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A THERMOCHEMICAL EXPLANATION OF DISSIMILAR REACTIVITIES OF AROMATIC LACTONES, CARBONATES, AND SULPHITES

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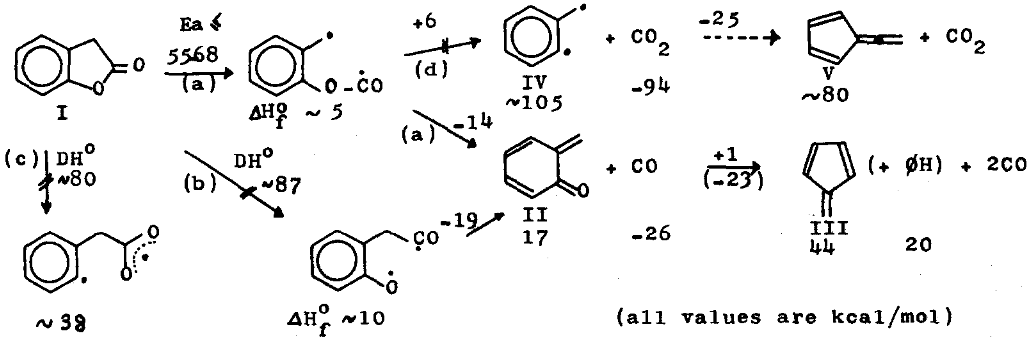
Two isomeric lactones, α-coumaranone (I) and phthalide (VI), undergo entirely different thermolyses in the gas-phase,[1] the former eliminating CO exclusively, the latter extruding predominantly CO_2. This difference is explained by simple thermochemical estimates. A similar difference exists between o-phenylenecarbonate (X) and o-phenylenesulphite (XVI), the former extruding CO_2, the latter only SO.[2] This difference has been explained by CNDO/2 calculations,[2] but the same conclusion may be reached much simpler on thermochemical grounds which, moreover, indicate that the CNDO/2 results are insufficient as an explanation.

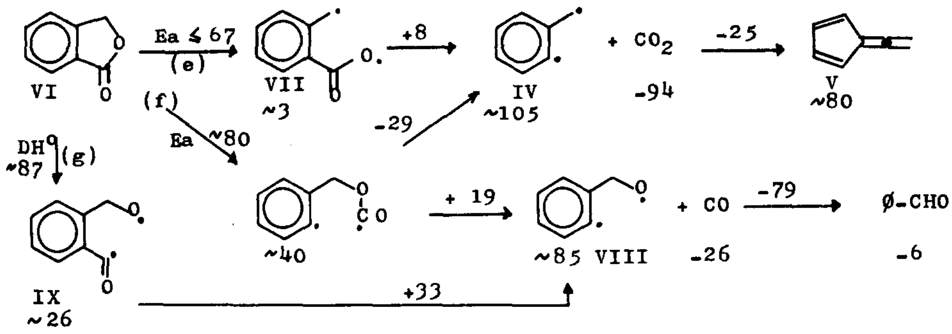
α-Coumaranone can in principle undergo ring-opening by three different paths, (a)-(c) (Scheme 1). The heats of formation of the biradicals formed are estimated from available data.[3-5] Paths (a) and (b) are thermodynamically favoured, and the non-occurrence of path (c), which would have led to CO_2-elimination and hence fulvenallene formation,[1] is essentially due to the high aryl-oxygen bond strength ($\sim$ 91 kcal/mol[5]). The activation energy for path (a) ring cleavage can be estimated as 55-68 kcal/mol from the analogous decomposition of phenylacetic acid.[3] Acyl-oxygen cleavage, path (b), does not usually occur in the pyrolysis of esters,[6] DH^o(RCO-OR) being $\sim$97 kcal/mol in the absence of resonance stabilization.[5] 2-Methylenecyclohexadienone[1] (II) can in principle result from both paths (a) and (b). This intermediate can only eliminate CO, with consequent formation of fulvene (III) and benzene, the observed products.[1] Even if path (a) were followed exclusively, the extrusion of CO from (II) would be favoured by ca. 20 kcal/mol over extrusion of CO_2; the Latter (path (d))

