

## SHORT COMMUNICATION

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### The thermal oxidation of pyrrolidine

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Thermal oxidation of most nitrogen-containing compounds causes yellow-brown substances to be formed, the depth of colour usually depending on the degree of oxidation. The product is always a complex mixture which is not susceptible to satisfactory analysis. In this study, the main product from the relatively mild thermal oxidation of pyrrolidine was identified. Subsequently, a pure sample of the main product was submitted to thermal oxidation and its main product was identified. Continuation of this step-wise process, with thin-layer chromatography as the main analytical method, enabled part of the chemical pathway by which pyrrolidine is transformed to a brown material to be elucidated. In the chain of compounds that has been identified, the last, 2-hydroxy-5-(N-2,5-dioxypyrrolidyl)-pyrrole contains a chromophore and readily undergoes polymerization to yield a brown resin. The evidence suggests that brown substances are polymeric and that they contain several different chromophores in the same molecule.

#### *Experimental*

Chromatographic plates were prepared in the standard manner with the Shandon equipment, the spreader gap being 250  $\mu\text{m}$ . The slurry consisted of silica gel GF<sub>254</sub> (Merck) and water (5 g+10 ml per 20 cm  $\times$  20 cm plate). After the freshly coated plates had dried (30 min), the adsorbent was activated by heating the plates at 105°C for 1 h. Chromatographic plates were stored in a desiccator until required.

Individual compounds were characterized by u.v. spectrometry (Unicam SP 500), i.r. spectrometry (Unicam SP 100) mass spectrometry and elemental microanalysis.

*Oxidation of pyrrolidine.* Air was bubbled through boiling pyrrolidine at 12.5 ml min<sup>-1</sup> for 5 h. The resulting brown mixture was evaporated under reduced pressure to near dryness, the residue was dissolved in some water, and a sample of the solution was chromatographed on silica gel together with the reference compounds pyrrolidine, 2-pyrrolidone and succinimide, with ethanol

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as eluent. Chromatograms were viewed in u.v. radiation ( $\lambda_{\max}=254$  nm and 365 nm) and also after treatment with iodine vapour and with Ehrlich's reagent<sup>1</sup>. Figure 1 shows that the oxidized sample contains components which have  $R_F$  values identical with those of pyrrolidine, 2-pyrrolidone and succinimide, as well as five other components, two of which (components 5 and 8) were rendered visible only with Ehrlich's reagent; presumably, they are trace components. Component 6 appears to be the main product.

Analytical quantities of component 6 were obtained by preparative thin-layer chromatography with ethanol as both the eluent and the extractive solvent (Found: 56.4% C, 8.45% H, 16.35% N; calculated for 2-pyrrolidone: 56.5% C, 8.2% H, 16.5% N). The i.r. spectrum of component 6 was identical with that of 2-pyrrolidone. Hence, component 6 is 2-pyrrolidone.

