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FLAME-INDUCED OXIDATION REACTION OF ALIPHATIC AMINES IN AN AQUEOUS SOLUTION

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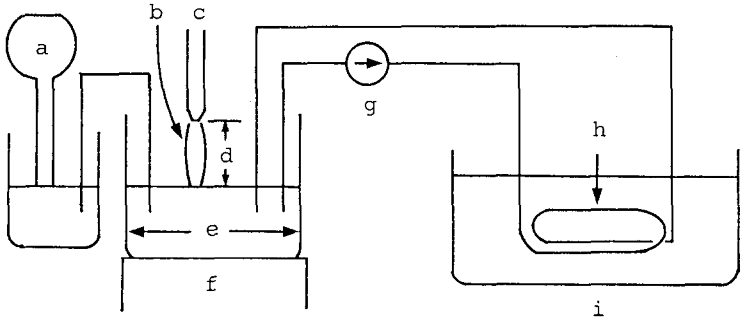
ABSTRACT: When a town gas-, a hydrogen-, and an ethylene-oxygen flame were blown against the surface of aqueous solutions of aliphatic amines, the amines were effectively oxidized to afford amino acids.

Little attention has been given to utilization of flames as an energy source for liquid-phase reactions. In the present study, it was found that flames of flammable gases, when blown against the surface of aqueous solutions of aliphatic amines, could oxidize amines to afford amino acids.

The flames used here were a town gas[1)]-, a hydrogen-, an ethylene-, and an acetylene-oxygen flame. Fig. 1 depicts the apparatus for the flame-induced oxidation reaction in an aqueous solution. A flame[2)] from a burner was kept in contact with the surface of an aqueous solution (ca. 500 ml) of an amine hydrochloride (ca. 5×10^{-4} mol/l) with stirring. The temperature of the solution was kept at 40-50 °C throughout the reaction by circulating it through a glass tube (4.5 m x 5 mmI.D.) in an ice bath. Water was supplied continuously from a reservoir to the reaction mixture, so as to make up for the solvent lost by evaporation[3)]. At reguler time intervals, 0.5 ml aliquots[4)] of the solution were withdrawn and analyzed with an amino acid analyzer.

Fig. 2 shows the results of oxidation of 1-amino-2-ethanol by a town gas flame[5)]. The substrate was smoothly oxidized and disappeared within 3 hours. The primary product of the oxidation was aminoacetaldehyde[6)], which was further oxidized to afford glycine. The aminomethyl group in the molecule resisted oxidation, since the amino group was protected in the form of an ammonium salt.



a: Water reservoir
b: Flame
c: Burner nozzle
d: 2-4 cm
e: 10 cm
f: Magnetic stirrer
g: Circulating pump
h: Glass tube (4.5 m x 5 mmI.D.)
i: Ice bath

