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Helium(I) Photoelectron Spectra of Organic Radicals

Sir:

We wish to report the results of our investigations of the He(I) photoelectron spectra of methyl and *tert*-butyl radicals. Our spectrum of methyl differs from those previously reported[1] in clearly showing two vibrational spacings for the methyl cation. The spectrum of *tert*-butyl has not previously been reported and our success indicates that the present technique should be useful for intermediates having fairly complicated structures.

The radicals were formed by flash vacuum pyrolysis[2] of azomethane and azoisobutane. The instrument used in this study was a modified Perkin-Elmer Model PS-18 photoelectron spectrometer. The modifications consisted primarily of an enlarged vacuum chamber, to accommodate an increased distance between the He(I) discharge lamp and the analyzer plate-detector assembly, necessitated by the sample heating system. The photoionization chamber was a 14-mm stainless steel tube with a 0.015 mm wide electron exit slit, which could be aimed by rotating the tube. An auxilliary pump and liquid N_2 cold trap served to differentially pump the transient species. Optimum resolution obtained with argon was less than 20 mV, room temperature.

Transient species were produced by resistance heating of a bifilar (noninductive) nichrome coil seated between two concentric quartz tubes, 140 mm in length. A third and innermost concentric tube served as a free photon path from the modified discharge lamp to the photoionization chamber. Temperatures were measured with a junction-type thermocouple in the pyrolysis region. Indicated temperatures in excess of 770° were easily obtained.

Figure 1a shows our spectrum of azomethane[3] at room temperature for calibration. The spectrum at 670° is shown as Figure 1b. The sharp peak at 9.82 ± .02 eV is due to the ionization of methyl radical to give the ground state methyl cation. Much more intense peaks (not shown) for nitrogen at 15.58 ($^2\Sigma_g^+$), 16.69, 16.92, and 17.15 eV ($^2\Pi_u$)[4] were also observed. The intensities of the 9.82 eV and nitrogen bands decreased with decreasing temperature and increased with increasing temperature. The half-width of the 15.76 eV argon peak at 670° was 30 meV.

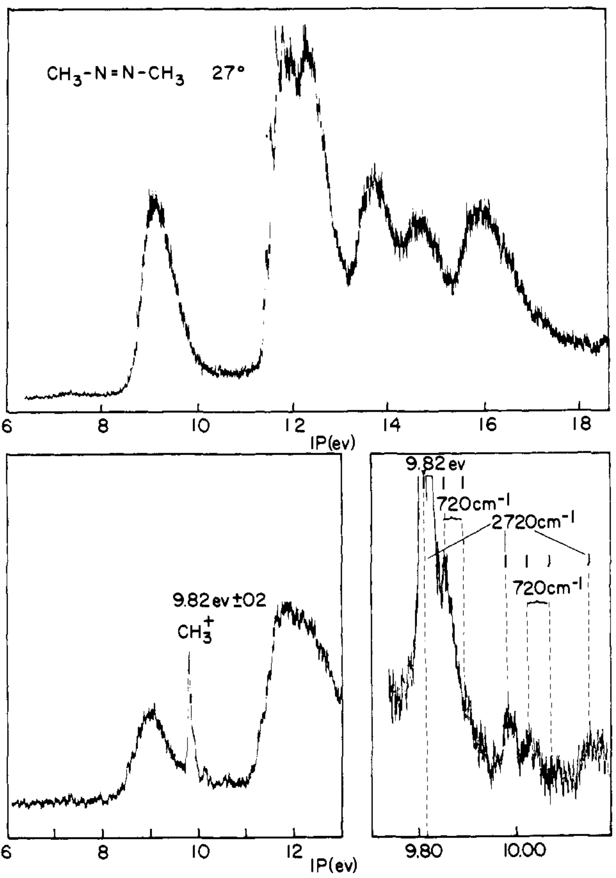

Figure 1. (a) Top, azomethane; (b) bottom left, methyl (9.52 eV) and residual azomethane; (c) bottom right, methyl, higher sensitivity. The main peak is off scale.

