and C_3, as required by the method of calculation.[12,16] The lowest $1\sigma_g$ and $1\sigma_u$ orbitals are consistently too high in energy, but these orbitals are not important in determining the electronic properties of the molecules. As expected from the method of calculation, the predicted orbitals of C_2O are roughly midway between the corresponding orbitals of CO_2 and C_3. The fourteen L-shell electrons of C_2O would fill the 1σ, $1\sigma'$, 2σ, $1\pi'$ and $2\sigma'$-orbitals, leaving two electrons for the 1π-orbital. Depending on the arrangement of the two electrons in the 1π-orbital, $^3\Sigma$, $^1\Delta$ and $^1\Sigma$ states can result. According to Hund's rules,[17] the $^3\Sigma$ state should be the ground state, with the $^1\Delta$ next and the $^1\Sigma$ state the highest in energy. Using the known splitting of the lowest electronic states of O_2, and allowing for the larger distances in C_2O, it is predicted that the $^1\Delta$ state lies 0.5 e.v. and the $^1\Sigma$ state 0.8 e.v. above the $^3\Sigma$ ground state.

Predictions could also be made on the expected absorption of C_2O. However, the small differences be-

(16) E. Clementi and A. D. McLean, *J. Chem. Phys.*, **36**, 45 (1962).

(17) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p. 135.

tween the upper π- and σ-orbitals in Fig. 3 depend on I_π and I_σ, which are only approximate large numbers. Therefore, little significance can be attached to the actual intervals shown. Considering the possible electronic states arising from the various excited configurations, it seems reasonable to expect several allowed electronic absorptions from both the $^3\Sigma$ and the $^1\Delta$ states in the range of 3 to 6 e.v. Thus a flash photolysis search for C_2O might prove fruitful.

The predicted existence of both low lying singlet and triplet states of C_2O, together with the evidence for two intermediates observed above, suggest that C_2O is the reactive intermediate in the photolysis of carbon suboxide both at long and short wave lengths. However, carbon suboxide molecules in excited electronic states could also be responsible. A decision between these two alternatives must await further experimental evidence.

Free Radicals by Mass Spectrometry. XXX. Ionization Potentials of Anilino and 2-, 3- and 4-Pyridylmethyl Radicals

BY T. F. PALMER[1] AND F. P. LOSSING

The vertical ionization potentials of the anilino and the 2-, 3- and 4-pyridylmethyl radicals have been measured by electron impact: anilino 8.26 v., 2-pyridylmethyl 8.17 v., 3-pyridylmethyl 7.92 v. and 4-pyridylmethyl 8.40 v. The appearance potentials for loss of a H-atom from 2-, 3- and 4-methylpyridines to give nominally pyridylmethyl ions do not reflect the differences in the radical ionization potentials, suggesting loss of orientational effects in the fragment ions.

Introduction

The replacement of ring H-atoms in the benzyl radical by various characteristic groups has been shown to cause relatively large changes in the vertical ionization potential of the radical.[2,3] The present work is an extension of these measurements to the effect of substitution of skeletal carbon atoms by nitrogen. The 2-, 3- and 4-pyridylmethyl radicals and the anilino radical have been produced by thermal decomposition reactions, and the vertical ionization potentials of the radicals have been measured by electron impact.

The three isomeric pyridylmethyl (picolyl) radicals

2-pyridylmethyl   3-pyridylmethyl   4-pyridylmethyl
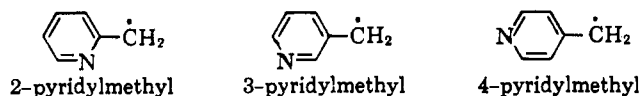
were produced by Roberts and Szwarc[4] in the thermal decomposition of the corresponding picolines using the toluene carrier technique. They found the bond dissociation energies $D(C_5NH_4CH_2-H)$ to be 75.5, 76.5 and 77.5 kcal./mole for the 2-, 3- and 4-picolines, respectively, essentially the same as their value for toluene.

The anilino radical C_6H_5NH has been observed by absorption spectroscopy in the flash photolysis of aniline in rigid matrices at low temperatures by Porter and co-workers.[5,6] They also observed the radical in

the flash photolysis of aniline in the vapor phase[7,8] and in hexane solution.[9] Its occurrence in the thermal decomposition of hydrazobenzene and phenylhydrazine has been postulated by Dewar,[10] who obtained D-$(C_6H_5NH-NHC_6H_5)$ = 35.4 kcal./mole, and D-$(C_6H_5NH-NH_2)$ = 48 kcal./mole.

No values for the ionization potentials of anilino or pyridylmethyl radicals appear to have been reported in the literature.

