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# Products and Mechanisms in the Anodic Oxidation of *N,N*-Dimethylbenzylamine in Methanol

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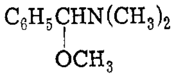
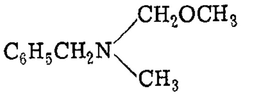
The anodic oxidation of *N,N*-dimethylbenzylamine has been studied in methanol–tetra-*n*-butylammonium fluoroborate and in methanol–potassium hydroxide. The major oxidation mechanism is of the ECE type and initiated by electron transfer from the amine substrate. The initially formed cation radical loses a proton and transfers an electron in subsequent steps to give cations, which react with available nucleophiles to yield the final products. The relative amount of attack on the methyl and benzyl positions is determined by the nature of the base participating in the proton transfer. When the base is the amine substrate, attack on methyl is strongly favored. When a strong base, *e.g.*, hydroxide ion or methoxide ion, is involved, the direction of attack is very nearly in accord with statistical expectations.

The anodic methoxylation of *N,N*-dimethylbenzylamine in methanol–potassium hydroxide affords two substitution products, α-methoxy-*N,N*-dimethylbenzylamine (I) and *N*-methoxymethyl-*N*-methylbenzylamine (II), in the ratio of 1:4.[1] Weinberg and Brown[1] proposed that this oxidation was initiated by electron transfer from the amine, but Smith and Mann[2] suggested that the oxidation resulted from the attack on the substrate of anodically generated methoxyl radicals. In later work[3] Weinberg supported his proposal by demonstrating that significant methoxylation occurs only at potentials greater than the half-wave potential for *N,N*-dimethylbenzylamine oxidation (0.92 V *vs.* sce at a rotating platinum microelectrode in acetonitrile containing 0.5 *M* lithium perchlorate).



$C_6H_5CH(OCH_3)N(CH_3)_2$

I



II

The preference for substitution of the methyl group was contrary to *a priori* expectation and was even more pronounced in the anodic cyanation of *N,N*-dimethylbenzylamine, where substitution occurred exclusively on the methyl group.[4] Both Weinberg[3] and Andreades[4] have invoked adsorbed intermediates, in which the methyl group of the adsorbed species is more accessible to chemical attack, to account for the observed direction of substitution.

However, many homogeneous, chemical oxidations of *N,N*-dimethylbenzylamine, all initiated by an electron transfer from the amine to form an aminium cation radical, show preferential attack on the methyl group. Some examples are the oxidation by chlorine dioxide in aqueous solution,[5] the oxidation by potassium hexacyanoferrate(III) in 2 *M* potassium hydroxide,[6] and the photochemical oxidation by 4-benzoylbenzoic acid in 2:1 *tert*-butyl alcohol–water.[7] It is, therefore, possible that the observed preferential attack on the methyl group is a, as yet incompletely understood, characteristic reaction of the amine cation radical and does not involve the intervention of the electrode surface. To explore this possibility we have carried out a more detailed study of the anodic oxidation of *N,N*-dimethylbenzylamine.

**Cyclic Voltammetry.** Fleischmann and Pletcher[8] have reported that the solvent decomposition potential, defined as the potential above which the current is greater than 10 mA/cm$^2$, for the acetonitrile–0.14 *M* tetraethylammonium fluoroborate electrolyte exceeds 3 V *vs.* Ag/Ag$^+$ $10^{-2}$ *M*. On cyclic voltammetry of dimethylbenzylamine in acetonitrile–0.1 *M* tetra-*n*-butylammonium fluoroborate, the peak current varied linearly with the amine concentrations, and the peak potential occurred at 0.86 V *vs.* sce, a value in reasonable agreement with the polarographic half-wave potential reported by Weinberg.[3]

Figure 1 shows a cyclic voltammogram for 0.6 *M* dimethylbenzylamine in methanol–0.5 *M* potassium hydroxide at a scan speed of 200 mV/sec. The concentrations are those used in the preparative experiments to be described later. Curve A is for the electrolyte alone and curve B is with added amine. Below 1.1 V *vs.* sce the observed currents are actually depressed by the addition of the amine, and this is in qualitative agreement with a similar observation, based on Tafel plots, made by Weinberg.[3] Above 1.1 V the currents are higher with the amine present. Both dimethylbenzylamine and methoxide ion are being oxidized simultaneously, and the waves for the two oxidations are not fully separable.

