

STUDY OF VARIOUS TYPES OF REACTIONS IN ELECTRO-ORGANIC SYNTHESIS FOR RADICALS

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Abstract

The reputation of electro organic chemistry as something for the synthesis might be traced to the standard Kolbe reaction, which often consists of the electrolysis of carboxylate ions ensuing in mixture and decarboxylation of the produced radicals. Nevertheless, at that moment, electro organic reactions weren't offered as an approach for the synthesis of complicated molecules. Excellent attempts were created to add electrochemical ideas into artificial natural chemistry. Electrocatalysis is among the secret keywords of electrochemistry; every event which concurs to increment the electrode fee is customarily called electrocatalysts. Even though views that are various are present, the established definition of electrocatalysts is the fact that of heterogeneous catalysis at giving electrodes viz., impact of the electrode content on the electrode reaction rate. These calls for the very idea of catalysis, i.e., decrease of the activation energy and / or maybe change in response mechanism. Thus in this particular paper we studied research of different types of reactions in electro organic synthesis for radicals.

1. INTRODUCTION

It became well known that upcoming chemical technologies must meet the brand new demands imposed on industry for lower and acceptable environmentally power routes, utilizing being sold & more affordable materials. In these conditions, electrosynthetic reactions started attracting a lot of interest among synthetic chemists because of the high energy efficiency of theirs, cleanness and also the application of such reaction started spreading into all of the fields of organic and natural chemistry.

Modified electrodes are discovering application for electrosynthesis, electroanalysis, energy transformation methods in addition to photo electrochemistry as well as bio electrochemistry. Chemically modified electrodes (CMEs) stand for a promising and new entirely sort of electrodes particularly in the situation of electro organic chemistry. Table 1.1 gives some present electro organic synthesis of essential chemicals.

Table 1: Current electro-organic technologies

Product	Starting material	Company
Acetoin	Butanone	BASF
Acetylenedicarboxylic Acid	1,4-butyndiol	BASF
Adipoin Dimethyl Acetal	Cyclohexanone	BASF
Adiponitrile	Acrylonitrile	BASF
4-Aminomethylpyridine	4-Cyanopyridine	Reilly Tar
Gluconic Acid	Glucose	Sandoz, India
Hexafluoropropyleneoxide	Hexafluoropropylene	Hoechst
Mucic Acid	Galacturonic Acid	EDF
p-Methoxybenzaldehyde	p-Methoxytoluene	BASF
Polysilanes	Chlorosilanes	Osaka Gas
p-t-Butylbenzaldehyde	p-t-Butyltoluene	BASF, Givaudan
Salicylic Aldehyde	o-Hydroxybenzoic Acid	CECRI, India
Succinic Acid	Maleic acid	India
3,4,5-Trimethoxybenzaldehyde	3,4,5-Trimethoxytoluene	Otsuka Chemical
3,4,5-Trimethoxytoluoyl Alcohol	3,4,5-Trimethoxytolue	Otsuka Chemical

2. TYPES OF REACTIONS IN ELECTRO-ORGANIC SYNTHESIS

Electron transfer between 2 reagents is the idea that provides typical definitions for reduction and oxidation. The idea is well known in inorganic redox response mechanisms. Though this particular idea of electron transfer got a lesser amount of interest in natural chemistry in earlier times. Organically grown chemical reactions that are happening in electrolytic cells by the passage of electric current is viewed as electro organic reactions. They're classified into two normal types of reaction

1. Indirect or perhaps homogeneous sort.
2. Heterogeneous or direct type

The manner by that the electron transfer is able to occur could be indirect or direct. The electrochemically produced radicals (radical anions or maybe cations) behave in a wide range of routes, possibly electrochemically or chemically to develop a range of things. These reaction pathways could be more complex when adsorbed intermediates communicate with these species. Classification of electro organic responses as indirect, direct and several examples of electro organic reactions as indirect electro organic synthesis are provided in Table two, three, and four.