Scheme 1

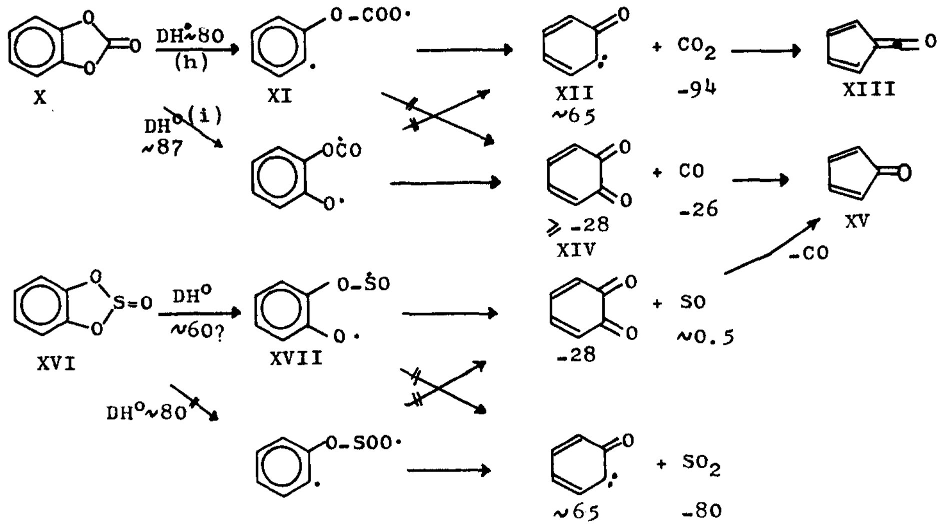


(all values are kcal/mol)

Scheme 2



Scheme 3



would have led to intermediate (IV) and fulvenallene (V).[1] [ΔH_f^o(IV) is estimated as $\Delta H_f^o(\not{0}CH_2^{\bullet})$ + $(\Delta H_f^o(\not{0}\cdot) - \Delta H_f^o(\not{0}H))$.[3,4] ΔH_f^o(II) is estimated from p-quinone,[7] assuming the same value for o-quinone, and group equivalents.[4]]

The heats of formation of fulvene[8] and fulvenallene are estimated[4,8] as 44 and 80 kcal/mol, respectively. The fulvene-forming reactions, II ⟶ III, are therefore nearly thermoneutral, while benzene formation is 23 kcal/mol exothermic, in accord with observations.[1] Interestingly however, the overall reaction (I) ⟶ fulvene + 2 CO is ca. 6 kcal/mol less exothermic than the non-observed (I) ⟶ fulvenallene + CO_2, thereby supporting the view that the reaction is not concerted, but proceeding via biradical ring-cleavage.

The possible reactions of phthalide (VI) are indicated in Scheme 2. The benzyl-oxygen cleavage[3,6b] is clearly favoured energetically (path (e)), and since the intermediate (VII) can only eliminate CO_2, fulvenallene (V) is the product.[1] The same product would result from path (f), which also accounts for the small yield of benzaldehyde.[1] The small amount of benzene formed in this reaction[1] may originate from loss of CO from either VIII or IX (path (g)).

The thermolyses of o-phenylenecarbonate (X) and -sulphite (XVI) are represented in Scheme 3. As pointed out by DeJongh and Thomson[2] aryl-oxygen cleavage is the preferred process, and accounts for the preponderance of cyclopentadienylideneketene (XIII) over cyclopentadienone (XV). It is due to the weakness of the SO bond[9] that o-phenylenesulphite (XVI) behaves differently: the intermediate XVII cannot lose CO_2, and loss of SO is ca. 13 kcal/mol more exothermic than loss of SO_2. Accordingly, only SO is lost, with consequent formation[2] of XIV and then XV.

It will be noted, however, that the overall process, o-phenylenecarbonate ⟶ XII + $\dot{C}O_2$ (path (h)) is not the thermodynamically favoured one: the process X ⟶ XIV + CO (path (i)) is ca. 25 kcal/mol more exothermic! When the CNDO/2 calculations,[2] which take account only of the intermediates XII, XIV, CO_2, and CO, give the correct result, this must then indicate that the CNDO/2 method produced entirely erroneous heats of reaction for paths (h) and (i), making the overall reaction (h) 21.7 kcal/mol more exothermic than path (i), and therefore that the agreement with experiment is coincidental. This is not surprising since the CNDO/2 method is not intended to give good absolute energies, although energies of isomeric species may reliably be compared. The observed contra-thermodynamic overall reaction again suggests the existence of the intermediate XI, which can only lose CO_2, although loss of CO would have been energetically preferred.[10]

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10. The estimated thermochemical data (especially bond strengths) are not expected to be precise. The differences between the various reaction paths are so large, however, that a considerable error will not affect the general conclusions.