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The Photolysis of Carbon Suboxide. II. Effect of Added Oxygen

BY KYLE D. BAYES

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The photolytic formation of allene from carbon suboxide and ethylene has been studied using monochromatic radiation. At short wave lengths oxygen has little effect on the production of allene, but at longer wave lengths oxygen efficiently quenches allene formation. It is shown that two distinct intermediates are involved, rather than one intermediate of gradually varying reactivity. The two intermediates can be correlated with two electronic transitions of carbon suboxide. Semi-empirical molecular orbital calculations on C_2O predict a triplet ground state and low lying singlet states. Thus the two intermediates could be C_2O in different electronic states. However, electronically excited carbon suboxide could also be involved.

Introduction

The insertion of a single carbon atom into olefinic bonds has been reported previously.^{1,2} When carbon suboxide is photolyzed in an excess of ethylene, allene and some methylacetylene are formed. An isotopic study of the product allene showed 92% of the inserted carbon to be in the middle position and 4% at each end position.³ The methylacetylene and the end-labeled allene could arise from the initial insertion of carbon into a C-H bond or from isomerization of an energetic allene molecule.

The nature of the reactive intermediate has not been established. By analogy with the ketenes, a C_2O intermediate is expected, but an electronically excited C_3O_2 could also be responsible. A recent measurement of the heat of formation of carbon suboxide rules out the possibility of a free carbon atom in the gas phase.⁴

The effect of added oxygen is often used as an indication that intermediates having unpaired spins are involved. Most free radical reactions are strongly inhibited by small amounts of oxygen.⁵ Gas phase fluorescence from triplet states is also quenched by oxygen.⁶ The reactions of CH_2 in its singlet state are not affected by oxygen, but when CH_2 decays to its triplet ground state, it reacts rapidly with any oxygen present.⁷ Initial studies of the photolysis of carbon suboxide showed that oxygen had little effect on the yield of products.¹ A further study of the effect of oxygen using monochromatic radiation is given below. The results suggest that there are two different intermediates involved, one which reacts rapidly with oxygen and one which reacts with ethylene even in the presence of excess oxygen. The possible nature of these two intermediates is discussed.

Experimental

The carbon suboxide was prepared and purified as described previously.² Research grade ethylene was passed through Ascarite to remove traces of CO_2 , then distilled under vacuum before use. Oxygen and nitric oxide were taken directly from commercial cylinders. The photolysis took place in a cylindrical quartz cell, 3 cm. in diameter and 30 cm. long, which was connected directly to the gas-handling system and a gas chromatograph. The light source was a high pressure mercury arc (General Electric BH6, 1000 watts) within an ellipsoid reflector which concentrated the light onto the entrance slit of a Bausch and Lomb 500-mm. grating monochromator. A Corning filter CS 9-54 between the light source and the monochromator absorbed light of wave length shorter than 2200 Å. The quartz cell was adjacent to the exit slit. Various spectral orders and slit widths were used. For each slit width, the monochromator was adjusted to the visible spectrum in the order to be used, and

the band pass of the monochromator determined by observing the transmitted light with a calibrated prism spectroscope. Since the grating was blazed for 7500 Å. in the first order, the monochromator was used in the third order for wave lengths shorter than 2900 Å., and in the second order for wave lengths of 2900 Å. and longer. Therefore, intense light of longer wave length also entered the photolysis cell, but it was not absorbed by the carbon suboxide or the reaction products. For runs with $\lambda > 3000$ Å., a thin piece of Pyrex glass was inserted between the exit slit and the cell to absorb scattered light of shorter wave length. Also, one run at 2400 Å. was made using a 1-cm. thick filter of 10% CCl_4 in CH_2Cl_2 , which absorbed >99% of $\lambda < 2450$ Å., but transmitted >75% of $\lambda > 2700$; only a trace of allene was formed, indicating that the intensity of scattered light of long wave length was less than 1% of the 2400 Å. intensity. The reaction cell was surrounded by cracked ice to prevent thermal decomposition of the suboxide. At least 30 minutes was allowed for mixing of the gases before sampling. The gas chromatograph was equipped with thermistor detectors and a 3.6-meter dimethylsulfolane column operated at 30°. Less than 2% of the suboxide was decomposed during a photolysis.

