

hexanes to afford 39 mg (51%) of 21 as a colorless solid: NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  2.13 (s, 3 H), 2.21 (bs, 9 H), 3.72 (s, 2 H), 4.20 (s, 4 H), 6.28 (d, 1 H,  $J = 13.5$  Hz), 6.42 (s, 1 H), 6.55 (s, 1 H), 7.20 (d, 1 H,  $J = 13.5$  Hz); IR ( $\text{CHCl}_3$ ) 3640, 3570, 3020, 2970, 2910, 1735, 1620, 1600, 1490, 1390, 1320, 1305, 1260, 1250, 1225, 1160, 1110, 1075, 1040, 1010, 990, 910, 855  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_6$ : C, 68.72; H, 6.30. Found: C, 68.79; H, 6.35.

It is likely that the yields for this reaction could be improved if the disiloxy ether was hydrolyzed by heating in methanol.<sup>2</sup>

***o*-Quinone Enol Ester 22.** Catechol 21 (20 mg, 0.052 mmol) was dissolved in 8 mL of dry benzene. Silver(I) oxide (120 mg, 0.52 mmol) was added, the flask purged with nitrogen, and the reaction mixture stirred at room temperature for 1 h. The silver salts were filtered from the solution, and the solvent was removed in vacuo to afford 20 mg of 22 as a red glass: NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05 (s, 3 H), 2.10 (bs, 9 H), 3.68 (s, 2 H), 4.22 (s, 4 H), 6.20 (s, 1 H), 6.30 (d, 1 H,  $J = 13.5$  Hz), 6.55 (s, 1 H), 7.18 (d, 1 H,  $J = 13.5$  Hz).

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work through Grant CHE-79-17570.

### Structure-Resonance Theory and the Kinetics of the Electrophilic Deuterium-Hydrogen Exchange in Benzenoid Hydrocarbons

Ahmad S. Shawali\*

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

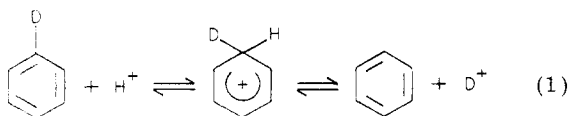
Cyril Párkányi\* and William C. Herndon\*

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968

Received August 18, 1981

Structure-resonance theory has recently been shown to correlate and to predict various physical and chemical properties of  $\pi$ -electron hydrocarbons.<sup>1,2</sup> Thus, e.g., the theory leads to quickly obtainable quantitative predictions of bond orders, charge distribution, heats of formation, bond lengths, NMR coupling constants, and relative stabilities of ground-state species and reaction intermediates. The major advantage of this theory is its simplicity. Its application requires only an enumeration of Kekulé structures, since it has been shown that an algorithm, logarithm of the Kekulé corrected structure count,<sup>3</sup> gives an excellent approximation of the ground-state eigenvalues of the structure-function Hamiltonian matrix.

The purpose of this contribution is to show that the structure-resonance theory can be used to correlate the rates of both the deuterium-hydrogen and hydrogen-deuterium exchange reactions of benzenoid hydrocarbons (eq 1). The kinetic data suitable for this purpose have been published.<sup>4-6</sup>



(1) W. C. Herndon, *J. Org. Chem.*, **40**, 3583 (1975).

(2) W. C. Herndon, *Israel J. Chem.*, **20**, 270 (1980), and references therein.

(3) R. Swinborne-Sheldrake, W. C. Herndon, and I. Gutman, *Tetrahedron Lett.*, 755 (1975).

(4) C. Párkányi and R. Zahradník, *Tetrahedron Lett.*, 1897 (1963).

### Results and Discussion

In previous publications,<sup>4,5</sup> a correlation of the log  $k$  values of protodeuteration with the Wheland HMO atom localization energies yielded three separate lines, depending on the type of the reaction site (benzene-like,  $\alpha$ -naphthalene-like, and *meso*-anthracene-like positions).<sup>5</sup> Similar splitting has been observed in the case of deuterodeprotonation, nitration, bromination, and other electrophilic aromatic substitutions.<sup>7,8</sup> This splitting into three dependences was explained as due to the differences in the electronic repulsion in positions of different classes of benzenoid hydrocarbons which are not taken into account in HMO calculations.<sup>5,6</sup> Thus, not surprisingly, a single regression line was obtained when SCF-MO localization energies were used.<sup>5</sup>

