TABLE II

EXPLANATION OF THE INTENSE BANDS IN THE DOUBLE BOND REGION

Vapor			CCl$_4$ soln.[b]			Liquid[b]	
Cm.$^{-1}$		Assignment	Cm.$^{-1}$	I	Assignment	Cm.$^{-1}$	
1676	s	2 × 838 = 1676	1675	s	2 × 840 = 1680	1689	vs, broad
		803 + 887 = 1690			804 + 875 = 1679		
		670(R) + 1007 = 1677			670(R) + 1006 = 1676		
1720	vs	C=C stretch	1708	vs	C=C stretch		
1776	m	2 × 887 = 1774	1752	s	2 × 875 = 1750	1744	m
1875	s	887 + 1007 = 1894[a]	1867	s	875 + 1006 = 1881[a]	1864	vs
1922	vs	C=O stretch	1900	vs	C=O stretch	1897	vs

R = Raman frequency. [a] Fermi resonance with C=O stretch. [b] Frequencies measured with CaF$_2$ prism.

cluded that the earlier work was incorrect, and that diketene exists in the 3-buteno-β-lactone form only.

An attempt was made to explain the temperature-induced changes observed by Miller and Koch. Their raw curves were re-examined, and there is no doubt that changes were clearly indicated. One possibility is that some component of the glyptal seal distilled into the cell at high temperature and condensed out at low temperature, even though a blank run was made to test this possibility. Since it is known that phthalic anhydride can be distilled out of glyptal, its vapor spectrum was determined. A glyptal resin (General Electric Company's No. 1202) also was examined by placing a sample at the bottom of the evacuated gas cell and heating to 200°. Neither material accounted for the earlier observations, and we are at a loss to explain them.

There is still the problem of accounting for the five strong bands in the 1650–1950 cm.$^{-1}$ region on the basis of the single 3-buteno-β-lactone structure. This structure would be expected to have only two fundamentals there. One is the carbonyl stretching frequency, which will be abnormally high because of being external to a 4-membered lactone, and which we can guess will be about 1830 cm.$^{-1}$.[9] The other is the olefinic stretching frequency, which also will be abnormally high because of being exocyclic to a four-membered ring.[9] We would predict it to be about 1720 cm.$^{-1}$. Actually the C=O frequency must be the band at 1900 in solution (1922 in the vapor) while the C=C stretch must be 1708 in solution (1720 in the vapor) (see Table II.) The intensity of the latter is remarkably high for an olefinic stretch.

The remaining three strong bands are then presumably to be explained as combination tones, in spite of their considerable intensity. Table II shows that this can be done as far as the frequencies are concerned, although it is still hard to understand their high intensity. It will be noted that in the pure liquid there are only four bands. The double bond frequency appears to be lower than its value of 1708 in the solution, and it apparently merges with the 1675 band to give a single very broad band at 1689.

(9) R. C. Lord and F. A. Miller, *App. Spectros.*, **10**, 115 (1956).

PITTSBURGH 13, PA.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Hydrogen Peroxide–Olefin Reactions in the Vapor Phase

BY E. R. BELL, W. E. VAUGHAN AND FREDERICK F. RUST

RECEIVED MARCH 2, 1957

Hydrogen peroxide has been decomposed in the presence of ethylene, propylene and isobutylene at temperatures between 435 and 630°. The products are traceable to an initial attack by hydroxy radical involving either addition to the double bond or abstraction of a hydrogen atom from the olefin. As a consequence of the latter process diallyl and dimethallyl are major products from propylene and isobutylene, respectively. Many other compounds must originate from radical association reactions. Much fragmentation of the olefins seems to have had its genesis in the initial addition of a hydroxy radical to the olefin double bond. In cases where the carbon skeleton has been retained, hydrogenation and dehydrogenation processes can be significant. Reaction steps which logically interpret the data have been proposed.

Introduction

Hydrogen peroxide has a thermal stability much greater than that of the organic peroxides and for this reason its significance to combustion phenomena in temperature regions beyond the cool flame zone is substantially greater. Moreover, this stability suggests that hydrogen peroxide may have useful properties as a high temperature reactant.

