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THE ULTRAVIOLET PHOTOELECTRON SPECTRUM OF O-BENZOQUINONE METHIDE [1]

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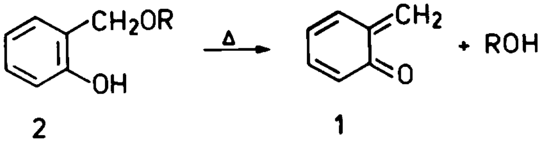
Highly reactive chemical species can be spectroscopically observed for longer periods of time by trapping them in an inert matrix [2]. Very recently, the method of matrix isolation could be supplemented by the method of variable temperature photoelectron spectroscopy [3] (VTPES). This technique can be used to study sensitive, short-lived molecules which otherwise form dimers, polymers or undergo chemical reactions. Typically, a suitable precursor molecule is vaporized under vacuum and heated so that the highly reactive species is generated in situ.

Simple quinone methides are very unstable molecules, which polymerise under ordinary circumstances [4]. The parent compound of the ortho series, o-benzoquinone methide (1) could be trapped as a solid at liquid nitrogen temperature by pyrolysis of 2-hydroxybenzyl methyl ether (2, R = CH_3) [5]. On warming to room temperature the trimer of 1 was obtained [5,6]. Matrix-isolated 1, thermally generated from 2-hydroxybenzyl alcohol (2, R = H), has been infrared spectroscopically observed [7].



In view of the interest in o-benzoquinone methide among organic chemists, a first study of the electronic structure would seem desirable. Thus 1 was generated by pyrolysis of 2 (R = H) in an heated and temperature-controlled target chamber and the UV photoelectron spectra of the pyrolysis products were recorded over the range of temperatures 100-600°C. The PE spectrum of the alcohol

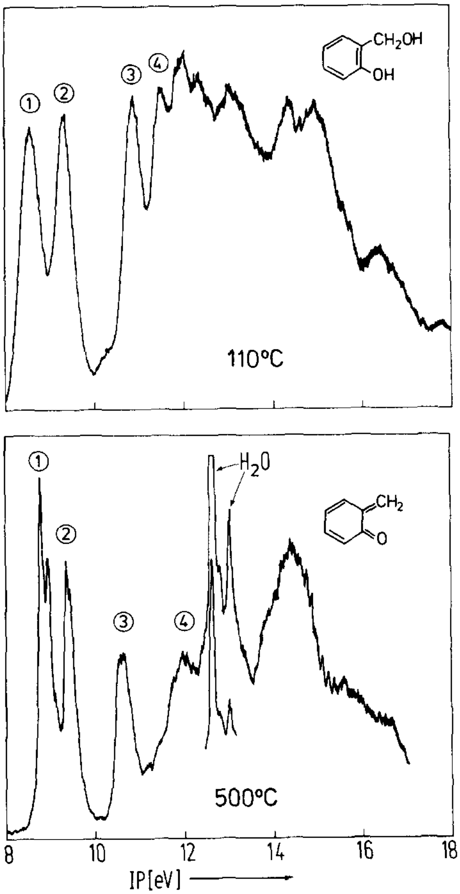
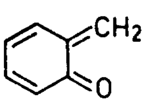
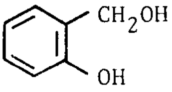
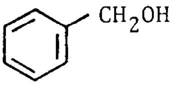


Figure 1. He(I) photoelectron spectra of 2-hydroxybenzyl alcohol (2, R = H) and o-benzoquinone methide (1).

2 (Figure 1) shows bands at 8.58 eV, 9.34 eV, 10.89 eV and 11.52 eV (Table 1). As indicated by the temperature dependent spectra the pyrolysis begins at ca. 350°C. From this temperature up to 500°C the precursor gradually disappears in the PE spectra, while a new compound together with H_2O (found for the first band: 12.63 eV, Literature [8]: 12.62 eV) appears (Figure 1). Between 500° and 600°C no changes were observed in the PE spectra. The well-resolved spectrum at 500°C exhibits bands at 8.80 eV, 9.37 eV, 10.63 eV and 12.02 eV (Table 1). The absence of starting material, the clean simple pattern of the spectrum at 500°C and the observation of H_2O indicates the complete formation of a new compound, which very likely is the o-benzoquinone methide (1). Further strong support for the identity of 1 arises from the very good agreement between the observed and calculated vertical ionization potentials for this compound (Table 1). The latter results are based on extensive PERTCI [9a] calculations using CNDO/S [9b] wavefunctions.

Table 1. Observed and Calculated Vertical Ionization Potentials.

Molecule	exp	IP (eV) PERTCI [a] (CNDO/S)	Assignment	Band
 [b] 1	8.80	8.56	π [c]	①
	9.37	9.40	n	②
	10.63	10.78	π	③
	12.02	11.85	π	④
 2	8.58		π [d]	①
	9.34		π	②
	10.89		n	③
	11.52		π	④
 3	9.23		π,π [d]	①,②
	10.58		n	③
	11.63			

(a) PERTCI (perturbational configuration interaction) Method [9a],

(b) geometry MNDO optimised. For the method see reference 10,

(c) assignments based on the good agreement between the observed and calculated results and in addition on the comparison with spectral data of reference compounds,

(d) assignments for 2 and 3 based on the direct comparison of the spectra of phenol (IP's assignment [11]: 8.74/π, 9.44/π, 11.58/π), 2 and 3.

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