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Preliminary communication

$\sigma \to \pi^*$, A REASSIGNMENT OF THE LONG WAVELENGTH UV TRANSITION IN ACYL-SILANES AND -GERMANES BY PHOTOELECTRON SPECTROSCOPY

BRIAN G. RAMSEY*
Department of Chemistry, San Francisco State University, San Francisco, California 94132 (U.S.A.)
ADRIAN BROOK, ALAN R. BASSINDALE
Department of Chemistry, University of Toronto, Toronto 5 (Canada)
and HANS BOCK**
Institute for Inorganic Chemistry, University of Frankfurt, Frankfurt/Main (West Germany)
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Summary

The first vertical ionization potentials, as measured by photoelectron spectroscopy, of $Me_3SiC(O)Me$ and $Me_3GeC(O)Me$ are found to be 8.6 and 8.5 eV respectively. On the basis of the broad photoelectron band width and modified CNDO/2 calculations, strong mixing between the localized oxygen lone pair and metal—carbon bond is suggested as the major origin of the shift of the 280 nm UV transition of aliphatic ketones to longer wavelengths in $R_3MC(O)R$ (370 nm) and $(R_3M)_2CO$ (500 nm), M is Si or Ge.

The acyl-silanes, -stannanes and -germanes, $R_3MC(O)R$ and $(R_3M)_2C{=}O$ (M is Si, Ge, Sn) possess UV transitions near 370 nm ($\epsilon = 10^2$) and 500 nm, respectively [1]***. These transitions have been universally accepted as $n \to \pi^*$ and numerous explanations offered [1, 2] for their lower transition energy, greater intensity, and increased vibrational structure, as compared to the 280 nm transition ($\epsilon \doteq 30$) of aliphatic ketones, $R_2C{=}O$.

Rationales most frequently invoked have been: (1) d_π—p_π^* interactions [1a, 2a] between metal *d* and carbonyl antibonding π^* orbitals, (2) an R_3M electron-releasing inductive effect [2b, c] on the oxygen lone pair, and (3) a combination [2d] of these with comparably important inductive and d_π—p_π^*

*Author to whom inquiries should be addressed.
**In the sequence of a continuing series of papers on photoelectron spectra and molecular properties by H. Bock and co-workers, this paper will be regarded as part XXXX by that laboratory.
***For reviews on the UV spectra of silyl and germyl ketones see ref. 1b.

effects. Several years ago it was also suggested [1b] by one of us that extensive mixing between metalloid—carbon bonds and hetero-atom lone pairs in $R_3MC(R)=\ddot{X}$— chromophores would increase the lone pair electron orbital energies and contribute to a decrease in $n\rightarrow\pi^*$ transition energy, where $\ddot{X}$— is $\ddot{O}$:, $\ddot{N}$—R, for example.

Photoelectron spectroscopy now provides an experimental method for evaluating these possibilities, since measured photoelectron vertical ionization potentials (within the validity of Koopman's theorem [3]) are equal to minus the SCF orbital energies.

The photoelectron spectra of formaldehyde and acetone [4] are textbook examples of lone pair ionization potentials; the vertical or most probable ionizations are also adiabatic; i.e., their first photoelectron bands consist of strong sharp peaks followed by short vibrational progressions of weaker intensity. Considering the substitution of Me_3M for Me in acetone, we can reasonably make the following limiting case predictions for the photoelectron spectra of $Me_3MC(O)Me$.

(1) For d_π—p_π bonding, the lone pair oxygen ionization potential should remain the same, or increase slightly relative to acetone (9.72 eV), as a result of decreased electron density at O.

(2) If an $R_3M\rightarrow$electron-releasing inductive effect on oxygen predominates a decrease of ~1.0 eV in lone pair ionization potential should be observed, corresponding to the differences between UV transition energies of $R_3MC(O)CH_3$ and $R_3CC(O)CH_3$*. Further, if we properly limit the term "inductive effect at oxygen" to changes in molecular orbital energy due only to change ($\delta\alpha$) in the diagonal matrix elements of the final self-consistent field Hartree—Fock Hamiltonian, this decrease in ionization potential should be given by $C_i^2\ \delta\alpha$ where C_i is the appropriate oxygen atomic orbital coefficient in the oxygen lone pair molecular orbital. Experimentally, if only an inductive effect is operative, the PE spectrum of $R_3MC(O)Me$ should retain the non-bonding lone pair characteristics exhibited by the spectra of acetone and formaldehyde.