Its thermal decomposition is apparently a complex of both heterogeneous and homogeneous processes. McLane[1] has reported that the decomposition in nitrogen begins to be essentially homogeneous only above 470° in reactors whose walls have been treated with boric acid. Although the reaction showed first-order kinetics in the temperature range 470–540°, the activation energy increased from 40 kcal. in a reactor whose surface to volume ratio was 7 cm.$^{-1}$ to 50 kcal. in one with a ratio of 3 cm.$^{-1}$. (A boric acid-coated reactor of surface–volume ratio 0.4 cm.$^{-1}$ has been chosen for these studies.)

The near coincidence of this high activation energy with the O–O bond strength in hydrogen perox-

(1) C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).

ide (53 kcal.[2,3]) suggests that this decomposition should be an effective source of hydroxy radicals.

Since it is known that hydrogen peroxide can be a significant product of hydrocarbon oxidation at temperatures in the region of 475°[4,5] a study of the high temperature peroxide–hydrocarbon reactions which must be proceeding concomitantly with the oxidation processes leading to hydrogen peroxide formation would seem to be desirable. One of the principal objectives of this investigation was to gain some insight into the behavior of certain of the simpler olefins when exposed to the radicals from decomposing hydrogen peroxide.

Experimental

A flow system was used in these experiments. The flow of hydrogen peroxide (30% aqueous solution) through a capillary was calibrated against the air pressure above the peroxide. The peroxide was then fed onto a vertically descending spiral glass rod (about 2 mm. o.d.) fused onto the inner wall of a 44 mm. glass tube. The outer wall of this tube was heated by a flexible tape heater. Its temperature was measured by a thermocouple between the heater and tube in the lower third of its length. For low peroxide flows, (0.3–0.5 g./min.) the wall was heated to 100°; for high (*ca.* 2.0 g./min.) the wall was heated to 180°. Tests of this vaporizer showed that negligibly small amounts of peroxide were decomposed. The hydrocarbon was metered as vapor and flowed through the vaporizer into the reactor.

The latter was a glass tube 48 mm. o.d. by 75 cm. long sealed directly to the vaporizer and heated by a "Hevi-Duty" furnace. This reactor was periodically soaked overnight with a saturated boric acid solution and then drained. For the experiment at 630° and high flow rates a "Vycor" reactor 18 mm. o.d. by 20 cm. long was used. It was found necessary to provide a baffle near the inlet to cause turbulence which accelerated the attainment of reaction temperature by the vapors.

The product collection system consisted of a water condenser followed by a trap at 0° and then a series of traps at −78°. The non-condensable gas was collected over brine. When the non-condensable gas was excessive, as with ethylene, an aliquot of the gas was collected by means of an interval timer and a solenoid valve arrangement while the remainder was vented through a wet test meter.

Product work-up consisted of the following steps: (1) the contents of the Dry Ice traps were distilled through a 3 ft. Vigreux column until the C_4 hydrocarbons had been taken overhead; (2) the bottoms from this distillation were combined with the contents of the 0° trap; (3) the aqueous and oil phases were separated and the oil phase washed several times with ice-water; (4) the oil phase, after it had been dried with anhydrous potassium carbonate, was distilled through a Piros–Glover micro-spinning band column or through a 20 theoretical plate helices-packed column; (5) the combined aqueous phase and washings were titrated iodometrically for residual peroxide; (6) the residual peroxide was decomposed by gentle warming of the aqueous phase over platinum oxide; (7) the aqueous phase was then analyzed by standard methods for acid, ester, α-glycol, formaldehyde, total carbonyl, saturated carbonyl, total hydroxyl and saturated hydroxyl; on occasion the aqueous phase was flashed to an overhead temperature of 100°, and the distillate redistilled through the 20-plate column to provide material for identification; (8) all gas samples and low temperature distillation cuts were analyzed by both mass spectrometric and Orsat methods; (9) the analysis of the C_5 fraction was obtained by Podbielniak distillation coupled with appropriate chemical and spectroscopic analyses of the fractions; (10) the other hydrocarbon fractions were characterized by boiling point, refractive index and infrared spectroscopy.

