

Electroorganic Preparations II. Oxidation of Carbinols

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An anodic voltammetric investigation of about thirty carbinols with a vibrating platinum electrode in acetonitrile containing sodium perchlorate is carried out. The electrode reaction corresponding to the first wave of anisyl alcohol is shown by controlled potential electrolysis to be an oxidation of anisyl alcohol to anisaldehyde.

Organic electrolytic oxidations have not been investigated as much as reductions, and no controlled potential electrolysis of irreversibly oxidizable compounds seems to have been reported, although it is still more important to control the potential in anodic than in cathodic processes in order to get a well defined product.

In this investigation the purpose was to find, from a current-potential curve of a micro electrode, conditions under which carbinols could be oxidized to carbonyl compounds. As the potential of a given electrode reaction found by means of an indicator micro electrode depends upon the electrode material and the medium the first aim was to find a suitable electrode material and reaction medium.

Electrode material. The ideal micro electrode must be unattackable in the potential range used and should be independent of its 'history'. It should be easy to make with a well defined shape and area and should possess a certain mechanical strength, because it is necessary to vibrate or rotate the electrode during the measurements¹.

As cathode the dropping mercury electrode comes very near the requirements, but as mercury is oxidized at a rather low potential its use as an anode is very restricted. It was, therefore, necessary to use a solid micro electrode and the greatest advantage of the mercury electrode — the continual renewal of the surface — is thus lost.

As material for micro electrodes have been described platinum^{1,2}, gold³, silver³, copper³ and amalgams of these, carbon^{2,4}, and lead dioxide². Of these lead dioxide, carbon and platinum have been tried in the present investigation.

The lead dioxide electrode was made according to Lord and Rogers² and their results that this electrode could only be used within a narrow potential range was confirmed.

The graphite electrodes were made according to Lord and Rogers² and Gaylor *et al.*⁴ Lord and Rogers coat the graphite electrode with Apiezon W carefully avoiding the Apiezon getting into the pores of the graphite, whereas Gaylor *et al.* impregnate the electrode with wax in such a way that the pores are filled with wax. One advantage of the carbon electrode is that a new surface can easily be produced by breaking off the tip of the electrode. Probably due to insufficient technique in preparing the electrodes the

carbon anodes gave in our hands too high residual currents and this together with the lack of mechanical strength caused us to abandon the carbon electrode as indicator electrode.

Preliminary investigations showed that platinized platinum did not possess advantages in preference to bright platinum so all further experiments were made with a bright platinum micro electrode. It had the required features, except that the surface could not easily be renewed, but as the main purpose was not analytical but to find the potential at which the electrode reaction took place this shortcoming was not deemed serious. In some cases it could even be an advantage as the electrode showed deformed curves in the cases, where the reaction products were ill-defined and tar-like.

Solvent. The solvent must not be oxidized in the potential range used, should have a high dielectric constant to diminish the resistance of the cell, be able to dissolve organic molecules as well as inorganic salts, and to take up and give off protons readily. It should be easily purified and not too expensive. The following solvents were tried: water, *t*-butanol, acetone, nitromethane, ethyleneglycol dimethylether, and acetonitrile.

Water evolves oxygen at the anode at too low potentials and this is also the case in mixtures with dioxan. *t*-Butanol has a rather low dielectric constant and its ability to dissolve inorganic salts is very limited. Nitromethane has a high dielectric constant, but a poor dissolving power for inorganic salts.

Acetone has some advantages, but as it is rather difficult to remove water and methanol to the required extent and as the current-potential curves were somewhat deformed in acetone this solvent was abandoned. Ethyleneglycol dimethylether was not found suitable as it was difficult to remove the monomethyl ether to a satisfactory degree.

Acetonitrile which was chosen as the solvent has a high dielectric constant, a good dissolving power for organic compounds and for some inorganic salts and is usable within a wide potential range. Its most serious shortcoming is its poor protolytic properties which make a buffering of the system difficult. The low protolytic capacity is not felt as much in the voltammetric investigations, where the number of reacting molecules is rather low, as in the preparative oxidations, where it is necessary to add a proton acceptor.

Supporting electrolyte. An indifferent supporting electrolyte is required to conduct the current in the solvent. Iodide, bromide, and chloride ions are oxidized at rather low potentials, nitrate a little higher, but only perchlorates were found satisfactory. Silver perchlorate and sodium perchlorate, for instance, are very soluble in acetonitrile giving solutions with a low resistance, and anhydrous sodium perchlorate in anhydrous acetonitrile is not attacked anodically until a potential at about 2.2 V *vs* the silver ion/silver electrode.