Fig. 1 The apparatus for the flame-induced oxidation reaction

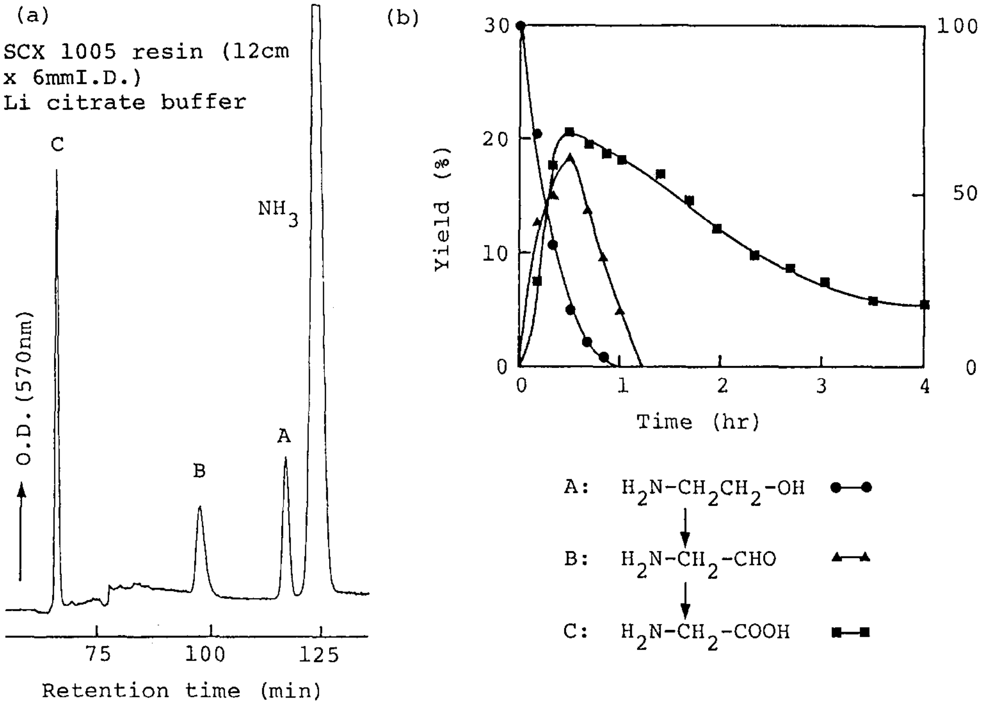


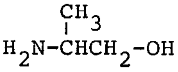
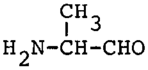
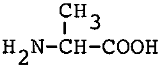
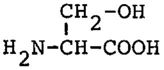
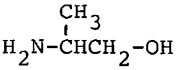
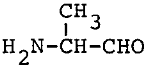
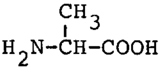
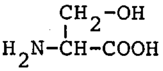
Fig. 2 Oxidation of 1-amino-2-ethanol by a town gas-oxygen flame
(a) The amino acid analysis of oxidation products at 30 min reaction
(b) The time course of the yields of products

The yield of glycine also decreased gradually on prolonged reaction, which may indicate that it was decomposed oxidatively to CO_2 and NH_3. There could be two possible reasons why the sum of the yields and the recovery did not reach 100% at any reaction time. First, another oxidation pathway might exist in which oxidation of the aminomethyl group of the substrate precedes that of the hydroxymethyl group, affording products undetectable with an amino acid analyzer. Second, the oxidation reaction would be vigorously proceeding in the vicinity of the solution surface exposed to the flame and therefore part of the substrate might be rapidly and completely decomposed there.

The results of oxidation of several amines by this method are summarized in the Table. Not only a town gas flame but an ethylene and a hydrogen flame proved to have the ability to oxidize organic compounds in water. In these reactions, amines or aminoalcohols afforded the corresponding amino acids via aminoaldehydes. The yields of hydroxylated products were generally low, due to their labilities to oxidation. The carbon-carbon bonds were cleaved oxidatively and the final product detected was glycine in all of the reactions.

In contrast to the above-mentioned results, an acetylene-oxygen flame practically failed to oxidize ethylamine under similar conditions. Thus, after

