Resonance Stabilization Energies in Polycyclic Aromatic Hydrocarbon Radicals

S. E. Stein and D. M. Golden*

Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025

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It is shown that relative values of π-bonding resonance stabilization energies for benzyl-type polycyclic aromatic radicals, as calculated by SCF–MO methods, closely correspond to energies calculated by the simple resonance theory approach of Herndon. The formula derived for the latter type of π-bonding resonance stabilization energy is $E_{\pi\mathrm{RSE}}$ (kcal mol^{-1}) = 22.68 ln [CSC(R·)] − 27.33 ln [CSC(RH)], where CSC(R·) and CSC(RH) are the corrected structure counts (number of stable Kekulé isomers) for the radical and parent molecule, respectively. Two methods are then suggested for modifying this formula to estimate empirical radical stabilization energies for use in predicting standard heats of formation of stabilized hydrocarbon radicals.

Herndon and co-workers[1] have shown that the number of stable Kekulé isomers (CSC, for corrected structure count) for polycyclic aromatic hydrocarbons (PCAH) can be related to resonance energies,[1,2] and reactivity parameters[3] derived from modern SCF–MO calculations. Herndon's resonance theory (HRT) has also been applied for the accurate calculation of bond orders,[4] ionization potentials,[4,5] and heats of formation[6] of PCAHs.

We have extended HRT to accurately reproduce SCF–MO π-bonding stabilization energy differences, $\Delta E_{\pi\mathrm{RSE}}$, for benzyl-type polycyclic aromatic radicals.

With available experimental measurements as a basis, we suggest modification of the $E_{\pi\mathrm{RSE}}$ formula to estimate thermodynamic radical stabilization energy, E_{RSE}. A paucity of relevant experimental values prohibits thorough testing of the absolute accuracy of this method, although estimates of this scheme do agree with existing data. Relative, if not absolute, estimates of E_{RSE} will find application in the guidance and interpretation of PCAH kinetics.

Method and Discussion

The π-bonding stabilization energy of a conjugated radical may be defined as the difference between the π-bonding energy of the radical, $E_\pi(\mathrm{R}\cdot)$, and the π-bonding energy in the parent molecule, $E_\pi(\mathrm{RH})$:

$$E_{\pi\mathrm{RSE}} = E_\pi(\mathrm{R}\cdot) - E_\pi(\mathrm{RH}) \qquad (1)$$

Herndon has shown that $E_\pi(\mathrm{RH})$ calculated by highly parameterized SCF–MO procedures are reproduced with an average deviation of 1.0 kcal mol^{-1} for 27 PCAHs by the formula[2]

$$E_\pi(\mathrm{RH})\ (\mathrm{kcal\ mol^{-1}}) = 27.33 \ln [\mathrm{CSC(RH)}] \qquad (2)$$

If we assume that $E_\pi(\mathrm{R}\cdot)$ is proportional to the logarithm of the number of resonance structures, and set this proportionality constant equal to 22.60 kcal mol^{-1}, then the resulting formula (3) (incorporating eq 1 and 2) reproduces published[7] relative $E_{\pi\mathrm{RSE}}$ values with an average deviation of 0.60 kcal mol^{-1} (see Table I).[9]

$$E_{\pi\mathrm{RSE}}\ (\mathrm{kcal\ mol^{-1}}) = 22.68 \ln [\mathrm{CSC(R\cdot)}] - 27.33 \ln [\mathrm{CSC(RH)}] \qquad (3)$$

Empirically, resonance stabilized radicals may be characterized by a total resonance stabilization energy, E_{RSE}. This energy, in effect, represents a lowering of the thermodynamic energy due to odd-electron delocalization over conjugated π bonds. By definition, E_{ESE} is the difference between the heat of the reaction $\mathrm{RX} \rightarrow \mathrm{R}\cdot + \mathrm{X}\cdot$ and the reaction $\mathrm{R_pX} \rightarrow \mathrm{R_p}\cdot + \mathrm{X}\cdot$, where R· is the resonance stabilized radical of interest and $\mathrm{R_p}\cdot$ is its paraffinic analogue.

In general, σ-bonding energies (E_σ) also contribute to E_{RSE}, since an increased stability in π-bonding system distorts the molecular σ-bonding framework. Formally,

$$E_{\mathrm{RSE}} = E_{\pi\mathrm{RSE}} + E_\sigma \qquad (4)$$

For instance, electron delocalization over the aromatic carbons in the benzyl radical reduces its heat of formation, while resulting steric interactions in the radical that are not present in its parent molecule can tend to work in the opposite direction. Therefore, generally $E_{\pi\mathrm{RSE}}$ is not expected to be equal to E_{RSE}. Also, the quantitative accuracy of calculated $E_{\pi\mathrm{RSE}}$ values is uncertain, although relative values are probably reliable.

