Studies of 2-Oxazolidinones. III. Kinetics of the Pyrolytic Decarboxylation of 2-Oxazolidinones

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Studies of the thermal decomposition of 2-oxazolidinones are important not only in order to synthesize ethylenimines or their polymers, but also in order to consider the thermal stability in some applications of 2-oxazolidinone derivatives to polymer chemistry(1). In the second paper of this series(2), the authors examined the pyrolysates from 3-substituted 2-oxazolidinones by means of infrared spectroscopy and discussed a two-step process, in which decarboxylation was followed polymerization. The present kinetic study has been undertaken to provide further insight into the mechanism of the decarboxylation step in this reaction. The effect of a 3-substituent on the decarboxylation rate and the rate-accelerating effect of various amines have been especially studied in detail.

Results and Discussion

Autocatalytic Nature of the Reaction. — The decarboxylation rates of some 2-oxazolidinones without either catalyst or solvent were measured. Figure 1 shows the results of plotting the decarboxylation rate, dx/dt, against the conversion x, for two representative 2-oxazolidinones. As is illustrated in this figure, the rate first increases as the reaction proceeds, but it comes to a maximum and then decreases(3). The basic products of the reaction —the corresponding ethylenimines and/orth eir polymers—appear to at as an auto-catalyst; this will be proved experimentally below.

Effect of the 3-Substituent on the Decarboxylation Rate.—The decarboxylation rates of various 3-substituted 2-oxazolidinones are summarized in Table I. Each of these values indicates a relative rate at 25% conversion taking as a standard the rate of the 3-phenyl

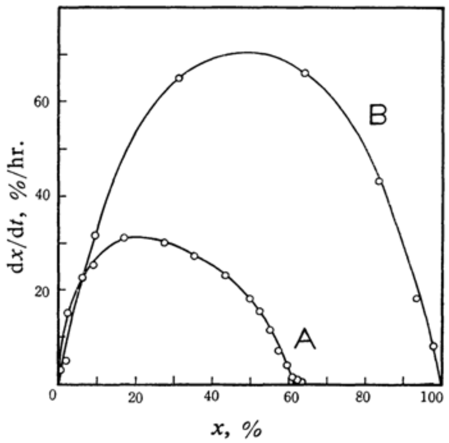

Fig. 1. Rate vs. conversion curves for the bulk decarboxylation of 2-oxazolidinones (0.02 mol.) without catalyst: A, 2-Oxazolidinone (at 200°C); B, 3-*o*-Nitrophenyl-2-oxazolidinone (at 230°C).

TABLE I. RELATIVE RATES FOR BULK DECARBOXYLATION OF 3-SUBSTITUTED 2-OXAZOLIDINONES WITHOUT CATALYST AT 230°C[a]

Run	Oxazolidinone[b]	Relative rate[c]
1	C_6H_5-Ox	1
2	*p*-CH_3-C_6H_4-Ox	0.7
3	*p*-C_2H_5OOC-C_6H_4-Ox	1.3
4	*p*-Cl-C_6H_4-Ox	1.9
5	*p*-NO_2-C_6H_4-Ox	130
6	*o*-NO_2-C_6H_4-Ox	140
7	$CH_3(CH_2)_3$-Ox	2.3
8	Ox-Ox	33[d]
9	Ox-$(CH_2)_2$-Ox	8.6[d]
10	Ox-$(CH_2)_4$-Ox	15[d]

a) In each run, 0.02 mol. of oxazolidinones was used.

b) The oxazolidinonyl group, $-\underbrace{N-CH_2CH_2OCO}$, abbreviated as Ox.

c) The volume of the compounds differs, but no correction for this is made, so that it is impossible to compare each rate value exactly.

d) This value has been divided by a statistical correction factor of two.

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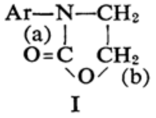
[1] e. g., J. R. Caldwell, U. S. Pat. 2656328 [*Chem. Abstr.*, **48**, 2415 (1954)]; W. H. Schuller and E. J. Kerle, U. S. Pat. 2786043 [*Chem. Abstr.*, **51**, 11758 (1957)]; R. Oda et al., *Chem. High Polymer Japan* (*Kōbunshi Kagaku*), **17**, 72 (1960); G. P. Speranza and W. J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958); E. K. Drechsel, ibid., **22**, 849 (1957).