Assuming that the hydrogen-deuterium exchange reactions involve the formation of a symmetrical Wheland transition intermediate (eq 1), the rates can be correlated with the differences in the resonance energy, RE, between the  $\pi$ -hydrocarbon substrate,  $\text{ArH}$ , and the  $\sigma$ -complex intermediate,  $\text{ArHD}^+$ . For the deuterodeprotonation and the protodeuteration reactions, the differences in resonance energies between the reactant and the intermediate can be expressed by eq 2 and 3, respectively.

$$\Delta\text{RE} = \text{RE}_{\text{ArHD}^+} - \text{RE}_{\text{ArH}} \quad (2)$$

$$\Delta\text{RE} = \text{RE}_{\text{ArHR}^+} - \text{RE}_{\text{ArD}} \quad (3)$$

The resonance energy of a given species has been shown to be given by eq 4, where SC is the structure count, i.e.,

$$\text{RE} = a \ln \text{SC} \quad (4)$$

the number of principal resonance structures of the species examined, and  $a$  is the proportionality constant (1.185).<sup>3</sup> Because the activation energy of a reaction is determined by the difference in the resonance stabilization of the intermediate I and the reactant R, one can write:

$$\ln k = a_0 + a_1 \ln \text{SC}_I - a_2 \ln \text{SC}_R \quad (5)$$

The constants  $a_1$  and  $a_2$  can be determined by regression analysis and sensible results require that the absolute values of these two constants should not be too different. Under such conditions, eq 5 can be rewritten in the form where  $\text{SC}(\text{ratio}) = \text{SC}_I/\text{SC}_R$ . Equations of the type 5 and 6 are therefore expected to correlate with the kinetic data

$$\ln k = a_0 + a \ln \text{SC}(\text{ratio}) \quad (6)$$

for deuterium-hydrogen exchange reactions of benzenoid hydrocarbons. The SC's for the benzenoid hydrocarbons and the corresponding  $\sigma$ -complex cations were determined with the coefficients of nonbonding molecular orbitals as previously described.<sup>9,10</sup> The results of the calculations and the rate constants used are summarized in Table I. When the data for the protodeuteration reaction were correlated by eq 5, the following linear relationship was obtained:

$$\ln k_{\text{D-H}} = -16.707 + 9.815 \ln \text{SC}_I - 9.810 \ln \text{SC}_R \quad (7)$$

with a correlation coefficient  $r = 0.973$  and a standard deviation  $s = \pm 0.723$ . The values of the constants  $a_1$  and  $a_2$  in eq 7 are indeed similar, their ratio being close to unity

(5) C. Párkányi, Z. Dolejšek, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **33**, 1211 (1968).

(6) G. Dallinga, A. A. Verrijn Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).

(7) R. Zahradník, *Chem. Listy*, **60**, 289 (1966).

(8) R. Zahradník and O. Chalvet, *Collect. Czech. Chem. Commun.*, **34**, 3402 (1969).

(9) W. C. Herndon, *Tetrahedron*, **29**, 3 (1973).

(10) W. C. Herndon, *J. Chem. Educ.*, **51**, 10 (1974).

Table I. Hydrogen Isotope Exchange Reactions of Benzenoid Hydrocarbons

compd (position of substitution)	$-\ln k_{D-H}^a$	$-\ln k_{H-D}^b$	$\ln SC_I$	$\ln SC_R$	$\ln SC_{I,h}$
1, benzene	13.378	10.361	1.099	0.693	1.609
2, naphthalene (1)	7.184	5.180	1.946	1.099	2.303
3, naphthalene (2)	9.348	7.207	1.792	1.099	2.197
4, anthracene (1)	5.825	3.569	2.485	1.386	2.773
5, anthracene (2)	7.391 <sup>c</sup>	5.181	2.303	1.386	2.639
6, anthracene (9)	3.638	-3.707	2.773	1.386	2.996
7, phenanthrene (9)	7.138	4.958 <sup>c</sup>	2.565	1.609	2.890
8, biphenyl (2)	9.279	6.747	2.197	1.386	2.565
9, biphenyl (4)	9.210	6.747	2.197	1.386	2.565
10, pyrene (1)		-0.990	3.045	1.792	3.296
11, benz[ <i>a</i> ]anthracene (7)		-2.533	3.367	1.946	3.584
12, benz[ <i>a</i> ]anthracene (12)		-2.533	3.296	1.946	3.526
13, perylene (1)		-1.221	3.611	2.197	3.829
14, perylene (3)		-1.221	3.689	2.197	3.892
15, triphenylene (1)		6.932	3.135	2.197	3.466
16, triphenylene (2)		8.061	3.091	2.197	3.434
17, chrysene (6)		2.833	3.258	2.079	3.526

