An investigation of the polymerization of pyridine with epoxy compounds

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The chemical reaction between pyridine and epoxy compounds has been investigated. This reaction disrupts the aromatic nature of the heterocyclic ring of pyridine, resulting in the formation of a polymeric material that contains cyclic amide structures. The polymer formed is not due to the homopolymerization of the epoxy groups. Based on the spectral studies, a reaction scheme is proposed. The order of reactivity for different pyridine derivatives has been obtained.

(Keywords: pyridine; epoxy ring; pyridinium salt; pyridone; *N*-substituted lactam)

INTRODUCTION

Pyridine and its derivatives exhibit full aromatic character. The similarity of pyridine to benzene with respect to their aromatic stability is well known. Pyridine also behaves as a weak monoacidic tertiary base. It was reported[1] that pyridine could induce the polymerization of epoxy compounds, albeit to a low degree. We found that pyridine derivatives, especially 4-alkylpyridine and pyridine, can combine with epoxy groups to form polymeric materials. These reactions do not result in the homopolymerization of the epoxy groups, but disrupt the aromatic nature of pyridine rings. In this paper we report the reactions, propose a possible reaction scheme and describe the structure of the reaction products.

EXPERIMENTAL

Pyridine derivatives and epoxy compounds were purchased from Aldrich Chemical Co. Inc. They were properly dried before use. Each pyridine derivative was mixed with an epoxy compound in a molar ratio of 1:1 or 1:2. The mixtures were heated to 110°C or 140°C. Samples were withdrawn and the structures were determined by Fourier transform infra-red spectroscopy (*FT*i.r.), ultraviolet absorption spectroscopy (u.v.) and gel permeation chromatography (g.p.c.).

RESULTS AND DISCUSSION

Spectrum A in *Figure 1* illustrates the initial mixture of 4-ethylpyridine and 1,4-butanediol diglycidyl ether in a molar ratio of 2:1. The mixture was a transparent colourless liquid. After heating at 140°C for 20 s, it became a yellow liquid. Continuous heating at this temperature changed the colour to dark blue, while the mixture became more viscous. After 5 min, a rubber-like solid material was formed. Spectrum B in *Figure 1* was obtained from the sample withdrawn from the reaction mixture just before solidification. Major spectral changes are apparent. After reaction, the intensity of the band at 915 cm^{-1}, which is assigned to a terminal epoxy group, was reduced by approximately 80%. The bands at 830 and 780 cm^{-1} are due to the CH out-of-plane bending modes of 4-substituted pyridine. The bands in the region 3030–3060 cm^{-1} are due to aromatic CH stretching modes. These bands are present in spectrum A, but their intensities are substantially reduced in spectrum B. All these spectral changes indicate that most of the epoxy ring and the aromatic ring of the reactants were consumed after the reaction had proceeded for 5 min at 140°C. This result was unexpected because the aromatic ring of pyridine is considered to be quite stable even under severe environments[2]. In order to follow the reaction, we carried it out at 110°C instead of 140°C, under nitrogen. The reaction rate was slowed down, and the possible influence of oxygen and water in the air was excluded. *Figure 2* shows the i.r. spectra of samples withdrawn at various reaction times. After reaction for 4 min, a new band appeared at 1670 cm^{-1} located in the region of the C=O stretching modes. After 12 min, a new band appeared at 1640 cm^{-1}, which is consistent with an unconjugated C=C group. The ring stretching modes, which display two strong absorption bands at 1600 and 1420 cm^{-1} and a weak absorption band at 1560 cm^{-1}, gradually reduced in intensity. The epoxy band at 915 cm^{-1} was reduced at the same time. All these spectral changes indicate that the epoxy ring and the pyridine ring of the reactants were disrupted, and the polymeric material formed in the reaction probably contains C=O and C=C groups.

