nmr ($CDCl_3$, δ) 8.1 (d, 1 H, J = 9 cps), 6.6 (d, 1 H, J = 9 cps), 3.2 (m, 4 H), 1.4 (m, 3 H); mass spectrum m/e (rel intensity) 181 (16), 152 (73), 151 (48), 135 (37), 105 (100), 65 (40), 50 (38), 44 (84), and 40 (81).

Registry No.—**1**, 6332-77-0; **2**, 934-03-2; **6** (radical anion), 11089-69-3; EDA, 107-15-3; EDA-d_8, 34281-22-6; DMEDA, 108-00-9; pyrazine radical anion, 11089-67-1; pyrazine radical anion-d_8, 11089-66-0; dihydropyrazine radical anion, 11089-68-2; nitrobenzene, 98-95-3; butyllithium, 109-72-8; sodium, 7440-23-5; lithium, 7439-93-2; nitrobenzene radical anion, 15753-78-3; pyrazine, 290-37-9; hydrogen, 1333-74-0.

Anodic Oxidations. VII. The Reaction Mechanism in the Electrochemical Oxidation of *N*,*N*-Dimethylformamide in Acetic Acid and in Methanol

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The anodic oxidation of *N*,*N*-dimethylformamide has been studied in methanol and in acetic acid, with fluoroborates, nitrates, and acetates as the supporting electrolytes. The operation of two oxidation mechanisms has been demonstrated. In the one, the primary reaction is an electron transfer from the amide to give a cation radical. In the other, the initiating reaction is an electron transfer from nitrate ion to give a nitrate radical. With a nitrate salt as the supporting electrolyte, both mechanisms operate, and the conditions under which each occurs have been defined.

There is evidence that, in acetic acid containing acetate ion, *N*,*N*-dimethylamides oxidize at a lower potential than acetate ion.[1,2] and the first step in the oxidations to form *N*-acetoxymethyl-*N*-methylamides is an electron transfer from the amide substrate. Nevertheless, when these reactions are run at constant current for preparative purposes, the coulombic efficiencies are low, and a significant portion of the charge passed is used in the Kolbe oxidation of acetate ion to give ethane and carbon dioxide.[1b]

The anodic oxidation of *N*,*N*-dimethylamides in alcohols, with nitrate salts as supporting electrolytes, is a good method for preparing *N*-alkoxymethyl-*N*-methylamides.[1c] However, there is uncertainty as to the mechanism. Current–potential curves, during electrolysis, support discharge of nitrate ion as the initiating reaction,[1c] but cyclic voltammetric curves show very similar peak potentials for *N*,*N*-dimethylformamide and for nitrate ion, suggesting that the amide and the anion oxidize simultaneously.[3]

The present research was undertaken to resolve some of these uncertainties. The anodic oxidation of *N*,*N*-dimethylformamide in both alcohols and acetic acid was studied using quaternary ammonium fluoroborates as the supporting electrolytes. Since the fluoroborate anion is known to oxidize at very high potentials,[4] it is certain that, in these systems, the amide oxidation is initiated either by direct oxidation of the amide or by oxidation of the solvent. For comparison purposes, these oxidations were also studied with quaternary ammonium nitrates as the supporting electrolytes.

(1) (a) S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Amer. Chem. Soc.*, **86**, 2745 (1964); (b) *J. Org. Chem.*, **31**, 128 (1966); (c) *J. Amer. Chem. Soc.*, **88**, 4657 (1966).

(2) L. Eberson and K. Nyberg, *ibid.*, **88**, 1686 (1966).

(3) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 9. The values given in Table 9-7 of this chapter for the peak potentials for the oxidation of aliphatic amides are in error and should all be higher by 0.6 V (private communication from Professor C. K. Mann).

(4) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).

Results

The electrochemical preparation of *N*-alkoxymethyl-*N*-methylformamides, using ammonium nitrate as the supporting electrolyte, has been described.[1c] In comparable oxidations, with a quaternary ammonium fluoroborate as the supporting electrolyte, the yields of product, isolated by distillation, varied from 60 to 90%. In a similar experiment in methanol, with sodium methoxide as the supporting electrolyte, the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 15%. In acetic acid the coulombic yield of isolated *N*-acetoxymethyl-*N*-methylformamide was >50% with a fluoroborate electrolyte but only 5.3% with sodium acetate as the supporting electrolyte.