Table 2: Classification of electro-organic reactions- Indirect type

- **Indirect: Charge transfer occurs with some other species, which then reacts with the substrate of interest**

a. with electro regenerated redox species	e.g., Cr^{6+} , Ce^{4+} , Ag^{2+} , Br_2 , etc.
b. With adsorbed intermediates generated during the course of a reaction	e.g., Cl_{ads} , CO_2 , HO_2 , H^+ or OH^-

Table 3: Classification of electro-organic reactions- Direct type

- **Direct: Charge transfer is the primary act with the organic substrate of interest**

a. Cation radical formation	$\text{R} \rightleftharpoons \text{R}^+ + \text{e}^-$
b. Anion radical formation	$\text{RX} \rightleftharpoons \text{RX}^- + \text{e}^-$ where X may be halogen, H or other functional group
c. Carbonium ion formation	$\text{RH} \rightleftharpoons \text{R}^+ + \text{H} + 2\text{e}^-$ e.g., $\text{CH}_3\text{-COO}^- \rightleftharpoons \text{CH}_3^+ + \text{CO}_2 + 2\text{e}^-$
d. Carbanion formation	$\text{RX} + 2\text{e}^- \rightleftharpoons \text{R}^- + \text{X}^-$
e. Reduction of carbonium ions or oxidation of anions	1) $\text{R}^+ + \text{e}^- \rightleftharpoons \text{R}^{\cdot}$ e.g., $\text{C}_6\text{H}_5\text{CH}=\text{N}^+(\text{CH}_2)_4 \rightleftharpoons \text{C}_6\text{H}_5\text{CH-N}(\text{CH}_2)_4$ $\text{C}_6\text{H}_5\text{CH-N}(\text{CH}_2)_4 \rightleftharpoons \text{product}$ (dimerizes on reation) 2) $\text{R}^- \rightleftharpoons \text{R} + \text{e}^-$ e.g., $\text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{e}^- \rightleftharpoons \text{product}$ (dimerizes on reation)

Consequently, numerous organic and natural responses are performed electrochemically, the standard tasks being anodic oxidation or maybe cathodic reduction frequently without having the usage of every other substance reagents. In general, attractive levels of highly reactive cation or even anion radicals can be produced electrochemically. Additional reactive species that could be easily made include halogens, hydrogen atoms, anion radicals, CO_2 , peroxide, hydroxyl radicals, and superoxide ions, including fluorine. An additional advantage with electrochemical routes for organic and natural synthesis will be the role played by the electrode substances, which may modify the course of reactions.

Table 4: Indirect electrolysis for electro-organic synthesis

Redox Couple	Electrochemical Conversion
Ti^{4+}/Ti^{3+}	Nitroaromatics → anilines, Quinine → hydroquinone
Fe^{3+}/Fe^{2+}	Acrylonitrile polymerization
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	Benzene oxidation
MnO_4^-/MnO_4^{3-}	Oxidation of aromatics
Ni^{3+}/NiF_6^{2-}	Electro fluorination
Ti^{3+}/Ti^+	1-Butene to methyl ethyl ketone
Co^{3+}/Co^{2+}	Oxidation of aromatics
Sn^{4+}/Sn^{2+}	Reduction of nitro compounds
Ce^{2+}/Ce^{3+}	Anthracene to anthraquinone
Cu^{2+}/Cu^+	Hydroxylation of aromatics
VO^{3-}/VO^{2+}	Oxidation of aromatics
HIO_4/HIO_3	Dialdehyde starch process
$NaHg/Hg$	Hydrodimerization
$NaOCl/NaCl$ $NaOBr/NaBr$	Propylene oxide from propylene or Oxidation of sugars

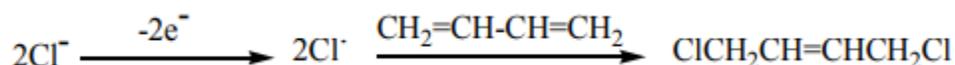
3. HOMOGENEOUS REACTIONS

A homogeneous, or perhaps indirect electro organic response is but one where the organic and natural compound doesn't swap electrons together with the electrode straight but by the intermediation of several electro proactive material. Electron transfer as well as chemical response could then occur in the majority of the answer until the healthy problems, items are obtained. Indirect reactions also can occur heterogeneously when one or maybe much more of the reactants or perhaps the electron mediators are assimilated or maybe immobilized in the electrode surface.

