Tetrahedron Letters No. 50, pp 4569-4572. 1976. Pergamon Press. Printed in Great Britain.

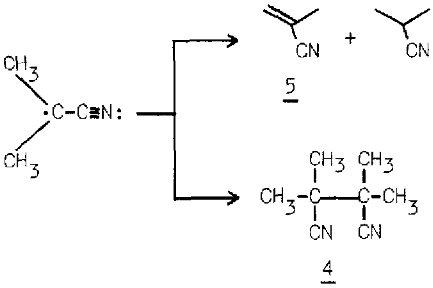
THE He(I) PHOTOELECTRON SPECTRA OF BENZYL AND α-CYANOISOPROPYL RADICALS

T. Koenig, W. Snell and J. C. Chang

Department of Chemistry
University of Oregon
Eugene, Oregon 97403

(Received in USA 7 September 1976; received in UK for publication 25 October 1976)

We wish to report our observation of the He(I) photoelectron spectra of α-cyanoisopropyl (1-cyano-1-methylethyl, 1) and benzyl (2) radicals. The spectrum of 1 (Figure 1) was obtained by flash vacuum pyrolysis[1] of AIBN (3) at temperatures between 300°C and 670°C. In this temperature range the azo compound (3) reacts completely[2] and a band (Figure 1) at 8.56 ± .06 eV appears which we assign to the first ionization potential of the radical. The solid product, isolated by warming the condensate of the 370° pyrolysis to room temperature was tetramethylsuccinonitrile (4). Neither the isolated product nor authentic 4 gives the 8.56 eV band with or without heating.



2

At higher temperatures, peaks due to methacrylonitrile (5) (10.37 eV, ν = 1240 cm^{-1}) are observed. This apparent change in product composition with temperature may be a surface effect. An alternative possibility is an appreciable activation energy difference for the disproportionation combination competition in the termination of 1, i.e. a nonzero value for E_a for one or both termination processes in the gas phase.

The present value for the first vertical ionization potential of 1 (8.56 ± .06 eV) is considerably lower than the published[3] estimate of its mass spectral appearance potential. A more recent investigation gives a value of 8.53 eV[4] which is in much better agreement with the present work. However, the onset of the pe band occurs at a value 0.16 eV lower than the band

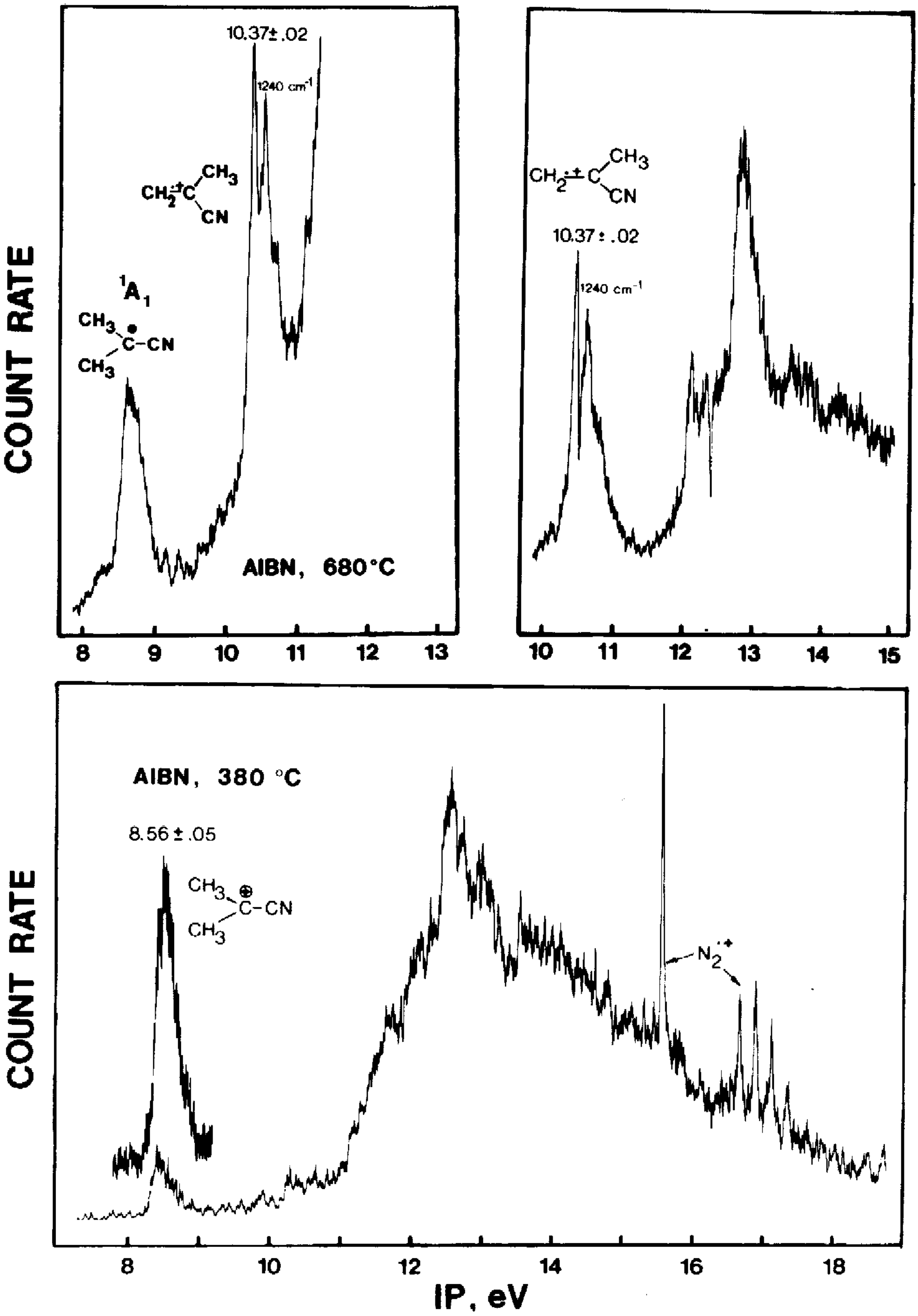

COUNT RATE
10.37±.02
1240 cm⁻¹
CH2=C(CH3)CN
¹A₁
CH3 C-CN CH3
AIBN, 680°C
8 9 10 11 12 13
CH2=C(CH3)CN
10.37±.02
1240 cm⁻¹
10 11 12 13 14 15
COUNT RATE
AIBN, 380 °C
8.56±.05
CH3 C-CN CH3
N2·+
8 10 12 14 16 18
IP, eV

