Free Radicals by Mass Spectrometry. XVIII. The Ionization Potentials of Conjugated Hydrocarbon Radicals and the Resonance Energies of Radicals and Carbonium Ions

BY A. G. HARRISON[1] AND F. P. LOSSING

The ionization potentials of the β-naphthylmethyl, α-naphthylmethyl and diphenylmethyl radicals have been measured by electron impact as 7.56 ± 0.05, 7.35 ± 0.1 and 7.32 ± 0.1 ev., respectively, in excellent agreement with calculations based on a self-consistent molecular orbital theory. The vertical resonance energies of the allyl, benzyl, α- and β-naphthylmethyl and diphenylmethyl radicals and carbonium ions have been estimated from experimental bond dissociation energies and ionization potentials. The results are compared with theoretical estimates.

Introduction

The simpler molecular orbital theories of the mobile electrons of conjugated systems, while giving a good account of many features, have not been satisfactory in dealing with the resonance stabilization of radicals and ions. For free radicals of the odd-alternant class the simple Hückel l.c.a.o. molecular-orbital (m.o.) approximation[2] implies that the resonance stabilization of a radical and the carbonium ion derived from that radical are the same, and, further, that the ionization potentials of all conjugated radicals are identical. These predictions are not in agreement with experimental results.

The basic reason for this discrepancy appears to lie in the neglect of electron interaction terms in the simple Hückel theory. To include these electron interactions in a strictly non-empirical calculation becomes far too complicated for any but the simplest systems. Recently it has been shown[3,4] that a set of simplifying approximations can be made which enable the electron repulsion terms to be included in a semi-empirical method applicable to larger molecules. Using these approximations, Pople and co-workers have developed a self-consistent molecular orbital theory which they have applied to various properties of conjugated hydrocarbon radicals and ions.

Whereas the simple m.o. theory predicts that the resonance energies of a conjugated free radical and its ion are equal, the inclusion of electron interaction terms leads to the conclusion[5] that the carbonium ion has an additional stability over that of the free radical. The theoretical estimates of resonance energies of carbonium ions and radicals based on this theory were in reasonable agreement with experimental data then available for the resonance stabilization of the allyl and benzyl free radicals and carbonium ions.

In a later paper Hush and Pople[6] extended the theory to the calculation of the ionization potentials and electron affinities of conjugated free radicals and molecules. Again because of the inclusion of electron interaction terms the results were in contrast with the predictions of the simple m.o. theory, in which the non-bonding orbital always has the

(1) National Research Council of Canada Postdoctorate Fellow, 1957–1959.
(2) E. Hückel, Z. Physik, 70, 204, 279 (1931).
(3) R. Pariser and R. G. Parr, J. Chem. Phys., 21, 767 (1953).
(4) J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
(5) A. Brickstock and J. A. Pople, ibid., 50, 901 (1954).
(6) N. S. Hush and J. A. Pople, ibid., 51, 600 (1955).

same energy. However, when electron interaction terms are included, this is no longer true, the theory predicting that the ionization potential of an odd alternant radical will be lower if the non-bonding orbital is more spread out. Support for these conclusions was provided by the good agreement between the calculated and experimental values for the ionization potentials of the allyl and benzyl free radicals.

While the theoretical approach of Pople and co-workers to the calculation of ionization potentials and resonance energies appears very promising, more experimental data are needed to test their conclusions. The present work reports the determination by electron impact methods of the ionization potentials of three conjugated free radicals: α-naphthylmethyl, β-naphthylmethyl and diphenylmethyl. The results are in excellent agreement with calculations based on the Hush and Pople method. Using recently published bond dissociation energies and these ionization potentials, experimental estimates of the resonance energies of several carbonium ions and free radicals have been made and compared with theoretical estimates calculated by the self-consistent molecular orbital theory.

Experimental

The radicals were produced by pyrolysis of suitable compounds in a low-pressure capillary reactor mounted directly above the ion source of the mass spectrometer. The reaction products, issuing from the reactor at a pressure of about 10^{-3} mm., passed into the ionization chamber through a small hole in the top plate. The mass spectrometer[7] and the "low pressure" thermal reactor[8] have been described previously. Because of the low vapor pressure of the compounds pyrolyzed, only the low pressure reactor was used and the compounds were admitted to the reactor through an adjustable metal valve on the low pressure side of the leak. The xenon standard was admitted through the leak in the usual manner.

Production of the Radicals. (a) Diphenylmethyl.—The diphenylmethyl radical was produced by pyrolysis of benzhydrylamine. The amine was prepared from benzophenone through formation of the oxime and reduction with zinc and acetic acid[9] and purified by recrystallization of the hydrochloride and vacuum distillation of the free amine.

