Studies of 2-Oxazolidinones. II. Products of the Pyrolysis of Some 2-Oxazolidinones

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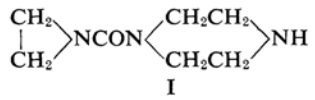
Among the various earlier studies of 2-oxazolidinones, some recent observations on the formation of ethylenimine and its polymer from 2-oxazolidinone[1-3] have been of great interest to us. Jones[3], studying the pyrolysis of 2-oxazolidinone at 210~235°C without a catalyst, isolated the following six products from ca. 42 g. of 2-oxazolidinone: ca. 11 g. of a polymer (A); 12.5 g. of a hygroscopic substance (B), b. p. 231~236°C/13 mmHg; 1.5 g. of a basic substance having the empirical formula of $C_7H_{13}N_3O$ (C), m. p. 244°C; 1 g. each of two distillates D and E, b. p. 86°C/13 mmHg and 136~160°C/13 mmHg respectively, and ca. 1 g. of ethanolamine. On the basis of infrared analysis, Jones suggested a poly(ethylenimine)

1) O. Sundén, Swed. Pat. 148559; *Chem. Abstr.*, **50**, 2679 (1956).
2) M. Crowther and W. R. Nummy, U. S. Pat. 2806839; *Chem. Abstr.*, **52**, 3405 (1958).
3) J. I. Jones, *Chem. & Ind.*, **1956**, 1454.

structure having a certain carbonyl group for A, and a tri- or tetrasubstituted urea structure such as I or II for C. However, there are some doubtful points in his assignments of A and C, and no information on the structure of B, one of the major products, has yet been obtained.



I

II

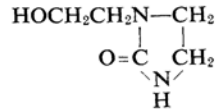
It is the purpose of this investigation to provide more detailed information on the structures of the pyrolysates from some 2-oxazolidinones and also to discuss a possible mechanism of the pyrolysis.

Results and Discussion

Products of the Pyrolysis of 2-Oxazolidinone.—2-Oxazolidinone was pyrolyzed at 230°C until the evolution of carbon dioxide ceased completely, this was done under the same conditions as Jones'[3], i. e., under the atmospheric pressure of dry nitrogen in the absence of a catalyst. Somewhat unexpectedly, the evolution of carbon dioxide ceased at ca. 61% of the theoretical amount. Moreover, in the infrared spectrum of the pyrolysate, the disappearance of the carbonyl band at 1760 cm^{-1}, which was found in 2-oxazolidinone, was accompanied by the formation of a new carbonyl band at the 1686 cm^{-1} position. These facts suggest that ca. 39 mol. % of 2-oxazolidinone was converted to another carbonyl compound which was thermally stable.

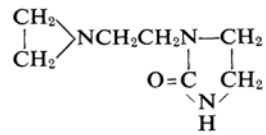
By careful fractionation, the pyrolysate (21 g.) could be separated into the following four fractions; probably ethanolamine (fraction 1), 1 g.; a hygroscopic product of b. p. 180~185°C/3.5 mmHg and m. p. 51.5°C, $C_5H_{10}N_2O_2$ (fraction 2), 11 g.; a basic powder of m. p. 234°C, $C_7H_{13}N_3O$ (fraction 3), 1 g.; and a semi-solid polymeric residue (fraction 4), 8 g. In comparison with Jones's results, our fractions 2 and 3 seem to correspond to his substances B and C respectively.

In the infrared spectrum of fraction 2 shown in Fig. 1A, three strong bands corresponding to amide I, II and III appeared at 1690, 1495 and 1279 cm^{-1} respectively; they are in nearly the same positions as in unsubstituted 2-imidazolidinone (1660, 1508 and 1270 cm^{-1})[4]. A characteristic hydroxyl band can also be found at 1067 cm^{-1}. Based on spectral and analytical data, formula III was proposed as the structure of fraction 2. This structure was further confirmed by a mixed melting point determination with an authentic sample prepared by an independent method.



