An Improved Energy Generator for the Study of Reactions of Thermal-Energy Electrons with Organic Compounds

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Summary

The products resulting from the reaction between thermal energy electrons and organic compounds have been investigated to further our knowledge of the mode of action of the electron-capture detector. Thermal energy electrons were generated by maintaining a corona discharge between a stainless steel cathode and a silver/silver chloride anode. The effects of electrode geometry, gas composition, gas flow rate, and the physical properties of the test substances were investigated. The design of the reactor was modified to minimize losses of unchanged substrate. Reaction products of benzaldehyde, tolualdehydes, chlorobenzaldehydes, and dichlorobenzenes were identified by combined gas chromatography — mass spectrometry.

Introduction

It is an embarrassing fact that, a quarter of a century after its introduction [1, 2], the mode of operation of the electron-capture detector is still not completely understood [3]. What has been done to elucidate its mechanism? One approach has been to perform a chromatographic analysis of the products of an actual electron-capture detector [4, 5]. Difficulties associated with this method arise because of the low concentrations of products obtained. A second electron-capture detector is used during the chromatographic analysis of the products produced in the first detector (since it is the only type of detector with a sufficiently low detection limit) yet, of course, it only responds to electron-capturing substances. No information is obtained about the non-electron-capturing products. The technique of plasma chromatography [6] has also been employed to study the interactions between thermal energy electrons and organic compounds, but only ionic products are detected.

To detect all of the neutral products produced in an electron-capture detector, it is necessary to use a device which mimics the function of the detector, and has either a much larger volume, and/or higher concentration of reactants. Such a device was first constructed by Lovelock [7], and it has been continually refined in our laboratory [8, 9]. We now describe additional modifications to enhance the performance of this simulator of the electron-capture detector.

Experimental

Materials

The following gases were high purity or ultra high purity from Iweco (Houston, TX): air, argon, argon/5% methane, argon/0.2% nitrous oxide, and nitrogen.

Suppliers of test compounds were Aldrich Chemical Co. (Milwaukee, WI) for 2-chlorobenzaldehyde, 3-methylcyclohexanone, and 1,3,5-trimethylbenzene, Baker Chemical Co. (Phillipsburg, NJ) for n-octanol; Fluka AG (Buchs, Switzerland) for 3-chlorobenzaldehyde, o-tolualdehyde, m-tolualdehyde, and p-tolualdehyde, and Mallinckrodt (St. Louis, MO) for o-dichlorobenzene and m-dichlorobenzene.

The Reactor

Thermal energy electrons are produced in a corona discharge in the device illustrated in Fig. 1. The walls of the reaction cell are made of borosilicate glass, and afford direct observation of the corona discharge and the reaction medium. The test compound (10—200 mg) lies on the silver/silver chloride in 1 M cesium chloride anode, a well-defined electrode which avoids the possibility of anode reactions. A stainless steel cathode is mounted 1—2 cm above the test compound, coaxially inside the inner glass tube through which there is a gas flow of 5—50 ml · min^{-1}.
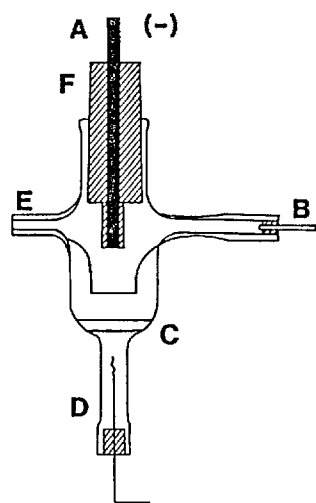
Fig. 1

Reaction cell which simulates the operation of the electron-capture detector. Thermal-energy electrons are generated in a corona discharge between a stainless-steel rod (A) and a cesium chloride solution containing a silver/silver chloride electrode (D). The test material (C) is placed above the cesium chloride solution. A 'carrier' gas flows through the cell from B to E. The stainless-steel cathode is insulated with a Teflon jacket (F).

The inner glass tube concentrates the gas flow around the cathode and allows limited diffusion of vapor molecules from the test substance to the region of ionization around the cathode. Teflon tubing is used for the gas supply lines to minimize contamination of the gas stream.

An appropriate potential difference is maintained between the electrodes using a Sorensen 230-2P high voltage DC power supply (Sorensen, South Norwalk, CT), and is monitored using a Keithly 177 digital multimeter (Keithly Instruments, Inc., Cleveland, OH).

The major difference from the previously employed reactor [9] is that the test substance is now isolated from the gas stream and the cathode by a sintered glass disk. This change in configuration has reduced the degree of loss of unchanged test substance and products.

Procedure

In a typical experiment, the gas flow is first adjusted using a micrometering valve and measured with a ball-type flow meter (Aalborg Instruments, Monsey, New York) and a bubble-type flow meter connected in series. The potential difference between the electrodes is then progressively increased to 5—15kV, thereby allowing a current of up to 200 μA to flow before complete breakdown of the gas takes place.

The reaction is allowed to proceed for 1—4hr before the products are extracted with a suitable solvent and examined by gas chromatography and/or combined gas chromatography — mass spectrometry.

Analysis

Gas chromatography was performed using a Perkin-Elmer Model 900 instrument equipped with 15m x 0.32mm (i.d.) DB-5 bonded-phase fused silica capillary column (J & W Scientific, Inc., Rancho Cordova, CA). Injector, column, and detector temperatures varied from experiment to experiment.

