A Spin-forbidden Predissociation in the Mass Spectrum of Isocyanic Acid

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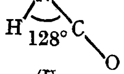
SOME mass-spectrometric fragmentation processes in small molecules have been shown to occur by predissociation onto repulsive energy surfaces.[1] The fragment ions should then be produced with excess kinetic energy and, if the predissociation is slow, we would expect to observe correspondingly wide metastable peaks[2] in the mass spectrum· We report an example in which the appearance of such a metastable peak can be explained by a spin-forbidden predissociation.

The main features of the mass spectrum of isocyanic acid (I) are shown in the Table. The appearance potentials of the fragment ions under electron impact were measured and the ionisation efficiency curves interpreted by semi-logarithmic plot and extrapolated voltage-difference methods. The



(I)

appearance potentials are certainly in the correct order but the values for NCO^+ and NH^+ are upper limits only, as the ionisation-efficiency curves for these fragments have quite different shapes from that of the parent ion. The metastable is rather weak in the ordinary spectrum, but in a double focussing machine it appears strongly in the refocussing method of Barber and Elliott.[3]

m/e	Species	Relative peak height (70 ev)	Appearance potential (ev)
43	$HNCO^+$	100	11·60†
42	NCO^+	21	<16·1
29	HCO^+	18	15·1—15·3
15	NH^+	9	<17·7

Metastable: wide, concave top and centred on *m/e* 19·6; corresponding to: $HNCO^+ \rightarrow HCO^+ + N$, with width corresponding to kinetic energy release (T) of 0·53 ev.

† Determined by photoelectron spectrometry.

It can be seen that HCO^+ formation is a slow process because it gives a metastable peak and although it has the lowest appearance potential, HCO^+ is not the most intense fragment ion.

The ground states of the products of the dissociation process of lowest energy are $^1\Sigma^+$ formyl ions and ^4S nitrogen atoms. These will only correlate with a quartet state of isocyanic acid ($^4A''$ if the plane of symmetry is retained during the dissociation). But we expect that the ground state of $HNCO^+$ will be $^2A''$ and that the formation of quartet states by electron impact will be relatively unlikely. If HCO^+ and N are formed in their ground states, they must be formed by a predissociation with $\Delta S = 1$,

$$\text{HNCO}^+\,(\text{doublet}) \xrightarrow{\Delta S=1} \text{HNCO}^+(^4A'') \rightarrow \text{HCO}^+(^1\Sigma^+) + \text{N}(^4S).$$

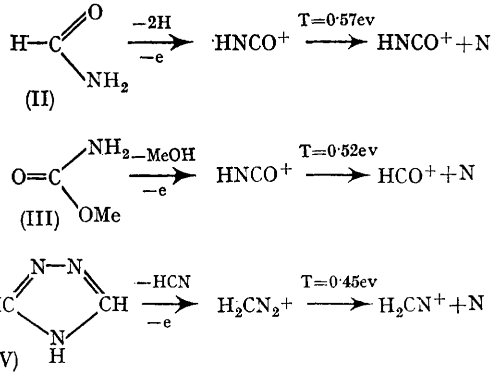
The slowness of the forbidden predissociation explains the appearance of a metastable for such a small molecule and repulsion between the closed shell formyl ion and the quartet nitrogen atom will lead to kinetic-energy release.

The heat of formation of isocyanic acid is not known, so we cannot prove this mechanism directly from the appearance-potential data. But if doublet, rather than quartet, nitrogen atoms were formed, the heat of formation of the products (16·86 ev) would be above the heats of formation of ground state $NH^+ + CO$ (16·04 ev) and to obtain the observed order of the appearance potentials, either NH^+ or CO would have to be formed in an excited state or their ground states would have to be formed *via* a large hump in the potential-energy surface. Since the ground states of NH^+ (doublet) and CO (singlet) correlate with a doublet state of $HNCO^+$ and since no rearrangement is required in the dissociation, we do not expect either formation of excited electronic states or significant activation energy for the association of the products.

Further confirmation that the mechanism involves a predissociation comes from the existence of the isoelectronic process in nitrous oxide,[4]

$$N_2O + h\nu\,(15{\cdot}01\text{ ev}) \xrightarrow{-e} NO^+(^1\Sigma^+) + N(^4S) + 0{\cdot}84\text{ ev}$$

Wide metastable peaks have been reported for the decomposition of $HNCO^+$ fragment ions in the mass spectra of formamide (II) and methyl carbamate (III).[5] We suggest that in these cases too, the appearance of the metastable peaks can be explained by a slow predissociation of doublet $HNCO^+$ fragments onto a repulsive quartet surface.



A kinetic energy releasing metastable peak has also been reported[6] for an isoelectronic process in the mass spectrum of *s*-triazole (IV). We feel that here also the metastable peak represents a similar, spin-forbidden, predissociation.

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