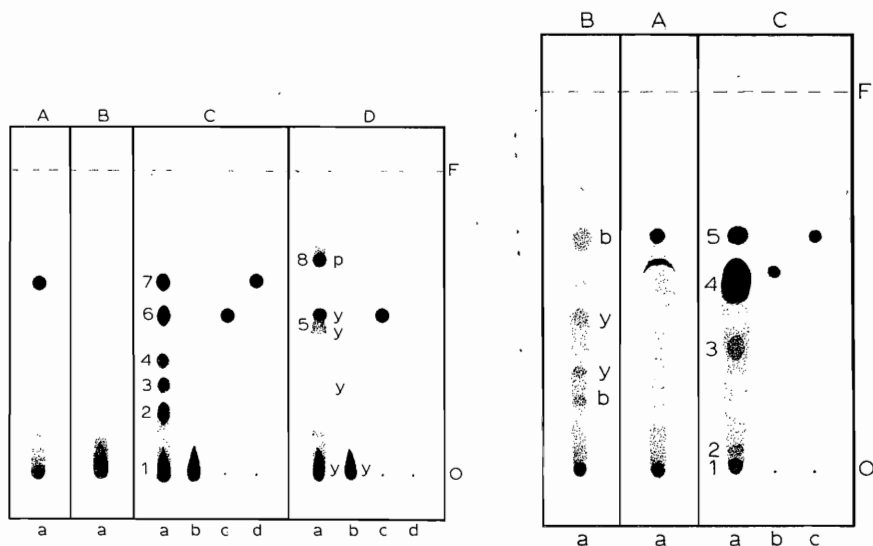


Fig. 1. Chromatogram of oxidized pyrrolidine on silica gel GF<sub>254</sub>. Solvent: ethanol. Detection: (A) u.v. light ( $\lambda_{\max}=254$  nm); (B) u.v. light ( $\lambda_{\max}=365$  nm); (C) iodine vapour; (D) Ehrlich's reagent. (a) Oxidized pyrrolidine (150  $\mu$ g); (b) pyrrolidine (25  $\mu$ g); (c) 2-pyrrolidone (25  $\mu$ g); (d) succinimide (25  $\mu$ g). p=Purple; y=yellow.

Fig. 2. Chromatogram of oxidised 2-pyrrolidone on silica gel GF<sub>254</sub>. Solvent: ethanol. Detection: (A), (B), (C) as in Fig. 1. (a) Oxidized 2-pyrrolidone (200  $\mu$ g); (b) 2-pyrrolidone (25  $\mu$ g); (c) succinimide (25  $\mu$ g). b=Blue; y=yellow.

**Oxidation of 2-pyrrolidone.** Air (at 12.5 ml min<sup>-1</sup>) was bubbled through 2-pyrrolidone maintained at 150°C for 15 h. The resulting brown liquid was dissolved in water, and a sample of the solution, together with samples of the reference compounds 2-pyrrolidone and succinimide, were chromatographed on silica gel with ethanol as the eluent. Figure 2 shows that component 5 has an  $R_F$  value identical with that of succinimide. Analytical amounts of component 5 were obtained by preparative t.l.c. After recrystallization from acetone and sublimation under reduced pressure, a sample had m.p. = 126°C (mixed melting point with authentic succinimide, 126°C). (Found: 48.65% C, 5.0% H, 14.25% N; calculated for succinimide: 48.5% C,

5.05% H, 14.1% N). The i.r. spectrum of component 5 was identical with that of succinimide. Hence component 5 is succinimide.

**Oxidation of succinimide.** Succinimide was boiled under reflux for 1 h in the presence of air, the resulting dark brown solid was treated with acetone, and the extract was examined by t.l.c. The only product appeared to be a brown material. Subsequently, the solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from acetone. After crystals of succinimide had been filtered off, this process was repeated to yield a mother liquor richer in oxidation products than the initial extract. A sample of this solution was chromatographed by the two-development technique with ethyl acetate as the eluent. Figure 3 shows that the mixture, although it contains many fluorescent compounds, contains essentially components 1, 2, and 3, the last component being succinimide. A small amount of compounds 1 plus 2 was obtained by preparative t.l.c. with ethyl acetate as the eluent and acetone as the extractive solvent. The crude sample (of compounds 1 plus 2) was dissolved in boiling ethyl acetate and filtered through a pre-washed plug of silica gel. After the solution had been evaporated to near dryness, the white, crystalline product was freeze-dried (24 h.).

Heat and u.v. radiation caused components 1 and 2 to isomerize (and, in the case of heat, to form brown compounds when the exposure time exceeded that described below) as is illustrated in Fig. 4. A sample (50  $\mu$ g.) containing a mixture of components 1 and 2 was chromatographed by the two-development technique in two dimensions with ethyl acetate as the eluent. After the first development,

