Identification of the Pyrolysis Products of Some Aromatic Amines using Microwave Spectroscopy

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The pyrolysis products of some aromatic amines have been identified using microwave spectroscopy. Aniline is found to produce 1-cyanocyclopenta-1,3-diene, *N*-methylaniline a mixture of 1-cyanocyclopenta-1,3-diene and benzonitrile, *N,N*-dimethylaniline produces benzonitrile, and *N,N*-dimethylpyridine-2-amine produces pyridine. In the pyrolysis of *N*-methylaniline the proportion of 1-cyanocyclopenta-1,3-diene to benzonitrile is estimated to be 4:1 from the integrated relative intensities of the low-resolution microwave band spectra of the two substances.

Pyrolysis followed by microwave spectroscopy has been used to prepare and identify a number of small molecules of chemical and astrophysical interest.[1] We have attempted to apply this combination of techniques to produce and identify larger molecules of more direct interest to organic chemists. Prompted by the observation that the pyrolysis of methylamine produces methylenimine[2] it was decided to see whether the pyrolysis of *N*-methyl aromatic amines would lead to the production of *N*-phenylimines. Although the desired products were not obtained, the results show that microwave spectroscopy can be used to identify relatively large pyrolysis products and they can also provide some information about the mechanisms involved in the pyrolysis of aromatic amines.

The high resolution and accurate frequency measurements of microwave spectroscopy along with the molecule-specific nature of microwave spectra mean that this method is ideally suited as an analytical technique.[3] In order to identify a molecule whose microwave spectrum is known it is only necessary to measure accurately the frequencies of a small number of lines. The identification of a molecule whose microwave spectrum is not known requires the analysis of the spectra of a sufficient number of isotopically labelled analogues of the molecule to be sure of its molecular structure. Tables of line frequencies[4] are useful for identifying lighter molecules such as ammonia, water, or methanol. The bibliography of Starck[5] which is catalogued by molecular type and molecule, provides summaries of the literature and contains tables of line frequencies and rotational constants.

In this work low-resolution microwave spectroscopy was found to be very useful as a preliminary means of identifying pyrolysis products. A number of types of molecular rotor give low-resolution band spectra.[6] The most common type of band spectrum is the μ_a *R*-branch type given by a near prolate rotor. Many monosubstituted and *para*-disubstituted benzenes and five-membered rings with a single substituent belong to this class of rotor. The band frequencies are given by equation (1), where

$$\nu = (J + 1)\,\overline{B + C} \qquad (1)$$

J is the rotational quantum number of the lower level involved in the transitions and $\overline{B + C}$ is very nearly equal to the sum of the ground vibrational state B_0 and C_0 rotational constants.