[2] R. Oda, M. Miyanoki and M. Okano, This Bulletin, **35**, 1910 (1962).

[3] In the decarboxylation of such 3-substituted 2-oxazolidinones as the 3-*o*-nitrophenyl or 3-*p*-chlorophenyl derivatives, the evolution of the theoretical amount of carbon dioxide was observed. In the case of unsubstituted 2-oxazolidinone, however, the evolution of carbon dioxide ceased at 61.4% of the theoretical amount; this is attributed to the fixation of the part corresponding to 38.6 mol.% as 1-substituted 2-imidazolidinones [see Ref. 2].

derivative. The results from runs 1—6 in Table I show that the reactivity of various 3-aryl derivatives depends on the electronic effect of the substitutent on the benzene ring; that is, an electron-attracting group such as *p*-nitro accelerates the decarboxylation, while an electron-releasing group such as *p*-methyl retards it. It may be inferred from this observation that the rate-determining step for this ring-cleavage is the fission of the N–C bond, (a) in I, rather than that of the O–C bond, (b) in I.



I

As is seen in runs 8–10, all bis-oxazolidinones showed high decomposition rates compared with that of *n*-butyl-2-oxazolidinone (run 7). This may be partially accounted for by the participation of the steric effect[4], but at present no complete solution is possible.

Aromatic Amine-Catalyzed Decarboxylation of 3-Aryl-2-oxazolidinone. — In both the presence and absence of *N*, *N*-diethyl-*p*-nitroaniline, the decarboxylation rates of 3-*p*-nitrophenyl-2-oxazolidinone in *o*-nitroanisole were measured. Rate vs. conversion curves are shown in Fig. 2[5]. Since the structure of the amine used is similar to that of *N*-*p*-nitrophenylethylenimine, which seems to be an initial product in this decomposition, and since the amount of the amine added is equivalent to that of the oxazolidinone, rate maximum would be expected to appear at the beginning of the reaction. As is shown in curve B, however, the rate increases gradually at first and comes to a maximum only after some conversion has occurred. This means that the pyrolysate formed, rather than the amine added, acts as the more effective catalyst.

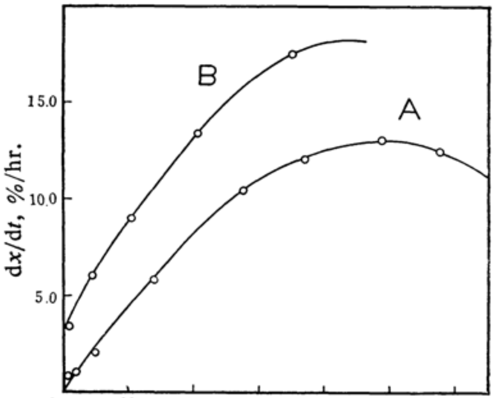


Fig. 2. Rate vs. conversion curves for the decarboxylation of 3-*p*-nitrophenyl-2-oxazolidinone (1 mol./l.) in the absence (A) and presence (B) of *N*,*N*-diethyl-*p*-nitroaniline in *o*-nitroanisole at 230°C. $[Ox]_0=[I]_0=1.00$ mol./l.

The rates of decarboxylation catalyzed by some *N*-ethylaniline derivatives for the same oxazolidinone were also measured. A comparison between the rates at 25% conversion are given in Table II. The order of the rates disagrees with that which would be expected judging from the basicities of the catalysts[6]. The larger accelerating effects of a polyamine (run 5) and of a small ring monoamine (run 4) as compared with an ordinary monoamine (run 2) suggest that the rates depend considerably on the steric requirements of amines.

TABLE II. RATE-ACCELERATING EFFECT OF ANILINE SERIES ON DECARBOXYLATION OF 3-*p*-NITROPHENYL-2-OXAZOLIDINONE IN *o*-NITROANISOLE AT 230°C[a]

Run	Catalyst added	Concn. mol./l.	Rate, d*x*/d*t* %/hr.
1	None	—	9.5
2	$C_6H_5N(C_2H_5)_2$	1.00	20
3	$C_6H_5NHCH_2CH_2NHC_6H_5$	0.50	30
4	$C_6H_5\underbrace{NCH_2CH_2}$	0.75	31
5	$(\text{-}\underset{C_6H_5}{N}CH_2CH_2\text{-})_n$	0.20/*n*	23

a) In each run, $[Ox]_0=1.00$ mol./l.