The solvent decomposition potential for methanol–0.4 *M* tetra-*n*-butylammonium fluoroborate is approximately 1.3 V *vs.* sce. In this electrolyte methoxide ion is absent, and the current increase above 1.3 V is due to oxidation of methanol. The cyclic voltammogram at a scan speed of 200 mV/sec for 0.6 *M* dimethylbenzylamine in this electrolyte is shown in Figure 2. The concentrations used are again those of preparative experiments. In this system the wave for the amine oxidation is clearly separable from the background, and the peak potential is 0.94 V *vs.* sce.

More detailed cyclic voltammetry studies in both acetonitrile and methanol, with 2.96 × $10^{-2}$ amine and 0.1 *M* tetra-*n*-butylammonium fluoroborate, satisfy the theoretical criteria, developed by Nicholson and Shain,[9] for an

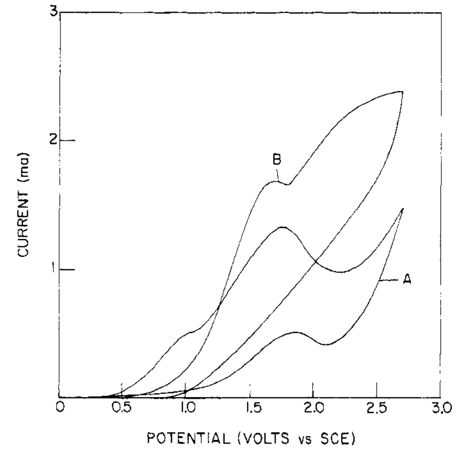


**Figure 1.** Cyclic voltammogram for 0.6 *M* *N*,*N*-dimethylbenzylamine in methanol–0.5 *M* potassium hydroxide at a scan speed of 200 mV/sec: A, background; B, amine.

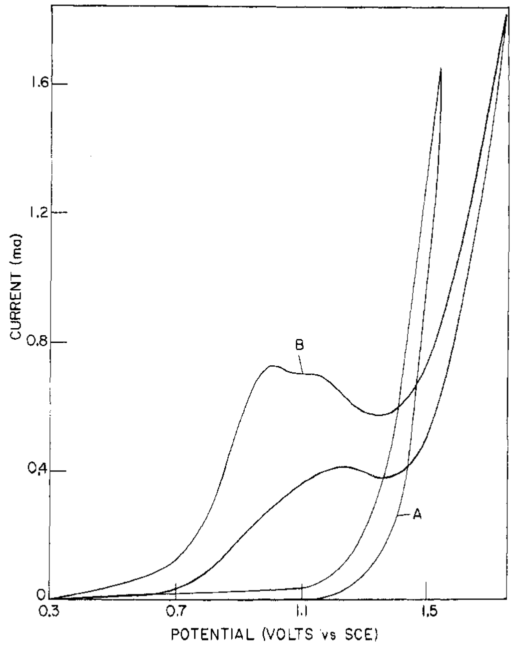


**Figure 2.** Cyclic voltammogram for 0.6 *M* *N*,*N*-dimethylbenzylamine in methanol–0.4 *M* tetra-*n*-butylammonium fluoroborate at a scan speed of 200 mV/sec: A, background; B, amine.

ECE mechanism and eliminate the possibility of an EC mechanism, involving disproportionation of the initially formed cation radical.[10] No detectable cathodic current was observed at scan rates as high as 50 V/sec. The number of electrons transferred in the reaction was found to be greater than one and very probably two.

**Product Studies.** A typical reaction mixture after electrolysis contains eight or more components. Our primary concern, in this study, was the relative amounts of attack on the methyl and benzyl positions of the starting substrate. We have, therefore, chosen to simplify the analytical problem by hydrolyzing the product mixture prior to analysis. After hydrolysis the reaction mixture contains the starting amine, benzaldehyde, resulting from attack on the benzyl position, and *N*-methylbenzylamine and benzyl-