The products of reaction of hydrogen peroxide with ethylene, propylene and isobutylene are summarized in Tables I, II and III. The oxygenated compounds have been identified by derivative preparation and quantitatively estimated by functional group analyses of the appropriate fractions. The gaseous products—C_1 to C_4—were analyzed by mass spectrometry. Fractionation of the higher boiling hydrocarbon components and infrared analysis of the fractions are the bases for the identification and estimation of the higher hydrocarbons.

Table I

Product Balance for Reaction of Hydrogen Peroxide with Ethylene

	Temp., 435°; contact time, ~26 sec.; feed ratio: C_2H_4, 17.1; H_2O, 4.4; H_2O_2, 1; peroxide decomposed, 98.5%; ethylene reacted, 2.8 moles/moles H_2O_2		Temp., 525°; contact time, ~10 sec.; feed ratio: C_2H_4, 20; H_2O, 4.4; H_2O_2, 1; peroxide decomposed, 100%; ethylene reacted, 1.4 moles/mole H_2O_2	
Product	Moles[a]/100 moles H_2O_2 reacted	Moles[a]/100 moles C_2H_4 reacted	Moles[a]/100 moles H_2O_2 reacted	Moles[a]/100 moles C_2H_4 reacted
H_2	..	..	11.8	8.3
CO	61.5	21.8	37.2	26.6
CO_2	4.9	1.8	2.0	1.4
CH_4	11.5	4.1	5.9	4.2
C_2H_6	21.5	7.5	6.0	4.3
C_2H_2	..	..	19.6	14.0
C_3H_8	7.2	2.5	..	..
C_3H_6	68.2	24.2	30.4	21.7
C_3H_4	0.2	0.1	..	..
C_4H_{10}[b]	3.0	1.1	..	..
C_4H_8[b]	5.7	2.0	1.8	1.3
C_4H_6	0.4	..	3.9	2.8
C_5 and higher[c]	19.0	6.7	10.0	7.0
Acid	5.5	1.9	0.2	0.1
Alcohol	11.3	4.0	.3	.2
α-Glycol	4.4	1.6	.3	.2
Acetaldehyde	14.0	5.0	..	..
Formaldehyde	6.3	2.2	5.8	4.1

[a] Calculated loss-free basis. [b] Almost entirely straight chain. [c] Calculated as C_6.

Discussion and Mechanism

A major problem in the study of the reaction of hydrocarbons with hydrogen peroxide is the known proclivity of hydrogen peroxide to decompose to water and oxygen by way of the chain reaction steps 1–4.[6]

$H_2O_2 \longrightarrow 2HO$ Initiation (1)

$HO + H_2O_2 \longrightarrow H_2O + HO_2$ Propagation (2)

$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + HO$ (3)

$HO + HO_2 \longrightarrow H_2O + O_2$ Termination (4)

When a hydrocarbon is present, its reaction with the most reactive species, hydroxy, becomes an important characteristic of the new system.

$$HO + RH \longrightarrow H_2O + R \qquad (5)$$

In principle, since the reaction of hydroxy with hydrocarbons is the subject of interest, step 5 and related reactions are promoted at the expense of 2–4 by operation with high hydrocarbon concentrations and the lowest practical peroxide concentrations. In practice it is not easy to conclude that this has been accomplished successfully since many products of the reaction of hydrocarbons with hydrogen per-

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(2) P. A. Giguere, *Can. J. Research*, **25B**, 135 (1947).

(3) K. H. Geib, *Ergeb. exakt. Natur.*, **15**, 44 (1936).

(4) P. J. Kooyman, *Rec. trav. chim.*, **66**, 5. 491 (1947).

(5) B. M. Sturgis, *S.A.E. Trans.*, **63**, 253 (1947).

(6) W. C. Schumb, C. N. Satterfield and R. H. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955, p. 457.

oxide are identical with those of the high temperature reaction with oxygen which might have come from peroxide decomposition.