Aliphatic Amine-Catalyzed Decarboxylation of 3-Aryl-2-oxazolidinones.—Using high boiling aliphatic amines as catalysts for the decarboxylation of 3-*p*-nitrophenyl- and 3-*p*-chlorophenyl-2-oxazolidinone, the kinetic order with respect to the catalysts and the rate constants have been determined. In all cases, there was a rate maximum at the beginning of the reaction, as expected. Figure 3 shows the rate vs. conversion curves for the *n*-dodecylamine-catalyzed decarboxylation in dibenzyl ether. From this

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[4] In the contiguous existence of two rings (intermolecular or intramolecular), the imino group resulting from one oxazolidinone ring would lie in a suitable position for promoting the decomposition of the other ring, though it appears to depend on the number of carbons in the polymethylene linkage.

[5] In this figure and hereafter, $[Ox]_0$ and $[I]_0$ represent the initial concentrations of oxazolidinone and amine respectively.

[6] The basicity constants of $(C_2H_5)_2NH$, $NH_2CH_2CH_2NH_2$, and $HN\Big\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}$ at 25°C are estimated to be 9.6×10^{-4}, 8.5×10^{-5}, 1.1×10^{-7} respectively. [a) "Handbook of Chemistry (Kagaku Binran)", New Ed., compiled by the Chemical Sociehy of Japan, Maruzen, Tokyo, (1958) p. 871; b) S. Searles et al., *J. Am. Chem. Soc.*, 78, 4918 (1959).] Presumably, those of $C_6H_5N(C_2H_5)_2$, $C_6H_5NHCH_2CH_2NHC_6H_5$, and $C_6H_5N\Big\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}$ would decrease in this order.

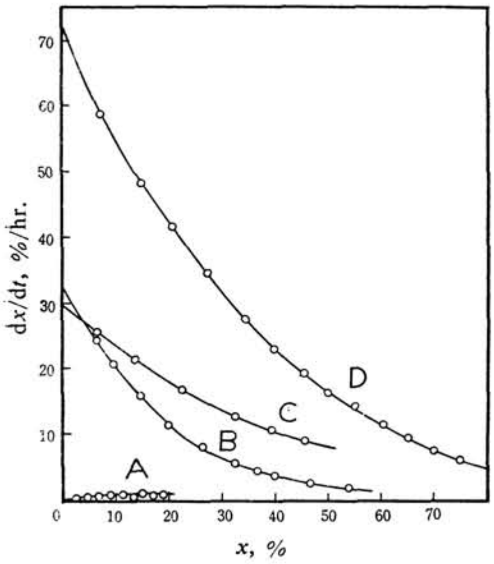
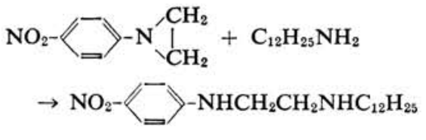


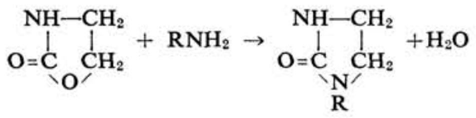
Fig. 3. Rate vs. conversion curves for the *n*-dodecylamine-catalyzed decarboxylation of 3-*p*-nitrophenyl- and 3-*p*-chlorophenyl-2-oxazolidinones in dibenzyl ether at 230°C: A, *p*-NO_2, non-catalyzed; B and D, *p*-NO_2, amine-catalyzed; C, *p*-Cl, amine-catalyzed. $[\mathrm{Ox}]_0=1.00$ mol./l.; $[\mathrm{I}]_0=1.00$ mol./l. in C and D, and 0.50 mol./l. in B.

figure, it can be seen that the rate of the decarboxylation of the *p*-nitrophenyl compound in the absence of a catalyst is very slow in comparison with that in the presence of the amine; hence, the participation of the non-catalyzed term is possibly negligible for the latter case.