The pyridine ring is quite stable to many chemicals owing to the conjugated structure of the six-membered ring. But there is a pair of unshared electrons on the nitrogen atom, which are not involved in conjugation or

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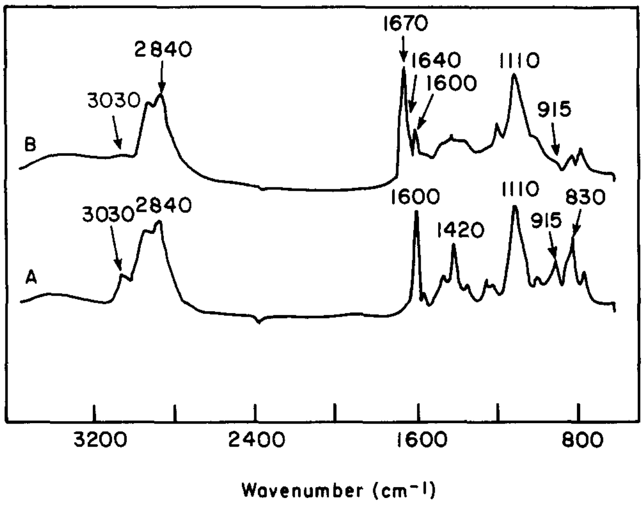

Figure 1 I.r. spectra of a mixture of 4-ethylpyridine and 1,4-butanediol diglycidyl ether: spectrum A, before reaction; B, after reaction

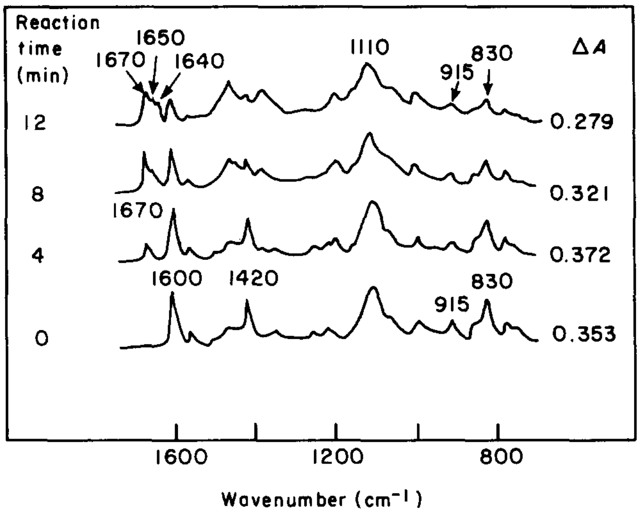

Figure 2 I.r. spectra of a mixture of 4-ethylpyridine and 1,4-butanediol diglycidyl ether after various reaction times

delocalization with the ring system. The unshared electrons are available for bonding with a proton to give a pyridinium cation. The pyridine may also form quaternary ammonium salts of various types[3,4]. Pyridinium salts differ from pyridine in their stability to nucleopholic attack. They are highly susceptible to attack by ammonia, water or sodium hydroxide, etc.[5,6]. In certain cases the nucleophilic attack results in the formation of *N*-alkylpyridone[7,8]. Pyridone has a vibration absorption in the i.r. region at 1650–1660 cm^{-1}, and a u.v. absorption at 300 nm (refs. 9 and 10).

By analogy, the nitrogen atom of pyridine may attack the three-membered epoxy ring upon heating, forming pyridinium salts, which are reactive and may undergo further reactions.

Figure 3 shows the u.v. spectra of 4-ethylpyridine (spectrum A), 1-methylpyridone (spectrum B) and the reaction mixture (spectrum C) that was withdrawn from the reaction system of 4-ethylpyridine and 1,4-butanediol diglycidyl ether. The bands at 253 nm in spectra A and C are assigned to the B-band absorption of pyridine[11]. The bands at 300 nm in spectra B and C are due to the pyridone structure. From the intensities of these bands, the molar absorptivities of each group and the concentration of the solution used for the u.v. determination, we calculated that, after the reaction has proceeded for 15 min at 110°C, 9% of the pyridine has changed to pyridone, 40% of it has remained as pyridine, and the polymeric material may account for the other 51%

According to our spectral studies and a literature survey, we propose a possible reaction scheme for the reaction of 4-ethylpyridine and an epoxy compound as shown in *Figure 4*. The reactions include salt formation as the first step. The R–CH–O$^-$ species of the salt is a strong nucleophilic reagent. It can be postulated that in the second step the R–CH–O$^-$ species attacks positions 2 or 6 of the pyridinium ring, forming a –N–C–O– structure, which may rearrange to carbonyl upon heating[12,13]. It should be noted that so far there is a conjugated 3,5-diene in the six-membered ring instead of whole-ring aromatic conjugation. The 3,5-diene can probably be polymerized through the Diels–Alder reaction. Accordingly there are two possible paths for –N–C–O– rearrangement. As the third step of the reaction, a polymer is formed through the polymerization of the 3,5-diene, and this is then followed by a rearrangement to form an amide structure. The polymer contains carbon–carbon isolated double bonds, which show i.r. absorption band at 1640 cm^{-1}, as well as amide bonds, which have i.r. absorption at 1670 cm^{-1}, as shown in *Figures 1* and *2*. Rearrangement may also occur before polymerization, forming a pyridone structure,

