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ELECTROCHEMICAL CHLORINATION OF HYDROCARBONS IN AN HCl-ACETIC ACID SOLUTION

William B. Mather, Jr., Hopewell Junction, and Edwin R. Kerr, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

A process of electrochemically halogenating hydrocarbons in an aqueous hydrohalic acid electrolyte comprising passing current from a cathode to an anode immersed in an electrolyte comprising a mixture of aqueous hydrohalic acid and 10–90 volume percent of an aliphatic acid of 2–4 carbon atoms. Typically, the process involves chlorinating an aliphatic, cycloaliphatic or aromatic hydrocarbon in an electrolytic cell employing graphite electrodes using a mixture of hydrochloric acid and acetic acid. Using the mixed acid electrolyte prevents rapid deterioration of the anodes and increases the solubility of the hydrocarbon starting material in the electrolyte.

BACKGROUND OF INVENTION

This invention relates to a process for halogenating hydrocarbons. More particularly, it relates to an improved method for electrochemically chlorinating or brominating hydrocarbons using a modified solvent-electrolyte mixture which increases the solubility of the hydrocarbon reactant in the electrolyte and aids in reducing the rate of deterioration of the electrodes during electrolysis.

Though for the purpose of brevity, the description of the present invention will be, for the most part, specific to chlorination reactions, bromination reactions are substantially analogous and they are intended to be included herein.

Electrochemical halogenation, particularly chlorination of organic compounds is well known and widely practiced. The synthesis of chlorohydrin from ethylene and a neutral aqueous chloride solution is a commercial process. The electrochlorination of n-dodecane with aqueous HCl has also been disclosed (Ruehlen et al.—J. Electrochem. Soc. 111, 1107 (1964)).

Electrolytic chlorinations are carried out in conventional electrolysis cells. The cell consists of a covered vessel containing electrolyte and equipped with an anode and a cathode extending down through the cover into the electrolyte. The cell is divided into interconnected anode and cathode compartments, each compartment being provided with a port to permit escape of gases produced during electrolysis. A source of DC power is connected across the electrodes.

Electrochemical chlorination involves the production of atomic chlorine or the chloronium ion (Cl^+) by electrolytic dissociation of a chlorine-containing compound in the electrolyte. As noted above, the chlorine compound may be one which gives neutral or acidic aqueous solutions. To commence electrochlorination, the compound to be chlorinated is added to the anode compartment and a DC potential is applied across the electrodes. At the cathode, hydrogen gas is formed from the reduction of hydrogen ions, and at the anode, chlorine is generated by dissociation of the chlorine-containing electrolyte. The chlorine generated at the anode reacts with the hydrocarbon present in the anode compartment to give the desired chlorohydrocarbon. Excess chlorine or hydrogen produced during electrolysis is vented through the electrolysis cell ports provided for this purpose.

In order for electrochemical chlorinations to be conducted in an economically feasible manner, the product yield and purity must be relatively high and the electrolytic cell, especially the electrodes, must be resistant to rapid deterioration during use.

From a standpoint of cell durability, it is preferred to conduct the chlorination in a neutral aqueous chloride solution since such electrolytes do not cause rapid deterioration of the cell and the electrodes. However, the neutral electrolyte process has several drawbacks which have an adverse impact upon its overall efficiency. The main drawbacks are the lack of solubility of the hydrocarbon starting material in the electrolyte, the relatively poor conductivity of the electrolyte and the problem of by-product alkali which is expensive to separate from residual sodium chloride. Other difficulties, such as the instability of the chloronium ion, necessary for the chlorination of olefin or aromatic hydrocarbons is much less stable in neutral than in acid solution.

The disadvantages attendant the use of a neutral electrolyte for chlorination of hydrocarbons are substantially avoided when the chlorination is carried out in a simple aqueous HCl electrolyte. Though it is advantageous from one standpoint to use an aqueous acidic electrolyte, aqueous acids cause rapid deterioration of the anode especially when a graphite anode is employed. Moreover, hydrocarbons used as starting materials are not generally soluble in aqueous HCl and since the solubility of the starting material is a determinant in product yields, yields of product based upon current input have not been as high as desired.

In view of this state of the art, it is an object of the present invention to provide a modified electrochemical chlorination process for converting hydrocarbons to chlorinated derivatives thereof. It is another object of the present invention to provide a new method of electrochemically chlorinating hydrocarbons wherein the electrolysis cell, especially the electrodes thereof, is not subjcet to rapid deterioration during electrolysis. Other objects will be apparent from the ensuing description of this invention.

