Chemical Structure and Kinetic Properties of Hydroaromatic Compounds

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The precise co-ordinates of alicyclic compounds have been determined by means of the force field method. Using the co-ordinates thus obtained, the binding energy of the compounds and their radicals were calculated from approximate theory by the INDO method and were correlated to the ease of their dehydrogenation. The order of ease of dehydrogenation is decalin < tetralin < 1,2-dihydronaphthalene < 1,4-dihydronaphthalene. The variation of hydrogen evolution with temperature for the compounds above described was measured by using g.l.c. and the results were analysed kinetically. The rate at decomposition of these compounds showed a similar trend to that of thermochemical binding energy.

HYDROGEN transfer in coal and/or solvents in coal liquefaction and carbonization plays an important role in the reaction process.[1-3]

It is recognized that the ability of donor solvents to donate hydrogen facilitates the hydrogenation of coal to liquid products.[4-6]

Hydroaromatic compounds such as tetralin and dihydronaphthalene may serve as models for donor solvents. Recently, Gangwer [7] proposed a heterogeneous mechanistic model for the kinetics of hydrogenation–dehydrogenation processes of hydroaromatic compounds in the gas phase.

Values for the thermochemical properties of some six-membered cyclic and polycyclic compounds included hydroaromatic derivatives related to coal have been calculated by Shaw et al.[8] However, few results [9] have been reported on correlations between the chemical structure of hydroaromatic compounds and the ability to transfer hydrogen.

The objectives of this paper are three-fold, to calculate the precise geometry of hydroaromatic compounds by means of the force field method, to apply INDO theory [10] to an evaluation of the binding energy of the hydroaromatic compounds and their radicals, and to find a correlation between the efficiency of hydrogen transfer and the chemical structures of donor compounds.

EXPERIMENTAL

Four hydrogen donor compounds as models, decalin, tetralin, 1,2-dihydronaphthalene (1,2-DHN), and 1,4-dihydronaphthalene (1,4-DHN) were selected. Decalin was obtained from Kishida, tetralin from Kantokagaku, 1,2-DHN from Aldrich, and 1,4-DHN from Tokyokasei.

The pyrolysis of the alicyclic compounds was carried out in a glass tube (10 mm diam. × 500 mm) with a rubber cap, in a vertical i.r. image furnace heated at a rate of 10 K min^{-1}. A gas-sampling syringe was inserted in the rubber cap and the hydrogen gas evolved was measured by g.l.c. (Shimazu GC-6A). The peak intensity of H_2 was calibrated from that for pure H_2.

RESULTS AND DISCUSSION

(i) *Molecular Geometry.*—Prior to calculating the binding energy by MO calculations based on the INDO

method,[10] it is necessary to determine the precise geometry of the atoms. Although many methods for solving molecular structures have been proposed, e.g. the heavy-atom method [11] from X-ray diffractometry data, in order to bypass the difficulties involved in the experimetal determination of molecular structure, the force-field method, i.e. the molecular mechanics method, was introduced by Allinger.[12,13] This method is constructed from a set of equations and parameters derived from classical mechanics and has been applied successfully to the analysis of dynamic molecular processes in organic chemistry.[14]

The theory of the force-field method may be summarized as follows. Molecular geometries may be defined by four types of structural parameter, bond angles θ, torsional angles ϕ, bond lengths r, and non-bonded distances d. The potential energy of molecule may thus be thought as the sum of four components [reaction (1)]. Each term in equation (1) is given by one of the equations (2)—(5). In equation (5), the C

$$E = E_r + E_\theta + E_\phi + E_d \tag{1}$$
$$E_r = \tfrac{1}{2}k_r(r - r_0)^2 \tag{2}$$
$$E_\theta = \tfrac{1}{2}k_\theta(\theta - \theta_0)^2 \tag{3}$$
$$E_\phi = \tfrac{1}{2}k_\phi(1 + \cos3\phi) \tag{4}$$
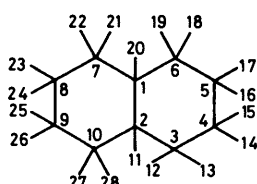$$E_d = [\varepsilon - (C_1/d^6) + C_2\exp(-C_3d)] \tag{5}$$

values are universal constants and ε is an energy parameter. In equations (2)—(4), the natural values (r_0, θ_0) and force constants (k_r, k_θ, k_ϕ) are calculated experimentally. This calculation involves systematically minimizing the total energy E in equation (1) by varying the structural parameters.