III

As is shown in Fig. 1B, fraction 3 also has three bands, corresponding to amide I, II and III, at 1690, 1500 and 1279 cm^{-1}. Their positions and intensities are just the same as those in fraction 2; this suggests a 1-substituted 2-imidazolidinone structure for fraction 3[5]. Futhermore, an absorption which is probably due to the C–H stretching vibration of a strained ethylenimine ring[6] is found at 3080 cm^{-1}. These data suggest that the most probable structure of fraction 3 is represented by formula IV. If Jones' tentative structure I or II were correct, its carbonyl frequency (amide I) should be lower than that of normal tri- or tetrasubstituted urea (cf. footnote 5) under the influence of a strained, three-membered ring[7]. Therefore, it is obvious that Jones's structures for fraction 3, which shows an amide I absorption in such a higher frequency region (near 1690 cm^{-1}), are erroneous.



IV

In polymeric fraction 4, the infrared spectrum was measured after its low boiling portion had been distilled off as completely as possible; the absorption curve is shown in Fig. 1C. Three amide absorptions (1695, 1495 and 1275 cm^{-1}) agreed with those in fractions 2 and 3. This would imply that the 2-imidazolidinone

4) R. Mecke, Jr. and R. Mecke, Sr., *Chem. Ber.*, **89**, 343 (1956).

5) Judging from the position of the amide I of the product, the possibility of some other carbonyl structure may be excluded. The amide I absorption of acyclic urethanes usually occurs in the 1705~1722 cm^{-1} region, while in cyclic systems such as 2-oxazolidinone, the carbonyl frequency falls in the range 1745~1760 cm^{-1} [e. g., S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).]. In acyclic *N,N'*-disubstituted ureas, the amide I absorption appears at a lower frequency than 1660 cm^{-1} [e. g., H. J. Becher, *Chem. Ber.*, **89**, 1953 (1956).], and in tri- or tetrasubstituted ureas, a further decrease in the frequency would be expected. However, the amide I band of fraction 3 was observed in another region. This is equally true for fraction 4.

6) H. T. Hoffman, Jr., G. E. Evans and G. Glockler, *J. Am. Chem. Soc.*, **73**, 3028 (1951).

7) Cf. L. J. Bellamy, "Infra-Red Spectra of Complex Molecules", Methuen, London (1958), p. 387.

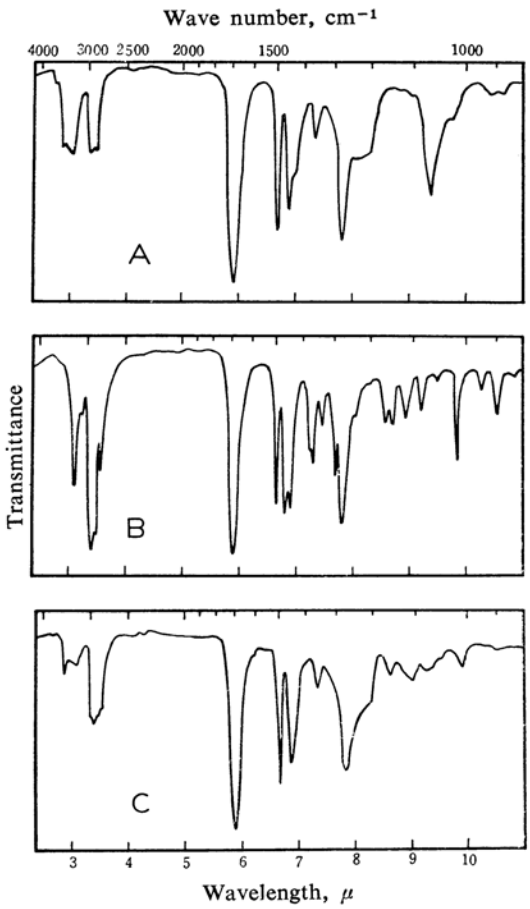
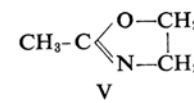


Fig. 1. Infrared spectra of each fraction of the pyrolysate from 2-oxazolidinone: A, fraction 2 (in $CHCl_3$ sol.); B, fraction 3 (in Nujol); C, fraction 4 (in $CHCl_3$ sol.).

rings are joined at the 1-position with the chain ends of some part, if not all, of the poly(ethylenimine) molecules[8].