SUMMARY AND DESCRIPTION OF INVENTION

In accordance with one aspect of this invention, it has been found that electrochemical halogenation, e.g., chlorination and bromination, can be conducted efficiently in a manner which does not result in rapid deterioration of the electrodes. The method involves conducting the electrolysis in an electrolyte comprising a carboxylic acid of 2–4 carbons such as glacial acetic acid, propionic and/or butyric acids and aqueous concentrated hydrochloric or hydrobromic acid. It has been found that the carboxylic acid provides two beneficial effects. It increases the solubility of the hydrocarbons in the electrolyte and it reduces the deterioration of the anode. Dry hydrogen halides can be used, but higher conductivity and better current efficiencies are achieved with aqueous concentrated hydrohalic acids, e.g., 12 N HCl or HBr. A preferred electrolyte contains 50% by volume of glacial acetic acid and 50% by volume of 12 N HCl. However, beneficial effects are obtained when as little as 10% by volume of carboxylic acid or as much as 90% is in the electrolyte. When the concentration of carboxylic acid is less than about 10%, solubility of the hydrocarbons is very low and deterioration of the graphite anode occurs. Too high a concentration of glacial acetic acid reduces the conductivity of the electrolyte thereby considerably increasing the voltage requirements for the reaction and raising the operating costs for the process.

The process of this invention is applicable to aliphatic, cycloaliphatic and aromatic hydrocarbons in general so

long as they are soluble in the electrolyte. Examples of useful compounds are paraffins of 3 to 20 carbon atoms such as propane, nonane, cetane, etc.; cycloalkanes of 4 to 12 carbon atoms such as cyclobutane, cyclohexane, etc.; olefins of 2 to 20 carbons such as ethylene, dodecene-1, etc.; cycloalkenes of 4 to 12 carbons such as cyclobutene, cyclohexene, etc.; and aromatics of 1–3 carbocyclic rings such as benzene, naphthalene, biphenyl anthracene and lower C_8 alkyl or alkenyl substitution products thereof such as toluene, xylene, cumene and styrene.

The hydrocarbon reactant need not be completely soluble in the electrolyte for the chlorination to proceed. However, chlorination by the process of this invention is more efficient for olefinic and aromatic compounds, than for the less soluble paraffins. Gaseous, liquid and solid hydrocarbons can be chlorinated so long as the reactant hydrocarbon is brought into intimate contact with the electrolyte. In the case of gaseous hydrocarbon reactants, the hydrocarbon is bubbled into the electrolyte by positioning the reactant feed inlet below the level of the liquid electrolyte in the anode compartment. Solid reactants can be comminuted prior to being introduced or dispersed by high shear agitation in the electrolyte cell, and maintained in suspension by agitation during electrolysis. Liquid hydrocarbon reactants which do not dissolve in the electrolytic cell can be suspended in the electrolyte by agitation during the chlorination reaction.

The chlorination process of this invention advantageously can be conducted in conventional electrolysis cells of the aforedescribed type. The electrodes can be fabricated of graphite, preferably of the high density type. One advantage of using a carboxylic acetic acid solvent in the electrolyte is that it permits use of low cost graphite electrodes without the previously encountered serious problem of rapid electrode deterioration due to spalling away of carbon during electrolysis. Not only does this surprising result beneficially influence the durability and efficiency of the cell, but it also leads to the production of chlorinated hydrocarbon product not contaminated by particles of the graphite electrodes.

The yield of product is determined by amount of current used, time of electrolysis, time to quench, voltage, temperature, electrolyte compaction, and in certain cases, the presence or absence of short wave UV radiation.

The amount of current theoretically required is that which yields the number of electrons required to effect a particular chlorination reaction. One equivalent of electrons is required for monochlorination, two for dichlorination, etc. The actual current requirement is based upon the "percent current efficiency," i.e., the number of electrons used to effect a particular reaction divided by the total electrons used and multiplied by 100. Current efficiency for any particular reaction increases until enough chlorine has been generated to react with the hydrocarbon starting material. The increase in current efficiency appears to be due to an initiation period in which current does not form products, because, it is speculated a certain concentration of chlorinating species (about 0.03 equiv.) must be generated before chlorination occurs. After the initiation period, there is a rapid increase in product formation until nearly all the hydrocarbon has reacted. After the equivalence point, current efficiency declines since there is no more hydrocarbon to react. Thus, the optimal use of current is fortunately achieved at highest starting material conversion levels. The electrolysis can be conducted at any temperature between ambient temperatures and the boiling point of the electrolyte.