A quantitative determination of the effect of oxygen on the formation of allene was made in the following way. A given mixture of ethylene and carbon suboxide was photolyzed and the rate of allene formation was measured by analyzing a single sample of the mixture with the gas chromatograph. Then, without disturbing the lamp or monochromator, a sample of oxygen was added and the photolysis was continued for a similar period of time. A second sample of the mixture was then analyzed. The rate of allene formation with oxygen present was calculated assuming the light intensity to be constant. Except for the longest wave lengths used, the amount of suboxide present was sufficient to absorb all of the quanta entering the cell, so that no correction was necessary for the 10% decrease in suboxide pressure caused by sampling. At the longer wave lengths, oxygen almost completely quenched the formation of allene, so a correction for the decrease in suboxide pressure was unnecessary. Also it has been shown that the yield of allene is not a strong function of pressure except at pressures approaching one atmosphere. For many of these experiments, the decrease in pressure caused by withdrawing a sample was offset by the addition of 10% oxygen, so that the total pressures during the first and second photolysis periods were the same. When the pressure changed significantly, a correction for the changing ratio of allene to methylacetylene was made, based on a previously measured curve.² Three runs were made to observe the effect of adding 16% NO on the rate of allene production. The effects at 2540, 2700 and 3130 Å. were identical, within the experimental error, to those observed with oxygen at the same wave lengths.

Several errors could contribute to the final results. Duplicate analyses with the gas chromatograph agreed to within 3%, and this is the error assumed for the data reported in Fig. 1. A change in the light intensity was a potential source of large error, since some runs lasted 8 hr. Changes of intensity up to 20% were sometimes noticed with new lamps, especially at short wave lengths. However, aged lamps, which were used for the measurements reported here, had intensities constant to within 2%. For the runs at large oxygen pressures, and probably to a lesser extent at lower oxygen pressures, a white crystalline solid formed in the front window of the cell. This solid could not be removed by pumping overnight, but heating in one atmosphere of pure oxygen quickly removed it. Frequent cleaning of the cell was necessary when working at high oxygen pressures, but at lower pressures the solid did not significantly change the light intensity during a run. This white solid is being investigated.

Results and Discussion

The experimental results are presented in the form of the ratio R

$$R = \frac{\text{rate of allene formation with } O_2 \text{ present}}{\text{rate of allene formation with no } O_2} \quad (1)$$

(1) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(2) K. Bayes, *ibid.*, **84**, 4077 (1962).

(3) R. T. Mullen and A. P. Woff, *ibid.*, **84**, 3214 (1962).

(4) R. Botter, "Advances in Mass Spectrometry," Vol. 2, edited by R. M. Elliott, Pergamon Press, Oxford, England, 1963.

(5) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

(6) B. Stevens, *Trans. Faraday Soc.*, **51**, 610 (1955); J. T. Dubois, *J. Chem. Phys.*, **25**, 178 (1956); see, however, D. W. Setser, *et al.*, *Can. J. Chem.*, **40**, 2179 (1962).

(7) H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).

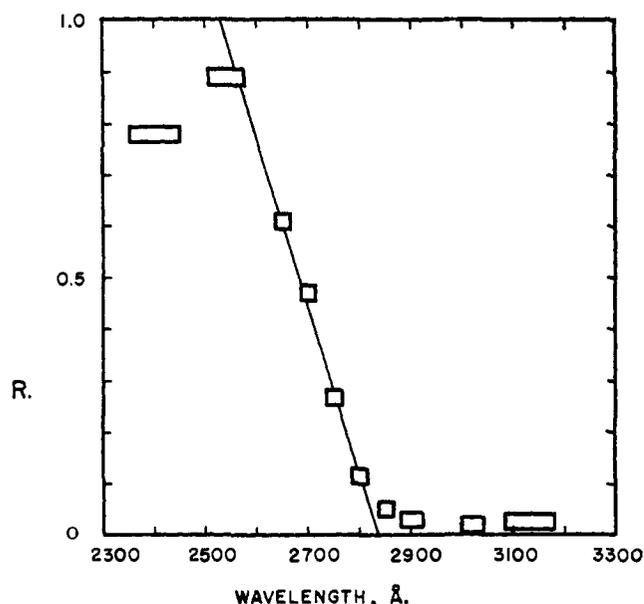
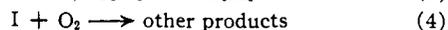
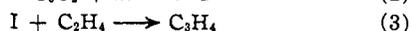


Fig. 1.—Values of R measured at 0° and about 100 mm. pressure, for different wave lengths. Oxygen/ethylene ratios of 0.20 ± 0.07 were used. The width of a rectangle gives the band pass of the monochromator. The straight line is arbitrary.

