

# The Electrooxidation of Absolute Methanol

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Tsutsumi and his collaborators<sup>1)</sup> first reported that several hydrocarbons give the corresponding methyl ethers upon the electrolysis of their methanolic solutions. They stated that the reaction proceeds through the formation of a methoxy-free radical.

As is well known,<sup>2)</sup> alkoxy-free radicals can generally be produced by neither irradiation nor thermal decomposition from their parent alcohol. Electrolysis, therefore, seems to be a quite specific method for producing alkoxy-free radicals.

In this paper, the electrolytic behavior of absolute methanol containing sodium methylate or certain inorganic salts as supporting electrolytes will be described. The reactions of several hydrocarbons in the methanolic media will be reported on successively.

## Experimental Procedures and Results

**General Description of the Experiment.**—Special grade methanol obtained from the Wako Pure Chemicals company was distilled once and dehydrated by the usual method before use. Smooth or platinized platinum was used for both the anode and the cathode electrode throughout the present investigation. The size of the electrode was changed with each experiment. The electrode potential was measured with reference to a saturated calomel electrode (SCE). Besides sodium methylate, some inorganic salts were examined as supporting electrolytes. Unless otherwise stated, the concentration of the electrolyte was kept at 0.1 mol./l. The solution was deaerated by nitrogen before each experiment.

**The Static Potential of the Platinum Electrode (Fig. 1).**—The electrode potential at a no-current flow was measured as a function of the sodium methylate concentration and of the hydrogen partial pressure, which was varied by mixing hydrogen with dry nitrogen. Both smooth and platinized platinum electrode were examined, but the data concerning the smooth platinum electrode were discarded because of their poor regularity.

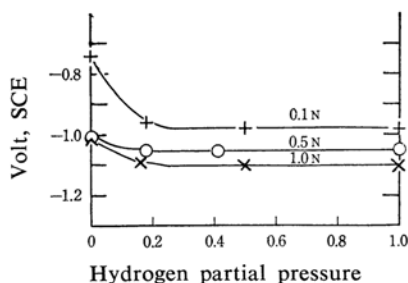


Fig. 1. Static electrode potential of Pt-Pt electrode in absolute methanol.  
+ : 0.1 N Sodium methylate  
O : 0.5 N Sodium methylate  
X : 1.0 N Sodium methylate

Although no quantitative conclusion can be obtained from this measurement, it is evident that the electrode potential is affected by the methylate concentration. The proportionality coefficient between the potential and the logarithm of concentration can roughly be estimated to be  $2RT/F$ .

**The Constant-current Polarization in the Stirred Solution.**—The current-potential and potential-time curves under the constant-current conditions were measured for sodium methylate solutions using a smooth platinum electrode with an apparent area of 30 cm<sup>2</sup>. During the experiment nitrogen was bubbled into the solution.

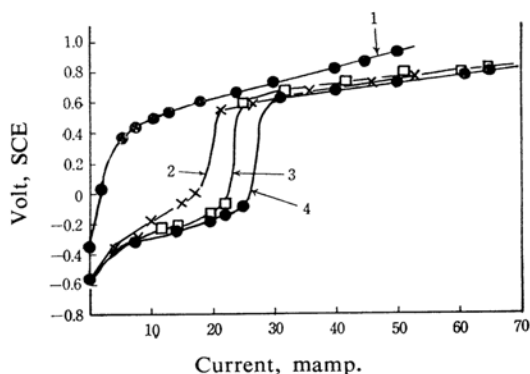


Fig. 2. Current-potential curves for various methylate concentrations.  
Curve 1, 0.24 mol./l.; 3, 1.9 mol./l.;  
2, 0.96 mol./l.; 4, 2.2 mol./l.

1) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **66**, 1659 (1963).

2) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

Figure 2 shows the  $i$ - $E$  curve obtained for solutions with different salt concentrations. It is significant that the  $i$ - $E$  curves show a sudden rise in potential at a certain current value. The current value at which the potential rises suddenly is shifted regularly to a lower value with a decrease in the methylate concentration. A similar shape of the polarization curve has often been reported in the case of Kolbe electrosynthesis.<sup>3-5)</sup>

In the latter case, it has been explained that the accumulation of carboxyl radicals, formed by the discharge of the carboxylate anion, on the electrode surface, causes the potential jump. In any case, it is clear, in the present experiment, that during the discharge of the methylate anion the electrode potential is kept at a lower value.

