A Specific Rearrangement of Doubly-charged Ions formed by Electron Impact

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DOUBLY-CHARGED ions in mass spectra are generally found in relatively low abundance (seldom $>1\%$ of the most abundant ion[1a]), and their use in structure determination has been primarily as an indicator of a high degree of unsaturation in the molecule.[1-3] Biemann comments that "no direct relationship between the intensity of the singly- and doubly-charged species should be expected";[2] the substantially higher energies involved† can help account for the scarcity of reports on specific decomposition pathways for the ions.[5] We report here a specific rearrangement in the spectra of benzophenone derivatives which yields $(M - \mathrm{CO})^{2+}$ ions[5b] whose abundances for particular derivatives are over 10% of the most abundant singly-charged ion in the spectrum.

Striking differences between the decompositions of singly- and doubly-charged molecular ions might be expected on the basis that the former are odd-electron (radical) ions, while the latter can contain either no *or two* unpaired electrons. The well known tendency for aromatic compounds to exhibit abundant doubly-charged ions may be due to the opportunity for complete electron pairing. Note that homolytic cleavage of a diradical doubly-charged ion can yield two odd-electron singly-charged ions (with kinetic energy of coulombic repulsion),† in contrast to the strong tendency of even-electron singly-charged ions to decompose to two even-electron products.[6]

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† Recent studies (ref. 4) of metastable decompositions of doubly-charged ions call attention to the fact that in all of those reported the decomposition is accompanied by the release of energy of at least 2 ev (ref. 4b).

In the mass spectra of substituted benzophenones, the formation of the benzoyl ion,[7a] the C_6H_5 ion,[7b] and their substituted counterparts[7c] are the most important processes for the decomposition of the singly-charged molecular ion; but the corresponding processes to form doubly-charged ions do not give significant peaks in these mass spectra. The opposite is true for ions formed by the expulsion of CO; $[(M - CO)^{2+}]/[M^{2+}]:[(M - CO)^{+}]/[M^{+}] > 100$. The Table presents the intensity ratios, Z,[7a] for the parent compound and the substituent effect on these ratios. The $(M - CO)$ ion is by far the most intense doubly-charged ion in the spectrum for this set of compounds at 75 ev. Thus further decomposition is relatively unimportant for the abundant $(M - CO)$ ions, allowing in these cases interpretation of these data in terms of a single rate-constant for formation of the ion.[7a]

TABLE

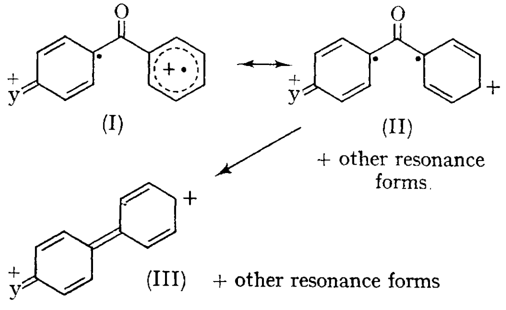
Substituent effects on [M — *CO*] *ion abundances*

$$Z = \frac{[YC_{12}H_9^{+}]}{[YC_6H_4CO{\cdot}Ph^{+}]}\,^{a} \qquad Z = \frac{[YC_{12}H_9^{2+}]}{[YC_6H_4CO{\cdot}Ph^{2+}]}\,^{b}$$

Y	log Z/Z_0	log Z/Z_0
p-Me_2N	$-0{\cdot}60$	$1{\cdot}61$
p-NH_2	$-0{\cdot}23$	$1{\cdot}65$
p-HO	$-0{\cdot}25$	$0{\cdot}82$
p-MeO	$-0{\cdot}70$	$0{\cdot}87^{c}$
p-Me	$-0{\cdot}31$	$0{\cdot}40$
p-Ph	$-0{\cdot}19$	$0{\cdot}95$
H	$0{\cdot}00$	$0{\cdot}00$
p-F	$0{\cdot}10$	$0{\cdot}67$
m-MeO	$-0{\cdot}10$	$-0{\cdot}96^{c}$
p-I	$-0{\cdot}60$	$0{\cdot}35$
p-Cl	$-0{\cdot}19$	$1{\cdot}13^{c}$
p-Br	$-0{\cdot}17$	$0{\cdot}44$
m-F	$0{\cdot}13$	$-0{\cdot}17$
m-Cl	$-0{\cdot}19$	$-0{\cdot}19^{c}$
m-Br	$-0{\cdot}68$	$-0{\cdot}61$
m-CN	$-0{\cdot}11$	$0{\cdot}28$
p-CN	$-0{\cdot}05$	$0{\cdot}64$
m-NO_2	$-0{\cdot}28$	$-0{\cdot}1 \pm 0{\cdot}3^{d}$
p-NO_2	$-0{\cdot}9^{d}$	$-0{\cdot}4 \pm 0{\cdot}3^{d}$