TABLE II

PRODUCT BALANCE FOR REACTION OF HYDROGEN PEROXIDE WITH PROPYLENE

Temp., 530°; contact time, 1.0 sec.; feed ratio: C_3H_6, 20.4; H_2O_2, 1; H_2O, 4.4; H_2O_2 reacted, 71.0%; C_3H_6 reacted, 1.8 moles/mole H_2O_2

Temp., 630°; contact time, 0.1 sec.; feed ratio: C_3H_6, 20.5; H_2O_2, 1; H_2O_2, 4.4; H_2O_2 reacted, 84.0%; C_3H_6 reacted, 1.7 moles/mole H_2O_2

Product	Moles/ 100 moles[a] H_2O_2 reacted	Moles/ 100 moles[a] C_3H_6 reacted	Moles/ 100 moles[a] H_2O_2 reacted	Moles/ 100 moles[a] C_3H_6 reacted
H_2	1.1	0.6	2.5	1.4
CO	12.6	7.0	13.5	8.0
CO_2	2.9	1.6	2.5	1.5
CH_4	16.2	9.0	21.0	12.5
C_2H_6	4.0	2.2	2.8	1.7
C_2H_4	23.3	13.1	8.5	5.0
C_2H_2	2.9	1.6	5.4	3.2
C_3H_8	9.4	5.2	..	..
C_3H_4	2.2	1.2	16.3	9.7
C_4H_{10}	0.7	0.4	0.4	0.3
C_4H_8	5.3	3.0	10.7	6.4
C_4H_6	1.4	0.8	0.2	0.1
C_5 HC's[d]	6.1	3.4	4.8	2.8
C_6 HC's other than diallyl[c]	5.6	3.1	2.5	1.5
Diallyl[b]	27.6	16.0	31.2	18.5
C_9's[e]	8.4	4.7	6.0	3.6
Sat. ROH	3.2	1.8	1.9	1.1
Allyl alcohol	4.7	2.6	4.4	2.6
α-Glycol	4.7	2.6	3.3	2.0
Acrolein	3.1	1.7	3.3	2.0
Sat. $C_2 + C_3$ carbonyl	5.8	3.2	6.5	3.8
H_2CO	1.3	0.7	0.9	0.6
Acid + ester	7.5	4.1	7.6	4.7

[a] Calculated on a loss-free basis. [b] Cut from 57–62, n^{20}_D 1.4030; lit. diallyl 59.4°, n^{20}_D 1.4040. [c] Cut from 62–90°. [d] Cut from 15–57°. [e] Hydrocarbon material boiling above 90°.

A further complication in interpretation arises because the high temperature oxidation of hydrocarbons is presumed to propagate to a significant extent by means of hydroxy radicals. Thus the distinction between the two systems is one of degree; oxidation involves a low concentration of hydroxy radicals in the presence of a high concentration of oxygen while the present system is designed for the study of a high concentration of hydroxy radicals in the presence of little or no oxygen.

The success in achieving this end must be judged in terms of those products which are peculiar to the hydrogen peroxide–hydrocarbon system and the trends of the product distribution with hydrocarbon to hydrogen peroxide ratio. It is felt that the results presented indicated a satisfactory suppression of hydrocarbon–oxygen reactions.

Two alternatives are open to hydroxy, *viz.*, hydrogen abstraction or addition to the olefinic double bond. Most of the products are ultimately traceable to one of these two initial modes of reaction.

TABLE III

PRODUCT BALANCE FOR REACTION OF HYDROGEN PEROXIDE WITH ISOBUTYLENE

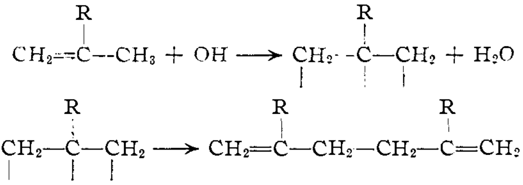
Temp., 530°; contact time, 9 sec.; feed composition, i-C_4H_8, 19; H_2O, 4.4; H_2O_2, 1; peroxide decomposed, 100%; isobutylene reacted, 1.76 moles/mole H_2O_2 converted