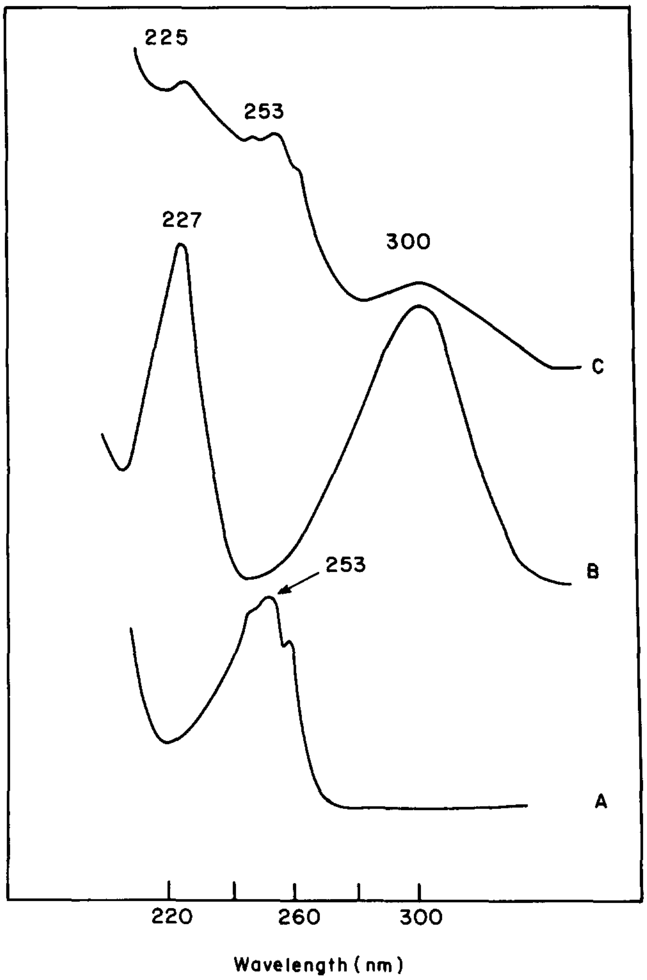

Figure 3 U.v. spectra of samples in ethanol solution: spectrum A, 0.006% 4-ethylpyridine; B, 0.002% 1-methylpyridone; C, 0.028% reaction mixture