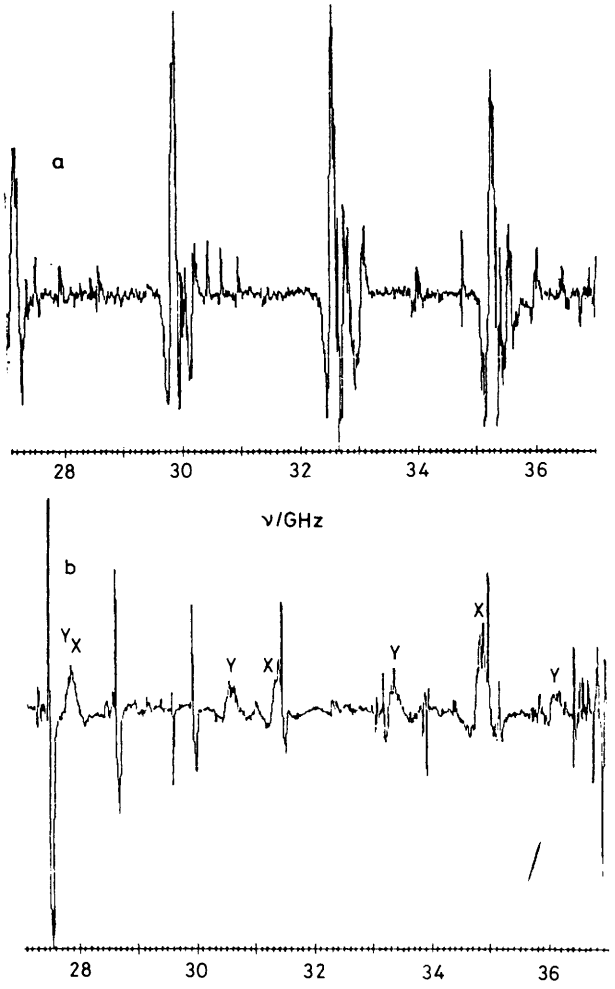


Figure 1. Low-resolution microwave spectrum of (*a*) *N*-methylaniline at room temperature and (*b*) the products of the pyrolysis of *N*-methylaniline at 1 300 K

Results

The first molecule investigated was *N*-methylaniline and its room-temperature low-resolution spectrum is shown in Figure 1(*a*). The value of $\overline{B + C}$ of 2 711 MHz, obtained by the application of equation (1), is in good agreement with the value reported previously.[7] As the temperature of the pyrolysis tube was increased the *N*-methylaniline bands disappeared and at

Table 1. Low-resolution band frequencies, rotational quantum numbers, and $\overline{B + C}$ constants for substance X (1-cyanocyclopenta-1,3-diene) and substance Y (benzonitrile)

	X			Y	
	ν/MHz			ν/MHz	
J	*N*-Methylaniline	Aniline	*J*	*N*-Methylaniline	*N*,*N*-Dimethylaniline
7	27 858	27 901	9	27 858	27 826
8	31 361	31 382	10	30 588	30 591
9	34 886	34 863	11	33 360	33 356
10		38 344	12	36 111	36 122
$\overline{B + C}$/MHz	3 485(3)[a]	3 487(1)		2 781(3)	2 780(1)

[a] Mean deviation in units of the least significant digit.

