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STUDIES ON COORDINATION COMPOUNDS

V. A CHROMATOGRAPHIC, MASS SPECTROMETRIC AND INFRARED SPECTROSCOPIC INVESTIGATION OF THE THERMAL DECOMPOSITION PRODUCTS OF SOME NICKEL(II) ANILINE CHLORIDE, BROMIDE, IODIDE, NITRATE AND SULPHATE COMPOUNDS

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ABSTRACT

Using chromatographic, infrared and mass spectrometric methods, 44 different organic compounds, besides water and ammonia have been separated and identified from the pyrolysis products of nickel(II) aniline nitrate hydrate. The nickel(II) aniline chloride, bromide, iodide and sulphate complexes, however, showed only aniline, formed by dissociation as an organic pyrolysis product; this is in accordance with previous conclusions drawn from thermogravimetric (TG) curves.

On the basis of these results it is advisable to proceed with a certain caution when drawing conclusions from TG curves on pyrolysis processes without specification analyses of the process products. This should be specially noted when the reaction is abrupt and not calculable from the corresponding part of the TG curve, that is not smooth, preferably of S-shape.

The formation of the main pyrolysis products through radical reactions is discussed.

INTRODUCTION

In an earlier investigation[1] it was shown that aniline combines with nickel(II) chloride, bromide, iodide, nitrate and sulphate to form the following complexes: $Ni(aniline)_2Cl_2 \cdot H_2O$, $Ni(aniline)_2Br_2 \cdot 2H_2O$, $Ni(aniline)_4I_2$, $Ni(aniline)_2(NO_3)_2 \cdot 4H_2O$ and $Ni(aniline)_2SO_4$. The thermogravimetric curves of the complexes in static air were presented and analyzed (Ref. 1, Fig. 1). A clear steplike progression was observed in the thermograms of the first three complexes and it was possible to calculate the thermal decomposition reactions step by step. The reactions begin with the loss of water (except with the iodide complex) then the loss of aniline followed and the reactions ended with the formation of halogen and nickel(II) oxide. However, after the water loss (100–183°C), first a slow but then a very rapid decomposition reaction followed in the thermal decomposition of the nickel(II) aniline nitrate complex. For this reason it was not possible to get a more detailed picture of the decomposition process. The decomposition process of the nickel(II) aniline sulphate complex was also not elucidated, although it was slower.

Even though the exact calculation of the runs of the thermal decompositions was possible for the halogen complexes from the thermograms, we wished to ascertain in this paper whether the organic ligand, aniline, escaped as such, or whether there were side-reactions that might change aniline to other compounds.

The preliminary experiments with the nickel(II) aniline nitrate complex showed that already a considerable part of aniline was converted to other compounds by an almost explosive, strongly exothermic decomposition reaction. An attempt was made to identify as many of the compounds formed as possible. The decomposition processes of the other nickel(II) complexes were also considered.

The present pyrolyses of the complexes were performed in dynamic helium atmospheres and as oxygenated products were obtained among the pyrolysis products under these conditions, it is to be expected that the pyrolysis processes would occur far more readily in the ways elucidated in static air atmospheres[1].

Attempts to derive mass spectra by direct probe insertion with low ionizing potentials (0–70 eV) from the solid complexes were unsuccesfull, because no molecular peaks were obtained due to the decomposition of the complexes in the high vacuum (10^{-6}–10^{-7} mm Hg). This led to the investigation method described in this paper.

EXPERIMENTAL

Apparatus

The pyrolysis apparatus was a Hamilton multi-purpose sampling system. For gas chromatographic separations the Perkin-Elmer gas chromatographs Models F 900 and F 7 and the automatic preparative gas chromatograph Model F 21 were used. The columns (stainless steel) and their coatings are described later in connection with the chromatograms. The usual thin-layer chromatographic method and distillation at normal and reduced pressures were also used to separate the pyrolysis products. The mass spectra were determined on a Perkin-Elmer Model 270B GC-DF analytical mass spectrometer. An ionizing potential of 70 eV was used. The infrared spectra were run with a Perkin-Elmer Model 457 infrared spectrometer.

Compounds and chemicals

The nickel(II) aniline complexes studied were those prepared several years ago in connection with the earlier studies[1]. The reference compounds were either synthesized or obtained commercially. All chemicals used were of the best commercial quality obtainable.

Pyrolyses of the complexes and separations and analyses of the pyrolysis products

The thermal decomposition of nickel(II) aniline nitrate hydrate was performed in the Hamilton multi-purpose sampling system. Although the equipment is intended to be used in such a way that the pyrolysis products are injected directly into a gas chromatograph for analysis, the method was not useful in this work. Specifically, it was impossible to inject a sufficiently large amount of the sample into the gas chromatograph in an adequately short time. The long injection time lowered the separation power of the chromatograph, because the sample was spread over a long area in the column. Therefore the pyrolysis products were first collected in a cooled flask and the analyses of the products were made after this. The experimental collection arrangement is shown in Fig. 1.

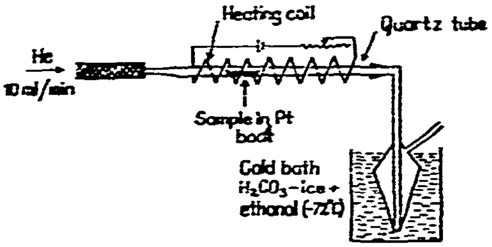


Fig. 1. Experimental arrangement for pyrolysis and collection of products.

The thermogravimetric curve[1] showed that the decomposition of the nickel(II) aniline nitrate complex had reached the NiO level when the temperature was 363 °C. (The heating rate was about 5 °C min^{-1}.) In the pyrolyses made in the present work the temperature was raised to 500 °C and held at this level for about 3 min. The heating rate was 70–90 °C min^{-1}.

Several pyrolyses with small samples were made to obtain a sufficient amount of the pyrolysis products. The observed weight changes in four pyrolyses were the following:

Amount of complex (mg)	*NiO residue*	
	mg	*% from the sample*
38.93	7.73	19.86
61.27	12.12	19.78
12.93	2.56	19.80
44.40	8.70	19.59
	Mean	19.76

For Ni(aniline)$_2$(NO$_3$)$_2$·4H$_2$O the yield of NiO should be 16.94%. The accuracy of weighing was about ±0.005 mg. Therefore over the years the complex had lost a great deal of its water of crystallization; the percentage 19.76 corresponding nearest to the composition Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O. However, it is most probable that the amount of water of crystallization does not effect the principal decomposition reaction, because the crystal water has escaped before the beginning of the main decomposition process. Hence it is assumed that the results obtained are also valid for the complex with its original composition ($4H_2O$).

A gas chromatogram of the total pyrolysis product immediately after the decomposition of the complex, without any handling of the product, is shown in Fig. 2. The chromatogram was obtained with the Model F 900 gas chromatograph of the Perkin-Elmer Model 270B GC-DF analytical mass spectrometer. The chromatographic conditions are given in the figure legend. Mass spectra were taken of some of the peaks of the chromatogram; the take-off places of the peaks are numbered on the chromatograms (Figs. 2–4, 6–11). The origins of the chromatographic peaks are also given in the figures.

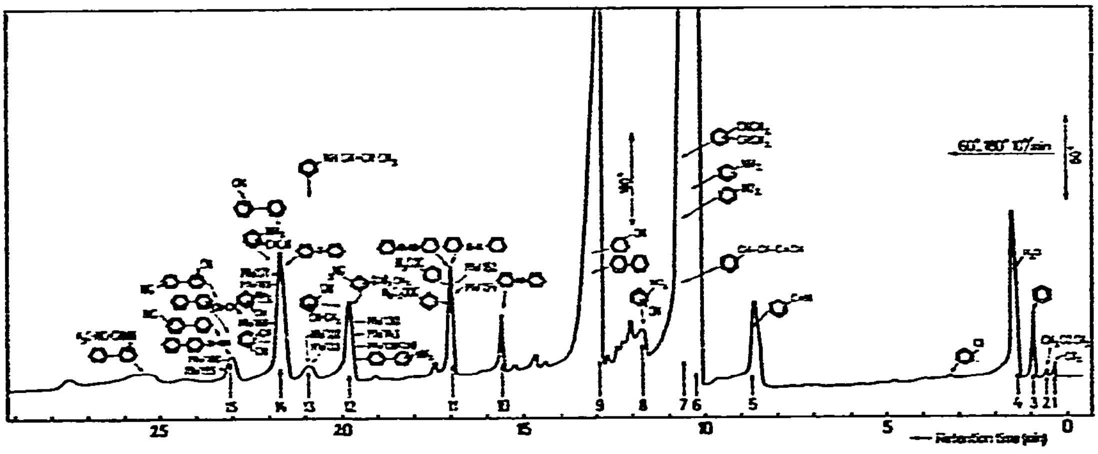


Fig. 2. Gas chromatogram of the total pyrolysis product of Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O. Column: Carbowax 20M, length 15 m, capillary. Carrier gas: He, 1 ml min^{-1}. Temperature programmed from 60 to 180°C, rate 10°C min^{-1}. Paper speed 20 mm min^{-1}. Sample volume: 0.5 μl (no solvent). The places where the mass spectra were taken are marked with numbers 1–15.

