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PYROLYSES OF AZOALKANES. PHOTOELECTRON SPECTRA OF SOME HYDROCARBON RADICALS

P. Bischof and G. Friedrich
Organisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 270, D-6900 Heidelberg(W.-Germany)

Summary. The pyrolyses of azocyclobutane (1)and azocyclopropylmethane (2) have been used to generate C_4H_7 radicals. The photoelectron spectra at various temperatures are presented and the results compared with the data obtained by pyrolyses of the corresponding methylnitrites.

The pyrolyses of appropriate precursors to generate short lived species close to the ionization region of a PE spectrometer has become a standard method to record photoelectron spectra of transients1).

For hydrocarbon radicals the corresponding methylnitrites and symmetrically substituted azocompounds have been found to produce the wanted radicals in high purity and yield at reasonably low pyrolyses temperatures:

$$R\text{-}CH_2\text{-}ONO \longrightarrow R^{\cdot} + CH_2{=}O + NO \qquad a)$$

$$R\text{-}N{=}N\text{-}R \longrightarrow 2\,R^{\cdot} + N_2 \qquad b)$$

The two alternative ways of radical generation open the possibility to compare the resulting photoelectron spectra and thus eliminate uncertainties in assigning observed bands in both spectra.

Very recently, Beauchamp et al2) published the results of their investigations of isomer C_4H_7 radicals which they produced by pyrolyses of the corresponding methylnitrites (pathway a described above).

We therefore wish to report the results of our studies on the pyrolyses of the alternative radical precursors azocyclobutane (1) and azocyclopropylmethane (2). The observed spectra at various pyrolyses temperatures are shown in Fig. 1, details about syntheses and spectra

