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ON THE USE OF THE L.F.E.R. RULE FOR THE QUANTITATIVE ESTIMATE OF THE SUBSTITUENT EFFECT ON THE BREAKDOWN OF THE BOND IN OZONIZATION

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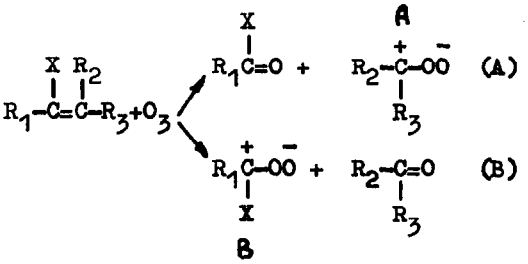
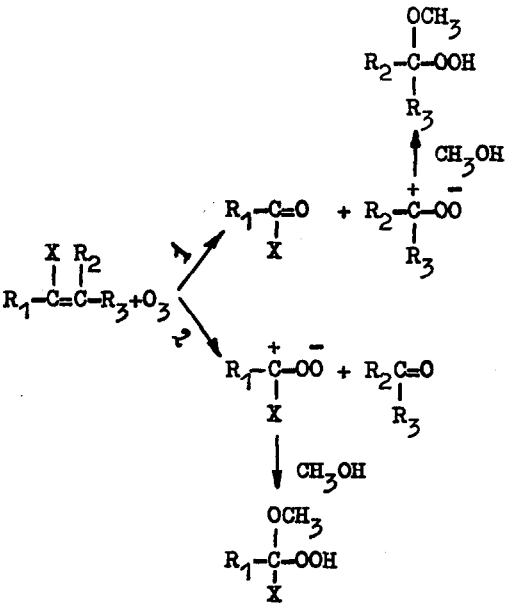
Abstract. The l.f.e.r. rule has been applied to the quantitative estimate of the substituent effect on the breakdown C=C bond on ozonization.

In a recent paper[1] an interesting effort of using the Hammet rule to the ozonization of nonsymmetric olefines has been made. The authors supposed that by the composition of the hydrolysis products of ozonides one could estimate the influence of the substituent on the preferential formation of zwitterion (A or B):



In fact they investigated the influence of the substituents on the ozonides hydrolysis since it was difficult to suggest that during hydrolysis the ozonides "remember" from which parts it had been synthesized, irrespectively of the introduced substituents nature. Probably a direct quantitative estimation of the formed zwitterion would better satisfy this aim. It is known that in the methanol solvent the ozonization reaction leads to the methoxydroperoxides formation[2].



Their quantitative estimation allows us to specify the zwitterions content of both reaction series in the system. Methoxyhydroperoxides have been analysed by gas-liquid chromatography of thermal decomposition products or of reduction by hydrogen iodide. In table 1 experimental results on ozonization, analysis of products and the values of induction constants σ are given.

olefines preferential zwitterion formation is observed at the carbon atom connected with electron-donating substituents ($H < R < CH_3 \ll 2CH_3$) $\frac{X_i}{X_o} > 1$ and on the contrary, zwitterion yields decrease in case of electron-acceptor substituents (C_6H_5) $\frac{X_i}{X_o} < 1$.

In Table 1 experimental results of calculation according to the "linear free energy relationships" rule (l.f.e.r.) are

Table 1

NN	Starting	Zwitterion Structure	$\frac{X_i}{X_o} = \frac{RCH-OO}{H_2C-OO}$	$\lg \frac{X_i}{X_o}$	$\sigma_{Exper.}$	$\sigma_{Liter.}$[3]
1	Ethylene	$H_2\overset{+}{C}-\overset{-}{O}O$	1	0	0	-
2	Hexene-1	$CH_3(CH_2)_3-\overset{+}{\underset{H}{C}}-\overset{-}{O}O$	1,12	0,05	-0,067	-0,07
3	Heptene-2	$CH_3-\overset{+}{\underset{H}{C}}-\overset{-}{O}O$	1,52	0,182	-0,242	-0,069
4	Isobutylene	$(CH_3)_2-\overset{+}{C}-\overset{-}{O}O$	only X_i	-	-	-
5	Styrene	$C_6H_5\overset{+}{\underset{H}{C}}-\overset{-}{O}O$	0,82	-0,086	+0,11	+0,06

During ethylene ozonization due to the olefine molecular symmetry the zwitterion formation is equally possible for both carbon atoms $\frac{X_i}{X_o}$. For nonsymmetric

given.[3,4] In literature as a rule equilibrium constants ratio is used. In our case relations of final products concentrations in two competing nonequilibrium

reactions (I and II) have been used. $\lg \frac{X_i}{X_0} = \rho\sigma$

where $\rho = 0{,}75$

This can be justified by the fact that $\Delta F \ll 1$ $\left(-\Delta F = 95 \frac{kcal}{mol}\right)$

and $\ln K_p \simeq \ln K_f \simeq -\frac{\Delta F}{RT}$

where K_p – equilibrium constant,

K_f – rate constant in the decomposition reaction.

The greatest deviation from literature data is observed for a methyl group.

Isobutene gives zwitterion only at a substituted carbon atom. It is well-known that in the presence of several substituents the l.f.e.r. rule is not satisfied quantitatively although the nature of the effect is preserved.[4]

Thus the l.f.e.r. rule can be used for a quantitative estimation of the substituent influence on the direction of the ozonization reaction and the product distribution, experimental values and nearly coinciding with these published in literature.

LITERATURE

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