

Anodic Oxidations. II. The Electrochemical Oxidation of Acetic Acid and Formic Acid in the Presence of Amides¹

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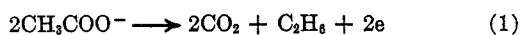
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The electrolysis of sodium formate in formic acid and potassium acetate in acetic acid, both in the presence of *N,N*-dimethylamides, results in the formation of *N*-acyloxymethyl-*N*-methylamides. In the electrolysis of sodium formate in formic acid in the presence of dimethylformamide, the ether amide, 2,6-diformyl-2,6-diaza-4-oxaheptane, is also obtained. Possible mechanisms for these reactions are discussed. The results afford evidence that the electrochemical oxidation of formic acid involves single-electron transfers at the anode rather than a concerted two-electron transfer.

It was reported, in a preliminary communication,² that when either potassium acetate in acetic acid or potassium formate in formic acid is electrolyzed in the presence of dimethylformamide, there is a sharp decrease in the rate of gas production at the anode, and an *N*-acyloxymethyl-*N*-methylformamide is formed. It is the purpose of the present report to describe these reactions in greater detail, to show that they can be observed with amides other than dimethylformamide, and to consider experiments designed to elucidate the mechanisms of these reactions.

As in the previous study,¹ measurement of the rate of gas production at constant current and determination of the gas composition served as a sensitive tool for determining whether or not a given added substrate participated in product-forming reactions at the electrodes. In these experiments hydrogen was always formed at the cathode in the theoretical amount, and a sharp decrease in the rate of gas production at the anode was a clear indication that the added substrate was either reacting with primary species formed at the anode or itself being discharged to give, in either case, nongaseous products.

When acetate ion is electrolyzed in 5 *N* aqueous acetic acid at high current density and high anodic potential³ or in glacial acetic acid,⁴ the over-all electrode reactions are almost exactly

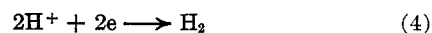
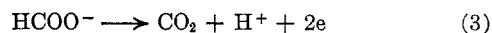


The current efficiency approaches 100%, and the coulombic yield approaches 2 moles of CO₂, 1 mole of H₂, and 1 mole of C₂H₆ per 2 f.

Table I shows the effect of adding amides in the electrolysis of potassium acetate (5.0 g.) in glacial acetic acid. In all of the experiments the temperature was 20°, and the current was held constant at 0.40 amp. (1-cm.² platinum electrodes at a separation of 0.6 cm.). Where the electrolysis was studied for an extended time period, acetic acid was added at periodic intervals to maintain the liquid volume in the cell. In the absence of an added amide, the rate of total gas production is 100 ± 1% of that demanded by eq. 1 and 2 above, with the ratio, CO₂/ethane, equal to 2.00 ± 0.02. These results are not measurably altered either by raising the temperature to 58° or lowering

the current to 0.2 amp. Addition of the three amides shown in Table I causes a marked decrease in the rate at which gas is produced at the anode. The magnitude of this decrease becomes greater as the amount of the amide initially added is increased and decreases with increasing electrolysis time. This suggests that the amide is a reactant and is being consumed. In all of these experiments the volume ratio, CO₂/ethane, does not vary significantly from 2, indicating that the amide is probably undergoing acetoxylation rather than methylation.¹

The electrolysis of formate ion in formic acid results in the formation of carbon dioxide at the anode and hydrogen at the cathode. Peroxides are not detectable, carbon dioxide is the sole anodic product, and hydrogen is formed only at the cathode. The over-all electrode reactions are⁵



The coulombic yield approaches 1 mole of CO₂ and 1 mole of H₂/2 f.⁶ The effect of added substrates on the course of this electrolysis is shown in Table II. As in the previous experiments, the temperature was 20°, and the current was maintained at 0.40 amp. (1-cm.² platinum electrodes at a separation of 0.6 cm.). In the absence of an added substrate the rate of production of gas at the anode is better than 99% of that demanded by eq. 3. The addition of dimethylcyclohexylamine or of either of the two imides, *N*-methylsuccinimide and *N*-methylphthalimide, is without significant effect on the rate of carbon dioxide formation. In contrast, all of the amides listed in Table II have a very large effect on the rate of gas formation at the anode, and in many instances the rate is decreased to less than 10% of its original value. For a given substrate a higher initial concentration results in a larger decrease, and with increasing time of electrolysis the rate of formation of anode gas increases. Both of these observations point to the incursion, in these systems, of some reaction which results in the consumption of the added amide.

Of the systems reported in Tables I and II, three were selected for study of the liquid products formed. These were the electrolysis of both acetic and formic acids in the presence of dimethylformamide and the electrolysis of acetic acid in the presence of dimethylacetamide. In addition, some studies were carried out in mixtures

(1) Paper I: S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

(2) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 2745 (1964).