The pyrolysis product was then fractionated by distillation. Fraction A: The distillation product at normal pressure up to 120°C; Fraction B: the distillation product at reduced pressure (3 mm Hg) up to 90°C; Fraction C: the distillation residue. The further fractionation and analysis of these main fractions are described below.

The other nickel(II) aniline complexes studied were pyrolysed and analysed by the same methods and these are also described in the following text.

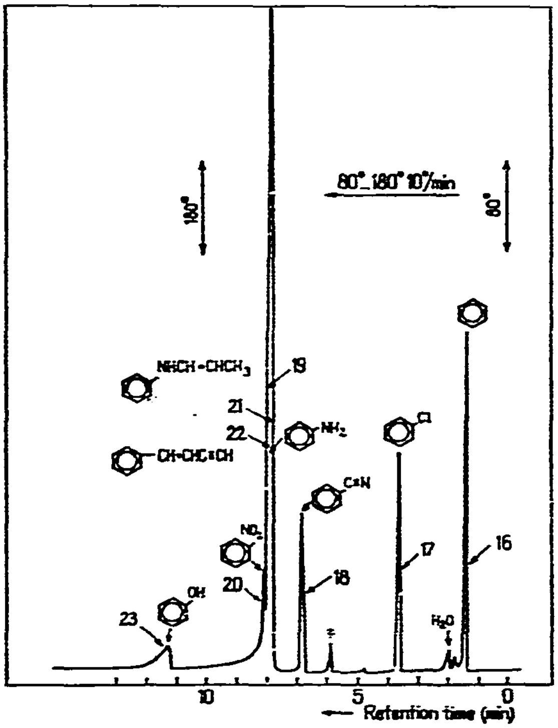
Over sixty mass spectra were used in the identification of the separated compounds. The spectra of identified well-known compounds are not presented.

RESULTS AND DISCUSSION

The analysis and identification of the decomposition products of the nickel(II) aniline complexes studied are described below. The results are combined with the earlier[1] TG results for the compounds. For the known mass spectra and fragmentation mechanisms of the previously identified compounds the reader is referred to Refs. 2 and 3 and the literature cited therein.

A. Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O

From the fifteen mass spectra (not shown) obtained (Fig. 2) it is reasonable to discuss spectra 1 and 2 first, because the compounds that the spectra represent disappeared in the further treatment of the pyrolysis products. According to spectrum 1, the molecular weight (MW) of the compound was 44. Its retention time in the gas chromatograph at 60°C was only 20 sec. This showed that the compound was gaseous at this temperature. On the basis of the molecular weight the compound could be CO_2 or $CH_3CH_2CH_3$. However, the absence of a strong M–15 (*m/e* 29) peak excluded propane, and therefore the compound should be carbon dioxide. This may be derived from the decomposition reaction or the cold bath. Spectrum 2 was due to acetone introduced by the injection syringe. It should also be considered that ammonia could not be detected chromatographically, but its presence among the decomposition products was ascertained on the basis of its strong smell.



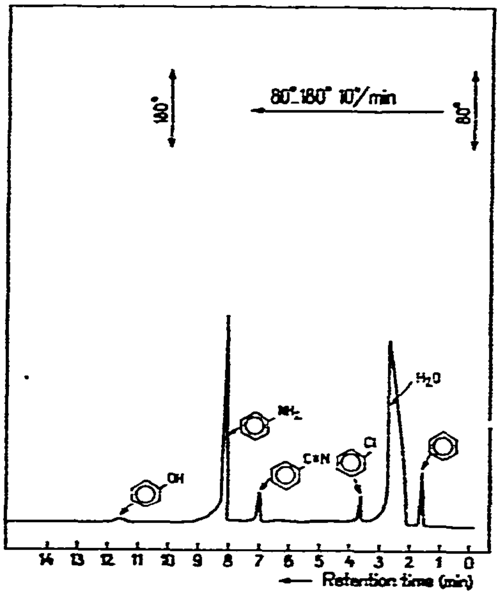


Fig. 3. Gas chromatogram of Fraction A1 (water insoluble). Column: Carbowax 20M, length 2 × 15 m, capillary. Carrier gas: He, 1 ml min^{-1}. Temperature: programmed from 80 to 180°C, rate 10°C min^{-1}. Paper speed: 10 mm min^{-1}. The places where the mass spectra were taken are marked with numbers 16–23.

Fig. 4. Gas chromatogram of Fraction A2 (water solution). Experimental conditions as in Fig. 3.

Fraction A obtained at normal pressure was further separated into two immiscible layers one of which appeared to be a water solution. The gas chromatograms of Fractions A1 (water insoluble) and A2 (water solution) are given in Figs. 3 and 4, respectively. The mass spectra were taken from the main peaks of the chromatograms in Figs. 3 and 4, and the corresponding compounds were identified for both chromatograms as described in the following text. Mass spectra Nos. 21 and 22 are given in Fig. 5 for the chromatogram in Fig. 3 and the identified compounds are marked in the chromatograms in Figs. 3 and 4.

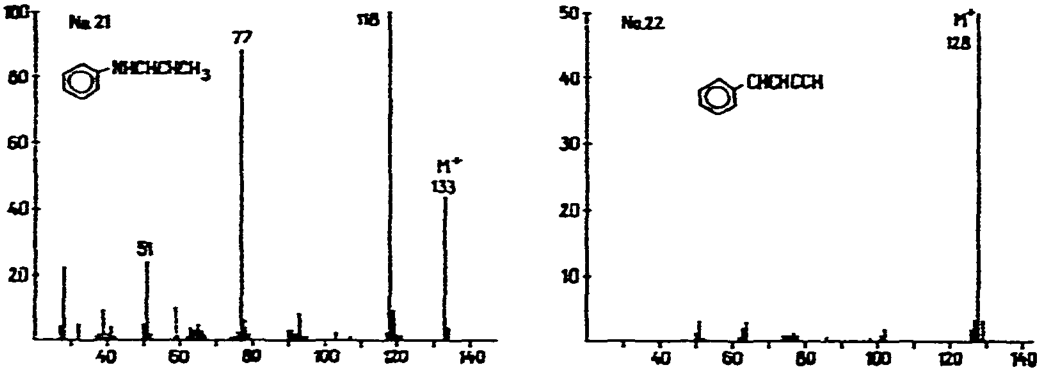


Fig. 5. Mass spectra 21 and 22 taken from the main peak of the gas chromatogram (Fig. 3) for Fraction A1 (water insoluble). Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O. Relative abundance is plotted against *m/e*.

On the basis of mass spectrum 16 and the retention time of the chromatographic peak (Fig. 3) benzene was identified[2,3].

Obviously, the nickel nitrate used to synthesize the complex contained chloride as an impurity, because chlorobenzene[2] was identified among the pyrolysis products through mass spectrum 17 and the retention time (Fig. 3).

To identify benzonitrile, it was collected with the preparative gas chromatograph (Perkin-Elmer F 21). The –C≡N absorption in the infrared spectrum and mass spectrum 18 confirmed the existence of benzonitrile. Further the retention time (Fig. 3) and the mass spectrum were identical with those of the synthesized reference compound.

The highest peak of the chromatogram (Fig. 3) (retention time about 8 min) could be divided by means of high resolution gas chromatography into four components. The gas chromatograph was a Perkin-Elmer Model F7, column (stainless steel), 4 m × 3/8 in. O.D.; packing, FFAP+Chromosorb G (5:95); gas flow-rate, 50 ml N_2 min^{-1}; temperature, 150 °C).

Aniline formed the greatest part of the content of the peak and could be identified[2,3] through its mass spectrum No. 19 (Fig. 3). The retention time also corresponded to that of aniline.

Another compound that could be identified was nitrobenzene[2,3]. Mass spectrum 20 (Fig. 3) and the retention time confirmed this.