### Table I
### Products Obtained after Anodic Oxidation of 0.1 Mol of Dimethylbenzylamine in Methanol, Passing 0.149 F of Charge at Constant Current, and Hydrolysis of the Reaction Mixture

| Current, A | Recovered $C_6H_5CH_2N(CH_3)_2$, % | Products $C_6H_5CHO$, % | $C_6H_5CH_2NHCH_3$, % | $C_6H_5CH_2NH_2$, % | % starting materials accounted for | Ratio attack on methyl/attack on benzyl |
|---|---|---|---|---|---|---|
| A. With 0.36 *M* Tetra-*n*-butylammonium Fluoroborate as Supporting Electrolyte | | | | | | |
| 2.0 | 73 | 8 | 7 | 2 | 90 | 1.4 |
| 1.0[a] | 57 | 10 | 20 | 4 | 91 | 2.8 |
| 0.5 | 35 | 7 | 48 | 4 | 94 | 8.0 |
| 0.1[b] | 29 | 7 | 58 | 2 | 94 | 8.9 |
| B. With 0.47 *M* Potassium Hydroxide as Supporting Electrolyte | | | | | | |
| 2.0 | 43 | 15 | 34 | 2 | 94 | 2.5 |
| 1.0[b] | 42 | 15 | 36 | 3 | 96 | 2.8 |
| 0.1[b] | 40 | 10 | 35 | 1 | 86 | 3.7 |

[a] Average of three experiments. [b] Average of two experiments.

### Table II
### Products Obtained after Anodic Oxidation of 0.0296 Mol of Dimethylbenzylamine in Methanol at Constant Potential and Hydrolysis of the Reaction Mixture

| Potential, V *vs.* sce | Charge passed, F | Recovered $C_6H_5CH_2N(CH_3)_2$, % | Products $C_6H_5CHO$, % | $C_6H_5CH_2NHCH_3$, % | $C_6H_5NH_2$, % | % starting materials accounted for | Ratio attack on methyl attack on benzyl |
|---|---|---|---|---|---|---|---|
| A. With 0.40 *M* Tetra-*n*-butylammonium Fluoroborate as Supporting Electrolyte | | | | | | | |
| +1.05 | 0.0296 | 44 | 4 | 40 | | 88 | 10.1 |
| +1.60 | 0.0296 | 48 | 5 | 35 | | 88 | 7.0 |
| +1.90 | 0.0296 | 59 | 5 | 23 | 3 | 90 | 5.8 |
| +2.30 | 0.0296 | 63 | 5 | 22 | 3 | 93 | 5.6 |
| B. With 0.47 *M* Potassium Hydroxide as Supporting Electrolyte | | | | | | | |
| +1.0 | 0.0122 | 73 | 4 | 8 | | 85 | 2.0 |
| +1.1 | 0.0300 | 62 | 9 | 21 | | 92 | 2.3 |
| +2.3 | 0.0750 | 16 | 24 | 42 | 6 | 88 | 2.3 |

amine, products from attack on the methyl positions. The justification for this simplifying procedure is given in the Experimental Section.

The results of experiments on the anodic oxidation of *N*,*N*-dimethylbenzylamine in methanol containing 0.36 *M* tetra-*n*-butylammonium fluoroborate as supporting electrolyte and in methanol containing 0.47 *M* potassium hydroxide as supporting electrolyte are shown in Tables I and II. Table I reports the results at constant current, and Table II gives the results at constant potential. The percentages shown in these tables indicate the amounts of starting material converted to a given product rather than coulombic yields. The last column of the two tables, headed, Ratio, attack on methyl/attack on benzyl, is obtained by adding the percentage yield of *N*-methylbenzylamine and two times the percentage yield of benzylamine and dividing the sum by the percentage yield of benzaldehyde. The factor of 2 for the benzylamine is necessary, since its formation results from two stages of oxidation, one on each methyl group, and an overall four-electron change.

In the experiments in the methanol–potassium hydroxide electrolyte the observed ratios of attack on the methyl position to attack on the benzyl position were essentially constant at the average value of 2.2 at constant anodic potentials of 1.0, 1.1, and 2.3 V, all *vs.* sce. In the constant-current experiments the ratios were 2.5 at 2.0 A, 2.8 at 1.0 A, and 3.7 at 0.1 A. From purely statistical considerations one would expect a ratio of 3. The present results, therefore, do not indicate any preference for attack on the methyl group in this electrolyte system.

In the methanol–fluoroborate electrolyte a very different situation is observed. At the lowest constant potential, 1.05 V *vs.* sce, the preference for attack on methyl is strong, and the observed ratio is 10. At 1.60 V there is a sharp drop to a ratio of 7.0, and then as the potential increases there is a further decrease in the ratio to values of 5.8 at 1.9 V and 5.6 at 2.3 V.