At a furnace temperature of 900° the decrease in the parent peak at mass 183 indicated about 85% decomposition of the benzhydrylamine. The diphenylmethyl radical was produced in reasonable yield as shown by the increase of the radical peak (mass 167) at an electron energy sufficient to ionize the radical but not sufficient to produce fragment ions. The corresponding hydrocarbon, diphenylmethane,

(7) F. P. Lossing, K. U. Ingold and A. W. Tickner, Discussions Faraday Soc., 14, 34 (1953).
(8) J. B. Farmer and F. P. Lossing, Can. J. Chem., 33, 861 (1955).
(9) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, 54, 710 (1932).

was formed during the pyrolysis presumably by hydrogen abstraction from material adsorbed on the walls of the reactor and ion source. At all temperatures at which pyrolysis occurred, a product was formed with a parent mass of 166. In attempts to produce the diphenylmethyl radical by pyrolysis of benzhydryl bromide no radical could be detected. The pyrolysis appeared to proceed exclusively to the formation of hydrogen bromide and the product of mass 166, tentatively identified as fluorene. The mechanism of the formation of fluorene is not clear, although one possibility is through the formation of the carbene with subsequent hydrogen migration
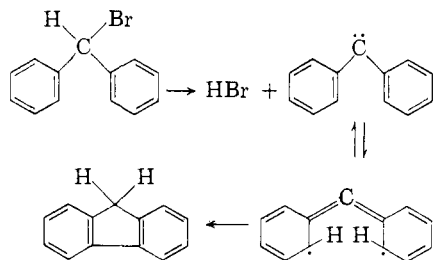
(b) α-Naphthylmethyl.—Similarly, the α-naphthylmethyl radical was obtained by pyrolysis of the corresponding amine. The method of preparation and purification of the naphthylmethylamine was similar to that used for the benzhydrylamine. The spectrum using 50 v. electrons showed large peaks for the parent ion (mass 157) and the loss of one hydrogen (mass 156). On pyrolysis these peaks decreased while the radical peak at mass 141 increased as did the peak at 142 characteristic of the hydrocarbon α-methylnaphthalene. Using low energy electrons a large increase was observed for the radical ion on pyrolysis. The radical yield was a maximum at 960°.

(c) β-Naphthylmethyl.—The β-naphthylmethyl radical was produced by the pyrolysis of β-naphthylmethyl bromide. The bromide was prepared by the reaction of N-bromosuccinimide with β-methyl-naphthalene in carbon tetrachloride[10] and was purified by recrystallization from petroleum ether and by vacuum distillation.

With 50 v. electrons the parent peaks for the bromide were much smaller than was the case for the amine, but they were still sufficiently large to serve as a guide to the extent of pyrolysis. At 960° the bromide was largely decomposed with formation of the radical of mass 141 in good yield. As was the case for the previous radicals no dimer was detected, but a considerable amount of the hydrocarbon β-methylnaphthalene was formed.

Measurement of the Ionization Potentials.—The technique of determining the ionization efficiency curves for the radical ion and the standard xenon gas has been described.[11] The net peak height for the radical at the appropriate mass was determined using 50 v. electrons by subtracting the contributions from the undecomposed parent substance and the hydrocarbon produced in the pyrolysis. The net radical peak remaining after these corrections was about 40–60% of the total peak and was generally about 100 cm. in height (2 × 10⁻¹² amp.).

The logarithm of the ratio of the peak height at a given electron accelerating potential to the net peak height at 50 v. was plotted against the electron accelerating potential. A typical set of ionization efficiency curves for the β-naphthylmethyl radical and the standard xenon is shown in Fig. 1. The two curves are essentially parallel from 1 to 0.1% in agreement with previous observations that the ionization efficiency curves for parent ions are generally parallel when plotted in this manner.

Results and Discussion

The experimentally determined ionization potentials for the β-naphthylmethyl, α-naphthylmethyl and diphenylmethyl radicals are recorded in Table I. Also included are the previously measured ionization potentials for the methyl,[11] allyl[11] and benzyl[11,12] free radicals. The limits of

(10) N. Buu-Hoi, *Ann.*, **556**, 18 (1944).