Products of the Pyrolysis of 3-Substituted 2-Oxazolidinones.—3-*p*-Chlorophenyl-2-oxazolidinone, which was less reactive than 2-oxazolidinone itself, was completely decarboxylated at 230°C. In the infrared spectrum of the pyrolysate, the carbonyl absorption which is found at 1740 cm^{-1} in the starting oxazolidinone completely disappears. This coincides with the fact that quantitative decarboxylation was observed. It therefore appears that the basic residue on the pyrolysis of this oxazolidinone is mainly composed of poly(*N*-*p*-chlorophenylethylenimine), in contrast with the polymeric product from unsubstituted 2-oxazolidinone. The pyrolysis of 3-*p*-nitrophenyl-2-oxazolidinone at 230°C gave essentially the same results. After half one of the theoretical amount of carbon dioxide had been evolved, the pyrolysis was stopped and the reaction mixture was examined by infrared analysis. The 1767 cm^{-1} absorption (in chloroform) due to the carbonyl group in 2-oxazolidinone was decreased to just half in transmittance, and no new carbonyl absorption was found.

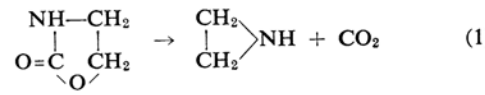
As a particular case, the pyrolytic decarboxylation of 3-acetyl-2-oxazolidinone at 195°C afforded a basic distillate of b. p. 110°C in addition to a polymeric residue. The infrared spectrum suggested that the distillate was 2-methyl-2-oxazoline V[9]. The structural assignment was established by a mixed melting point determination of its picrate with an authentic sample prepared by an independent route. This substance probably results from the rearrangement of *N*-acetylethylenimine, which seems to be an intermediate in pyrolysis. The above



V

consideration appears reasonable in view of the fact that *N*-benzoylethylenimine thermally rearranged to 2-phenyl-2-oxazoline with ease[10].

Mechanism of the Pyrolysis of 2-Oxazolidinones.—All experimental results, including our data, seem to indicate that the pyrolysis proceeds through the intermediate formation of ethylenimine.



(1)

It is well known that ethylenimine is rather stable in strong alkaline media, but that in the presence of acids (including carbon dioxide) it easily polymerizes to give poly(ethylenimine) according to a step-wise mechanism[11,12] promoted by the ethylenimmonium cation. In connection with our work, an initiation by carbon dioxide is interesting; it seems to arise from the following equilibrium:

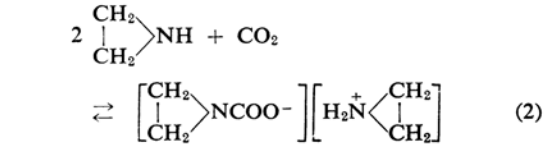
8) It is known that the shift of amide I frequency is of the order of 20 cm^{-1} to the lower side, with the structure varying from secondary to tertiary amide (Ref. 7, p. 211), from secondary to tertiary urethane [S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).], and from *N*-monosubstituted to *N*,*N*-'disubtituted urea [H. J. Becher et al., *Chem. Ber.*, **89**, 1593 (1956); *Naturwiss.*, **43**, 467 (1956).]. If fraction 3 or 4 had any 1, 3-disubstituted 2-imidazolidinone structure, a similar frequency decrease would be expected. Therefore, there is no possibility that the 2-imidazolidinone ring is sandwiched in between two poly(ethylenimine) residues.

9) The same compound has been obtained as a by-product in the preparation of 3-acetyl-2-oxazolidinone from *N*-(2-hydroxyethyl)-acetamide and methyl trichloroacetate. [G. Y. Lesher and A. R. Surrey, *J. Am. Chem. Soc.*, **77**, 639 (1955)].

10) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2933 (1895).

11) G. D. Jones et al., *J. Org. Chem.*, **9**, 125 (1944).

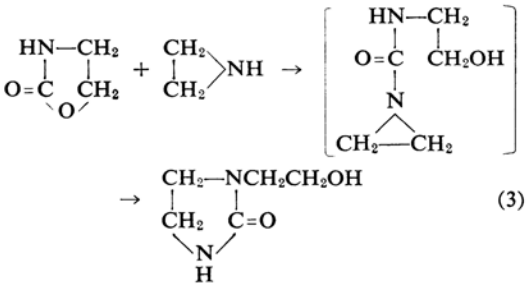
12) W. G. Barb, *J. Chem. Soc.*, **1955**, 2564, 2577.