The potential-time curve obtained by constant current electrolysis is shown in Fig. 3. In this case, the concentration of methylate is kept constant. The figure shows that the time required for the potential rise is lengthened by the decrease in the current applied.

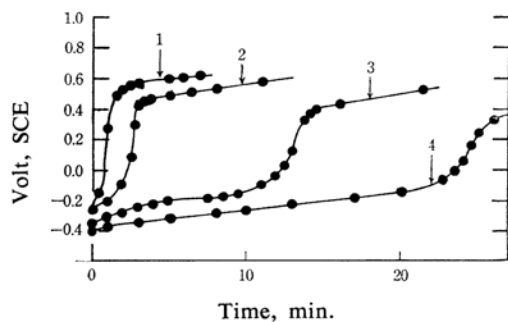


Fig. 3. Potential-time curves in the stirred solution.

Curve 1, 25 mamp.; 3, 12.2 mamp.;  
2, 19 mamp.; 4, 8.6 mamp.;  
0.1 mol./l. sodium methylate

**Constant-current Polarization under Unstirred Conditions (Chronopotentiometry).**— Another from of potential-time relationship was obtained under unstirred conditions. A schematic diagram of the cell for this measurement is shown in Fig. 4a. The  $E$ - $t$  curves were obtained by an automatic pen-recorder. Platinized platinum (0.5 mm. in diameter and 5 mm. long) was used as the working electrode.

The most striking feature observed in this experiment is that the shape of the chrono-

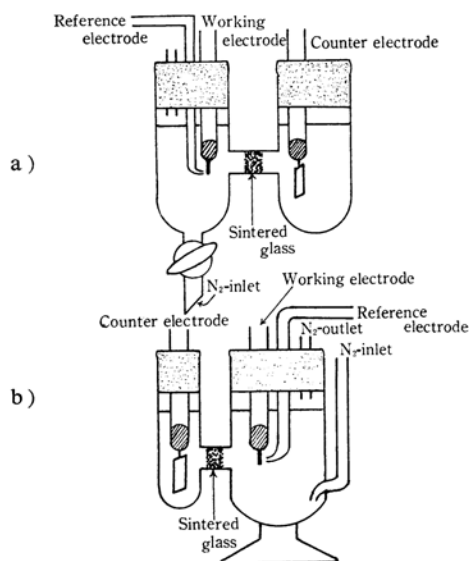


Fig. 4. Electrolysis cells.

a) for chronopotentiometry  
b) for potentiostatic voltammetry

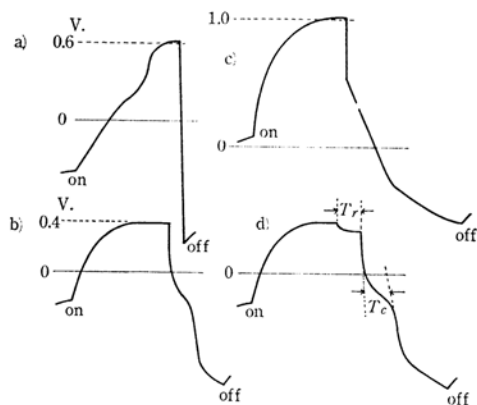


Fig. 5. Chronopotentiograms of current reversal in absolute methanol.

a) Sodium methylate, b) Sodium perchlorate, c) Ammonium chloride

Curve d illustrates the notations used in Fig. 7.

potentiogram is determined solely by the kind of supporting electrolyte used (Figs. 5a—c).

When sodium methylate was examined as a supporting electrolyte, the normal potential arrest (the chronopotentiometric "transition time") was observed in the process of anodic polarization. Upon the immediate reversal of the direction of the current flow, the potential decreased steeply without any characteristic change (Fig. 5a). The potential arrest observed in the anodic process satisfied approximately the requirement of the constancy of  $i\tau^{1/2}$ . This is illustrated in Fig. 6, which depicts the

3) N. Sato, T. Sekine and K. Sugino, 29th Annual Meeting of the Electrochem. Society of Japan, Sendai, 1962.

