form, 57362-50-2; **14b** charged form, 57362-51-3; **14b** uncharged form, 57362-52-4; **14c** charged form, 38938-48-6; **14c** uncharged form, 38938-36-2; **14d** charged form, 57362-53-5; **14d** uncharged form, 57362-54-6; **14e** charged form, 57362-55-7; **14e** uncharged form, 57362-56-8; **14f** charged form, 57362-57-9; **14f** uncharged form, 57362-58-0; **14g** charged form, 57362-59-1; **14g** uncharged form, 57362-60-4; **14h** charged form, 57362-61-5; **14h** uncharged form, 57362-62-6; **16**, 4443-91-8; **17** charged form, 57362-63-7; **17** uncharged form, 57362-64-8; potassium amide, 17242-52-3; *n*-butyllithium, 109-72-8; methyl iodide, 74-88-4; trimethylchlorosilane, 75-77-4; *n*-butyl iodide, 542-69-8; trihhenylphosphinehexanoylmethylene charged form, 57362-65-9; triphenylphosphinehexanoylmethylene uncharged form, 33803-58-6; *o*-phthalaldehyde, 643-79-8.

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Atomic Oxygen. V. Reactions of Enol Ethers with Oxygen (^{3}P) Atoms[1]

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The products of the gas-phase reactions of ground state (^{3}P) oxygen atoms with methyl vinyl ether, ethyl vinyl ether, 2-methoxypropene, 1-methoxy-2-methylpropene, 2,3-dihydrofuran, and dihydropyran are reported. The oxygen atoms were generated by the mercury photosensitized decomposition of nitrous oxide. The reactions produced alkoxyoxiranes, α-alkoxycarbonyl compounds, esters, and fragmentation products. Novel alkoxy radical rearrangements and a reinvestigation of the acid-catalyzed reaction between 3-hydroxy-3-methyl-2-butanone and methanol are reported.

The reactions of atomic oxygen are of continuing interest because of their application to mechanisms of photochemical air pollution,[2] upper atmosphere chemistry,[3] and combustion. Oxygen atom reactions have also been applied to the synthesis of new or labile organic compounds. For example, 3-butenal is produced by reaction of 1,3-butadiene with oxygen (^{3}P) atoms.[4]

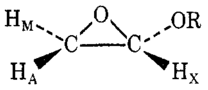
Ground state (^{3}P) oxygen atoms react with olefins of formula C_nH_{2n} to produce epoxides, aldehydes, and ketones of formula $C_nH_{2n}O$. Cvetanovic[5] has proposed that O(^{3}P) atoms add to olefins to form short-lived carbon–oxygen 1,3-biradicals. These biradicals can either close to epoxides or rearrange to aldehyde and ketones. The 1,2 migration of a hydrogen atom is intramolecular, but alkyl groups become at least partially detached during rearrangement. The rearrangement of hydrogen atoms and alkyl radicals in 1,3-biradicals is significant, because these groups do not commonly migrate in monoradical systems.

It was expected that reaction of atomic oxygen with enol ethers would produce enol ether epoxides (or alkoxyoxiranes). Four methods have been applied to the synthesis of simple enol ether epoxides: (a) reaction of diazomethane with esters,[6] (b) epoxidation of enol ethers with peracids,[7,8] (c) reaction of α-halocarbonyl compounds with sodium methoxide,[9] and (d) base-induced ring closure of alkoxy-substituted chlorohydrins.[10] Each of these alkoxyoxirane syntheses has disadvantages.

Reaction Conditions. In this study, conditions for the gas-phase production and reaction of atomic oxygen were derived from the pioneering work of Cvetanovic and coworkers.[5] Ground state (^{3}P) oxygen atoms were produced by the mercury photosensitized decomposition of nitrous oxide.[11] The reaction apparatus and conditions have been described previously.[12] The total pressure before photolysis was 0.9 atm, and the reaction temperature was 25–30°.

