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THE PHOTOCHEMICAL AMINATION OF CYCLOHEXANE WITH HYDRAZINE[1]

Y. OGATA, Y. IZAWA and H. TOMIOKA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University,
Nagoya, Japan

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Abstract—The UV light-induced amination of cyclohexane in a liquid phase at room temp has been studied. The amination with hydrazine forming cyclohexylamine is possible, the best yield being 45% on the basis of hydrazine, one of the by-products being cyclohexanol. The effect of reaction conditions and photocatalysts on the yield of amination has been examined. Initial concentration of hydrazine is important and the lower concentration tends to raise the yield. Zinc oxide is an effective photocatalyst.

ALTHOUGH there are many methods for the preparation of aliphatic amines, the only paper on the photochemical amination of alkanes is the Gesser's report[2] which discusses the photochemical decomposition of ammonia in which isopropylamine is produced in poor yield.

In preliminary experiments on the photochemical reaction of cyclohexane with hydrazine, we discovered that amination is possible. The present paper describes the UV light-induced amination of cyclohexane with hydrazine in t-butanol.

RESULTS AND DISCUSSION

The reaction products and experimental conditions. In Table 1 the photochemical reaction of cyclohexane with hydrazine in a solution homogenized with t-butanol at room temperature (25–30°) is given. The best yield (45%) of cyclohexylamine was obtained with 0·0103 M hydrazine, 0·0195 M cyclohexane and irradiation for 40 hr.

TABLE 1. THE YIELDS OF CYCLOHEXYLAMINE AND CYCLOHEXANOL IN THE PHOTOCHEMICAL REACTION OF CYCLOHEXANE WITH HYDRAZINE IN t-BUTANOL AT 25–30°

Molar ratio, $[N_2H_4]:[C_6H_{12}]$	$[N_2H_4]$ M	$[C_6H_{12}]$ M	Irradiation time, hr	Yield, %	
				$C_6H_{11}NH_2$[a]	$C_6H_{11}OH$[b]
1:2	0·0103	0·0195	20	33	10
			40	45	15
	0·0575	0·111	20	21	5·0
			40	28	6·5
	0·111	0·242	20	6·4	4·4
			40	10	5·1
	0·196	0·399	20	5·3	1·8
			40	4·3	4·5
1:5	0·174	0·885	20	4·1	0·4
			40	2·3	0·7
1:10	0·160	1·605	20	3·2	0·3
			40	3·2	0·5
3:1	0·578	0·192	20	3·8	1·9
			40	0·7	3·3

[a] On the basis of hydrazine. [b] On the basis of cyclohexane.

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[1] Contribution No. 81.

[2] H. Gesser, *J. Amer. Chem. Soc.* 77, 2626 (1955).

Figure 1 shows the correlation of the yield of cyclohexylamine to the concentration of hydrazine with the molar ratio of hydrazine vs. cyclohexane 1:2. An increase of the concentration of hydrazine above 0·0103 M results in a decrease in the yield and the correlation curve becomes linear above 0·1 M hydrazine. In contrast, an increase of the molar ratio of hydrazine vs. cyclohexane with constant concentration of hydrazine results in a small decrease in the yield. Furthermore, when the amination is carried out with 2·0 M hydrazine, no cyclohexylamine was detected even after irradiation for 50 hr. The data indicates that for a higher yield of cyclohexylamine the initial concentration of hydrazine is more important than the molar ratio of hydrazine vs. cyclohexane. The difference between the yield for 40 hr and that for 20 hr decreases with the concentration of hydrazine. As to the amination with over 0·17 M hydrazine the yield for 40 hr is lower than that for 20 hr. These lower yields may be explained by the photochemical decomposition of cyclohexylamine induced by hydrazine, i.e., the abstraction of amino hydrogen from cyclohexylamine by radicals $N_2H_3\cdot$ and/or $NH_2\cdot$ produced in the photolysis of hydrazine becomes more pronounced at higher concentrations of hydrazine. A similar phenomenon has been observed in the photolysis of n-hexylamine in n-hexane solution.[3] In the present reaction, one of the by-products is cyclohexanol (Fig. 2). The content of cyclohexanol increases with the irradiation time. It is rational that cyclohexanol is produced by the photo-oxidation of cyclohexane with dissolved oxygen; i.e., the preliminary removal of dissolved oxygen by bubbling nitrogen gas into the reaction mixture results in less cyclohexanol being produced, while the preliminary introduction of oxygen gas into the mixture gives ca. a tenfold higher yield of cyclohexanol. Furthermore, no cyclohexanol was detected during the irradiation of an oxygen-free t-butanol solution of cyclohexylamine and hydrazine, although Pouyet[4] has reported that n-hexanol is produced by the photodecomposition of an aqueous solution of n-hexylamine;—his decomposition experiments were probably done in the presence of dissolved oxygen. The product corresponding to the peak (IV) in the gas chromatograph

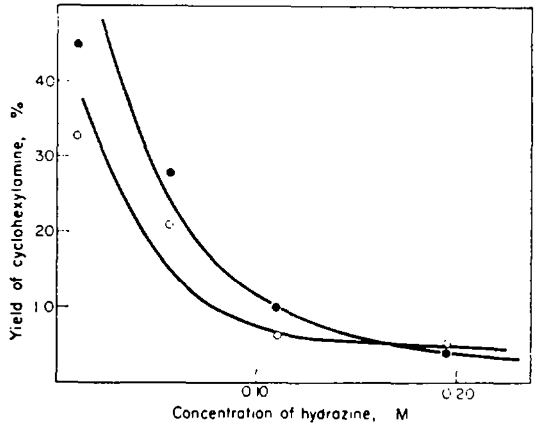

Fig. 1. The correlation between the yield of cyclohexylamine and the concentration of hydrazine: ○, irradiation for 20 hr; ●, for 40 hr.