(11) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).
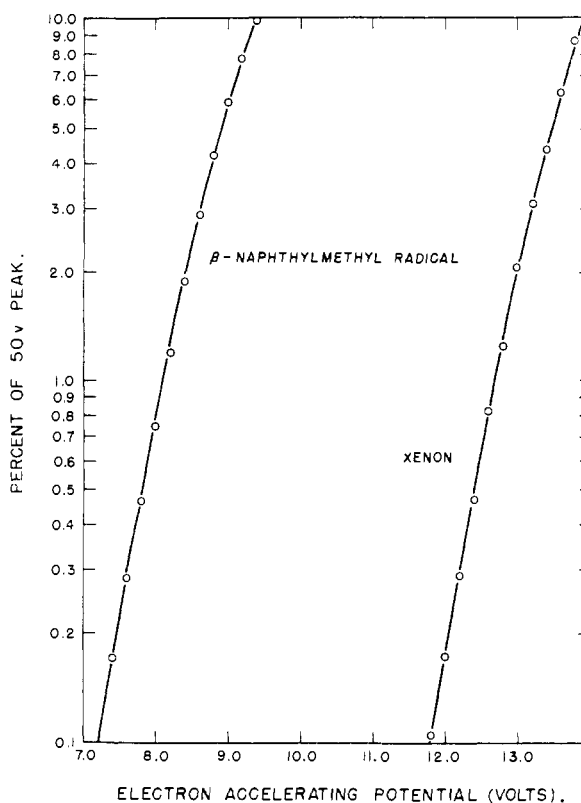
Fig. 1.—Ionization efficiency curves for the β-naphthylmethyl radical and the xenon standard.

error represent the average deviation of three or more determinations, not an estimate of the absolute error.

TABLE I

IONIZATION POTENTIALS OF CONJUGATED RADICALS

Radical	Ionization potential		Calcd.
	Measured		
Methyl	9.95 ± 0.03[a]		9.50[d]
Allyl	8.16 ± .03[a]		8.23[d]
Benzyl	7.76 ± .08[a,b]		7.78[d]
β-Naphthylmethyl	7.56 ± .05[c]		7.57[c,e]
α-Naphthylmethyl	7.35 ± .1[c]		7.35[d,e]
Diphenylmethyl	7.32 ± .1[c]		7.26[d,e]

[a] Ref. 11. [b] Ref. 12. [c] This work. [d] Ref. 6. [e] A recent calculation by A. Streitwieser (private communication) gives 7.42 v. for I(diphenylmethyl) and preliminary values of 7.5 and 7.7 v. for α- and β-naphthylmethyl, respectively.

The ionization potentials determined by electron impact are usually considered to correspond to vertical transitions and therefore may differ somewhat from the adiabatic ionization potential. It should be pointed out, however, that the calculated ionization potentials in column 3, Table I, are also vertical ionization potentials since the method of calculation necessarily assumes no changes in bond length or angle between the radical and ion. The calculated values are taken from Hush and Pople[6] with the exception of β-naphthylmethyl which has been evaluated in this work using the same method.

The excellent agreement between the experimental and theoretical values for the ionization

(12) J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *ibid.*, **22**, 1948 (1954).

potentials offers striking support for the theory of electron interaction developed by Pople and co-workers. As previously mentioned, the simple molecular orbital theory, neglecting electron interaction, would have predicted the same ionization potentials for all the conjugated radicals in Table I.

Closely related to the ionization potential of the free radical is the question of the resonance stabilization of the radical and carbonium ion. Brickstock and Pople,[5] using the self-consistent molecular orbitals, have calculated resonance energies of the allyl, benzyl and diphenylmethyl radicals and carbonium ions. Recently Mason[13] has extended the calculations to the α- and β-naphthylmethyl radicals and ions. Estimates of the resonance energies of these radicals and ions can be obtained indirectly from experimental data. The resonance energy of the radical RCH_2 is obtained from bond dissociation energies through the relation

$$E_R(RCH_2) - E_R(RCH_2X) = D(RCH_2-X) - D(CH_3-X) \quad (1)$$

By combining the ionization potentials recorded in Table I with the bond dissociation energies, the resonance energies of the carbonium ions are obtained, following Halpern's method,[14] from the relation

$$E_R(RCH_2^+) - E_R(RCH_2X) = I(RCH_2) + D(RCH_2X) - [I(CH_3) + D(CH_3X)] \quad (2)$$

Table II records theoretical and experimental estimates of the resonance energies of radicals and carbonium ions. The theoretical estimates are based on the calculations of Brickstock and Pople[5] and Mason[13] and neglect any resonance due to the CH_2X group in the undissociated compounds. The experimental estimates were obtained from equations 1 and 2 using the ionization potentials from Table I, these bond dissociation energies for the methyl derivatives

$$D(CH_3-H) = 102 \text{ kcal./mole}[15]$$
$$D(CH_3-Cl) = 80.5 \text{ kcal./mole}[15]$$
$$D(CH_3-Br) = 67.0 \text{ kcal./mole}[15]$$

and the bond dissociation energies for RCH_2 derivatives recorded in column 4 of Table II.