At present, the only well-established E_{RSE} value for benzyl-type aromatic radicals is for the benzyl radical itself. This is accepted[8] as 13 ± 1.5 kcal mol^{-1}. Since $\mathrm{CSC(C_6H_5CH_2\cdot)} = 5$ and $\mathrm{CSC(C_6H_5CH_3)} = 2$, formula 3 yields $E_{\mathrm{RSE}} = 17.6$ kcal mol^{-1}; formally, $E_\sigma = -3.6$ kcal mol^{-1}. Based on these values, we suggest two formulas for deriving E_{RSE} for larger benzyl-type resonance stabilized radicals.

The first method simply scales down formula 3 to yield 13 kcal mol^{-1} for the benzyl radical:

$$E_{\mathrm{RSE}}\ (\mathrm{kcal\ mol^{-1}}) = 16.75 \ln [\mathrm{CSC(R\cdot)}] - 20.19 \ln [\mathrm{CSC(RH)}] \qquad (5)$$

This scheme may be viewed as a result of either of two assumptions: (1) E_σ is negligible ($E_{\mathrm{RSE}} \cong E_{\pi\mathrm{RSE}}$), and for absolute accuracy, $E_{\pi\mathrm{RSE}}$ values must be multiplied by a factor 13.0/17.6 = 0.74, or (2) $E_{\pi\mathrm{RSE}}$ is an accurate absolute value, and $E_\sigma = -0.26E_{\pi\mathrm{RSE}}$ for all benzyl-type resonance stabilized radicals.

A second formula may be derived, based on the assumptions that $E_\sigma = -3.6$ kcal mol^{-1}, and $E_{\pi\mathrm{RSE}}$ is accurate for these stabilized radicals:

$$E_{\mathrm{RSE}}\ (\mathrm{kcal\ mol^{-1}}) = E_{\pi\mathrm{RSE}} - 3.6 \qquad (6)$$

In Table II are given E_{RSE} values estimated by using these two formulas for a number of benzyl-type PCAHs. The average difference in estimated E_{RSE} values from these two formulas is 1.4 kcal mol^{-1}; this is of the same magnitude as experimental uncertainty in E_{RSE} determinations. However, for the more highly stabilized radicals, such as 9-anthryl and 5-naphthacenyl, predictions of these two formulas differ by more than 3 kcal mol^{-1}. For these species, accurate experimental determinations can potentially distinguish between these two models.

In Table III predictions using eq 5 are compared with measured E_{RSE} values for other conjugated hydrocarbon radicals. Intuitively, one expects E_σ, and perhaps $E_{\pi\mathrm{RSE}}$, to vary with the class of radical; however, E_{RSE} calculated for alternant radicals are generally within the experimental

Table I. Calculated Differences in π-Bonding Stabilization Energies[a] (kcal mol^{-1}) for a Series ot Benzyl-Type Polycyclic Aromatic Radicals

Radical	CSC(R·)	CSC(RH)	ΔE_{RSE}(SCF)[b]	$\Delta E_{\pi RSE}$(SCF) − $\Delta E_{\pi RSE}$(method A)	$\Delta E_{\pi RSE}$(SCF) − $\Delta E_{\pi RSE}$(method B)
Benzyl	5	2	(0.0)	(0.0)	(0.0)
3-Phenanthryl	17	5	1.38	−1.33	−2.62
2-Triphenylenyl	31	9	1.57	−1.29	−2.60
1-Triphenylenyl	32	9	1.75	−0.75	−2.83
2-Naphthyl	9	3	1.75	0.50	−0.62
1-Phenanthryl	18	5	3.21	−0.80	−1.53
1-Naphthyl	10	3	4.04	0.60	0.30
9-Phenanthryl	18	5	4.10	−0.09	−0.64
6-Chrysyl	34	8	4.93	0.66	−1.97
2-Anthryl	14	4	4.96	−0.55	0.59
1-Anthryl	16	4	7.84	−0.40	1.73
1-Pyrenyl	27	6	8.12	0.11	0.48
9-Anthryl	20	4	11.97	0.53	2.96
Average deviation				0.60	1.45

[a] $E_{RSE} = A \ln$ [number stable Kekulé structures for radical] − $B \ln$ [number stable Kekulé structures for molecule], $\Delta E_{\pi RSE} = E_{\pi RSE}$(radical) − $E_{\pi RSE}$(benzyl). Method A: $A = 22.38$; $B = 27.33$; B value from Herndon, ref 2. Method B: $A = B = 13.0$. [b] Reference 7.