If oxygen has no effect on the reaction, R will be unity. If oxygen completely quenches the photolytic formation of allene, R will be zero. The observed dependence of R on wave length is shown in Fig. 1. Each point represents the average of at least two runs, except for the points at 2650, 2750 and 3020 Å.

At long wave lengths, very little allene is formed when 20% oxygen is present. Values of R for $\lambda > 2900$ Å., although nearly zero within the experimental error, were consistently slightly larger than zero. At 2900 Å. the short wave length Pyrex filter could not be used, so that some scattered light could be contributing to the experimental R . At shorter wave lengths R increases, reaching a maximum of about 0.9 at 2540 Å., then decreases somewhat at still shorter wave lengths. Values of R less than unity at short wave lengths were not caused by scattered light of longer wave length (see above).

The change of R from near zero at 2900 Å. to near unity at 2500 Å. is approximately linear in wave length. In order to determine whether this transition is a single effect of varying degree, or a mixture of two effects, the dependence of R on the ratio of oxygen to ethylene was measured. If an intermediate, I , is formed during the photolysis which can react with either oxygen or ethylene



then a steady state treatment gives the equation

$$\frac{1}{R} = 1 + \frac{k_4(O_2)}{k_3(C_2H_4)} \quad (5)$$

where R is defined in (1) and k_3 and k_4 are the rate constants corresponding to (3) and (4). Figure 2 shows the experimental dependence of R^{-1} on the mole ratio of oxygen to ethylene at three different wave lengths. At the long wave length, eq. 5 is obeyed very well. The slope of the line gives a ratio of k_4/k_3 of 230 at 3020 Å. This means that the addition of only 0.5% oxygen to the ethylene will reduce the allene production by a factor of two. Values of R^{-1} at 2540 Å. give a plot of questionable linearity. Even with O_2/C_2H_4 equal to 6.0, the observed R^{-1} was still 1.76. Thus the ratio of k_4/k_3 at 2540 Å. has a maximum value of 0.5 (the

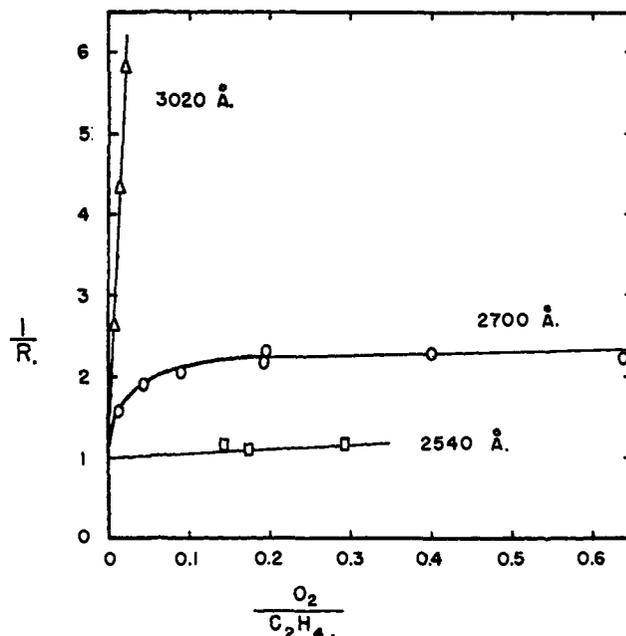


Fig. 2.—The reciprocal of R plotted against the ratio oxygen/ethylene for three wave lengths. The band passes were similar to those used in Fig. 1.

line shown in Fig. 2), and could be as small as 0.1. Therefore the ratio k_4/k_3 is 500 to 2000 times larger at 3020 Å. than at 2540 Å.

The dependence of R^{-1} on the ratio O_2/C_2H_4 at 2700 Å. clearly shows that the transition region of Fig. 1 is due to a mixture of the two extreme effects, and not to a gradual change in the ratio k_4/k_3 . The curve at 2700 Å. has a large slope for small oxygen additions, corresponding to the long wave length dependence. But at about $R^{-1} = 2$, the slope approaches that of the short wave length curve. It seems evident from the above observations that there are two distinct intermediates formed when carbon suboxide is photolyzed. The intermediate formed at long wave lengths reacts readily with oxygen, while the short wave length intermediate reacts with ethylene even when an excess of oxygen is present. At 2700 Å. a mixture of the two intermediates is formed. Even at the short wave lengths, some of the "long wave length intermediate" is probably formed, resulting in short wave length R -values less than unity in Fig. 1.