Table Flame-induced oxidation of aliphatic amines in an aqueous solution

Substrate	Flame*	Product (Maximum yield, Reaction time**)		
$H_2N\text{-}CH_2CH_3$	A	$H_2N\text{-}CH_2CH_2\text{-}OH$ (3.8%, 15min)	$H_2N\text{-}CH_2\text{-}CHO$ (7.9%, 30min)	$H_2N\text{-}CH_2\text{-}COOH$ (21.3%, 60min)
$H_2N\text{-}CH_2CH_2\text{-}OH$	A	$H_2N\text{-}CH_2\text{-}CHO$ (18.2%, 30min)	$H_2N\text{-}CH_2\text{-}COOH$ (20.1%, 30min)	
$H_2N\text{-}CH_2CH_2CH_3$	A	$H_2N\text{-}CH_2CH_2CH_2\text{-}OH$ (8.9%, 15min) $H_2N\text{-}CH_2\text{-}COOH$ (26.3%, 60min)	$H_2N\text{-}CH_2CH_2\text{-}CHO$ (7.1%, 15min)	$H_2N\text{-}CH_2CH_2\text{-}COOH$ (28.7%, 30min)
$H_2N\text{-}CH_2CH_2CH_2\text{-}OH$	A	$H_2N\text{-}CH_2CH_2\text{-}CHO$ (3.6%, 20min)	$H_2N\text{-}CH_2CH_2\text{-}COOH$ (15.1%, 60min)	$H_2N\text{-}CH_2\text{-}COOH$ (5.3%, 140min)
 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}HCH_2\text{-}OH$	A	 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}H\text{-}CHO$ (18.6%, 30min) $H_2N\text{-}CH_2\text{-}COOH$ (2.0%, 120min)	 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}H\text{-}COOH$ (14.1%, 60min)	 $H_2N\text{-}\overset{\overset{CH_2\text{-}OH}{\mid}}{C}H\text{-}COOH$ (small amount)
$H_2N\text{-}CH_2CH_3$	B	$H_2N\text{-}CH_2CH_2\text{-}OH$ (0.9%, 30min)	$H_2N\text{-}CH_2\text{-}CHO$ (2.6%, 30min)	$H_2N\text{-}CH_2\text{-}COOH$ (18.4%, 60min)
$H_2N\text{-}CH_2CH_2\text{-}OH$	B	$H_2N\text{-}CH_2\text{-}CHO$ (9.3%, 10min)	$H_2N\text{-}CH_2\text{-}COOH$ (24.5%, 20min)	
$H_2N\text{-}CH_2CH_2CH_3$	B	$H_2N\text{-}CH_2CH_2CH_2\text{-}OH$ (small amount) $H_2N\text{-}CH_2\text{-}COOH$ (28.4%, 90min)	$H_2N\text{-}CH_2CH_2\text{-}CHO$ (5.3%, 10min)	$H_2N\text{-}CH_2CH_2\text{-}COOH$ (24.9%, 30min)
$H_2N\text{-}CH_2CH_2CH_2\text{-}OH$	B	$H_2N\text{-}CH_2CH_2\text{-}CHO$ (18.2%, 10min)	$H_2N\text{-}CH_2CH_2\text{-}COOH$ (29.0%, 30min)	$H_2N\text{-}CH_2\text{-}COOH$ (22.9%, 60min)
 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}HCH_2\text{-}OH$	B	 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}H\text{-}CHO$ (15.7%, 20min) $H_2N\text{-}CH_2COOH$ (3.7%, 90min)	 $H_2N\text{-}\overset{\overset{CH_3}{\mid}}{C}H\text{-}COOH$ (16.0%, 30min)	 $H_2N\text{-}\overset{\overset{CH_2\text{-}OH}{\mid}}{C}H\text{-}COOH$ (2.2%, 60min)
$H_2N\text{-}CH_2CH_2\text{-}OH$	C	$H_2N\text{-}CH_2\text{-}CHO$ (16.1%, 10min)	$H_2N\text{-}CH_2\text{-}COOH$ (34.2%, 45min)	

* A: town gas-oxygen flame, B: hydrogen-oxygen flame, C: ethylene-oxygen flame.

** The reaction time taken to reach the maximum yield.

exposure to this flame for 3 hours, the starting material did not decrease in the solution and no product was detected. Judging from this fact, the flame-induced oxidation reported here could not be due to a thermal decomposition and an air oxidation of the substrates, but would be caused by some reactive species which passes from the flames into the solution. Reactive species that exist in flame7) and oxidize organic compounds in an aqueous solution might be mainly various kinds of radicals, especially a OH and a OOH radical. Taking into account the higher reactivity of the former than that of the latter, the OH radical in the flames is considered to oxidize amines in solution. The fact that the acetylene flame lacks the oxidation-inducing ability might indicate that it is poor in OH radical, possibly because of the lower hydrogen content of acetylene (C_2H_2) than those of the other flammable gases. Further studies are now in progress to make this problem clearer.

It is noteworthy that the water-phase reaction induced by flames proved not to be so complex as compared with gas-phase combustion reactions, but to proceed by a stepwise oxidation mechanism. This study will provide new experimental evidences of aqueous phase reactions which are effected by reactive species generated in a gas phase.

Notes

1) The composition of the town gas used is as follows; methane: 88%, ethane: 5%, propane: 5%, butane: 2%.

2) The conditions concerning flames are summarized in the following table.

Flame	Burner nozzle (mmI.D.)	Flow rate of gas (l/min) Flammable gas	Oxygen
Town gas-O_2 flame	9	1.4	3.5
Hydrogen-O_2 flame	1.5	1.8	0.9
Ethylene-O_2 flame	6	0.8	1.4
Acetylene-O_2 flame	1.5	1.5	1.0

3) About 400 ml of water was added in the course of reaction for 6 hours.

4) The samples were immediately frozen and kept in a freezer before analysis.

5) The yields of products and the reaction times taken to reach the maximum yields fluctuated to some extent on repeated runs.

6) The concentration of aminoaldehyde was determined from an increase of the corresponding aminoalcohol on sodium borohydride treatment of the reaction mixture.

7) Besides the active species stated in the text, excited molecules and small amounts of ionic species are present in flames and ultraviolet light is emitted from flames.

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