Reference electrode. The silver/silver chloride electrode in acetonitrile has been investigated by Ulich and Spiegel^{5,6} who found it reproducible within 0.1 mV. The silver ion/silver electrode was found by Pleskow⁷ to be reproducible within 0.1 mV. Although both electrodes were found satisfactory the latter was preferred, because it was necessary to keep the former in a separate compartment, as the chloride ions were oxidized at a too low potential. The silver ions were only in special cases undesirable in the anode compartment.

RESULTS

In Table 1 are given the half-wave potentials of a number of aromatic alcohols and one aldehyde. For the compounds giving deformed waves is given the 'half-peak' potential. All the potentials are measured against the 0.1 N silver ion/silver electrode and the half-wave potentials are corrected for iR drop in the solution. The potentials are measured in solutions containing the oxidizable compound in concentrations 10^{-4} — 10^{-3} M with a voltage scanning rate of about 200 mV/min.

In the first column is given the compound, in the second one the half-wave potential and in the third one the shape of the current-voltage curve. 'Normal' means that the curve is S-shaped without peak, whereas 'deformed' indicates the appearance of a peak on the curve. Curves taken successively in

Table 1. Half-wave potentials of the investigated compounds in unbuffered acetonitrile containing 0.5 M sodium perchlorate measured against the 0.1 N silver ion/silver electrode in acetonitrile.

		1. wave $E_{\frac{1}{2}}$	shape	2. wave $E_{\frac{1}{2}}$	shape
I	<i>p</i> -Methoxybenzyl alcohol	1.22	normal	1.64	normal
IA	Anisaldehyde	1.63	normal		
II	<i>m</i> -Methoxybenzyl alcohol	1.28	normal		
III	<i>o</i> -Methoxybenzyl alcohol	1.25	normal		
IV	α -Naphthyl carbinol	1.25	normal	1.63	normal
V	β -Naphthyl carbinol	1.25	nearly normal		
VI	<i>p</i> -Chlorobenzyl alcohol	1.79	normal		
VII	<i>m</i> -Chlorobenzyl alcohol	1.85	normal		
VIII	<i>o</i> -Chlorobenzyl alcohol	1.84	normal		
IX	<i>p</i> -Bromobenzyl alcohol	1.75	normal		
X	<i>p</i> -Iodobenzyl alcohol	1.58	normal	1.91	normal
XI	<i>p</i> -Methylbenzyl alcohol	1.59	normal		
XII	Furfuryl alcohol	1.33	normal	1.82	normal
XIII	Cinnamyl alcohol	1.36	normal	1.77	normal
XIV	<i>p</i> -Nitrocinnamyl alcohol	1.72	normal		
XV	Methyl <i>p</i> -methoxyphenyl carbinol	1.24	normal		
XVI	Methyl <i>p</i> -chlorophenyl carbinol	1.80	normal		
XVII	Methyl <i>p</i> -iodophenyl carbinol	1.58	normal		
XVIII	Methyl β -naphthyl carbinol	1.29	normal		
XIX	Fluorenol	1.31	deformed		
XX	2,7-Dichlorofluorenol	1.32	deformed		
XXI	4-Methoxybenzhydrol	1.23	normal		
XXII	4,4'-Dimethoxybenzhydrol	1.22	normal		
XXIII	Phenyl α -naphthyl carbinol	1.27	deformed		
XXIV	4,4'-Dichlorobenzhydrol	1.77	deformed		
XXV	Benzhydrol	> 2.0			
XXVI	Methyl phenyl carbinol	> 2.0			
XXVII	Benzyl alcohol	> 2.0			
XXVIII	<i>o</i> -Nitrobenzyl alcohol	> 2.0			
XXIX	<i>p</i> -Bromophenacyl alcohol	> 2.0			
XXX	<i>p</i> -Bromophenyl ethylene glycole	1.62	normal		
XXXI	Cyclohexanol	> 2.0			
XXXII	Allyl alcohol	> 2.0			

the same solution of a compound giving deformed curves are not identical, unless the electrode is cleaned in between. The fourth column gives the half-wave potential of a second wave and the fifth one the shape of this wave.

DISCUSSION

In comparing the half-wave potentials of different compounds it must be remembered that empirical rules of any significance can only be expected when the reaction mechanisms are the same and when factors as energy of activation vary only slightly. As the half-wave potentials of the carbinols are closely related to those of the parent compounds a discussion of the half-wave potentials will be postponed to a later communication.

It is seen from Table 1 that the investigated compounds can be divided into three groups, the first one containing alcohols giving a normal voltammetric curve, the second group carbinols giving deformed waves and the third one not participating in any electrode reaction in the experimentally accessible potential range.