The experiments compiled in Table I were carried out to obtain more accurate data on coulombic yields and to compare the reactions in the presence of fluoroborates with those using nitrates as supporting electrolytes. The solutions electrolyzed contained 0.05 mol of the supporting electrolyte, 0.13 mol of *N*,*N*-dimethylformamide and 140 ml of either acetic acid or the appropriate alcohol. The amount of charge passed was in every case 0.112 F, and the products formed were determined by vpc.

To elucidate the reaction mechanisms in these systems, the interdependence of the electrode potential and the electric current for the anodic oxidation of *N*,*N*-dimethylformamide was studied by potentiostatic steady-state measurements and by cyclic voltammetry. As was anticipated, electrooxidations in the presence of the fluoroborate anion proved the most straightforward in mechanism. The polarization curves shown in Figure 1 correspond to the steady-state behavior of the electrolyte (tetrabutylammonium fluoroborate in methanol) (curve a) and of added dimethylformamide at two different concentrations (curves b and c). In the absence of added dimethylformamide, the oxidation of methanol is self-inhibiting, and the current density remains low (i < 10 mA cm^{-2}) until the oxidation of

TABLE I

ANODIC OXIDATION OF *N,N*-DIMETHYLFORMAMIDE AT CONSTANT CURRENT

Solvent	Supporting electrolyte	Current, A	Product	Coulombic yield, %
Methanol	Tetraethylammonium fluoroborate	2.0	$HCON(CH_3)CH_2OCH_3$	100
Methanol	Tetraethylammonium nitrate	2.0	$HCON(CH_3)CH_2OCH_3$	88.4
Ethanol	Tetra-*n*-butylammonium fluoroborate	1.0	$HCON(CH_3)CH_2OC_2H_5$	90.0
Ethanol	Tetraethylammonium nitrate	1.0	$HCON(CH_3)CH_2OC_2H_5$	61.4
1-Butanol	Tetra-*n*-butylammonium fluoroborate	0.5	$HCON(CH_3)CH_2OC_4H_9$	87.5
1-Butanol	Tetraethylammonium nitrate	0.5	$HCON(CH_3)CH_2OC_4H_9$	62.3
Acetic acid	Tetra-*n*-butylammonium fluoroborate	0.5	$HCON(CH_3)CH_2OOCCH_3$	54.5
Acetic acid	Tetraethylammonium nitrate	1.0	$HCON(CH_3)CH_2OOCCH_3$	68.6

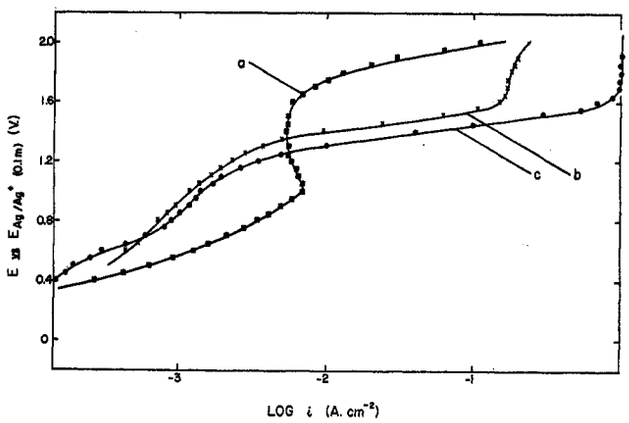


Figure 1.—Potentiostatic, steady-state polarization curves obtained at a platinum electrode in a solution of 0.33 *M* tetra-*n*-butylammonium fluoborate in methanol: curve a, electrolyte alone; curve b, electrolyte containing 0.25 *M* *N,N*-dimethylformamide; curve c, electrolyte containing 1.25 *M* *N,N*-dimethylformamide.