4) G. S. Pande and S. N. Schulka, *Electrochem. Acta*, **4**, 215 (1961).

5) T. Dickinson and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **58**, 382, 388, 400 (1962).

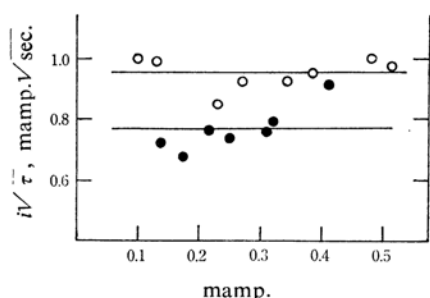


Fig. 6. Relation between  $i\tau^{1/2}$  and current for methylate solution obtained from two separate runs; apparent area of Pt-Pt electrode is  $0.08 \text{ cm}^2$ .

results obtained from two separate runs.\*

The anodic chronopotentiogram for sodium perchlorate, on the other hand, showed no characteristic potential arrest and reached the final plateau gradually. In this case, however, a definite potential arrest appeared in the cathodic half cycle (Fig. 5b). It is interesting that the potential arrest,  $T_c$ , is affected by the duration of the current rupture,  $T_r$ , between the anodic and cathodic half-cycles. Notations are illustrated in Fig. 5d.

As Fig. 7 shows, the cathodic arrest time decreases proportionally with the square root

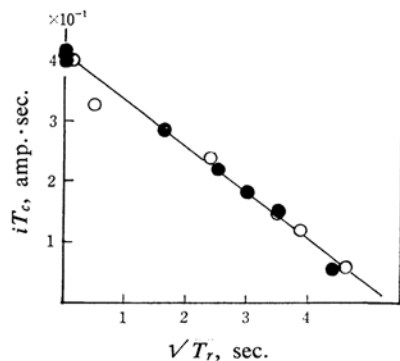


Fig. 7. The effect of the current rupture on the cathodic transition time in the perchlorate system.

Full and empty circles represent the results obtained by polarizing current of 330 and 770  $\mu\text{amp.}$ , respectively.

\* By using the mean value of these two experiments, and by evaluating the apparent surface area of the electrode, the concentration of methylate can be estimated as  $0.3 \text{ mol./cc.}$  If the true area of the platinized platinum electrode is 2000 times greater than the apparent one,<sup>6)</sup> the figure calculated above agrees roughly with the real one. This treatment, however, seems to be too arbitrary. In the rigorous sense of the terminology, this case must be treated as the solution containing no supporting (in-different) electrolyte. Accordingly, the chronopotentiometric transition time will be affected by the electric migration.<sup>7)</sup>

6) J. S. Mayell and S. H. Langer, *J. Electroanal. Chem.*, **7**, 288 (1964).

7) J. J. Lingane, *ibid.*, **6**, 300 (1963).

of the time of the current rupture. Although no active materials in this cathodic potential arrest are known, it is clear that such materials are produced during the anodic half-cycle but disappear from the electrode surface according to some simple kinetic rule.

By EPR measurement, Maki and Geske<sup>8)</sup> observed the perchlorate-free radical formed electrolytically in an acetonitrile solution. Their results were confirmed in our laboratory, although no EPR signal was detected in the methanolic media.<sup>9)</sup>

Although the shape of the chronopotentiogram of the ammonium chloride solution (Fig. 5c) is not simple enough for us to say more, it is at least clear that no potential arrest is observed in the anodic half-cycle.

The three types of chronopotentiograms obtained above suggest that methanol, as it is, can be oxidized electrochemically only with difficulty. In other works, the primary electroactive species in the electrooxidation of absolute methanol are the supporting electrolytes, not methanol itself or anything else which is derived from methanol.

The fact that the final values of the anodic potential for three kinds of electrolytes differ from each other may be a support for this statement.

