acted **8** was recovered. At 340 and 305° for 72 and 35 hr, respectively, only black carbonized, insoluble material was obtained; combustion analysis of this showed *ca.* 95% carbon. Heating of **8** as a 3% solution in *p*-diisopropylbenzene in an evacuated sealed tube for 50 hr at 250° gave a 60% yield of **9**: white crystals; mp 250–255°;[9] nmr (CCl_4) δ 1.30–2.10 (m, adamantyl and allylic protons), 5.20 (ill-defined t, olefinic protons), ratio *ca.* 30:1; mass spectrum (70 eV) parent ion at m/e 618, not 616 as would be expected for 1; ir 2890 (s), 2850 (s), 2630 (m), 1445 (s), 1350 (m), 1340 (m), 1310 (m), 1100 (m), 1090 (m), 970 (s); uv$_{max}$ (pentane) 209 nm (shoulder). Ultraviolet spectra of bent butadienes often have no maxima above 210 nm, *e.g.*, 2,3-di-*tert*-butyl-1,3-butadiene[13] and 2,3,4,5-tetramethyl-2,4-hexadiene.[14] These results are in agreement with structure **9**, the product expected for hydrogen transfer to **2** from *p*-diisopropylbenzene. A mixture of aromatic products was also obtained from the reaction but the components have not yet been identified. Although it is possible to account for **9** by other mechanisms than that involving **2**, these seem less likely, and isolation of **9** constitutes added evidence for the two-step, biradical mechanism for allene dimerization. Further attempts are underway to find conditions which will give even low yields of dimers from 1,3-diadamantylallene and an attempt will be made to prepare the optically active allene.

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Thomas L. Jacobs,* R. Craig Kammerer
Contribution No. 3033, Department of Chemistry
University of California, Los Angeles, California 90024

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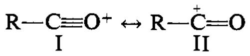
Electron Spectroscopy of Organic Ions. III.[1] Alkyl- and Aryloxocarbenium Ions (Acyl Cations)

Sir:

Since the first stable acyl cations were observed,[2] considerable effort has been directed toward elucidating their structure. Nmr, ir, and X-ray studies[3] have indicated that they are resonance hybrids of the oxonium (I) and oxocarbenium ion (II) forms without evaluating



$$\underset{\text{I}}{R{-}C{\equiv}O^+} \leftrightarrow \underset{\text{II}}{R{-}\overset{+}{C}{=}O}$$

the relative contributions of these forms. An important forward step in structural investigations of acyl cations in now provided by X-ray electron spectroscopy (es). Core electron binding energies (E_b) are closely related to molecular charge distribution, reflecting important changes in the valence shell.[4,5] Es has been particularly useful in studying both carbocationic[1,6] and oxonium ion[7] species.

We wish now to report the results of the es study of a series of alkyl- and aryloxocarbenium ions as thermally stable salts.[8] All samples were prepared under dry nitrogen atmosphere using the previously described powder technique.[6] The spectra were recorded with a Varian VIEE-15 instrument equipped with a spherical electrostatic analyzer. The analyzer energy was 100 V. Peak positions were taken as the intensity maxima. Because the salts were extremely sensitive to moisture and in some cases slowly decomposed under vacuum, the spectra were sometimes complicated by lines belonging to minor hydrolysis and/or decomposition products.[9] Impurity (as well as vacuum oil contamination) lines overlap with the lower E_b lines of the ionic species, altering the expected intensity ratios.

Figure 1 shows the C 1s spectrum of methyloxocarbenium and phenyloxocarbenium ions as hexafluoroantimonate salts. In both cases, the higher binding energy signal is assigned to the carbonyl carbon. Table I lists the differences in C 1s binding energies, ΔE_b, between the two principal types of carbon atoms present in the oxocarbenium ions studied. Also included are the relative intensities of the two signals indicating the extent of hydrolysis and/or decomposition processes in the case of alkyloxocarbenium ions.

A comparison between ΔE_b of the acetyl cation (6.0 eV) and that of acetaldehyde (2.6 eV)[10] reveals the substantial effect of formal hydride abstraction from the aldehyde. Since the oxonium ion form (I) of the acetyl cation is isoelectronic with acetonitrile, we have measured the es spectrum of the latter and found ΔE_b = 3.0 eV. The difference $\Delta E_b(CH_3CO^+) - \Delta E_b(CH_3CN)$ = 3.0 eV mainly accounts for the effect of the positive charge (the effect of the smaller electronegativity of N as compared with that of O should also be taken into consideration, but this effect is expected to be significantly smaller).

Veillard and Weiss[11] have calculated a ΔE_b value of 5.1 eV for the methyloxocarbenium ion and 4.9 eV

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[9] The acetyl and isobutyryl cations are subject to proton elimination from the α carbon with subsequent acylation of the resulting ketene. The new acyl ions broaden the lines and alter their relative intensities. The aryloxocarbenium ions are significantly more stable (there is no α hydrogen to allow the above described secondary reactions). Therefore, their spectra show the expected intensity ratios.

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[11] We thank Professors A. Veillard and R. Weiss for communicating their results prior to publication.