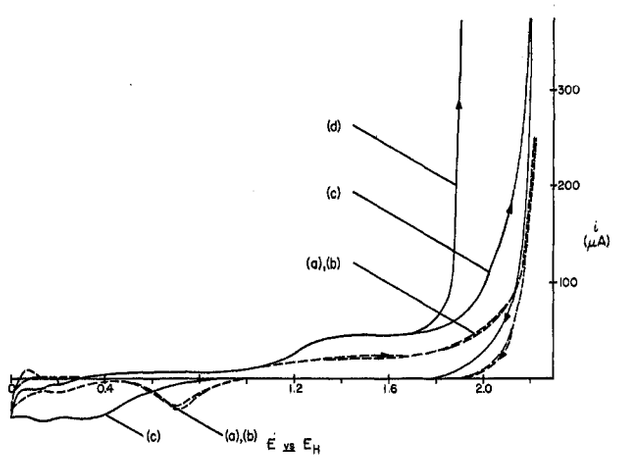


Figure 2.—Current–potential curves obtained by cyclic voltammetry at a scan rate of 50 mV sec^{-1} at a platinum electrode in a solution of 1.0 *M* potassium acetate in glacial acetic acid: curve a, electrolyte alone; curve b, electrolyte containing approximately 0.1 *M* *N,N*-dimethylformamide; curve c, electrolyte containing approximately 4 *M* *N,N*-dimethylformamide; curve d, electrolyte containing approximately 4 *M* *N,N*-dimethylformamide and 0.06 *M* anisole.

the fluoroborate anion becomes a significant Faradaic process, *i.e.*, at potentials more anodic than 1.8 V *vs.* *E*, $Ag|Ag^+$ (0.1 *M*). The addition of dimethylformamide suppresses the oxidation of methanol, and the amide itself is oxidized at potentials appreciably less anodic than those required to oxidize the fluoroborate anion.

The Tafel slope of 125–130 mV/decade of current, obtained from the steady-state log (current) *vs.* potential curves for the oxidation of dimethylformamide in methanol, and the observed electrochemical reaction order, $(d \log i/d \log C_r)E = 1$, where C_r is the bulk concentration of the amide, are consistent with an electrode reaction in which the rate-determining step is an irreversible one-electron transfer process.

The results of cyclic voltammetric studies of the oxidation of dimethylformamide in 1.0 *M* potassium acetate in acetic acid are shown in Figure 2. Curve a is the current–potential relation obtained for the electrolyte alone. The anodic sweep shows a large increase in current at $E > 2.1$ V *vs.* E_H (hydrogen reference electrode) due to the onset of the Kolbe oxidation of acetate ion. Addition of 0.1 *M* dimethylformamide (curve b) did not affect the anodic trace, and there is no indication that the amide is oxidized at potentials less anodic than 2.1 V *vs.* E_H, *i.e.*, the region of potential at which the Kolbe reaction also occurs. However, at high concentrations of the amide, *e.g.*, 4.0 *M* (curve c), the currents in the potential region, 2.0–2.4 V, are significantly larger, and this increase is attributable to oxidation of dimethylformamide. In contrast, the addition of a small amount of anisole[5] brought about a large increase in the current at potentials less anodic than 1.95 V *vs.* E_H (curve d).

The potentiostatic, steady-state polarization behavior of a solution of tetraethylammonium nitrate in methanol, containing tetra-*n*-butylammonium fluoroborate as the supporting electrolyte, is shown as curve b in Figure 3. The linear (Tafel) behavior in the potential region, 1.2–1.6 V *vs.* *E*, $Ag|Ag^+$ (0.1 *M*), corresponds to the electrooxidation of the nitrate anion. By comparing curve c in Figure 1 with curve b in Figure 3, it can be seen that, with 0.33 *M* nitrate ion and 1.25 *M* dimethylformamide, the oxidation of nitrate ion is a significant reaction in spite of the larger concentration of the amide. For the purpose of comparison it is instructive to define an "oxidation potential" as that potential at which the steady-state current is 10 mA cm^{-2}. The results for 0.33 *M* fluoroborate ion, 0.25 *M* dimethylformamide, 1.25 *M* dimethylformamide, and 0.33 *M* nitrate ion are 1.75 V, 1.40 V, 1.32 V, and 1.24 V, (V *vs.* *E*, $Ag|Ag^+$ (0.1 *M*), respectively.