In all of the constant-potential experiments attack on the methyl group is, therefore, strongly favored. The experiments at constant current exhibit a similar trend. The highest ratio, 8.9, is observed at the lowest current, 0.1 A. At 0.5 A the ratio drops to 8 and at 1.0 A to 2.8. At the smaller currents, 0.1 and 0.5 A, there is still a preference for methyl group attack, but at 2.0 A the ratio drops to 1.4, where it is now attack on the benzyl group that is favored.

## Experimental Section

**Materials.** Baker and Adamson, electronic grade, acetone-free methanol was used without further purification. DPI acetonitrile containing less than 0.1% water was purified as described by Mann[11] and distilled from phosphorus pentoxide directly into the electrochemical cells. DPI *N*,*N*-dimethylbenzylamine was distilled from calcium hydride, bp 55° (9 mm). Tetra-*n*-butylammonium fluoroborate was prepared and purified as previously described.[12]

***N*-Benzyl-*N*-methylformamide** was prepared by heating *N*-methylbenzylamine (24.2 g, 0.2 mol) with formamide (10 g, 0.22 mol) at 100° until ammonia evolution ceased. Distillation at 1 mm yielded 24.8 g (83.2%) of the amide, bp 104°.

**Cyclic Voltammetry.** These studies were performed with a PAR 170 Electrochemistry unit. A single-compartment cell, fitted with a Pt button working electrode, a Pt sheet auxiliary electrode, and a saturated calomel reference electrode, was used. The supporting electrolyte was 0.1 *M* tetra-*n*-butylammonium fluoroborate. For current function studies a Tektronix Type 564 storage oscilloscope was used.

**Justification of Analytical Method.** In a screening experiment a solution containing 0.1 mol of dimethylbenzylamine and 0.05 mol of tetra-*n*-butylammonium fluoroborate in 140 ml of methanol was electrolyzed at a constant current of 1 A until 0.152 F of charge had been passed. Analysis of the solution by vpc indicated that 64% of the starting amine was unreacted. The products found included 2.0% benzaldehyde, 2.1% *N*-methylbenzylamine, and 1.7% *N*-methyl-*N*-benzylformamide. This accounts for 69.8% of the starting amine. In addition the vpc tracing showed the presence, in lesser quantities, of four compounds, probably methoxy-substituted dimethylbenzylamines, with retention times shorter than that of *N*-methyl-*N*-benzylformamide, and one, possibly the amino ether III, reported by Weinberg,[3] which had a much longer retention time than the amide.

$$(C_6H_5CH_2NCH_2)_2O$$

III

After acid hydrolysis the above reaction mixture afforded 61% recovered amine, 11% benzaldehyde, 12% *N*-methylbenzylamine, and 3.6% benzylamine. These products account for 87.6% of the starting *N*,*N*-dimethylbenzylamine. The formation of *N*-methyl-*N*-benzylformamide, found prior to hydrolysis, requires a four-electron oxidation and represents two stages of oxidation on a methyl group. Therefore, to the extent that some of the *N*-methylbenzylamine results from hydrolysis of the amide, the ratios reported in the last column of Tables I and II are slightly low. In the experiment described above 1.7% of amide was present prior to hydrolysis and 12% of *N*-methylbenzylamine was found after hydrolysis. The amide, therefore, accounts for only 14% of the *N*-methylbenzylamine found.

**Constant-Potential Electrolyses.** The PAR instrument with ir compensation was used. The electrolysis cell was a single compartment, water-jacketed cell, cooled by a continuous flow of tap water. A Teflon cap, which held two Pt sheet electrodes (5.5 × 2.5 cm) 2.5 cm apart, was fitted to the top of the cell, and the sce reference electrode was placed in close proximity to the anode through a hole in the cap. The electrolysis solution was stirred with a magnetic stirring bar.

In a typical experiment a solution of *N*,*N*-dimethylbenzylamine (4.0 g, 0.0296 mol) and tetra-*n*-butylammonium fluoroborate (6.6 g, 0.02 mol) in methanol (50 ml) was electrolyzed under the conditions indicated in Table II. After completion of the electrolysis the solution was transferred to a round-bottomed flask with the aid of additional methanol (20 ml). Water (10 ml) and concentrated hydrochloric acid (10 ml) were added, and the solution was refluxed overnight. The methanol was separated by distillation at atmospheric pressure through a Vigreux column, and this methanol distillate was analyzed by vpc for any products that codistilled.