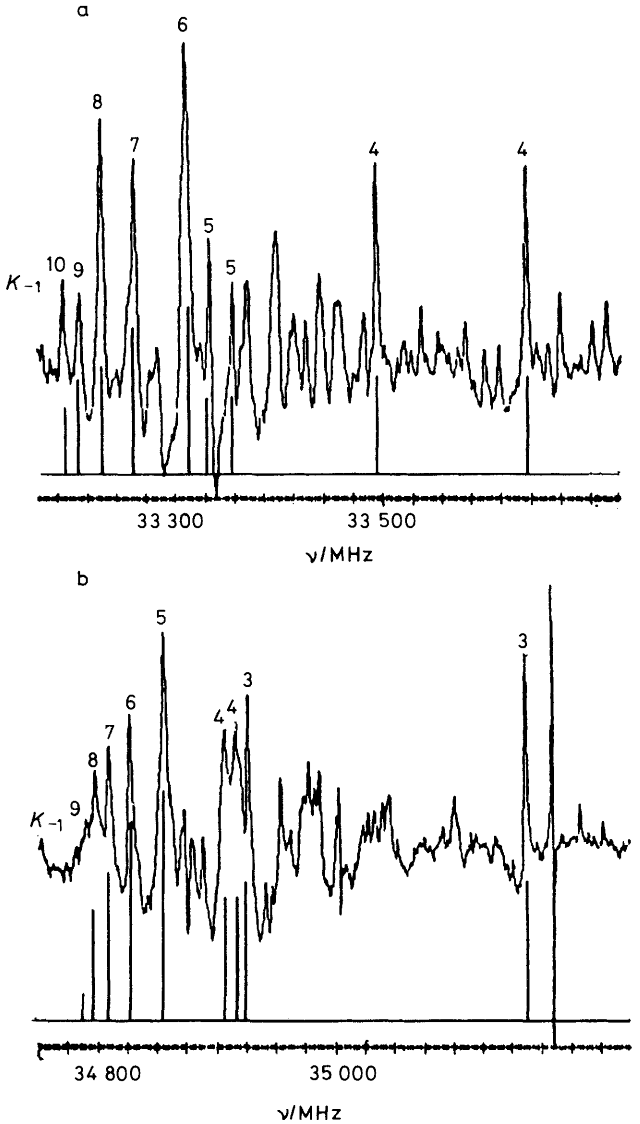


Figure 2. High-resolution spectra of (*a*) the $J = 12 \leftarrow 11$ band of the substance Y (benzonitrile) and (*b*) the $J = 10 \leftarrow 9$ band of the substance X (1-cyanocyclopenta-1,3-diene) showing the assigned ground-vibrational-state lines

1 300 K the spectrum shown in Figure 1(*b*) was observed. The narrow strongest absorptions are single lines due to ammonia, but two series of bands labelled X and Y in the Figure are apparent. The band frequencies and the $\overline{B + C}$ constants are given in Table 1.

Table 2. Comparison of the ground-vibrational-state rotational constants of 1-cyanocyclopenta-1,3-diene and benzonitrile determined with those reported previously

	X	1-Cyano-cyclopenta-1,3-diene[12]	Y	Benzo-nitrile[10]
A_0/MHz	8 352.2(6)[a]	8 356(5)	5 661(4)	5 656.7(1.8)
B_0/MHz	1 904.24(5)	1 904.24(2)	1 547.0(1)	1 546.84(2)
C_0/MHz	1 565.36(5)	1 565.36(2)	1 214.3(1)	1 214.41(2)
Δ_{JK}/kHz	2.40(9)		1.1(1)	
Δ_c/10^{-45} kg m^2	50.71	50.24	−3.87	−1.54

[a] Standard errors in units of the least significant digit.

Figure 2 shows the $J = 10 \leftarrow 9$ band of X and the $J = 12 \leftarrow 11$ band of Y under higher resolution. These spectra served as starting points for analyses intended to obtain the ground-vibrational-state rotational constants (A_0, B_0, C_0) of the substances giving rise to the X and Y spectra. The assignment of lines was made on the basis of expected relative intensities and Stark effects and from fitting of line frequencies to rigid-rotor theory. The stick diagrams beneath the spectra in Figure 2 show the assigned ground-vibrational-state lines and their calculated relative intensities. The lines are labelled by K_{-1}, the limiting prolate symmetric-top quantum number. This procedure gave preliminary rotational constants for X and Y which were used to predict the frequencies of other lines. The final analyses of the measured line frequencies was made using a semirigid rotor Hamiltonian[8] with a single centrifugal distortion constant (Δ_{JK}). The rotational and centrifugal distortion constants are given in Table 2.

The spectra of the pyrolysis products of aniline and *N*,*N*-dimethylaniline are shown in Figure 3. Both spectra show a single series of bands as well as a number of strong single lines most of which are due to ammonia. Table 1 shows that the bands from the pyrolysis of aniline correspond to the bands X and those from the pyrolysis of *N*,*N*-dimethylaniline correspond to the bands Y from *N*-methylaniline. The accurate frequency measurements of a number of transitions of both pyrolysis products confirmed that these were identical with the pyrolysis products of *N*-methylaniline.

The products X and Y were identified using the following considerations. For a rigid planar molecule the quantity Δ_c,

$$\Delta_c = I_a + I_b - I_c$$

where I_a, I_b, and I_c are the principal moments of inertia[9], is zero and for molecules in their ground vibrational state this quantity is typically ±(1—5) × 10^{-45} kg m^2. Table 2 shows that for Y Δ_c is of the order of magnitude expected for a planar molecule.

