radical pairs returns to starting material,[10] this may be considered evidence for a nonradiative decay of the state *via* a bond-breaking and re-forming process.

[10] According to the calculated electron spin correlation time,[3a] this should be less than 1%.

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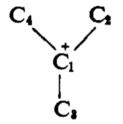
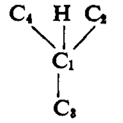
Received August 17, 1970

Photoelectron Spectroscopy of Organic Ions. I. Carbon 1s Electron Binding Energies of the *tert*-Butyl, Trityl, and Tropylium Cations

Sir:

Direct measurements of carbon 1s electron binding energies in several hydrocarbons by means of the recently developed X-ray photoelectron spectroscopy[1] yielded a rather narrow range of chemical shifts.[2] For instance, one cannot make a distinction between the carbon atoms of neopentane and those of benzene because their 1s binding energies are virtually the same (290.4 eV). Ethane (290.6), ethylene (290.7), and acetylene (291.2 eV) carbon 1s binding energy differences are well below the presently attainable resolution.[3] These results are in agreement with theoretical expectations. Core electrons are barely affected unless their screening against nuclear attraction is modified by a significant change in the outer (valence) electron shell. In other words, core electron binding energies are mainly dependent on the formal charge of the corresponding atom and on the electronegativity of attached atoms or groups of atoms. The fact that such factors are minimal in hydrocarbons accounts for the small differences described above.

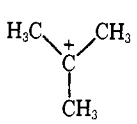
Table I. *Ab Initio* and Experimental Data for *tert*-Butyl Cation and Isobutane

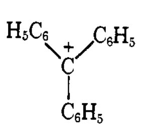
Compd	Calcd E_b		Exptl E_b		Calcd ΔE_b	Exptl ΔE_b	Calcd charge	
	C_1	C_2, C_3, C_4	C_1	C_2, C_3, C_4	$(C_1 - C_2)$	$(C_1 - C_2)$	C_1	C_2, C_3, C_4
	312.06	307.61	288.6	285.2	4.45	3.4	+0.328	−0.216
	300.52	300.11	283.9		0.41	<0.5	−0.014	−0.176

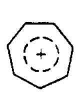
However, X-ray photoelectron spectroscopy should be particularly useful for the investigation of the corresponding ions. Within such molecules the formal charge is generally unequally shared by different atoms. Consequently, the core electrons of these atoms are differently screened and show increasing binding energies with increasing positive charge localization. In the latter cases, the energy differences should be large enough to give rise to separate K-shell photoelectron lines.

We wish now to report the first soft X-ray photoelectron spectra of carbenium ions obtained in frozen superacid solutions or as isolated salts. To illustrate the potential and limitations of the method, we have chosen two types of ions: the *tert*-butyl cation (**1**) (with charge localization) and the trityl (**2**) and tropylium (**3**) cations (with charge delocalization).

The *tert*-butyl cation was generated at −78° from *tert*-butyl chloride in a 1:1 (v/v) SbF_5–SO_2 solution.[4]


1


2


3

Sulfur dioxide was subsequently removed by the usual freeze–thaw procedure. A thin layer of the viscous SbF_5 solution was deposited on the precooled sample holder, in a dry nitrogen atmosphere. The spectrum was recorded at liquid nitrogen temperature.[5]

The binding energies E_b (defined as differences between the Fermi level and the 1s atomic level energies) are given by the equation

$$E_b = E_{h\nu} - E_k - \Phi_s$$

where $E_{h\nu}$ is the energy (1485.6 eV) of the exciting radiation (Al Kα X-rays), E_k is the measured kinetic energy of the photoejected electron, and Φ_s (= 4.6 eV) is the spectrometer work function (the energy necessary to bring the electron from the Fermi level to the free-electron level). The analyzer energy was 30 eV. The photoelectron spectrum of *tert*-butyl cation (Figure

[1] (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA, Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy," Almquist and Wiksells Boktryckeri, AB, Uppsala, 1967; (b) for reviews on this subject see: J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970); D. Betteridge and A. D. Baker, *Anal. Chem.*, **42**, 43A (1970); D. M. Hercules, *ibid.*, **42**, 20A (1970), and references cited therein.

[2] T. D. Thomas, *J. Chem. Phys.*, **52**, 1373 (1970).

[3] With half-line widths of 1.0–1.8 eV, peak separations of about 0.5 eV are currently possible using a deconvolution program or a curve resolver. Line-position measurements are accurate to ±0.1 eV; reproducibility is ±0.03 eV.

[4] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

[5] Varian IEE (Induced Electron Emission) spectrometer, with spherical electrostatic analyzer.