The identity of the two other separated compounds is still unknown, since the amounts were too small to allow the taking of infrared spectra.

Mass spectra 21 and 22 (Fig. 5) gave molecular weights of 133 and 128, respectively. The compound of molecular weight 133 is certainly aromatic, because the mass spectrum (21 in Fig. 5) showed a strong *m/e* 77 peak. The M–15 (*m/e* 118) peak indicates that the compound may have a methyl group. Further the odd number of the molecular weight showed the compound to contain one nitrogen atom. On the basis of these considerations the configuration $C_6H_5{\cdot}NHCH{=}CHCH_3$ is proposed.

The compound corresponding to molecular weight 128 is obviously also aromatic, although the intensity of the peak at *m/e* 77 is weak (22, Fig. 5). The configuration $C_6H_5{\cdot}CH{=}CHC{\equiv}CH$ is postulated.

The existence of phenol[2,3] in the pyrolysis products was confirmed through its smell, mass spectrum 23 and retention time (Fig. 3). The presence of water was ascertained by the retention time (Fig. 3) and the mass spectrum.

Fraction B, collected by vacuum distillation, showed a gas chromatogram (Fig. 6) that contained no new compounds as compared with Fraction A. The greatest peak (retention time = 13 min) also contained the previously discussed compounds with molecular weights 128 and 133. The fraction was used for gas chromatographic separations (Perkin-Elmer F 7).

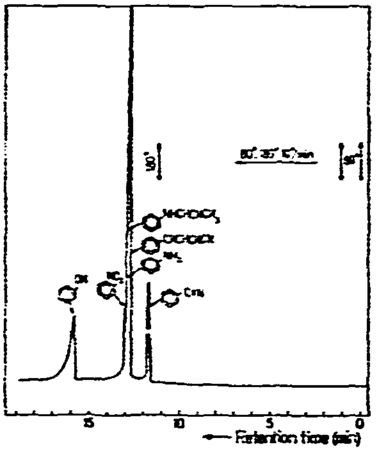


Fig. 6. Gas chromatogram of Fraction B (by vacuum distillation). Experimental conditions as in Fig. 3.

The study of the red-brown solid residue, Fraction C, left after the vacuum distillation, was first tried using gas chromatography. However, none of the several columns already available was suitable. In many cases the compounds were left fully in the column. It is known, that the organic bases in question here are difficult to separate by gas chromatography because they are adsorbed strongly on the stationary phase of the column. After several experiments the combination Chromosorb W–Carbowax 20M–KOH (75:10:15, w/w/w) was found to be a good bed material for the column. The packing was prepared by mixing Chromosorb W with potassium hydroxide dissolved in absolute ethanol and the solvent was evaporated under vacuum. This product was further mixed with Carbowax 20M dissolved in chloroform and then chloroform was distilled out under vacuum. The gas chromatogram in Fig. 7 was obtained from Fraction C with a column filled with this bed material.

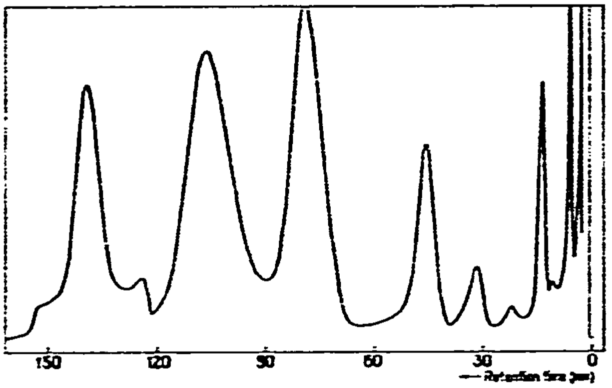


Fig. 7. Gas chromatogram of Fraction C (distillation residue). Column: Chromosorb W–Carbowax 20M–KOH (75:10:15), 90 cm × 3/8 in. O.D. Carrier gas: N_2, 90 ml min^{-1}. Temperature: 170 °C. Paper speed: 10 mm 5 min^{-1}. Gas chromatograph: Perkin-Elmer F21.

Biphenyl, biphenylamine and azobenzene were separated by thin-layer chromatography of the distillation residue, Fraction C. In the thin-layer chromatographic separation a 0.5 mm thick Al_2O_3 layer was used. The elution solvent was n-pentane–ethanol (97:3, v/v). After elution the layers of the compounds were extracted with ether and Al_2O_3 was filtered off. The ether solutions were concentrated.

Mass spectrum No. 24 (not shown) was identical with that obtained from pure biphenyl[2]. The retention time in the gas chromatograph also confirmed the structure.

The existence of biphenylamine was ascertained by the mass spectrum (No. 25, not shown) and the retention time.

The synthesized azobenzene and the product separated from the distillation had similar mass spectra (No. 26, not shown) and retention times.

Fraction C was further divided with the preparative gas chromatograph into four Fractions C1, C2, C3 and C4, using a 180 cm × 3/8 in. O.D. column, the carrier gas was nitrogen at a flow-rate of 70 ml min^{-1}, the temperature was 180 °C and the packing was Chromosorb W–Carbowax 20M–KOH (75:10:15). These four fractions were separated into their components gas chromatographically as shown in Figs. 8–11. Some of the mass spectra obtained from the peaks of these gas chromatograms are given in Figs. 12–15. The ordinal numbers of the mass spectra are the same as the peak numbers in the gas chromatograms in Figs. 8–11.

Fraction C1 (Fig. 8) contained at least twelve components. Some of these have already been identified above.

The compound corresponding to the molecular weight 152 (spectrum No. 27, Fig. 12) was certainly not aromatic because all mass numbers characteristic of aro-

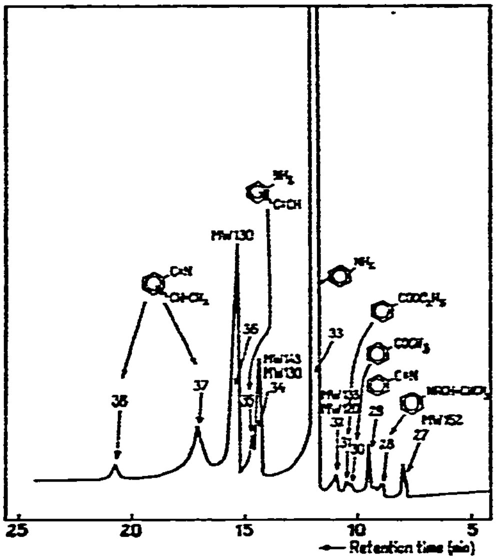


Fig. 8. Gas chromatogram of Fraction C1. Column: Carbowax 20M, length 2 × 15 m, capillary. Carrier gas: He, 1 ml min^{-1}. Temperature: programmed to 90°C in 4 min, from 90 to 170°C at 4°C min^{-1}. Paper speed: 10 mm min^{-1}. The places where the mass spectra were taken are marked with numbers 27–38.

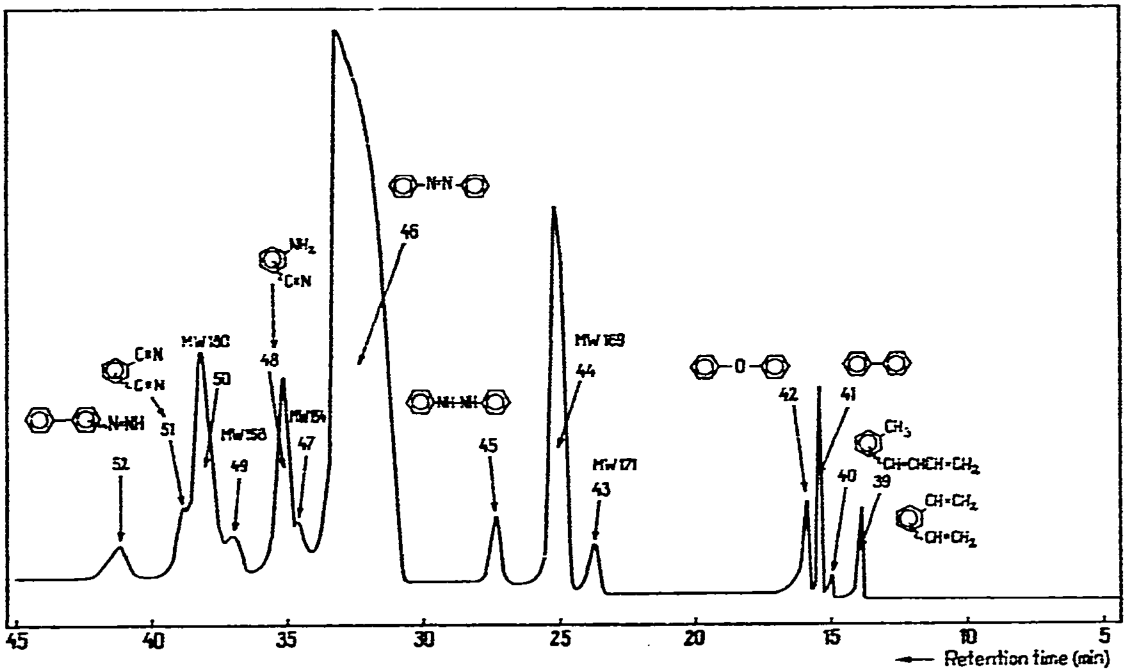


Fig. 9. Gas chromatogram of Fraction C2. Experimental conditions as in Fig. 8. The places where the mass spectra were taken are marked with numbers 39–52.

maticity were missing from the spectrum. It is not possible to identify the compound on the basis of the mass spectrum.