Product yields reported below are based on the quantity of nitrogen produced. Two experimental conditions were used to limit the reactions to primary processes. First, a high ratio of nitrous oxide to substrate (>15) was maintained in order to minimize mercury photosensitized reactions of substrate or products. Second, conversion of organic substrate was limited to <30% to minimize secondary oxidations and reactions of products.

Enol Ether Reactions. Methyl Vinyl Ether. Oxygen atoms react with methyl vinyl ether to produce methoxyoxirane (**1**, 45% yield), methoxyacetaldehyde (26%), methyl acetate (2%), and carbon monoxide (13%). The total yield of oxygenated product is 86%.



1, R = CH_3
2, R = C_2H_5

Methoxyoxirane (**1**) has been prepared previously by reaction of diazomethane with methyl formate, but no spectra of this material were given.[6] The NMR spectrum of **1** shows a well-resolved AMX system and a singlet at δ 3.45.

Positions and coupling constants of the AMX system follow: H_A δ 2.56, H_M δ 2.74, and H_X δ 4.50; J_{AM} = 3.9, J_{AX} = 2.3, and J_{MX} = 1.2 Hz. These assignments are consistent with epoxide spectral parameters reported by Lehn and Riehl.[13]

Epoxide **1** is stable in $CDCl_3$ solution for several hours at room temperature. However, an attempt to isolate **1** by short-path distillation (atmospheric pressure) of the combined product mixtures of several reactions led to decomposition of the epoxide. A purified sample of **1** did not survive gas chromatography under mild conditions. The sample apparently polymerized in the instrument, since no $C_3H_6O_2$ products (other than the methyl acetate impurity known to be present by NMR) eluted from the GC.

Ethyl Vinyl Ether. The reaction of atomic oxygen with ethyl vinyl ether produced ethoxyoxirane (**2**, 50% yield); ethoxyacetaldehyde (18%); ethyl acetate (3%); and carbon monoxide (9%). The total product yield was 80%.

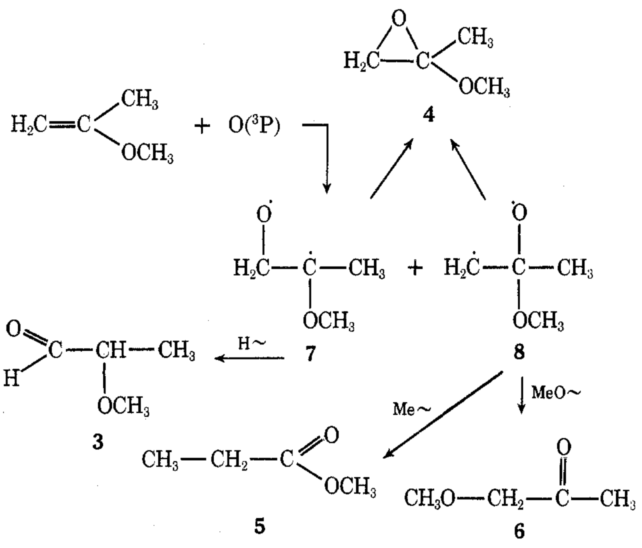
Epoxide **2** is also thermally labile. The NMR spectrum of its AMX system is quite similar to that of compound **1**.

2-Methoxypropene. The products of the reaction of 2-methoxypropene with oxygen (^3P) atoms were 2-methoxypropanal (**3**, 49% yield); 2-methoxy-2-methyloxirane (**4**, 21%); methyl propionate (**5**, 2.4%); methoxyacetone (**6**, 1.3%); and carbon monoxide (10%). The total yield of product was 84%.

The reaction of 2-methoxypropene with atomic oxygen is of mechanistic interest, because it provides information on both orientation of atom addition and migratory aptitudes in 1,3-biradical systems (Scheme I).