(3) K. Sugino, T. Sekine, and N. Sato, *Electrochem. Tech.*, **1**, 112 (1963).

(4) C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4290 (1956).

(5) B. E. Conway and M. Dziechiuch, *Can. J. Chem.*, **41**, 21 (1963).

(6) K. Hopfgartner, *Monatsh.*, **32**, 523 (1911); F. Müller, *Z. Electrochem.*, **33**, 173 (1927); E. Baur, *Helv. Chim. Acta*, **11**, 372 (1928).

TABLE I
THE EFFECT OF ADDED AMIDES ON THE PRODUCTION OF GAS IN THE ELECTROLYSIS OF POTASSIUM ACETATE (5.0 g.)
IN GLACIAL ACETIC ACID

| Substrate | Vol., ml. | Vol. of HOAc, ml. | Electrolysis time, hr. | % of theoretical Kolbe anode gas | Volume ratio of CO ₂ /ethane |
|---------------------|-----------|-------------------|------------------------|----------------------------------|---|
| None | | 60 | | 100 ± 1 | 2.00 ± 0.02 |
| Dimethylformamide | 20 | 40 | 1.5 7.4 28.5 | 74.7 77.8 84.3 | 2.00 2.09 2.06 |
| Dimethylformamide | 30 | 30 | 2.1 31.5 | 58.7 79.4 | |
| Dimethylacetamide | 5 | 55 | 2.1 24.1 75.0 | 75.6 89.7 98.4 | 2.02 |
| Dimethylacetamide | 10 | 50 | 3.5 46.3 78.8 | 59.0 85.3 96.0 | 2.05 2.04 |
| Dimethylacetamide | 30 | 30 | 2.0 7.8 31.6 | 17.1 22.6 36.6 | |
| N-Methylpyrrolidone | 30 | 30 | 1.3 25.5 | 28.9 59.7 | |

TABLE II
THE EFFECT OF ADDED SUBSTRATES ON THE PRODUCTION OF GAS IN THE ELECTROLYSIS OF FORMATE ION IN FORMIC ACID

| Substrate | Vol., ml. | Formate salt (g.) | Vol. of HCOOH, ml. | Electrolysis time, hr. | % of theoretical anode gas |
|-----------------------------|-----------|-----------------------|--------------------|---------------------------|----------------------------|
| None | | K ⁺ (5) | 60 | | >99 |
| Dimethylcyclohexylamine | 20 | K ⁺ (4) | 40 | 1.1 7.1 | 90.1 94.8 |
| N-Methylsuccinimide | 33.9 g. | K ⁺ (4.2) | 40 | 1.3 4.3 | 95.8 99.5 |
| N-Methylphthalimide | 11 g. | K ⁺ (4.2) | 53 | 4.4 31.6 71.5 | 92.2 92.4 91.8 |
| Dimethylformamide | 5 | K ⁺ (4.2) | 55 | 4.0 | 21.1 |
| Dimethylformamide | 20 | K ⁺ (4.2) | 40 | 1.8 4.3 7.3 20.8 | 6.3 7.3 9.4 12.8 |
| Dimethylformamide | 20 | Na ⁺ (3.4) | 40 | 2.0 23.3 | 6.9 13.7 |
| Dimethylformamide and water | 20 10 | K ⁺ (4.2) | 30 | 1.3 23.6 | 5.5 10.9 |
| N-Methylformamide | 20 | K ⁺ (4.2) | 40 | 2.0 24.0 | 30.6 38.5 |
| Diethylformamide | 25 | Na ⁺ (3.4) | 35 | 2.8 | 19.1 |
| Dimethylacetamide | 20 | K ⁺ (4.2) | 40 | 3.5 54.7 94.9 | 7.7 48.1 96.6 |
| N-Methylpyrrolidone | 20 | K ⁺ (4.2) | 40 | 1.3 25.8 | 2.9 27.5 |

of acetic and formic acids, and an attempt was made to determine, at least qualitatively, the effect of dimethylformamide on the anodic discharge potentials for acetate and formate.

Experimental Section

Rates of Gas Production and Gas Analysis.—The electrolysis cell and the apparatus and methods used to collect and analyze the gases formed have been described previously.^{1,7}

Electrolysis of Potassium Acetate in Dimethylacetamide and Acetic Acid.—A solution of potassium acetate (5 g., 0.05 mole) in dimethylacetamide (28.1 g., 0.32 mole) and acetic acid (31.5 g., 0.52 mole) was electrolyzed at 0.40 amp. for 32 hr. The cell and electrodes were those used in measuring rates of gas formation. During the electrolysis, acetic acid (8 ml.) was added.