If the amine concentration remains constant during a run, the reaction will be in pseudo-first-order; hence, a plot of $\mathrm{d}x/\mathrm{d}t$ vs. x should be linear. However, first-order plots with a downward curvature were obtained, as is shown in B, C and D of Fig. 3. This observation may be interpreted as follows: By the reaction with the *N*-arylethylenimines formes as reaction intermediates, *n*-dodecylamine is partially converted to the less effective *N*-aryl-*N'*-*n*-dodecylethylenediamines, and the low catalytic activity of these amines may lead to a slower rate. Judging from the experimental data (see below), it is appearent that a secondary aliphatic amine is less effective than a primary one as a catalyst. Additionally, no appreciable rate acceleration by the aromatic amine in dibenzyl ether was observed in a preliminary test.


(1)

Another consumption of the amine which is due to the condensation with oxazolidinone to afford 1-substituted 2-imidazolidinone may also be considered[7] (cf. our previous paper[2]). In another experiment[8], however, it has been found that the existence of a 3-substituent on the oxazolidinone ring makes this condensation difficult. Therefore, such consumption would be negligible.


(2)

Since the rate did not fit the simple pseudo-first-order rate equation, as has been mentioned above, the initial second-order rate constants, k, were computed from the values of the initial rate, $(\mathrm{d}x/\mathrm{d}t)_{x=0}$, which were extrapolated graphically in Fig. 3, using the following equation:

$$(\mathrm{d}x/\mathrm{d}t)_{x=0}=k[\mathrm{Ox}]_0[\mathrm{I}]_0 \qquad (3)$$

In Table III-A, a little increase of k with an increase in the amine concentration is observed; this may be ascribed to a small contribution of the second-order term with respect to amine.

TABLE III. RATE CONSTANTS OF DECARBOXYLATION OF 3-*p*-NITROPHENYL-2-OXAZOLIDINONE CATALYZED BY VARIOUS AMINES IN DIBENZYL ETHER AT 230°C[a]

Amine added	Concn. of amine mol./l.	Initial second-order rate constant, l. mol^{-1} min^{-1} $k\times10^3$
A series		
n-Dodecylamine	0.50	10.7
n-Dodecylamine	1.00	12.0
N-Ethyl-*n*-dodecylamine	1.00	8.75
Bis(2-ethylhexyl)-amine	1.00	1.40
N, *N*-Diethyl-*n*-dodecylamine	1.00	1.90
B series		
Tetraethylenepentamine	0.125	73
Triethanolamine	0.20; 0.40	33[b]

a) In each run, $[\mathrm{Ox}]_0=1.00$ mol./l.
b) Mean value for two different amine concentrations.

Rate vs. conversion curves for similar decarboxylations in the presence of aliphatic secondary or tertiary amines (e.g., *N*-ethyl-*n*-dodecylamine, bis(2-ethylhexyl)-amine and *N*, *N*-diethyl-*n*-dodecylamine) are shown in Fig. 4. In contrast with Fig. 3, the plots of A and B in Fig. 4 are very close to straight lines; hence, it appears that the concentration of the catalyst remains constant, at least in the range

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[7] S. Gabriel and G. Eschenbach, *Ber.*, 30, 2495 (1879).
[8] R. Oda and K. Yamamoto, Unpublished data.

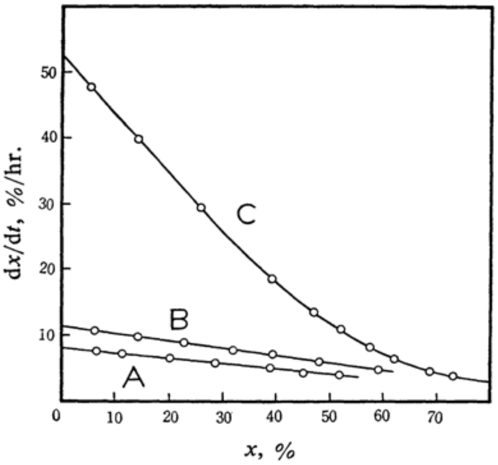


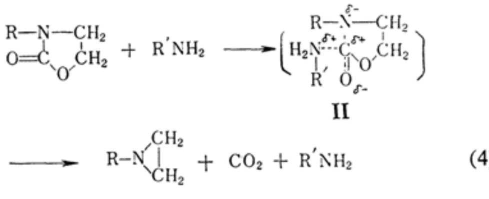
Fig. 4. Rate vs. conversion curves for the aliphatic amine-catalyzed decarboxylation of 3-*p*-nitrophenyl-2-oxazolidinone in dibenzyl ether at 230°C: A, Bis(2-ethylhexyl)-amine; B, *N*,*N*-Diethyl-*n*-dodecylamine; C, *N*-Ethyl-*n*-dodecylamine. $[\mathrm{Ox}]_0=[\mathrm{I}]_0=1.00$ mol./l.