The addition of an oxygen atom to carbon 1 of the olefin would yield 1,3-biradical **7**, with a tertiary carbon radical site, while addition to carbon 2 produces biradical **8**, containing a primary carbon radical. As would be expected from conventional radical stabilities, formation of **7** is preferred over formation of **8**. If one assumes that biradicals **7** and **8** produce epoxide **4** at equal rates, then the ratio of addition to carbon 1 vs. carbon 2 is 13 [as indicated by the product ratio **3**/(**5** + **6**)]. This ratio is similar to the addition ratio observed in the reaction of atomic oxygen with 2-methylpropene,[5] where addition to carbon 1 vs. carbon 2 is 14.

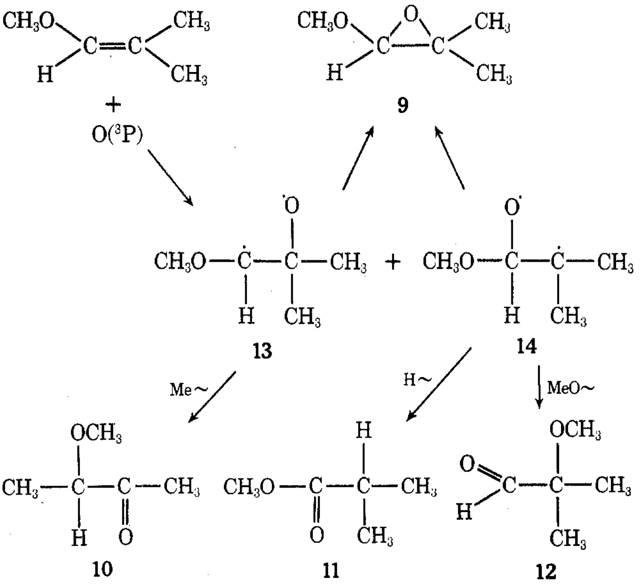
Scheme I



Products **5** and **6** are formed from the minor biradical intermediate **8** by 1,2 migration of a methyl radical and a methoxy radical, respectively. The ratio of these products indicates the relative migratory aptitudes of the two groups: Me~/MeO~ = **5**/**6** = 1.8. There is no apparent literature precedent for the 1,2 rearrangement of an alkoxy group in a monoradical or biradical system.

1-Methoxy-2-methylpropene. Atomic oxygen reacts with 1-methoxy-2-methylpropene to produce 3,3-dimethyl-2-methoxyoxirane (**9**, 46% yield); 3-methoxy-2-butanone (**10**, 15%); methyl isobutyrate (**11**, 10%); 2-methoxy-2-methylpropanal (**12**, 5%); and carbon monoxide (1%). The total product yield is 77%. A scheme for the formation of these products is shown in Scheme II.

Scheme II



If one assumes that biradicals **13** and **14** close to epoxide **9** at equal rates, then the ratio of the carbonyl products [**10**/(**11** + **12**) = 1.0] indicates the orientation of addition. This product ratio means that one methoxy substituent directs the orientation of addition (to form biradical **13**) as well as two methyl groups (to form biradical **14**).

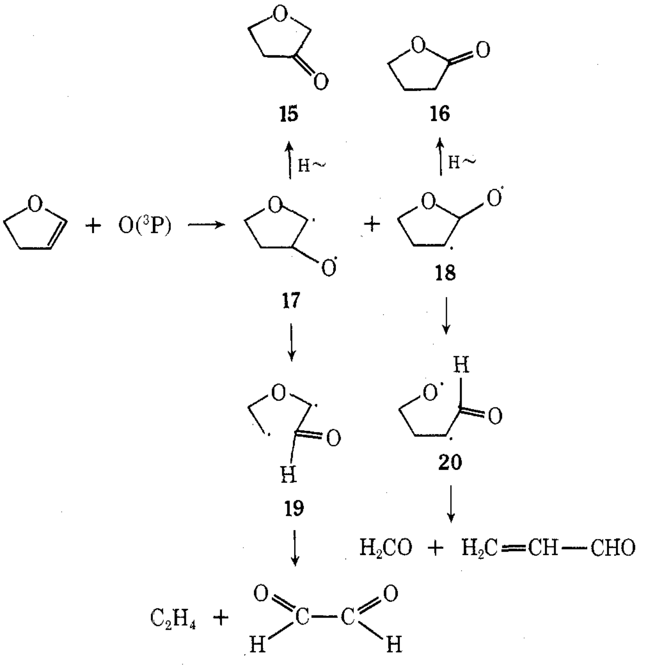
Products **11** and **12** are formed from 1,3-biradical **14** by competing 1,2 rearrangements of a hydrogen atom and a methoxy radical, respectively. The ratio of these two products indicates that hydrogen migrates twice as fast as methoxy.