(7) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

The solvent and excess reagents were removed from the cell contents with a water pump using a hot-water bath kept at or below 80°. Ether (300 ml.) was added to the semisolid residue, and the solid was separated by filtration. Ether was removed from the solution at atmospheric pressure, and the remainder was distilled *in vacuo*, yielding a main fraction of 19.4 g., b.p. 50–72° (0.08–0.35 mm.), *n*_D²⁰ 1.4438. This product was redistilled, and a fraction of 10.9 g. (23.5%) was taken: b.p. 51–56° (0.005–0.02 mm.) (largely 56°), *n*_D²⁰ 1.4457. The infrared spectrum was identical with that reported for N-acetoxymethyl-N-methylacetamide.⁸

Electrolysis of Potassium Acetate in Dimethylformamide and Acetic Acid.—A solution of potassium acetate (5 g., 0.05 mole) in dimethylformamide (28.34 g., 0.388 mole) and acetic acid (31.5 g., 0.52 mole) was electrolyzed at 0.40 amp. for 31.6 hr. in the apparatus used in the experiment above. Acetic acid (25 ml., in two portions) was added during the electrolysis. Most of the solvent was removed with the water pump. Ether

(8) W. Walter, M. Steffen, and K. Heyns, *Chem. Ber.*, **94**, 2462 (1961).

was added to the dark semisolid residue, and the ether solution was filtered. The residue was warmed several more times with ether, and the extracts were filtered. Ether was distilled from the combined extracts through a Vigreux column, and the residue was distilled at 0.4 mm. to give four fractions, each of which was shown by v.p.c. analysis to contain some N-acetoxymethyl-N-methylformamide. The last three fractions were combined and redistilled to give 3.6 g. (7.1%) of product, b.p. 53–55° (0.007–0.012 mm.), n_D^{24} 1.4393. This material was shown by its infrared spectrum to be identical with a sample of N-acetoxymethyl-N-methylformamide, prepared by reacting N-hydroxymethyl-N-methylformamide with acetic anhydride and pyridine.

Electrolysis of Sodium Formate in Dimethylformamide and Formic Acid.—A solution of sodium formate (3.4 g., 0.05 mole) in dimethylformamide (18.9 g., 0.258 mole), dried over barium oxide and magnesium sulfate and redistilled, and formic acid (43.8 g., 1.06 moles), 98–100% acid dried over and distilled from magnesium sulfate, was electrolyzed as above at 0.4 amp. for 23.7 hr. The cell contents were washed out with ether and distilled at water-pump pressure, heating with a water bath at 80°. The distillate was analyzed for unreacted dimethylformamide by v.p.c. Ether was added to the distillation residue, and the precipitated sodium formate was filtered and washed several times with ether. The combined ether solutions were dried over magnesium sulfate, and the ether was removed by distillation through a Vigreux column. The residue was analyzed by v.p.c. for both dimethylformamide and the ester amide, N-formyloxymethyl-N-methylformamide. The analyses indicated that 0.131 mole of the ester amide was formed and that 0.092 mole of dimethylformamide remained unreacted. The yield of N-formyloxymethyl-N-methylformamide, based on dimethylformamide consumed, was 78.9%. By distillation at 0.08 mm. it was possible to isolate 13.4 g. of the ester amide, b.p. 63–65°, n_D^{24} 1.4445. The yield was 68.7% based on the dimethylformamide consumed and 44.2% based on the starting dimethylformamide. A sample redistilled for analysis had b.p. 44–45° (0.005 mm.), n_D^{24} 1.4471.

Anal. Calcd. for $C_6H_9NO_3$: C, 41.03; H, 6.03; N, 11.96. Found: C, 41.16, 41.16; H, 6.11, 6.12; N, 11.84, 11.76.

The residue from the first distillation above was dissolved in ethyl acetate, ether was added, and two crops, 1.74 g. (0.0109 mole), of 2,6-diformyl-2,6-diaza-4-oxaheptane, m.p. 61–62°, were obtained. A mixture melting point with an authentic sample of this ether, prepared as directed by Robson and Reinhart,⁹ showed no depression.

When water (10 ml.) was added to the solution prior to the electrolysis, the distillation of the product was accompanied by extensive decomposition as evidenced by a strong odor of formaldehyde and difficulty in maintaining the vacuum. The distillate was largely N-methylformamide but did contain some N-formyloxymethyl-N-methylformamide, and larger amounts of 2,6-diformyl-2,6-diaza-4-oxaheptane were obtained from the distillation residue.

N-Formyloxymethyl-N-methylformamide was prepared on a larger scale by using an electrolysis cell consisting of a water-jacketed, 1-l. 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 separation of 2 cm. In a typical experiment a solution of sodium formate (5 g.) in dimethylformamide (200 ml.) and formic acid (400 ml.) was electrolyzed at a current of 4 amp. and applied voltage of 43 v. until a total charge of 5.5 f. was passed through the solution. The yield of N-formyloxymethyl-N-methylformamide, isolated as above, was 191.4 g. (62.2%).

