dissociation. $\Delta H_f{}^+(C_2H_3O)$ for a non-cyclic is 174 kcal./mole,[2] supporting this conclusion. The value of $\Delta H_f{}^+(C_2H_3O)$ obtained from the appearance potential study of ethylene oxide is 215 kcal./mole, only in fair agreement with that determined from propylene oxide. Although the agreement is within approximately the accumulative quoted errors, it is possible that this ion is cyclic and also that this ion be CH_2CHO^+. It is fairly certain the ion is not CH_3CO^+.

m/e **44.**—Ionization of ethylene oxide requires 10.65 ± 0.10 e.v., giving $\Delta H_f{}^+(C_2H_4O) = 234$ kcal./mole. This indicates the cyclic nature of this ion. The *m/e* 44 ion abundance in the spectrum of C_3H_6O was too small to allow a determination of its appearance potential.

m/e **57.**—Ionization and dissociation of C_3H_6O to $C_3H_5O^+$ and H is responsible for the observed ion at *m/e* = 57. From the experimental appearance potential, $\Delta H_f{}^+(C_3H_5O)$ is found to be 193 kcal./mole. We suggest that this ion retains its cyclic structure.

m/e **58.**—This ion could only result from ionization without further dissociation of propylene oxide. Thus, $\Delta H_f{}^+(C_3H_6O)$ is 204 kcal./mole, and for this ion it is reasonable to assume a cyclic structure. $\Delta H_f{}^+(C_3H_6O)$ for non-cyclics, although depending on the structure, is about 180 kcal./mole.[2]

From the above data, we concluded that $\Delta H_f(C_2H_3O) = 33 \pm 5$ kcal./mole. Assuming the C–H bond energy to be about 100 kcal./mole, and taking the appearance potentials of the ions from their respective molecules, the ionization potentials of the radicals C_3H_5O and C_2H_3O are calculated to be approximately 7.2 and 7.8 e.v., respectively.

The low values for the appearance potentials of *m/e* 43 and 29 and their large abundances suggests these ions are formed directly from the parent molecule ion. The less abundant *m/e* 42, 28, 16 and 14 ions indicates these are likely due to secondary dissociation. *m/e* 15 is likely the result of a secondary process and involves rearrangement, as does *m/e* 16. Further theoretical considerations of the construction of the mass spectrum will be treated in more detail in a future publication.

Acknowledgments.—The authors wish to express their appreciation to Dr. J. L. Franklin for his helpful comments and suggestions. We also thank Dr. Werner H. Wahl and V. Čermák for their discussions and criticisms of this work and Mr. Brice Hobrock for aiding in taking some of the experimental data.

[CONTRIBUTION, ISSUED AS N.R.C. No. 6094, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, ONTARIO, CANADA]

Free Radicals by Mass Spectrometry. XXI. The Ionization Potentials of Some *meta* and *para* Substituted Benzyl Radicals

BY A. G. HARRISON,[1] P. KEBARLE[2] AND F. P. LOSSING

RECEIVED SEPTEMBER 6. 1960

The ionization potentials of a number of *meta* and *para* substituted benzyl radicals have been determined by electron impact. The substituents, in order of decreasing ionization potential of the radical, were *m*-CN, *m*-NO_2, *p*-CN, *m*-F, *p*-Cl, *p*-F, *p*-*i*-Pr and *p*-CH_3O. The results are in agreement with the known electron-releasing or electron-attracting powers of the substituents. Since the effect of the substituents on the stability of the radicals themselves is very small, the results permit a consideration of the stabilization of ions in the gas phase where solvation plays no role.

Introduction

Since the ionization potentials of hydrocarbon free radicals reflect the effects of structural factors on the stabilities of radicals and ions, a knowledge of the ionization potentials of a wide variety of radicals is of importance both in the development of theoretical methods in molecular structure and in the understanding of the reactivities of radicals and carbonium ions. The ionization potentials of a number of conjugated hydrocarbon radicals, measured directly by electron impact,[3,4] are in excellent agreement with values calculated by a semi-empirical molecular orbital method.[5] Recently the simple molecular orbital theory has been modified[6] to permit the examination of the hyperconjugative effect of a methyl group on ionization potentials. Ionization potentials of a number of methyl substituted allyl, benzyl and alkyl radicals calculated by this method[6] are in reasonable agreement with experimental values obtained by electron impact.[7-9]

Such theoretical calculations have not been made as yet for radicals containing hetero-atoms, presumably because of the mathematical complexity of the calculations and the lack of experimental data for comparison. Some experimental data on the effect of halogen hetero-atoms on the ionization potential of the methyl radical has been published recently,[10] and it appears desirable to examine further the effect of such hetero substituents on radicals of various types. The present paper is

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[1] National Research Council postdoctorate fellow 1957–1959.