(2)

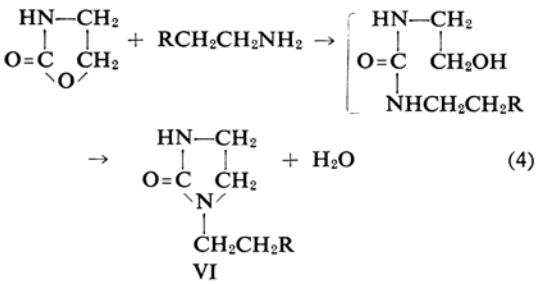
The same reaction path would be expected in the formation of ethylenimine polymer by pyrolysis. In default of equilibrium 2, however, the pyrolytic polymerization of 3-aryl- or 3-acyl-2-oxazolidinone seems to be initiated by some acidic impurity (e. g., traces of water).

Furthermore, the fact that, in the pyrolysis of unsubstituted 2-oxazolidinone, some 1-substituted 2-imidazolidinones including the polymer were isolated, as has been described above, is strikingly different from the result in other cases, so that some explanation seems to be necessary. First, the formation of 1-(β-hydroxyethyl)-2-imidazolidinone could be understood in terms of a nucleophilic attack of ethylenimine having active hydrogen on a cyclic



(3)

urethane, 2-oxazolidinone, followed by cyclization of the resulting adduct. However, in this mechanism, it is necessary for the reactants to be unsubstituted at the 3-position of 2-oxazolidinone and the 1-position of ethylenimine; this requirement is fulfilled in 2-oxazolidinone itself. Secondary, a similar attack of the terminal amino group of the polymer on 2-oxazolidinone, followed by dehydration of the adduct, may also lead to the formation of a 2-imidazolidinone derivative, as is shown in Eq. 4:



(4)

(R: Any group derived from ethylenimine)

Actually, a compound corresponding to R= $-\underset{|}{N}CH_2CH_2-$ in VI, as well as a polymer having a VI type structure, was isolated as described above. In this connection, Gabriel and Eschenbach[13] long ago investigated a similar reaction, which involved the formation of 1-phenyl-2-imidazolidinone from 2-oxazolidinone and aniline. Further, the water formed in Eq. 4 seems to be consumed by the ring-cleavage of ethylenimine itself and by the terminal ethylenimine ring of the polymer.

Under such severe conditions as bulk pyrolysis, the contribution of more complicated reactions may also be considered. However, the discussion above seems to be sufficient to explain all the products of the pyrolysis.

Finally, we wish to point out the difference in mechanism between this reaction and the formation of polypeptide from 2, 5-oxazolidinedione (Leuchs' anhydride), which involves a similar decarboxylative polymerization. On the formation of ethylenimine from 2-oxazolidinone, the ethylenimine and its polymer act only as a catalyst for the decarboxylation[14] and cannot directly initiate the polymerization, so the decarboxylation and the polymerization are two entirely independent steps. On the other hand, in the formation of polypeptide, the reaction proceeds by the repeated attack of the propagating chain on the monomer (Leuchs' anhydride); that is, the decarboxylation and the polymerization occur simultaneously.

Experimental

Materials.—2-Oxazolidinone was prepared by the condensation of ethanolamine with diethyl carbonate according to Homeyer's procedure[15]. The yield was 70%. It melted at 89~90°C after recrystallization from tetrahydrofuran.

3-Acetyl-2-oxazolidinone was prepared from acetylchloride and 2-oxazolidinone by the method of Close[16]. The yield was 70%. It melted at 69°C after recrystallization from benzene. 3-*p*-Chlorophenyl- and 3-*p*-nitrophenyl-2-oxazolidinone were prepared as previously desribed[17]. The *p*-chlorophenyl derivative, m. p. 121°C; the *p*-nitrophenyl derivative, m. p. 154.5°C.

General Procedure of Pyrolysis. — The material was placed in a small flask fitted with a nitrogen inlet and a delivery tube which was connected with a potash-bulb through a trap, and then heated under a stream of dry nitrogen in a silicone oil bath maintained at the descired temperature. The extent of pyrolysis was determined from the amount of absorbed carbon dioxide. After the evolution of carbon dioxide has ceased completely, the syrupy or resinous mass remaining in the flask was cooled and examined by infrared analysis. The amount

13) S. Gabriel and G. Eschenbach, *Ber.*, **30**, 2495 (1897).
14) A detailed study of the catalytic action of bases will be presented in a following paper.
15) A. H. Homeyer, U. S. Pat. 2399188; *Chem. Abstr.*, **40**, 4084 (1946).
16) W. J. Close, *J. Am. Chem. Soc.*, **73**, 97 (1951).
17) R. Oda, M. Miyanoki and M. Okano, This Bulletin, **35**, 1309 (1962).

of evolved carbon dioxide was 61.4% of the theoretical value in the case of 2-oxazolidinone and quantitative in the case of its 3-substituted derivative (e. g., *p*-chlorophenyl, 101%). The pyrolysate from 2-oxazolidinone was further fractionated (as described below). However, the fractionation of no other pyrolysate was undertaken. Their molecular weights were not very high, this may be due to the simultaneous depolymerization cited by Barb[12].