The low yield of carbon monoxide from this reaction (1%) is consistent with previous results.[5] Simple alkenes show decreased fragmentation with increased substitution of the olefin.

2,3-Dihydrofuran. The reaction of 2,3-dihydrofuran with oxygen atoms produced carbon monoxide (45%); dihydro-3(2*H*)-furanone (**15**, 20%); ethylene (17%); acrolein (1.9%); and dihydro-2(3*H*)-furanone (**16**, 1.4%). The NMR spectrum of the product mixture showed no peaks that could be attributed to the epoxide, 2,6-dioxabicyclo[3.1.0]hexane. Other possible products, formaldehyde, glyoxal, and hydrogen, would not have been detected under the reaction and analysis conditions used.

The reaction of 2,3-dihydrofuran with O(^3P) should proceed in a manner similar to the reaction of cyclopentene, which has been studied extensively by Cvetanovic and coworkers.[14] A mechanism for the formation of the observed products is proposed in Scheme III.

Scheme III

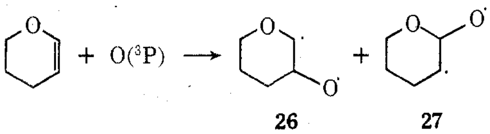


The ambiguous origin of the carbon monoxide formed in this reaction makes an exact calculation of the orientation of addition somewhat doubtful. However, it is apparent from the high ratio of products attributable to biradical **17** (ketone **15** and ethylene) vs. products derived from biradical **18** (lactone **16** and acrolein) that formation of biradical **17** is preferred.

Precedence for the extensive ring opening of 1,3-biradicals **17** and **18** to form 1,4-biradicals **19** and **20** is seen in the reaction of cyclopentene with atomic oxygen.[14] 1,4-Biradicals formed in other atomic oxygen systems consistently show β-cleavage as their major reaction.[1,4,14] The large yield of carbon monoxide from the dihydrofuran reaction may arise by decomposition of excited glyoxal and formaldehyde.

Dihydropyran. The reaction of dihydropyran with atomic oxygen differed markedly from the 2,3-dihydrofuran reaction in that the dihydropyran reaction produced no detectable carbon monoxide (detection limit ≅0.5% yield). The products of the dihydropyran reaction follow: 2,7-dioxabicyclo[4.1.0]heptane (**21**, 48% yield); dihydro-2*H*-pyran-3(4*H*)-one (**22**, 32%); tetrahydrofurfural (**23**, 0.4%); pentanedial (**24**, 0.4%); and tetrahydro-2*H*-pyran-2-one (**25**, 0.1%). In addition, three minor peaks with a total yield of 2% appeared in the GC of the product mixture. Two of these minor peaks may have been 5-hydroxy-2-pentenal and 3-oxa-5-hexenal. The formation of these two products is predicted by analogy with the reaction between cyclohexene and oxygen (^3P) atoms.[1]

The initial biradical intermediates formed by addition of O(^3P) to dihydropyran are shown below.



The distribution of carbonyl products shows that there is a large preference for formation of the oxygen-substituted biradical **26** over the carbon-substituted biradical **27**.

