

through smaller rings. We therefore favor a rotaxane-like structure for the complexes.

The definitions of the macroscopic association constants, $K_1 = [C \cdot M]/([C][M])$, $K_2 = [C \cdot M_2]/([C \cdot M][M])$, yield the ratio $K_1/K_2 = [C \cdot M]^2/([C][C \cdot M_2])$ which can be determined directly from the proton NMR spectra. We find $K_1 = 4(\pm 0.1)K_2$. However, these constants must be corrected for statistical effects since C·M has two ways to form and C·M₂ has two ways to dissociate. Therefore the statistically corrected (intrinsic) association constants K_1^1 and K_2^1 are equal; the system is noncooperative. Hill plots of the data⁷ indeed give straight lines with slope $\bar{n} = 1$, with midpoints between 10⁻³ and 10⁻⁴ M free metal.

The finding that the two sites act independently in the present case may be rationalized in entropic terms. Binding at one site fixes only one of the many rotational degrees of freedom enjoyed by the remote polyether ring. In order for positive cooperativity ($K_2 > K_1$) to be observed, binding at one site must fix a larger fraction of the variables at the remote site. We are pursuing this goal through the construction of more rigid subunit systems.¹¹

Acknowledgment. We are indebted to Professor J. Coetzee for advice and to the National Institutes of Health for financial support.

(11) For unusual cooperativity in oxygen binding to models for hemoglobin, see: Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 3224-3237.

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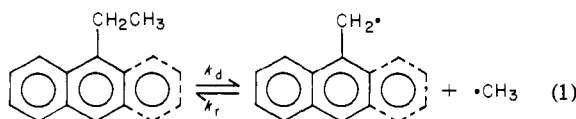
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Highly Stabilized Radicals: Benzylic Radicals in Polycyclic Aromatic Systems

Sir:

We wish to report (1) measurements of the rates and equilibria of gas-phase benzylic bond scission for ethylbenzene, 1-ethyl-naphthalene, and 9-ethylanthracene (reaction 1), (2) the enthalpies



of formation of the highly stabilized arylmethyl radicals produced in these reactions, and (3) the extent to which these values validate a recently developed technique¹ for estimating resonance-stabilization energies in polycyclic aromatic hydrocarbon radicals.

In recent publications, Herndon and co-workers have shown² that π -bonding energies in polycyclic aromatic hydrocarbons (PAH) calculated by highly parameterized SCF-MO procedures are reproduced with an average deviation of 1.0 kcal/mol for 27 polycyclic aromatic hydrocarbons by means of a one-parameter equation involving the number of stable Kekule isomers [CSC(RH)]: $E_r(\text{RH})/(\text{kcal mol}^{-1}) = 27.33 \ln [\text{CSC}(\text{RH})]$. Stein and Golden have speculated¹ that a similar relationship holds for benzylic radicals in these same polycyclic aromatic systems. They have suggested an expression of the form

$$R_{\text{RSE}}/(\text{kcal/mol}) = A \ln [\text{CSC}(\text{R}\cdot)] - B \ln [\text{CSC}(\text{RH})] \quad (2)$$

The values of the constants A and B were derived by (1) taking

(1) Stein, S. E.; Golden, D. M. *J. Org. Chem.* **1977**, *42*, 839.
(2) (a) Herndon, W. C.; Ellsey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631. (b) Herndon, W. C. *Ibid.* **1973**, *95*, 2404; (c) *Israel J. Chem.* **1980**, *20*, 270.