Table II. Estimated E_{RSE} (kcal mol^{-1}) for Benzyl-Type Radicals

Radical	CSC(R·)	CSC(RH)	Eq 5	Eq 6	Δ
1-Naphthyl	10	3	16.4	17.6	1.2
2-Naphthyl	9	3	14.7	15.2	0.5
1-Phenanthryl	18	5	16.0	17.0	1.0
2-Phenanthryl	16	5	14.0	14.3	0.3
3-Phenanthryl	17	5	15.0	15.7	0.7
4-Phenanthryl	17	5	15.0	15.7	0.7
9-Phenanthryl	18	5	16.0	17.0	1.0
1-Anthryl	16	4	18.5	20.4	1.9
2-Anthryl	14	4	15.3	17.4	2.1
9-Anthryl	20	4	22.3	25.5	3.2
1-Pyrenyl	27	6	19.1	21.2	2.1
2-Pyrenyl	19	6	13.2	13.3	0.1
4-Pyrenyl	23	6	16.2	17.6	1.4
1-Chrysyl	31	8	15.5	16.5	1.0
2-Chrysyl	27	8	13.3	13.4	0.1
3-Chrysyl	29	8	14.5	15.0	0.5
4-Chrysyl	29	8	14.5	15.0	0.5
5-Chrysyl	29	8	14.5	15.0	0.5
6-Chrysyl	34	8	17.1	18.6	1.5
1-Naphthacenyl	23	5	20.1	22.6	2.5
2-Naphthacenyl	20	5	17.7	19.4	1.7
5-Naphthacenyl	32	5	25.6	30.1	4.5
1-Triphenylenyl	32	9	13.7	14.0	0.3
2-Triphenylenyl	31	9	13.2	13.3	0.1
1-Perylenyl	46	9	19.8	22.2	2.4
2-Perylenyl[a]	9	3	14.7	15.2	0.5
3-Perylenyl	49	9	20.9	23.7	2.8

[a] For this radical species, no stable resonance structures can be written for electron delocalization in a naphthyl moiety. As a result, this radical is formally identical with the 2-naphthyl species.

uncertainties. Predictions of eq 6 are not appreciably different.

For the nonalternant cyclopentadienyl and cycloheptatrienyl radicals, predicted E_{RSE} values are clearly too large if CSC(R·) is defined as the number of resonance isomers. For alternant radicals, structures contributing to the CSC have the radical "centered" on roughly half of the carbon atoms within the π-bonding framework. Since for nonalternant radicals, the radical site may be on any carbon within the π-bonding system, we are tempted to define the CSC for these stabilized radicals as one-half of the total number of Kekulé structures. By doing so, calculated E_{RSE} match experimental values well (Table III).

Conclusions

The computational scheme proposed by Herndon for resonance energy calculation has been shown to be capable of yielding relative π-bonding stabilization energies for benzyl-type radicals of SCF–MO quality. Comparison of these calculated energies with the measured thermodynamic stabilization energy for the benzyl radical has led us to suggest two simple formulas for estimating E_{RSE} for other benzyl-type radicals. These two formulas lead to fairly similar values for E_{RSE}. This method has also been applied for calculation of E_{RSE} values to other classes of alternant conjugated radicals, and has been shown to yield E_{RSE} generally within experi-

Table III. Comparison of Experimental and Estimated E_{RSE}

	CSC(R·)	CSC(RH)	E_{RSE} (eq 3)	E_{RSE} (exptl)	Exptl ref
Allyl	2	1	11.6	10.0 ± 1.5	*a*
Cyclohexen-3-yl	2	1	11.6	12.5 ± 1.0	*b*
Methylallyl	2	1	11.6	12.5 ± 1.5	*a*
1,3-Hexadien-5-yl	3	1	18.4	18 ± 3	*a,c*
1,3-Cyclohexadien-5-yl	3	1	18.4	24 ± 6	*d,e*
Cyclopentadienyl	5[h]	1	27.0	17.5 ± 2.5	*f*
Cyclopentadienyl	5/2[i]	1	15.4	17.5 ± 2.5	*f*
Cycloheptatrienyl	7[h]	1	32.6	21.5	*g*
Cycloheptatrienyl	7/2[i]	1	21.0[g]	21.5	*g*

