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ORGANIC MASS SPECTROMETRY IX*. THE REDUCTIVE REACTION OF 1,2-QUINONES IN THE MASS SPECTROMETER

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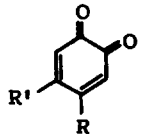
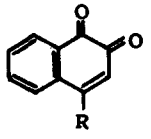
Mass spectrometry of 1,4-quinone derivatives has been investigated by several workers (1-9). During the investigation of mass spectrometry of 1,2-benzoquinones and 1,2-naphthoquinones, we found that the M+2 peak appears

Table I The Relative Intensities of the M^{+} and M+2 Peaks in the Spectra of 1,2-Quinones (Heating Inlet 230°C).





Compds.	R	R'	M^{+}	M+1	M+2	Base peak
I	CH_3	H	100	77	92	M^{+}
II	SCH_3	H	2	3	100	M+2
III	SCH_3	OCH_3	6	10	38	M-CO
IV	H	-	27	6	22	M-CO
V	OCH_3	-	5	1	6	M-CO
VI	SCH_3	-	17	7	16	M-CO
VII	S-Ø	-	17	11	23	M-CO

* Part VIII : A. Tatematsu, H. Yoshizumi, E. Hayashi and H. Nakata, Tetrahedron Letters, 1967, No. 31 in press.

strongly in the spectra of these compounds. As shown in Table I, M+2 peak in these cases shows a comparable intensity with that of $M^{\dagger}$, especially, in the case of 4-methylthio-1,2-benzoquinone (II) the M+2 peak becoming the base peak.

The relative intensities of both molecular and M+2 peaks vary by changing temperature of the ionization chamber and/or by use either an all-glass inlet or a direct inlet system, as shown in Table II. Furthermore, intensity of the M+2 peak increases gradually with time (Fig.1). This tendency is stronger for benzoquinones than for naphthoquinones.

Table II Ratio of Heights of $M^{\dagger}$ and M+2 Peaks in various Temperature.

Compds.	Heating Inlet Temp. 230°	130°	Direct Inlet Temp. 120°
I	52 : 48	58 : 42	57 : 43
II	2 : 98	2 : 98	23 : 77
III	14 : 86	17 : 83	19 : 81
IV	55 : 45	83 : 17	76 : 24
V	45 : 55	90 : 10	77 : 23
VI	52 : 48	69 : 31	70 : 30
VII	43 : 57	45 : 55	45 : 55

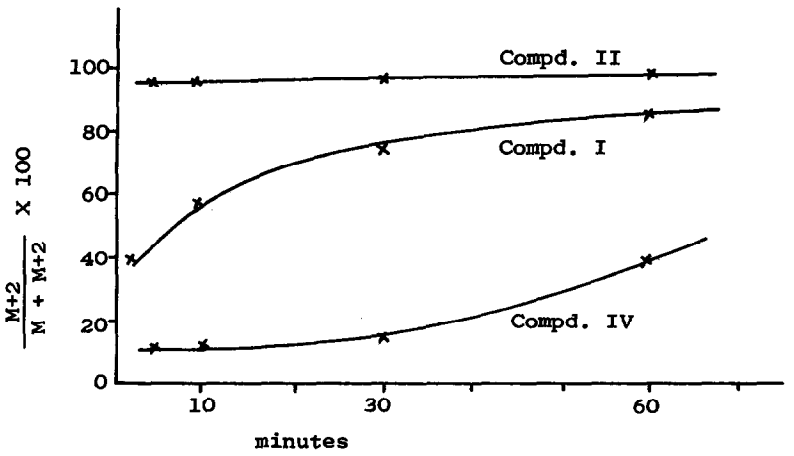


Fig.1 Plots of [(M+2) / $M^{\dagger}$ + (M+2)] in the spectra of the 1,2-quinones at 130°C. vs. time.

From these results, it seems that 1,2-quinones are reduced by moisture in the mass spectrometer to give the M+2 peak. This is supported by the following experiment: when deuterium oxide was introduced in the mass spectrometer before introduction of the sample, strong M+3 and M+4 peaks observed in the spectrum of II thus obtained. Incidentally, that the 1,2-quinones are not contaminated by the corresponding hydroquinones are checked by UV and NMR spectra. From these facts, it is suggested that the compounds which have a high oxidation potential such as 1,2-quinones may be reduced by moisture in the mass spectrometer.

In the case of 1,4-naphthoquinones (1) appearance of appreciable M+2 peak has not been pointed out (10). 1,4-Benzoquinones (2) usually give M+2 peak, whose intensity is slightly stronger than that calculated from the natural abundance, but it is rare case that the intensity of M+2 peak exceeds one tenth of that of M^{+} peak (8). It was reported (5,6,9) that some of 1,4-benzoquinone derivatives having an unsaturated side chain, such as plastoquinones and ubiquinones, gave a fairly intense M+2 peak in their mass spectra, whereas no M+2 peak was observed in the spectra of the corresponding quinones having a saturated side chain. Interestingly, a compound, which gives intense M+2 peak (67 % of M^{+} peak), reported by Aplin et al.(8) has an unsaturated side chain. It was also suggested by Aplin et al. that in the 1,4-quinone spectra water is the probable origin of the hydrogen molecule responsible for the M+2 peak. In these cases, however, role of the unsaturated side chain has not been clarified.

Detailed fragmentation patterns of these 1,2-quinones will be reported elsewhere.

All spectra of the present work were measured by Hitachi RMU-6E Type double-focussing mass spectrometer, using an all-glass heated inlet and a direct inlet system. The ionizing energy was kept at 70 eV. and the ionizing total current at 80 μA.

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(10) The mass spectra of some of 1,4-quinones measured by us, however, showed slightly larger M+2 peak than that calculated from natural abundances.