N-Acetoxymethyl-N-methylacetamide.—N-Acetoxymethyl-N-methylacetamide was prepared by permitting a solution of N-hydroxymethyl-N-methylacetamide (0.5 mole), prepared as previously described,^{10,11} in pyridine (50 ml.) and acetic anhydride (75 ml.) to stand at room temperature for 24 hr. The product was isolated by the procedure described by Chupp and Speziale.¹¹ The yield was 11.8 g. (17.5%), b.p. 56° (0.005 mm.), n_D^{24} 1.4449. The infrared spectrum of this product was identical with that previously reported⁸ and with that of the product obtained by electrolysis.

N-Acetoxymethyl-N-methylformamide.—Pyridine (50 ml.) and acetic anhydride (75 ml.) were added, with cooling, to N-

hydroxymethyl-N-methylformamide (0.5 mole), prepared as directed by Bamford and White.¹² The reaction mixture was left standing at room temperature overnight. The excess reagents were removed with the water pump, and the residue was distilled, yielding 56.4 g. (86%) of product, b.p. 44–45° (0.01–0.03 mm.), n_D^{24} 1.4404. This product contained some N-methylformamide. Redistillation at 1.3 mm. gave 34.7 g. (52.9%) of product,¹³ b.p. 80–87°, n_D^{24} 1.4420. This product and the product obtained by electrolysis gave identical infrared spectra. A sample redistilled for analysis had b.p. 66–67° (0.3 mm.), n_D^{24} 1.4420.

Anal. Calcd. for $C_6H_9NO_3$: C, 45.80; H, 6.92; N, 10.68. Found: C, 45.90; 45.90; H, 6.79, 6.84; N, 10.67, 10.66.

N-Formyloxymethyl-N-methylformamide.—N-Acetoxymethyl-N-methylformamide (11.18 g., 0.0853 mole) in 98–100% formic acid (61 g., 1.33 moles) was left standing overnight at room temperature. The solution was taken up in ether (600 ml.), and the ether solution was stirred magnetically with sodium carbonate (141 g., 1.33 moles) being added portionwise. The ether solution was filtered and concentrated to a volume of 100 ml. V.p.c. analysis of this solution indicated that both the amide formate and the amide acetate were present in a weight ratio of approximately 4 to 1. The remaining ether was removed, and the residue was distilled at 0.03 mm., yielding two fractions, one of 3.6 g. having b.p. 60–61°, n_D^{24} 1.4459, and the other of 4.1 g. having b.p. 60–61°, n_D^{24} 1.4463. V.p.c. analysis indicated that no separation had been effected by the distillation. Both fractions contained approximately 80% of the formate and 20% of the acetate. The residue from this distillation, crystallized from ethyl acetate-ether, yielded 0.2 g. of 2,6-diformyl-2,6-diaza-4-oxaheptane, m.p. 60–62°.

If N-acetoxymethyl-N-methylformamide was treated four times successively with formic acid as above, the final product isolated by distillation was free from the acetate but contained appreciable amounts of N-methylformamide as an impurity.

N-Formyloxymethyl-N-methylformamide was also obtained by esterification of N-hydroxymethyl-N-methylformamide with formic acid. The product proved difficult to isolate from the reaction mixture, and the yields in this preparation were erratic and never exceeded 17%.

Methyl-(2-hydroxynaphthylmethyl)amine Hydrochloride.^{10,14}—A mixture of N-formyloxymethyl-N-methylformamide (1.17 g., 0.01 mole), β -naphthol (1.50 g., 0.0104 mole), ethanol (5 ml.), and concentrated hydrochloric acid (1 ml.) was refluxed overnight. The mixture was cooled, and ether was added. The product, 2.1 g. (93.7%), had m.p. 190–193° dec. A sample crystallized from ethanol-ether, then ethanol, had m.p. 205–206° dec.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.85. Found: Cl, 16.17.

Both N-acetoxymethyl-N-methylformamide and N-acetoxymethyl-N-methylacetamide reacted as above to give the same amine hydrochloride.

Potential Measurements.—Anode potentials were measured during electrolysis of formic and acetic acids both with and without added dimethylformamide. The anode was a platinum wire, 0.035 cm. in diameter, sealed into glass with a 0.217-cm. length exposed to the solution. The working electrolysis cathode was platinum foil while a large mercury pool was used as a reference cathode for potential measurements. Nitrogen was bubbled through the cell before and during the electrolysis, entering the solution just above the electrodes. Electrolysis current was varied randomly (over the ranges 0–440 μ a. for acetic acid and 0–280 μ a. for formic acid) and was measured with a sensitive meter, while the corresponding potentials were measured with a standardized potentiometer-galvanometer circuit.

Measurements were first made on a solution of 4.9180 g. (0.050 mole) of potassium acetate in 50.0 ml. of acetic acid, and these were followed immediately by measurements on the same solution with 2.0 ml. of dimethylformamide added. A series of measurements on a solution of 3.4007 g. (0.050 mole) of sodium formate in 50.0 ml. of formic acid was followed immediately by measurements on this same solution with 2.0 ml. of dimethylformamide added.