Recently, Kao and Allinger [15] extended their theory to the molecular mechanics of conjugated hydrocarbon systems. A variable electronegativity self-consistent-field (VESCF) calculation was carried out on the π-system to obtain bond orders which are used to assign stretching and torsional parameters.

In order to calculate the co-ordinates of the atoms in the model compounds, the COORD, MMI, and MMPI [16] programs were used. Our program is basically divided

into two parts, which are called MMI (molecular mechanics I) and MMPI. MMPI is used for molecules which contain conjugated π-systems. MMI is used for molecules which do not, but which may have double and triple bonds, as long as they are not conjugated. Approximate co-ordinates of atoms, bond lengths and dihedral angles obtained from a molecular model of the donor compound were input into the COORD program. Accordingly, the energy of a molecule with co-ordinates corresponding to the initial geometry was calculated and then by using the MMI and MMPI programs, the energy minimization were conducted to give the final steric energy and most stable structure. The final co-ordinates of the four model donor compounds are in Tables 1—4.

TABLE 1

Final atomic co-ordinates of decalin

Atom	x	y	z
C(1)	0.185 84	0.256 31	0.238 32
C(2)	1.660 78	0.409 46	0.654 19
C(3)	2.533 40	0.535 36	−0.597 12
C(4)	2.226 74	1.842 75	−1.349 95
C(5)	0.788 92	2.338 73	−1.120 38
C(6)	−0.167 04	1.154 38	−0.964 51
C(7)	−0.220 16	−1.200 40	−0.037 62
C(8)	0.210 26	−2.168 81	1.066 02
C(9)	1.724 41	−2.075 37	1.276 00
C(10)	2.107 31	−0.648 81	1.673 40
H(11)	1.808 75	1.376 36	1.169 23
H(12)	2.336 93	−0.341 57	−1.227 82
H(13)	3.604 85	0.473 97	−0.352 45
H(14)	2.924 30	2.638 89	−1.044 23
H(15)	2.413 11	1.692 31	−2.425 28
H(16)	0.704 78	2.959 38	−0.215 61
H(17)	0.475 64	3.007 04	−1.939 65
H(18)	−1.217 03	1.483 41	−0.910 12
H(19)	−0.094 22	0.593 55	−1.906 33
H(20)	−0.403 71	0.581 14	1.113 89
H(21)	0.239 57	−1.548 96	−0.972 28
H(22)	−1.308 19	−1.259 65	−0.200 89
H(23)	−0.080 50	−3.202 61	0.815 73
H(24)	−0.316 36	−1.917 42	1.998 61
H(25)	2.253 64	−2.354 71	0.353 53
H(26)	2.047 74	−2.795 54	2.045 91
H(27)	3.191 90	−0.578 58	1.849 92
H(28)	1.635 56	−0.443 08	2.647 50

TABLE 2

Final atomic co-ordinates of tetralin

Atom	x	y	z
C(1)	0.108 51	−0.098 40	−0.121 33
C(2)	1.474 92	0.268 53	−0.097 82
C(3)	1.888 74	1.703 31	0.133 00
C(4)	0.763 77	2.725 40	−0.041 86
C(5)	−0.486 10	2.249 49	0.703 05
C(6)	−0.975 03	0.931 16	0.100 06
C(7)	−0.230 85	−1.431 72	−0.328 38
C(8)	0.753 00	−2.416 80	−0.537 77
C(9)	2.090 32	−2.054 22	−0.533 85
C(10)	2.441 39	−0.708 37	−0.315 09
H(11)	2.758 84	1.955 30	−0.490 33
H(12)	2.234 67	1.716 81	1.175 96
H(13)	0.532 13	2.830 77	−1.112 36
H(14)	1.083 52	3.718 10	0.315 26
H(15)	−1.282 49	3.010 86	0.666 91
H(16)	−0.240 89	2.094 44	1.764 45
H(17)	−1.375 91	1.117 16	−0.906 09
H(18)	−1.796 26	0.500 95	0.691 35
H(19)	−1.282 73	−1.727 97	−0.340 62
H(20)	0.464 15	−3.458 93	−0.704 51
H(21)	2.866 80	−2.807 69	−0.696 99
H(22)	3.499 58	−0.435 37	−0.307 21
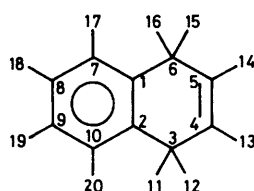
TABLE 3