[2] National Research Council postdoctorate fellow 1956–1958.

[3] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

[4] A. G. Harrison and F. P. Lossing, THIS JOURNAL, **82**, 1052 (1960).

[5] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[6] A. Streitwieser and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

[7] J. B. Farmer, F. P. Lossing, D. G. H. Marsden and C. A. McDowell, *J. Chem. Phys.*, **24**, 52 (1956).

[8] C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

[9] F. P. Lossing and J. B. deSousa, THIS JOURNAL, **81**, 281 (1959).

[10] F. P. Lossing, P. Kebarle and J. B. deSousa, "Advances in Mass Spectrometry," Pergamon Press, London, 1959, p. 431.

concerned with the effects of hetero-groups in the *meta* and *para* positions on the ionization potential of the benzyl radical. The benzyl radicals substituted in these positions comprise a particularly interesting group since the substituent is sufficiently removed from the nominal site of the free electron that it exerts its influence only by electronic effects and not by steric effects.

The ionization potentials of these radicals are also of considerable interest in relation to the reactions of substituted aromatic systems in solution. The reactions have often been interpreted in terms of the effect of the substituents on the stability of charged species formed during the course of the reaction. The importance of solvation effects has been a source of uncertainty in conclusions reached from these kinetic studies. It appeared that a knowledge of the effect of substituents on the energetics of ionization processes in the gas phase might be of assistance in interpreting substituent effects in solution reactions. Since the bond dissociation energies of *meta* and *para* substituted benzyl derivatives show very little dependence on the nature of the substituent,[11] the change of ionization potential with substitution is a direct measure of the energy required for ion-pair formation in the gas phase. The relevant energy relations are shown in Fig. 1 for the case of the substituted benzyl bromides.

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 reactor[12] and mass spectrometer[13] have been described previously. The technique of measuring the ionization potentials was the same as that used for the xylyl[7] and arylmethyl[4] radicals.

For the substituted benzyl radicals of interest in this work, pyrolysis of the corresponding bromide or iodide was found to be a satisfactory method of preparation, with the exception of the *p*-methoxybenzyl radical for which a somewhat more subtle approach was necessary owing to the thermal instability of the radical. Table I records the derivatives pyrolyzed to produce the respective radicals.

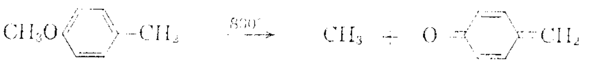
TABLE I

IONIZATION POTENTIALS OF SUBSTITUTED BENZYL RADICALS

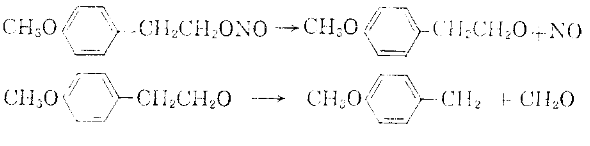
Substituent	Source of radical	Ionization potential (volt)
m-CN	Bromide	8.58 ± 0.1
m-NO_2	Bromide	8.56 ± .1
p-CN	Bromide	8.36 ± .1
m-F	Bromide	8.18 ± .06
p-Cl	Bromide, iodide	7.95 ± .1
p-F	Bromide	7.78 ± .1
H	Iodide, amine	7.76 ± .08
m-CH_3	Iodide	7.65 ± .03
3,4-C_4H_4	Bromide	7.56 ± .05
p-CH_3	Iodide	7.46 ± .03
p-i-Pr	Iodide	7.42 ± .1
p-CH_3O	β-(*p*-methoxyphenyl)-ethyl nitrite	6.82 ± .1

Analysis, with 50 v. electrons, of the products issuing from the reactor showed that the main products of decomposition of the bromides and iodides were the corresponding benzyl radical and the halogen atom. Similar results were observed previously for the pyrolysis of the xylyl iodides.[7] The pressures in the present reactor favor wall reactions with the result that the main non-radical products were the respective substituted toluenes, and in only a few cases were significant amounts of the products of radical dimerization detected.

The *para*-methoxy benzyl radical appeared to be relatively unstable thermally. At the temperature necessary for pyrolysis of the amine or bromide no radical could be detected at mass 121. Instead, methyl radicals and a product of mass 106 were formed, suggesting that the following decomposition of the radical was occurring at the high temperatures.