(12) C. H. Bamford and E. F. T. White, *J. Chem. Soc.*, 1860 (1959).

(13) Our previous report³ of a 96% yield in this reaction was for a product which was later shown by v.p.c. to contain N-methylformamide as an impurity.

(14) W. J. Burke, M. J. Kolbezen, and C. W. Stephens, *J. Am. Chem. Soc.*, **74**, 3601 (1952).

(9) J. H. Robson and J. Reinhart, *J. Am. Chem. Soc.*, **77**, 2453 (1955).

(10) H. Böhme, A. Dick, and G. Driesen, *Chem. Ber.*, **94**, 1879 (1961).

(11) J. P. Chupp and A. J. Speziale, *J. Org. Chem.*, **28**, 2592 (1963).

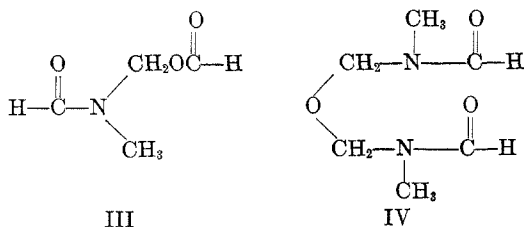
Discussion

As shown in Tables I and II, the addition of N-methyl-substituted amides effectively suppresses the rate at which gas is produced at the anode in the electrolysis of acetate ion in acetic acid and of formate ion in formic acid. The gaseous products that were found are those that result from the normal Kolbe electrolyses¹⁵ of acetate ion and formate ion. Since hydrogen is formed at the cathode in the theoretical amount during these reactions, the added amide is either reacting with a primary species formed at the anode or is itself being discharged to give, in either case, nongaseous products.

For three systems the nongaseous products formed in the presence of the amide have been isolated and identified. In the electrolysis of potassium acetate in dimethylacetamide and acetic acid, the product formed is the known N-acetoxymethyl-N-methylacetamide (I),^{8,10,11} having characteristic carbonyl absorptions at 5.8 and 6.0 μ .⁸

The electrolysis of potassium acetate in dimethylformamide and acetic acid gave N-acetoxymethyl-N-methylformamide (II), which has been prepared previously by reacting dimethylformamide with *t*-butyl peracetate under the influence of ultraviolet light and copper ions.¹⁶ II, prepared by treating N-hydroxymethyl-N-methylformamide¹² with acetic anhydride and pyridine, and the product isolated from the electrolysis gave identical infrared spectra, with carbonyl absorptions at 5.79 and 5.97 μ in agreement with the values reported by Sosnovsky.

The electrolysis of potassium formate in dimethylformamide and formic acid gave two products, N-formyloxymethyl-N-methylformamide (III) and 2,6-diformyl-2,6-diaza-4-oxaheptane (IV). The ether amide

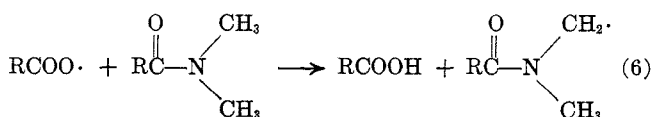
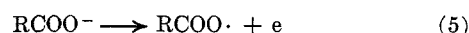


IV is a known solid, readily prepared by allowing N-methylformamide to react with 95% paraformaldehyde and concentrated hydrochloric acid.⁹ The ester amide III was not known, but its structure is indicated by comparison of its infrared spectrum, which shows carbonyl absorption at 5.83 and 5.97 μ , with the spectra of I and II and by its analysis. It has now also been prepared, but in poor yield, by esterification of N-hydroxymethyl-N-methylformamide with formic acid and, in a somewhat more satisfactory reaction, by treating II with formic acid. This latter reaction, which involves an acyl group exchange, is indicative of facile carbonium ion formation in the ester amides I, II, and III.¹⁷ It makes them highly useful reagents, capable of transferring the grouping, $\text{RCON}(\text{CH}_3)\text{CH}_2^-$, to a nucleophile. This possibility has been explored, and the re-

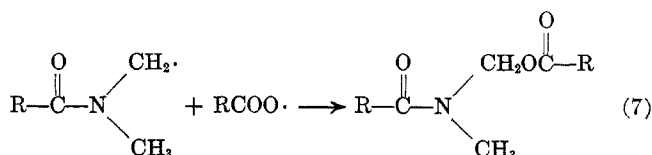
sults will be reported in another connection. It is also of interest that the electrochemical reaction is clearly the method of choice for the preparation of III. Unlike the other two reactions it goes cleanly and in good yield and permits the isolation of III in high purity.