Product	Moles/ 100 moles[a] H_2O_2 reacted	Moles/ 100 moles[a] i-C_4H_8 reacted
H_2	2.7	1.5
CO	6.8	3.8
CO_2	1.0	0.5
CH_4	15.1	8.6
C_2H_4	6.9	3.9
C_2H_6	0.5	0.3
C_3H_4	2.2	1.2
C_3H_6	4.3	2.5
C_3H_8	0.8	0.4
C_4H_{10}	7.0	4.0
C_5's[b]	2.8	1.5
C_6's[c]	7.1	4.0
C_7's[d]	6.8	3.8
C_8's other than dimethallyl[f]	6.0	3.4
C_{10}'s[g]	5.3	3.0
Dimethallyl[e]	36.6	20.8
Sat. alcohol	3.2	1.9
Sat. carbonyl	4.7	2.7
Ester	6.5	3.7
Unsat. alcohol	7.5	4.3
Methacrolein	4.1	2.4
α-Glycol	5.1	2.9
H_2CO	2.4	1.3

[a] Calculated on a loss-free basis. [b] Distilled +15–37°. [c] Distilled +38–90°. [d] Distilled +90–111°. [e] Distilled 111–118°; n^{20}_D 1.4300–1.4310; lit. dimethallyl 114.3°; n^{20}_D 1.4293. [f] Distilled 118–164°. [g] Bottoms.

Depending upon the olefin and the point of attack, the resultant radical R will be either an allylic or vinylic radical—in the case of ethylene entirely vinylic, and for propylene and isobutylene largely allylic, although it should be borne in mind that the selectivity of attack customary at lower temperatures will be less obvious at 500°.

The high yields of diallyl from propylene, and dimethallyl from isobutylene are probably the most notable characteristics of the high temperature reactions with hydrogen peroxide. They present probably the most convincing evidence that molecular oxygen from decomposing peroxide is an insignificant factor in these studies because these diolefins have never been reported to be formed in the presence of oxygen. There can be little doubt that formation of these diolefins takes place as

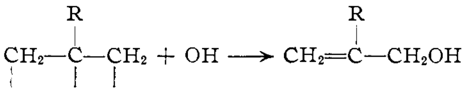


$$CH_2{=}\overset{\overset{R}{|}}{C}{-}CH_3 + OH \longrightarrow \underset{|}{CH_2}\cdots\underset{|}{\overset{\overset{R}{|}}{C}}{-}\underset{|}{CH_2} + H_2O$$

$$2\underset{|}{CH_2}{-}\underset{|}{\overset{\overset{R}{|}}{C}}{-}\underset{|}{CH_2} \longrightarrow CH_2{=}\overset{\overset{R}{|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{R}{|}}{C}{=}CH_2$$

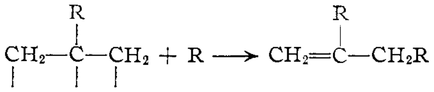
where R is H or CH_3.

Allyl (or methallyl) alcohol is then a logical consequence of



$$\underset{|}{CH_2}{-}\underset{|}{\overset{\overset{R}{|}}{C}}{-}\underset{|}{CH_2} + OH \longrightarrow CH_2{=}\overset{\overset{R}{|}}{C}{-}CH_2OH$$

and the olefins, which are formed in substantial quantity, of



$$\underset{|}{CH_2}—\underset{|}{\overset{\overset{R}{|}}{C}}—\underset{|}{CH_2} + R \longrightarrow CH_2{=}\overset{\overset{R}{|}}{C}—CH_2R$$

1-butene from propylene by way of allyl and methyl is an example of the foregoing.

At a temperature of 630° the hydrogen peroxide–propylene reaction is noticeably productive of C_3H_4 (allene). Inasmuch as radical–radical association reactions are important paths to some end products, it is not unreasonable to ascribe other compounds, *e.g.*, allene, to radical–radical disproportionations.

$$\underset{|}{CH_2}—\underset{|}{CH}—\underset{|}{CH_2} + R \longrightarrow CH_2{=}C{=}CH_2 + RH$$

The importance of allyl radical reactions in the case of propylene is demonstrated by the fact that 55 and 70% of the reacted propylene at 530 and 630°, respectively, yields products traceable to allyl radical precursors. Products which stem from initial abstraction of vinylic hydrogen atoms are evident, particularly in the case of ethylene and in the higher temperature region.