**Potentiostatic Polarization.**—Potentiostatic measurements were also made using sodium

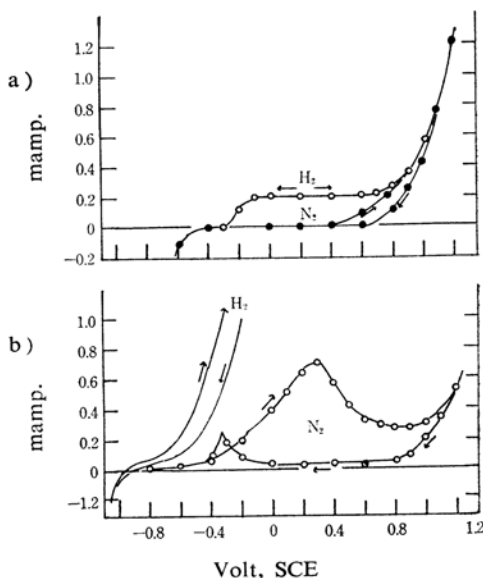


Fig. 8. Potentiostatic  $i$ - $E$  curves for sodium perchlorate (Fig. 8a) and sodium methylate solution (Fig. 8b).

8) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).

9) K. Sasaki and T. Ichikawa, unpublished work.

methyrate and sodium perchlorate as the supporting electrolytes. The platinized platinum electrode used in the chronopotentiometry was used again in this experiment. The rate of voltage scanning was 0.05 V./min. The electrolysis cell is shown in Fig. 4b. During the experiment, nitrogen or hydrogen gas was bubbled in order to agitate the solution.

In accordance with the results of the chronopotentiometry, the potentiostatic  $i$ - $E$  curve was greatly affected by a change in the kind of electrolyte used. Figure 8a represents the results with a perchlorate solution. If the solution was under the nitrogen atmosphere, the  $i$ - $E$  curve was quite simple and the anodic and cathodic scan curves were on almost the same line. When the solution was saturated with hydrogen, however, a definite diffusion limiting current was observed. The reverse scan curve coincided with the curve of forward scan. The fact that the anodic and cathodic scan curves are on the same line suggests that the complication of the surface change of platinum electrode encountered in the aqueous phase experiment<sup>10)</sup> can be ignored in the methanolic media, at least if the scan speed is not exceptionally large.

Figure 8b presents the results concerning the methyrate solution. In this case, the shape of the  $i$ - $E$  curve is quite similar to that obtained in the aqueous solution of methanol. For instance, the anodic current shows a peak in the moderate potential range.

Furthermore, the potential at which the anodic current peak appears in the course of the cathodic scan is shifted to a less positive potential than in the case of the foregoing scan. In addition, the peak value of the

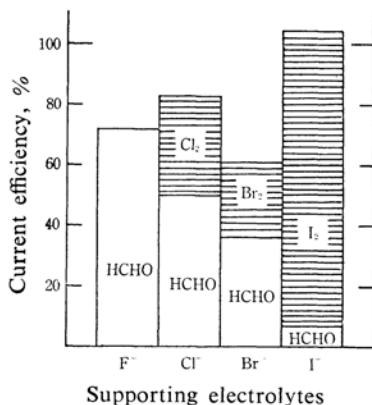


Fig. 9. Current efficiencies for the formation of formaldehyde (empty area) and free halogen (shaded area) with respect to four ammonium halides.

anodic current is successively decreased when the scan is multiplied. In this case the accumulation of electrolytically-inert material may be significant.

**Product Analysis.**—Methanol in an aqueous solution, especially in an acidic medium, is oxidized anodically to carbon dioxide, but the final product in absolute methanol is carbon monoxide. This was confirmed by mass spectrometric analysis.<sup>11)</sup> In the present experiment, the products in the liquid phase was analyzed. One hundred cubic centimeters of absolute methanol containing either one of four ammonium halides or sodium methyrate was electrolyzed for two hours at 100 mamp. The electrolysis cell was then cooled by ice-water mixture in order to minimize the evaporation. The results of the analysis of free halogen and formaldehyde as determined by iodometric titration are shown in Fig. 9. In this figure, the product yield is expressed in terms of current efficiency. It can be seen that the formation of both formaldehyde and free halogen molecules is affected by the change in the supporting electrolyte.