The most striking result emerging from the experimental estimates in Table II is the confirmation they provide for the theoretical prediction that the resonance energy of the carbonium ion is greater than that of the radical. In addition the good numerical agreement between the theoretical and experimental estimates of resonance energies for both the radicals and ions provides further support for the theoretical picture of electron interactions proposed by Pople and co-workers.

Two other features of the estimates in Table II are worthy of mention. First, the experimental estimates of the resonance energies for both the diphenylmethyl radical and ion are considerably lower than the theoretical estimates. The theoretical estimates are based on the assumption of

(13) S. F. Mason, J. Chem. Soc., 808 (1958).
(14) J. Halpern, J. Chem. Phys., 20, 744 (1952).
(15) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

TABLE II
THEORETICAL AND EXPERIMENTAL ESTIMATES OF RESONANCE ENERGIES

Energy	Theor. est.	Exp. est.	Comments
E_R(Allyl)	31.0[d]	24	D(allyl-H) = 78[a]
E_R(Allyl$^+$)	60.2[d]	66	
E_R(Benzyl) $-E_R$(Benzene)	21.9[d]	19–24	D(benzyl-H) = 78–83[b]
E_R(Benzyl$^+$) $-E_R$(Benzene)	61.6[d]	69–74	
$E_R(\beta\text{-}C_{10}H_7CH_2)$ $-E_R(C_{10}H_8)$	22.0[e]	26 22	$D(\beta\text{-}C_{10}H_7CH_2\text{-H}) = 76^c$ $D(\beta\text{-}C_{10}H_7CH_2\text{-Br}) = 45^d$
$E_R(\beta\text{-}C_{10}H_7CH_2{}^+)$ $-E_R(C_{10}H_8)$	66.6[e]	81 77	
$E_R(\alpha\text{-}C_{10}H_7CH_2)$ $-E_R(C_{10}H_8)$	23.3[e]	26 27	$D(\alpha\text{-}C_{10}H_7CH_2\text{-H}) = 76^c$ $D(\alpha\text{-}C_{10}H_7CH_2\text{-Br}) = 40^b$
$E_R(\alpha\text{-}C_{10}H_7CH_2{}^+)$ $-E_R(C_{10}H_8)$	72.8[e]	86 87	
E_R(Diphenyl methyl) $-2E_R$(Benzene)	46.7[d]	23.0 24.5	D(Diphenylmethyl-Br) = 44[b] D(Diphenylmethyl-Cl) = 56[b]
E_R(Diphenyl-methyl$^+$) $-2E_R$(Benzene)	102.9[d]	83.7 85.0	

[a] Based on best estimate ΔH^0_f (allyl) = 31 from pyrolytic and electron impact data, C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, Can. J. Chem., 34, 345 (1956). [b] A. Sehon and M. Szwarc, Ann. Rev. Phys. Chem., 8, 439 (1957). [c] M. Szwarc, Chem. Revs., 47, 75 (1950). [d] Ref. 5. [e] Ref. 13.

planarity of the radical and ion. It has been suggested[16] that triaryl carbonium ions are not planar, although the evidence for the diaryl ions is not as conclusive. The low experimental values for the resonance energies of the diphenylmethyl radical and ion could be explained on the basis of non-planarity in the diphenylmethyl system.

Secondly, with the exception of the diphenylmethyl system the theoretical estimates for the resonance energies of the carbonium ions are consistently some 10 kcal./mole lower than the experimental estimates. It is interesting to note that in the equation derived by Hush and Pople[6] for the ionization potentials of the free radicals

$$-I = -U + \frac{1}{2}\gamma_{11} - \frac{1}{2}\sum_{\mu\nu} \chi^2_{N\mu}\chi^2_{N\nu}\gamma_{\mu\nu}$$

The term U can be identified with the ionization potential of the methyl radical and the term

$$\frac{1}{2}\gamma_{11} - \frac{1}{2}\sum_{\mu\nu}\chi_{\mu}{}^2\chi_{N\nu}{}^2\gamma_{\mu\nu}$$

is identical with the expression derived by Brickstock and Pople[4] for the difference in resonance energy of the carbonium ion and radical. To obtain the best fit with experimental data for the more complex free radicals, it was necessary to take U, the ionization potential of methyl, as 9.50 ev. If this value, instead of the experimental value of 9.95 ev., had been used in the experimental estimates of the carbonium ion resonance energies in Table II, the estimates would be lower by 10 kcal./mole. It would thus appear that with the exception noted above, the theory of Brickstock and Pople underestimates the carbonium ion resonance energies by about 10 kcal./mole.

OTTAWA, CANADA

(16) For a discussion of the evidence see D. Bethell and V. Gold, Quart. Rev., XII, 173 (1958).