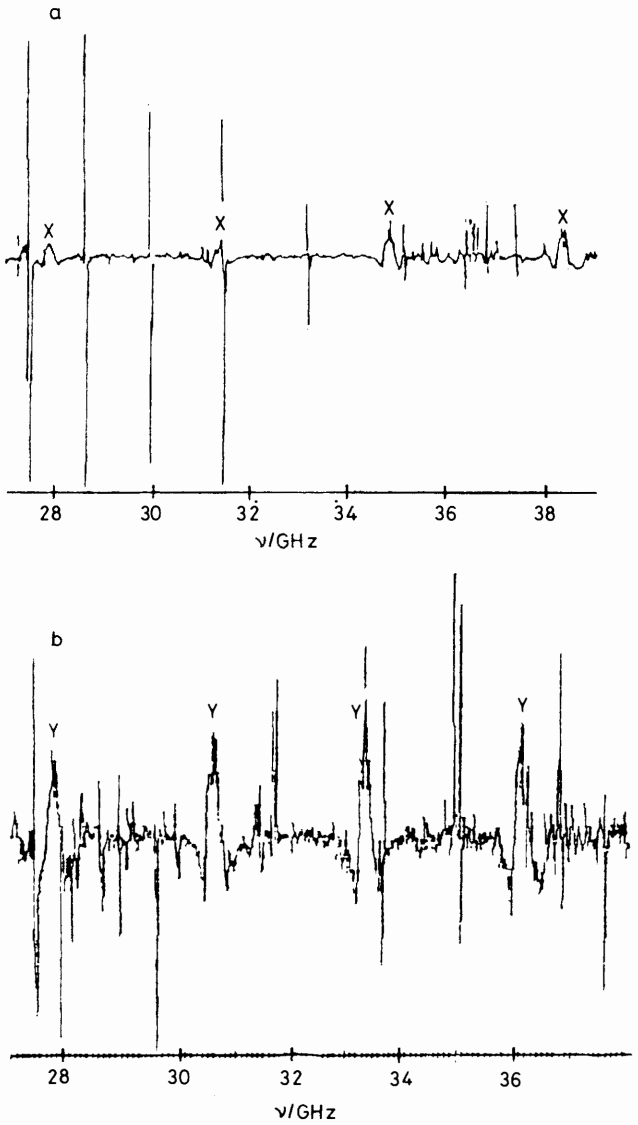


Figure 3. Low-resolution microwave spectrum of the pyrolysis products of (*a*) aniline at 1 200 K and (*b*) *N*,*N*-dimethylaniline at 1 200 K