The results of cyclic voltammetric studies in acetonitrile are shown in Figure 4. A current–potential curve obtained at a platinum electrode in a solution of 0.33 *M* tetra-*n*-butylammonium fluoroborate is shown as curve a. It can be seen that, within the chosen range of potentials [0 to 2.5 V *vs.* *E*, $Ag|Ag^+$ (0.1 *M*)],

(5) The half-wave potential for anisole oxidation in 0.5 *M* sodium acetate in acetic acid, as reported by Eberson and Nyberg,[2] is 1.67 V *vs.* sce.

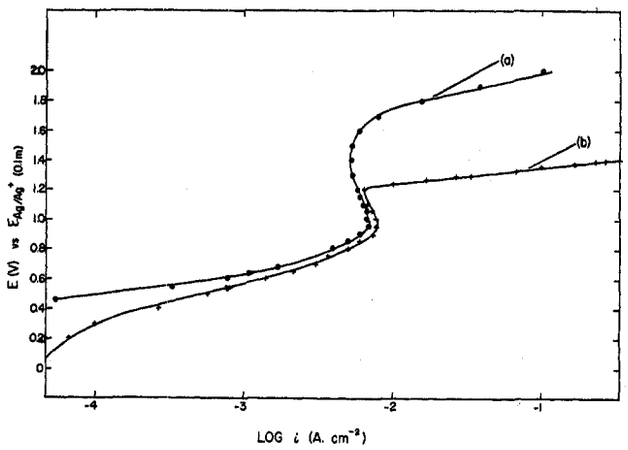


Figure 3.—Potentiostatic, steady-state polarization curves obtained at a platinum electrode in a solution of 0.33 *M* tetra-*n*-butylammonium fluoroborate in methanol: curve a, electrolyte alone; curve b, electrolyte containing 0.33 *M* tetraethylammonium nitrate.

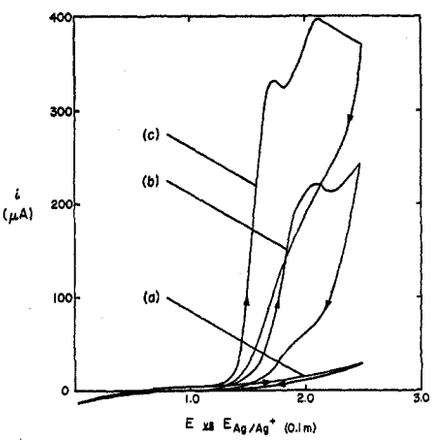


Figure 4.—Current–potential curves obtained by cyclic voltammetry at a scan rate of 100 mV sec^{-1} at a platinum electrode in a solution of 0.33 *M* tetra-*n*-butylammonium fluoroborate in acetonitrile: curve a, electrolyte alone; curve b, electrolyte containing ~0.05 *M* *N*,*N*-dimethylformamide; curve c, electrolyte containing ~0.05 *M* *N*,*N*-dimethylformamide and ~0.05 *M* tetraethylammonium nitrate.

no significant Faradaic process occurs prior to the oxidation of the anion of the supporting electrolyte.

The effect of adding dimethylformamide (concentration ≃0.05 *M*) is shown in curve b, where the currents over the potential range, 1.8–2.4 V, correspond almost entirely to oxidation of the amide. Analysis of a series of current–voltage curves obtained at various scan rates indicated an irreversible, diffusion-controlled reaction, and at fast scan rates ($dE/dt > 2$ V sec^{-1}), there was no evidence of a reduction peak.

Tetraethylammonium nitrate was then added to the solution (concentration ≃0.05 *M*), and the resulting current–potential profile (curve c) showed two peaks, corresponding to the oxidation of the anion and of dimethylformamide. The peak potential for the oxidation of nitrate ion occurred at a potential 0.4 V less anodic than that for the amide. Owing to distortion of the current–voltage curves in cases of consecutive peak currents,[6] it is difficult to correlate the peak current corresponding to the oxidation of dimethylformamide with that obtained in curve b.