(3) If the lower UV transition energy of $R_3MC(O)Me$ relative to that of MeC(O)Me results from strong oxygen lone pair—metal carbon bond mixing, again we should observe an approximate 1 eV decrease in the $R_3MC(O)R$ first ionization potential. However, in contrast to the inductive effect only case 2, the photoelectron band shape should be broadened with a low adiabatic ionization probability.

The first vertical ionization potential of $Me_3SiC(O)Me$ (8.6 eV) and $Me_3GeC(O)Me$ (8.5 eV) have now been measured by photoelectron spectroscopy (Fig. 1), and a decrease found of 1.1 to 1.2 eV relative to acetone (9.7 eV). The very broad photoelectron bands (half width 0.5 eV) demonstrate the essentially σ bond character of the ionized electron in these molecules and dramatically confirm the importance of metal—carbon bond mixing with adjacent heteroatom electron lone pairs.

These experimental conclusions are further supported by modified CNDO/2 calculations on acetone, $Me_3SiC(O)Me$, and $(H_3Si)_2C=O$. The modification of the

*$(CH_3)_3CC(O)CH_3$ λ_{max} 277 nm (4.5 eV); $CH_3C(O)CH_3$ λ_{max} 279 nm (4.5 eV); $Me_3SiC(O)CH_3$ λ_{max} 372 nm (3.4 eV); $Me_3GeC(O)CH_3$ λ_{max} 359 nm (3.5 eV); $Et_3GeC(O)Me$ λ_{max} 365 (3.4 eV).

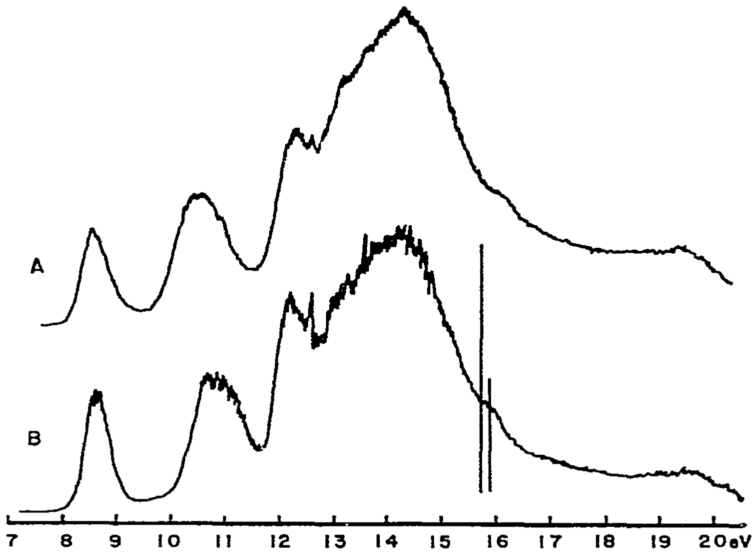

Fig. 1. The photoelectron spectra of $Me_3MC(O)Me$ calibrated against Ar (15.76 eV). Instrument calibrated against MeI (9.54, 10.15 eV): (A) M is Ge, (B) M is Si.

CNDO/2 program used here is essentially that of Jaffe and Del Bene [5] extended to 3rd row elements and programmed by Kroner and Proch at the University of Munich, and Bock and Fuss at the Univ. of Frankfurt [6]. This CNDO/2 method has been found to be particularly appropriate for photoelectron spectra since it was originally developed for the calculation of UV transition energies. An ionization potential difference of 1.2 eV between acetone and $Me_3SiC(O)Me$ is calculated (obs. 1.1 eV). Of this 1.2 eV decrease, only 0.1 eV calculated from $\delta\alpha$ (oxygen) results from the inductive effect of R_3M. Thus according to our calculations, 90% of the change in first ionization potentials of $Me_3SiC(O)Me$ relative to acetone is the result of σ(Si—C)n_O mixing in which the highest filled orbital is largely an antibonding combination of oxygen and carbon $2p_y$ orbitals.