Final atomic co-ordinates of 1,2-DHN

Atom	x	y	z
C(1)	0.028 32	−0.057 22	0.057 47
C(2)	1.430 75	−0.073 67	0.031 54
C(3)	2.171 52	1.194 04	0.155 04
C(4)	1.555 42	2.380 21	−0.006 05
C(5)	0.088 36	2.445 50	−0.340 45
C(6)	−0.688 66	1.258 06	0.227 04
C(7)	−0.670 85	−1.266 25	−0.069 41
C(8)	0.009 48	−2.479 08	−0.185 68
C(9)	1.410 20	−2.496 90	−0.168 59
C(10)	2.114 78	−1.300 98	−0.051 43
H(11)	3.249 26	1.166 33	0.337 51
H(12)	2.133 90	3.309 43	0.046 54
H(13)	0.030 63	2.435 15	−1.437 86
H(14)	−0.337 24	3.387 49	0.038 03
H(15)	−1.716 95	1.215 24	−0.159 17
H(16)	−0.763 48	1.362 86	1.318 65
H(17)	−1.763 53	−1.264 96	−0.061 54
H(18)	−0.547 62	−3.416 33	−0.277 65
H(19)	1.946 09	−3.447 62	−0.247 63
H(20)	3.207 53	−1.322 25	−0.044 01

(ii) *Binding Energy*,—The binding energies of the alicyclic compounds were calculated by the approximate INDO method. The difference between the total energy of a molecule at the equilibrium geometry and the sum of the atomic energy of the component atoms, *i.e.* the binding energy is relevant to an understanding of the stability of molecule at equilibrium.

In general, the dehydrogenation reaction accompanied by pyrolysis of an alicyclic compound can be written as equation (6) where HA is an alicyclic compound and A· its radical.
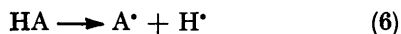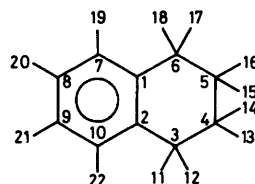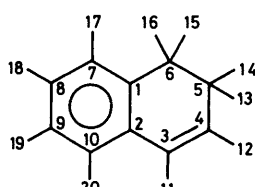
$$HA \longrightarrow A^{\cdot} + H^{\cdot} \qquad (6)$$

Let us assume that the ease of dehydrogenation from an alicyclic compound is correlated with the binding energy difference (ΔE) of HA and A·. That is, compounds with smaller values of ΔE are able to produce radicals more easily than those with larger values of ΔE. In order to check the validity of this assumption we have performed calculation of the binding energy of the

TABLE 4

Final atomic co-ordinates of 1,4-DHN

Atom	x	y	z
C(1)	0.041 08	0.020 28	0.138 71
C(2)	1.442 66	0.061 59	0.176 66
C(3)	2.119 45	1.391 60	0.402 41
C(4)	1.349 17	2.528 61	−0.215 38
C(5)	0.011 05	2.489 09	−0.252 51
C(6)	−0.723 92	1.307 97	0.324 26
C(7)	−0.605 80	−1.199 06	−0.092 90
C(8)	0.126 24	−2.376 28	−0.277 73
C(9)	1.520 82	−2.335 04	−0·241 07
C(10)	2.171 51	−1.117 17	−0·019 11
H(11)	3.136 73	1.361 59	−0.008 22
H(12)	2.162 52	1.558 10	1.485 69
H(13)	1.886 68	3.405 54	−0.592 33
H(14)	−0.555 49	3.333 45	−0.660 08
H(15)	−1.713 58	1.218 78	−0.141 54
H(16)	−0.836 15	1.470 33	1.403 21
H(17)	−1.697 24	−1.240 34	−0.125 59
H(18)	−0.389 96	−3.324 89	−0.453 66
H(19)	2.100 58	−3.251 29	−0.388 16
H(20)	3.263 67	−1.094 17	0.006 40

hydroaromatic compounds and radicals by the INDO method. The INDO method is based on semiempirical MO theory and it has often led to good results for the ground-state properties of organic molecules. The precise geometries of the model donor compounds obtained by application of the force field method (Tables 1—4) were used for input data for the INDO method. Table 5 summarizes the binding energy of the donor compounds and their radicals and binding energy difference.

