# **1187.** *The Dissociation of* o-*Nitrotoluene Under Electron Impact*

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The mechanism whereby neutral carbon monoxide is ejected from the (*p*-OH)$^+$ ion from *o*-nitrotoluene under electron impact has been studied. The compound *o*-nitro[*Me*-$^{13}$C]toluene was prepared in order to assist this study.

It has been shown [1] that the *o*-nitrotoluene molecule ion dissociates under electron impact, losing OH, to form the ion of *m*/*e* 120. This ion, the most abundant in the mass spectrum, could possibly arise in two different ways. If the molecular ion undergoes rearrangement to the nitrite form before dissociation (as it presumably does in the reaction characteristic

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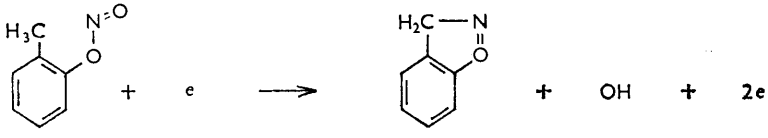
[1] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. chim. belge*, 1964, **29**, 311.

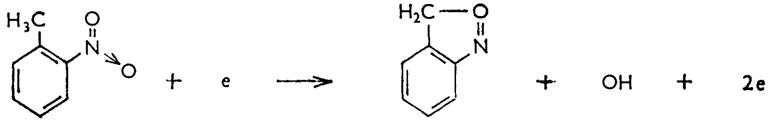
of aromatic nitro-compounds $RNO_2^+ \longrightarrow RO^+ + NO$), it is envisaged that the loss of OH will occur as at (*a*).

(*a*)



Alternatively, if the nitro group retains the configuration usually associated with the neutral molecule, the dissociation may be considered to proceed as at (*b*).

(*b*)



The ion of *m*/*e* 120 can be shown to dissociate further, losing CO, to form the ion of *m*/*e* 92. A " meta-stable peak " is observed at *m*/*e* 70·5 corresponding to this transition, *i.e.*,

$$(p\text{-}OH)^+ \longrightarrow (p\text{-}OH\text{-}CO)^+ + CO$$

where p represents the parent, or molecule ion. The carbon atom of the CO group ejected in this last fragmentation could be derived either from the methyl group or from the benzene ring. This will depend upon which of the two fragmentation routes postulated above is responsible for the production of the *m*/*e* 120 ion. In order to distinguish between the two possibilities, a sample of *o*-nitro[*Me*-$^{13}$C]toluene was prepared, and its mass spectrum obtained under conditions of high resolution. If the peak at *m*/*e* 92 is " shifted " to *m*/*e* 93 one would assume that the carbon atom in the ejected CO group comes from the ring, and that the molecular ion rearranges to the nitrite form before undergoing any fragmentation. Conversely if the peak at *m*/*e* 92 is not " shifted " to *m*/*e* 93 the carbon atom must be derived from the methyl group.

The labelled compound could not be prepared in a pure state. It was actually produced in 54% concentration in admixture with unlabelled *o*-nitrotoluene. The spectra of this mixture and of the unlabelled compound were obtained, and the spectrum of the pure labelled compound was obtained by subtraction of one spectrum from the other.

## RESULTS AND DISCUSSION

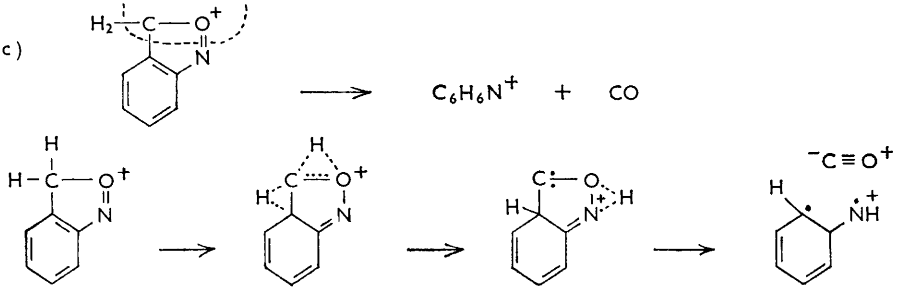
The high resolution spectra of the unlabelled and $^{13}$C-labelled compounds at *m*/*e* 92 and 93 are given in the Table; the figures in parentheses represent the percentage abundances of the ions where the *m*/*e* 120 ion is taken as 100% in the spectrum of *o*-nitrotoluene and the *m*/*e* 121 ion is taken as 100% in the spectrum of *o*-nitro[*Me*-$^{13}$C]toluene.

