1,2 and 2,3 rotations during the process. Any Z conformation of the zwitterion should collapse with alcohol more or less randomly.

[2 + 2] Cycloadditions via diradical intermediates show lower stereospecificity[16] than those through 1,4 zwitterions which are often completely stereospecific.[17] Our finding emphasizes that the zwitterions *must be created from the* $_{\pi}$*2 reactants in U conformations* which are favored by Coulomb potential and CT interactions.[18]

Supplementary Material Available. A listing of calculated coordinates for hydrogen and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5285.

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(9) It was easier to grow fingernail size crystals than well-shaped small ones.
(10) Some big crystals gave levo- or dextrorotary solutions, others turned out to be racemic.
(11) Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 61.29; H, 6.61; N, 20.43. Found: C, 61.27; H, 6.59; N, 20.60. Stable under dry nitrogen, the colorless crystals develop a brown amorphous coat on longer exposure to air.
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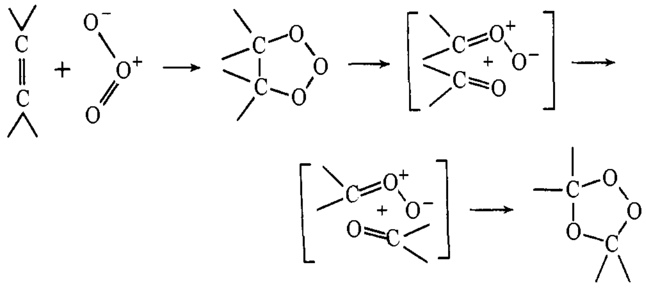
New Evidence in the Mechanism of Ozonolysis of Olefins

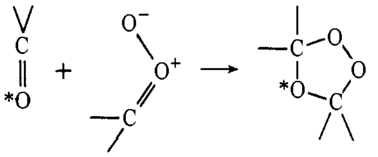
Sir:

Considerable controversy has surrounded the mechanism of ozonolysis. The most accepted mechanism today is a refinement of the Criegee mechanism,[1] the Bauld–Bailey syn-anti zwitterion mechanism.[2] Since this paper does not involve syn and anti zwitterions, only the basic Criegee mechanism (2 + 3 exchange reaction) is shown below.

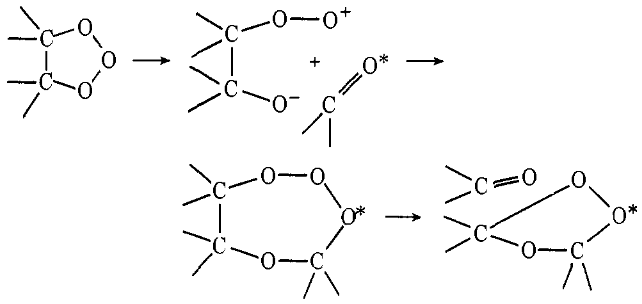


This mechanism was challenged by Story[3] and given the most serious blow by some exchange experiments.[3c] When *trans*-diisopropylethylene was ozonized in the presence of an excess of ^{18}O enriched acetaldehyde, some 75% of the ^{18}O label ended up in the peroxide bridge.

Such results cannot be accommodated by the Criegee mechanism since all the label should end up in the ether position.



On the basis of this and other evidence, Story suggested various alternative mechanisms for ozonolysis. His aldehyde interchange mechanism illustrating the incorporation of ^{18}O into the peroxide bridge is shown below.

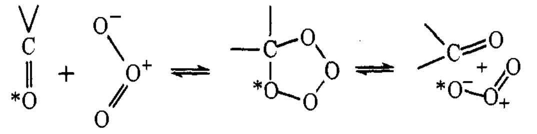


Since then numerous experimentalists[4] have tried to confirm these results by other methods but failed to find the high proportions reported by Story. However, under some specific conditions, ^{18}O is undoubtedly incorporated into the peroxide bridge as was shown by several researchers using various olefins and ^{18}O enriched aldehydes.[5]

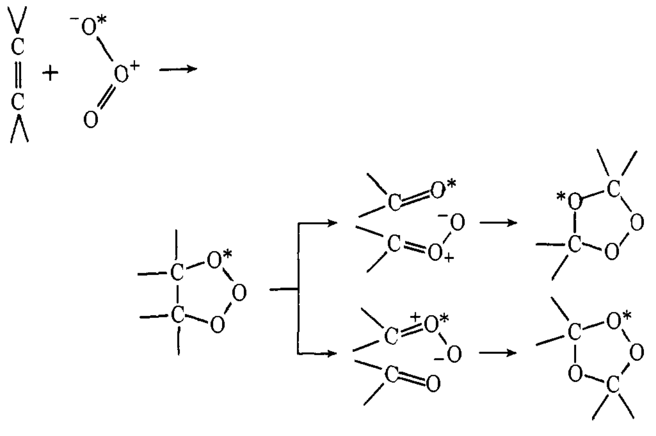
With the exception of the preceding piece of disturbing evidence, however, the Criegee mechanism, with refinements, has held up quite well. It is supported not only by molecular orbital symmetry considerations[6] but also by a large accumulation of experimental data.[7]

The fact that, on the other hand, the mechanism advocated by Story invokes an unfavorable 2 + 2 concerted path prompted us to reexamine the supporting experimental facts. In the process of doing this, we found and present here evidence that the disturbing observations reported above might be simple artifacts and cannot be used as evidence against the Criegee mechanism.

We hypothesized that aldehydes may react with ozone in the same fashion as olefins, i.e., via a favorable (2 + 3) exchange reaction.[6]



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 tetraazaannulenes[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-