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Preliminary communication

Oxidation of olefins to unsaturated alcohols by aqueous mercuric sulfate

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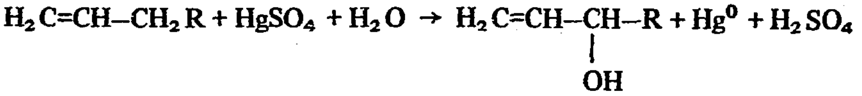
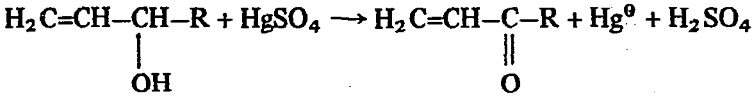
Previous publications describing the oxidation of olefins by aqueous mercuric salts disagree regarding the principal reaction products. For example, the mercuric ion oxidation of propylene in water reportedly yielded in one case, exclusively acetone[1]; while in another similar case, a mixture of principally acrolein with some acetone and propionaldehyde was observed[2]. Studies of the oxidation of other olefins were equally confusing since both saturated[3,4] and unsaturated[5,6] ketones were reported as major products. Detailed examinations of the oxidation of olefins by other aqueous metal ions, *i.e.*, Pd^{2+} [7,8,9] and Tl^{3+} [10,11] have been reported. However, similar studies of the aqueous mercuric system have not been performed due in part to the variety of products observed.

We have now found that unsaturated alcohols, previously unreported products, are obtained when terminal olefins are oxidized by aqueous mercuric sulfate (Eqn. 1). This reaction not only is novel but also appears to be an intermediate step in the overall oxidation of olefins to unsaturated carbonyl compounds (Eqn. 1 and 2).



$$H_2C{=}CH{-}CH_2R + HgSO_4 + H_2O \rightarrow H_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R + Hg^0 + H_2SO_4 \tag{1}$$



$$H_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R + HgSO_4 \longrightarrow H_2C{=}CH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R + Hg^0 + H_2SO_4 \tag{2}$$

Consequently, this reaction suggests a rationale for the variety of products which had previously been reported.

The results summarized in Table 1 show that reasonable yields of unsaturated alcohols are obtained as primary products from the oxidation of terminal olefins by mercuric sulfate. These results also show (Table 1) that under identical reaction conditions, the primary products are rapidly (< 1 hour) converted to secondary products, vinyl ketones, in practically quantitative yields (Eqn. 2). This suggests that the difficulty associated with recovering high yields of unsaturated alcohol is not due to the poor selectivity of reaction 1 but rather the high rate of reaction 2.

Table 1

PRODUCTS OBTAINED FROM MERCURIC SULFATE OXIDATION OF OLEFINS

Olefin	Primary product	Yield[a] (mole %)	Secondary product	Yield[b] (mole %)
Propylene[c]	Allyl alcohol	51	Acrolein	87
1-Butene[c]	1-Buten-3-ol	41	1-Buten-3-one	100
	2-Buten-1-ol	0[d]	1-Buten-3-one	100
trans-2-Butene[c, e]	2-Butanone	81	No reaction	–
1-Pentene[c]	1-Penten-3-ol	33	1-Penten-3-one	92
	2-Penten-1-ol	8	1-Penten-3-one	86
cis-2-Pentene[c, e]	2-Pentanone	53	No reaction	–
	3-Pentanone	27	No reaction	–
1-Hexene	2-Hexen-3-ol	35	1-Hexen-3-one	91
1-Dodecene	1-Dodecen-3-ol	6	Not examined	–
Cyclohexene[e]	Cyclopentane Carboxyaldehyde	74	No reaction	–

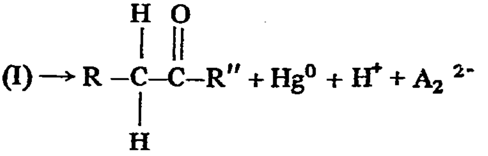
[a] Yields of isolated products were on reduced mercury. [b] Yields of isolated ketones were based on reacted alcohols. Yields based on reduced mercury were ~ 90 mole %. Reaction conditions were 90° and 1 hour. Yields of ketone starting from the corresponding olefin were consistently 20% less. [c] Reaction conditions were 90° and 5 hours. [d] 2-Buten-1-ol is very rapidly isomerized to 1-buten-3-ol by aqueous acid solutions at 90°. [e] The same products were observed when $Hg(NO_3)_2$ or $Hg(ClO_4)_2$ was used.

In contrast to this reaction with mercuric sulfate, the terminal olefins listed in Table 1 were oxidized by mercuric nitrate or mercuric perchlorate to saturated methyl ketones in greater than 80% yield. Under identical reaction conditions, internal olefins were oxidized to saturated ketones by all three mercuric salts (Table 1).