All three of the ester amides react with β -naphthol in ethanol in the presence of concentrated hydrochloric acid to give methyl-(2-hydroxynaphthylmethyl)amine hydrochloride in good yield.^{10,14} In all three cases an N-methylaminomethyl group has been transferred to β -naphthol. These reactions, therefore, constitute further support for the structures of I, II, and III.

Three possible mechanisms for the formation of the N-acyloxymethyl-N-methylamides warrant consideration. The first possibility involves a one-electron transfer at the anode to form an acyloxyl radical, which then abstracts a hydrogen from the amide (eq. 5 and 6).

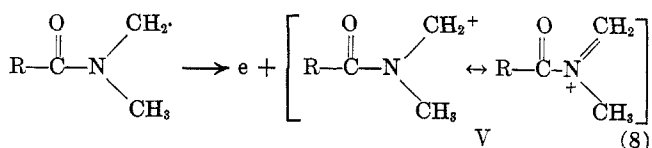


Coupling of the amide radical with the acyloxyl radical would give the final product as shown in eq. 7.



In the experiments with acetate ion in acetic acid the quantities of methane produced were negligible with respect to the amounts of I and II isolated. If this mechanism is operating, it must, therefore, be the acetoxy radical rather than the methyl radical which abstracts the hydrogen, and it would follow that the acetoxy radical, when generated at an electrode surface, is sufficiently stabilized by its environment to permit its reaction with a suitable substrate or radical.¹⁸

A second possibility for the formation of the N-acyloxymethyl-N-methylamides involves the anodic oxidation of the radical formed in eq. 6 to give the carbonium ion V, which could then react either with solvent or



with the anion to give the final product. There is evidence for the anodic generation of carbonium ions,¹⁹ and such a process may be favored where the carbonium ion formed is stabilized by electron delocalization.

Finally, there is the possibility that it is the substrate rather than the anion that is discharged at the anode. This mechanism is highly probable when the substrate is an aromatic compound such as naphthalene or ani-

(15) For review articles, see B. C. L. Weedon, *Quart. Rev. (London)* **6**, 380 (1952); *Advan. Org. Chem.*, **1**, 1 (1960); A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.*, **32**, 30 (1963).

(16) G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963); *Tetrahedron*, **21**, 871 (1965).

(17) S. G. Cohen, *J. Am. Chem. Soc.*, **66**, 1395 (1944).

(18) For a discussion of the stability of the acetoxy radical and arguments for and against its participation in reactions, see H. J. Shine and J. R. Slagle, *ibid.*, **81**, 6309 (1959); H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963); J. C. Martin and E. H. Drew, *ibid.*, **88**, 1234 (1961).

(19) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2465 (1960); E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); L. Ebersson, *Acta Chem. Scand.*, **17**, 1196 (1963).

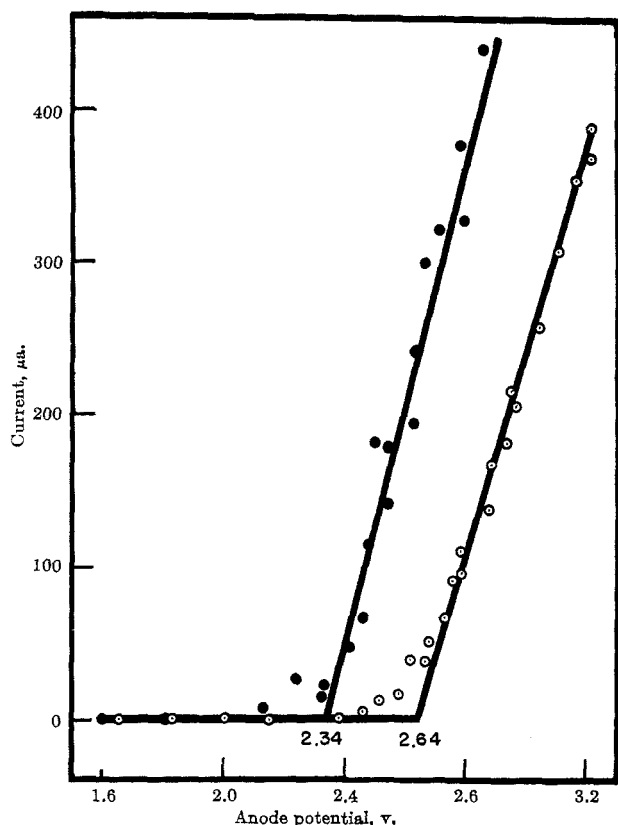


Figure 1.—Plot of current vs. anode potential (relative to Hg pool) for electrolysis of solution containing 0.050 mole of potassium acetate in 50.0 ml. of acetic acid: ○, without dimethylformamide; and ●, with 2.0 ml. of dimethylformamide added.

