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MASS SPECTRA OF s-TETRAZINES. REDUCTION TO DIHYDRO-s-TETRAZINES IN THE ION SOURCE OF THE MASS SPECTROMETER

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Current interest in redox reactions of quinones occurring in the heated inlet system or the ion source (direct insertion) of the mass spectrometer (1,2) prompts us to report a related phenomenon observed during the mass spectrometric study of some s-tetrazine derivatives (Table I).

The 3,6-diacyl-s-tetrazines I-IV (3) on admission by a direct insertion system to the ion source have been found to exhibit abnormally high M+2/M abundance ratios in their spectra; other s-tetrazines (V-X) show a similar, but less pronounced effect (4). The M+2/M ratios in the spectra of dihydro-3,6-dibenzoyl-s-tetrazine (XI) (5) and 3,6-di-p-methoxybenzoyl-pyridazine (XII) are close to normal.

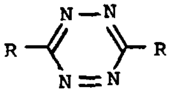
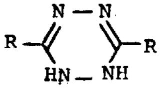
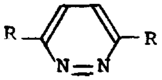
The possibility that the abnormally intense M+2 peaks originate from the corresponding dihydrotetrazines present as impurities in the tetrazine samples was excluded in the case of I by recording the mass spectrum of a sample after treatment with D_2O in dioxan. The spectra of the original and the D_2O-treated I were very similar; in particular, the abundance ratios M+1/M, M+2/M, M+3/M+2, and M+4/M+2 were essentially the same in both spectra.

In correspondence with the observation made by Aplin and Pike (1) in the case of p-benzoquinone we have found that water is the probable origin of the hydrogen incorporated into the M+2 ion. Thus, when the spectrum of

I was recorded after equilibration of the source with D_2O (6 x 10^{-6} mm., 195°), the most prominent peaks in the M to M+5 region appeared at M+3 and M+4 (404 and 879, respectively, relative to M = 100). Methanol can also serve as a source of hydrogen: continuous introduction of water or methanol (2 - 3 x 10^{-6} mm.) to the source at 190° resulted in a very high M+2/M ratio - 33:1 in each case. The spectra returned to normal after the introduction of methanol or water was stopped.

The appearance of relatively intense M+2 peaks in the mass spectra of the tetrazines can best be rationalized in terms of the reduction of the s-tetrazines to dihydro-s-tetrazines prior to ionization. This process may be related to catalytic reduction effected by atomic or molecular hydrogen, with reaction occurring on the surface of the ionization chamber (6). The greater importance of this process in the case of the tetrazines with acyl substituents (I-IV) is in accord with the expectation that they would be more readily reduced than the tetrazines V-X. The alternative possibility that M+2 ions arise by an ion-molecule reaction of the molecular ions of the tetrazines is remote at the sample pressure routinely employed (5 x 10^{-7} mm.) and is further contraindicated by the observation than small increases in the sample pressure lead to a decrease of the M+2/M abundance ratio in the spectrum of I. This observation can be interpreted in terms of prereduction of the tetrazine, however, since increased sample pressure could result in less efficient reduction due to competition for a restricted amount of reducing agent.

TABLE I. Relative Intensities of M+1 and M+2 Peaks[a,b]

	Compound		M+1		M+2	
			Calc.[c]	Found	Calc.[c]	Found
	I	R = C_6H_5CO	19.0	30.7	2.1	513
	II	R = *p*-$MeOC_6H_4CO$	21.4	24.7	3.0	303
	III	R = *p*-MeC_6H_4CO	21.3	23.0	2.6	77
	IV	R = 2,4,6-$Me_3C_6H_2CO$	25.7	25.0	3.6	138
	V	R = C_6H_5	16.3	18.2	1.3	9.8
	VI	R = *p*-$MeOC_6H_4$	19.1	19.6	2.1	10.0
	VII	R = $C_6H_5CH_2$	19.0	20.8	1.7	6.8
	VIII	R = C_6H_5CHOH	19.1	17.0	2.1	10.0
	IX	R = *p*-$MeOC_6H_4CHOH$	21.4	22.2	3.0	6.1
	X	R = 2,4,6-$Me_3C_6H_2CHOH$	25.8	28.0	3.6	17.2
	XI	R = C_6H_5CO (5)	19.1	19.6	2.1	2.6
	XII	R = *p*-MeC_6H_4CO	22.7	23.0	2.9	3.5

[a] Relative to M = 100. [b] Spectra were recorded with an ionization energy of 70 eV and an emission current of 96 μA. The source temperature was 180-210°, except for compounds III (140°), VII (60°), and XII (130°). [c] Calculated from natural isotopic abundances.

REFERENCES

1. R. T. Aplin and W. T. Pike, Chem. and Ind. (London), 2009 (1966).
2. S. Ukai, K. Hirose, A. Tatematsu, and T. Goto, Tetrahedron Letters, 4999 (1967).
3. P. Yates, O. Meresz, and H. Morrison, Tetrahedron Letters, 77, 1575 (1967).
4. The abundances of the molecular ions of I-X relative to the base peaks ranged from 1 to 40%.
5. This is either the 1,2- or 1,4-dihydro derivative.
6. Compound I undergoes facile chemical reaction with water in a different fashion, yielding phenylglyoxal 2-(N-phenylglyoxalyl)hydrazone.