Experimental

The free radicals were produced by the thermal decomposition of suitable derivatives in a fused-silica capillary furnace leading directly to the ionization chamber of a mass spectrometer.[11] The method of comparison of the ionization efficiency curves for the parent radical ion with that of an added standard gas was the same as employed formerly.[12]

The 3-pyridylmethyl radical was produced in fair yield by the thermal decomposition of 3-aminomethylpyridine at 1050°.
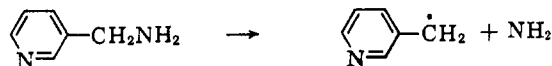
Other products were ammonia and a smaller amount of 3-picoline. The decomposition of 2- and 4-aminomethylpyridines yielded large amounts of the 2- and 4-picolines, but only traces of the corresponding radicals. These radicals were therefore produced from the thermal decomposition of α- and γ-dihydrostilbazole at 1000°.

(1) National Research Council Postdoctorate Fellow 1960–1962.

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

(3) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961).

(4) J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **16**, 981 (1948).

(5) I. Norman and G. Porter, *Proc. Roy. Soc.* (London), **A230**, 399 (1955).

(6) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

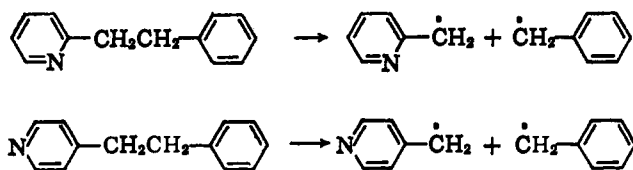(7) G. Porter and F. J. Wright, *ibid.*, **51**, 1469 (1955).

(8) G. Porter, *Chem. Soc. Special Publ.*, **No. 9**, 139 (1958).

(9) G. Porter and E. J. Land, Fifth International Symposium on Free Radicals, Preprints B4, 1961.

(10) Cited by M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

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

(12) R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1523 (1962).

For both radicals the yield appeared to be considerably smaller than the yield of benzyl radicals. This resulted mainly from the formation of appreciable amounts of the 2- and 4-picolines, presumably by abstraction of H-atoms from substances adsorbed on the walls of the reactor or the ionization chamber. It is not clear why pyridylmethyl radicals should be so much more effective than benzyl radicals in abstracting H-atoms in this way.

Since the ionization potentials of the pyridylmethyl radicals (mass 92) were higher than that of benzyl radical (mass 91), the lower energy portions of their ionization efficiency curves had to be corrected for ^{13}C-contributions from the benzyl radical. At the lowest electron energies this correction became quite large, amounting to some 40% of the mass 92 peak for 2-pyridylmethyl radical.

The anilino radical was produced in fair yield by the thermal decomposition of N-allylaniline at 870°. Other major products were allyl radicals and aniline. The absence of significant amounts of allene ruled out the formation of aniline by disproportionation between the anilino and allyl radicals. Consequently the aniline must have been produced by a reaction of anilino radicals with substances adsorbed on the walls. Above 870°, the concentrations of aniline and its precursor, the anilino radical, decreased, and increasing amounts of the cyclopentadienyl radical and a compound of mass 27 were formed. It would appear that the anilino radical decomposes by loss of HCN (or HNC) in a manner analogous to the elimination of CO from the phenoxyl radical[13,14] and of CS from the phenyl sulfide radical.[15]
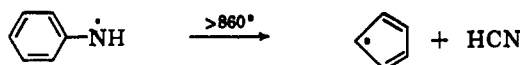
The corresponding reaction by which C_2H_2 could be eliminated from benzyl radical or the pyridylmethyl radicals does not occur even at temperatures in excess of 1000°. Evidently the necessary H-atom migration is not easily effected.
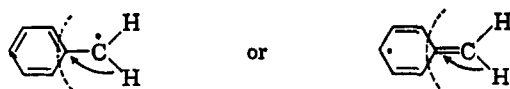
Materials.—The three picolines, the 2-, 3- and 4-aminomethylpyridines and N-allylaniline were commercial samples of good purity. They were distilled under reduced pressure, and a middle fraction was used in each case. α-Dihydrostilbazole was prepared by the reaction of 2-picoline with sodamide and benzyl chloride.[16] The final product was distilled under reduced pressure and a middle fraction collected. Mass spectral analysis of the purified product showed that it contained no volatile impurity. γ-Dihydrostilbazole was prepared in the same manner using 4-picoline as the starting material. The product was purified by pumping under vacuum followed by repeated recrystallization from small amounts of alcohol. The melting point was 71° (lit.[16] 72°).