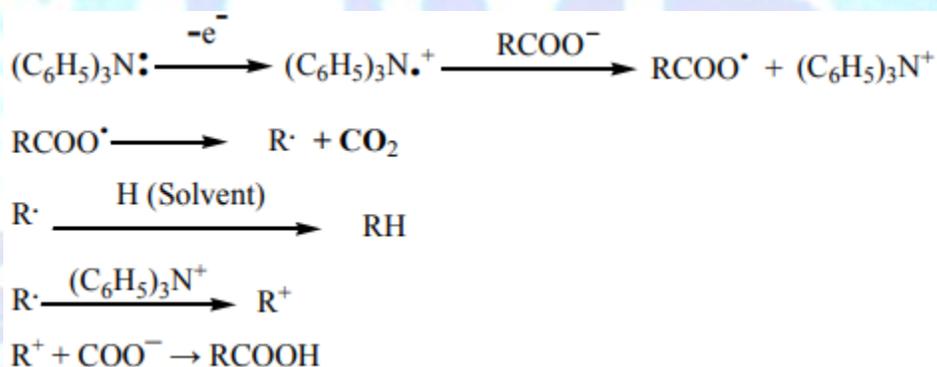
4. HOMOGENEOUS OR INDIRECT REACTION RATE

Homogeneous or indirect electro organic reactions happen through a minimum of one intermediary stage in general pattern of the reaction. The heterogeneous reaction might involve an inorganic or even an organic species. Certainly, the speed of the complete response is dependent on the rate of the heterogeneous response that establishes the focus of the electrolytically formed proactive agents responding with the organic and natural substrate. Indirect responses in cases that are most are homogeneous electrocatalytic reactions since the immediate electroactive species might be reused and also may be utilized solely in catalytic quantities. Indirect synthesis could be attained by constantly electro generating among the

reactants: for instance, superoxide ion O_2^- , from oxygen bubbled through the electrolysis medium for oxygenations, or by forming NO_2^+ from anodic oxidation of NO_2 for nitration of aromatics; or as in chlorination via continuous anodic formation of Cl_2 , or Cl^- from Cl^- ion:



Most homogeneous electro catalysts have been oxidative redox-type mediated reactions. Anodically regenerated oxidants, such as $Cr_2O_7^{2-}$, MnO_4^+ , Ce^{4+} , Mn^{3+} , Co^{3+} , Br^- , Cl^- , I^- and natural radical cations, for instance (triphenylamine) $^+$, are used. It will be very well to mention that homogeneous electrocatalysis could provide items that are different, out of exactly the same substrate, from what heterogeneous electrocatalysis would do, since the catalytic course could be changed. Metal oxoanion catalysts are able to act by oxygen transfer or maybe hydride abstraction from the organically grown substrate. The indirect oxidation of carboxylates might result in esters as well as alkanes instead of to Kolbe dimers, when it's catalysed by triphenylamine major cation, primarily due to relative awareness consequences.



5. HETEROGENEOUS ELECTROCATALYSTS

Heterogeneous electrocatalysis for organic and natural synthesis aims largely at decreasing the over possibility of direct electro organic reactions. In probably the broadest sense throughout the electrodes are looked upon as catalysts insofar as the electrode is just the website of the electrochemical response and it is not used in the procedure.

Heterogeneous electrocatalysis is assisted by adsorption forces in between the organically grown substrate as well as the adsorbing electrode stage. Adsorption lowers the activation power based on just how powerful the binding is and just how it impacts the adsorbed species physically and chemically. Electrodes could be seen as special types of catalysts, different in amount as well as specificity based on the chemical of theirs as well as bodily states of being. For heterogeneous electrocatalysis the aim is modifying or even triggers the electrode surface to facilitate the electro response in a selective manner.

A requirement for catalysis on blank electrode surfaces on the whole is adsorption of the responding species onto the electrode top. For adsorption to become catalytic the transition between electrode area websites as well as reactants would need to be stabilized to enable the activation energy barrier of the counter response being decreased. Harsh adsorption generally implies strong catalysis. Electrosorption or adsorption, when it happens under the effect of an electrical area, involves 3 primary steps:

1. Transport of reactants from the majority of the means to fix the surface area of the catalyst.
2. Physical and , and chemical interactions thereupon and also
3. Transport of items on the solution.