Figure 1

maximum so that the agreement between the two methods is not as precise as a superficial numerical comparison would indicate.

The difference in the ionization potential of 1 and t-butyl is 1.63 eV which represents the effect on the ionization process of replacing a methyl group with a cyano group. The corresponding differences for the change from methyl acetylene to cyanoacetylene and isobutylene to methacrylonitrile are 1.23 eV and 0.98 eV respectively. An appreciably larger cyano shift for the radical ionization is expected if the cyano group stabilizes the ground radical more than an olefinic group.

The spectrum of benzyl (Figure 2) was obtained by pyrolysis of the corresponding oxalate.[5] The product isolated by warming the condensate to room temperature, was bibenzyl (>90% by pmr). The pe spectrum of the total product (inset, Figure 2) is nearly identical to that of authentic bibenzyl and does not show the low energy peak (7.43 ± .06 eV) which we assign to the first vertical ionization potential of 2. The mass spectrometry IP was given[6] to be 7.27 ± .03 eV.

The second and third band maxima in the spectrum from the pyrolysis stream are similar to those of bibenzyl. However, there is a feature on the high energy side (∿10.1 eV) in the transient spectrum which is not attributable to the final isolated products. The second (singlet triplet set) ionization potential is expected to occur between 9 and 11 eV with twice the intensity of the first band. Using the wavelength reported[7] for the lowest (presumed) $^1A_1 \rightarrow {}^1B_2$ transition of benzyl cation in solution (3.4 eV) suggests the corresponding band in

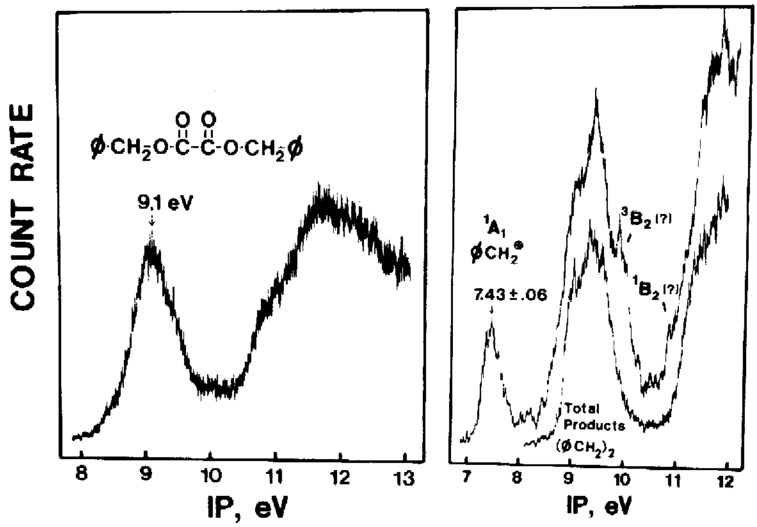


Figure 2

the pe spectrum should be near 10.9 eV. INDO[8] calculations suggest the corresponding triplet to lie 0.5 eV below suggesting a pe band near 10.4 eV. We are therefore inclined to assign the 10.1 eV feature to the $^3B_2$ state of the cation though this assignment must be regarded as tentative.

The spectra of both 1 and 2 give indications of vibrational structure but the required instrumental resolution for its analysis has not yet been achieved under pyrolytic conditions.

Acknowledgment : We are greatful to the National Science Foundation for financial support of this work.

References

1) E. Hedaya, Acc. Chem. Res. 2, 367 (1969). F. P. Lossing and G. P. Semeluk, Can. J. Chem., 48, 955 (1970). Our adaptation of a Perkin Elmer PS-18 Photoelectron Spectrometer for this experiment has been described previously: T. Koenig, T. Balle and W. Snell, J. Amer. Chem. Soc., 97, 662 (1975).

2) The pe spectrum of 3 has been described previously. K. N. Houk, Y. Chang and P. Engel, J. Amer. Chem. Soc., 97, 1824 (1975). (First vertical IP 9.62 eV, n_-.)

3) R. Pottie and F. P. Lossing, J. Amer. Chem. Soc., 83, 4737 (1961).

4) F. P. Lossing, private communication.

5) W. Trahanovsky, C. Ong and J. Lawson, J. Amer. Chem. Soc., 90, 2839 (1968).

6) F. P. Lossing, Can. J. Chem., 49, 357 (1971).

7) R. Jones and L. Dorfman, J. Amer. Chem. Soc., 96, 5715 (1974).

8) J. A. Pople, D. L. Beveridge and P. A. Dobosh, J. Chem. Phys., 47, 2026 (1967). The calculated difference in energies of the lowest configuration for 1 and its cation is 8.94 eV (vs. 8.56 eV, expt.). For 2 and its cation the calculated difference is 8.14 eV (vs. 7.46 eV, expt.). The $^3B_2$ ionic configuration is calculated at 12.32 eV above the $^2B_1$ ground state radical.