In most electrochlorinations in accordance with this invention, current efficiency and product selectivity are not greatly influenced by incident light and generally the reaction proceeds equally well in room light and with no light. However, the bromination of paraffins is significantly affected by radiation which is capable of dissociating halogen molecules into halogen atoms. Wavelengths shorter than 500 mμ will dissociate halogen molecules into halogen atoms to some extent although maximum dissociation is around 340 mμ or lower. In the case of paraffin halogenation the active species is atomic halogen and therefore the higher level of halogen dissociation aids in the attainment of greater conversion rates for the paraffin strating material. In the case of olefins or aromatic hydrocarbons, the active species is either the chloronium or the bromonium ion. Since UV light does not facilitate the formation of the latter, and in fact, may inhibit their formation, only a minor or even a negative effect is noticed when aromatics or olefins are halogenated in the presence of light with wavelengths shorter than 500 mμ.

The major products of the electrohalogenation reaction of the present invention and mono and dihalogenated derivatives of the hydrocarbon starting material. In the case of olefin starting materials, the major products are dihalo derivatives of the starting materials, whereas in the cases of paraffin and aromatic compounds the major products are monohalo derivatives of the starting materials. The products of halogenation can be separated from the electrolyte by conventional extraction or chromatographic separation techniques, the choice of which is dependent upon the nature of the product and the degree of product purity which is desired.

The following examples are presented to further illustrate the present invention.

EXAMPLE 1

Chlorination of dodecene-1

An electrolysis cell was made from a laboratory beaker which was fitted with a cover through which was passed a ⅜" graphite rod anode and a 1" (I.D.) bottomless Pyrex tube extending to ¾" above the bottom of the beaker. Another ⅜" graphite rod was used as the cathode within the Pyrex tube. The beaker was equipped with a magnetic stirrer and a Teflon-coated stirring bar.

When the electrolysis was conducted in the absence of light, the beaker was wrapped with black plastic tape to exclude all outside light. A strip of the tape was removable to give an area 2 centimeters wide and 5 centimeters high to admit light into the cell. 8 watt long wave (about 360 mμ peak) and short wave (about 254 mμ peak) discharge bulbs were placed next to the untaped area of the electrolysis beaker. The Pyrex glass in the beaker transmits ultraviolet light down to 280 mμ. The short wave length UV light had a peak intensity at 254 mμ but a long radiation tail into the visible region. The long wave UV light had a peak intensity at 360 mμ and a short wave cutoff at 300 mμ. Since chlorine absorbs radiation below 480 mμ to form chlorine atoms, both lights dissociated electrogenerated chlorine molecules.

The electrolyte, usually consisting of glacial acetic acid and concentrated aqueous HCl, was mixed with the hydrocarbon in the cell and the solution (or suspension) was stirred vigorously. A current was passed through the cell and voltage and current measurements were taken. After a predetermined time, the current was shut off and the reaction was allowed to stand for some hours in order to allow the chlorine to react further. The mixture was then diluted with an equal volume of water and the reaction quenched with excess sodium sulfite. Products were separated directly or extracted with chloroform and then weighed and analyzed.

Analyses were carried out on an Aerograph model 202 gas chromatograph (T.C. detector) using a 5 ft. by ¼" column of 20% SE–30 on 60/80 Chromsorb W with isothermal operation. Effluent peaks were collected and identified by IR or NMR quantitative determinations.

Using the foregoing equipment and procedures, a series of experiments was conducted in which dodecene-1 was

electrochlorinated in 250 milliliters of an electrolyte consisting of 50% glacial acetic acid and 50% 12 N HCl. Current, concentration, time of electrolysis, time to quench, equivalents of current and light conditions were varied. Products from each experiment were isolated, weighed and analyzed, and the current efficiency and product selectivity for 1,2-dichlorodecane were calculated. The results are given in Table I.