We have previously proposed the structure $C_6H_5 \cdot NH\text{–}CH{=}CH\text{–}CH_3$ for the compound of molecular weight 133 (spectrum No. 21, Fig. 5). Spectrum No. 28

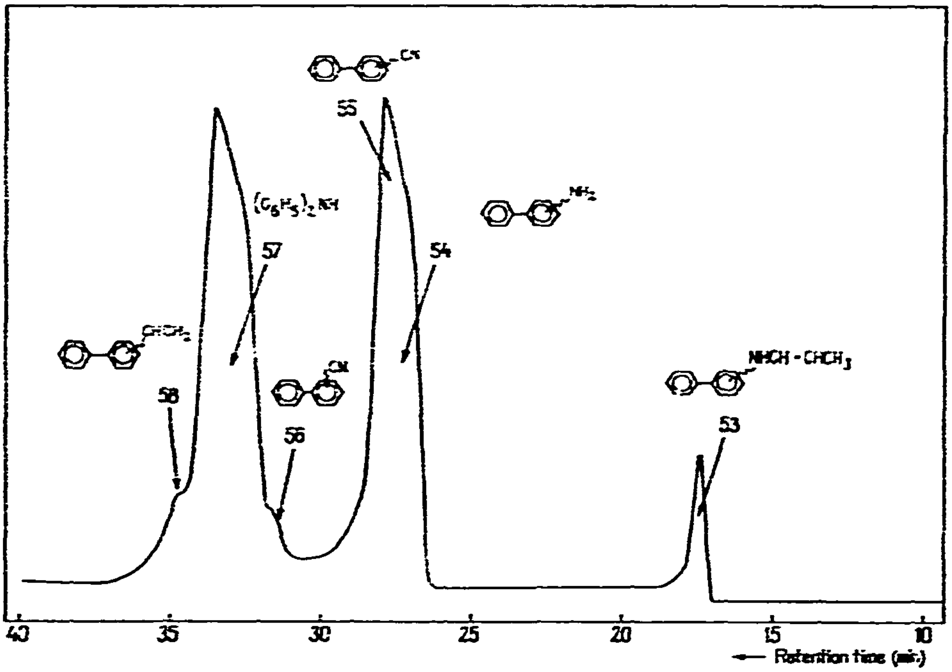


Fig. 10. Gas chromatogram of Fraction C3. Column: Carbowax 20M, length 15 m, capillary. Other conditions as in Fig. 8. The places where the mass spectra were taken are marked with numbers 53–58.

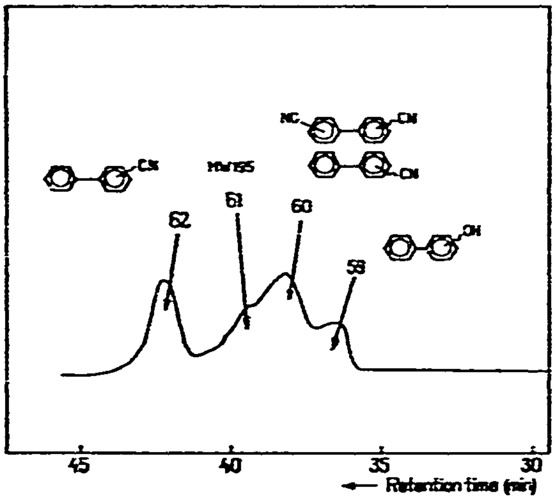


Fig. 11. Gas chromatogram of Fraction C4. Experimental conditions as in Fig. 10. The places where the mass spectra were taken are marked with numbers 59–62.

(Fig. 8) was similar and the structure could be held to be confirmed by the mass spectra.

The compound of molecular weight 103 (spectrum No. 29, Fig. 8) was the previously identified benzonitrile, $C_6H_5 \cdot CN$.

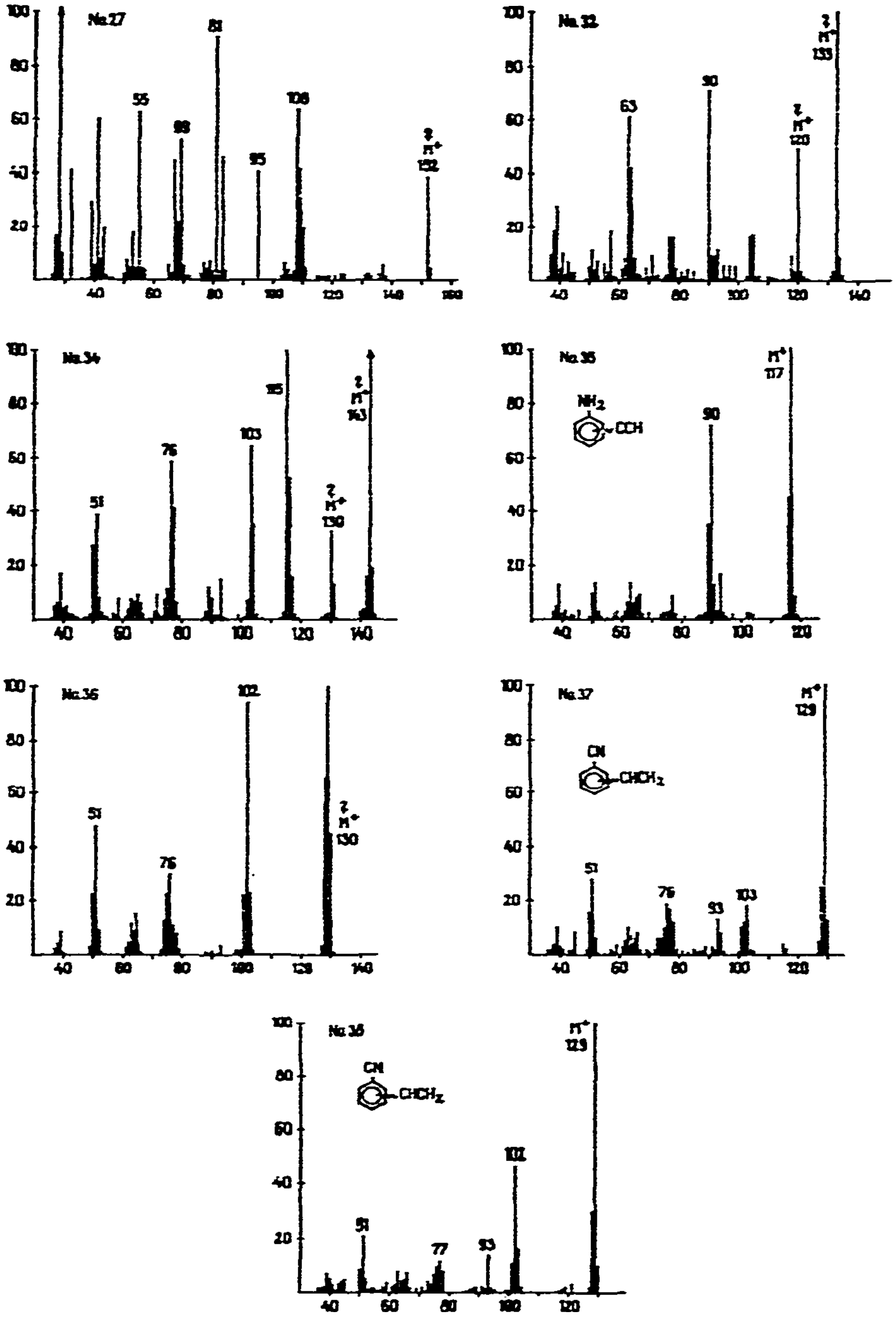


Fig. 12. Mass spectra 27, 32 and 34–38 taken from the peaks of the gas chromatogram of Fraction C1 (Fig. 8). $Ni(aniline)_2(NO_3)_2 \cdot 0.5H_2O$. The relative abundance is plotted against *m*/*e*.