It was found, however, that the radical could be prepared by the thermal decomposition of β-(*p*-methoxyphenyl)-ethyl nitrite. Although the intermediate oxy radical was not detected, it is probable, by analogy with the alkyl nitrites,[9] that the decomposition proceeded by



This sequence of reactions occurred at a temperature of about 400°, some 400° lower than the pyrolysis of the bromide or amine. As a consequence the radical was present in sufficient yield to permit determination of its ionization efficiency curve. At higher temperatures the radical peak rapidly decreased with formation of methyl radicals and the product of mass 106. The relatively unstable propyl and butyl radicals have recently been obtained[9] in a similar manner by pyrolysis of the appropriate nitrites.

Materials.—The *meta*-nitrobenzyl bromide was a commercial sample of high purity. The remainder of the substituted benzyl bromides were prepared by the bromination of the appropriate toluene with N-bromo-succinimide in carbon tetrachloride.[14] The bromides were purified either by fractional distillation or by recrystallization from petroleum ether. The iodides were prepared from the respective chlorides by reaction of sodium iodide in acetone.[15] All chlorides were available commercially with the exception of *para*-isopropyl benzyl chloride which was prepared by the chloromethylation of cumene.[16]

The β-(*p*-methoxyphenyl)-ethyl nitrite was prepared from the alcohol by reaction with sodium nitrite in dilute sulphuric acid.[17] The alcohol was obtained by the reduction of *para*-methoxyphenyl acetic acid with lithium aluminum hydride.[18]

Results and Discussion

The vertical ionization potentials measured for the substituted benzyl radicals are given in Table I. Included in the table are the previously measured ionization potentials for the benzyl,[3,19] β-naphthylmethyl[4] and *meta*- and *para*-xylyl radicals.[7] The limits of error given in the table are the average deviations of three or more determinations and are not intended to represent the absolute error.

The results clearly indicate that, in general, the ionization potential of the benzyl radical, and thus the energy required for ion-pair formation, is affected by the substituents in the manner one would expect from the known electronic effects

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(11) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

(12) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(13) F. P. Lossing, K. U. Ingold and A. W. Tickner, *Discussions Faraday Soc.*, **14**, 34 (1953).

(14) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

(15) R. C. Fuson and H. G. Cooke, Jr., THIS JOURNAL, **62**, 1180 (1940).

(16) L. Bert, *Bull. Soc. Chim. France*, [4] **37**, 1252 (1925).

(17) "Organic Syntheses," Vol. XVI, John Wiley and Sons, Inc., New York, N. Y., 1936.

(18) J. H. Hunter and J. A. Hogg, THIS JOURNAL, **71**, 1922 (1949).

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

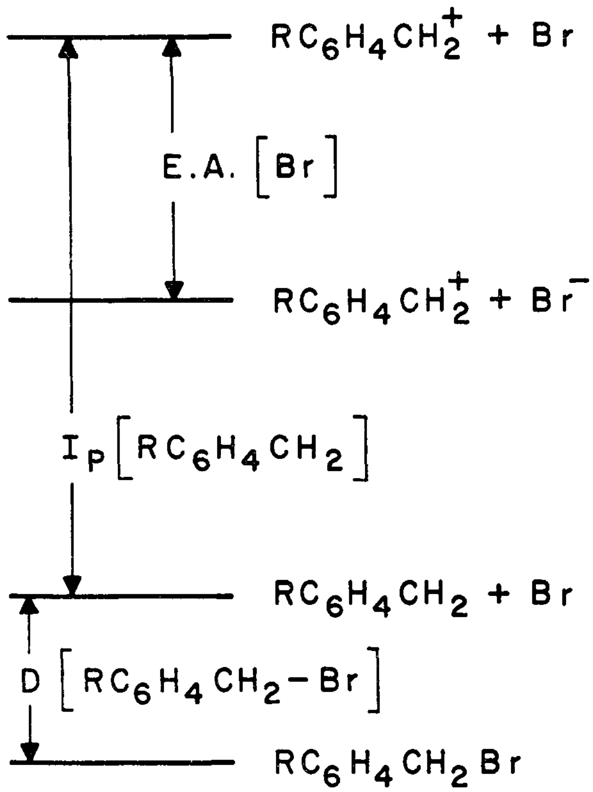


Fig. 1.—Energy relations for ion pair formation in the gas phase.

of the substituents.[20] Thus the cyano and nitro groups, being electron attracting by both the inductive and conjugative mechanism, decrease the stability of the carbonium ion and cause an increase in the ionization potential compared to the benzyl radical. On the other hand the methoxy group, although weakly electron attracting by the inductive mechanism, is strongly electron donating by the conjugative mechanism. In the *para* position where the methoxy group can conjugate with the positive charge a striking lowering of the ionization potential results.