TABLE I.—ELECTROCHLORINATION OF DODECENE-1

Run No.	Starting material (moles)	Current used (equiv.)	Products separated (moles)	U.V. light	Gas chromotographic analysis (moles in product) Dodecene-1	Chlorododecane	1,2-dichlorododecane	2-acetoxy-1-chlorododecane	Current eff. for chlorination, percent
1	.225	1.00	.230	(1)	.005		.163	.041	41
2	.225	.46	.223	(1)	.016		.166	.019	80
3	.113	.166	.119	(1)	.058	.002	.049	.007	68
4	.115	.074	.128	(1)	.112	.004	.016	.001	60
5	.115	.238	.110	(1)	.009		.075	.017	77
6	.113	.047	.113	(1)	.099	.001	.011	.002	55
7	.113	.392	.112	(1)	.003	.001	.074	.023	50
8	.113	.609	.117	(1)	.002		.083	.019	33
9	.113	.331	.113	No.	.004		.074	.020	57
10	.113	.082	.125	No.	.103	.002	.015	.0003	46
11	.113	.117	.115	No.	.085		.024	.004	48
12	.113	.037	.117	No.	.113	.0015	.0021	.003	17
13	.113	.179	.115	No.	.060	.002	.039	.009	55
14	.113	.174	.127	No.	.080	.004	.031	.009	48
15	.113	.065	.116	No.	.104		.009	.002	34
16	.113	.024	.114	No.	.110	.0014	.0027		28
17	.113	.056	.113	No.	.116	.003	.011	.003	55
18	.113	.284	.110	No.	.003		.072	.023	68
19	.113	.119	.117	lw.	.078	.002	.027	.007	60
20	.113	.406	.112	lw.	.003		.083	.017	50
21	.113	.068	.109	lw.	.096	.002	.009	.002	35
22	.046	.0306	.043	lw.	.0385	.0008	.0029	.0004	24
23	.047	.0164	.044	lw.	.0422	.0004	.0013	.0001	19
24	.046	.0080	.043	lw.	.0417	.0003	.0008	.0002	29
25	.045	.0312	.044	sw.	.0411	.0008	.0022	.0003	19
26	.047	.0134	.046	sw.	.0438	.0009	.0012	.0001	26
27	.045	.0609	.0445	sw.	.0396	.0014	.0029	.0005	13

[1] No attempt to exclude light.

EXAMPLE 2

Using the procedures and equipment described in Example 1, n-nonane and n-dodecane were electrochlorinated under varying conditions of current, light, time, etc. and the products were isolated and analyzed. For purposes of comparison, two runs were made in which an equivalent amount of sodium chloride was substituted for HCl as the source of chloride ions in the electrolyte. The results are presented in Table II.

TABLE II.—ELECTROCHLORINATION OF N-NONANE, N-DODECANE

n-Nonane	Starting material (moles)	Current used (equiv.)	Products separated (moles)	UV light	Gas chromatographic analysis (moles in product) Nonane	Chlorononane	Dichlorononane	Trichlorononane	Current eff. for chlorination, percent
Run No.:									
1	.056	.061	.042	sw.	.038	.003	.001		9.0
2	.056	.238	.040	sw.	.025	.012	.002	.001	7.6
3	.140	.476	.124	sw.	.072	.044	.008		12.5
4	.140	1.245	.144	sw.	.011	.062	.060	.012	17.3
5	.140	.539	.127	sw.	.120	.006	.002		1.6
6	.140	.289	.135	sw.	.089	.042	.004		17.4
7	.140	2.00	.078	sw.	.018	.057	.003		3.2
8	.140	.887	.138	No.	.125	.011	.002		1.6
n-Dodecane					**Dodecane**	**Chlorododecane**	**Dichlorododecane**		
9	.110	1.71	.088	No.	.079	.007	.002		0.66
10	.110	.713	.125	sw.	.073	.031	.021		10.2
11	.110	1.033	.097	sw.	.060	.037			3.6
12	.110	1.29	.076	sw.	.044	.033			2.6
13	.110	.478	.112	sw.	.079	.027	.007		8.6
14	.110	.597	.123	sw.	.064	.049	.013		12.6
15	.110	1.47	.093	sw.	.023	.031	.039		7.3
16	.110	3.14	.107	sw.	.014	.049	.045		4.4
17	.110	1.255	.082	No.	.081	.001			.09

EXAMPLE 3

Using the equipment and following the procedures described in Example 1, benzene and cumene were electrochlorinated in 250 milliliters of a 50% glacial acetic acid and 50% 12 N HCl electrolyte. The results are presented in Table III.

TABLE III.—ELECTROCHLORINATION OF BENZENE AND CUMENE

Benzene	Starting material (moles)	Current used (equiv.)	Products separated (moles)	Gas chromatographic analysis (moles of product) Benzene	Chlorobenzene	o-Dichlorobenzene	p-Dichlorobenzene	Current eff. for chlorination, percent
Run No.								
1	.281	.130	.147	.092	.052	.002		43
2	.281	.061	.152	.130	.022			36
3	.281	.249	.091	.018	.071	.001	.0025	31
4	.281	.575	.168	.006	.173	.0085	.016	50
5	.281	.428	.072		.037	.012	.023	25
6	.281	.363	.139	.019	.111	.003	.006	36
7[1]	.281	.358	.144	.016	.116	.004	.008	39
8	.562	1.16	.251		.0102	.0052	.0097	35
Cumene				**Cumene**	**o-Chlorocumene**	**p-Chlorocumene**		
9	.358	.415	.307	0.128	.087	.092		58

[1] All runs except No. 7 were run in taped beaker (no exposure to light). Run No. 7 was exposed to long wave ultraviolet light (360 mμ).