Although there are several ion species present at both *m*/*e* 92 and *m*/*e* 93 it is clear, from a study of the results in the Table, that the major contribution to the $(p - OH - CO)^+$ ion in the spectrum of the labelled compound is due to the $C_6H_6N^+$ ion of *m*/*e* 92, and only a small contribution is noted at *m*/*e* 93 due to $C_5{}^{13}CH_6N^+$. Therefore, the major fragmentation mode that results in the loss of CO from the $(p - OH)^+$ ion involves the loss of the carbon from the methyl group, as at (*c*).

| *m*/*e* | *o*-Nitrotoluene | | *o*-Nitro[Me-$^{13}$C]toluene | |
|---|---|---|---|---|
| 92 | $C_6H_4O^+$ | (2·5) | $C_6H_4O^+$ | (0·8) |
| | $C_6H_6N^+$ | (41·5) | $C_6H_6N^+$ | (35·2) |
| | $C_6{}^{13}CH_7{}^+$ | (5·0) | $C_6{}^{13}CH_7{}^+$ | (63·8) |
| 93 | $C_6H_5O^+$ | (2·7) | $C_5{}^{13}CH_4O^+$ | (0·9) |
| | $C_6{}^{13}CH_6N^+$ | (3·0) | $C_6H_5O^+$ | (1·8) |
| | $C_6H_7N^+$ | (1·6) | $C_5{}^{13}CH_6N^+$ | (2·6) |
| | | | $C_6H_7N^+$ | (0·3) |

It is difficult to postulate a precise mechanism whereby this product ion is formed, or to visualise the transition states involved in transferring the two hydrogen atoms from the methyl group, but it seems possible that one of these hydrogens will transfer to the adjacent ring carbon, whilst the other transfers to the nitrogen *via* the oxygen atom, as shown.

(c)



The configuration of the charged fragment in the last stage of this process is not intended to represent the final structure of the $C_6H_6N^+$ ion. It is probable that it will undergo further rearrangement, possibly to the azepinyl form, but clearly there is no evidence to support this.

The other ion species of *m*/*e* 92 are $C_6H_4O^+$ and $C_6{}^{13}CH_7{}^+$. The former arises by loss of $CH_3$ and NO from the molecular ion, and the latter is probably the $^{13}C$ labelled tropylium ion formed by loss of the nitro group from the molecular ion.

## EXPERIMENTAL

o-*Nitro*[Me-$^{13}$*C*]*toluene*.—The Grignard reagent from magnesium (1·5 g.) and bromobenzene (10 ml.) in ether (50 ml.) was treated at −20° with the carbon dioxide from barium carbonate (6·24 g., 54 atom-% $^{13}$C) and sulphuric acid (50 ml.) to give 3·2 g. of [*carboxy*-$^{13}$C] benzoic acid. Esterification with methanol and sulphuric acid, followed by reduction with lithium aluminium hydride gave 2·1 g. of [*methylene*-$^{13}$C] benzyl alcohol. The remaining steps were to be reduction to toluene, nitration, and isolation of the *o*-isomer by gas–liquid chromatography. The benzyl alcohol was therefore first diluted with zone-refined *p*-xylene (10 ml.) to minimise subsequent loss of toluene by evaporation, dilution with *p*-xylene being unobjectionable in view of the automatic removal of *p*-xylene and 2-nitro-*p*-xylene during the chromatographic separation of *o*-nitrotoluene from its *p*-isomer. The solution of benzyl alcohol in *p*-xylene was hydrogenolysed using 3% palladium–charcoal (1 g.) and hydrogen at atmospheric temperature and pressure. The resulting solution of [*Me*-$^{13}$C] toluene in *p*-xylene was dried over sodium sulphate (1 g.), which was filtered off and washed with *p*-xylene. The resulting 10·8 g. of solution was added to a mixture of sulphuric acid (5·7 g.) and water (2·5 g.), and stirred below 20° whilst a mixture of sulphuric acid (12·6 g.), nitric acid (7·7 g., *d* 1·5) and water (3 g.) was slowly added. The temperature was raised to 45° during 10 minutes and kept at 45—50° for 30 minutes. After cooling and adding to water, the product was extracted with ether, washed with water, dilute sodium hydroxide solution, water, dilute hydrochloric acid, and water. The ether was then removed to leave 8·9 g. of oil.

The sample of *o*-nitrotoluene (mixed labelled and unlabelled) was separated from toluene, *p*-xylene, *m*- and *p*-nitrotoluene, dinitrotoluene and nitro-*p*-xylene, and collected by gas chromatography (5 ft. silicone gum column operated at 170°).

The mass spectra were recorded on an AEI MS9 mass spectrometer using 70 ev ionising electrons and a resolving power of about 20,000.

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