Quantitative correlations between the changes in ionization potential and the electronic effect of the substituents, as derived from the study of organic reactions, are shown in Fig. 2. The upper graph shows a plot of the ionization potentials against the Hammett σ values[21,22] for the substituents, while the lower graph shows a similar plot in which Brown's σ^+ values[23] were used. A satisfactory linear correlation is observed in both plots, although, significantly, the points for the β-naphthylmethyl and p-methoxybenzyl radicals show considerable deviation from the straight line in the σ plot but fall well in line when plotted against σ^+.

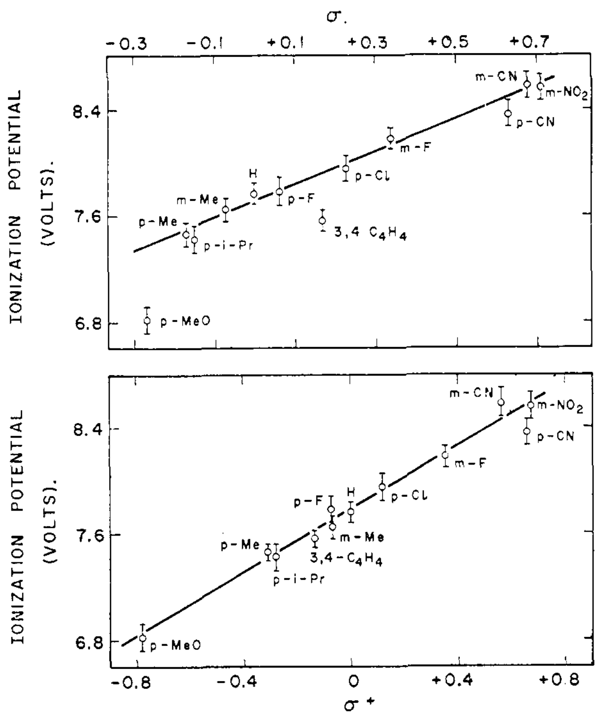
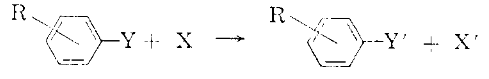


Fig. 2.—Ionization potentials of substituted benzyl radicals plotted against Hammett σ values (upper graph) and Brown σ^+ values (lower graph).

The Hammett σ values arose from observations during the 1930's that the effect of substituents in many reactions involving benzene derivatives could be correlated with the acid strengths of the corresponding substituted benzoic acids. This led Hammett to introduce a general relation between the nature of the substituent in the *meta* or *para* position and the reactivity of benzene derivatives. For the generalized reaction



The Hammett relation takes the form

$$\log \frac{k_R}{k_H} = \rho\sigma \qquad (1)$$

where k_R is the rate constant for the substituted compound, k_H the rate constant for the unsubstituted compound, σ is the substituent constant depending only on the nature and position of the substituent and ρ is the reaction constant which depends upon the reaction, the conditions under which it is studied and the nature of the side chain Y. The magnitude of the reaction constant ρ is often considered to be a measure of the susceptibility of the reaction under consideration to the electronic effect of the substituents.

Although the Hammett relation has provided a satisfactory description of substituent effects on the reactions of benzene derivatives in a wide variety of reactions, it has been observed that for reactions involving the formation of an electron-deficient reaction center, such as a fully or partially formed carbonium ion, the correlation between relative rates and σ values was unsatisfactory. This situation was particularly noticeable in cases where

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(20) For a discussion of the electronic effect of substituents see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 60 and ref. 21 and 22.

(21) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chap. VII.

(22) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(23) H. C. Brown and Y. Okamoto, THIS JOURNAL, **80**, 4979 (1958).