The mass peaks at *m/e* 51 and 77 in spectrum No. 30 (Fig. 8) of the compound with MW = 120 confirmed that it was aromatic. The M–15 peak (*m/e* 105) showed the cleavage of a methyl group. Because the compound contained no nitrogen and the intensity of the *m/e* 91 peak was weak the only possible structure was acetophenone, $C_6H_5 \cdot COCH_3$. A reference mass spectrum verified the structure.

On the basis of mass spectrum No. 31 (Fig. 8) it was assumed that the corresponding compound (MW = 150) was ethylbenzoate, $C_6H_5 \cdot COOC_2H_5$. Comparison with the mass spectrum of pure ethylbenzoate substantiated the assumption.

Spectrum No. 32 (Fig. 12) is obviously due to two compounds with MW = 133

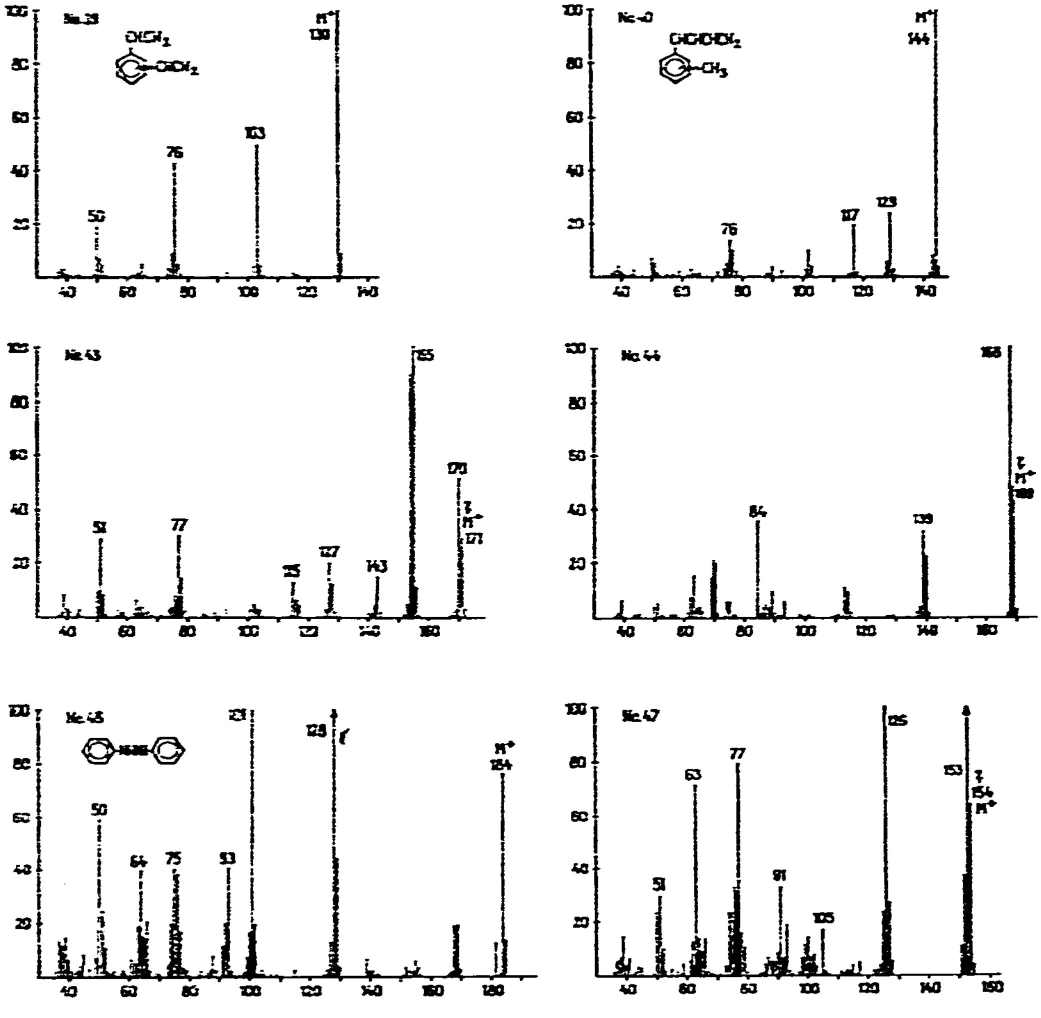


Fig. 13a.

Fig. 13a. Mass spectra 39, 40, 43–45, 47. b. Mass spectra 48–52 taken from the peaks of the gas chromatogram of Fraction C2 (Fig. 9). $Ni(aniline)_2(NO_3)_2 \cdot 0.5H_2O$. The relative abundance is plotted against *m/e*.

and 120, because the cleavage M − 13 is impossible. The structures of the compounds are not known at present.

Spectrum No. 33 (Fig. 8) confirmed the presence of aniline (MW = 93) among the pyrolysis products.

In spectrum No. 34 (Fig. 12) we are again dealing with a mixture of two compounds of aromatic character. The molecular weights are 130 and 143, the latter containing a nitrogen atom. The structures could not be elucidated on the basis of the mass spectrum.

The compound with MW = 117 corresponding to mass spectrum No. 35 (Fig. 12) is a nitrogen-containing aromatic with molecular formula C_8H_7N. It must have one carbon–carbon triple bond. The possible structural formulae are then: $C_6H_5{\cdot}NHC{\equiv}CH$, $C_6H_5{\cdot}C{\equiv}CNH_2$ or $H_2N{\cdot}C_6H_4{\cdot}C{\equiv}CH$ (*o*-, *m*- or *p*-isomers). The strong M − 27 (*m/e* 90) peak eliminates the first and second possibilities. From the

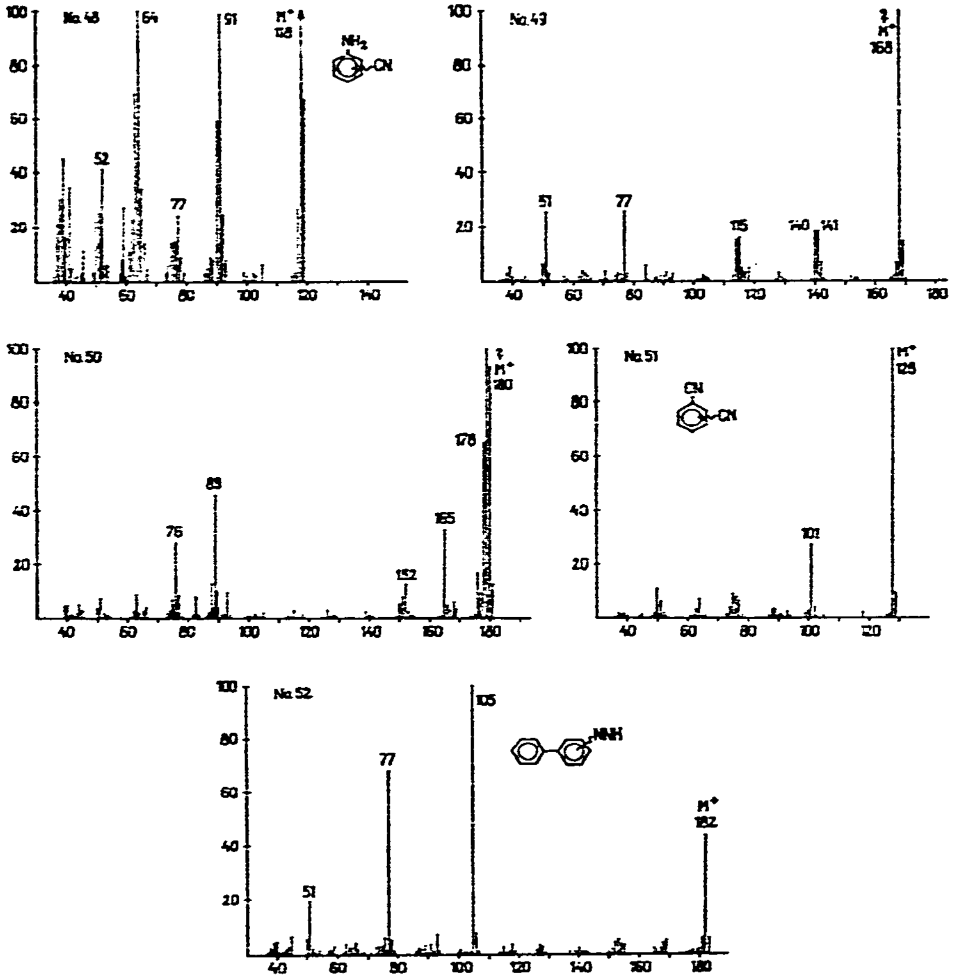


Fig. 13b.

three compounds left the *m*-isomer is outside the range of possibilities, because of the *ortho–para*-directing property of the NH_2 group. The compound is therefore the *ortho* or *para* isomer of $H_2N \cdot C_6H_4 \cdot C \equiv CH$.