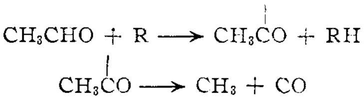
$$CH_2{=}CH_2 + OH \longrightarrow CH_2{=}CH— + H_2O$$
$$2CH_2{=}CH— \longrightarrow CH_2{=}CH—CH{=}CH_2$$
$$CH_2{=}CH— \longrightarrow CH{\equiv}CH + H$$

Although vinyl radicals can be postulated as intermediates in other reactions, butadiene and acetylene seem to be devoid of reasonable alternate antecedents. A significant yield of acetylene (5.4%) from propylene seems likewise to be a result of vinyl hydrogen removal.

$$CH_3CH{=}CH_2 + OH \longrightarrow CH_3CH{=}CH— + H_2O$$
$$CH_3CH{=}CH— \longrightarrow CH_3 + CH{\equiv}CH$$

Addition of a hydroxy radical to the double bond must be the single most important reaction with ethylene even at 525° and must be progressively less important with propylene and isobutylene. The resultant hydroxyalkyl radicals can be stabilized as alcohols by hydrogen capture, but evidently the more usual evolution of hydroxyalkyl leads to eventual fragmentation of the molecule. Methane, carbon monoxide and formaldehyde are important products of the hydrogen peroxide–ethylene experiments and in the propylene studies these plus, in particular, ethylene must be accounted for. The initial hydroxyethyl radical which seems to be a step in the breakdown of ethylene, shows little evidence of instability and, in fact, rather limited reaction opportunities. The complete absence of hydrogen at 435° precludes a β-scission of a carbon–hydrogen bond so that it can only be concluded that hydroxyethyl is a hydrogen donor. That some donor of considerable efficiency is present can be deduced from the important yields of ethane. The reaction steps suggested then become

$$—CH_2CH_2OH + X \longrightarrow CH_2{=}CHOH + XH$$
$$X = \text{olefin or radical}$$
$$CH_2{=}CHOH \longrightarrow CH_3CHO$$



$$CH_3CHO + R \longrightarrow CH_3\overset{|}{C}O + RH$$
$$CH_3\overset{|}{C}O \longrightarrow CH_3 + CO$$

At 435° acetaldehyde is a significant product and its decomposition to methyl and carbon monoxide frequently has been demonstrated.[7] Thus, this course of fragmentation for ethylene—and for propylene—seems reasonable.

The production of hydrocarbons of higher carbon number is surely a consequence of radical addition to olefin double bonds. Indicative of the number of processes yet to be explored is the analysis of a broad product fraction boiling from 15 to 57°—identified among the products as C_5's. The C_5 hydrocarbons in the fraction were identified as pentanes 2.9%, amylenes 32.2%, pentadienes 32.8%, cyclopentane 2.5%, cyclopentene 13.2% and cyclopentadiene 2.1%.

EMERYVILLE, CALIF.

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[7] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd Ed., Reinhold Publishing Co., New York, N. Y., 1954, p. 206.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Intramolecular Oxidation. The Autoxidation of Some Dimethylalkanes

BY FREDERICK F. RUST

RECEIVED MARCH 2, 1957

The products from the liquid phase, non-catalytic oxidations of 2,3-dimethylpentane (I), 2,4-dimethylpentane (II), 2,5-dimethylhexane (III) and 2,6-dimethylheptane (IV) have been identified and related to one facet of the mechanism of hydrocarbon oxidation. In the cases of II and III, the 2,4- and 2,5-dihydroperoxides, respectively, were made in extraordinarily high yields despite the fact that less than 10% of the hydrocarbons reacted. The results show that intramolecular peroxy radical attack is highly efficient at the β-position, somewhat less so at the γ-position and apparently of little or no significance at either the α- or Δ-positions. The efficiency of intramolecular oxidation appears to be favored by attachment of the peroxy radical to a tertiary carbon atom.

Introduction

Although the oxidation of aliphatic hydrocarbons is conventionally represented as an intermolecular process of the type

$$RO_2 + RH \longrightarrow RO_2H + R$$
$$R + O_2 \longrightarrow RO_2$$

increasing evidence indicates that an oxidation chain does not necessarily propagate from molecule to molecule, but, depending on conditions, can propagate from one point to another within the molecule. The formation of β-dicarbonyl compounds and oxirane rings in the gas phase oxidation