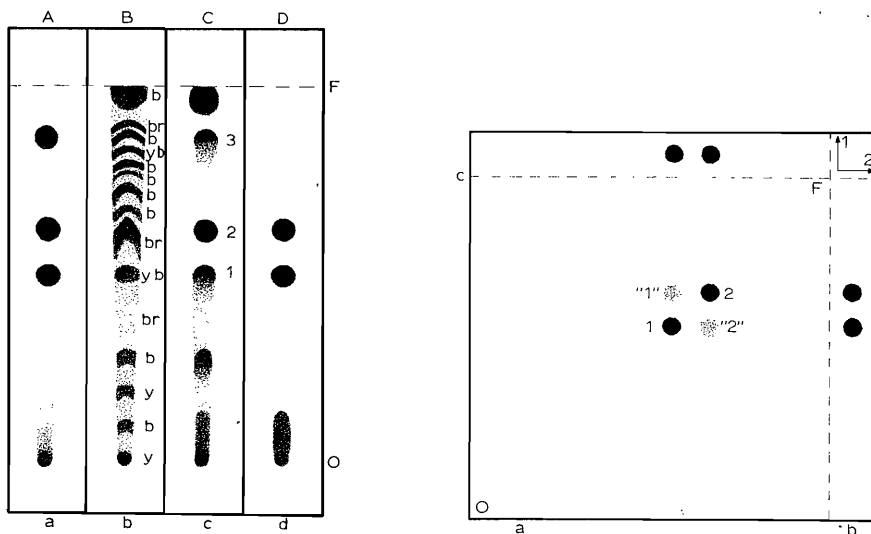


Fig. 3. Chromatogram of oxidised succinimide on silica gel GF<sub>254</sub>. Solvent: ethyl acetate; two developments, each to a distance of 15 cm. Detection: (A), (B), (C) as in Fig. 1; (D) concentrated sulphuric acid. (a), (b), (c), and (d) = Oxidized succinimide (50  $\mu$ g), Y = yellow; b = blue; br = brown.

Fig. 4. Chromatogram of the oxidation products of succinimide on silica gel GF<sub>254</sub>. Solvent: ethyl acetate in both directions; two developments in each direction, each to a distance of 15 cm. Spray: concentrated sulphuric acid. (a), (b), and (c) A mixture of components 1 and 2 (25  $\mu$ g).

the chromatoplate was heated at 110°C for 5 min before it was developed in the second direction. In this chromatogram, unchanged compounds will lie on the diagonal OF (*i.e.* components 1 and 2) whereas compounds formed during the intermediate heating process will be situated away from the diagonal (*i.e.* components "2" and "1"). Figure 4 shows that some of component 1 has been converted to component 2, and some of component 2 to component 1 by the action of heat. Hence, components 1 and 2 are interconvertible.

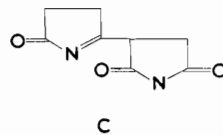
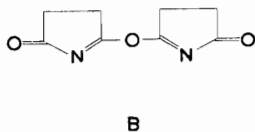
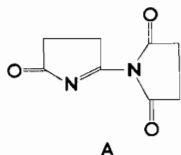
An exactly similar experiment in which the chromatoplate was exposed to u.v. radiation ( $\lambda_{\max}=254$  nm) for 1 h, produced a chromatogram identical with that shown in Fig. 4. Hence, u.v. energy also causes the isomerization.

On changing the pH of a solution containing components 1 and 2, with aqueous 1% hydrochloric acid or ammonia, different ultra-violet absorbing species are formed, and the conversion is reversible provided that the exposure to alkali is short; this indicates keto-enol tautomerism. (Found: 53.25% C, 4.55% H, 15.35% N, corresponding to the empirical formula,  $C_8H_8N_2O_3$ .) The i.r. spectrum of components 1 plus 2 shows several carbonyl peaks, but yields very little other information concerning their structure. The mass spectrum of a mixture of components 1 and 2 shows a molecular ion peak at  $m/e=180$ . Two abundant fragments have  $m/e$  values of 96 and 84. After hydrolysis of a sample of the mixture with thoroughly degassed 6 *M* hydrochloric acid (1.5 ml.) at 110°C for 24 h in a sealed tube, t.l.c. showed that the hydrolysate consisted mainly of succinic acid together with a small amount of an oxygen-rich, unstable polybasic acid.

