along the chain, and this is presumably how the reaction occurs.

An arrangement of the atoms within a chain of molecules of I in the solid state which would be "completely ideal" for the nucleophilic substitution would be identical with that of the transition state for reaction, and such a crystal is therefore by definition not isolable.[9] The structure of I is almost, but not quite, ideal, and converson to the transition state structure requires just enough energy to allow isolation of the material at room temperature. This, combined