From the foregoing examples, it can be seen that product yields and product selectivity are quite high in the case of olefins and aromatics, and considerably lower in the case of paraffins. Thus, dodecene-1 was chlorinated to a mixture containing 1,2-dichlorododecane (70% selectivity) and 2-acetoxy-1-chloro-dodecane (20% selectivity) representing a 50% yield of the dichloro compound. Paraffins were chlorinated in the same system with about 1% current efficiency in the absence of light, but up to 17% current efficiency in the presence of short wave ultraviolet (254 mμ peak) light. Aromatics, like olefins, were chlorinated with high current efficiency. The initial product of benzene chlorination was chlorobenzene formed in about 40% yield. Further chlorination yielded only o-dichlorobenzene (33%) and p-dichlorobenzene (66%) with no more than 5% of the meta isomer. Overall current efficiency for benzene chlorination was therefore between 30 and 50%. Cumene was chlorinated in a 50% yield to o-chlorocumene (49%) and p-chlorocumene (51%) with no more than n-chlorocumene in the product.

Analogous bromination products are obtained when the foregoing procedures are modified by substituting HBr for HCl in the electrolytic composition.

EXAMPLE 4

Using the equipment and the procedures of Example 1, toluene was chlorinated in two separate runs with and without glacial acetic acid in the electrolyte. The reaction conditions and results are presented in Table IV.

TABLE IV.—ELECTROCHLORINATION OF TOLUENE

Run No.	Starting material		Anode	Solvent (ml.) plus electrolyte (gm.)	Voltage applied	Current used			Time of elec.	Product sep. (gm.)	Remarks
	Gm.	Moles				Current	Amph	Equiv.			
1	43.4	.470	graphite rod	HOAc (125) plus HCl (125)	4.3-4.7	.25-.30	34.8	1.30	119	43.1	Ring substitution (NMR).
2	43.4	.470	do	H_2O (125) plus HCl (125)	2.6-5.5	.17-.30	14.9	.56	72		Anode badly attacked.

From the results of Example 4, it can be noted that the presence of glacial acetic acid in the electrolyte was critical to the attainment of a substantial amount of the product and the preservation of the graphite anode.

EXAMPLE 5

Electrochlorination of methylcyclopentane

Following the procedure of Example 1 except for the substitution of methylcyclopentane for dodecene-1, a product having the expected monochlorocyclopentane and dichlorocyclopentane was obtained.

EXAMPLE 6

Electrochlorination of cyclohexane

Following the procedure of Example 1 except for the substitution of cyclohexane for dodecene-1, a product having monochlorocyclohexane and dichlorocyclohexane was obtained.

In the cases of Examples 5 and 6, there were no signs of deterioration of the graphite anode after electrolysis had been completed.

What is claimed is:

1. In the process of electrolytically halogenating hydrocarbons in an aqueous hydrochloric or hydrobromic acid electrolyte by passing current from a cathode to an anode immersed in said electrolyte whereby active halogen species is formed and reacts with the hydrocarbon to produce the desired chlorinated or brominated derivatives, the improvement which comprises incorporating in the electrolyte between 10 and 90% by volume of an aliphatic carboxylic acid of 2–4 carbon atoms.

2. The process of claim 1 wherein the anode and cathode are fabricated of graphite.

3. The process of claim 1 wherein the hydrocarbon is an olefin of 2–20 carbon atoms.

4. The process of claim 1 wherein the hydrocarbon is an aromatic compound of 1–3 carbocyclic rings.

5. The process of claim 1 wherein the hydrocarbon is a paraffin of 3–20 carbon atoms.

6. The process of claim 5 wherein the electrolyte is exposed to short wave UV radiation during the halogenation.

7. The process of claim 1 wherein the carboxylic acid is glacial acetic acid.

8. The process of claim 1 wherein hydrochloric acid is employed.

9. The composition of claim 1 wherein the electrolyte is a 50%–50% by volume mixture of aqueous concentrated hydrohalic acid and glacial acetic acid.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

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