We propose the following reaction scheme to explain the formation of either saturated or unsaturated products as a function of the nature of the olefin (*i.e.*, terminal or internal double bond) and the ionic character of the mercury-anion bond. The first step is the very rapid oxymercuration of the olefin[12] (Eqn. 3).

$$R'HC{=}CHR'' + HgA_2 + H_2O \longrightarrow \underset{(I)}{(A_2Hg{-}CR'H{-}CH(OH)R'')^{-}} + H^+ \qquad (3)$$

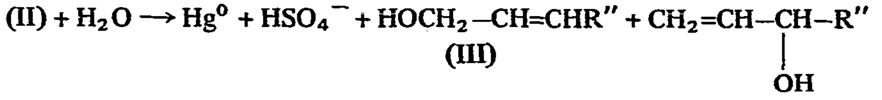
The subsequent steps depend on the nature of the olefin and/or the anion A_2^{2-} [$(ClO_4)_2^{2-}$, $(NO_3)_2^{2-}$, or SO_4^{2-}]. When R' and R'' are alkyl groups, a secondary carbon–mercury bond is formed which is relatively reactive regardless of the anion A_2^{2-} and demercuration occurs, yielding a saturated ketone (Eqn. 4). When R' is hydrogen and R'' is an alkyl group, a primary carbon–mercury bond is formed and demercuration takes place when A_2^{2-} is $(NO_3)_2^{2-}$ or $(ClO_4)_2^{2-}$. However, when A_2^{2-} is SO_4^{2-}, the carbon–mercury bond is sufficiently inert to allow dehydration of the oxymercurial (I) (Eqn. 5). The allylmercurial (II) demercurates rapidly (Eqn. 6) to form an allyl carbonium ion and finally a mixture of the allylic alcohols (III) and (IV).



$$(I) \longrightarrow R{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R'' + Hg^0 + H^+ + A_2^{2-} \qquad (4)$$

$$\text{(I)} \longrightarrow (\text{SO}_4\text{Hg–CH}_2\text{–CH=CHR}'')^- + \text{H}_2\text{O} \qquad (5)$$

(II)



$$\text{(II)} + \text{H}_2\text{O} \longrightarrow \text{Hg}^0 + \text{HSO}_4^- + \text{HOCH}_2\text{–CH=CHR}'' + \text{CH}_2\text{=CH–}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{–R}'' \qquad (6)$$

(III)

(IV)

The subsequent oxidation of (III) yields the unsaturated aldehyde while (IV) is converted to a vinyl ketone. Dehydration of (I) involving the 1 and 2 carbon atoms yields a vinylmercurial which demercurates to form a saturated aldehyde. The formation of propionaldehyde★ from propylene is the only example of this reaction observed to date.

The proposed mechanism depends to a great extent on the variable reactivity of carbon–mercury bonds. In this regard, Jensen *et al.*[14] have demonstrated that secondary carbon–mercury bonds are at least 10^4 times as reactive as primary bonds. In addition, experiments with the cyclohexyl-mercuric spcies[15] have demonstrated that the rate of demercuration depends on the ionic character of the mercury–anion bond. The more ionic the bond, the more rapid the demercuration.

We tested certain aspects of this oxidation mechanism. Allylmercuric sulfate, synthesized from the corresponding iodide, was demercurated in aqueous H_2SO_4 to yield allyl alcohol (87 mole %) at 70° (Eqn. 6). The inability to isolate an allylmercuric species from the oxidation reaction medium is consistent with the high reactivity of this carbon–mercury bond.

The literature contains evidence that β-hydroxyethylmercuric chloride will dehydrate in basic alcohol[16]. Our indirect evidence regarding this dehydration (Eqn. 5) was obtained by treating isopropanol, butan-2-ol, and pentan-2-ol under conditions identical to the oxidation conditions but in the absence of mercuric ion. The isolation of the corresponding olefin in 15 to 30% yield after 1 hour of heating suggests that dehydration of the oxymercurial in aqueous acid solution is possible.

The saturated products observed during oxidation of olefins by aqueous Pd^{2+} and Tl^{3+} are consistent with the high reactivity of carbon–palladium and carbon–thallium bonds.

The allylic oxidation of olefins by mercuric acetate in acetic acid appears to involve a solvent elimination step, similar to Eqn. 5[17,18]. This observation is consistent with the fact that the mercuric–acetate bond is relatively non-ionic.

EXPERIMENTAL

Propylene, butenes, and pentenes (200 mmoles) were oxidized at 90° by $HgSO_4$ (50 mmoles) in 150 ml of aqueous H_2SO_4 (0.3 *M*). The reaction was performed in a 300 ml stirred autoclave and required 5 hours. 1-Hexene, 1-dodecene, and cyclohexene (200

★Allyl alcohol has been reported to isomerize to propionaldehyde[13] but this was not observed under our conditions.

mmoles) were oxidized at 100° for 5 hours using the same reaction solution in an open flask. Additional olefin (0.1 mole/hour) was continuously added and a portion of the product was removed from the reactor by steam distillation.

Unsaturated alcohols (200 mmoles) were oxidized at 90° in 150 ml of aqueous H_2SO_4 (0.3 *M*) by the slow addition of $HgSO_4$ (50 mmoles). The $HgSO_4$ addition took 1 hour and the reaction was virtually complete in this time. When saturated ketones were treated in the same manner no unsaturated ketones were observed.

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