<sup>a</sup> The rate constant for the protodeuteration reaction,<sup>5</sup> in s<sup>-1</sup>. <sup>b</sup> The rate constant for the deutero-deprotonation reaction,<sup>6</sup> in h<sup>-1</sup>. <sup>c</sup> Calculated using the equation:  $\ln k_{H-D} = 0.883 \ln k_{D-H} + 1.345$ ;  $r = 0.996$  (from ref 5).

Table II. Statistical Treatment of the  $\ln k_{D-H}$  Data Using Various Resonance Energy Parameters

parameter <sup>a</sup>	<i>n</i> <sup>b</sup>	<i>i</i> <sup>c</sup>	$\rho$ <sup>d</sup>	<i>r</i> <sup>e</sup>	$\pm s$ <sup>f</sup>
$\sigma^+$	9	-12.561	13.829	0.971	0.610
$L_r^+$	9	29.048	-15.798	0.913	1.049
$N_R$	9	7.342	-8.193	0.955	0.761
$\Delta E_\pi(\text{CNDO}/2)$	7	-62.281	4.137	0.962	0.768
$\Delta E_\pi(\text{PPP})$	9	-11.253	4.205	0.933	0.924
$\ln SC(\text{ratio})$	9	-16.704	9.835	0.973	0.590

<sup>a</sup> For the explanation of the symbols, see the text.

<sup>b</sup> The number of points. <sup>c</sup> Intercept of the regression line. <sup>d</sup> Slope of the regression line. <sup>e</sup> Correlation coefficient. <sup>f</sup> Standard deviation.

( $a_2/a_1 = 0.999$ ). This leads to a good correlation of the same rate data with the algorithm,  $\ln SC(\text{ratio})$ . The least-squares regression line corresponding to this relationship is expressed by eq 8.

$$\ln k_{D-H} = -16.704 + 9.835 \ln SC(\text{ratio}) \quad (8)$$

$$r = 0.973, s = \pm 0.590$$

The results of correlating the  $\ln k_{D-H}$  data with other resonance energy indices such as the localization energy constant  $\sigma^+$ , HMO localization energy  $L_r^+$ , Dewar's MO reactivity number  $N_R$ ,<sup>11</sup> and  $\Delta E_\pi(\text{CNDO}/2)$  and  $\Delta E_\pi(\text{PPP})$  are given in Table II for comparison.

Statistical treatment of the rate data for deutero-deprotonation (Table I), using eq 5 and 6, leads to the correlations expressed by eq 9 and 10, respectively.

$$\ln k_{H-D} = -15.764 + 17.280 \ln SC_I - 20.723 \ln SC_R \quad (9)$$

$$r = 0.981, s = \pm 0.911$$

$$\ln k_{H-D} = -17.628 + 13.664 \ln SC(\text{ratio}) \quad (10)$$

$$r = 0.945, s = \pm 1.401$$

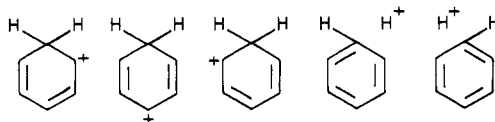
The reason for the difference in the quality of the correlations expressed by eq 9 and 10 (cf. the values of the correlation coefficients) is not obvious. However, it is clear that the logarithms of the structure counts of the reactant and of the intermediate are good reactivity indices for electrophilic aromatic substitution reactions.

The above treatment was based on the assumption that the intermediate  $\text{ArHD}^+$  is stabilized only by  $\pi$ -resonance. Recently, it has been shown that  $\sigma$ -complex intermediates

Table III. Constants for Linear Correlations of Rate Data with  $\ln SC_{I,h}$  Using Eq 5 and 6

eq	constant	$\ln k_{D-H}$	$\ln k_{H-D}$
5	$a_0$	-25.035	-29.654
	$a_1$	13.085	23.327
	$a_2$	-12.421	-26.559
	<i>r</i>	0.966	0.983
	<i>s</i>	$\pm 0.811$	$\pm 0.787$
	<i>n</i>	9	17
6	$a_0$	-24.968	-28.772
	<i>a</i>	13.714	18.764
	<i>r</i>	0.965	0.951
	<i>s</i>	$\pm 0.673$	$\pm 1.327$
	<i>n</i>	9	17

are stabilized by both  $\pi$ -resonance and hyperconjugation as depicted below for the cation derived from benzene.<sup>12</sup>