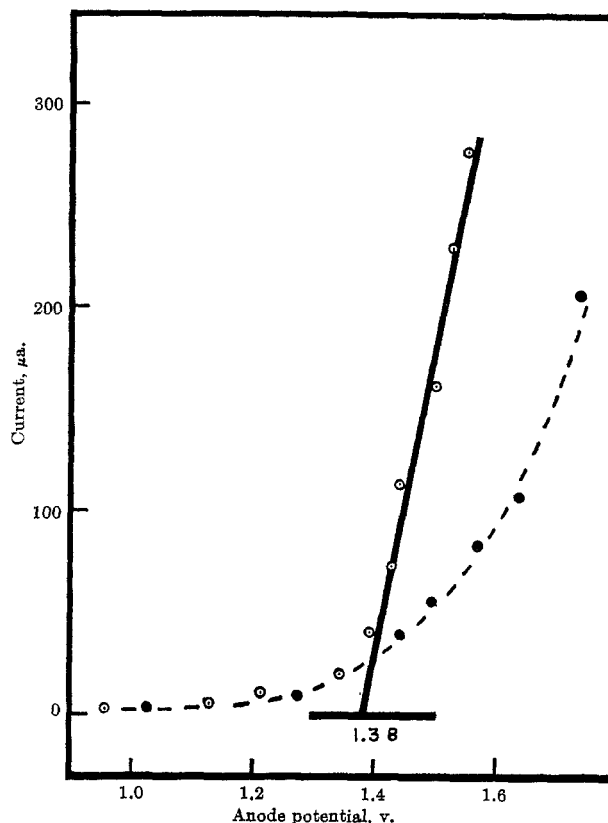
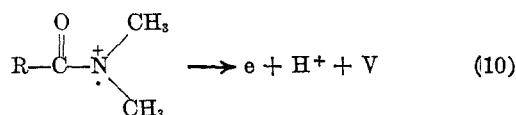
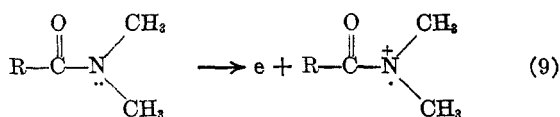


Figure 2.—Plot of current vs. anode potential (relative to Hg pool) for electrolysis of solution containing 0.050 mole of sodium formate in 50.0 ml. of formic acid: ○, without dimethylformamide; and ●, with 2.0 ml. of dimethylformamide added.

sole^{1,20} and must be considered in this case also. The formulation of such a mechanism for an N-methyl-substituted amide is not immediately obvious. One possibility that may be reasonable involves the transfer of two electrons to the anode, the discharge of a proton and formation of the carbonium ion, V. It may be formulated in two steps as shown in eq. 9 and 10.



This last mechanism is probable only if the amide is discharged at a potential measurably lower than that for the acid or its conjugate base. This question is amenable to experimental testing, and the pertinent discharge potentials have been investigated as described in the Experimental Section. The results for the acetate-acetic acid system are shown in Figure 1, and the results for the formate-formic acid system are presented in Figure 2.

In acetic acid the addition of dimethylformide results in a clear lowering of the potential at which the current rises rapidly. It is, therefore, highly probable that the amide is discharged at the anode at a lower potential than the acid in this system. A report from Professor

Eberson that he has succeeded in oxidizing dimethylformamide in acetate ion-acetic acid at an anode potential which does not allow the Kolbe reaction to take place makes this probability a virtual certainty.²¹

In formic acid it is equally clear that the addition of dimethylformamide does not result in a lowering of the potential at which the current increases rapidly. With dimethylformamide added the current begins to increase at essentially the same potential, but the curve of current vs. potential falls below that for the system without dimethylformamide and was observed to drift still lower with time. This suggests that a product of the electrolysis may be adsorbed to some extent on the anode, thus decreasing the area available for the normal electrochemical reaction. At any rate, it may be concluded that the mechanism represented by eq. 9 and 10 is relatively improbable in this system.

It is not possible to relate the potentials measured in the two systems. It is, however, clear that formate ion is discharged at a potential much lower than that required for acetate ion. If an equimolar mixture of formic and acetic acids is electrolyzed at 0.4 amp. as in the other experiments, the gaseous products are almost entirely carbon dioxide and hydrogen, and the rate of gas production is almost exactly that expected for discharge of formate ion only. The two possibilities are readily distinguishable, since for every 2 f. of charge passed the discharge of acetate ion generates 4 moles of gas while the discharge of formate ion generates 2 moles of gas. The results thus present a consistent picture in which formate ion has the lowest discharge poten-

(20) L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963); L. Eberson and K. Nyberg, *ibid.*, **18**, 1568 (1964); M. Leung, J. Herz, and H. W. Salsberg, *J. Org. Chem.*, **30**, 310 (1965).

(21) Private communication from Professor Lennart Eberson, Department of Organic Chemistry, University of Lund, Lund, Sweden.

tial, acetate ion the highest potential, and dimethylformamide a potential in between.