The strong fractional number mass peaks in spectrum No. 36 (Fig. 12) (e.g. *m/e* 64.5) point to a compound containing nitrogen. The even molecular weight (130) indicated that there were two nitrogen atoms in the molecule. Furthermore the compound is aromatic but the structure is unknown.

An aromatic compound containing one nitrogen atom (MW = 129) corresponds to spectrum No. 37 (Fig. 12). The M − 27 peak (*m/e* 102) points to the cleavage of HCN. The proposed structure is the *o*-, *m*- or *p*-isomer of $NC \cdot C_6H_4 \cdot CH{=}CH_2$.

Spectrum 38 is similar to spectrum No. 37 (Fig. 12) indicating an isomer of the above compound with MW = 129.

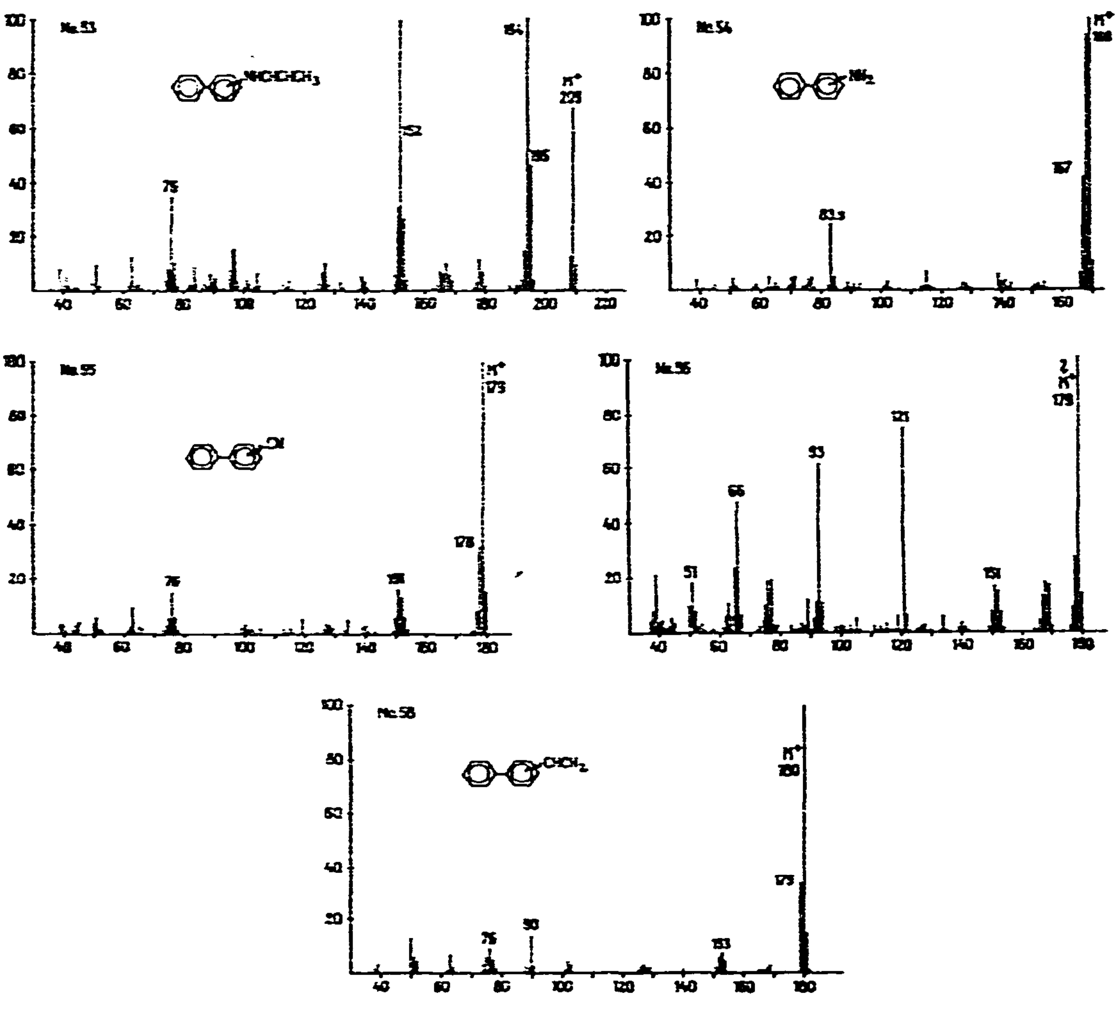


Fig. 14. Mass spectra 53–56 and 58 taken from the peaks of the gas chromatogram of Fraction C3 (Fig. 10). $Ni(aniline)_2(NO_3)_2 \cdot 0.5H_2O$. The relative abundance is plotted against *m/e*.

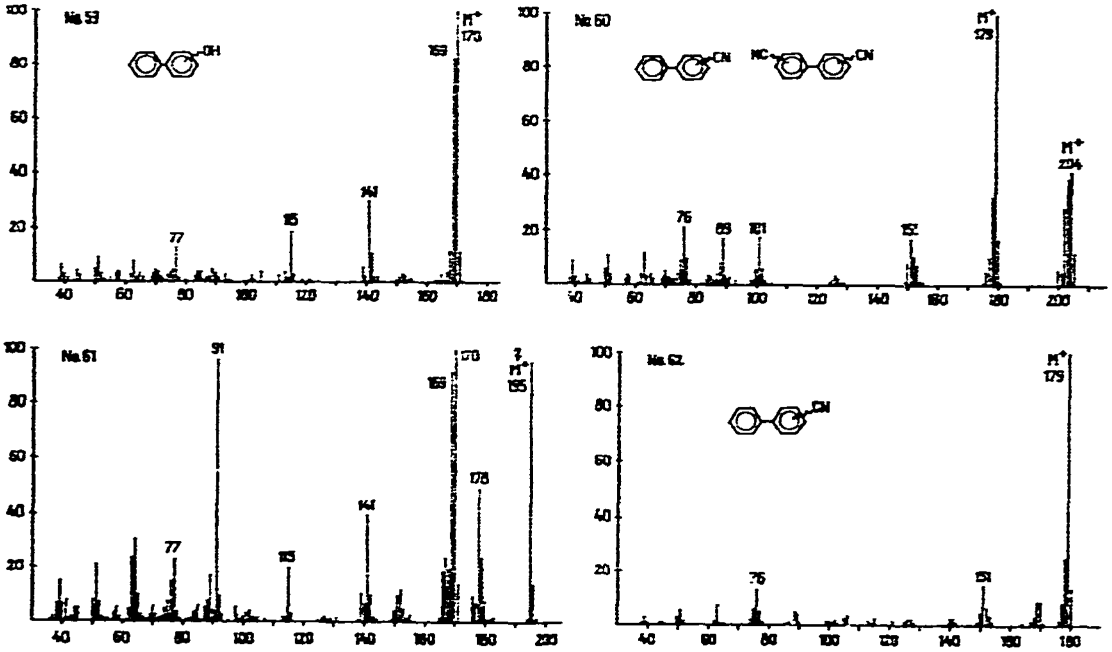


Fig. 15. Mass spectra 59–62 taken from the peaks of the gas chromatogram of Fraction C4 (Fig. 11). Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O. The relative abundance is plotted against *m/e*.