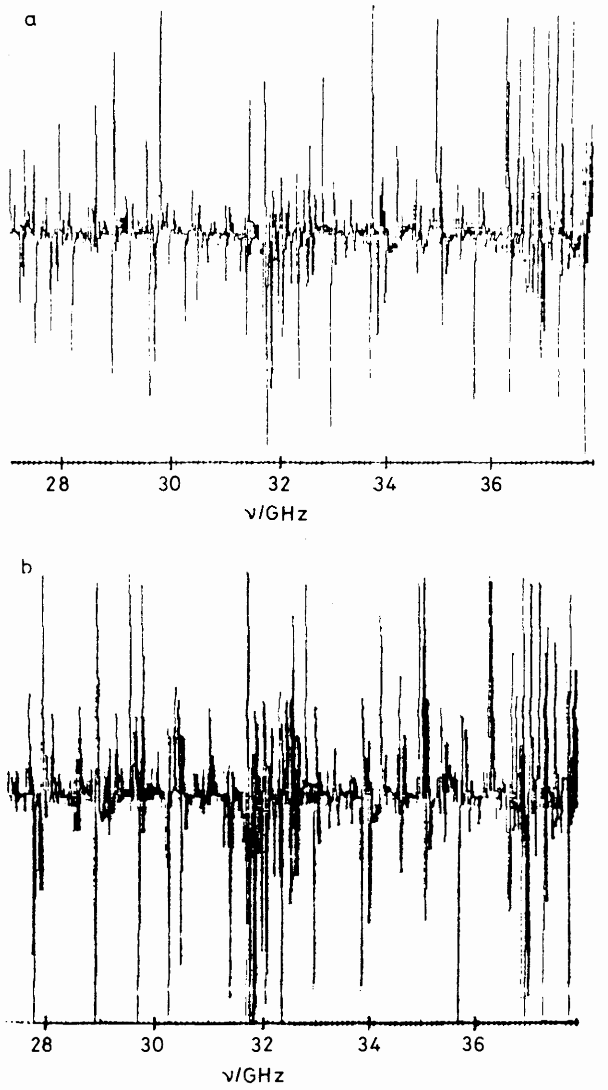


Figure 4. Low-resolution microwave spectra of (*a*) the pyrolysis products of *N*,*N*-dimethylpyridine-2-amine at 1 200 K and (*b*) a sample of pyridine

The value of Δ_c for X (Table 2) is typical of that for a molecule in which the only out-of-plane atoms belong to a methylene or a methyl group. It was noticed that A_0 rotational constant of substance Y was similar to that of a number of monosubstituted benzenes and a search of the Starck bibliography[5] showed the rotational constants of Y to be identical with those of benzonitrile[10] (Table 2). The lack of any intense vibrational satellites in the spectrum of the pyrolysis product X also indicated this to be an unsaturated ring molecule since an acyclic molecule would have at least one low-frequency torsional vibration and a saturated cyclic molecule at least one low-frequency ring-puckering vibration.[11] The larger A_0 rotational constant of X compared with that of Y indicated a narrower ring and a search through the data for five-membered rings in the Starck bibliography showed the rotational constants of X to be identical with those of 1-cyanocyclopenta-1,3-diene[12] (Table 2).

The ratio of the concentration of 1-cyanocyclopenta-1,3-diene to that of benzonitrile produced in the pyrolysis of *N*-methylaniline has been estimated from the ratios of the integrated intensities of the low-resolution bands. The method and some of the approximations used by Bellott and Wilson[13] have been adopted. The integrated intensity (*I*) of a low-resolution microwave band is given in equation (2) where μ_a is

$$I \propto \mu_a^2 N \nu_0^2 (A_0 B_0 C_0)^{\frac{1}{2}} \sigma \Sigma e^{-E_i/kT} S_i \qquad (2)$$

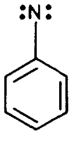
the component of the electric dipole moment along the *a* inertial axis, *N* is the number of molecules in the cell of the species giving rise to the low-resolution band, A_0, B_0, and C_0 are the ground-vibrational-state rotational constants, σ is the symmetry number of the molecule, E_i is the energy of the lower level of the *i*th transition, and S_i is the line strength of this transition. The summation in equation (2) is carried out over the transitions which contribute to the band and are modulated by the Stark effect. For 1-cyanocyclopenta-1,3-diene the μ_a electric dipole component[12] is 1.418×10^{-29} C m and the symmetry number is 1, while for benzonitrile[14] the μ_a electric dipole component is 1.381×10^{-29} C m and the symmetry number is 2. The integrated intensities were estimated by cutting the bands out of recordings of the spectra and weighing them. In this way the ratio of the concentration of 1-cyanocyclopenta-1,3-diene to that of benzonitrile was estimated to be 4:1 with an estimated error of 25% in the ratio.

A final series of experiments was carried out on *N*,*N*-dimethylpyridine-2-amine. This substance shows a weak and complicated spectrum at room temperature. The spectrum of the pyrolysis products shown in Figure 4(*a*) is much stronger than that of *N*,*N*-dimethylpyridine-2-amine but contains no regular series of bands. Figure 4(*b*) shows that the room-temperature spectrum of pyridine is very similar to that of the pyrolysis products shown in Figure 4(*a*). The accurate measurement of the frequencies of a number of lines of the pyrolysis products and those of pyridine confirmed the presence of pyridine in the pyrolysis products.