The implications of the foregoing electrochemical experiments for the reaction mechanisms involved were further explored by carrying out appropriate electrolyses of *N*,*N*-dimethylformamide at controlled potential. The first experiment was designed to confirm the fact that constant current oxidations in methanol, with a fluoroborate electrolyte, were also at an essentially constant potential and one lower than that required for oxidation of the fluoroborate anion. The oxidation was carried out at 1.65 V *vs.* $Ag|Ag^+$ (0.1 *M*) in a methanol solution that was 0.5 *M* in tetra-*n*-butylammonium fluoroborate and 1.0 *M* in the amide and the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 100%, the same as that observed in the constant current experiment.

The constant current oxidation of the amide in acetic acid with tetra-*n*-butylammonium fluoroborate as the supporting electrolyte is at a potential which involves simultaneous oxidation of both the substrate and the fluoroborate anion. In a typical experiment (Table I), the coulombic yield of the product, *N*-acetoxymethyl-*N*-methylformamide, was 54.5%. When the oxidation was run at a constant potential of 1.6 V *vs.* $Ag|Ag^+$ (0.1 *M*), oxidation of the fluoroborate anion was avoided, and the coulombic yield of product increased to 89.5%.

Finally, dimethylformamide was oxidized in a methanol solution, 0.13 *M* in tetraethylammonium nitrate and 0.052 *M* in the amide, at a constant potential of 1.55 V *vs.* $Ag|Ag^+$ (0.1 *M*). The electrochemical measurements indicate that, at this potential and at these relative concentrations of amide and nitrate ion, no more than 15% of the charge passed is used for direct oxidation of the amide. Nevertheless, the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 71.9%. Since at least 85% of the charge passed in this experiment is used in oxidizing nitrate ion to nitrate radical, it follows that the mechanism in which the nitrate radical is formed in the primary step can lead to the normal amide oxidation product in relatively high yield.

Experimental Section

Materials.—DPI, White Label *N*,*N*-dimethylformamide was distilled from calcium hydride and a middle cut, bp 51° (16 mm), was used. Spectroquality acetonitrile from Matheson Coleman and Bell was used without purification. ACS reagent grade glacial acetic acid and ACS reagent grade methanol, both from Allied Chemical, were used without purification. The preparation of tetraethylammonium nitrate has been described.[7] Tetraethylammonium fluoroborate was prepared by the procedure given by Moe.[8] Tetra-*n*-butylammonium fluoroborate was prepared by adding with magnetic stirring an excess of 48–50% fluoroboric acid to a dilute aqueous solution of tetra-*n*-butylammonium bromide. The product, which precipitates immediately, was crystallized first from methanol–water and then from 2-propanol–ether, yield 86%, mp 160–162°.

Constant Current Electrolyses.—The same equipment was used both for those experiments in which the objective was to isolate the oxidation product and for the electrolyses in which the amount of product obtained was determined analytically. The electrolysis cell consisted of a water-jacketed, 200-ml beaker, fitted with a magnetic stirring bar, a thermometer, and a Teflon cover to which were attached two platinum electrodes, 0.025 cm thick, 2.5 cm wide, immersed to a depth of 7 cm and at a separa-

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, p 129.

(7) S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 4155 (1957).

(8) N. S. Moe, *Acta Chem. Scand.*, **19**, 1023 (1965).

tion of 2 cm. Current was supplied by a voltage regulated dc power supply.

Where the objective was to isolate the oxidation product, a mixture of *N*,*N*-dimethylformamide (75 ml, 0.97 mol), a quaternary ammonium fluoroborate (0.05 mol) and 75 ml of the alcohol or acetic acid was electrolyzed at constant current, enough charge being passed to oxidize no more than half of the amide. The products were isolated by distillation and their identities were verified by comparing their retention times on vpc with the retention times of authentic samples.[1c]

For the experiments in which the products formed were determined by vpc, the solutions electrolyzed contained 0.05 mol of the supporting electrolyte, either a fluoroborate or a nitrate, *N*,*N*-dimethylformamide (0.13 mol), and 140 ml of either acetic acid or the appropriate alcohol. The amount of charge passed was in every case 0.112 F.

To prepare the reaction mixtures for vpc analysis, the solvent was first removed with the water pump using a water bath at 50° or below. Dry ether (400 ml) was added. The mixture was cooled, and the quaternary ammonium salt which precipitated was filtered. The ether was removed, and the residue was made up to 25 ml with acetone for analysis.