Experimental and theoretical evidence for hyperconjugative stabilization of cationic centers has been discussed by DeFrees, Hehre, and co-workers.<sup>13,14</sup> In an attempt to evaluate the importance of hyperconjugation effects in the hydrogen isotope exchange reactions under investigation, the rate data for both reactions were recorelated with the algorithms of the structure counts of the intermediates,  $\ln SC_{I,h}$ , corrected for hyperconjugation.<sup>12</sup> The results of regression analyses are summarized in Table III. A comparison of the values of the correlation coefficients obtained in this case with those for the above eq 7-10 indicates that inclusion of hyperconjugation effects leads to a slight improvement of the correlation for the deutero-deprotonation reaction. On the other hand, the quality of the correlation for the protodeuteration reaction is slightly diminished. Thus, it is not unreasonable to conclude that hyperconjugation does not play any significant role in the stabilization of the intermediates in the reactions studied.

(12) W. C. Herndon, *J. Phys. Chem.*, **85**, 3040 (1981).

(13) D. J. DeFrees, W. J. Hehre, and D. E. Sunko, *J. Am. Chem. Soc.*, **101**, 2323 (1979).

(14) D. J. DeFrees, M. Taagepera, B. A. Levi, S. K. Pollack, K. D. Summerhays, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 5532 (1979).

(11) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

Finally, the results reported in this contribution clearly indicate that differences in resonance energies determine the differences in reactivities of benzenoid hydrocarbons and that the hydrogen isotope exchange reactions follow the simple pathway expressed by eq 1 rather than the more complex pathway proposed by Gold and Satchell.<sup>15</sup>

### Conclusion

Logarithms of the rates of deuterodeprotonation of nine alternant hydrocarbons and protodeuteration of five hydrocarbons containing 17 and 12 different reaction sites, respectively, are correlated with the logarithms of the structure counts of the intermediate,  $\ln SC_I$ , and the reactant,  $\ln SC_R$ , and with their ratio,  $\ln (SC_I/SC_R)$ . The quality of the correlations is very good. The results indicate that the differences in reactivities of benzenoid hydrocarbons in aromatic substitution reactions are due to differences in their resonance energies and that hyperconjugation does not play a significant role in the stabilization of the intermediates in the reaction studied.

It is interesting to note that the correlations of the rate data with the calculations based on the structure-resonance theory are much better than those obtained with the HMO localization energies, although both approaches are highly empirical. This is a situation similar to that presented in another recent paper.<sup>16</sup> However, no detailed theoretical explanation for this difference in the quality of the respective correlations can be offered at the present time.

**Acknowledgment.** Financial support of this work by the Robert A. Welch Foundation, Houston, TX, is gratefully acknowledged. A.S.S. thanks the Robert A. Welch Foundation for a postdoctoral fellowship.

**Registry No.** 1, 1120-89-4; 2, 875-62-7; 3, 2430-34-4; 4, 14056-37-2; 5, 80160-90-3; 6, 4485-03-4; 7, 4819-99-2; 8, 4819-96-9; 9, 4819-98-1; 10, 80160-91-4; 11, 64615-22-1; 12, 80160-92-5; 13, 80160-93-6; 14, 80160-94-7; 15, 80160-95-8; 16, 80160-96-9; 17, 80160-97-0; benzene, 71-43-2; naphthalene, 91-20-3; anthracene, 120-12-7; phenanthrene, 85-01-8; biphenyl, 92-52-4; pyrene, 129-00-0; benz[a]anthracene, 56-55-3; perylene, 198-55-0; triphenylene, 217-59-4; chrysene, 218-01-9.

(15) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955).

(16) B. A. Hess, Jr., L. J. Schaad, W. C. Herndon, D. Biermann, and W. Schmidt, *Tetrahedron*, 37, 2983 (1981).