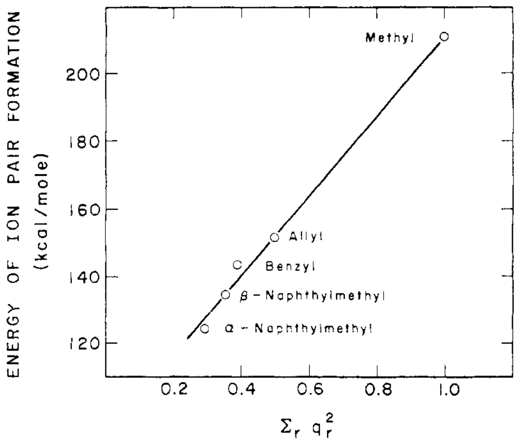

Fig. 3.—Plot of the energy for ion pair formation against $\Sigma_r q_r^2$ (see text).

strongly electron-releasing substituents were in a position permitting conjugation with the developing carbonium ion. The Brown σ^+ values, on the other hand, were derived from a study of the solvolysis of substituted phenyldimethylcarbinyl chlorides, a reaction proceeding by the formation of such an electron-deficient reaction center. The σ^+ values are therefore expected to describe the effect of substituents on the rates of such electrophilic reactions in a more satisfactory manner. Both the 3,4,-C_4H_4 and p-CH_3O substituents are examples of electron-releasing substituents in a position which permits conjugation with the developing charge, therefore it would be expected in the present case that a more satisfactory correlation would be obtained with the σ^+ values.

The data of Fig. 2, when plotted in the usual manner of equation 1, lead to a ρ value of approximately -20. Since, as discussed above, the bond dissociation energies of substituted benzyl compounds are nearly independent of the nature of the substituent, this ρ value is essentially a measure of the susceptibility of the energy for ion-pair formation in the gas phase to the electronic effect of substituents. Consequently it is of interest to compare this reaction constant with similar constants obtained from solvolytic reactions of benzyl derivatives in the liquid phase, particularly those proceeding by the S_N1 mechanism and therefore involving at least partial ion pair formation in the rate-controlling step. For electrophilic aromatic side chain reactions a recent summary[23] shows that such reactions give ρ values in the range -2.5 to -4.7. The most extensive investigation of an S_N1 solvolysis reaction has been the study by Brown and co-workers[24] of the solvolysis of substituted phenyldimethylcarbinyl chlorides in 95% aqueous acetone. This reaction yields a reaction constant $\rho = -4.54$, considerably less than that found in the present work for ion pair formation in the gas phase.

In general, therefore, it would appear that S_N1 solvolysis reactions are much less susceptible to the electronic effect of substituents than is the similar gas phase ionization. In the gas phase ionization the positive charge is fully developed and the substituents can exert their maximum influence on the stability of the ions through changes in the extent of charge delocalization. On the other hand, for the solvolysis reaction the influence of the substituents can be diminished not only by incomplete charge formation in the transition state but also by solvation effects. These solvation effects may manifest themselves either by specific solvation of the localized charge, thus decreasing the charge delocalization and the effect of substituents on the delocalization, or by systematic changes in the solvation energy with change in substituent.

In this regard Mason[25] has suggested recently that for arylmethyl carbonium ions the free energy of solvation decreases with increasing charge dispersal. Mason has modified the simple Born expression for the free energy of solvation to take into account charge dispersal or delocalization and has obtained the following expression.

$$-\Delta F_s = \Sigma_r q_r^2 e^2 (1 - 1/D)/2R_e \qquad (2)$$

where q_r is the fraction of the positive charge on atom r, R_e is the equivalent radius of the solvation sheath, and the other letters have their usual significance. For the arylmethyl ions $\Sigma_r\ q_r^2$ can be calculated from the coefficients of the non-bonding molecular orbital by the method of Longuet-Higgins.[26] For the present discussion it is of interest to note that for the arylmethyl ions, where data is available, the energy required for ion pair formation is, within the limits of error, a linear function of $\Sigma_r q_r^2$, as shown in Fig. 3. The energy of ion pair formation has been calculated for the reaction

$$ArCH_2Br \longrightarrow ArCH_2^+ + Br^-$$

using the known bond dissociation energies,[11,27] ionization potentials previously reported[3,4] and the electron affinity of bromine.[28] Assuming the validity of equation 2 the free energy of solvation should decrease linearly with decreasing energy of ion pair formation for the arylmethyl system.

It is obviously impossible to transfer this argument in a quantitative fashion to the case of the hetero substituted benzyl compounds, however one might logically expect the free energy of solvation to be a linear function of the energy of ion pair formation in this case as well. It is possible therefore that the low susceptibility of solvolysis reactions to the effect of substituents results partially from systematic changes in the solvation free energy and not necessarily from incomplete charge formation in the transition state.

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(24) See ref. 23 and earlier references quoted therein.

(25) S. F. Mason, *J. Chem. Soc.*, 808 (1958).

(26) J. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).

(27) A. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957)

(28) F. H. Field and J. L. Franklin, "Electron Impact Phenomena,' Academic Press, Inc., New York, N. Y., 1957.