As for ammonium iodide, the current is consumed almost completely in the liberation of the free iodine molecule. No free fluorine was detected, perhaps because of the immediate formation of hydrogen fluoride. It is interesting to notice that the formation of free halogen increased and formaldehyde decreased in the following order of supporting electrolytes: F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>.

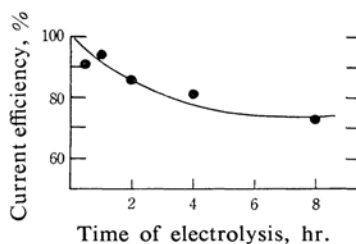


Fig. 10. The current efficiency of the formation of formaldehyde and the duration of the electrolysis. Supporting electrolyte is sodium methyrate.

Except the case of iodide, the total current efficiency for the formation of free halogen and formaldehyde differed greatly from 100%. This is also true when sodium methyrate is used as the electrolyte. In the latter case, the current efficiency for the aldehyde formation is reduced by the duration of electrolysis (Fig. 10). The remainder of the current is consumed by the further oxidation of the

10) K. Ohashi, K. Sasaki and S. Nagaura, *J. Electrochem. Soc. Japan*, **32**, 515 (1964).

11) K. Sasaki and S. Nagaura, *This Bulletin*, **37**, 1086 (1964).

aldehyde, yielding carbon monoxide. In addition, since the present analysis does not cover the vapor phase, the evaporation of the products may be another reason for this discrepancy.

### Summary

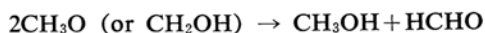
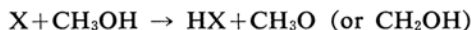
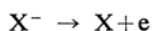
From the several experiments described above, it can be concluded that the electroactive species in the anodic reaction of methanol in the moderate potential range is the methylate anion only.

The evidence for this conclusion will be summarized below.

The static potential of the platinized platinum electrode in absolute methanol is affected by the methylate concentration.

It is confirmed that a definite transition time in an anodic chronopotentiogram is observed only for the case of the methylate ion. The results from the potentiostatic experiments also support this conclusion.

Although this is the case, methanol is still electrolyzed to form formaldehyde at a higher potential range. Product analysis shows that the yield of formaldehyde is affected appreciably by the kind of supporting electrolyte. Except fluorine, an appreciable number of free halogen molecules is detected in the solution after electrolysis. Even in the case of an iodine/iodide couple, the thermodynamic potential is far more positive than that of methanol. It may be understood from this fact that the electrooxidation of neutral methanol is strongly irreversible. Furthermore, it seems quite plausible that some part of the methanol is decomposed by the attack of the free radicals (or atoms) formed by the discharge of salt anion. The reaction scheme can be formulated as follows:



Coinciding with this hypothesis, the current efficiencies of formaldehyde formation are increased in the order of the hydrogen-abstracting power of the four halogen atoms examined, i. e.,  $I < Br < Cl < F$  (see Fig. 9).

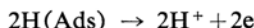
The mechanism of the electrolytic oxidation of methanol in aqueous solution has been studied by many authors, but no mechanism has yet been accepted without any ambiguity.

The static electrode potential observed in an aqueous methanol solution rests near the thermodynamic redox couple:



It is evident, however, that the real process does not proceed through such a simple reversible path.

Another mechanism proposed is the catalytic dehydrogenation:



This mechanism seems somewhat plausible, and some indirect evidence for it has been pointed out by the present authors.<sup>12)</sup>

Although it is difficult to state a definite conclusion about the reaction mechanism in the aqueous solution, the present conclusion, emphasizing the importance of the methylate ion, seems applicable in the case of the aqueous phase reaction. The fact that the performance of the methanol fuel cell in the alkaline medium is superior to that in the acidic one can thus be understood if the following reaction is taken into account:



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12) K. Sasaki and S. Nagaura, 4th Symposium on the primary cell, Kawasaki, October, 1963.