### On the Thermodynamic Stability and Reactivity of Alkyl-Substituted Alkenes

M.-H. Whangbo\*† and K. R. Stewart

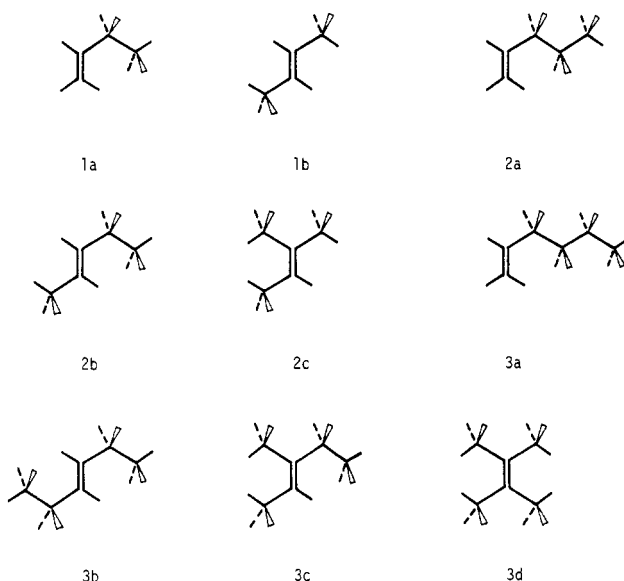
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

Received September 15, 1981

From heats of formation and heats of hydrogenation data,<sup>1,2</sup> it is observed that the thermodynamic stability of an alkene increases with alkyl substitution. In the hyperconjugation rationale,<sup>3</sup> alkyl group conjugation with a double bond is considered as stabilizing in nature so that an alkene with more alkyl substituents is predicted to be more stable. An alternative rationale focuses upon the C-C and C-H bond energies.<sup>4</sup> Provided that the sum of the  $C_{sp^3}-C_{sp^2}$  and  $C_{sp^3}-H$  bond energies exceeds that of the

\* Camille and Henry Dreyfus Teacher-Scholar, 1980-1985.

Chart I



$C_{sp^3}-C_{sp^3}$  and  $C_{sp^3}-H$  bond energies, the stability of an alkene is expected to increase with alkyl substitution. Those explanations are primarily concerned with the thermodynamic stability of an alkene and do not deal with the change in the reactivity of a double bond induced by alkyl substituents.<sup>5-7</sup>

Alkyl substitution is known to greatly enhance the susceptibility of a double bond toward electrophilic attack<sup>5-7</sup> and also to lower the ionization potential of double bond  $\pi$  electrons.<sup>8</sup> From the viewpoint of molecular orbital theory, those results are brought about because alkyl substitution raises the alkene HOMO level.<sup>9</sup> That is, the  $\pi$ -electrons of a double bond become less tightly bound upon alkyl substitution and hence act as a destabilizing factor for the overall thermodynamic stability of the alkene.

Thus, the enhancement of the alkene thermodynamic stability and the raising of the alkene HOMO level are two important aspects to reckon with in any satisfactory explanation of the alkyl substitution effect in alkenes. This effect is an example which counters the empirical observation<sup>10,11</sup> that the HOMO of a molecule parallels the total energy during the course of a molecular conformational change. This observation implies that the most stable isomer of a given molecule would be the one with the lowest-lying HOMO. In order to investigate the alkyl substitution effect in some detail, we have performed ab

(1) (a) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, NY, 1953, pp 108-119.

(2) (a) A. Liberles, "Introduction to Theoretical Organic Chemistry", MacMillan, New York, 1968, pp 214-216; (b) M. J. S. Dewar and H. N. Schmeising, ref 3b, pp 83-95.

(3) (a) M. J. S. Dewar, "Hyperconjugation", Ronald Press, New York, 1962, and references therein. (b) V. J. Shiner, Jr., and E. Campaigne, Eds., "Conference on Hyperconjugation", Pergamon Press, New York, 1959.

(4) (a) S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, 97, 3337 (1975); (b) M. J. S. Dewar, ref 3, pp 61-70.

(5) G. H. Schmid and D. G. Garratt, "The Chemistry of Double-Bonded Functional Groups", S. Patai, Ed., Wiley, New York, 1977, Part 2, Chapter 9, and references cited therein.

(6) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 4285 (1965).

(7) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968).

(8) D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, 52, 2622 (1970).

(9) N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, 100, 29 (1978).

(10) M.-H. Whangbo and S. Wolfe, *Isr. J. Chem.*, 20, 36 (1980), and references cited therein.

(11) B. M. Deb, *J. Am. Chem. Soc.*, 96, 2030, 2040 (1974).