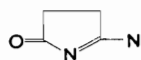
Another sample of brown solid from the oxidation of succinimide was dissolved in water and dialysed against tap-water (72 h) and distilled water ( $3 \times 2$  l; 24 h each). The resulting solution was evaporated to dryness under reduced pressure to yield a brown solid. (Found: 53.2% C, 3.55% H, 15.0% N; *cf.* components 1 and 2, 53.25% C, 4.55% H, 15.35% N.) The i.r. spectrum of the brown material was uninformative. A chromatographic investigation of this material showed that it contained neither succinimide nor components 1 and 2, and its dialytic behaviour indicates that it is polymeric.

### Discussion

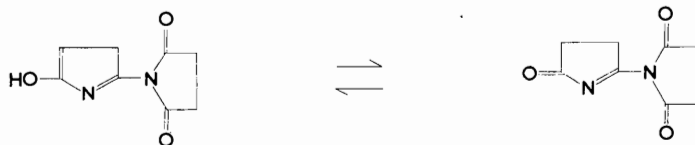
The empirical formula of components 1 and 2 (from the oxidation of succinimide) is  $C_8H_8O_3N_2$ , the molecular weight is 180 and they are formed from succinimide. Three possible structures are:



All of these can form tautomers but only structure A is supported by the mass spectrum which indicates fragments having molecular masses of 96 and 84, corresponding to:



It is concluded that components 1 and 2 are, respectively,



and the polymeric brown substances have the idealized structures:

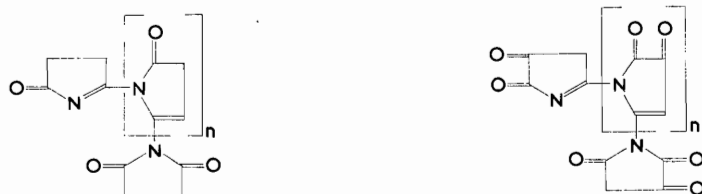


Table 1 shows the compositions of the repeating units in these oligomers. The brown product from the oxidation of succinimide is not likely to be a mixture of these two model oligomers, because the repeat units are interchangeable; in any particular molecule they may occur in any ratio.

In polymers of this type, the magnitude of an individual chromophore, *i.e.*, the wavelength at which it exhibits maximum absorption, depends on the extent to which it has been oxidized as well as on the size of the molecule. Consequently, a mixture composed of oligomers will absorb energy of many different wavelengths and will appear brown. Although these ideas have been developed from experiments based on derivatives of pyrrolidine, investigations not described here indicate that they are also applicable to the formation of brown materials from other cyclic compounds containing nitrogen, *e.g.*, piperidine and caprolactam.

### Conclusion

Pyrrolidine is oxidized to brown material via 2-pyrrolidone and succinimide which undergoes dimerization, thus:

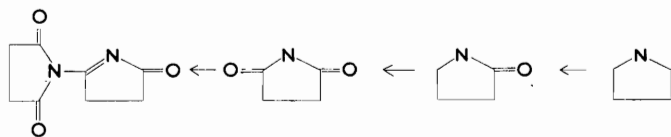


TABLE I

COMPOSITION OF BROWN MATERIAL AND VARIOUS POSTULATED MODEL COMPOUNDS

Calculated for repeat unit	C (%)	H (%)	N (%)	O (%)
$C_4H_3N_1O_1$	59.3	3.7	17.3	19.7
$C_4H_1N_1O_2$	50.5	1.1	14.7	33.7
Found	53.2	3.5	15.0	28.25

Subsequently, the dimer polymerizes to yield the brown material. The observed composition of the brown material is consistent with the composition of the polymer which would result by continuing the condensation.

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#### REFERENCES

- 1 J. G. Kirchner in E. S. Perry and A. Weissberger (Eds.), *Technique of Organic Chemistry*, Vol. XII, Interscience, New York, 1967, p. 158.