Primary alcohols of the first group show two waves unless the first wave occurs at a potential so positive that a possible second wave would be expected to occur outside the accessible potential range. It seems natural to assume that the electrode reaction corresponding to the first wave is a two electron oxidation of the carbinol to a carbonyl compound, and that the electrode reaction corresponding to the second wave is a two electron oxidation of the aldehyde to the oxidation state of a carboxyl compound.

This assumption is confirmed by the following facts. Hydroquinone and *p*-methoxybenzyl alcohol give nearly the same wave height in the same molar concentration. The molecular weight and thus the diffusion coefficient are nearly the same for both compounds, and as hydroquinone is oxidized in a two electron electrode reaction it is very likely that the same is true for anisyl alcohol. That the wave height of anisyl alcohol is diffusion-controlled is qualitatively shown by the fact that the wave height increases when the amplitude of the vibration increases. Furthermore, anisaldehyde gives a wave with very nearly the same half-wave potential as the second wave of anisyl alcohol.

Although these facts are suggestive a proof of the course of the electrode reaction can only be obtained from a preparative oxidation at a suitable potential and, as will be mentioned later, the preparative oxidation showed that the electrode reaction corresponding to the first wave was indeed an oxidation of the carbinol to a carbonyl compound.

No preparative oxidations have been performed at potentials more positive than the half-wave potential of the second wave and no conclusive evidence of the course of the reaction can be given here. From the height of the wave it is known that it is a two electron oxidation, but as no oxygen is present in the deaerated solution except in the perchlorate ions the formation of a carboxyl group is dubious.

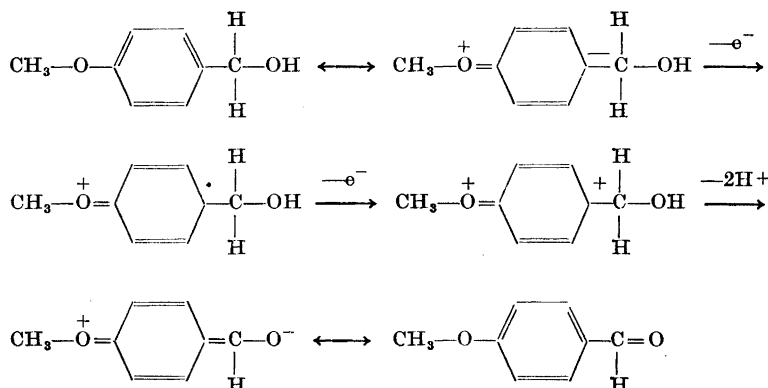
Addition of anhydrous perchloric acid in acetonitrile (from 100 % H_2SO_4 and $\text{Ba}(\text{ClO}_4)_2$) does not affect the half-wave potential of anisyl alcohol, whereas addition of pyridine lowers the half-wave potential from 0.05 to 0.1 V. The second wave of anisyl alcohol (and that of anisaldehyde) disappears on addition of pyridine.

Carbinols giving waves with half-wave potentials below + 1.65 V are not affected by the presence of silver ions, whereas carbinols having half-wave potentials at higher potentials or not producing any wave in the accessible potential range in the presence of silver ions produce a wave about + 1.69 V. The nature of this wave is not known.

The carbinols giving deformed waves with peaks are not oxidized to the carbonyl compounds, but yield unidentified products which cover the electrode with a visible, black layer. The electrode is thereby insulated from the solution and as the current is inversely proportional to the resistance of the cell it drops, giving the current-voltage curve its characteristic peak. At low concentrations the curves are more normal because the electrode is not covered com-

pletely with the reaction product during the voltammetric measurement. More often than not the electrode could be cleaned by wiping off the black layer, but in some cases it was necessary to burn it off.

As will be shown in later communications on electrolytic oxidation of hydrocarbons, heterocyclic compounds, phenols, and amines, it is likely that the primary step in the electrode reaction is a loss of an electron from the aromatic system. The radical formed is stabilized by the removal of a second electron and two protons after the following outline which gives a possible route for the oxidation of anisyl alcohol. Not all the resonance possibilities of the radicals are given.



It is essential for the formation of an aldehyde that the radical is stable long enough for the removal of two protons from the carbinol carbon atom and that seems to require that the electron deficiency is localized during a considerable time at the carbon atom next to the carbinol carbon atom.