The addition of ether to the above distillation residue precipitated the fluoroborate salt. Both the salt and the solution were extracted copiously with ether. The ether extracts were combined, dried over magnesium sulfate, and concentrated to a volume of 25 ml for vpc analysis.

The aqueous residue from the above extractions was made basic by the addition of a concentrated solution of sodium hydroxide. This was then again extracted with ether, and the ether extracts were dried and concentrated to a volume of 25 ml for vpc analysis.

For the experiments with the methanol–potassium hydroxide electrolyte the procedure was as shown above except that the hydrolysis was carried out after the addition of 75 ml of water and 20 ml of concentrated hydrochloric acid.

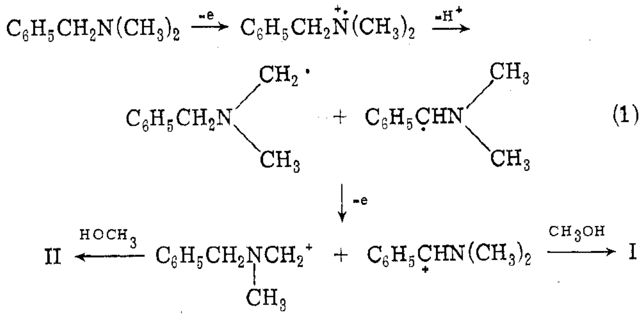
**Constant-Current Electrolyses.** These were carried out using the cell and electrode configuration previously described.[12] The work-up procedure was essentially the same as that described above for the constant-potential electrolyses except that proportionately larger volumes of reagents were used to take care of the larger scale on which the constant current electrolyses were run.

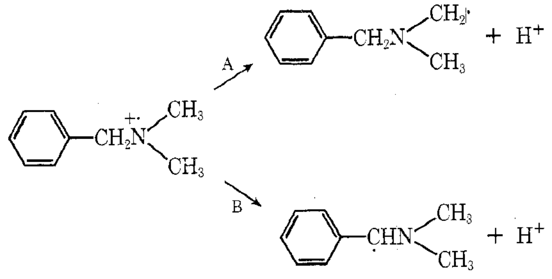
**Vpc Analyses.** These were done under isothermal conditions on an F & M Model 72 dual column gas chromatograph using thermal conductivity detection and a helium carrier gas. Using a 6-ft column packed with 10% SE-30 on 60-80 Diataport S, benzylamine was determined at 100°, benzaldehyde at 120°, and *N*-methyl-*N*-benzylformamide at 160°. Using a 6-ft column packed with 10% polyphenyl ether (six ring) on Diataport S, benzaldehyde, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine were determined simultaneously at 140°. The unknown solutions were compared with standards prepared from the identified components.

## Discussion

An adequate mechanism for the anodic oxidation of *N*,*N*-dimethylbenzylamine in methanol must account, at one and the same time, for both the observed electrochemical parameters and the very large difference in the direction of attack when the supporting electrolyte is changed from potassium hydroxide to tetra-*n*-butylammonium fluoroborate. In the methanol–potassium hydroxide electrolyte the divergence from statistical expectations is small. In the methanol–fluoroborate electrolyte the preference for attack on the methyl group is very large at 1.05 V *vs.* sce, where cyclic voltammetry indicates that electron transfer is occurring only from the amine, but decreases significantly at potentials greater than 1.3 V, where cyclic voltammetry indicates that the amine and the methanol solvent are being oxidized simultaneously.

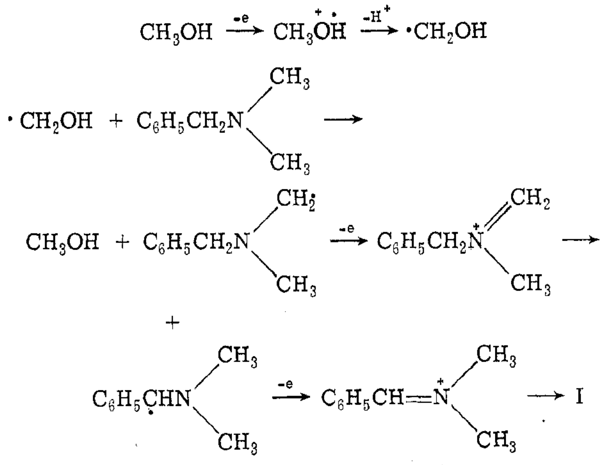
In the synthetic experiment at a constant anodic potential of 1.05 V with methanol–fluoroborate electrolyte (Table II), the oxidation mechanism is unambiguous. At this potential electron transfer can occur only from the amine, and cyclic voltammetry is consistent with an ECE mechanism. The only possible formulation is that shown in eq 1. Yet it is in this very experiment that we found the greatest preference for attack on methyl, the observed ratio for methyl attack/benzyl attack being 10. If, in fact, eq 1 is a correct representation of the reaction mechanism, it follows that in the proton transfer step (eq 2) the rate constant for path A is approximately 3.5 times larger than the rate constant for path B.