Reinvestigation of the Reaction of 3-Hydroxy-3-methyl-2-butanone with Methanol. Thorne[15] has reported that the acid-catalyzed reaction of 3-hydroxy-3-methyl-2-butanone (**28**) with anhydrous methanol produces 2-methoxy-2,3,3-trimethyloxirane (**29**). This result is surprising in light of the observations of Stevens[8] concerning the facile ring opening of alkoxyoxiranes under these conditions.

Upon reinvestigation of the reaction reported by Thorne, it was found that the material boiling at the point reported for epoxide **29** was really the hydroxy ketone reactant, **28.** In addition, the NMR spectrum of the crude reaction mixture shows no absorptions other than those due to starting materials. Thus, no acid-catalyzed reaction takes place between **28** and methanol under the conditions reported by Thorne.

Conclusions

With the exception of 2,3-dihydrofuran, the gas-phase reactions of enol ethers with atomic oxygen produce good yields of alkoxyoxiranes, α-alkoxycarbonyl compounds, and smaller amounts of esters and other products. The mild and neutral reaction and work-up conditions allow for the isolation of alkoxyoxiranes which either are not available or are difficultly prepared by other methods.

In order that the reactions described herein and other reactions can be scaled up to make larger amounts of oxygenated material, we are currently investigating convenient solution phase precursors of atomic oxygen. Research is also underway to elucidate the nature of the fragmentation processes observed in atomic oxygen reactions.

Experimental Section

Reactants. Commercial reactants were distilled or trap-to-trap distilled before reaction. 2-Methoxypropene was made by the method of Newman and Vander Zwan.[16] 1-Methoxy-2-methylpropene was prepared by the method of Wenkert et al.[17]

2,3-Dihydrofuran was prepared by the method of Hubert et al.[18] A stirred mixture of 50 g of 2,5-dihydrofuran and 2 g of iron pentacarbonyl was irradiated with a sun lamp for 3 days. The reaction mixture was filtered and distilled to give 2,3-dihydrofuran (bp 55–57°) in 85% yield. The NMR spectrum of this material matched a reported spectrum.[19]

Reaction Procedures. The apparatus and techniques for atomic oxygen reactions have been described previously.[12] A typical product analysis is discussed below.

Methyl Vinyl Ether. The crude mixture of organic products was isolated by trap-to-trap distillation into a −107° trap (isooctane slush). Integration of the NMR spectrum of this fraction (with benzene added as an internal integration standard) allowed calculation of the yields of the methoxyoxirane and methoxyacetaldehyde products.

In another reaction, a sample of methoxyoxirane (1) which was contaminated with 3% methyl acetate (as determined by NMR) was obtained by distillation through a −96° trap (acetone slush) into a −106° trap. Gas chromatography of this sample (NMR reported in the results section) showed elution of only the methyl acetate impurity. This demonstrated lack of rearrangement of **1** under GC conditions allowed for determination of the methyl acetate to methoxyacetaldehyde product ratio by GC of the crude product mixture.

Other spectra of the purified methoxyoxirane (**1**) follow: high-resolution MS of parent peak, obsd, 74.0355 (calcd for $C_3H_6O_2$, 74.0367); low-resolution MS (70 eV) *m/e* (rel intensity) 74 (9), 73 (5), 59 (100), 57 (42), 43 (93), 41 (35), 31 (67); ir (vapor phase), 3020, 2960, 2860, 1470, 1382, 1297, 1288, 1280, 1217, 1130, 1160, 910, 828, and 745 cm^{-1}.

Products. For comparison of GC retention times and spectra, samples of products **5, 6, 11, 16, 24, 25,** methyl acetate, ethyl acetate, ethylene, and acrolein were obtained commercially. Tetrahydrofurfural (**23**) was prepared by the oxidation of tetrahydrofurfuryl alcohol with chromium trioxide–pyridine.[20] Spectra of GC-purified products **15** and **22** matched literature spectra of these compounds.[21–23] Spectra of other α-alkoxycarbonyl products, **3, 10, 12,** methoxyacetaldehyde, and ethoxyacetaldehyde, were simple and unambiguous.