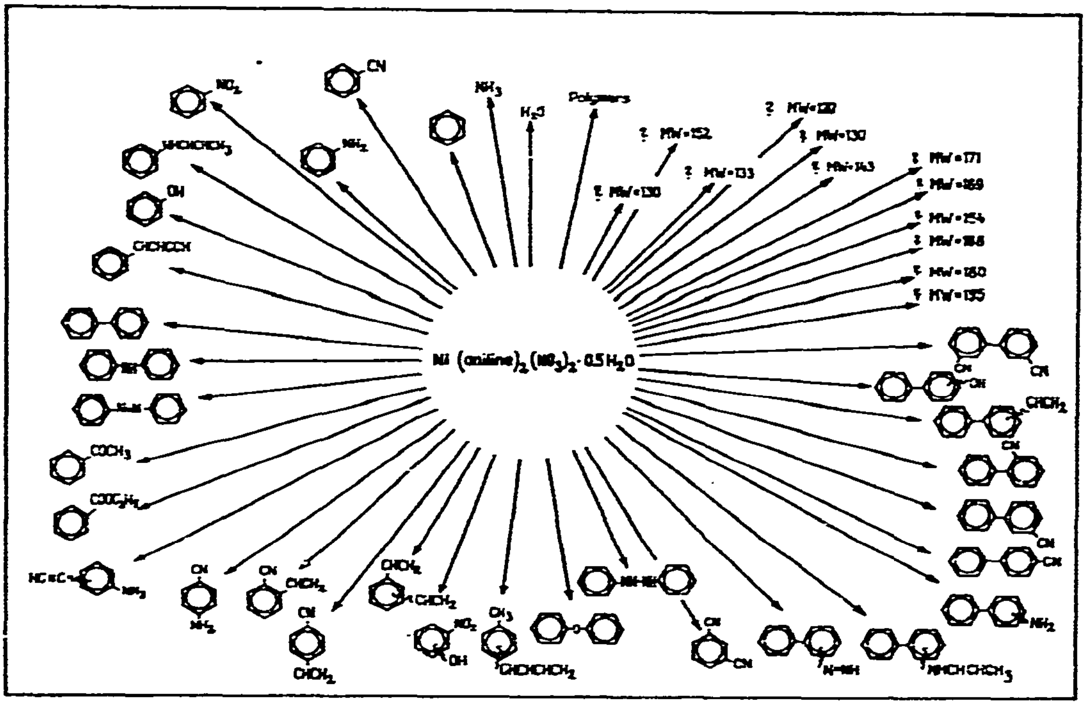


Fig. 16. Summary of the most probable pyrolysis products of Ni(aniline)$_2$(NO$_3$)$_2$·0.5H$_2$O.

On the basis of the mass spectra (a part in Fig. 13) taken from the gas chromatographic peaks (Fig. 9) of Fraction C2 we could assign the following structures to the separated substances.

The compound (MW = 130) represented by spectrum No. 39 (Fig. 13) is aromatic and does not contain nitrogen (cf. spectrum No. 36, Fig. 12). The M − 27 peak (*m/e* 103) can correspond to the cleavage of $\cdot CH{=}CH_2$. Because the intensity of the *m/e* 103 peak is high and that of the peak at *m/e* 77 is low, the compound may be an *o*-, *m*- or *p*-isomer of $C_6H_4 \cdot (CH{=}CH_2)_2$.

The peaks M − 15 (*m/e* 129) and M − 27 (*m/e* 117) in spectrum No. 40 (Fig. 13) of the compound with MW = 144 showed that a $\cdot CH_3$ and $\cdot CH{=}CH_2$ group could be removed from the compound. Furthermore the compound is aromatic and contains no nitrogen. The molecular formula is $C_{11}H_{12}$ and the structural formula may be the *o*-, *m*- or *p*-isomer of $H_3C \cdot C_6H_4 \cdot CH{=}CHCH{=}CH_2$.

The compound corresponding to spectrum No. 41 (Fig. 9) is the previously identified biphenyl $(C_6H_5)_2$, (MW = 154).

Spectrum 42 (Fig. 9) was thought to be from biphenylether, $(C_6H_5)_2O$ (MW = 170) and this was confirmed through a reference spectrum.

Spectrum 43 (Fig. 13) represents an aromatic nitrogen-containing compound (MW = 171), that is a benzene derivative, not a biphenyl derivative. The structure could not be elucidated from the spectrum.

The M − 30 peak (*m/e* 139) in spectrum 44 (Fig. 13) points to the cleavage of NO from an aromatic nitro compound (MW = 169). The compound is a derivative of nitrobenzene. The structure could not, however, be elucidated on the basis of the mass spectrum.

The similarity between spectrum 45 (Fig. 13) and spectrum 46 azobenzene $C_6H_5{-}N{=}N{-}C_6H_5$ (MW = 182) points to hydrazobenzene $C_6H_5 \cdot (NH)_2 \cdot C_6H_5$ (MW = 184).

Spectrum 47 (Fig. 13) corresponds to an aromatic benzene derivative (MW = 154). The structure is unknown.

The compound represented by spectrum 48 (Fig. 13) is an aromatic compound containing two nitrogen atoms (MW = 118). The suggested structure is the *o*-, *m*- or *p*-isomer of $H_2N \cdot C_6H_4 \cdot C{\equiv}N$.

A benzene derivative, probably not containing nitrogen, is represented by spectrum 49 (Fig. 13). The molecular weight is 168, but the structure is unknown.

The compound corresponding to spectrum 50 (Fig. 13) is also an aromatic benzene derivative (MW = 180). The structure is unknown.

Spectrum 51 (Fig. 13) represents an aromatic compound (MW = 128) that can lose HCN. The structure is probably one of the *o*-, *m*- or *p*-isomers of $C_6H_4 \cdot (CN)_2$.

The *o*-, *m*- or *p*-isomer of $C_6H_5 \cdot C_6H_4 \cdot N{=}NH$ (MW = 182) corresponds to spectrum 52 (Fig. 13).

The mass spectra corresponding to the compounds giving the gas chromatographic peaks of Fraction C3 in Fig. 10 are presented in Fig. 14 and discussed below.

The compound (MW = 209) pictured by spectrum 53 (Fig. 14) is a biphenyl derivative that includes at least one easily removable methyl group and one nitrogen atom. There are many possible molecular structures. One of the most probable is the *o*-, *m*- or *p*-isomer of $C_6H_5 \cdot C_6H_4 \cdot NH \cdot (CH)_2 \cdot CH_3$, which could be formed from the compound corresponding to mass spectrum 28 (Fig. 8) through the addition of a phenyl group.

Spectrum 54 (Fig. 14) is very similar to that (spectrum 57) of biphenylamine. The compound (MW = 169) is probably one of the three isomers of aminobiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NH_2$.

The compound (MW = 179) represented by spectrum 55 (Fig. 14) is obviously one of the isomers of biphenylnitrile, $C_6H_5 \cdot C_6H_4 \cdot CN$.

Spectrum 56 (Fig. 14) includes peaks at *m/e* 93 and 121 of very high intensity that are not observed in spectrum 55. The molecular weight is 179 and the compound may be one of the isomers of $C_6H_5 \cdot C_6H_4 \cdot CN$.

The already identified biphenylamine $(C_6H_5)_2NH$ (MW = 169), was also due to spectrum 57 (Fig. 10).

On the basis of spectrum 58 it is suggested that the corresponding compound (MW = 180) is one of the *o*-, *m*- or *p*-isomers of $C_6H_5 \cdot C_6H_4 \cdot CH{=}CH_2$.

The gas chromatographic separation of the components of Fraction C4 was poor (Fig. 11). Therefore it was not possible to get mass spectra of pure compounds.

Mass spectrum 59 (Fig. 15) represents *o*-, *m*- or *p*-hydroxybiphenyl (MW = 170), $C_6H_5 \cdot C_6H_4 \cdot OH$.

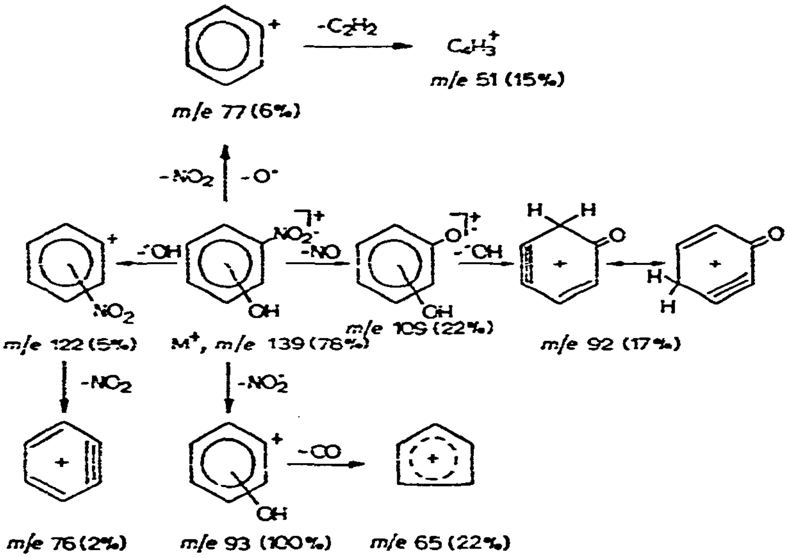
Spectrum 60 (Fig. 15) certainly includes the mass spectra of two compounds (MW = 204 and 179), because the fragmentation *m/e* 204 → 179 is not possible. The compound with MW = 179 could be one of the isomers of the compound represented by mass spectrum 55 (Fig. 14) or one of the biphenylnitriles, $C_6H_5 \cdot C_6H_4 \cdot CN$. The compound with molecular weight 204 is probably one of the isomers of biphenylnitrile, $(C_6H_4 \cdot CN)_2$.