Substrate	Temp., K	k_d^{uni} , s ⁻¹	K_d , m ⁻¹	k_r^{∞} , 1-m/s	$\Delta(\Delta H_{\text{d},300}^{\circ})$	k/k^{∞}	$\log A_{\text{d},T}$	$E_{\text{d},T}$	$\Delta H_{\text{d},300}^{\circ}$	$\Delta(\Delta H_{\text{d},300}^{\circ})$	$\Delta(\Delta H_{\text{d},300}^{\circ})$ (calcd.) ^d	$\Delta H_{\text{f},300}^{\circ}$ ArCH ₂ ·
ØEt	1000	0.11	—	—	(0)	0.30	15.85 ^b	(74.7) ^c	(75.00)	(0)	(0)	—
ØØEt	1000	0.60	—	—	—	0.52	—	—	—	—	—	—
	1100	8.9	1.01 × 10 ⁻⁸	2 × 10 ⁹	4.5 ± 1.5	0.37	15.65 ^e	71.8	72.1 ± 1.3 ^f	2.9 ± 1.0	2.9	59.6 ± 1.5 ^f
ØØØEt	1000	5.9	3.24 × 10 ⁻⁹	4 × 10 ⁹	8.3 ± 1.5	0.45 ^g	15.60 ^e	66.5	66.8 ± 1.3	8.3 ± 1.0	7.8	79.9 ± 1.5

^aBased on $\Delta H_{\text{f},300}^{\circ} = 47.3$ for the benzyl radical (Reference 6). Units in kcal mole⁻¹.

^bDerived from the RRK fitting of experimental values of k_d^{uni} and an assumed value⁶ of 74.7 kcal mole⁻¹ for $E_{\text{d},1000}$.

^cDerived from $\Delta H_{\text{d},300}^{\circ} = 75.0$ kcal mole⁻¹ (Ref. 6) and the considerations outlined in Reference 12a and Note 13.

^dCalculated with equation (2), where $A = 14.21$ and $B = 17.14$.

^eDerived by adjustment of $\log A_{\text{d},1000} = 15.85$ for ethylbenzene, where the most important consideration is the fact that increase in the external moments of inertia as the complex is formed gets smaller as the size of the aromatic system increases.

^fError limits assigned on basis of one standard deviation in rate constants and probable error limit in estimated A factors.

^g k/k^{∞} is slightly less for ethylanthracene than it is for ethylnaphthalene because the lower activation energy and a lower collision frequency for ethylanthracene outweigh the effect of the larger number of oscillators.

Table I. Bond Dissociation Data and Derived Thermochemical Values

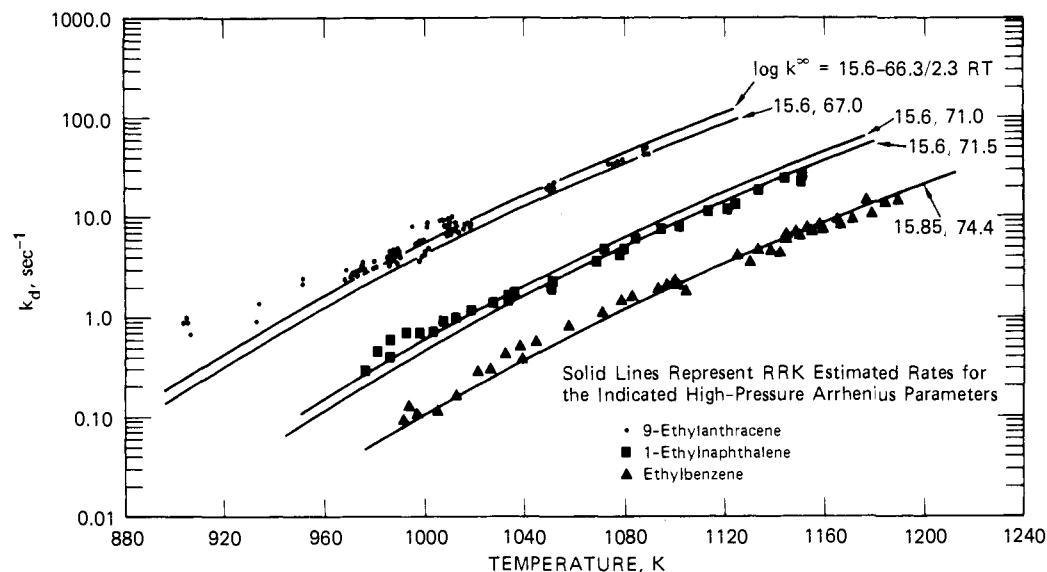


Figure 1. Rates of unimolecular decomposition of 9-ethylanthracene, 1-ethylnaphthalene, and ethylbenzene as a function of temperature.