An authentic sample of 3,3-dimethyl-2-methoxyoxirane (**9**) was prepared by the reaction of 2-chloro-2-methylpropanal with sodium methoxide.[9] It should be noted that freshly prepared sodium methoxide was needed for this reaction. Three attempts to prepare **9** with commercial sodium methoxide, which had been vacuum dried, were unsuccessful. The NMR spectrum of **9** showed absorptions at δ 1.21 (s, 3 H), 1.31 (s, 3 H), 3.44 (s, 3 H), and 4.22 (s, 1 H).

Epoxides of enol ethers, other than **1**, were not separated from other reaction products, but their yields were calculated by NMR integration vs. other major reaction products and internal integration standards. Ethoxyoxirane (**2**) was determined by its AMX system at δ 4.45–4.60 and 2.45–2.85; 2-methoxy-2-methyloxirane (**4**) by singlets at δ 2.58 and 2.64; 3,3-dimethyl-2-methoxyoxirane (**9**) by its singlet at δ 4.23; and 2,7-dioxabicyclo[4.1.0]heptane (**21**) by its doublet at δ 4.61 and its multiplet at δ 2.98.[10]

Attempted Reaction of 3-Hydroxy-3-methyl-2-butanone (28) with Methanol. Following the procedure of Thorne,[15] a mixture of 14 g of distilled **28**, 50 ml of anhydrous methanol, and 0.012 mol of anhydrous hydrogen chloride was stirred for 4 hr. The NMR spectrum of the mixture showed only starting materials. The reaction mixture was neutralized with Ag_2CO_3, filtered, and vacuum distilled. The fraction boiling at 83–85° (100 mm) contained only **28** by NMR, ir, and mass spectrometry (85% recovery).

This reaction was repeated several times using halved and doubled HCl concentrations, K_2CO_3 neutralization, and reaction times up to 48 hr. In each case, only starting materials were recovered.

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Registry No.—**1,** 57346-02-8; **2,** 53332-61-9; **4,** 57346-03-9; **9,** 26196-04-3; **21,** 286-26-0; **28,** 115-22-0; methyl vinyl ether, 107-25-5; ethyl vinyl ether, 109-92-2; 2-methoxypropene, 116-11-0; 1-methoxy-2-methylpropene, 17574-84-4; 2,3-dihydrofuran, 1191-99-7; dihydropyran, 110-87-2; atomic oxygen, 17778-80-2; methanol, 67-56-1.

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Reactions of Cation Radicals of EE Systems. III. Chlorination of 9,10-Diphenylanthracene[1]

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Stopped-flow kinetic studies of the reaction of 9,10-diphenylanthracene (DPA) cation radical ($DPA\cdot^{+}$) with chloride ion in acetonitrile gives rise to a rate law which is second order in $DPA\cdot^{+}$, first order in Cl^{-}, and independent of DPA. The product of the reaction of electrogenerated $DPA\cdot^{+}$ with Cl^{-} was shown to be 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (**1**), which undergoes both surface catalyzed and thermally induced rearrangement to 2-chloro-DPA (**2**) via loss of HCl. The mechanism proposed for the addition of Cl^{-} to $DPA\cdot^{+}$ to form **1** involves an associative equilibrium and is of a form which accounts for the observed kinetics as well as those previously reported for the hydroxylation and pyridination of $DPA\cdot^{+}$, which followed a different rate law.

Investigators in several laboratories have examined the reactions of various nucleophiles with the cation radicals derived from aromatic hydrocarbon and heterocyclic fused ring systems such as 9,10-diphenylanthracene (DPA),[1–8] thianthrene,[9–17] dibenzodioxin,[9,18,19] and phenoxathiin.[9,20] Each of these substrates exhibits EE electrochemistry in that one observes two successive monoelectronic oxidation steps, initially to the cation radical and subsequently to the corresponding dication at increasingly anodic potentials. While these aforementioned substrates exhibit strikingly similar electrochemical behavior, the mechanisms postulated for various nucleophilic additions to the cation radi-