Electrochemical Measurements.—A two-compartment cell was used for all electrochemical measurements. The reference electrode was connected to the main compartment by a Luggin capillary, which terminated close to the study electrode. A closed, solution-sealed stopcock was used to separate effectively the two compartments yet allow electrolytic contact between them.

In all experiments and with all three solvents, methanol, acetic acid, and acetonitrile, the concept of a constant ionic medium in forming liquid junctions with the reference electrode was employed. Hence, the electrolyte, solvent plus supporting electrolyte, was always common to both the main and the reference electrode compartments, and silver perchlorate, to give a solution containing 0.1 *M* silver ion, was added only to the reference electrode compartment.[9] It should be noted that comparisons of voltammetric or steady-state polarization data should only be made within the same solvent, since the reference electrode is then constant within experimental error.[10,11] Attempts to refer all the measured potentials to a particular aqueous reference electrode, *e.g.*, the normal hydrogen electrode or the standard or saturated calomel electrode, lead to some uncertainty in the results. Butler[10] has pointed out that the potential difference between the $Ag|Ag^+$ electrode in acetonitrile and an aqueous saturated calomel electrode is dependent on such factors as the nature of the supporting electrolyte, the nature of the salt bridge, and even on whether or not a salt bridge is used.

Conventional circuitry was used for both the steady-state measurements and cyclic voltammetry. A Wenking potentiostat, Model No. 68FRO.5, provided the potential control, and potentials were measured with a Keithley Electrometer, Model No. 610A. A Wavetek function generator was used to superimpose the triangular wave required for cyclic voltammetry, and both single-scan and multiscan techniques could be used. The transient currents were passed through a calibrated resistor, and the resulting potential differences were recorded on an oscilloscope (Tektronix 501) or on a high impedance XY recorder (Hewlett-Packard Model No. 7030 AM). Some of the voltammetric studies were carried out using a Princeton Applied Research Model 170 electrochemistry system.

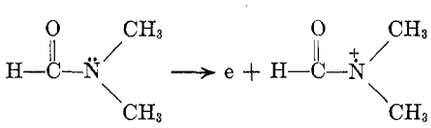
Controlled Potential Electrolyses.—These were carried out in the cell used for the electrochemical measurements, but the working electrode was of larger surface area (geometric area approximately 3 cm^2). The cell was jacketed with a copper coil, through which water was circulated, to control the temperature. The potential was controlled with the Princeton Applied Research electrochemistry system, and the total charge passed during an electrolysis was determined by the weight of copper deposited in a copper coulometer, connected in series with the auxiliary electrode. The amount of product formed was determined by vpc analysis after work-up of the reaction mixtures in the manner described for the constant current electrolyses.

Analysis by Vpc.—The vpc analyses were carried out with a Perkin-Elmer Model 154B vapor fractometer using helium as the carrier gas. The column used was a Perkin-Elmer large-diameter Golay column of 0.06-in. i.d. and 300-ft length, in which the stationary phase was Ucon polyglycol LB 550-X. The unknown solutions were compared with standards prepared from the identified components.

Discussion

In a methanol solution of a quaternary ammonium fluoroborate, it is possible to observe some anodic oxidation of methanol, but the reaction is self-inhibiting, and the current densities involved are small until the potential at which fluoroborate anion is oxidized is attained.[12]

The addition of *N*,*N*-dimethylformamide further inhibits the methanol oxidation, and the amide is oxidized at potentials appreciably lower than those required to oxidize fluoroborate ion. The electrochemical reaction order in the amide and the Tafel slope over the potential region of amide oxidation are consistent with an electrode reaction in which the rate-determining step is an irreversible, one-electron transfer. For the oxidation of *N*,*N*-dimethylformamide, it is highly probable that this transfer occurs in the primary step and results in a cation radical as shown in eq 1.



(1)

In the oxidation of dimethylformamide in acetic acid, with tetra-*n*-butylammonium fluoroborate as the supporting electrolyte, the electrochemical evidence again supports an irreversible, one-electron transfer as the rate-determining step. In this solvent an electrolysis at constant current can attain an anode potential high enough to permit oxidation of fluoroborate ion, and a controlled potential electrolysis, which prevents this side reaction, results in a higher coulombic yield of *N*-acetoxymethyl-*N*-methylformamide.