(1)


(2)

It is an obvious corollary of the above that, contrary to all *a priori* expectations, the methyl hydrogens in the *N,N*-dimethylbenzylamine cation radical are much more reactive than the methylene hydrogens, or, stated alternatively, that the positive charge density is greater on the methyl hydrogens of the cation radical than on the methylene hydrogens. It is fortuitous that INDO calculations have been carried out on this cation radical by Lars Cedheim at the University of Lund in Sweden, and we are very much indebted to Professor Lennart Eberson, who conveyed the results to us. These calculations assign positive charge densities to all of the methyl and methylene hydrogens. If one assumes a transition state for the proton abstraction reaction that is close to the cation radical, these results indicate that the methyl hydrogens should be roughly twice as reactive as the methylene hydrogens. Taking the statistical factor into account one would expect a reactivity ratio of 6:1 for attack on methyl and methylene hydrogens, respectively. These results afford us some confidence in the validity of our observations and in the correctness of our interpretation.

Still to be explained is the drop in the observed ratios at anodic potentials of 1.5 V and higher. At these potentials electron transfer is occurring simultaneously from both the amine and the methanol solvent, and we would suggest that a second oxidation mechanism becomes possible and competes at these higher potentials. This mechanism, shown in eq 3, is ECE overall, but involves a hydrogen atom abstraction, not by the methoxyl radical, but rather by the hydroxymethyl radical. Since the hydrogen atom abstraction occurs on the amine molecule rather than the cation radical, we can be confident that abstraction from the secondary methylene position will be preferred.


(3)

The synthetic experiments at constant current are in qualitative agreement with the foregoing. At the lowest current (lowest potential) the ratio is highest and decreases regularly with increasing constant current. At the highest constant current used, 2.0 A, the observed ratio, 1.4, actually indicates a preference for attack on the methylene position. This is possible, if, under this condition, eq 3 represents the predominant oxidation mechanism.

It is the presently prevailing view that, in the methanol–potassium hydroxide electrolyte, amine oxidation products result only from the reaction sequence shown in eq 1, where the initiating electron transfer is from the amine substrate. This is based on Weinberg's finding that amine oxidation products are formed only at high enough potentials to permit electron transfer from the amine. This implies that at lower potentials methoxide ion may be oxidized to methoxyl radical, but the radical so formed does not abstract a hydrogen from the substrate amine. We have confirmed this view in a qualitative sense at least. In addition to the experiments shown in Table II, we have done a preparative experiment at a constant anode potential of 0.80 V *vs.* sce. At this potential there is presumably no direct oxidation of amine, and the currents observed (10–15 mA) must be attributed to methoxide ion oxidation. In this experiment there was, in fact, some oxidation of the amine, but the coulombic efficiency (~1%) was almost negligible, and the only oxidation product found was benzaldehyde. This is exactly what might be expected if, in this experiment, the only amine oxidation mechanism available was a counterpart of eq 3 with methoxyl radical as the abstracting species and if the methoxyl radical was extremely inefficient in the abstracting process.

These results pose an apparent contradiction. In both electrolyte systems the predominant oxidation mechanism is that shown in eq 1, yet in methanol–fluoroborate this results in a strong preference for attack on the methyl group, but in methanol–potassium hydroxide the direction of attack approaches statistical expectations. The difficulty is readily overcome if one takes due cognizance of the proton-accepting base in the two experiments. In the methanol–

fluoroborate electrolyte the only available base is the amine substrate, but in the methanol–potassium hydroxide electrolyte the much stronger bases, hydroxide ion and/or methoxide ion, are present at a combined concentration of 0.47 *M*. It is reasonable that the weaker base should attack the positions of higher positive charge density in a discriminating fashion and that the much stronger base should attack more randomly in a nondiscriminating reaction.