[a] Reference 8. [b] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3,** 93 (1970). [c] K. W. Egger and M. Jola, *ibid.*, **2,** 265 (1970); H. M. Frey and A. Krantz, *J. Chem. Soc. A*, 1159 (1969). [d] D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **64,** 2752 (1968). [e] S. W. Benson, "Thermochemical Kinetics", 2d ed, Wiley, New York, N.Y., 1976. [f] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3,** 237 (1971). [g] G. Vincow, H. J. Dauben, F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91,** 2823 (1969). [h] CSC has not been previously defined for such nonalternant systems; it is assumed to be equal to the total number of distinct resonance structures. [i] E_{RSE} (eq 3) is derived using CSC(R·) defined as one-half of the number of resonance structures.

mental uncertainty. The current paucity and inaccuracy of existing data, however, make a convincing test of these methods impossible. For nonalternant conjugated radicals, the proposed estimation method yields E_{RSE} substantially higher than measured values. By halving the total structure count to yield a corrected structure count for these radicals, E_{RSE} predictions accurately match the measured values.

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Registry No.—Benzyl, 2154-56-5; 3-phenanthryl, 61062-76-8; 2-triphenylenyl, 61062-77-9; 1-triphenylenyl, 61062-78-0; 2-naphthyl, 10237-50-0; 1-phenanthryl, 61062-79-1; 1-naphthyl, 2510-51-2; 9-phenanthryl, 20199-82-0; 6-chrysyl, 61062-80-4; 2-anthryl, 61062-81-5; 1-anthryl, 27735-76-8; 1-pyrenyl, 27735-78-0; 9-anthryl, 27735-77-9; 2-phenanthryl, 61062-82-6; 4-phenanthryl, 61062-83-7; 2-pyrenyl, 61062-84-8; 4-pyrenyl, 61062-85-9; 1-chrysyl, 61062-86-0; 2-chrysyl, 61062-87-1; 3-chrysyl, 61062-88-2; 4-chrysyl, 61062-89-3; 5-chrysyl, 61062-90-6; 1-naphthacenyl, 61062-91-7; 2-naphthacenyl, 61062-92-8; 5-naphthacenyl, 61062-93-9; 1-perylenyl, 61062-94-0; 2-perylenyl, 61092-32-8; 3-perylenyl, 61062-95-1; allyl, 1981-80-2; cyclohexen-3-yl, 15650-80-3; methylallyl, 15157-95-6; 1,3-hexadien-5-yl, 61062-96-2; 1,3-cyclohexadien-5-yl, 15819-51-9; cyclopentadienyl, 2143-53-5; cycloheptatrienyl, 3551-27-7.

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(9) Table I also shows the results of optimizing an equation of the form $E_{\pi RSE} = A \ln [\mathrm{CSC(R\cdot)}]/[\mathrm{CSC(RH)}]$. Equation 3 is better.

Production of Nitric Oxide in the Pyrolysis of Aromatic Nitro Compounds

C. W. Hand*

University of Alabama, University, Alabama 35486

C. Merritt, Jr., and C. DiPietro

Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760

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The pyrolysis of nitrobenzene in the temperature range 400–600 °C was studied in a continuous-flow apparatus consisting of pyrolyzer, gas chromatograph, and mass spectrometer. Several of the observed products (benzene, biphenyl, naphthalene) could arise from phenyl radical, but, in contrast to earlier suggestions, there is no evidence supporting a primary fission to phenyl radical and nitrogen dioxide. Pyrolysis of nitrosobenzene yields products similar to those from nitrobenzene, and a two-step mechanism, nitrobenzene → nitrosobenzene → phenyl, is proposed. Although the details of the mechanism are not conclusively proven, there is considerable evidence for a heterogeneous mechanism and none supporting a homogeneous mechanism.

Recent experience in this laboratory[1] and others[2] has shown that nitric oxide is a prominent product of the pyrolysis of aromatic nitro compounds, and that nitrogen dioxide is not produced in detectable quantities. This is not necessarily a surprising result inasmuch as the possible rearrangement to an aryl nitrite leads to compounds which should readily undergo homolytic fission to nitric oxide plus aryloxy radicals. Photochemical nitro–nitrite rearrangements are known,[3] and the analogous rearrangement of the positive ion occurs in the mass spectrum of nitrobenzene.[4] Even though there is little