Results and Discussion

The vertical ionization potentials found for the 2-, 3- and 4-pyridylmethyl radicals and the anilino radical are given in Table I. The limits of error given are the average deviations from the mean of three or more determinations and do not represent the limits of absolute error. The radicals, which are stabilized by resonance, can in principle combine to form several possible dimers. Since the mass spectra of these dimers are unknown, the net 50-volt peak height for the radicals could not be calculated. The ionization efficiency curves for the radical and the standard gas were therefore matched in curvature by vertical displacement.[12,17] For comparison with earlier results, the ionization potentials of the benzyl and allyl radicals formed in

the preparation of the 2- and 4-pyridylmethyl and the anilino radicals were also measured. The values obtained were: benzyl 7.74 ± 0.05 v. (average of seven determinations), and allyl 8.22 v. (average of two determinations). These results are in satisfactory agreement with the earlier measurements: benzyl 7.73 ± 0.08 v.,[18] 7.81 ± 0.08 v.[19] and allyl 8.16 ± 0.03 v.[18] It would appear, therefore, that the energy scale is sufficiently well established to show that the substitution of N for CH in benzyl radical brings about significant increases in the vertical ionization potential, which depend on the position of substitution.

TABLE I
VERTICAL IONIZATION POTENTIALS OF RADICALS

Radical	Radical source	I.p. (volts)
2-Pyridylmethyl	α-Dihydrostilbazole	8.17 ± 0.1
3-Pyridylmethyl	3-Aminomethylpyridine	7.92 ± .1
4-Pyridylmethyl	γ-Dihydrostilbazole	8.40 ± .15
Anilino	N-Allylaniline	8.26 ± .1

It can be seen from Table I that substitution of N for CH in the m-position of the ring has a minimum effect on the ionization potential of the benzyl radical, raising it by only about 0.2 v. In the o- and p-positions, however, and in the side chain, substitution of CH by N increases the ionization potential by 0.4–0.7 v. These results can be explained in a qualitative way on the basis of differences in charge delocalization. Considering the radicals as odd alternant species,[20] the positive charge in the ions will reside mainly on the starred positions
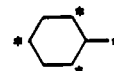
The 3-pyridylmethyl radical ion is the only one of the four in which a part of the charge need not be located at a N-atom. In the other three radical ions the electrophilic nature of the N-atom will act to impede the full development of the charge delocalization and to raise the ionization potential. Assuming little or no positive charge to reside on the N-atom, structural considerations would predict that the delocalization of charge over the three starred carbon atoms would be greater in the 2-pyridylmethyl radical ion than in the 4-pyridylmethyl or anilino radical ions. On this basis, the latter two radicals would have the highest ionization potentials, in agreement with the experimental results.

The situation appears to be quite different for the vertical ionization potentials of the corresponding picolines.[21] These show much smaller orientational effects, which are, in fact, in the opposite direction to those in the radicals. Since methyl substitution in pyridine caused a much smaller decrease in the ionization potential than substitution in benzene, the authors[21] concluded that ionization of picolines involved an electron from the nitrogen lone pair, rather than a π-electron. The ionization potentials of the pyridylmethyl radicals, on the other hand, are about 1.5 v. lower than those of the picolines, and almost certainly involve the electron from the non-bonding orbital. The orientational effects in the radicals are consequently much greater.

(13) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, J. Am. Chem. Soc., 82, 5593 (1960).
(14) R. F. Pottie and F. P. Lossing, ibid., 85, 269 (1963).
(15) T. F. Palmer and F. P. Lossing, ibid., 84, 4661 (1962).
(16) A. E. Tchitchibabine, Bull. soc. chim. France, 3, 1607 (1936).
(17) S. N. Foner and R. L. Hudson, J. Chem. Phys., 25, 602 (1956).

(18) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, ibid., 22, 621 (1954).
(19) J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, ibid., 22, 1948 (1954).
(20) C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London), A192, 16 (1947).
(21) H. Baba, I. Omura and K. Higasi, Bull. Chem. Soc. Japan, 29, 521 (1956).

It is of interest to attempt to fit these radical ionization potentials to the linear relationship between Hammett σ-constants and ionization potential found for other substituted benzyl radicals.[3] In Table II are given values of σ predicted from the σ–i.p. relationship,[3] together with $\sigma_{exp.}$ and $\sigma_{calcd.}$ values for the reactivity of side chains in pyridines given by Jaffé.[22,23] The latter were derived from standard MO–LCAO theory. It can be seen that although all three sets agree as to the order of reactivity (and ionization potential) of the three species, the actual values of σ differ greatly from set to set.

TABLE II

σ-CONSTANTS FOR THE REACTIVITY OF SIDE CHAINS IN PYRIDINES

| | | σ-Constants | |
Position	Predicted from ionization potentials	Experimental[a]	Calculated[a]
2	0.39	0.81, 0.40	0.46
3	.18	.62 ..	0.35
4	.58	.93 ..	1.07

[a] Ref. 22.