Cyclic voltammetric studies of the oxidation of dimethylformamide in 1.0 *M* potassium acetate in acetic acid afford no evidence that the amide is oxidized at a potential significantly less anodic than that at which the Kolbe reaction occurs, and the results indicate that the amide and acetate ion oxidize simultaneously. Since the initial acetate ion oxidation products, acetoxy and/or methyl radicals, do not lead to oxidation of the amide, the poor coulombic yields observed in this system are explained.

Potentiostatic, steady-state polarization studies of solutions of tetraethylammonium nitrate and of *N*,*N*-

(9) When a solution of tetraethylammonium perchlorate (0.1 *M*) in acetonitrile was used as the common electrolyte, the change in the potential difference between an $Ag|Ag^+$ (0.1 *M*) electrode placed in the reference electrode compartment and an $Ag|Ag^+$ (1.0 *M*) electrode placed in the main compartment was only 5 mV after 36 hr. Diffusion of silver ion to or from the separated compartment is, therefore, negligible within the time of the electrochemical measurements or controlled potential electrolyses.

(10) J. Butler, *Advan. Electrochem. Electrochem. Eng.*, **7**, 77 (1970).

(11) G. Charlot, J. Badoz-Lambling, and B. Tremillon, "Electrochemical Reactions," Elsevier Publishing Co., Amsterdam, The Netherlands, 1962, Chapter 13.

(12) The oxidation of methanol in both neutral and basic solution can give rise to methoxy radicals by the reactions i and ii. In neutral solution,

$$CH_3OH \rightarrow e + H^+ + CH_3O\cdot \quad \text{(i)}$$

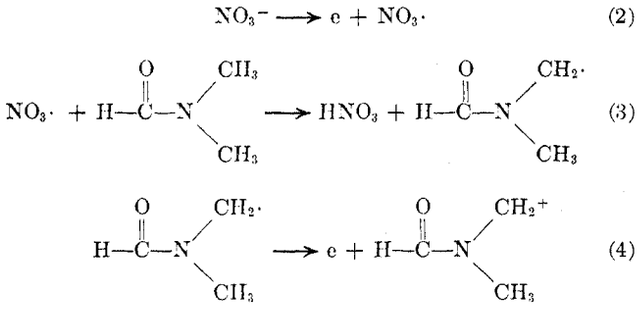
$$CH_3O^- \rightarrow e + CH_3O\cdot \quad \text{(ii)}$$

e.g., in the reaction with tetraethylammonium fluoroborate as the supporting electrolyte, the oxidation of methanol is of no consequence, since the coulombic yield of amide oxidation product is 100%. In basic solution, *e.g.*, with sodium methoxide as the supporting electrolyte, oxidation of methoxide ion is an important reaction, and the coulombic yield of *N*-methoxymethyl-*N*-methylformamide is only 15%. In this system, the initially formed methoxy radicals are relatively ineffective in attacking the amide, and formaldehyde is probably the major oxidation product.

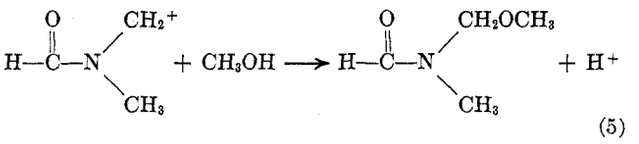
dimethylformamide demonstrate that nitrate ion is oxidized at a lower anodic potential than the amide. This conclusion is also supported by the results of cyclic voltammetric studies in acetonitrile.

The steady-state currents at constant potentials for oxidation of nitrate ion and the amide are such that, when the ratio of the two concentrations, $C_{amide}/C_{NO_3^-}$, is 3, the two oxidations proceed at nearly equal rates. When the ratio is 0.3, ~90% of the charge passed goes into oxidation of nitrate ion. For 90% of the charge to go into amide oxidation, the ratio would have to be ~30.

In a controlled potential experiment, with the initial ratio, $C_{amide}/C_{NO_3^-}$, such that at least 85% of the charge passed was going into nitrate oxidation, the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 71.9%. It, therefore, follows that oxidation of nitrate ion can initiate a sequence of reaction steps that leads ultimately to the amide oxidation product. The first step in this sequence must necessarily be that shown in eq 2, and this reaction has also been proposed by Mann.[13] Reasonable subsequent steps are eq 3–5.

