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OBSERVATION BY PMR SPECTROSCOPY OF THE INTERMEDIATE ALKOXYCARBONIUM IONS IN THE ACID-CATALYSED DECOMPOSITION OF ORGANIC HYDROPEROXIDES

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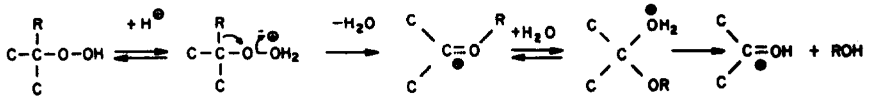
The acid-catalysed decomposition of hydroperoxides to ketones (or aldehydes) and alcohols (or phenols) is generally believed[1-4] to proceed via the following steps:



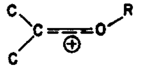
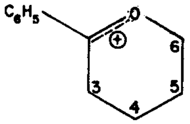
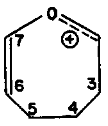
I

II

R = $\underline{a}$ CH_3, $\underline{b}$ C_2H_5, $\underline{c}$ i-C_3H_7, $\underline{d}$ $C_6H_5CH_2$, $\underline{e}$ C_6H_5, $\underline{f}$ p-$CH_3C_6H_4$, $\underline{g}$ p-(tert-C_4H_9)C_6H_4, $\underline{h}$ $C(CH_3) = CH_2$

We now report the observation, by PMR spectroscopy, of several alkoxycarbonium ions II, formed via an instantaneous reaction of the corresponding hydroperoxide I with FSO_3H/SbF_5 (5:1) at -40 °C In no case was the protonated hydroperoxide detected, even at -60 °C.

Table PMR spectroscopic data of alkoxycarbonium ions in FSO_3H/SbF_5 (5:1)

Structure	Chemical shift[a], ppm (multiplicity, J in Hz)	
	CH_3	R
IIa R = methyl	3.08	4.89 (s)
IIb R = ethyl	3.05	CH_2 5.21 (q,7); CH_3 1.83 (t,7)
IIc R = isopropyl	3.05; 3.02[b]	CH 5.87 (spt, 6); CH_3 1.79 (d,6)
IIg R = p-tert-butylphenyl	3.36; 3.04[b]	t-Bu 1.45 (s); phenyl H 7.77, 7.30 (d,9)
IV 	$C(3)H_2$ 3.89 (t,~7) $C(4+5)H_2$ 2.2 (m) $C(6)H_2$ 5.41 (t,7)	
VI 	$C(3)H_2$[c] 2.65 (t,7.5); $C(4)H_2$ 2.07 (q,7); $C(5)H_2$[c] 2.95 (t,7) of (d,2); C(6)H 8.87 (t,2); C(7)H 9.11 (s)	

a) Measured against tetramethylammonium ion (δ = 3.20) as internal reference.

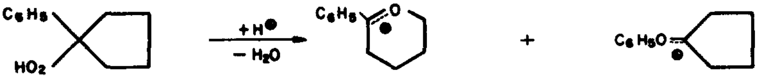
b) Methyl groups syn and anti with respect to R.

c) Assignments for 3 and 5 positions may be reversed.

Treatment of Ia with FSO_3H/SbF_5 yielded >99% of IIa (cf. ref. 5 and 6). Similarly, Ib and Ic afforded IIb and IIc in 66 and 70% yield, respectively, the balance consisting of the hydrolysis products of these ions; no (<1%) products arising from methyl migration were observed.

The reactions of Id, e and f with FSO_3H/SbF_5 only led to the hydrolysis products (protonated acetone and protonated alcohol or phenol) of the intermediate ions. Obviously, ROH is a better leaving group when R = aryl or benzyl than when R = alkyl. In contrast, Ig afforded IIg in ca. 50% yield. It is not clear why IIg is more stable to hydrolysis than IIf.

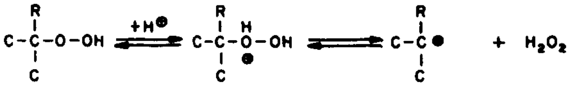
With III the rates of alkyl and phenyl shift are similar[7]. This suggests that the stability of the product is reflected in the transition state, as cyclic cations analogous to IV are known[3,8] to be stabler than their acyclic counterparts V.



III IV V

The reaction of III with FSO_3/SbF_5 gave IV[9] in 11% yield together with the hydrolysis products (protonated cyclopentanone and protonated phenol) of V in 64% yield. The 6:1 ratio of phenyl to alkyl shift is in good agreement with a previous study[7] of the acid-catalysed decomposition of III. Ion IIh could not be observed in the reaction of Ih with FSO_3H/SbF_5 owing to its rapid hydrolysis to two moles of protonated acetone. However, 3-hydroperoxycyclohexene afforded VI in ca. 50% yield (together with unidentified products; no cyclohexenone, the product expected from H shift, was found). We attribute this difference in ease of observation to the greater stability in general of cyclic carbonium ions compared to their acyclic analogues[3,8].

In two cases we observed VII, formed via C–O heterolysis. Thus, III afforded the 1-phenylcyclopentyl ion (25 %) and Ig gave VII (R = p-tert-butylphenyl) in 50 % yield.



I VII

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