The appearance potentials of the radical ions from 2-, 3- and 4-picolines were also measured (Table III). From these, the ionization potentials of the radicals and the relationship

$$A(R^+) - I(R) \geq D(R-H)$$

we get values for $D(R-H)$ which are some 20 kcal./mole higher than those found by Roberts and Szwarc[4] in their pyrolytic work. It is evident, therefore, that the threshold for loss of an H-atom from the picolines by dissociative ionization does not correspond to formation of pyridylmethyl ions with little or no excitation. The situation may have some parallels with the dissociative ionization of toluene, for which a discrepancy of about the same magnitude was found.[2] Later work on the formation of the "benzyl" ion in the dissociative ionization of benzyl derivatives led to the conclusion that an isomerization occurs in this process, with the formation of a symmetrical tropylium ion.[24] One may speculate, therefore, concerning the formation (from dissociative ionization of picolines) of the analogous 7-membered ring with a N-atom, the azepinyl ion

(22) H. H. Jaffé, J. Chem. Phys., 20, 1554 (1952).
(23) H. H. Jaffé, Chem. Rev., 53, 191 (1953).
(24) P. N. Rylander, S. Meyerson and H. M. Grubb, J. Am. Chem. Soc., 79, 842 (1957); S. Meyerson and P. N. Rylander, J. Chem. Phys., 27, 901 (1957); S. Meyerson, P. N. Rylander, E. Eliel and J. D. McCollum, J. Am. Chem. Soc., 81, 2606 (1959).

Recently Harrison, et al.,[25] have pointed out that differences in the ionization potentials of m- and p-substituted benzyl radicals should be paralleled by differences in the appearance potentials of these radical ions in the dissociative ionization of the m- and p-derivatives. The absence of such differences can on this basis be taken as evidence of a loss of ring orientation in the ion and consequently of the formation of ions with the tropylium structure. Following this reasoning, the observation that there is no appreciable difference in appearance potentials of the parent-minus-one ions in the three picolines (Table III) would suggest formation of the azepinyl ion. This rearrangement is of course highly conjectural, in the absence of other evidence for an ion of this type. The mass spectra of picolines,[26] for instance, do not show any metastable peaks arising from dissociation of an ion of mass 92 comparable to the well known loss of neutral C_2H_2 from $C_7H_7^+$.[24] The intensity of the $C_6NH_6^+$ peak in the mass spectra of picolines is in fact much lower than that of $C_7H_7^+$ in toluene. The possibility of the formation of a symmetrical $C_6NH_7^+$ parent ion in the ionization of D- and N^{15}-labeled anilines has been examined.[27] Although there is some evidence for symmetrical ion formation, it is only for certain minor dissociation paths. In aniline, and probably also in picolines, the dissociation pattern does not seem to be dominated by formation of a symmetrical precursor ion as it is in alkylbenzenes. It seems, therefore, that at present one can say only that formation of $C_6NH_6^+$ ion from picolines proceeds from dissociation of an excited state or states of the molecular ions in which orientational energy differences are small.

TABLE III

APPEARANCE POTENTIALS OF RADICAL IONS

Ion	Source	Appearance potential, v.
$C_6NH_6^+$	2-Picoline	12.38 ± 0.1
	3-Picoline	$12.31 \pm .1$
	4-Picoline	$12.22 \pm .1$
	Aniline	See text

The ionization efficiency curve for $C_6NH_6^+$ ion from aniline was found to have a long tail extending over several volts. No meaningful value for the appearance potential could be assigned using the present technique.

(25) J. M. S. Tait, T. W. Shannon and A. G. Harrison, ibid., 84, 4 (1962).
(26) See for example the spectrum of 2-methylpyridine, No. 1535 in the A.P.I. Project 44 catalog of mass spectra.
(27) P. N. Rylander, S. Meyerson, R. Eliel and J. D. McCollum, presented before A.S.T.M. Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

Quantitative Raman Spectroscopy for the Determination of Base Strengths of Weak Organic Bases[1]

BY N. C. DENO AND MAX J. WISOTSKY[2]

RECEIVED JANUARY 18, 1963

The protonation equilibria and base strengths of acetamide, methanol, dioxane, acetone and acetonitrile have been studied in aqueous sulfuric acids using a Cary 81 Raman spectrophotometer.

The common organic functional groups such as olefin, alcohol, ether, ketone, amide and nitrile are too weak to be measurable by pH meters and the methods applicable to dilute aqueous solutions. In the aliphatic series, the methods based on ultraviolet spectra that