[3] G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.* 188 (1952).

[4] M. B. Pouyet, *C.R. Acad. Sci., Paris* **258**, 2317 (1964).

(Fig. 2), and which increases with the irradiation time and results in decreasing yields of cyclohexylamine, is probably due to decomposition of cyclohexylamine, since the peak in the gas chromatograph is identical with that which appears during the irradiation of a t-butanol solution of cyclohexylamine and hydrazine. The product has not yet been identified.

The effect of photocatalysts. The effect of ordinary catalysts, such as oxides of titanium, zinc and molybdenum, on the photochemical amination are listed in Table 2. These catalysts, especially zinc oxide, are effective in a 0·111 M hydrazine solution. Zinc oxide is effective even with 0·2 M hydrazine.

TABLE 2. THE EFFECT OF PHOTOCATALYSTS ON THE YIELDS OF CYCLOHEXYLAMINE AND CYCLOHEXANOL PRODUCED FROM CYCLOHEXANE AND HYDRAZINE IN t-BUTANOL AT 25–30°

Photocatalysts	$[N_2H_4]$ M	$[C_6H_{12}]$ M	Irradiation time, hr	Yield, % $C_6H_{11}NH_2$[a]	Yield, % $C_6H_{11}OH$[b]
TiO_2	0·111	0·242	20	10	2·4
			40	10	4·7
ZnO	0·111	0·242	20	15	3·9
			40	13	5·8
TiO_2	0·198	0·406	20	3·5	0·4
			40	6·0	1·6
ZnO	0·198	0·406	20	6·3	1·4
			40	13	3·6
MnO_2	0·198	0·406	20	2·8	1·1
			40	4·3	1·8

[a] On the basis of hydrazine.

[b] On the basis of cyclohexane.

The higher yields obtained after 40 hr′ irradiation in the presence of catalysts may imply that the decomposition of cyclohexylamine is retarded by the adsorption of hydrazine on the surface of catalysts and the consequent lowering of hydrazine concentration. The lower yield of cyclohexanol in the presence of catalysts may also be due to the strong adsorption of hydrazine on the surface of catalysts causing deactivation of the photo-oxidizing sites.

EXPERIMENTAL

Materials. Anhydrous hydrazine, b.p. 113·5–114·0° (lit.[5], 113·5°), n_D^{22} 1·4691 (lit.[5] 1·4670), was prepared by refluxing hydrazine hydrate with NaOH for 2 hr followed by rectification. Cyclohexane was purified by duplicate distillations after passing through dry silica gel, b.p. 80·4–80·6° (lit.[6], 80·7°), no benzene being detected by UV spectrophotometry. t-Butanol was purified by distillation over CaO, b.p. 81·5–83·0° (lit.[7], 82·0–83·0°).

The photochemical amination of cyclohexane with hydrazine. In a quartz tube (30 × 300 mm) filled with a rubber stopper hydrazine (0·01–0·6 M), cyclohexane (0·02–1·6 M) and t-butanol (30 ml) was illuminated with the UV light by Toshiba H-400 P at a distance of 20 cm at room temp for 20–40 hr.

The photocatalyst, when used, (ca. 0·1 g) was suspended in the t-butanol solution (30 ml) containing hydrazine (0·1–0·2 M) and cyclohexane (0·2–0·4 M).

The identification and estimation of products. Analysis of the low boiling reaction products was done by means of gas chromatography employing a Yanagimoto Model GCG-220 operated with a 1·0 m × 4 mm column packed with Silicone DC 550 (30 wt.%) on Celite 545 of 80–100 mesh using

[5] L. F. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine* p. 48, J. Wiley, New York (1951).

[6] R. W. Crowe and C. P. Smith, *J. Amer. Chem. Soc.* **73**, 5406 (1951).

[7] A. A. Moryott, *J. Amer. Chem. Soc.* **63**, 3079 (1941).

a He as a carrier gas (90 ml/min) at 72°. The similarity of the retention times of the peaks of authentic materials with those of the sample established their identity. The estimations of cyclohexylamine and cyclohexanol were made by means of t-butanol as an internal standard. The results of gas chromatography are shown in Fig. 2.

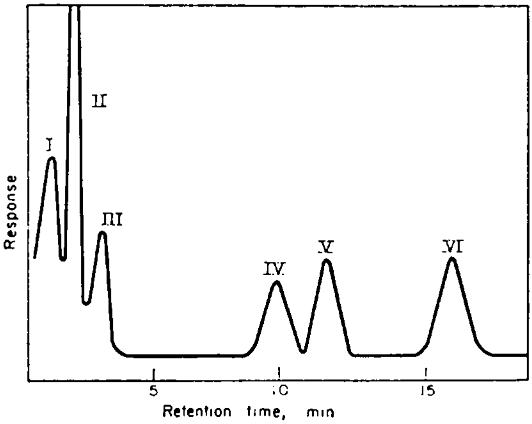

FIG. 2. The gas chromatograph of the reaction products of cyclohexane with hydrazine in t-butanol at 25–30°: I, hydrazine; II, t-butanol; III, cyclohexane; IV, photolysis product of cyclohexylamine; V, cyclohexylamine; VI, cyclohexanol.

Cyclohexylamine was further identified by the Schiff's base formed by condensation with salicylaldehyde; λ_{max} at 410 mμ and near IR absorption with λ_{max} at 1740 and 1810 mμ. Cyclohexanol was identified by comparison with an authentic specimen in gas chromatography using a 1·5 m × 4 mm column packed with PEG #4000 (25 wt.%) on Celite 545 of 60–80 mesh with He as a carrier gas (123 ml/min) at 125°.

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