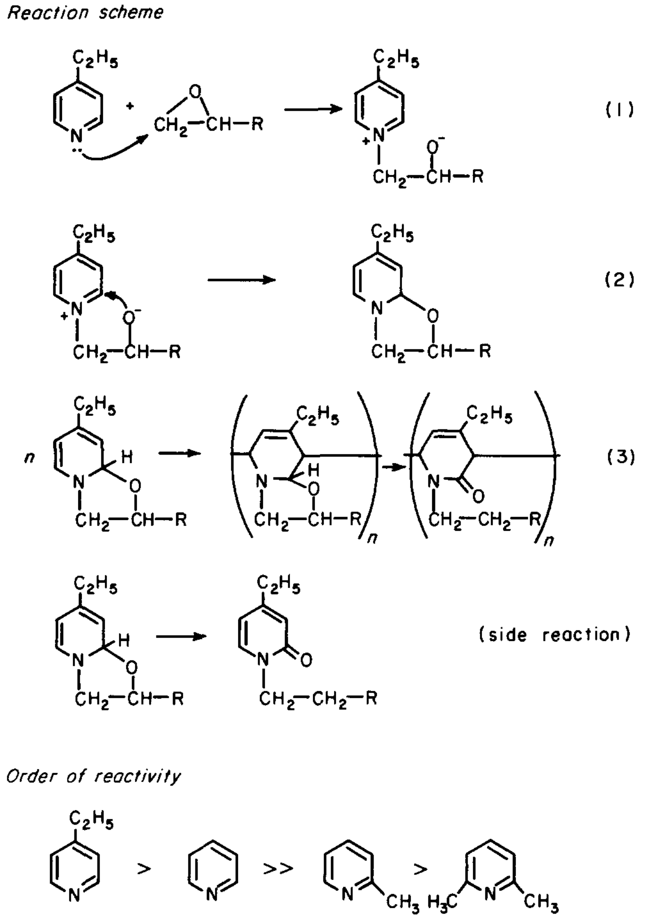

Figure 4 Proposed reaction scheme for 4-ethylpyridine and an epoxy compound. R represents the remaining part of the epoxy compound. Also shown is the order of reactivity of various pyridine derivatives

which shows i.r. absorption at 1650 cm^{-1}. According to the u.v. study, pyridone formation is a side reaction.

Pyridine and its derivatives can react with many kinds of epoxy compounds. With a diepoxide, such as 1,4-butanediol diglycidyl ether, a rubber-like polymer forms owing to crosslinking, and does not dissolve in solvents. With a monoepoxide as the reactant, such as allyl glycidyl ether or styrene oxide, linear polymer chains can form. These linear chains can be dissolved in some polar solvents, such as acetone, alcohols, etc. They do not dissolve in non-polar solvents, such as cyclohexane.

Evidence of combination of pyridine and epoxy group was obtained by g.p.c. *Figure 5* shows the chromatogram of the reaction mixture of 4-ethylpyridine with allyl glycidyl ether, after reaction for 25 min at 110°C. The molecular weight scale is calibrated with standard polyoxymethylene for the low-molecular-weight materials and a u.v. detector was used. One can see the peaks due to pyridine, pyridone and oligomers, which are tentatively assigned to dimer, trimer and tetramer. Owing to the limited solubility of the polymer in THF (tetrahydrofuran, a solvent used in g.p.c.), we cannot obtain the peaks for polymer. The chromatogram shows evidence of the combination of pyridine and the epoxy groups, because only pyridine and its reaction products show u.v. activity in this system and therefore can be detected.

Since pyridine was reported to induce the polymerization of epoxy resins[1], it is necessary to distinguish the homopolymerization of the epoxy groups and the polymerization with pyridine as we proposed above. As we know, the homopolymerization of the epoxy groups will increase the amount of ether structure. I.r. spectra of alkyl ethers display an antisymmetric C–O–C stretching band at 1110 cm^{-1}. In *Figures 1* and *3*, the spectra of the initial mixtures of 1,4-butanediol diglycidyl ether and pyridine show strong absorption at 1110 cm^{-1}. After reaction, the intensity of this band does not show any major increase as compared with the CH stretching mode at 2853 cm^{-1}. *Figure 6* shows a more precise comparison. Spectrum A in *Figure 6* is the initial mixture of 1,4-butanediol diglycidyl ether and 4-ethylpyridine with an equal weight of chloroform. After the reaction has proceeded for 15 min at 110°C, a sample was withdrawn, mixed with an equal weight of chloroform, and spectrum B was obtained. Care was taken to minimize the evaporation of chloroform during the handling and i.r. examination. The band at 758 cm^{-1}, which is due to the CCl group, is used as the internal thickness band. Comparison of the intensity of the C–O–C band at 1110 cm^{-1} shows that the amount of alkyl ether did not significantly increase after reaction. Recently, it has been