Fractionation of the Pyrolysate from 2-Oxazolidinone.—The pyrolysate (21 g.) obtained by the decomposition of 2-oxazolidinone (30.5 g.) at 230°C under the atmospheric pressure of nitrogen was distilled under reduced pressure to yield 1 g. of a water-soluble base boiling below 100°C at 4 mmHg, probably ethanolamine (fraction 1), and 11 g. of a viscous liquid, b. p. 185°C/3.5 mmHg (fraction 2). The addition of chloroform to the resulting residue gave 1 g. of a white powder, m. p. 234°C (fraction 3) which was removed by filtration; the filtrate was then evaporated to yield 8 g. of a polymeric residue (fraction 4). Treatment of this fraction at 240°C/3 mmHg for a short time to remove its low boiling portion gave a pale yellow mass which solidified on cooling.

Redistillation of fraction 2 gave hygroscopic crystals, m. p. 51.5°C, having an empirical formula of $C_5H_{10}N_2O_2$ (Found: C, 45.96; H, 8.51; N, 21.27. Calcd. C, 45.79; H, 8.45; N, 21.36%.). This compound was presumed to be 1-(β-hydroxyethyl)-2-imidazolidinone, and no depression in melting point was observed when it was mixed with an authentic sample, which had been prepared in a 68% yield according to Wilson's procedure[18] except that diethyl carbonate was used instead of urea as a carbonyl source.

In basic fraction 3, its empirical formula $C_7H_{13}N_3O$ (Found: C, 53.41; H, 8.57; N, 27.13. Calcd. C, 54.17; H, 8.44; N, 27.08%.) agreed with Jones' result, but its melting point was 10°C lower than that he reported. A higher value was not obtained by repeated recrystallizations from chloroform. This fraction is believed to be 1-(β-aziridinylethyl)-2-imidazolidinone.

Fraction 4 was strongly basic and hygroscopic. On the basis of infrared analysis, it was assumed to be a mixture of low molecular weight poly(ethylenimine) partially terminated with 2-imidazolidinone ring.

On the pyrolysis of 2-oxazolidinone under a reduced pressure of 20 mmHg at 170°C a similar result was obtained.

Distillate of the Pyrolysis of 3-Acetyl-2-oxazolidinone.—When 16.5 g. of 3-acetyl-2-oxazolidinone was thermally decarboxylated at 195°C, 4.4 g. of a basic oil having a pyridine-like odor was distilled out in addition to a polymeric residue. The redistilled liquid boiled at 110°C. Its picrate recrystallized from absolute ethanol melted at 151°C. The infrared spectrum of the free base is identical with that of 2-methyl-2-oxazoline. Furthermore, a mixed melting point of its picrate with an authentic sample prepared according to Wenker's procedure[19] showed no depression.

Summary

The products obtained by the pyrolytic decarboxylation of 2-oxazolidinones have been investigated, chiefly by infrared analysis. In the case of 2-oxazolidinone, the products are 1-(β-hydroxyethyl)-2-imidazolidinone, 1-[β-(1-azilidinyl)ethyl]-2-imidazolidinone (somewhat uncertain), and poly(ethylenimine) having a 2-imidazolidinone ring at the chain end. On the other hand, the only products from 3-*p*-chlorophenyl- and 3-*p*-nitrophenyl-2-oxazolidinone are believed to be low molecular weight polymers of the corresponding ethylenimines. From 3-acetyl-2-oxazolidinone, a considerable amount of 2-methyl-2-oxazoline, which seems to arise from the rearrangement of *N*-acetylethylenimine, is isolated, in addition to the corresponding poly(ethylenimine). On the basis of the products obtained, a possible mechanism for the pyrolysis has been proposed.

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18) A. L. Wilson, U. S. Pat. 2517750; *Chem. Abstr.*, **45**, 1627 (1951).

19) H. Wenker, *J. Am. Chem. Soc.*, **57**, 1079 (1935).