

OXIDATIONS OF AMINES VI. PLATINUM-CATALYZED AIR
OXIDATIONS OF N-METHYL TERTIARY AMINES*

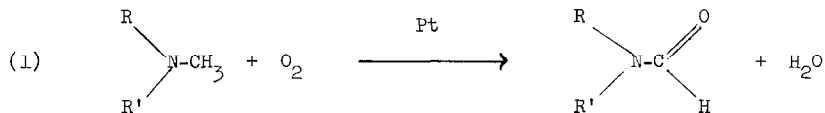
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Fragmentary reports exist concerning transition metal-catalyzed air oxidations(1,2) or dehydrogenations of primary amines(3,4) or secondary amines(5).

None of these results suggest that the catalytic systems are effective for oxidations of tertiary amines. In fact, Balandin and Vasyunina(3) were able to dehydrogenate a primary amine function in the presence of a tertiary function without altering the tertiary amine functional group. Most of the results reported involved vigorous conditions, e.g., 320-400° (3,4,5) or in refluxing xylene(2), though one example(1) involved reactions at ambient temperatures.

We have now discovered that platinum is an effective catalyst for the molecular oxygen oxidation of N-methyl groups in tertiary amines to give N-formyl groups. The reaction is remarkably selective, inasmuch as N-benzyl groups or N-ethyl groups in tertiary amines are not similarly attacked. Furthermore, the oxidations occur at ambient temperatures, requiring only stirring of the platinum catalyst with the amine in a solvent. Clean yields of N-formyl compounds are obtained, with evidence of only trace quantities of side-products (by vapor phase chromatography). The general equation is indicated in eq (1).



* Paper number V of this series, "Oxidations of Amines. V. Duality of Mechanism in the Reactions of Aliphatic Amines with Permanganate", D. H. Rosenblatt, G. T. Davis, L. A. Hull, and G. D. Forberg, J. Org. Chem., 33, 1649 (1968).

Though the benzyl group of benzyldimethylamine is not oxidized in this system, dibenzylamine is readily oxidized to give a mixture of benzaldehyde (16 percent) and benzylbenzaldimine (51 percent). Yields obtained by vapor phase chromatography are presented in the table below:

Platinum-Catalyzed Oxidations of Amines in Benzene at Room Temperature			
Amine	Reaction Time (Hrs.)	Principal Products	Yields (percent)
Trimethylamine	48	Dimethylformamide	74
Benzyldimethylamine	24	N-Benzyl-N-Methylformamide	85
N-Methylpiperidine	20	N-Formylpiperidine	100
Dibenzylamine	22.5	Benzylbenzaldimine	51
Tribenzylamine	16	Benzaldehyde	Trace
Triethylamine	20	None detected	---

A typical procedure is as follows: To 0.50 g of platinum black catalyst in a 50 ml vaccine bottle was added 5 ml of a 0.200 M solution of the amine in benzene. The air was displaced with an oxygen atmosphere. After magnetically stirring the stoppered flask for 16-48 hours, the contents were analyzed on an F and M Model 400 Biomedical Gas Chromatograph equipped with a flame ionization detector. Most analyses were made on a 4 ft column of 15 percent Silicone QF-1 on 80-100 S. (Analyses establishing the absence of N-methylpiperidine or piperidine following oxidation of N-methylpiperidine were made on 4 ft 4 percent Silicone SE-30 and 3 percent Versamid 900 on 80-100 S). Identity of products was obtained by comparison of retention times with authentic samples, and by comparison of infrared spectra of residues obtained on evaporation of the benzene solvent with infrared spectra of authentic samples. N-Benzylbenzaldimine was isolated by preparative gas chromatography. In all cases, the infrared spectra were identical with the authentic specimens.

In a preparative run, 0.1 mole of benzyldimethylamine was oxidized in 100 ml benzene in the presence of 2.00 g of platinum black. After reacting for 24 days, a yield of 35 percent purified N-benzyl-N-methylformamide was obtained. There was recovered 29 percent of starting amine as the hydrochloride.

REFERENCES

1. H. Wieland and F. Bergel, *Ann.* 439, 196 (1924).
2. K. W. Rosenmund and G. Jordan, *Ber.* 58B, 51 (1925).
3. A. A. Balandin and N. A. Vasyunina, *Zhur. Obschie Khim.*, 18, 398 (1948).
4. A. A. Balandin and N. A. Vasyunina, *Doklady. Akad. Nauk S.S.S.R.*, 103, 831 (1955).
5. J. K. Dixon, *Chem. Abstr.*, 44, 3040 (1950), U. S. Patent, 2,474,782.