Support for this point of view can be mustered from other oxidation studies of *N*,*N*-dimethylbenzylamine. In both the oxidation with chlorine dioxide[5] at pH 8 and in the oxidation with potassium hexacyanoferrate (III) in 2 *M* potassium hydroxide[6] there is exhibited only a modest preference for attack at the methyl position. We have repeated the latter oxidation. The oxidation products obtained were benzaldehyde, *N*-methylbenzylamine, and *N*-benzyl-*N*-methylformamideand the ratio of methyl attack to benzyl attack was 2.8. The electrochemical dealkylation of *N*,*N*-dimethylbenzylamine at pH 12 at a glassy carbon electrode involves a mechanism similar to that shown in eq 1, and again there is no special preference for removal of the methyl group.[13] All of the above reactions are in the presence of a strong base where the proton transfer step would be expected to be nondiscriminating. By contrast, the photochemical oxidation of dimethylbenzylamine, where the strongest base present is the amine substrate, shows a very strong, albeit not quantitatively determined, preference for attack on the methyl group.[7]

**Registry No.**—*N*-Benzyl-*N*-methylformamide, 17105-71-4; *N*-methylbenzylamine, 103-67-3; formamide, 75-12-7; *N*,*N*-dimethylbenzylamine, 103-83-3.

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# Peroxodisulfate Oxidation of Guanosine and Deoxyguanosine in Alkaline Aqueous Solution[1]

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The peroxodisulfate oxidation of the common nucleosides has been investigated. Only guanine nucleosides show appreciable reaction with peroxodisulfate in 1 *M* $Na_2CO_3$ solution at 40°. Rate *vs.* pH plots suggest that the guanosine anion is the kinetically significant reactant. No reaction between guanosine and peroxodisulfate was observed under neutral or mildly acidic conditions at 40°. Radical traps have no effect on either the rate or extent of peroxodisulfate disappearance or on the rate or extent of product formation. Products identified as a result of peroxodisulfate oxidation of guanosine were guanidine, urea, ribose, ribosylurea, and ribonic acid. Those products identified for deoxyguanosine oxidation were guanidine, urea, and deoxyribosylurea. Alkaline peroxodisulfate oxidation shows promise as a selective chemical method for the modification of polynucleotides at the site of guanine residues.

Our studies on the peroxodisulfate oxidation of the common nucleic acid bases[2] have shown that guanine reacts much more rapidly under all conditions than any other base. The relative rates of oxidation in 1 *N* KOH at 40° are as follows: adenine, 1; thymine, 5.5; uracil, 5.2; cytosine, 8.6; guanine, 338. We have further shown that the rates of these oxidations are dependent upon pH, since it is only the dianions of thymine and uracil and the monoanions of adenine and cytosine which react at a significant rate with peroxodisulfate ions. In contrast, both the mono- and dianions of guanine are reactive. It appeared probable, therefore, that of the nucleosides, only guanosine would be oxidized. We present evidence in this paper to substantiate this supposition. This suggests that peroxodisulfate ions can be used to modify polynucleotides, particularly polydeoxyribonucleotides, in a highly selective way.

## Materials and Methods

Adenosine, uridine, thymidine, cytidine, guanosine, and deoxyguanosine were purchased from P & L Biochemicals Inc., Milwaukee, Wis. Guanidine hydrochloride was obtained from Heico, Inc., Delaware Water Gap, Pa. D-Ribose was purchased from Pfanstiehl Laboratories, Waukegan, Ill. Ribonolactone was obtained from the Sigma Chemical Co., St. Louis, Mo. 2-Deoxy-D-ribose and 8-hydroxyguanine were purchased from the Aldrich Chemical Company, Milwaukee, Wis. Potassium peroxodisulfate was a Baker Analyzed reagent, Phillipsburg, N. J., and was recrystallized from water for use in kinetic experiments. All other inorganic chemicals were Baker Analyzed reagents and were used without further purification. Ribosylurea was synthesized by the method of Benn and Jones[3] but was not isolated. Deoxyribosylurea was prepared by permanganate oxidation of deoxyguanosine by the method of Jones and Walker.[4] Ribonic acid was prepared by hydrolysis of ribonolactone in aqueous sodium hydroxide solution.

Ultraviolet absorption spectra were measured using a Perkin-Elmer Model 202 spectrophotometer. Colorimetric measurements were carried out on a Klett-Summerson colorimeter.