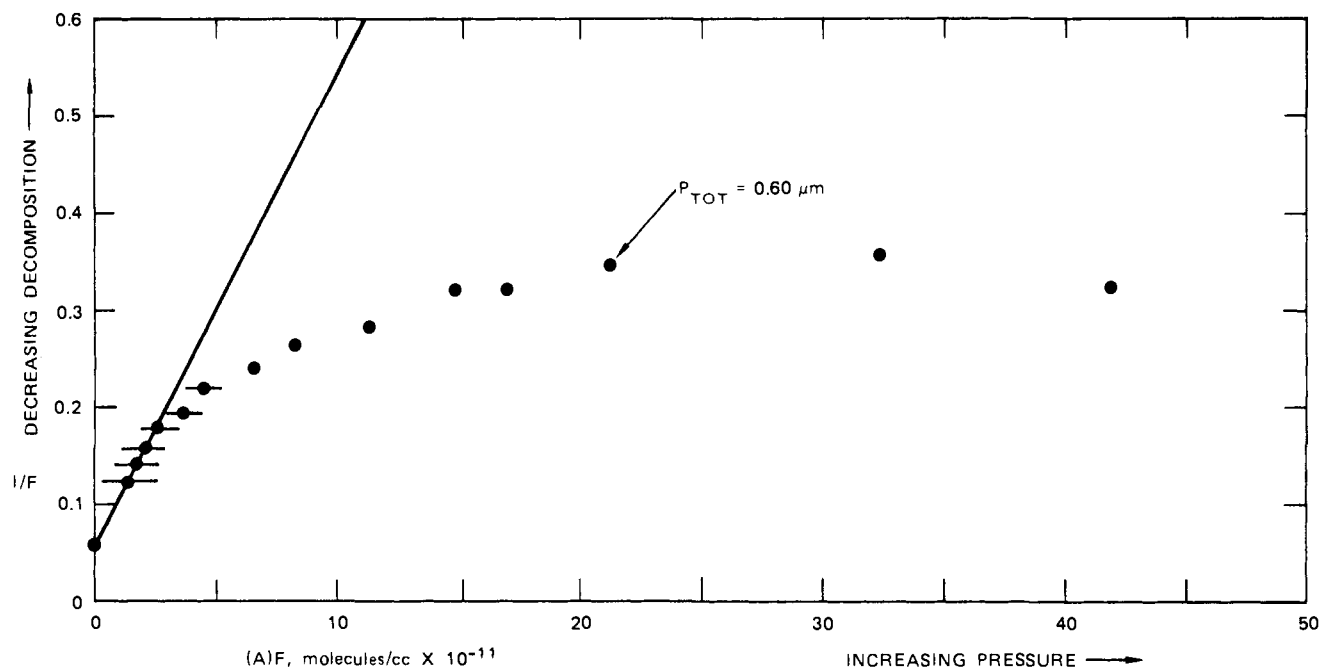


Figure 2. Ratio of ethylnaphthalene escaped to ethylnaphthalene decomposed as a function of pressure at 830 °C with 0.0047-cm² aperture.

$B = 27.33$ from Herndon,² (2) adjusting A so that eq 2 reproduces published (SCF) relative π -stabilization energies,³ and (3) scaling both constants to fit the accepted value for the only benzylic radical whose net stabilization energy has actually been measured.^{4,5} This procedure, when used with the currently accepted value for benzyl radical⁶ ($\Delta H_f^\circ_{298} = 47$ kcal/mol, RSE = 11 kcal/mol), results in the prediction that the 1-naphthylmethyl, 9-phenanthrylmethyl, and 9-anthrylmethyl radicals will exhibit 2.9, 2.5, and 7.8 kcal/mol additional resonance stabilization energy (RSE) relative to the benzyl radical.