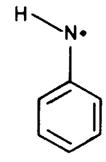
Discussion

The work described here shows that in favourable circumstances microwave spectroscopy can be used to identify relatively large pyrolysis products, a process which is greatly facilitated if they give rise to low-resolution microwave band spectra. In the case of a mixture of products the relative integrated band intensities can be used to estimate the proportions of the products in the mixture. This may be considered to be complementary to the more usual method based on the relative peak or integrated intensities of high-resolution lines.[3] A disadvantage of using microwave spectroscopy to identify pyrolysis products is that non-polar molecules such as benzene do not have a pure rotational spectrum and cannot be detected. A second disadvantage is illustrated in Figure 4(*a*) where the intense and complicated spectrum of pyridine would obscure the spectra of products with weaker and simpler spectra.

Finally we would like to propose possible mechanisms involved in the pyrolysis of aromatic amines. Under the conditions used in this work, temperatures of 1 200—1 400 K, pressures of 3—7 Pa, and relatively slow flow rates it seems likely that the initial stages of reaction involve bond homolysis with the production of radicals. 1-Cyanocyclopenta-1,3-diene has been observed as the principal product in the pyrolysis of phenyl azide,[15] benzotriazole,[15] and isatin.[16] The initial stage in the pyrolysis of phenyl azide is thought to be the formation of phenyl nitrene (**1**) while for benzotriazole and isatin the diradical (**2**) is proposed.



(**1**)

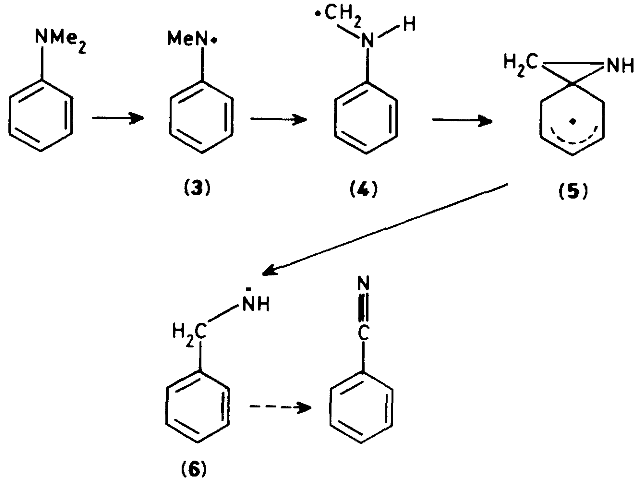


(**2**)

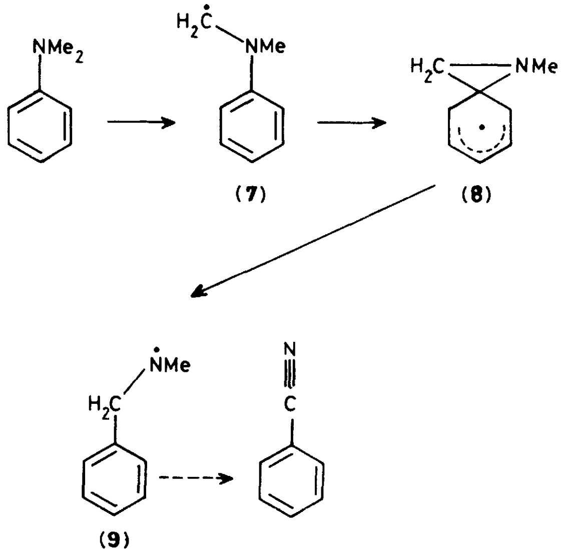
The subsequent steps involved in the formation of 1-cyanocyclopenta-1,3-diene have also been discussed.[15–18] The formation of either (**1**) or (**2**) from aniline requires the homolysis of either the two N–H bonds or an N–H and the *ortho* C–H bond. The fact that lines due to ammonia are observed in the spectrum of the pyrolysis products of aniline also indicates some homolysis of the C–N bond and the production of benzene must occur. The microwave spectrum of ammonia is one of the most intense that has been observed[4] and although the ammonia lines in Figure 2(*a*) are many times more intense than the 1-cyanocyclopenta-1,3-diene bands the relative proportion of benzene formed in the pyrolysis of aniline is unlikely to be more than 10%.