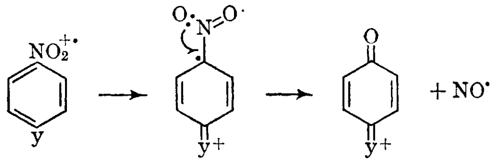
[a] $Z_0 = 0{\cdot}040$; [b] $Z_0 = 4{\cdot}5$, estimated from isotope peak at 77·5 (for Y = H, $[C_{12}H_{10}^{2+}]/[M^{+}] = 0{\cdot}060$); [c] interference by singly-charged ions; estimated from isotope peaks; [d] ions of very low intensity.

This reaction involves the formation of an even-electron doubly-charged ion by decomposition of an even-electron ion; from the discussion above, a possible explanation for its unusually high rate is that the precursor is a diradical species, while all of the electrons are paired in the product ion.‡ This is consistent with the large rate-enhancement caused by substitution of electron-donating substituents in the *para*-position.



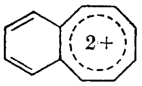
(I) (II) (III)

The spectrum of a bis-substituted derivative, *pp'*-dimethoxybenzophenone exhibits the highest rate enhancement observed: log $Z/Z_0 = 1{\cdot}77$, indicating a similar enhancement of the radical site in the second ring. The substituent effects observed here bear a qualitative relationship to those found in the loss of NO from nitroaromatics,[8] and suggest that partial localization of the radical site at the carbon atom attached to the nitro-group may be an important driving force[9] in addition to the stabilization of the product ion from the NO· loss.



(IV) (V) (VI)

An alternative driving force could be the formation of the Hückel-aromatic benzocyclo-octatetraene dication.§



(VII)

The effect of substituents on the formation of singly-charged $YC_{12}H_9^{+\cdot}$ ions is obscured by the

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‡ Since triplet–singlet conversions are slow, the electrons in the molecular ion must be spin-paired, though in different orbitals, for the reaction to be relatively rapid.

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possibility for further decomposition; low-voltage studies[7] were not attempted because of the low ion abundances. However, the effect of most substituents—to lower the net abundance of $YC_{12}H_9^{+\cdot}$—is quite similar to the net substituent effect on the abundance of $YC_6H_4^+$ in the 75 v spectra of the same compounds.[7c]

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[1] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960: (*a*) p. 345, (*b*) p. 375, (*c*) p. 401, (*d*) p. 261.

[2] K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill, New York, 1962, p. 157.

[3] F. L. Mohler, National Bureau of Standards Technical Note 243 (1964); for an unusual exception see M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, 1965, **77**, 5510.

[4] (a) W. Higgins and K. R. Jennings, *Chem. Comm.*, 1965, 99; (b) J. H. Beynon and A. E. Fontaine, *Chem. Comm.*, 1966, 717.

[5] (a) Beynon (ref. 1b) points out that abundant $(M - O)^{2+}$ ion in the spectrum of maleic anhydride may be due to the formation of the stable ion $^+O{\equiv}C{\cdot}CH{=}CH{\cdot}C{\equiv}O^+$; for most ions, such as $(M - 6H)^{2+}$, (ref. 1c) it is more difficult to formulate plausible "specific" mechanisms; (b) Beynon (ref. 1d) has noted analogous doubly-charged ions in the spectrum of fluorenone corresponding to M^{2+} and $(M - CO)^{2+}$, plus a "metastable" peak for $M^{2+} \rightarrow (M - CO)^{2+}$.

[6] (a) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, New York, 1963, p. 309; (b) F. W. McLafferty, "Interpretation of Mass Spectra," Benjamin, New York, 1966, p. 30.

[7] (a) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 529; (b) *ibid.*, p. 4484; (c) *ibid.*, 1967, **89**, 1.

[8] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5023.

[9] F. W. McLafferty, *Chem. Comm.*, 1966, 78.