The Diels-Alder Reaction. A Quantitative Probe for Resonance Energies

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Summary The free energies of activation for aromatic hydrocarbon–maleic anhydride Diels-Alder reactions have a linear relationship with respect to calculated resonance energy differences, and this relationship is used to estimate resonance energies in annulenes.

Rates and selectivities of Diels–Alder reactions correlate with the results of molecular orbital calculations.[1] The qualitative parallel between *para*-localization energies and the ease with which aromatic hydrocarbons undergo cycloadditions is a well known example.[2] Relevant quantitative relationships have been demonstrated for reactions of maleic anhydride[3] and singlet oxygen ($O_2\ {}^1\Delta_g$)[4] with aromatic hydrocarbons. The logarithms of the rate constants of the maleic anhydride reactions also correlate[5] with resonance energy differences calculated using an empirical structure–resonance theory based solely on Kekulé structures.[6]

Additional examples of maleic anhydride–aromatic hydrocarbon reactions are listed in Table 1, extending the previous studies to a wider range of reactivities. Free energies of activation, ΔG^*, are calculated using the Eyring equation.[8] Resonance energy differences, ΔRE, refer to the π systems of aromatic reactant and adduct, and were obtained using the structure–resonance method outlined previously.[6]

A linear relationship between ΔG^* and ΔRE, expressed by the equation $\Delta G^* = 27{\cdot}8 - 0{\cdot}55\ (\Delta\text{RE})$, is illustrated in the Figure. Even though these reactions were carried out by different investigators, in different solvents, and at widely varying temperatures, the correlation coefficient between calculated ΔRE and ΔG^* is $-0{\cdot}994$, and the average deviation of experimental and calculated ΔG^* is $\pm 0{\cdot}4$ kcal mol^{-1}. The slope of the ΔG^* *vs.* ΔRE line leads one to infer that 55% of the resonance energy differences between reactants and products is reflected in the transition

Table 1. Diels–Alder reactions of aromatic compounds with maleic anhydride

Reactant	Rate constant /l mol^{-1} s^{-1}	Temp./°C	ΔG^*/kcal mol^{-1}	ΔRE/kcal mol^{-1}
Naphthalene[a]	$1{\cdot}03 \times 10^{-4}$	155·7	33·2	−9·9
Dibenz[*a,j*]anthracene[b]	$6{\cdot}75 \times 10^{-5}$	129·7	31·5	−6·2
Dibenz[*a,c*]anthracene[b]	$3{\cdot}58 \times 10^{-4}$	129·7	30·2	−6·7
Benz[*a*]anthracene[b]	$6{\cdot}92 \times 10^{-4}$	129·7	29·7	−2·8
Dibenz[*a,c*]naphthacene[c]	$1{\cdot}75 \times 10^{-3}$	120·1	28·2	−0·2
Anthracene[b]	$7{\cdot}55 \times 10^{-3}$	129·7	27·7	+1·9
Benz[*a*]naphthacene[c]	$4{\cdot}98 \times 10^{-3}$	70·0	23·8	+7·0
Naphthacene[b]	$2{\cdot}08 \times 10^{-3}$	39·7	22·2	+10·2
Benz[*a*]pentacene[c]	$4{\cdot}31 \times 10^{-3}$	0·0	18·9	+15·3
Pentacene[c]	$5{\cdot}86 \times 10^{-3}$	0·0	18·7	+16·5

[a] Evaluated from equilibrium constant and decomposition of 50:50 mixture of *endo* and *exo* adducts (ref. 7) in dimethyl succinate solution. ^{1}H n.m.r. determination. [b] Ref. 3. [c] *o*-Xylene solution. Spectrophotometric determination.

TABLE 2. Diels-Alder reactions of potential annulenes

Reactant	Rate constant[a] /l mol^{-1} s^{-1}	ΔG^*/kcal mol^{-1}	ΔRE/kcal mol^{-1}
Dehydro[12]annuleno[*c*]furan (**1**)	$1{\cdot}67 \times 10^{-4}$	22·5	−4·2
Dehydro[16]annuleno[*c*]furan (**3**)	$1{\cdot}33 \times 10^{-3}$	21·2	−1·8
'Open' model compound (**5**)	$7{\cdot}33 \times 10^{-3}$	20 2	0·0
Dehydro[18]annuleno[*c*]furan (**4**)	$2{\cdot}83 \times 10^{-2}$	19·4	+1·4
Dehydro[14]annuleno[*c*]furan (**2**)	$4{\cdot}50 \times 10^{-2}$	19·2	+1·8

[a] Reactions with maleic anhydride at 23 °C. Ref. 10.

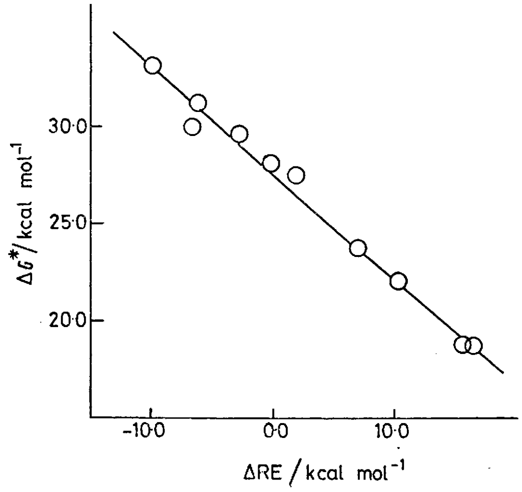
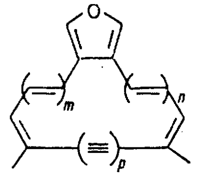


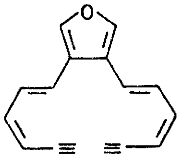
FIGURE. Resonance energy changes and free energies of activation for Diels-Alder reactions.

states for these reactions. Small, comparable secondary deuterium isotope effects for both forward and retro-Diels–Alder reactions[9] of anthracene can be interpreted on this basis.

Kinetic data of this type can be used to estimate resonance energies in other types of ring systems. To exemplify, Table 2 lists the results of Sondheimer, *et al.*[10] for cycloadditions that give rise to annulene systems. The resonance energy increments were obtained by noting that the reaction of the 'open' model compound introduces no annulene resonance, and by assuming that the factor of 1/0·55 could be used to calculate the resonance energies introduced upon cycloaddition.



(1) $m = n = p = 1$
(2) $m = n = 1, p = 2$
(3) $m = 1, n = p = 2$
(4) $m = n = p = 2$



(5)

The results indicate that the [12]- and [16]-annulenes are slightly anti-aromatic, whereas the $4n+2$ [14]- and [18]-annulenes are resonance stabilized to a small degree, in agreement with qualitative deductions of Sondheimer, *et al.*[10] These small resonance energies for large annulenes are also in accord with the predictions of structure–resonance theory, and with the results of molecular orbital calculations.[11] The resonance energy for [18]annulene, 100[12] or 37[13] kcal mol^{-1}, obtained from heats of combustion, is not consonant with the results in Table 2. A large ΔG^*, ΔRE factor would be required to yield a resonance energy of the order of 30—100 kcal mol^{-1}, which would imply a very early transition state for the Diels–Alder reactions of furan derivatives. The small secondary isotope effects observed in retro-Diels–Alder reactions of furan–maleic anhydride adducts[14] do not agree with this latter implication.

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