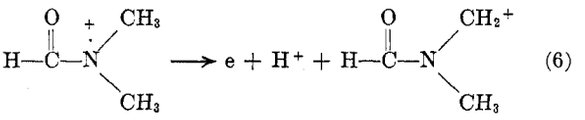


(13) R. R. Rao, S. B. Mulliken, S. L. Robinson, and C. K. Mann, *Anal. Chem.*, **42**, 1076 (1970).



The above sequence constitutes an over-all ECEC reaction, in which nitrate ion functions as a catalyst, which is consumed in eq 2 but regenerated in eq 3.[14]

When the initial electron transfer is from the amide, the primary step is that shown in reaction 1, and possible subsequent reactions are 6, followed by 5. The over-all sequence is EEC. Reaction 6 has been written



as a concerted reaction involving the simultaneous transfer of a proton to a base and an electron to the anode. It is possible that eq 6 involves two discrete steps, a proton transfer followed by a separate electron transfer, in which case the over-all sequence is ECEC.

Registry No.—*N*,*N*-Dimethylformamide, 68-12-2; methanol, 67-56-1; ethanol, 64-17-5; butanol, 71-36-3; acetic acid, 64-19-7; tetraethylammonium fluoroborate, 429-06-1; tetraethylammonium nitrate, 1941-26-0; tetra-*n*-butylammonium fluoroborate, 429-42-5; nitrate radical, 34236-35-6.

(14) G. Cauquis and D. Serve [*C. R. Akad. Sci., Ser. C*, **262**, 1516 (1966)] have proposed the electrochemical oxidation of nitrate ion to give the nitronium ion. The nitronium ion could abstract a hydride ion from the methyl

$$NO_3^- \rightarrow e + NO_2^+ + {}^1/_2O_2$$

group of the amide and thus lead to the observed *N*-methoxymethyl-*N*-methylformamide. A corollary of this mechanism is that oxidation of the amide is accompanied by conversion of the quaternary ammonium nitrate to a nitrite. Since the nitrate can be recovered unchanged from the present reactions, this mechanism is eliminated.

The Crystal and Molecular Structure and Absolute Configuration of *d*-Spiro[3.3]heptane-2,6-dicarboxylic Acid at −160°

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The crystal and molecular structure of *d*-spiro[3.3]heptane-2,6-dicarboxylic acid or *d*-Fecht acid, $C_9H_{12}O_4$, at −160° has been solved by conventional X-ray diffraction methods. The dimensions of the monoclinic cell are a = 8.486, b = 7.609, c = 6.928 Å; β = 93.25°; space group $C2$, Z = 2. The structure was refined by least-squares techniques, R = 0.056 and R_w = 0.062 for 2314 independent reflections. From a determination of the absolute configuration by use of the anomalous scattering of oxygen and carbon, a strong indication was obtained that *d*-Fecht acid has the *R* configuration shown in Figure 1. The molecules have twofold symmetry. The four-membered rings are puckered with a dihedral angle of 152.6°, resulting in an approximate equatorial position of the carboxylic acid groups. The bond lengths and angles in the ring range from 1.539 to 1.564 (0.0013) Å and from 88.0 to 88.9 (0.08)°, respectively. The C–C–C angles at the central spiro carbon atom vary from 114.8 to 126.2°.

The isolation and identification of *dl*-spiro[3.3]heptane-2,6-dicarboxylic acid or Fecht acid was first reported by Fecht[2a] in 1907. The resolution of the acid in its optical antipodes was achieved by Backer and Schurink[2b] in 1928 by fractional crystallization of the brucine salts.

Recently the acid has aroused interest as a suitable starting material for the synthesis of optically active 2,6-disubstituted spiro[3.3]heptane derivatives.[3] A knowledge of the absolute configuration of Fecht acid would establish the absolute configuration of this whole series of compounds. Wynberg and Houbiers[3] on the basis of ORD and CD measurements and making use of the application of Lowe's rule[4] to the spiro[3.3]-

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