For a mixture of two intermediates, a steady state approximation yields

$$\frac{1}{R} = 1 + x \left[\frac{0.1p(1 + 230x) + 230(1 + 0.1x)}{p(1 + 230x) + (1 + 0.1x)} \right] \quad (6)$$

where x is O_2/C_2H_4 , p is the ratio of short wave length intermediate to long wave length intermediate being formed, and values of 230 and 0.1 have been used for k_4/k_3 for the long wave length and the short wave length intermediates, respectively. The experimental values of R at 2700 Å. yield a consistent value for p of 0.89 when treated by 6. Using this value of p , eq. 6 is plotted as a solid line in Fig. 2. The agreement is within experimental error.⁸

The two intermediates can be correlated with the absorption spectrum of carbon suboxide. Thompson and Healey observed that the first region of strong absorption in carbon suboxide, from 3300 to 2400 Å., consisted of two different transitions.⁹ The first transition gives a large number of bands, extending

(8) The author wishes to thank Dr. Delano Chong for suggesting eq. 6 and pointing out the good agreement with the experimental data.

(9) H. W. Thompson and N. Healey, *Proc. Roy. Soc. (London)*, **A167**, 331 (1936).

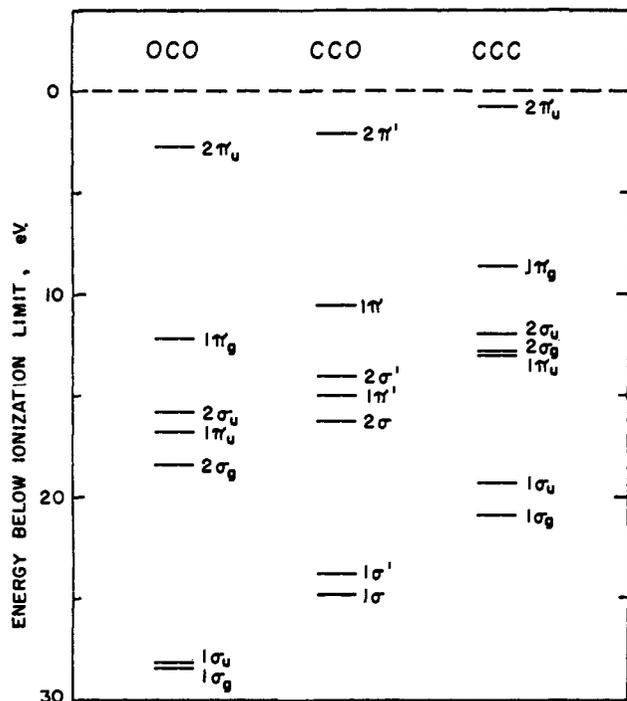


Fig. 3.—Results of the molecular orbital calculations on CO_2 , C_2O and C_3 . Since C_2O does not have a center of symmetry, its orbitals cannot be labeled g or u; those levels which were constructed like ungerade orbitals are primed.

from 3300 Å. to shorter wave lengths. The second transition results in a continuum extending from about 2800 to 2400 Å. Comparing these wave length limits with Fig. 1, it is reasonable to associate the banded absorption with the long wave length intermediate, and the continuum with the short wave length intermediate.

Measurements with the unfiltered light used previously indicated about one-third of the long wave length intermediate was formed for the conditions of reference 2. It was expected that the ratio of methylacetylene/allene would depend on the nature of the intermediate; however, there was only a small effect. Values of methylacetylene/allene measured with monochromatic light and a total pressure of about 100 mm. were: 0.20 (3130 Å.), 0.20 (2800 Å.), 0.26 (2470 Å.), 0.25 (2400 Å.).

The reactivity with oxygen and nitric oxide suggests that the long wave length intermediate has unpaired electrons. When carbon suboxide absorbs a quantum, it could undergo a radiationless transition into a triplet state, which would be metastable with respect to radiation to the singlet ground state, and thus could react with other molecules. The only available evidence suggests that this is not occurring. Thomson and Healey could not observe fluorescence of carbon suboxide when they excited it with a mercury lamp.⁹ While the absence of fluorescence does not disprove the participation of a metastable triplet state, it slightly favors a dissociation of the suboxide molecule as a primary step in the long wave length region. Carbon suboxide in a triplet state could conserve spin by dissociating to a ground state CO and a C_2O molecule in a triplet state. As will be shown below, the predicted ground state of C_2O is a triplet state.

