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A HAMMETT TYPE RELATIONSHIP IN OZONOLYSIS OF ACETYLENES

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Recently it was shown that the anomalous ozonolysis of 2-substituted naphthoquinones (1,2) as well as the ozonolysis of 1,2-dibenzoylethylenes of Bailey and coworkers (3) could be satisfactorily explained by the aid of a Hammett type relationship. Within the limits of the experimental errors the zwitterion formation at the "preferred" carbon atom C_i was expressed by the equation:

$$\text{Log}\ \frac{x_i}{x_o} = \rho\Delta_i$$ where x_o is a mole fraction = 0.5 and x_i a mole fraction in the range 0.5 - 1.0 representing the amount of zwitterion formed at C_i . Δ_i is a net substituent constant assumed to express the degree of electronic asymmetry in the ozonolysis intermediate, and ρ is a reaction constant.

Accidentally or due to structural relationship between the naphtoquinones and the dibenzoylethylenes a common ρ value could be used for both series.

As only a few quantitative determinations of directive influences of substituents in ozonolysis reactions are known, it may be of interest to test whether the Hammett type relationship can be applied to the ozonolysis of phenylacetylene and 1-phenylpropyne reported by Bailey and coworkers (4).

These authors found that with both acetylenic compounds the zwitterion was formed predominantly at the carbon atom carrying the phenyl group. Based on a quantitative determination of reaction products, the preferred zwitterion formation could be calculated to approximately 72 and 67 per cent respectively.[*] It was concluded that the ozonolysis was best understandable on the assumption that ozone adds to the tripple bonds in the same manner as to olefins, forming a simple five membered ring adduct. The cleavage of this instable ring intermediate was, in the two actual cases, supposed to be predominantly controlled by the resonance effect of the phenyl group. The existence of a five membered ring intermediate in ozonolysis and the cleavage of this being controlled by resonance and inductive effects of the substituents, is in line with the hypothesis of Bernatek, Kolsaker and Ledaal. Besides this a striking similarity exists between the ozonolysis results for the two acetylenes and for the 2-substituted naphtoquinones. In phenylacetylene and 2-phenylnaphthoquinone the only substituent is a phenyl group. In both cases the ozonolysis results is the same, i.e. about 72 per cent zwitterion formation at the carbon atom carrying the phenyl group.

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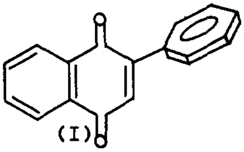
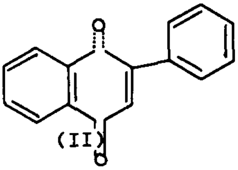
[*] Based on results with methanol as solvent.

For 2-phenylnaphthoquinone two limiting conformations may exist, (I) being the sterically more favourable and (II) being favoured by the higher resonance stabilization.


(I)


(II)

In (I) the σ_m value and in (II) the σ_p value of the phenyl group have to be used in calculating Δ_i, resulting in Δ_1 values of 0.218*) and 0.236. The arithmetic mean of these two Δ_1 values equals exactly the experimental $\Delta_1 = 0.227$ calculated by applying the observed x_i and a ρ value of 0.693 in the Hammett type equation. This may indicate that the 2-phenylnaphthoquinone exists either with the conformations (I) and (II) equally populated or more likely in one single intermediate conformation giving the best compromise between steric strain and maximum resonance stabilization.

In phenylacetylene only one pair of π-electrons may be in resonance interaction with the phenyl group at a given moment, the other being localised in a π-orbital perpendicular to the plane of resonance and thus easily available for ozone attack. The primary ozone adduct can then be assumed to have an initial conformation as given in (III), where the plane of the five membered ring is at right angle to the plane of the benzene ring.

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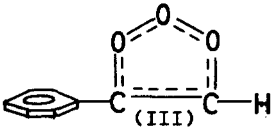
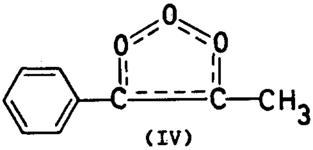
*) Hammetts $\sigma_{mC_6H_5}$



(III)

In this case the only substituent effect is a destabilizing + I-effect of the phenyl group, causing an asymmetric cleavage of the primary ozonide to occur so rapidly that no other conformation of the intermediate will exist.
The usual calculation therefore simply gives Δ_1 equal to σ_m for phenyl = 0.218, which by insertion in the Hammett type equation together with the experimental x_i value and solving for ρ gives a ρ value of <u>ca</u> 0.70.
For phenylpropyne the stabilizing effect of the methyl group will enable the more stable intermediate conformation (IV) having the phenyl group coplanar with the oxygen ring to play the role as ozonolysis key intermediate.



(IV)

Calculation of Δ_i for (IV): $\sum\sigma C_1 = \sigma_{pCH_3} = + 0.17$

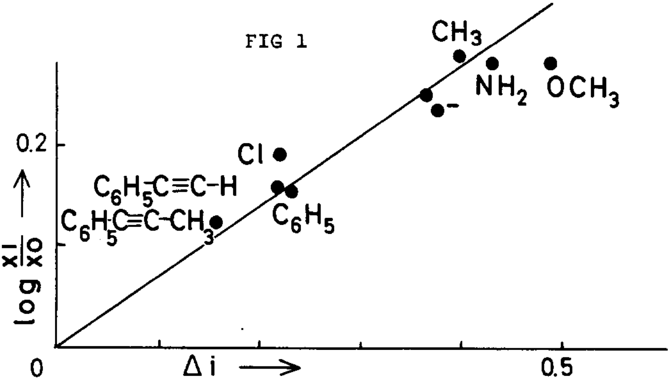
$\sum\sigma C_2 = \sigma_{pC_6H_5} = + 0.009$[*)]): $\Delta_1 = 0.161$

By inserting the experimental x_i and the calculated Δ_1 in the Hammett type equation the same ρ value is found as before.

[*)] The substituents are here acting on the more remote carbon atom of the ozonide ring through the remaining double bond.

Fig. 1 shows approximate linearity between log $\frac{x_i}{x_o}$ and Δ_i and that the ozonolysis results for phenylacetylene and phenylpropyne fits very well into the relationship found for anomalous ozonolysis of naphthoquinones.

FIG 1



No safe conclusions can of course be drawn on the basis of so few experimental results, but some interesting features have been indicated above:

1) The Hammett type relationship seems to be applicable for ozonolysis reactions of different types of olefinic as well as of acetylenic compounds.

2) The found common reaction constant may be a general reaction constant of ozonolysis.

3) In order to obtain coincidence between experimental and calculated values, special conformations of the ozonolysis intermediates in many cases have to be assumed. These conformations seem to be those most resonable or the only ones that may exist.

The Hammett type relationship of ozonolysis may thus not only be used to precalculate the relative amounts of zwitterion formed at either side, but may also give useful indication about the conformation of the compounds being ozonised or of the ozonolysis intermediates in the moment before their cleavage. The conformations in question can of course only be indicated to the extent that quantitative methods for determination of cleavage products are available and coincidence between experimental and calculated Δ_i values is found.

The possibility that $\rho = 0.693$ is a general ozonolysis constant may be understandable on the assumption that there exists but one type of a primary ozonolysis intermediate, i.e. a five membered ring ozone adduct which always is cleaved with the formation of zwitterions being controlled by the degree of electronic asymmetry in the ring.

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