The methyl cation band in Figure 1b is qualitatively similar in appearance to that of ref 1a. However, Figure 1c shows that at least two members of a vibrational progression with a frequency of 720 ± 50 cm^{-1} are present in addition to those corresponding to the 2720 ± 30 cm^{-1}. Both of these frequencies are in good agreement with those previously observed[5] for Rydberg transitions.

The 720-cm^{-1} vibrational component can be assigned to the out of plane C–H bending frequency of the carbonium ion. The conclusion from such an assignment is that there must be a change in the degree of planarity upon going from the methyl radical to the methyl cation. All chemical

Table I. Ionization Potentials and Vibrational Spacings

Compound	IP_{vert}, eV	ν_θ, cm^{-1}	ν_R, cm^{-1}
Azomethane	8.95[a]		
Methyl	9.82[b]	720[c]	2720[d]
Azoisobutane	8.33		
tert-Butyl	6.95[e]	410[f]	800[g]
Isobutylene	9.39		1290

[a] ±0.05 eV, lit. 8.95 eV, assignment n^{-3}. [b] ±0.02 eV, lit. 9.83,[1a] 9.843,[5] and 9.86 eV.[1b] [c] ±50 cm^{-1}, out of plane bending mode, intensity ratios in the main ν_R band; $I_0 = 1.0$, $I_1 = 0.3$, and $I_2 = 0.1$. [d] ±20 cm^{-1}, C–H stretching modes, intensity ratios $I_0 = 1.0$, $I_1 = 0.1$, and $I_2 = 0.06$. [e] ±0.05 eV, lit. 6.93 eV.[2a] [f] ±20 cm^{-1}, out of plane bending mode, intensity ratios in the main ν_R band, $I_0 = 0.1$, $I_1 = 0.3$, $I_2 = 0.5$, $I_3 = 0.7$, $I_4 = 1$, and $I_5 = 1.0$. [g] Coupled C–C stretch C–C–H bend; ±100 cm^{-1}.

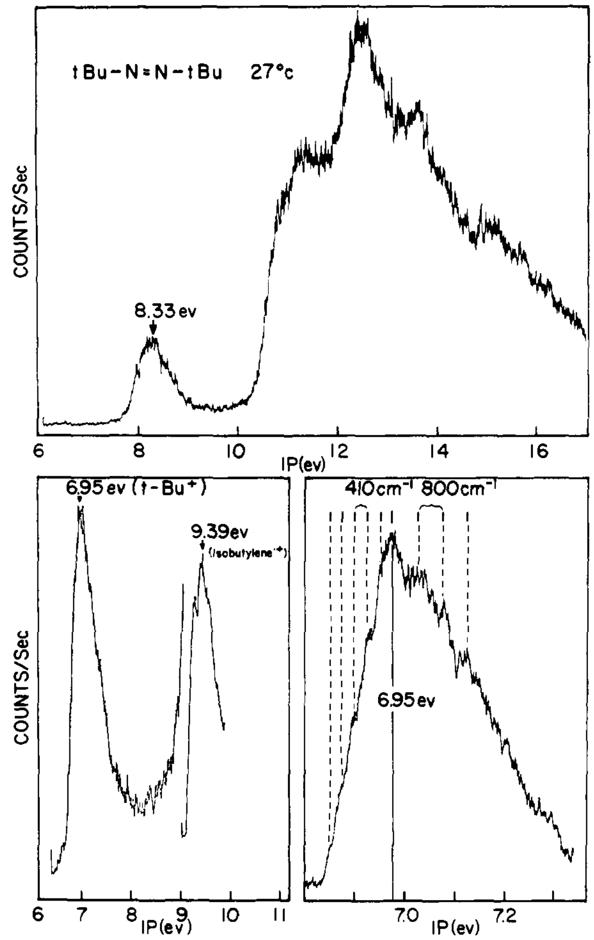

Figure 2. (a) Top, azoisobutane; (b) bottom left, *tert*-butyl (6.95 eV) and isobutylene (9.39 eV); (c) bottom right, *tert*-butyl, expanded.