of ca. 50% conversion. Probably this means that these amines react only slowly with the intermediate *N*-aryl-ethylenimine. The initial second-order rate constants calculated from Eq. 3 are also listed in Table III-A. In a series of amines, a variation in structure from primary to secondary and from secondary to tertiary leads to a decrease in the catalytic effect; this order disagrees with that of their basicities[9]. Such behavior would be caused by steric hindrance to the approach of the oxazolidinone molecule. Actually, in the case of highly hindered bis(2-ethylhexyl)-amine, an unexpectedly low rate was observed.

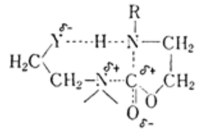
It can be seen from Table III that a polyamine is more effective as a catalyst than a monoamine in the aliphatic as well as in the aromatic series (cf. Table II). In order to make the rate constant for the tetraethylenepentamine-catalyzed reaction comparable with the value obtained from monoamine-catalyzed decomposition, a statistical correction factor of 5 has to be applied. The calculated rate constant per amino group, 14.6×10^{-3} mol. $\mathrm{l}^{-1}\cdot\mathrm{min}^{-1}$, is somewhat larger than the observed values in other cases. Considering that this polyamine contains three secondary amino groups, which are less effective than primary groups, the larger value would be expected. Therefore it seems, clear that polyamine acts as a bi-functional (or polyfunctional) catalyst in this decarboxylation. This suggests a push-pull mechanism which involves the nucleophilic attack of one amino group on the positive carbon of the carbonyl group in oxazolidinone and the simultaneous electrophilic attack of the hydrogen of the other amino group on the nitrogen of the urethane group in the same molecule of oxazolidinone. Since the hydroxyl group is known to be more acidic than the amino group, triethanolamine, which has both groups, may be expected to be a more powerful catalyst[10]. As is shown in Table III-B, the decomposition rate in the presence of this amine is much larger than that for the ordinary tertiary amine-catalyzed reaction. Additionally, it was ascertained experimentally that just aliphatic alcohols such as *n*-dodecyl alcohol showed no accelerating effect on the rate. Therefore, the first-order dependence with respect to triethanolamine strongly supports a concerted mechanism, in which the hydroxyl group in the catalyst acts as electrophile and the amino group act as a nucleophile simultaneously.

The above considerations may also be applied to the problem of two amino groups in separate molecules; that is, the slight second-order dependence with respect to amine, which has been observed in the monoamine-catalyzed reaction, can be understood by a similar explanation.

In summary, it may be concluded that amine-catalyzed decarboxylations proceed by two different mechanisms depending on the structure of the amine. When simple monoamine is used as a catalyst, the reaction occurs mainly through transition state II, as is shown in Eq. 4. On the other hand, in the reaction catalyzed by an amine having an active hydrogen group, such as NH_2 or OH, on the β-carbon, the activated complex may be approximated by structure III:



(4)



Y=NH or O

III

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[9] e.g., the basicity constants of $C_2H_5NH_2$, $(C_2H_5)_2NH$, and $(C_2H_5)_3N$ at 25°C are estimated to be 3.4×10^{-4}, 9.6×10^{-4} and 5.65×10^{-4} respectively (Ref. 6a).

[10] In fact, it has been reported in patent literature [O. Sunden, Swed. Pat. 148559; *Chem. Abstr.*, **50**, 2679 (1956)] that the use of triethanolamine on the decarboxylation of 2-oxazolidinone leads to a satisfactory yield of ethylenimine.