At shorter wave lengths, the inertness toward oxygen and nitric oxide suggests a singlet state for the reactive intermediate. This could be either an electronically excited C_3O_2 or a C_2O molecule. By analogy with the photolysis of the ketenes, it seems most likely that the initial step is a cleavage of a carbon-carbon double

bond forming a singlet C_2O and a ground state CO. The C_2O could then attack carbon-carbon double bonds in preference to reaction with oxygen, as has been found for singlet CH_2 .⁷

Although the C_2O intermediate has been postulated in several systems,^{10,11} it has not yet been observed spectroscopically. A rough idea of the expected electronic states of C_2O can be derived by considering the isoelectronic species CO_2^{++} . If the molecular orbitals of the latter are similar to the parent CO_2 ,¹² the ground state configuration of the doubly charged ion should be

$$K, K, K, 1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 1\pi_u^4, 2\sigma_u^2, 1\pi_g^2$$

which would result in a ${}^3\Sigma_g^-$ ground state and low lying ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ states.

The above considerations justified a more careful approach to the molecular orbitals of C_2O . A semi-empirical MO calculation has been made, based on the methods developed by Mulliken.¹³ Similar calculations were also made for CO_2 and C_3 , and the parameters adjusted somewhat to give agreement with the more sophisticated calculations for these molecules.

Molecular orbitals were constructed using linear combinations of 2s- and 2p-Slater type orbitals. The σ -orbitals were constructed using s-p-hybrid orbitals on the terminal atoms, and s- or p-orbitals on the central atom, depending on whether the MO was even or odd. The orbitals for CCO were constructed as if the molecule had a center of symmetry, since the difference in effective nuclear charge between the C and O atoms should cause only small changes in the molecular orbitals. The π -orbitals were constructed from p_x - and p_y -orbitals. The energies of the orbitals were calculated using the simplified formula

$$E_i = -AI_i \frac{S_i}{1 + S_i}$$

where E_i is the energy of the i th orbital relative to I_i , the average ionization energy of the electrons participating in the orbital. The factor A is a constant, taken to be 1.0 for σ -orbitals and 1.5 for π -orbitals. The overlap integrals, S_i , were calculated using published tables and recommended values for the effective nuclear charges.¹⁴ Known interatomic distances were used for CO_2 and C_3 , while the bond distances in C_2O were assumed to be the same as observed in C_3O_2 .¹⁵ The values of I_i require an average over the atoms in appropriate "valence states."¹³ The actual values used were adjusted somewhat to give better agreement with the machine-calculated energy levels of CO_2 and C_3 . The parameters used in the calculations are collected in Table I. The energies of the molecular orbitals are shown in Fig. 3.

TABLE I
THE PARAMETERS USED IN THE MO CALCULATIONS OF ENERGY LEVELS

	CO_2	C_2O	C_3
$r(\text{CO})$, Å.	1.163	1.160	...
$r(\text{CC})$, Å.	...	1.279	1.281
I_π , e.v.	12.3	10.7	9.0
I_σ , e.v.	20.0	17.0	14.0

The calculated energies of the higher orbitals agree within one or two e.v. with previous results for CO_2

(10) H. von Weyssenhoff, S. Dondes and P. Harteck, *J. Am. Chem. Soc.*, **84**, 1526 (1962).

(11) H. B. Palmer and T. J. Hirt, *ibid.*, **84**, 113 (1962).

(12) J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).

(13) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950); *J. Phys. Chem.*, **56**, 295 (1952).

(14) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(15) L. Pauling, "The Nature of the Chemical Bond," Third Edition, Cornell Univ. Press, Ithaca, N. Y., 1960, p. 268.

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.

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

By T. F. PALMER¹ AND F. P. LOSSING

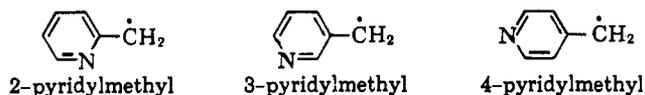
RECEIVED JANUARY 17, 1963

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



were produced by Roberts and Szwarc⁴ 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-picoline, 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-picoline, 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.

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(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.

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