information indicates that carbonium ions show a strong preference for planarity. We therefore interpret the 720 cm^{-1} vibrational progression in Figure 1c as an indication *that methyl radical is not strictly planar* although the degree of nonplanarity is small.[6] Assignment of the 2720-cm^{-1} frequency as a C–H stretch similarly implies a change in the C–H bond length for the cation compared to the radical. Such changes are not unexpected since the $^{2}A_1''$ ionic state of ammonia also shows[7] such N–H perturbations.

The spectrum of azoisobutane has not been reported previously and is also shown, for comparison, as Figure 2a. Figure 2b shows the first two bands which were observed at 370°. The first band maximum is at 6.95 ± .05 eV in excellent agreement with the ionization potential for *tert*-butyl, measured using the mass spectrometry technique.[2a] The second band is identical, in position and shape, with isobutylene passed through the furnace at approximately the same temperature. The starting azo compound is completely absent under the conditions giving Figure 2b.

Figure 2c shows an expanded view of the *tert*-butyl band. Two vibrational spacings are apparent as shown ($\nu_1 \sim 410$ and $\nu_2 \sim 800$ cm^{-1}). The 410-cm^{-1} frequency could be assigned to a C–C out of plane bending and the 800-cm^{-1} spacing to a C–C–H bending.[8] If taken at face value these assignments would indicate that *tert*-butyl radical is strongly pyrimidal and that there is considerable change in the C–C–H bond angle in the *tert*-butyl cation as compared to the radical. However, the degree of nonplanarity, implied by the length of the 410-cm^{-1} progression, appears to be too large to be consistent with esr results.[9] An alternative explanation of the 410-cm^{-1} progression is that the *tert*-butyl radical is formed in a highly excited (C–C–C bending) vibrational state. This explanation would require a lifetime, for the excited vibrational states, of the order of 10^{-4} sec^{-1} which also seems too long.

While some ambiguities remain in the interpretation of the band shape of the *tert*-butyl spectrum, a considerable geometric reorganization of the cation relative to the radical seems clearly indicated. The observation of the *tert*-butyl spectrum also establishes that this technique is not restricted to small molecules such as methyl and should be generally useful for the study of organic intermediates.

Studies of the deuterated analogs of the present examples as well as a quantitative analysis of the Frank-Condon factors[10] are presently in progress. Investigation of other alkyl radicals and diradicals have also been initiated.

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Tryptoquivaline and Tryptoquivalone, Two Tremorgenic Metabolites of *Aspergillus clavatus*

Sir:

The fungus *Aspergillus clavatus* collected from a sample of mold-damaged rice produces two nontoxic metabolites kotanin and desmethylkotanin[1] and minor amounts of the highly toxic cytochalasin E.[2] More recently we have separated from the same mold isolate two tremor producing metabolites[3] and now report on their structures.

The more polar metabolite, now called tryptoquivaline (**1**) (mp 153–155°; $[\alpha]^{25}\text{D}$ 142° (*c* 1.05, $CHCl_3$); *m/e* found 546.2155,[4] calcd for $C_{29}H_{30}N_4O_7$ 546.2114; ir ($CHCl_3$) 3520, 1790, 1735, 1680, 1615 cm^{-1}; uv$_{max}$ (EtOH) 228 nm (ϵ 37,000), 275 (8550), 305 (3800), 317 (3040); nmr ($CDCl_3$) δ 1.03 (d, 3, J = 7 Hz), 1.17 (d, 3, J = 7 Hz), 1.50 (s, 3), 1.52 (s, 3), 2.19 (s, 3), 2.63 (m, 1), 3.10 (d, 1, J = 10 Hz), 3.15 (d, 1, J = 10 Hz), 3.63 (b, 1), 4.04 (b, 1), 5.00 (s, 1), 5.61 (d, 1, J = 9 Hz), 5.70 (t, 1, J =