This is illustrated strikingly in the cases of α - and β -naphthyl carbinol, *p*- and *m*-methoxybenzyl alcohol and fluorenol. Whereas α -naphthyl carbinol produces two normal waves β -naphthyl carbinol gives only one slightly deformed wave. The methoxybenzyl alcohols give the same picture. The *p*-isomer gives two normal waves, the *o*-isomer one normal and one with a smaller wave height than corresponding to a two-electron oxidation and the *m*-isomer produces only one normal wave. Fluorenol gives a very pronounced peak.

The difference between α - and β -naphthyl carbinol is, according to the explanation given above, due to the wellknown fact that there are more resonance possibilities where the electron deficiency is in the α -position than in the β -position, but as the difference in resonance possibilities between the α - and the β -position is not great, the tendency of the β -naphthyl carbinol to produce a deformed wave is not pronounced. In fluorenol, however, where the probability of an electron deficiency at the carbon atoms neighbouring the 9-position is very low, the chances of getting the carbinol oxidized to a carbonyl compound are few. The oxidation takes place in some other part of the molecule (probably in the 2 and 7 positions) and it seems likely that the polymerization product thus formed would be ill-defined and tar-like, thus explaining the great tendency of fluorenol to produce deformed curves.

PREPARATIVE OXIDATIONS

The controlled potential anodic electrolysis was undertaken in order to prove the course of the electrode reaction corresponding to the first wave in the voltammetric diagram. As representative for the first group was chosen anisyl alcohol, for the second group giving deformed voltammetric curves fluorenol and as a compound between the first and the second group β -naphthyl carbinol.

When anisyl alcohol was oxidized in a medium of 0.5 M sodium perchlorate in acetonitrile at an anode potential about + 1.35 V only about 5 % of the theoretical amount of electricity was consumed and no carbonyl compounds could be detected in the reaction medium. When the same medium, however, contained a proton acceptor as pyridine in a concentration sufficiently high to combine with all the protons formed in the electrode reaction the consumption of electricity was nearly theoretical and anisaldehyde could be isolated in a yield of 72 % as its 2,4-dinitrophenyl hydrazone. As proton acceptor pyridines or quinolines could be used, but not aliphatic or aromatic amines, as they themselves gave off electrons at a potential lower than the half-wave potential of anisyl alcohol.

Oxidation of fluorenol in acetonitrile yielded both in the absence and presence of pyridine a black, insoluble tar which covered the electrode in a very short time. No fluorenone could be detected in the tar or in the solution.

Neither did β -naphthyl carbinol yield its aldehyde on electrolytic oxidation at +1.40 V, but the covering of the electrode was slower than in the case of fluorenol.

EXPERIMENTAL

Apparatus. For the voltammetric investigation a Sargent-Heyrovsky photographic recording polarograph Model XII was used. The electrode potential was controlled by a Lingane-Jones potentiostat⁸. The coulometer used was an electromechanical current integrator⁹.

The construction of the platinum micro electrode is shown in Fig. 1. The electrode tip is a platinum wire 4.0 mm long with a diameter of 0.5 mm. The vibrator was manufactured by Fisher Scientific Company, Switzerland. The advantages of this electrode are its simplicity in construction and absence of rotating parts, which makes the exclusion of oxygen easy. It has the disadvantage that the amplitude of the vibration is difficult to measure exactly, and for analytical purposes the rotating electrode is more appropriate.

The electrolysis cell was similar to that used in Part I¹⁰. The reference electrode was a silver wire in a 0.1 M silver perchlorate and 0.5 M sodium perchlorate solution in acetonitrile separated from the test solution by a fritted glass diaphragm.

Materials. The acetonitrile (Eastman, white label) was purified according to Walden and Birr¹¹. The acetonitrile purified in this manner shows less infra-red absorption than Eastman's 'Spectro grade' acetonitrile. The pure acetonitrile is only slightly hygroscopic and can be stored for a month in a flask equipped with an effective drying tube.

The acetone was purified according to Livingstone¹².

Sodium perchlorate (Riedel-de-Haën, p.a.) was dried without further purification at 145°–150° for 24 h and finally in vacuum over P₂O₅ at 150°. As the dry product is very hygroscopic it was stored over P₂O₅.