TABLE IV. RATE CONSTANTS OF DECARBOXYLATION OF 2-OXAZOLIDINONE CATALYZED BY *n*-DODECYLAMINE IN DIBENZYL ETHER AT 230°C

Initial concn. of oxazolidinone mol./l.	Initial concn. of amine mol./l.	Initial second-order rate constant l. mol^{-1} min^{-1} $k\times 10^3$	Initial third-order rate constant l. mol^{-1} min^{-1} $k'\times 10^3$
0.50	0.50	1.00	2.00
0.50	0.75	0.98	1.96
1.00	0.50	2.33	2.33
1.00	0.75	2.37	2.37

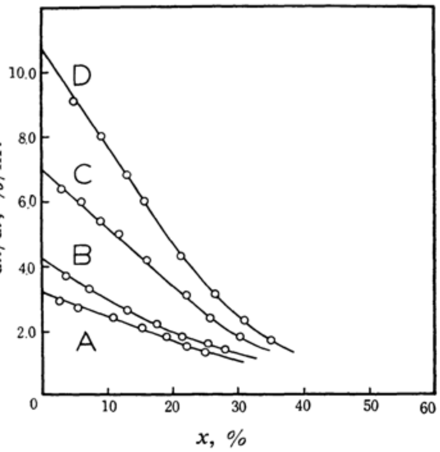


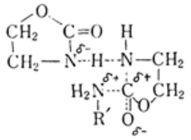
Fig. 5. Rate vs. conversion curves for the *n*-dodecylamine-catalyzed decarboxylation of 2-oxazolidinone in dibenzyl ether at 230°C. $[\mathrm{Ox}]_0=1.00$ mol./l. in C and D, and 0.50 mol./l. in A and B. $[\mathrm{I}]_0=0.75$ mol./l. in A and C, and 0.50 mol./l. in B and D.

Aliphatic Amine-Catalyzed Decarboxylation of 2-Oxazolidinone. — Finally, in the presence of an amine catalyst, the rate of the decarboxylation of 2-oxazolidinone itself was measured. As is shown in Fig. 5, rate vs. conversion curves for the *n*-dodecylamine-catalyzed reaction in dibenzyl ether tend to converge at a point near 60%-conversion; similar behavior has also been observed in the non-catalyzed reaction (cf. Fig. 1).

The initial second-order and third-order rate constants, k and k', for various concentrations of oxazolidinone and amine, were evaluated by using Eqs. 3 and 5 respectively. These values are listed in Table IV.

$$(\mathrm{d}x/\mathrm{d}t)_{x=0}=k'\,[\mathrm{Ox}]_0^2\,[\mathrm{I}]_0 \qquad (5)$$

In the table, the k value changes for the two initial concentrations of oxazolidinone, while the k' value becomes nearly constant, though one can not overlook a slight increase in k' with an increase in the oxazolidinone concentration. Therefore, the amine-catalyzed decarboxylation of 2-oxazolidinone would proceed mainly by a concerted mechanism, in which the added amine attacks oxazolidinone as a nucleophile and, simultaneously, another oxazolidinone molecule attacks it as an electrophile. The transition state may be represented as IV[11]:



IV

Experimental

Materials. — All 2-oxazolidinones used in this work were prepared by methods previously described[2,12]. The following constants were observed: 3-substituent, b. p. or m. p.; none, m. p. 90°C; *n*-butyl, b. p. 113°C/4.3 mmHg; phenyl, m. p. 49°C; *p*-tolyl, m. p. 61°C; *p*-nitrophenyl, m. p. 116°C; *o*-nitrophenyl, m. p. 70.5°C; *p*-carbethoxyphenyl, m. p. 145°C; *p*-chlorophenyl, m. p. 69°C; bis, m. p. 97°C; ethylene-bis, m. p. 136°C; tetramethylene-bis, m. p. 118°C. The solvents (*o*-nitroanisole and dibenzyl ether) and the aliphatic and aromatic amines, except those described below, were of the best grade commercially available and were used after sufficient purification.

N,N-Diethyl-p-nitroaniline. — The amine was prepared according to the procedure of Behr et al.[13] from *p*-chloronitrobenzene and diethylamine in a 94.5% yield. Recrystallization from ethanol afforded the pure product, m. p. 77°C.

N-Phenylethylenimine and its Polymer.—*N*-(β-Bromoethyl)-aniline was treated with aqueous sodium hydroxide according to the method of Heine et al.[14] The *N*-phenylethylenimine thus obtained boiled at 62～65°C/10 mmHg. The polymer was purified by reprecipitation using dimethylformide as a solvent and water as a precipitator.

N-Ethyl-n-dodecylamine. — A mixture of 25 g. of

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11) Though the existence of an oxazolidione dimer has been known 〔Cf. S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4102 (1956); E. Fischer, *J. Chem. Soc.*, **1952**, 4525〕, the dimer seems to be inferior in reactivity because of the lower reactivity of the carbon atoms of its carbonyl groups. Therefore, the possibility of the nucleophilic attack of amine on the dimer may be eliminated from the main route of the reaction. However, the appearance of a third order term with respect to oxazolidinone, though in a slight degree, seems to indicate the participation of such an attack.