The relevant oxygen lone pair and carbonyl carbon $2p_y$ atomic orbital mixing coefficients for the highest filled MOs are given as follows: (O-$2p_y$; C-$2p_y$) MeC(O)Me (−0.80; 0.32), $MeC(O)SiMe_3$ (−0.66; 0.46); $(H_3Si)_2C$=O (−0.60; 0.60). Thus although according to the calculations, in acetone 64% of the ionized electron density is from the oxygen atomic $2p$ lone pair orbital, less than 44% of the ionized electron density is from the oxygen atomic $2p$ in the case of $R_3SiCOMe$, and in the case of $(H_3Si)_2CO$ only 36% is from oxygen. In all cases the remaining electron density is distributed over the remaining σ molecular framework.

On the basis of photoelectron spectra and CNDO/2 calculations we now conclude that the predominant character of the highest occupied orbitals of α-metalloid ketones such as $R_3MC(O)R$ and $(R_3M)_2CO$ (M is Si or Ge) is σ, an antibonding combination of O lone pair and M—C localized orbitals, rather than oxygen lone pair. The observed longest wavelength singlet—singlet transitions are then better regarded as $\sigma \to \pi^*$ than $n_O \to \pi^*$ (especially in the case of $(R_3M)_2C$=O). Whether the transition is labelled $n \to \pi^*$ or $\sigma \to \pi^*$, the symmetry classification remains the same, i.e. ${}^1A \to {}^1A_2$ under local C_{2v} symmetry. Within a $\sigma \to \pi^*$ classification, the observed red shifts, increase in intensity, and increased vibrational structure of the first UV transitions of acyl-silanes and -germanes (α-silyl and α-germyl ketones) are readily understood at least semi-quantitatively.

Even though the first ionization potential of $Me_3GeC(O)Me$ is 0.1 eV less than that of $Me_3SiC(O)Me$, the $\sigma \to \pi^*$ transition energy is slightly greater (0.1 eV) [5]. This may reflect either $d_\pi - p_\pi{}^*$ bonding by silicon, reduced in Ge, or a difference in the respective molecular orbital exchange and Coulomb integrals between σ and π^* orbitals since the transition is determined by these as well as the orbital energies. The dangers of equating molecular orbital and electronic transition energy differences are further illustrated in that the sum of the σ (or n) orbital destabilization energy (1.1 eV) and previously estimated [2d] $d_\pi - p_\pi{}^*$ stabilization (0.2-0.3 eV), is greater than the $Me_3SiC(O)Me—Me_2CO$ difference in longest wavelength UV-visible transition energies (1.1 eV).

The $\sigma \to \pi^*$ classification may be chemically important in explaining the ease and frequency with which α-silyl ketones when photolyzed form oxycarbenes, $R_3Si—O—\ddot{C}—R$, as compared with the relative rarity of this mechanism in hydrocarbon ketones [7]. In the $\sigma \to \pi^*$ excited state the silicon—carbon bond (or silicon atom) becomes electron deficient and attack at the high electron charge density of oxygen (eqn. 1) is easily rationalized. (Of course, to the extent that transition state resembles product, the greater strength of the Si—O bond, as compared to C—O, also favors siloxycarbene formation.)

$$R_3Si{:}\overset{\overset{O}{\|}}{C}—R \xrightarrow{h\nu} [R_3Si\cdot\underset{\delta+}{\overset{\overset{O\cdot}{\|}}{C}}—R]^* \longrightarrow R_3Si—O—\ddot{C}—R \qquad (1)$$

The five membered ring cyclic oxycarbenes are a major product in the photolysis of cyclobutanones [8], and an analogous rationalization might also apply here, since important mixing between oxygen lone pair and the highest-occupied cyclobutane Walsh type orbitals can be expected.

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