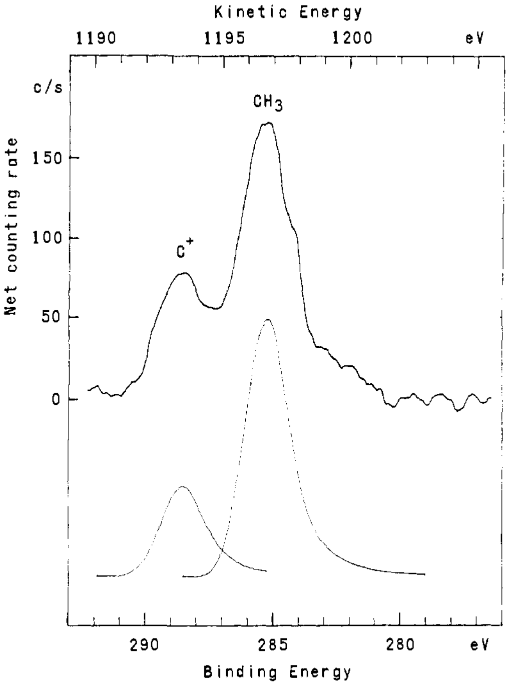


Figure 1. Carbon 1s photoelectron spectrum of *tert*-butyl cation (see text).

1, upper trace) exhibits two clearly separate peaks with E_b = 285.2 and 288.6, respectively.

The lower traces in Figure 1 represent the result given by a curve resolver[6] assuming two gaussian peaks with an integrated area ratio of 1:3. However, for a best fitting, we had to apply a slight skewing on the right wings of the curves. This suggests that the distribution is not perfectly gaussian. The background is not represented in Figure 1.

The precursor (*tert*-butyl chloride) gave a single, slightly broader line centered at 284.1 eV. No distinction of the central carbon peak was possible. It must be pointed out that these values do not represent absolute binding energies. We have used the carbon 1s line of graphite as reference (E_b = 284 eV), but no study of the effect of superacid on graphite itself and on the work function and surface potential has yet been carried out. We feel, however, that relative (internal) chemical shifts are very important in determining the electronic structure of a given cation. Indeed, our data correlate satisfactorily with *ab initio* calculations carried out by Pople and coworkers.[7] (Their absolute values given in Table I are 5–8% higher than the experimental ones.)

The experimental carbon 1s binding energy difference (3.4 eV) between the carbenium ion center and the remaining three carbon atoms is about 1 eV smaller than that predicted by *ab initio* calculation (4.45 eV).

Trityl and tropylium hexafluoroantimonates were measured in solid state. A few milligrams of fine powder (mixed with graphite) was uniformly spread on an adhesive tape and wrapped around a cylindrical sample holder. The trityl cation peak (E_b = 284.7 eV) does not exhibit any significant broadening (in comparison with triphenylmethyl chloride). Thus it is obvious that an extensive positive charge delocalization occurs in this ion. The tropylium cation also gives a single 1s line at practically the same position as the trityl cation.

We are presently carrying out further investigations in order to find a suitable internal standard reference. We are also extending the photoelectron spectroscopic studies to other organic ions. Detailed aspects of this work will be reported in a full paper.

Acknowledgment. We are grateful to Professor John A. Pople for communicating results of his calculations ahead of publication.

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Received October 2, 1970

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(6) Du Pont Model 310 curve resolver.

(7) J. A. Pople, L. Radom, and P. v. R. Schleyer, personal communication.

The Total Synthesis of DL-Alnusenone

Sir:

An earlier report[1] from this laboratory presented the advantages to a program directed toward the total synthesis of a variety of pentacyclic triterpenes of a scheme that had as its initial goal the synthesis of members of the friedelin group. The specific synthetic plan designed for this task has as its central feature the construction of the pentacyclic diether **9**, which after sequential modification of the terminal aromatic rings would provide access to the triterpenoid ketone alnusenone (**13**).[2] The realization of this initial goal in preliminary form is the subject of this report and sets the stage for the broader investigation of the transformations of pentacyclic derivatives most readily available through synthesis.

The results of our previous investigation[1] suggested that the synthetically most difficult structural feature of the pentacyclic diether **9** was not so much its pentacyclic character but the trans-oriented C-6a and C-14a angular methyl groups. Subsequent work[3] has therefore focused on overcoming this problem early in the synthetic program. One such approach entails the establishment of the desired trans orientation of the potential C-6a and C-14a angular methyl groups in an appropriate tricyclic intermediate from which the desired B/C trans-fused pentacyclic diether **9** can be formed through closure of ring B by an acid-catalyzed process.

In order to realize the logistic advantages of a convergent synthesis[4] we chose to investigate the sequence outlined in Chart I. Our plan called for the formation of the requisite tricyclic olefin mixture **7** through the agency of conjugate cyanide addition to the readily available[1] α,β-unsaturated ketone **3** (bp 193–195° (0.01 mm)). In fact, utilization of the elegant pro-

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(1) R. E. Ireland, D. A. Evans, D. Glover, G. M. Rubottom, and H. Young, *J. Org. Chem.*, 34, 3717 (1969).

(2) J. M. Beaton, F. S. Spring, and R. Stevenson, *J. Chem. Soc.*, 2616 (1955).

(3) R. E. Ireland, M. I. Dawson, J. Bordner, and R. E. Dickerson, *J. Amer. Chem. Soc.*, 92, 2568 (1970); R. E. Ireland, D. R. Marshall, and J. W. Tilley, *ibid.*, 92, 4754 (1970.)

(4) L. Velluz, J. Rallo, and G. Nominé, *Angew. Chem., Int. Ed. Engl.*, 4, 181 (1965); see also R. E. Ireland, "Organic Synthesis," Prentice-Hall, Englewood Cliffs, N. J., 1969, pp 28–30.