Correlation Between Resonance Energies Per π Electron and Sondheimer's Rates of Formation of Macrocyclic Annulenes

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Summary An excellent correlation of the rates of formation of [12]-, [14]-, [16]- and [18]-annulenes with their calculated resonance energies per π electron (REPE) has been found.

RECENTLY Sondheimer and his co-workers[1] suggested that the rate of the Diels–Alder addition of maleic anhydride to dehydro[*n*]annuleno[*c*]furans might be related to the resonance stabilization of the annulene formed as the product. They found that two furans which formed $4n+2$

annulenes reacted faster and two which formed $4n$ annulenes reacted more slowly than an 'open-chain' furan.

A least-squares fit of our Hückel resonance energies per π electron (REPE)[2] to the logarithm of Sondheimer's rate constants gives a good straight line with a standard deviation, σ, of 0·091 [equation (1)]. Although Dewar and de Llano's calculations usually agree fairly closely with ours, they appear to predict the $4n$ annulenes to be too aromatic, and their numbers[3] show little correlation (σ 1·1) with Sondheimer's results,[1,4] as shown in the Table. Calculated rate constants for annulenes not listed in the Table are easily obtained using equation (1) and Krygowski and Kruszewski's formula for REPE.[5]

$$\log k_B = 60{\cdot}5\ \text{REPE} - 0{\cdot}475 \qquad (1)$$

TABLE. A comparison of rates of reaction of dehydro[*n*]-annuleno[*c*]furans with maleic anhydride with Dewar resonance energies per electron (DREPE) and REPE of the product annulene.

n	DREPE/eV	k_B	REPE/β
14	+0·011	2·7	+0·016
18	+0·007	1·7	+0·012
(acyclic)	0·000	0·44	0·000
16	+0·008	0·08	−0·011
12	+0·007	0·01	−0·024

We have also calculated resonance energies using the graph theoretical method of Aihara[6] and Trinajstić[7] and found a fit (σ 0·16) only slightly worse than that of equation (1). Herndon's valence bond method[8] has also been successful for a wide range of compounds, but he neglected contributions from cyclic systems with more than 10 electrons, and hence would predict zero resonance energy and identical rates for all Sondheimer's compounds. Sondheimer's data might provide a convenient way for giving parameters of the contribution of these larger cyclic systems by the Herndon method.

It might be anticipated that total resonance energy rather than resonance energy per electron would be a more appropriate fit to log k_B, but in all cases, except Dewar's, this gives a somewhat worse standard deviation: Hess–Schaad (0·23); Aihara–Trinajstić (0·24); Dewar–de Llano (1·04).

Finally, it is implicit in Sondheimer's discussion that the conjugated furan reactants themselves all have equal resonance stabilization. We have computed the resonance energies of these systems and found them to be small relative to those of the annulenes. A plot of REPE of the annulene minus that of the furan *vs.* log k_B also gives a good linear relationship. It would be interesting to have the total Dewar resonance energy for the furans to see whether total resonance differences might correlate with log k_B.

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