12) R. Oda, M. Miyanoki and M. Okano, This Bulletin, 35, 1309 (1962).

13) L. C. Behr, E. J. Kirby, R. N. MacDonald and C. W. Todd, *J. Am. Chem. Soc.*, **68**, 1296 (1946).

n-dodecylbromide and 25.8 g. of 70% aqueous ethylamine was allowed to stand in a sealed tube at 80°C for 24 hr. The resulting mixture was gradually made acidic with hydrochloric acid. After the extraction of the organic layer with ether, the aqueous layer was made strongly alkaline with aqueous potassium hydroxide, and the amine formed was extracted with ether. After the resulting ethereal solution had been dried over anhydrous potassium carbonate and the ether had then been evaporated, distillation in vacuo gave 19 g. (90%) of the fraction of *N*-ethyl-*n*-dodecylamine, b. p. 107~110°C/2 mmHg. The redistilled product boiled at 108°C/2 mmHg.

Found: C, 78.59; H, 14.43; N, 6.69. Calcd. for $C_{14}H_{31}N$: C, 78.79; H, 14.64; N, 6.56%.

N, N-Diethyl-n-dodecylamine.—The amine was prepared according to the method of Coan et al.[15] in an 87% yield by the reaction of *n*-dodecylbromide with diethylamine. The product boiled at 155°C/16.5 mmHg, and its hydrochloride melted at 116°C.

Kinetic Measurement.—Pyrolytic decarboxylation was carried out in glass tubes of ca. 5 or 10 ml. volume for bulk and solution experiments respectively; these tubes were immersed in a constant temperature bath of silicone oil. The evolved carbon dioxide was swept out by a stream of purified nitrogen and absorbed in a potash-bulb. Figure 6 shows an outline of the apparatus. After the immersion of the reaction vessel, a period of 10 min. was allowed for establishment of the temperature equilibrium, and then the rate was measured by weighing the potash-bulb at appropriate time intervals.

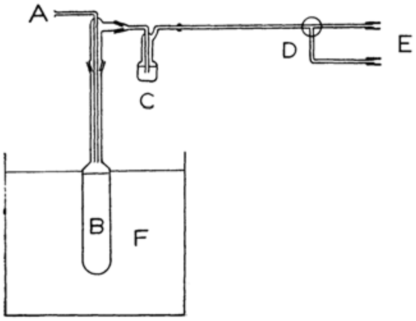

Fig. 6. Apparatus.

A: Dry nitrogen inlet
B: Reactor (Pyrex tube)
C: Trap containing concd. sulfuric acid
D: Switching cook
E: To potash-bulb
F: Thermo-regulated silicone oil bath

In the complete decarboxylation of 3-*p*-chlorophenyl- and 3-*o*-nitrophenyl-2-oxazolidinone, the amounts of evolved carbon dioxide were nearly quantitative (101 and 98% respectively). Therefore, it is believed that the above estimation method leads to responsible results.

Summary

The kinetics of the pyrolytic decarboxylation of 3-substituted 2-oxazolidinones have been studied and the following results obtained. (1) This decomposition is an autocatalytic reaction, in which the amine formed acts as a catalyst. (2) In the decarboxylation of 3-aryl-2-oxazolidinones, the electronic effect of the substituent on the benzene ring indicates that the fission of the N–C bond of the urethane group in the 2-oxazolidinone ring is rate-determining. (3) The initial rate of the aliphatic amine-catalyzed decarboxylation of 3-aryl-2-oxazolidinones is of the pseudo-first-order; it also depends on the concentration and structure of the amine. A mechanism has been proposed which involves a nucleophilic attack of amine on the carbonyl-carbon atom. An amine having an hydroxyl or amino group on the β-carbon shows a large rate-acceleration; this suggests the simultaneous electrophilic participation by the active hydrogen of these groups. (4) The initial rate of the decarboxylation of 2-oxazolidinone itself, catalyzed by aliphatic amine, is of the second-order in oxazolidinone and of the first-order in amine. From this a concerted mechanism has been inferred, in which the amine acts as a nucleophile and the other oxazolidinone acts as an electrophile.

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