

Ozonization of Amides

Synopsis

Ozonization of various amides was carried out as a model reaction for the degradation of polyamides with ozone. *N*-alkylamides and *N,N*-dialkylamides were found to be reactive compared with those amides which have no alkyl group on the nitrogen atom, and it was suggested that ozone attacks preferentially *N*-methylene or *N*-methyl group of amides in the first step of ozonization.

INTRODUCTION

Amides have often been used as model compounds in the investigation on the degradation of polyamides.¹⁻⁷ For example, the result of the oxidative degradation of nylon-6 was interpreted on the basis of the result of the oxidation of ϵ -caprolactam with molecular oxygen.⁸ However, there has been no report on the ozonization of amides.

This paper deals with an investigation on the ozonization of various amides as a model reaction for the degradation of polyamides with ozone.

EXPERIMENTAL

Commercial amides, catalase (2000–5000 sigma unit/mg dry weight) and other reagents were used without further purification.

40 g of amides were charged into 150 mL reaction vessels and were stirred using a magnetic agitator. Ozonized oxygen (ozone concentration of 3.0 vol %) produced by Nippon Ozone 0-3-2 ozone generator was introduced into the vessels at a flow rate of 540 ml/min.

Products were analyzed using a Hitachi 063 gas chromatograph, a Varian T-60A ¹H NMR spectrometer, a Hitachi 215 infrared spectrophotometer, and a Hitachi RMU 6L mass spectrometer.

The amount of peroxide was determined by an iodometric titration of the reaction mixture which was pretreated with catalase to decompose hydrogen peroxide.

RESULTS AND DISCUSSION

The result of the ozonization of amides is shown in Table I. Formamide is fairly stable, and the reactivity of acetamide and propionamide is as low as that of formamide, which shows that alkyl groups adjacent to carbonyl group are not susceptible to ozone. Substitution of *N*-hydrogen atoms with alkyl groups increases the reactivity of amides (compare run 1 with runs 4, 5, and 6, or run 2 with runs 7, 8, 9, and 10). This seems to indicate that ozone attacks *N*-alkyl groups. *N,N*-dialkylamides are more reactive than *N*-alkylamides (compare runs 4 and 5, 7 and 8, or 9 and 10). The alkyl group adjacent to carbonyl group increases the reactivity of *N*-alkylamides and *N,N*-dialkylamides (compare runs 4 and 7, 5 and 8, or 6 and 10).

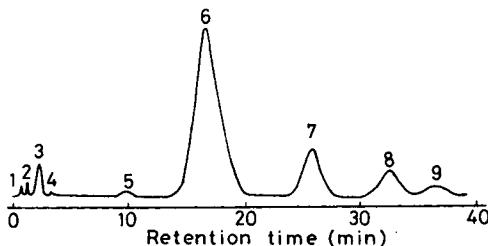


Fig. 1. Gas chromatogram of ozonized *N,N*-diethylacetamide. Column packing: Ethylene glycol adipate polyester (2 m); column temperature: 130°C; carrier gas: He (30 mL/min). (3) Acetaldehyde; (5) water; (6) *N,N*-diethylacetamide, (7) *N*-ethylacetimide; (8) *N*-ethylacetamide. (1), (2), (4), and (9) Unknown products.

TABLE I
 Ozonization of Amides^a

Run	Amide	Temp (°C)	Reaction time (h)	Amide consumed (%)	Peroxide ^b formed (%)	H ₂ O ₂ ^b formed (%)
1	HCONH ₂	90	2	<3 ^c	0.2	0.02
2	CH ₃ CONH ₂	90	2	<1 ^c	0.3	0.09
3	CH ₃ CH ₂ CONH ₂	90	2	<2.5 ^c	0.2	0.02
4	HCONHCH ₃	40	4	8.7	1.0	0.4
5	HCON(CH ₃) ₂	40	4	20.7	5.8	0.7
6	HCON(CH ₂ CH ₃) ₂	40	4	25.9	6.2	0.9
7	CH ₃ CONHCH ₃	40	4	12.5	5.4	0.2
8	CH ₃ CON(CH ₃) ₂	40	4	43.3	19.0	1.3
9	CH ₃ CONHCH ₂ CH ₃	40	4	18.8	6.4	0.3
10	CH ₃ CON(CH ₂ CH ₃) ₂	40	4	41.1	13.7	1.5
11	HCONHC(CH ₃) ₃	40	4	9.6	2.4	1.0
12	ε-Caprolactam	90	4	16.9	6.4	0.1
13	α-Pyrrolidone	40	4	8.2	4.4	1.1

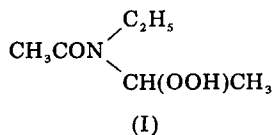
^a Flow rate of ozonized oxygen (ozone concentration of 3.0 vol %): 540 mL/min. Initial amount of amides charged was 40 g.

^b Based upon the amount of amide charged.

^c Reproducibility of the analysis was poor and the maximum analytical values are shown.

Figure 1 shows the result of the gas chromatographic analysis of the reaction mixture of ozonized *N,N*-diethylacetamide. The compounds corresponding to peaks 3, 5, 6, 7, and 8 were found to be acetaldehyde, water, *N,N*-diethylacetamide, *N*-ethylacetamide, and *N*-ethylacetamide respectively. The product corresponding to peak 9 contained acetyl and ethyl group; however, it could not be identified. The yield of the products corresponding to peaks 1, 2, and 4 were too low to be identified.

Peroxide formed in the ozonization of *N,N*-diethylacetamide was identified as *N,N*-diethylacetamide hydroperoxide (I) on the basis of its ¹H NMR spectrum and mp (74°C).³



It was found that adipimide and *N*-methylacetamide were obtained as main products in the ozonization of ε-caprolactum and *N,N*-dimethylacetamide, respectively.

The results obtained here suggest that ozone attacks preferentially *N*-methyl or *N*-methylene groups of amide in the first step of ozonization.

High reactivity of *N*-methyl or *N*-methylene groups of various amides in the photoinduced,^{5,7} transition metal-hydroperoxide catalyzed,⁹ and thermal,^{2,8,10} oxidation of amides or in the reaction of photochemically excited acetone with amides¹¹ has been reported. Sharkey and Mochel⁷ stated that *N,N*-dialkylamides are more reactive than *N*-alkylamides in the photoinduced oxidation, which is the same phenomenon observed in this work. The higher reactivity of *N,N*-dialkylamides compared with that of *N*-alkylamides may be attributed to the increase in the number of the sites of attack by ozone. The promoting effect of alkyl group adjacent to the carbonyl group of *N*-alkylamides and *N,N*-dialkylamides remained unknown.

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SEI-ICHIRO IMAMURA
KOJI NISHII
HIROSHI TERANISHI

Department of Chemistry
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto 606, Japan

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