Clearly, the binding energy difference (ΔE) is largest for decalin and smallest for 1,4-DHN with the order: decalin > tetralin > 1,2-DHN > 1,4-DHN.

(iii) *Kinetics Studies.*—The variation of hydrogen evolution with temperature for the model compounds is shown

in the Figure. The order of release of hydrogen is as follows: decalin < tetralin < 1,2-DHN < 1,4-DHN. The extent of dehydrogenation is strongly dependent upon the chemical structure of the model compound. These results are in good agreement with those of Virk et al.,[17] i.e. 1,2- and 1,4-DHN are more active than
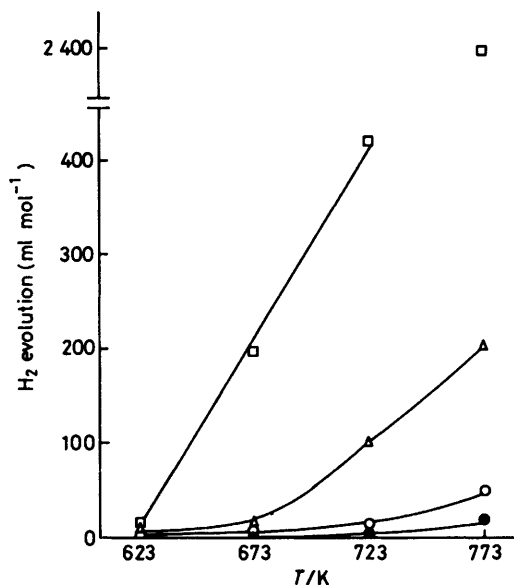

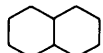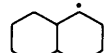FIGURE Hydrogen evolution of hydroaromatic model compounds: □, 1,4-DHN; △, 1,2-DHN; ○, tetralin; ●, decalin
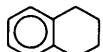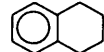
tetralin and decalin in transferring hydrogen to anthracene.
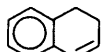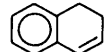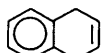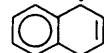
The efficiency of hydrogen donation of hydroaromatic compounds is basically a kinetic problem. Therefore, we have carried out a kinetic analysis of hydrogen evolution from hydroaromatic compounds.

Assuming an irreversible first-order reaction, the rate of hydrogen gas evolution can be written as (7) where x

$$dx/dt = k(1 - x) \qquad (7)$$

TABLE 5

Binding energy of model donor compounds, radicals, and their binding energy difference

HA E (a.u.)		A˙ E (a.u.)		ΔE (a.u.)
	−11.9439 (−7 490.26) *		−11.6265 (−7 291.21)	0.3174 (199.1)
	−10.7882 (−6 765.50)		−10.4753 (−6 569.27)	0.3129 (196.2)
	−10.3707 (−6 503.67)		−10.0657 † (−6 312.40)	0.305 (191.3)
	−10.3558 (−6 494.33)		−10.0576 (−6 307.32)	0.2982 (187.0)

1 a.u. = 6.2712 × 10² kcal mol⁻¹

* Values in the parentheses are in units of kcal mol⁻¹.   † This radical was identified by e.s.r.

is the amount of hydrogen evolved at time t, and k is the apparent rate constant and is given by Arrhenius equation (8). For a constant rate of heating, equation

$$k = A \exp\left(-\Delta E/RT\right) \qquad (8)$$

(7) is non-linear and hence must be solved numerically. However, if the heating operation can be approximately expressed equation (9) where T_0 and T are temperatures

$$\frac{1}{T_0} - \frac{1}{T} = \frac{1^j}{q_H}(t - t_0) \qquad (9)$$

at times t_0 and t, respectively, and q_H is an experimental constant. Then equation (7) can be integrated analytically and can be written as (10) where x_0 denotes the

$$\ln\frac{1 - x_0}{1 - x} = A\frac{Rq_H}{\Delta E}\exp\left(-\frac{\Delta E}{RT_0}\right)$$
$$\left[\exp\frac{\Delta E}{Rq_H}(t - t_0) - 1\right] \qquad (10)$$

amount of H_2 evolution at t_0. Furthermore, by differentiating equation (10) and taking logarithms, equation (11) can be obtained.[18]

$$\ln(1 - x)\left(\frac{dx}{dt}\right) = \left(\ln A - \frac{\Delta E}{RT_0}\right) + \frac{\Delta E}{Rq_H}(t - t_0) \qquad (11)$$