The compound (MW = 195) represented by spectrum 61 (Fig. 15) is a nitrogen-containing aromatic. The structure could not be elucidated.

The compound (MW = 179) of spectrum 62 (Fig. 15) is an isomer of the compound $C_6H_5 \cdot C_6H_4 \cdot CN$ given by spectrum 55 (Fig. 14).

In the preparative separation of Fraction C a considerable amount of brown solid substance remained at the beginning of the column at the end of the work. Considering the gas chromatographic conditions (Fig. 7) it was concluded that the substance was composed of different high boiling and high molecular weight polymers.

In the context of mass spectrum 8 (Fig. 2) taken directly from the total pyrolysis products of nickel(II) aniline nitrate it was interesting to note that in the later separations of the products we did not find the compound giving mainly mass spectrum 8. The compound must have disappeared during the separation processes. On the basis of mass spectrum 8 we could, however, conclude that the compound most probably had been *o*-, *m*- or *p*-nitrophenol, $O_2N \cdot C_6H_4 \cdot OH$ (MW = 139). The fragmentation patterns considered on the basis of the main peaks shown by the mass spectrum are given in the following scheme:



The relative abundances of the mass peaks are given in percentages. The fragmentation first through the nitro group is dominating. The cleavage *m/e* 139 → 111 was not observed. The main peaks presented were all accompanied by satellite peaks with smaller or larger *m/e* ($\leqslant 3-2$ units), the intensity decreasing rapidly with increasing *m/e* increment.

The decomposition products of the nickel(II) aniline nitrate complex considered above have been collected in Fig. 16. The most probable structure or structures have been selected from the many *o*-, *m*- or *p*-isomers previously considered when presenting the structural formulas. The probabilities are based on the substituent-directing properties of the groups situated in the benzene ring.

The distribution of the separated compounds presented in Fig. 2 is to a certain extent, hypothetical. It was based on comparison of the mass spectra 1–15 with those of the separated compounds.

B. $Ni(aniline)_2Cl_2 \cdot H_2O$

According to the previous thermogram (Fig. 1, Ref. 1) water and aniline are lost between 30 and 333 °C in the decomposition process. In the present work the temperature was raised to 350 °C. The decomposition products were collected in a cold bath and analyzed by mass spectrometry. The analysis showed no other compounds besides water and aniline.

C. $Ni(aniline)_2Br_2 \cdot 2H_2O$

The temperature was raised in the decomposition to 350 °C. The collection and analysis of the products carried out as above indicated only water and aniline.

D. $Ni(aniline)_4I_2$

In the decomposition 270 °C was the final temperature. Only aniline was detected.

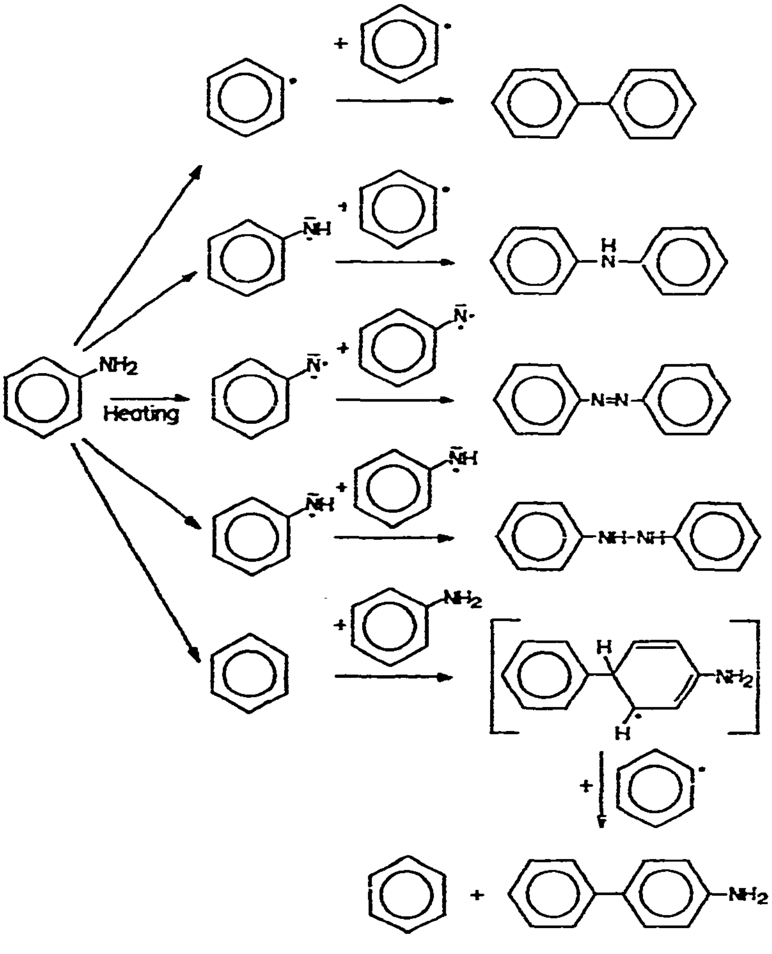
E. Ni(aniline)$_2$SO$_4$

In the case of the decomposition of the nickel(II) aniline sulphate complex, a part of the nickel(II) sulphate formed decomposed before a plateau was reached (Fig. 1, Ref. 1). In the present work the temperature was allowed to rise little by little, when a colourless liquid was condensed into the collection flask in the cold bath. At about 370°C distillation ceased. The analysis confirmed the liquid to be aniline.

CONCLUSION

In the present work it has been possible to show with certainty that by heating the nickel(II) aniline chloride, bromide and iodide complexes the thermal decomposition processes for the organic ligand occur as calculated earlier from the thermograms of the complexes[1].

The process of aniline escape had been completed in the thermal decomposition of the nickel(II) aniline sulphate complex when the temperature had reached 370°C.



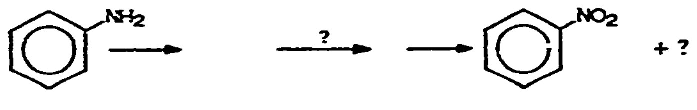
Scheme A.

The weight changes observed after this temperature (370–833 °C) in the thermogram (Fig. 1, Ref. 1) were due to the decomposition reactions of nickel(II) sulphate as concluded earlier[1].

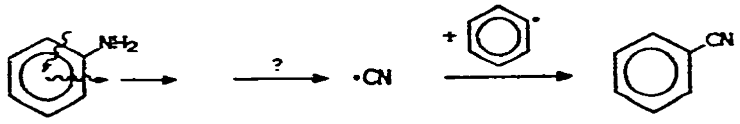
The thermal decomposition of the nickel(II) aniline nitrate complex happens at explosive speed after the temperature has reached a certain value (Fig. 1, Ref. 1). The greatest part of aniline is conserved unchanged. A proportion of the aniline molecules, however, may decompose to fragments of different sizes from which a group of new compounds is formed through combinations. The oxidation of aniline or its fragments may also take place when nitrate groups of the complex act as oxygen donors.

It is not possible to say anything certain about the mechanisms of the reactions without isotope labelling. It is, however, to be expected that the greatest part of the reactions occur as radical reactions. The formation of benzene, biphenyl, biphenylamine, azobenzene, hydrazobenzene and aminobiphenyl (e.g.) from aniline may be assumed to take place as in Scheme A on p. 127.

Nitrobenzene is probably formed directly from aniline by oxidation:



The formation of benzonitrile and other CN-containing compounds is possible only through the rupture of the benzene ring:



It is likely that the formation of different mono- and dialkyl-substituted aniline and benzene derivatives requires the breakdown of benzene rings. The formation of phenol, acetophenone and ethylbenzoate may be thought to take place in so many different ways that it is not reasonable to speculate on the basis of the present data.

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