Common Intermediates in the Electron Impact Decomposition of Substituted Nitrobenzenes and Anisoles

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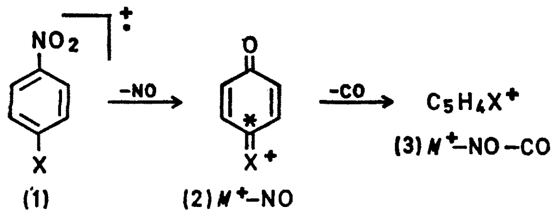
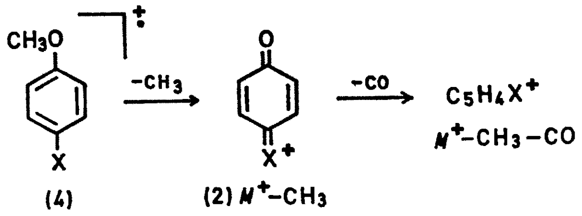
Summary The shapes of "metastable peaks" are used to establish that $M^{+} - \text{NO}$ ions from substituted nitrobenzenes and $M^{+} - \text{CH}_3$ ions from substituted anisoles decompose further *via* common intermediates, and that in this further decomposition *m*- and *p*-substituents are not randomised relative to the reaction centre.

THE observation that *p*-substituted nitrobenzenes lose NO from their molecular ions (**1**) with kinetic energy release in the instances of ***para*** electron-donating substituents, but that the same reaction in the *m*-substituted isomers proceeds without kinetic energy release, leads to the conclusion that substituent orientation is not lost in such reactions, and further that quinoid stabilised ions [*e.g.* (**2**)] are almost certainly formed from the *p*-substituted nitrobenzenes.[1-3]



The most general reaction undergone by the $M^{+} - \text{NO}$ ions is loss of CO [*e.g.* (**2**) → (**3**)]. In the case of *p*-nitroaniline (**1**; $X = NH_2$), it has been reported that the $M^{+} - \text{NO}$ ion (**2**; $X = NH_2$), when enriched with ^{13}C at the carbon indicated by an asterisk, loses approximately one sixth of the enrichment when CO is eliminated.[4] This surprising finding suggests that the oxygen atom may become randomly attached to any of the six carbon atoms prior to CO elimination. Such an interpretation of the data necessitates a deep seated isomerisation of (**2**; $X = NH_2$) prior to CO loss, and leads to the expectation that the $M^{+} - \text{NO}$ ions from *p*- and *m*-substituted nitrobenzenes might isomerise to common structures prior to CO loss, and so lose CO by reaction over a common potential surface.



Metastable transitions occurring from common states over the same potential surfaces will give rise to "metastable peaks" of the same shape. Using this criterion we have first sought additional evidence for the structure (**2**), by generating $M^{+} - \text{CH}_3$ ions from *p*-substituted anisoles (**4**). These $M^{+} - \text{CH}_3$ ions decompose by loss of CO, and in so doing give "metastable peaks" identical in shape (within the limits of experimental error) with those for CO loss from the $M^+ - NO$ ions of the substituted nitrobenzenes (Table).

Widths of "metastable peaks" for the reactions ($M^+ - NO$) $\rightarrow$ ($M^+ - NO - CO$) *occurring in substituted nitrobenzenes* (**1**) *and for the reactions* ($M^+ - CH_3$) $\rightarrow$ ($M^+ - CH_3 - CO$) *occurring in substituted anisoles* (**4**)

	Anisoles (**4**)		Nitrobenzenes (**1**)	
Substituent	Peak width (m.u.)[a]	T(ev)[b]	Peak width (m.u.)[a]	T(ev)[b]
p-NH_2	0·96	0·38	0·93	0·35
p-OMe	0·86	0·23	0·88	0·24
p-Br	*ca.* 0·8	*ca.* 0·11	—	—
p-Cl	—	—	0·52	0·15
p-OH	0·50	0·10	0·52	0·11
p-Ph	0·64	0·08	*ca.* 0·6	*ca.* 0·07
p-Me	—	—	Gaussian	*ca.* 0·0
p-CN	Gaussian	*ca.* 0·0	—	—
H	Gaussian	*ca.* 0·0	Gaussian	*ca.* 0·0
m-NH_2	Absent	—	*ca.* 0·51	*ca.* 0·11
m-OMe	Absent	—	*ca.* 0·44	*ca.* 0·06

[a] A dash in this column indicates that the compound was not examined. [b] T(ev) is the release in kinetic energy, calculated from the peak width (ref. 2).

It may be concluded that the ions generated by loss of NO from nitrobenzenes, and by loss of CH_3 from the anisoles, have the same structure [almost certainly (**2**) at the threshold], and that subsequent loss of CO occurs from a common structure [either (**2**) or a common rearranged structure]. Somewhat surprisingly, those ions (**2**) which are most highly stabilised by electron donation through a mesomeric effect (*e.g.* X = *p*-NH_2 and *p*-OMe) lose CO with the largest release of kinetic energy (Table). There is no significant release of kinetic energy in the absence of a *p*-substituent, and in the presence of an electron-withdrawing substituent (*p*-CN). Thus it is precisely those *p*-substituted nitrobenzenes [*e.g.* (**1**; X = NH_2 and OMe)] which release relatively large amounts of kinetic energy in NO loss[1-3] that also release relatively large amounts of kinetic energy in subsequent loss of CO. In addition, the loss of CO from the $M^+ - NO$ ions derived from *p*-amino- and *p*-methoxy-nitrobenzenes proceeds with a larger release of kinetic energy than does the corresponding loss of CO from the $M^+ - NO$ ion derived from *m*-amino- and *m*-methoxy-nitrobenzenes (Table). Thus it must be concluded that in these compounds the $M^+ - NO$ ions losing CO (or, at least, a large fraction of such ions) do so over different potential surfaces, and therefore the *m*- and *p*-substituents cannot be randomised with respect to the reaction centre. There does not appear to be a simple interpretation which will satisfy both the ^{13}C labelling results[4] and the present data.

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