We have used the very low-pressure pyrolysis (VLPP) technique to measure the rates at which 1-ethylnaphthalene and 9-ethyl-

anthracene undergo benzylic bond cleavage to produce two of the above benzyl radical analogues. The VLPP technique has been previously described in detail;⁷ it consists essentially of pyrolysis in a Knudsen cell reactor where the reactant pressure is maintained low enough (typically, 0.01–1 μm) that reactive fragments formed in the initial bond-breaking step escape from the reactor to the mass spectrometric detection system before they undergo enough gas-gas collisions to result in secondary reactions of the starting material. The reactor used for the current measurements⁸ is very similar to that recently described,⁷ except that a second thermostatted Knudsen cell containing liquid substrate is connected through heated transfer lines of minimum length (~ 15 cm) to the VLPP reactor to provide reproducible and measurable flow

(3) Unruh, J. D.; Gleicher, G. J. *J. Am. Chem. Soc.* **1971**, *93*, 2008.

(4) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(5) Reference 3 presents a correlation between measured rates of liquid-phase H abstraction by trichloromethyl radical from arylmethanes and SCF calculated values of π -bonding resonance stabilization energies. The success of the correlation is noteworthy, but it provides no experimental measure of absolute energy differences and uses a series of abstractions by an electrophilic radical that are exothermic by 10–20 kcal/mol.

(6) (a) Rossi, M.; Golden, D. M. *Int. J. Chem. Kinet.* **1979**, *11*, 715. (b) Davis H. G.; private communication.

(7) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223.

(8) The VLPP reactor has a volume of 145 cm³, large and small aperture escape rate constants of $4.69 (T/M)^{1/2}$ and $0.175 (T/M)^{1/2} \text{ s}^{-1}$, respectively, and a gas-wall collision frequency of $4.18 \times 10^3 (T/M)^{1/2} \text{ s}^{-1}$. Defined first-order decomposition rate constants measured with the large aperture showed no significant dependence on flow rate (i.e., pressure) over the range 8×10^{13} – 2×10^{15} molecules/s. Unimolecular rate constants were measured by using the large aperture at flow rates typically $\leq 5 \times 10^{14}$ molecules/s.

rates of the low vapor pressure substrates used in this work.⁹

Figure 1 shows the unimolecular decomposition rates for reaction 1, for ethylbenzene, 1-ethylnaphthalene, and 9-ethylanthracene, determined with the large reactor aperture exposed. Under these conditions, the reactant pressure is very low (e.g., 0.05 μm), and the defined first-order rate constants, k_d^{uni} , are independent of flow rate. The solid lines are calculated values of k_d^{uni} corresponding to the indicated high-pressure Arrhenius parameters. Under our experimental conditions, the decomposition of all three substrates is slightly in the pressure-dependent or falloff region ($k/k_\infty \approx 0.3$ to 0.6). The values of k_d^{uni} , which reflect this falloff, were calculated by the RRK procedure, which has been shown to be adequate near the high-pressure limit.¹⁰ Table I lists the values of the activation energies and shows their relationship to ΔH°_{300} for the reaction, and thus the stabilization energies of the requisite radicals.

The VLPP technique was also used to measure equilibrium constants in reaction 1 as a more direct and potentially more accurate route to values of ΔH°_d at 300 K. The measurement simply involves observing the decrease in net extent of decomposition as a function of increasing substrate pressure in the VLPP reactor when the small aperture is exposed and the pressure is high enough that recombination of initially formed radicals competes with escape from the reactor.¹¹

Figure 2 shows data for decomposition of ethylnaphthalene at 1103 K, plotted essentially¹² as the reciprocal of fractional decomposition vs. substrate pressure in the reactor. The slope is a measure of k_r/k_d , and the intercept is a measure of k_d in the limit of zero pressure.¹¹ Table I lists the results of the above-described rate and equilibrium measurements at 1000 and 1100 K for ethylbenzene, 1-ethylnaphthalene, and 9-ethylanthracene.

The principal conclusions to be drawn from the data in Table I are as follows:

(1) Values of ΔH°_{300} derived from $E_{d,1000}$ by means of an assumed activation energy for recombination at 1000 K and adjustment to 300 K (columns 11 and 12) agree within 0.1 and 1.5 kcal/mol with the equilibrium constant based values (columns

6 and 7) if a rotational transition-state model is used as the basis¹³ for obtaining the required activation energy for recombination¹⁴ at 1000 K.

