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A THERMODYNAMIC INTERPRETATION OF THE HAMMETT TYPE RELATIONSHIP IN OZONOLYSIS.

T. Ledaal

Universitetets Kjemiske Institutt, Blindern, Oslo 3, Norway.

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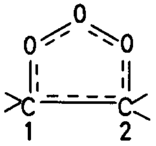
In previous papers (1,2,3,4) a Hammett type relationship has been reported which could account for the ozonolysis results of different naphthoquinones, dibenzoylethylenes and acetylenes. The relationship is

$$\log \frac{x_i}{x_o} = \rho\Delta_i$$

where x_o is a mole fraction = 0.5 and x_i is a mole fraction in the interval 0.5 - 1.0 expressing the amount of zwitterion formed at C_i.

ρ is a reaction constant, and Δ_i is a net substituent constant, assumed to give a relative measure of electronic asymmetry in an ozonolysis intermediate of the general type I.



I

The electronic asymmetry factor Δ_i was defined:

$$\Delta_1 = |\sum\sigma c_1| + |\sum\sigma c_2| \text{ when } |\sum\sigma c_1| > |\sum\sigma c_2|$$

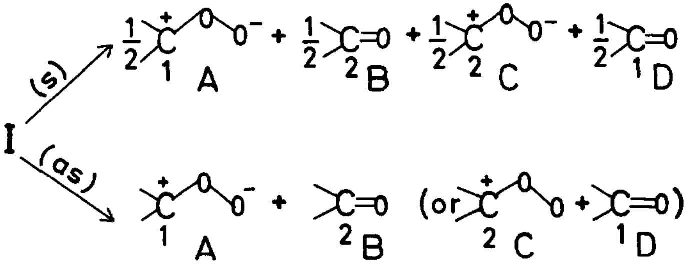
and $$\Delta_2 = |\sum\sigma c_2| + |\sum\sigma c_1| \text{ when } |\sum\sigma c_2| > |\sum\sigma c_1|$$

where $|\sum\sigma c_i|$ denotes the numerical value of the arithmetic sum of the Hammett σ constants for the substituents at carbon atom c_i. $\Delta_i = 0$ corresponds to symmetric cleavage i.e. equal zwitterion formation at c_1 and c_2.

The constant ρ was determined from ozonolysis experiments in the naphthoquinone series, and was found to have a mean value of approximately 0.70. The fact that the same ρ-value could be used with success on the ozonolysis results for dibenzoylethylenes and acetylenes of Bailey and Coworkers (4), and that the experimental value coincides with ln 2 may not be accidental. The empirical relationship

$$\log \frac{x_i}{x_o} = \rho\Delta_i$$ may, as will be seen in the following, have a simple thermodynamic interpretation.

For a generalised intermediate of type I, which may be assumed as a key intermediate of ozonolysis, two limiting reaction paths exist, i.e. fully symmetric cleavage (s) and 100 per cent asymmetric cleavage (as) as shown by the scheme:



The Gibbs energy of the symmetric cleavage $\Delta G(s)$ amounts to:

$$\Delta G(s) = \tfrac{1}{2}(\mu_A^o + RT \ln a_A + \mu_B^o + RT \ln a_B + \mu_C^o + RT \ln a_C + \mu_D^o + RT \ln a_D) + \mu_I^o + K,$$

where μ_i^o denotes the thermodynamic potential of the different species, a_i their activities, and K is a constant. For the asymmetric cleavage the change in Gibbs energy is:

$\Delta G(as_1) = \mu_A^o + RT \ln a_A + \mu_B^o + RT \ln a_B + \mu_I^o + K$ (or for the cleavage in the opposite direction

$\Delta G(as_2) = \mu_C^o + RT \ln a_C + \mu_D^o + RT \ln a_D + \mu_I^o + K$).

If one assumes that $(\mu_A^o + \mu_B^o)$ is nearly equal to $(\mu_C^o + \mu_D^o)$, then $\tfrac{1}{2}(\mu_A^o + \mu_B^o + \mu_C^o + \mu_D^o)$ representing the arithmethic mean of the two former sums, must be very nearly equal to either of them. (For symmetrically substituted ozonolysis intermediates the three sums are, of course, identical.. Also for asymmetric intermediates, however, the differences are certainly small, as the species are of the same type, and as a difference in the μ^o-values of the two possible zwitterions A and C must be nearly compensated by a difference of opposite sign for the μ^o-values of the corresponding carbonyl compounds B and D).

As the ozonolysis solution is very dilute, and we are considering relative differences only, the activities of the different species may with good approximation be substituted with the respective concentrations.
Based on the assumptions mentioned above $\Delta G(as) + \Delta G(s) = \Delta(\Delta G)$ amounts to 2RT ln 2.

The cleavage of the intermediate into a zwitterion and a carbonyl fraction as proposed by Criegee, is in effect the result of a total polarisation of an O-O and a C-C bond. If no electronic asymmetry is introduced into the ring intermediate by the substituents, statistically the same number of polarisations leading to cleavage in one as in the other direction will occur. To bring about totally asymmetric cleavage, the Gibbs energy difference of 2RT ln 2 favouring symmetric cleavage must be compensated by an asymmetry of the ring.

By use of the relationships

1) $\Delta G = \Delta H + T\Delta S$ and

2) $\Delta S = +(1+x)R \ln(1+x)+xR \ln x$ + a constant is seen that

$\Delta(\Delta S) = \Delta S_{(as)} + \Delta S_{(s)} = +2R \ln 2 = + \frac{\Delta(\Delta G)}{T}$): $\Delta(\Delta H) = 0.$

From $\Delta(\Delta G) = 2RT\ 2.3 \log \frac{x_{(as)}}{x_{(s)}} = 2RT\ 2.3\ \rho\Delta_{(as)}$

is seen that with $\Delta_{(as)} = \log e$, $\rho = \ln 2 = 0.693$ in accordance with the ρ-value found experimentally.

Quite generally $\Delta_i = \frac{1}{2.3} \frac{\Delta(\Delta G_i)}{\Delta(\Delta G)} = \log e \frac{\Delta(\Delta S_i)}{\Delta(\Delta S)}$

showing it to be a numeral as primarely postulated.

As we here apparently are dealing with an entropy effect, conformational relationships must as found play an important role in the Hammett type relationship of ozonolysis.

The cleavage of an ozonolysis intermediate with formation of a zwitterion constitutes a total polarisation in analogy to the dissociation of an acid. This may be the reason why the original Hammett σ-constants, which were based on the relative dissociation constants of differently substituted benzoic acids, are the type of substituent constants best fitting the Hammett type relationship of ozonolysis.

A similar relationship may hold for a primary ozonide like that isolated by R. Criegee (5), provided a cleavage into a zwitterion and a carbonyl fraction and not some other type of reaction occur. As primary and ordinary ozonides probably have sp^3-hybridised bonds, the Δ_i values might be calculated in a somewhat different way, using σ_m-rather than σ_p-substituent constants and taking account of their signs. The zwitterion should in such cases be formed predominantly at the carbon atom being most electron-donating i.e. having the lower value of $\sum \sigma c_i$.

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