Silver perchlorate. To a stirred solution of 24.5 g dry sodium perchlorate in 100 ml acetonitrile is added drop by drop a solution of 34 g silver nitrate in 100 ml acetonitrile. The precipitate of sodium nitrate is filtered off, the solution evaporated to 50 ml and

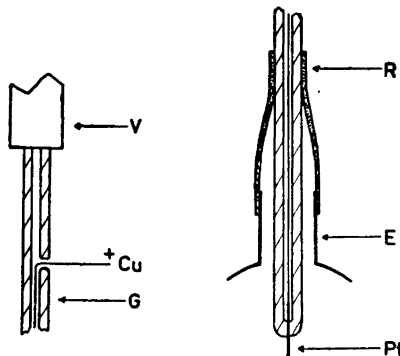


Fig. 1. Vibrating platinum electrode. V is a vibrator, Cu a copper wire soldered to the platinum wire Pt. G is a glass capillary tube, R a rubber tube, and E the electrode chamber.

traces of sodium nitrate are removed by centrifuging. On addition of dry ether the silver perchlorate is brought to crystallization. The crystals are washed with a mixture of ether and acetonitrile, 1:1, and dried in vacuum. The composition of the crystals correspond to $\text{AgClO}_4 \cdot 3 \text{CH}_3\text{CN}$ (found: Ag 31.5, Calc. for $\text{C}_6\text{H}_5\text{N}_3\text{AgClO}_4$: Ag 32.6). On heating, the crystals dissolve in their acetonitrile. If this acetonitrile is evaporated at elevated temperature a solid cake of silver perchlorate remains, which is known¹³ to be explosive. The crystals containing acetonitrile were, therefore, used and the solutions were made up according to the silver analysis.

The following carbinols were prepared from the corresponding acids or acid derivatives by reduction with LiAlH_4 : IV, m.p. 61° (59.5° – 60° ¹⁴); V, m.p. 81° (80.5° ¹⁵); X, m.p. 72° (72° – 73° ¹⁶). From the carbonyl compounds by reduction with LiAlH_4 : XIX, m.p. 154° (155° – 56° ¹⁷); XXIII, m.p. 85° (84° – 86° ¹⁸); XXV, m.p. 68° (68° ²⁰). From the carbonyl compounds by reduction with aluminium isopropoxide: VI, m.p. 71.5° (71° – 72.5° ²⁰); VII, b.p. 128° – $30^\circ/10 \text{ mm}$ (242° ²¹); VIII, m.p. 69.5° (70° ²¹); IX, m.p. 76° (76° – 76.5° ²⁰); XVIII, m.p. 71° (71° ²²); methyl *p*-iodophenyl carbinol, m.p. 52° – 52.5° , has not been described before. It was recrystallized from heptane. (Found: C 38.71; H 3.79; I 51.00. Calc. for $\text{C}_8\text{H}_9\text{OI}$: C 38.76; H 3.66; I 51.13); XX, m.p. 161° (161° – 62° ²³).

From a carbonyl compound and a Grignard compound: XVI, b.p. 84° – $88^\circ/1 \text{ mm}$ (87° – $89^\circ/2 \text{ mm}$ ²⁴); XV, b.p. 105° – $10^\circ/10 \text{ mm}$ ($95^\circ/1 \text{ mm}$ ²⁵); XXI, m.p. 66° (65° – 66° ²⁶).

XI, m.p. 59° was made according to Ref.²⁷; XXIX, m.p. 136° according to Ref.²⁸; XXX, m.p. 102° according to Ref.²⁹.

Electrolytical oxidation of anisyl alcohol. 35 ml 0.5 N sodium perchlorate in acetonitrile were deaerated with purified nitrogen³⁰ and oxidizable impurities were removed by electrolysis at an anode potential of $+1.50 \text{ V}$. When the current had reached a stationary value (residual current) 59.3 mg (0.43 mMole) of anisyl alcohol and 106.5 mg (1.35 mMole) of pyridine were added and the carbinol was oxidized at an anode potential of $+1.35 \text{ V}$ vs. the 0.1 N silver ion/silver electrode. The platinum anode had an area of 10 cm^2 ; the initial current was 60 mA and decreased in the course of 5 h to about 1 mA. The amount of electricity used was, after correction for residual current, 81 coulombs (theoretically 82 coulombs for 100 % oxidation).

4 ml of the anode chamber solution was evaporated and the residue extracted with carbon tetrachloride. An infra-red spectrum of this solution was identical with that of actual anisaldehyde in carbon tetrachloride. The rest of the anode solution was evaporated through a small column and the residue dissolved in ethyl alcohol. The carbonyl compound was precipitated as its 2,4-dinitrophenyl hydrazone. After recrystallization from xylene were obtained 89 mg (m.p. 249° – 51° (253° – 54° ³¹). The 89 mg (plus those from the test) correspond to a yield of 72 % of anisaldehyde, but the actual yield may have been somewhat higher.

This investigation was carried out at the Chemistry Department of Harvard University, Cambridge 38, Mass. 1954–1955. The author wishes to express his thanks to Dr. L. F. Fieser and Dr. J. J. Lingane for their kind interest and for many facilities which have been put at his disposal.

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Received December 15, 1956.