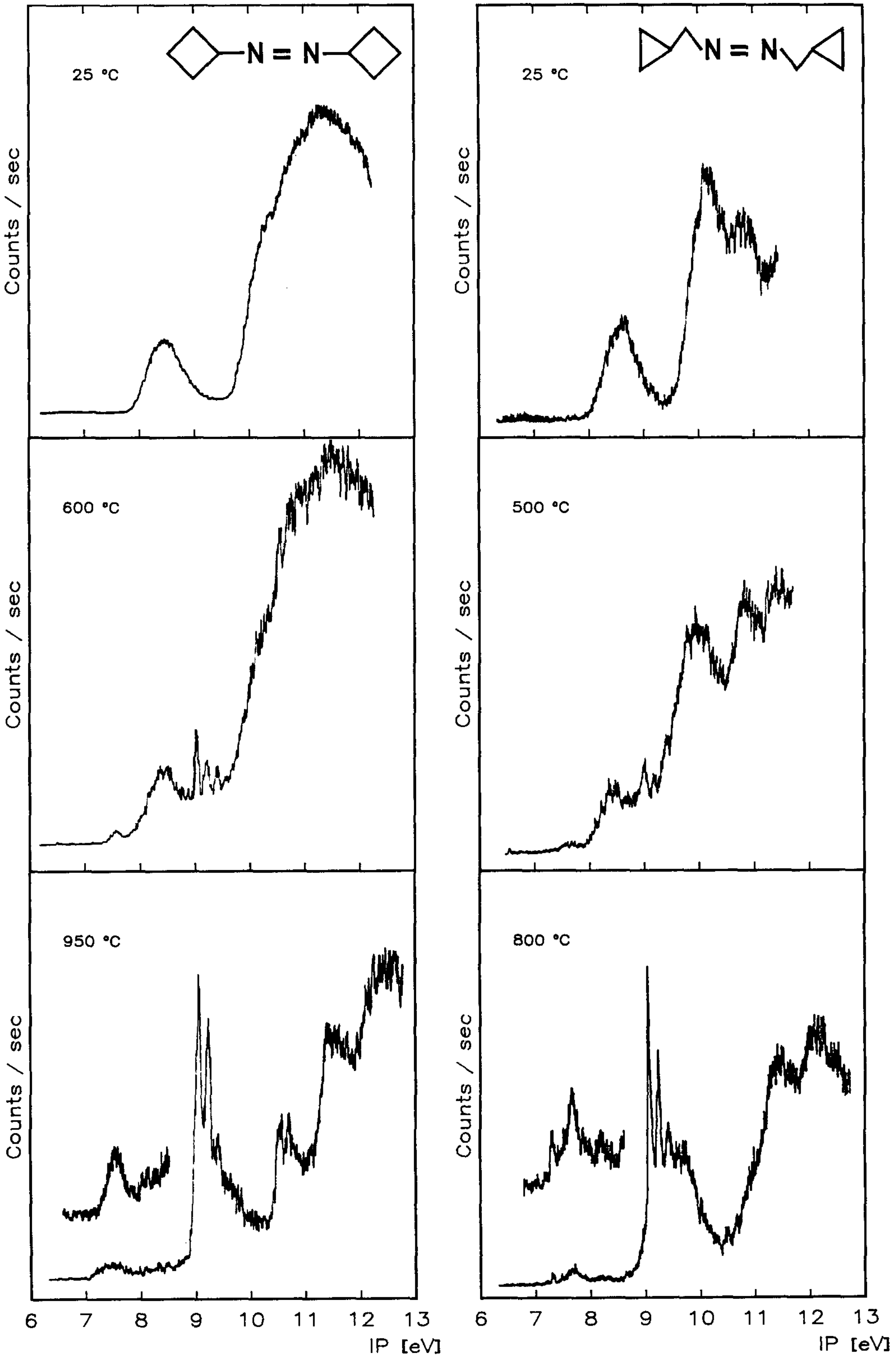

Figure 1

recording shall be given elsewhere[3].

The thermodynamic stability of the precursors can be estimated by observing the intensity of the first band as a function of temperature. While the pyrolyses of 1 starts at temperatures around 600°C, the azocyclopropylmethane (2) is fully decomposed in the same range of temperatures and fragmentation is clearly observed above 500°C. These observations strictly parallel those reported for the methylnitrites for which the same minimal pyrolyses conditions have been reported[2].

We shall first focus on the pyrolyses of azocyclobutane 1:

At temperatures above 600°C a well separated band is raising in the spectrum with a principal maximum at 7.55 eV starting with a relatively steep onset at 7.35 eV. This band can be assigned to the primary cyclobutylradical, the observed IP's being in full accord with the reported values[2]. However, even at this low temperature, the spectrum reveals the presence of secondary reaction products: The sharp, well resolved peaks at 9.03, 9.21, 9.43 and 10.5 eV prove the presence of butadiene[4], cyclobutene[5] and ethylene[6], respectively. While the peaks at 9.03 and 9.21 show a strictly parallel positive temperature dependence, the band at 9.43 eV becomes weaker with increasing temperature. Hence the former two peaks can be assigned to the first two progression lines in the PE-spectrum of butadiene[4], the latter must therefore be due to a different fragmentation product and can by comparison be ascribed to the spectrum of cyclobutene[5]. At temperatures above 1000°C, the ethylene band at 10.51 eV becomes the dominant feature in this spectrum. We shall now turn to the pyrolyses of 2:

The observed spectrum reveals a complex manifold of secondary fragmentation products. This not only leads to many different signals in the spectrum, but also to a complex relative temperature dependence of the individual bands. It is this observation which at the time makes it impossible to assign the recorded data to the individual fragments. At 500°C, a dominant peak has been recorded with a principle maximum at 10.1 eV. This strong band vanishes with increasing temperature. We conclude from its position and typical bandshape, that it signals the presence of an alkylsubstituted cyclopropane[7], probably the dimer of the cyclopropylcarbinylradical. At higher temperatures, the spectrum exhibits dominant ring opening which finally leads to the large concentration of butadiene observed in the reaction mixture. The high intensity of the first vibrational progression line leads to a relatively strong He-Iß band recorded at 7.16 eV. Ethylenegeneration is obviously much less pronounced compared to the pyrolyses of 1. The most evident feature however is the observation of the bands at 7.6 and 8.55 eV. They can be assigned to the ionizations of 1-Methylallyl and 3-Butenylradicals respectively. The former assignment is tentative and the cyclobutylradical might as well be responsible for the appearance of the band at 7.6 eV. However, the absence of the expected cyclobutenebands in the spectrum and the comparison with Beauchamp's results$^{2)}$ support our intuitive assignment.

Experimental: The spectra were recorded on a modified$^{3)}$Perkin Elmer PES-18 spectrometer at pressures of approx. 0.1 torr, the individual temperatures are listed in Fig. 1.

Concluding Remarks: Even at low temperatures, both spectra exhibit a complex chemical equilibrium in the gas phase. Further information about the thermodynamical stabilities of the species involved as well as about the relative reaction rates might well be obtained by careful registration of the temperature dependences of the individual band intensities.

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