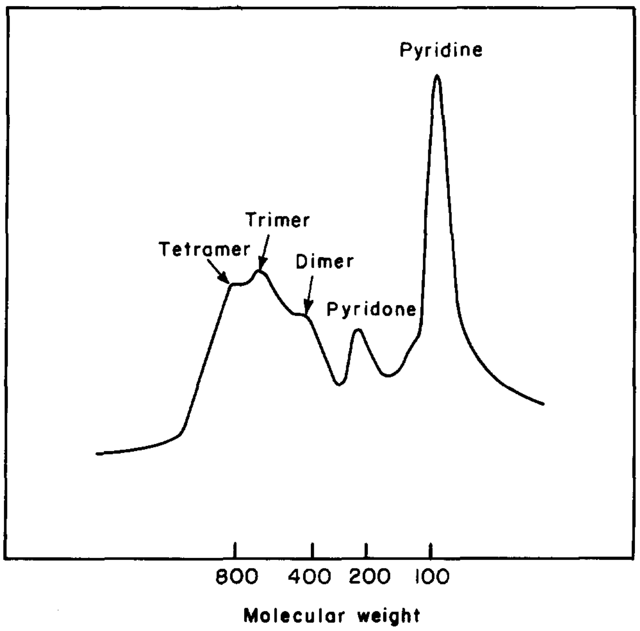

Figure 5 G.p.c. chromatogram of the reacted mixture of 4-ethyl pyridine and allyl glycidyl ether

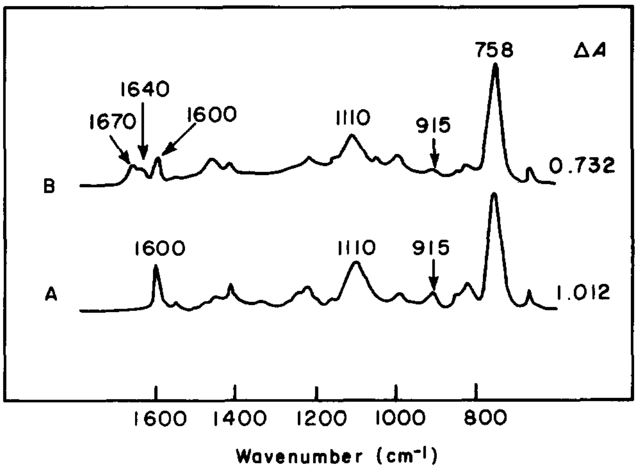

Figure 6 I.r. spectra of the reaction system with an equal weight of chloroform: spectrum A, before reaction; B, after reaction

reported that cyclic amides, such as pyridone or lactams, act as inhibitors of the homopolymerization of epoxy compounds[14–16]. In general, the inhibitor is preferably present in an amount by weight of about 0.02% to about 1.5% of the composition. In the system we studied, the molar ratio of pyridine to the epoxy group was 1:1. After heating, the *N*-substituted lactams were formed in a large amount (the polymeric units), leading to the inhibition of the homopolymerization of the epoxy groups. The disappearance of the epoxy group is, therefore, mainly due to the reaction with pyridine.

With the same epoxy compound, different derivatives of pyridine show different reactivities. The order of reactivity is shown in *Figure 4*. This result strongly supports the reaction scheme that we proposed. The first step of the reaction was proposed as salt formation. The ethyl group in 4-ethylpyridine is an electron donor; the salt formed between 4-ethylpyridine and the epoxy group is more stable than that formed from pyridine. So, 4-ethylpyridine reacts faster than pyridine. The 2-methylpyridine opens the epoxy ring at a lower rate than pyridine due to steric hindrance of the methyl group in the position 2 of the ring. The second step proposed involves nucleophilic attack on the positions 2 or 6 of the pyridinium ring. If one of these positions is occupied by the methyl group, the nucleophilic attack would be expected to proceed at a lower rate. For these two reasons, the reaction of pyridine is much faster than that of 2-methylpyridine. In the case of the 2,6-dimethylpyridine, both positions adjacent to the nitrogen are occupied by methyl groups and, as we expected, almost no reaction was observed. Hence, the observed order of reactivity is consistent with the reaction scheme proposed above.

CONCLUSIONS

Polymerization of pyridine or alkylpyridine with epoxy groups, which resulted in the loss of the aromatic structure of the pyridine rings, has been studied.

Based on *FT*i.r., g.p.c. and u.v. analyses, a reaction scheme and the structure of the products are proposed. With monofunctional epoxy compounds, pyridine can react to form linear polymers containing cyclic amide structure. With diglycidyl ether, crosslinking takes place with the formation of a rubber-like material. Further study shows that the polymers formed are due to the polyaddition of the intermediate of the reaction between the pyridine and the epoxy groups, rather than the homopolymerization of the epoxy groups.

Since pyridine and its derivatives have been considered to have great stability in most situations, the discovery of the reaction of pyridine and the epoxy compound introduces a new phenomenon in the area of organic chemistry. A further study concerning the structure and properties of the polymer formed in this reaction may yield interesting results.

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