A possible mechanism for the formation of benzonitrile in the pyrolysis of *N*,*N*-dimethylaniline is given in Scheme 1 and an alternative in Scheme 2.

In the case of the pyrolysis of *N*,*N*-dimethylpyridine-2-amine the deactivating effect of the imino group may be expected to make the formation of the intermediates analogous to (**5**) or (**8**) from those analogous to (**4**) and (**7**) rather difficult. The production of pyridine could arise from the homolysis of the C–N bond in *N*,*N*-dimethylpyridine-2-amine or in the intermediates analogous to (**3**) and (**4**) or (**7**).



Scheme 1.



Scheme 2.

In the pyrolysis of *N*-methylaniline two pathways are open: one similar to that in the pyrolysis of aniline and leading to 1-cyanocyclopenta-1,3-diene and the second similar to that described for the pyrolysis of *N*,*N*-dimethylaniline and leading to benzonitrile. It has been observed that methyl cyanocyclopentadienes under pyrolysis conditions aromatize to give benzonitrile,[17,19] so yet another mechanism for the production of benzonitrile from *N*-methylaniline or *N*,*N*-dimethylaniline could involve the migration of a methyl group into the benzene ring followed by the formation of a methyl cyanocyclopentadiene and its aromatization to give benzonitrile.

Experimental

The apparatus used in the experiments described here is shown schematically in Figure 5. The microwave spectrometer was a computer-controlled Stark modulation instrument[20] which can be swept under computer control over a microwave waveguide band[21] in order to produce low-resolution spectra. The

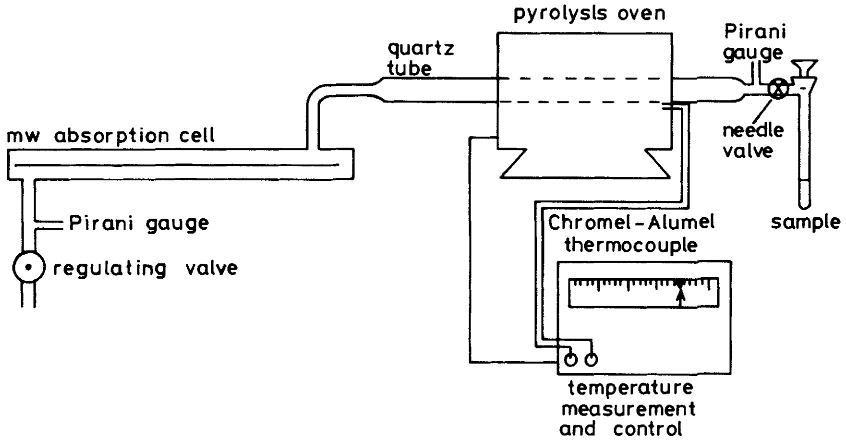


Figure 5. Schematic diagram of the pyrolysis apparatus used

pyrolyses were carried out in a 21-mm diameter (outside) quartz tube heated over a length of 42 cm in an electric furnace capable of reaching a temperature of 1 400 K. Pressure measurement and control were made using Pirani or thermocouple gauges and regulating and needle valves located as shown in Figure 5. Temperature measurement and control were made with a Chromel–Alumel thermocouple inserted in the furnace alongside the pyrolysis tube. Typically, a sample pressure of 4—7 Pa was maintained in the region in front of the oven and the flow rate was adjusted to give a pressure of 3—4 Pa at the exit from the microwave absorption cell. Under these conditions the aromatic amine was consumed at a rate of *ca.* 10 µmol h^{-1}.

The samples of *N*-methylaniline and *N*,*N*-dimethylaniline (supplied by Carlo Erba; both 99% pure by g.l.c.) were those used in previous microwave studies.[7,22] Aniline (supplied by Merck; 99.5% pure by g.c.) and *N*,*N*-dimethylpyridine-2-amine (supplied by Aldrich–Europe; 97% pure by i.r.) were used without further purification.

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