Using equations (8) and (11), we can obtain apparent rate constants k for dehydrogenation reaction of hydroaromatic compounds from the view point of hydrogen gas evolution. Apparent rate constants thus obtained are summarized in Table 6. The order of rate constants (k) is decalin $<$ tetralin $<$ 1,2-DHN $<$ 1,4-DHN.

TABLE 6

Apparent rate constants of hydroaromatic compounds for dehydrogenation reaction

Compound	k/min^{-1} at 723 K
Decalin	1.32×10^{-5}
Tetralin	1.32×10^{-4}
	(1.74×10^{-4}) *
1,2-DHN	9.98×10^{-4}
1,4-DHN	5.74×10^{-3}

* Ref. 19.

From the analysis of the kinetics, we can conclude that 1,4-dihydronaphthalene was the most effective donor compound of the hydroaromatic compounds tested.

Conclusions.—The binding energy differences (ΔE) of alicyclic compounds and their radicals for decalin, tetralin, 1,2-DHN, and 1,4-DHN were calculated by means of the force-field and INDO methods. The values obtained were 199, 196, 191, and 187 kcal mol^{-1}, respectively. The variation of hydrogen evolution with temperature for the compounds was measured by using g.l.c. and was analysed kinetically. The order of release of hydrogen was decalin $<$ tetralin $<$ 1,2-DHN $<$ 1,4-DHN. The trends in the decomposition kinetics of model compounds was interpreted in terms of the trends in binding energy difference.

REFERENCES

1 H. Marsh and R. C. Neavel, *Fuel*, 1980, **59**, 511.
2 T. Yokono and H. Marsh, *Fuel*, 1980, **59**, 362.
3 T. Yokono, H. Marsh, and M. Yokono, *Fuel*, 1981, **60**, 607.
4 I. Schwager and T. F. Yen, *Fuel*, 1978, **57**, 100.
5 M. H. Storch ' Chemistry of Coal Utilization,' ed. H. H. Lower, Wiley, New York, 1945, vol. II, ch. 38, p. 1750.
6 A. M. Squires, *Appl. Energy*, 1978, **4**(3), 161.
7 T. Gangwer, D. Mackenzle, and S. Casans, *J. Phys. Chem.*, 1979, **83**, 2013.
8 R. Shaw, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, 1977, **81**, 1716.
9 H. H. King and L. M. Stock, *Fuel*, 1981, **60**, 748.
10 J. A. Pople and G. A. Segal, *Chem. Phys.*, 1966, **44**, 3289; J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, 1965, **43**, 129.
11 M. Hegue, W. Horne, S. E. Cremer, and J. T. Most, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1000.
12 N. L. Allinger, *Adv. Phys. Org. Chem.*, 1976, **13**, 1.
13 N. L. Allinger and Y. H. Yah, QCPE, 1980, **11**, 318.
14 E. Ōsawa, K. Aigami, and Y. Inamoto, *J. Chem. Soc., Perkin Trans. 2*, 1979, 172, 181.
15 J. Kao and N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 975.
16 The MMI/MMPI force field was used, N. L. Allinger, QCPE, 1980, **11**, 318.
17 P. S. Virk, D. H. Bass, C. P. Eppig, and D. J. Ekpenyoung, Am. Chem. Soc. Div. of Fuel Chem. Meeting, 1979, Abstracts, p. 144.
18 K. Miyazawa, T. Yokono, T. Chiba, Y. Sanada, E. Yamada, and S. Shimokawa, ' Adv. in Chem. Ser.,' Am. Chem. Soc., Washington, 1981, vol. 192, p. 59.
19 H. Tominaga, *J. Fuel Soc., Japan*, 1980, **59**, 791.