Table I. Carbon 1s Binding Energies and Atomic Charge Differences in Oxocarbenium Ions

Compound	ΔE_b, eV	$E_b(C^+)$, eV	Rel areas, C^+/C	$\Delta q(C^+ - C)$
$CH_3CO^+SbF_6^-$	6.0 ± 0.5[b]	291.8[a]	1.0/1.5[b]	1.09 ± 0.08
$(CH_3)_2CHCO^+SbF_6^-$	6.4 ± 0.5[c]	290.0[a]	1.0/5.5[c]	1.16 ± 0.08
$C_6H_5CO^+SbF_6^-$	5.1 ± 0.3	289.9[a]	1.0/6.0	0.92 ± 0.05
p-$CH_3C_6H_4CO^+SbF_6^-$	5.3 ± 0.3	288.8[a]	1.0/7.0	0.96 ± 0.05
p-$CH_3OC_6H_4CO^+SbF_6^-$	5.0 ± 0.3	289.4[a]	1.0/7.0	0.90 ± 0.05
2,4,6-$(CH_3)_3C_6H_2CO^+SbF_6^-$	4.8 ± 0.3	288.5[a]	1.0/9.0	0.87 ± 0.05

[a] Absolute values always have a greater inherent uncertainty, due to surface potential (charging of the sample) and other solid state effects. [b] This was the best ratio we could obtain. The salt is very sensitive to moisture. [c] This compound decomposes under vacuum, which may account for the high degree of extraneous signal in the lower E_b region of the spectrum.

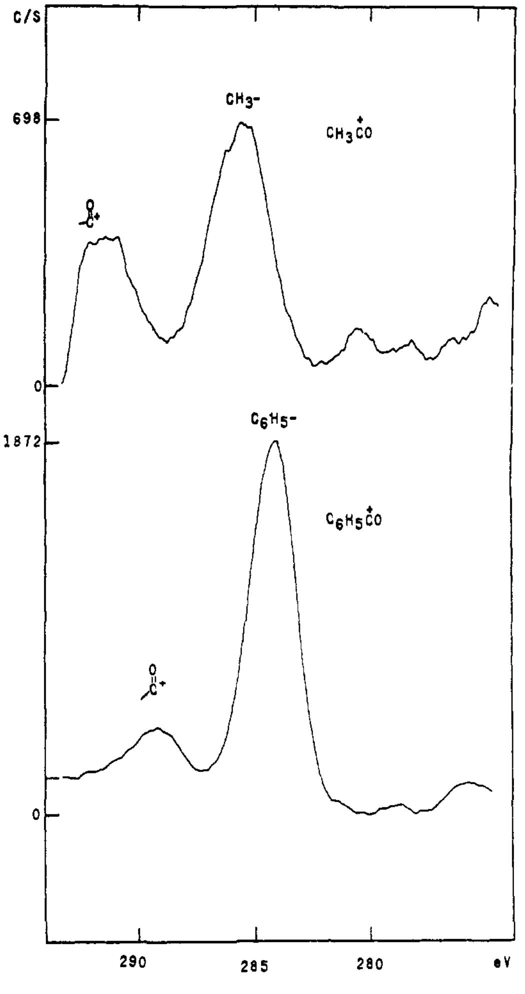

Figure 1. Carbon 1s electron spectra of methyloxocarbenium (a) and phenyloxocarbenium (b) hexafluoroantimonate.

for the isopropyloxocarbenium ion (for the difference between the C 1s levels of the α carbon and the carbonyl carbon). There is reasonable agreement between their calculated ΔE_b and our experimental results. The absolute values of the calculated binding energies are, however, higher (by 25–30 eV) than those found experimentally. The same calculations also predict that the β carbon C 1 signal in isopropyloxocarbenium ion should be 2.42 eV lower than that of the α carbon. We were unable to resolve these two carbon signals. Based on the ΔE_b of the corresponding C 1s levels in other isopropyl substituted compounds,[12] one would not expect to see such a large shift difference.

A qualitative comparison of the ΔE_b values of studied alkyloxocarbenium ions with those of aryloxocarbenium ions (see Table I) reflects the ring and ring substituent participation in charge delocalization. Thus, 2,4,6-$(CH_3)_3C_6H_2CO^+$ presents the smallest ΔE_b (4.8 eV).

In an attempt to establish a first approximation for the C–O bond order in oxocarbenium ions we have plotted measured ΔE_b values *vs.* Δq, the difference in calculated atomic charge of the two types of carbon taken into consideration, for a series of 27 compounds. The atomic charge q was calculated using the Pauling electronegativity approach.[4,13] In this approach $q = \Sigma I + Q$, where I is the partial ionic character of the bond and Q is the formal charge. A reasonably linear correlation was found. Using the experimental ΔE_b of CH_3CO^+ (6.0 ± 0.5 eV) a $\Delta q = 1.09 \pm 0.08$ was found. The calculated Δq values for the methyloxocarbenium ion in its carbenium and oxonium forms are 1.3 and 1.15, respectively. This shows that the bond order is very much displaced toward 3, emphasizing the major contribution of the oxonium ion form. In spite of its high degree of approximation this result is in good agreement with X-ray crystal-structure determination[3d] and is complementary to existent ir data.[3b,c]

In arylcarbenium ions contribution from resonance forms involving charge delocalization into the ring decreases both E_b and ΔE_b. The overlapping of the O 1s and Sb $3d_{5/2}$ lines prevents the measurement of O 1s binding energies in hexafluoroantimonate salts. Oxygen chemical shifts will be obtained in continuing work using different counterions (BF_4^-, AsF_6^-, PF_6^-).

Acknowledgments. Support of our work by the National Institutes of Health is gratefully acknowledged.

[12] For example, the ΔE_b of diisopropyl ether is 1.4 eV. The C 1s levels of isopropyl groups bound to a neutral carbon are essentially identical.[4,10]

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(14) NIH Postdoctoral Fellow.

(15) NDEA Predoctoral Fellow.

Gheorghe D. Mateescu, J. Louise Riemenschneider[14]
James J. Svoboda,[15] **George A. Olah***
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106
Received April 10, 1972

Ratio of Terminal to Central Addition of Fluorine Atoms to Propylene

Sir:

Quantitative studies of the addition of fluorine atoms to simple asymmetric alkenes have been few because of the general experimental difficulties in the handling of fluorine atoms and the eventual reaction products.