For the path by which III is formed in formic acid the choice to be made is between the first two mechanisms. Both mechanisms involve the discharge of a formate ion to give a formyloxy radical, which then abstracts a hydrogen atom from dimethylformamide. For either mechanism, it follows that the electrochemical oxidation of formic acid involves single-electron transfers at the anode rather than a concerted two-electron transfer. The first mechanism involves only radical intermediates, whereas the second mechanism involves the carbonium ion V as well.

It was hoped that this last distinction would provide a basis of choice between the two possibilities. Since only formate ion is discharged when a mixture of acetic and formic acids is electrolyzed, it might be expected that electrolysis of an equimolar mixture of the acids in the presence of dimethylformamide would result only in III if the first mechanism is correct but in a mixture of II and III if the carbonium ion is an intermediate. The experiment, in fact, resulted in a mixture of II and III, but the result is inconclusive, since it was later shown that II added to formic acid gives a mixture of II and III. This experiment led to the previously described conversion of the acetate, II, to the formate, III. The present experiments, thus, do not permit a definite choice between these two possible mechanisms.

The genesis of the ether amide IV is subject to the same uncertainty. This product is probably not a primary one, and it almost certainly results from etherification of N-hydroxymethyl-N-methylformamide. None of our experiments were done under rigorously anhydrous conditions, and all most likely contained sufficient water to account for the amounts of IV isolated. It is pertinent that addition of water

prior to the electrolysis of potassium formate in dimethylformamide and formic acid results in a greatly diminished yield of III, indications of formaldehyde formation during distillation and the presence of appreciable quantities of N-methylformamide, a decomposition product of the hydroxymethyl compound, in the distillate. It is also pertinent that IV may be obtained by electrolysis of dimethylformamide with 5–10 vol. % of 1 M sulfuric acid²² and that IV may be prepared by treating N-methylformamide with paraformaldehyde and acid.⁹ Furthermore, it can be demonstrated that III is readily hydrolyzed under our experimental conditions.²³ The ester III is a possible precursor of N-hydroxymethyl-N-methylformamide, but the latter compound could also arise from reaction of V with water. This question is not resolved by our experiments.

In the electrolyses in acetic acid, dimethylformamide is discharged at a lower potential than acetate ion, and the third mechanism is the most probable one. This is the strongest statement that is permissible, since the results in Table I indicate that acetate ion is also being discharged under our experimental conditions.²⁴ Therefore, some of the products I and II could be the result of the first and/or the second mechanism. It is an attractive possibility that in both solvents the carbonium ion V is the critical intermediate but that this intermediate arises *via* different paths in the two solvents.

(22) D. E. Couch, *Electrochim. Acta*, **9**, 327 (1964).

(23) In a solution of III (1 ml.) in dimethylformamide (10 ml.), water (1 ml.), and formic acid (0.5 ml.) approximately 30% of III had reacted within 20 hr. at room temperature. If the solution was then warmed, another 30% reacted within minutes.

(24) The maximum current density involved in the experiments used to investigate the discharge potentials is about one order of magnitude less than that which obtains in the preparative electrolyses.

Reactions of N-Formyloxymethyl-N-methylformamide. A Useful Electrophilic Reagent

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The acid-catalyzed reactions of N-formyloxymethyl-N-methylformamide with carboxylic acids, alcohols, a mercaptan, β -naphthol, anisole, phenol, and thiourea have been studied, and the products have been determined. All of the reactions proceed by the AAL1 mechanism and involve the carbonium ion, III, as an intermediate.

A previous report from this laboratory¹ has described a convenient electrochemical procedure for preparing N-formyloxymethyl-N-methylformamide (I). It was also shown that I can be obtained by treating N-acetoxymethyl-N-methylformamide with formic acid. Such acyl group exchange is indicative of facile carbonium ion formation.² In Ingold's classification, the mechanism is of the AAL1 type³ and may be written as shown in Scheme I in which the rate-determining step is the unimolecular heterolysis of II to give the carbonium ion, III.

(1) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

(2) S. G. Cohen, *J. Am. Chem. Soc.*, **66**, 1395 (1944).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

This result suggested that N-acyloxymethyl-N-methylformamides would prove to be useful electrophilic reagents, reacting with other nucleophiles under acid catalysis to give a variety of products. This possibility has been explored with N-formyloxymethyl-N-methylformamide (I), and the results are reported in the present communication.

Acyl-exchange reactions were also successfully effected on I by benzoic acid and propionic acid. In both reactions small amounts of concentrated hydrochloric acid served as catalyst. The reaction with benzoic acid was run in dimethylformamide as solvent and gave the known N-benzoyloxymethyl-N-methylformamide.⁴ In the reaction with propionic acid, the

(4) C. H. Bamford and E. F. T. White, *J. Chem. Soc.*, 1860 (1959).