(2) The good agreement, particularly in the case of ethylanthracene, between rate constant and equilibrium constant based values, i.e., the successful closure of the thermochemical cycle, significantly increases the confidence in the derived ΔH°_{300} values. Among other things, this agreement indicates that k_d values do not reflect substantial surface contribution, since anomalously high values of k_d would be matched by correspondingly high values of k_r , leaving k_d/k_r unchanged.

(3) The extents of bond strength decrease predicted by eq 2 (2.9 and 7.8 kcal/mol) are in excellent agreement with the average of the two measures of bond strength decrease (columns 7 and 12), 3.7 and 8.2 kcal/mol for ethylnaphthalene and ethylanthracene, respectively.

(4) A measured recombination rate constant for anthrylmethyl radical with methyl radical (column 5) in the same range as for small alkyl radicals suggests that there are no stringent steric requirements for recombination of even large extensively delocalized radicals.

The accuracy with which stabilization energies for ethylnaphthalene and ethylanthracene were predicted by use of a one-point parameterization of eq 2 is striking. Studies are currently under way to see if this accuracy is maintained for two somewhat different systems, 9-ethylphenanthrene and 9,9-dimethyldihydroanthracene. 9-Ethylphenanthrene is isomeric with 9-ethylanthracene, but is predicted to exhibit only 2.6-kcal/mol additional stabilization energy, less than even 1-ethylnaphthalene. Dimethyldihydroanthracene will undergo C-C bond scission to produce a substituted cyclohexadienyl radical for which eq 2 predicts a resonance-stabilization energy ~ 20 kcal/mol greater than that of the cyclohexadienyl radical. Confirmation of the accuracy of eq 2 in these two additional systems would provide a calibration of the estimation technique over essentially its entire range of application to hydrocarbon structures.

Acknowledgment. We gratefully acknowledge support from the Department of Energy, Contract No. DE-AC03-79ER10483, under whose sponsorship the ethylanthracene studies were performed. Studies on ethylnaphthalene were performed under Contract No. EF-76-C-01-2202.

(9) Maintenance of the temperature within ± 0.2 in this reservoir results in flow rates that are constant within $\pm 1.4\%$.

(10) (a) Solly, R. K.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1971**, *75*, 1338. (b) McMillen, D. F.; unpublished work.

(11) Golden, D. M.; Spokes, G. N.; Benson, S. W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 534.

(12) Derivation of the equation on which Figure 2 is based is shown in ref 11. This equation is

$$\frac{(1)}{F} = \frac{(A)}{(A)_0 - (A)} = \frac{k_{eA}}{k_d} + \frac{k_r}{k_d} \frac{F(A)}{(3.39)}$$

where (A) corresponds to the reactant concentration that escapes the reactor undecomposed, $(A)_0$ corresponds to what the reactant concentration would have been with no decomposition, k_d is the rate of unimolecular decomposition, k_r is the rate of radical recombination to regenerate the substrate, and k_{eA} is the rate constant for reactant escape from the reactor.

(13) For a consideration of the appropriateness of a rotational transition state model, see: (a) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (b) Smith, G. P.; Golden, D. M. *Int. J. Chem. Kinet.* **1978**, *10*, 489. (c) Baldwin, A. C.; Golden, D. M. *J. Phys. Chem.* **1978**, *82*, 644.

(14) Activation energy for recombination at 1000 K is based on the assumption that $\Delta E^\circ_r(0 \text{ K}) = 0$, and therefore that $E_{r,1100} = {}_0(\Delta C_p^{\circ*})_{(1100-300)} + R(1100)$. Then $\Delta H^\circ_{300} = \Delta H^\circ_{1100-300}(\Delta C_p^{\circ*})_{1100(1100-300)} = E_{d,1100-300}(\Delta C_p^{\circ*})_{1100(1100-300)}$. The heat capacity of activation for recombination, $\Delta C_p^{\circ*}$, is defined by the transition-state model over the interval 300–1100 K. $\Delta C_p^{\circ*}$ is typically 2 cal/mol $^\circ\text{C}$ more positive for a vibrational model than for a rotational model. Uncertainties in an estimated values of $\Delta C_p^{\circ*}$ and ΔS°_{300} are second-order considerations relative to this difference in $\Delta C_p^{\circ*}$. The impact of all these uncertainties is discussed in a forthcoming paper.

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