As respect to the electron transfer reaction, contemporary point of view reject the idea that the catalytic power of the electrode is a characteristic of the job function of the metal and attribute the catalytic properties on the capability of the electrode components to develop selectively synthetic bonds with the substance species taking part in the electrochemical response

6. HETEROGENEOUS REACTION RATES

As respect to the electron transfer itself, it's frequently thought that electrons are transferred one after the other, although time in between successive transfers may be as smaller as that associated with a molecular vibration. The speed of an electrode response as conveyed by websites current is connected to the over capability by the equation

$\eta = a \pm b \log i$ which is known as Tafel's equation, which is a special form of the Butler-Volmer equation

$$i = i_0 \{ \exp [\alpha n F/RT] - \exp [(1-\alpha) n F/RT] \}$$

Anywhere i , i_0 as well as α are found today's, exchange present and transport coefficient respectively, and additional symbols have the typical meanings of theirs. The over possibilities is the activation of possible plus it's a degree of the modification in activation power for the electron transfer reaction. The particular value of the electrode opportunity E_a contains the equilibrium possible E_{eq} . The activation over possible is identified as $\eta = E - E_{eq}$, where E is the potential in excess of the E_{eq} . The concentration over potential E_c , and the ohmic over potential IR , and any liquid junction potentials which are usually neglected in synthetic work so that the assured electrode potential in an electrosynthesis is

$$E_a = E_{eq} + \eta + E_c + IR$$

In plotting Tafel lines E_c and IR over potentials must be absent or minimized. The Tafel equation can be written so as to indicate the theoretical values of the constants a and b as follows

$$\eta = -2.3 (RT/ \alpha n F) \log i_0 + 2.3 (RT/\alpha n F) \log i$$

Because activation over potential relative to true equilibrium potential is very seldom known, the Tafel equation is written as

$$E = a + b \log I$$

Wherever E denotes a relative electrode opportunity assessed against any guide electrode ideal for an electrosynthesis. From such useful Tafel associations it's feasible to evaluate the electrocatalytic qualities of electrodes and additionally to infer plausible response mechanisms, and to choose perfect applied potentials with regard to selectivity and rates of reactions. Electro catalysis aims at decreasing the over possible and therefore enhancing both the reaction fee as well as the reaction selectivity. As a rule, the taller the over opportunity is, that's, much more bad for cathodic reactions, or even better for anodic reactions, the higher the reactivity of main solutions will be, and therefore the smaller the response selectivity is. In case the electrode is a certain electrocatalyst for a certain response, setting the electrode possibility in a good printer is going to affect mainly the electronation or maybe deelectronation speed of the sought-after reaction can't be likely to be managed exclusively by the possibility of the electrode

7. CONCLUSION

In conclusion, electroorganic synthesis will transform from a niche technology to a common synthetic method. Therefore, electrosynthesis also has to find its place in teaching and student training. The sustainability of this particular approach will make the use of this method inevitable at an academic and a technical level.

REFERENCES

- [1].Ramezanali M. and Mohammadreza H. (2008), 'On the application of electrochemical machining for inner surface polishing of gun barrel chamber', Journal of Materials Processing Technology, Vol. 202, Nos. 1-3, pp. 307-315.
- [2].Shi HyoungRyu (2008), 'Micro fabrication by electrochemical process in citric acid electrolyte', Journal of Materials Processing Technology, Vol. 209, No. 6, pp. 2831-2837.
- [3].Haisch T., Mittemeijer E. and Schultze J.W. (2001), 'Electrochemical machining of the steel 100 Cr6 in aqueous NaCl and NaNO₃ solutions: microstructure of surface films formed by carbides' ElectrochimicaActa, Vol. 47, Nos. 1-2, pp.235-241.
- [4].AhmetHascalik and UlasCaydas (2007), 'A comparative study of surface integrity of Ti-6Al-4V alloy machined by EDM and AECG', Journal of Materials Processing Technology, Vol. 190, Nos. 1-3, pp. 173-180.

- [5].Hewidya M.S., Ebeid S.J., Rajurkar K.P. and El-Saftia M.F. (2001), 'Electrochemical machining under orbital motion conditions,' Journal of Materials Processing Technology, Vol. 109, No. 3, pp. 339-346.
- [6].Sun J.J., Taylor J. and Srinivasan R. (2001), 'MREF-ECM process for hard passive materials surface Engineering', Journal of Materials Processing Technology, Vol. 108, No. 3, pp. 356-368.
- [7].Ebeid S.J. and Abdel Mahboud A.M. (2008), 'High speed electrochemical boring', Precision Engineering, Vol. 10, No. 2, pp. 80-84.
- [8].Zawistowski F. (2009), 'New system of electrochemical form machining using universal rotating tools', International Journal of Machine Tools and Manufacture, Vol. 30, p. 475.