Combined gas chromatography — mass spectrometry was performed using a Finnigan Model 1020/OWA instrument equipped with a 11m x 0.32mm (i.d.) DB-5 bonded-phase fused silica capillary column connected directly to the ion source. The electron energy was 70eV. Spectra were recorded from m/z 45 to m/z 400 every 0.5sec.

Results and Discussion

Evaluation of reactor design

Benzaldehyde had previously been studied using earlier prototypes of our reaction cell [8, 9]. Seven products were obtained, with an overall yield of 40% [9], so benzaldehyde was an appropriate choice of substrate for evaluating refinements to the system.

Operating characteristics of the reaction cell have been investigated in detail for argon and nitrogen. These data were obtained using a 1cm electrode gap. When benzaldehyde is present on the anode, the relationship between applied potential difference and current flow is time-dependent. The establishment of a corona discharge requires a gradual increase in the applied potential difference. At low potential differences, the current flow pulsates. As the potential difference is increased, a vibration of the organic surface becomes perceptible. At some point (depending upon the gas used), a small additional increase in the potential difference leads to a marked increase in current flow, from 0.1 μA to 100 μA. A pale blue corona appears first, then several mobile luminous spots are seen on the surface of the cathode. These spots cover only a portion of the periphery of the cathode, and progressively become more numerous with an increase in the applied potential difference while, simultaneously, a greater current flows through the cell. The current reaches a plateau when the electrode is totally surrounded by the corona: a further increase in applied potential difference results in only a small increase in current. At still higher applied potentials, the corona discharge degenerates into an arc discharge, characterized by a drop in potential difference between the electrodes and a much higher current. As noted above, the induction of a corona discharge is time-dependent: if the voltage between the two electrodes is increased suddenly, arcing will invariably occur.

Once the corona discharge is fully established and the applied potential difference is kept constant, the current flow through the cell increases for a period of time and then decreases. It is thought that the increase in current flow is due to vaporization of the organic sample and its reaction products as the reactor becomes warmer. As the irradiation proceeds, less volatile products are formed and, as they condense, the current flow decreases. Indeed, as the reaction progresses, droplets of reaction products condense upon the inner walls of the reaction vessel.

When a sharp-tipped cathode was employed the onset of corona discharge was almost instantaneous, but the volume encompassed by the discharge was relatively small and the yield of reaction products was low. Much greater yields were obtained with the flat-tipped cathode, and the induction of a corona discharge was not unduly difficult to obtain.

In principle, any conducting material could be employed as an anode. Experiments with metallic anodes were, however, less than completely successful. An organic layer on a flat anode acts as a dielectric insulator, and a current does not flow until arcing occurs as the applied potential difference is increased to 20–30kV. With a cup-shaped aluminium anode, a corona discharge was established only between the two points on the anode and cathode, respectively, which were in closest proximity. Thus, the reaction yields were very low. An appropriate corona was obtained only when an electrolytic solution was employed as the anode, as illustrated in Fig. 1.

A corona discharge could be maintained with electrode gaps of 0.5 to 2.0cm. With smaller gaps the organic vapors tend to condense on the cathode, while with larger gaps degeneration of the corona into an arc discharge occurs more frequently. Most experiments were conducted with a gap of 0.8 to 1.3cm.

If there is no gas flow through the cell the pale blue color of the corona turns to a more intense yellow color, the organic sample pyrolyses, dark products accumulate on the corona, and arcing occurs. Too great a gas flow through the cell, however, will flush out the test substance and its reaction products, reducing the yield. Flow rates of $50\,ml \cdot min^{-1}$ were used with the earlier prototypes, but we were able to obtain improved yield with the modified reactor, which could be operated with a gas flow of 10 to $15\,ml \cdot min^{-1}$.

Gases which we evaluated were air, argon, argon + 5% methane, argon + 0.2% nitrous oxide, and nitrogen. An applied potential difference of 5kV induced a corona discharge in argon and its mixtures, while a potential difference of 9kV was required for air and nitrogen. The yields obtained with benzaldehyde (20mg) were compared for an electrode gap of 1cm, a gas flow rate of $15\,ml \cdot min^{-1}$, a current of $60\,\mu A$, and a reaction time of 90min. For each experiment, the reaction mixture was extracted with 0.4ml of methylene chloride, which was then diluted to 1.0ml. Three individual 1-μl aliquots were examined by gas chromatography with on-column injection. The precision of the analyses was close to 10%. The yields of the two major products, benzophenone (PhCO·Ph) and benzil (PhCO·CO·Ph), which represent 80% of the reaction products, are shown in Table I, relative to the yields obtained in argon. Also given are the recovery of organic material after extraction (%R) and the overall conversion yield (%C). The amounts of organic material recovered are independent of the gas employed, although

the degree of reaction is. The greatest quantity of reaction products is formed when pure argon is employed as the gas. This observation is seemingly in contradiction with the situation in an actual electron-capture detector. In such a detector, however, all of the reactions take place in the vapor phase, whereas in our reactor, some reactions also take place in the liquid phase and at the gas-liquid interface. When oxygen is present in the gas, most of the benzaldehyde is oxidized to benzoic acid.

It had occurred to us that some reaction products might be formed by direct ionization of the test substance, rather than reaction with thermal-energy electrons. This possibility was eliminated by the observation that 3-methylcyclohexanone, n-octanol, and 1,3,5-trimethylbenzene (which do not capture electrons) afford no detectable products, even after irradiation for 4hr.

In all of the experiments which follow, argon was employed as the gas.

Benzaldehyde

Relative yields of products from benzaldehyde are given in Table II. Benzoic acid was not included since it is an oxidation product formed by reaction with traces of oxygen in the gas. Previously, only seven products were obtained [9]. In the current study, five new products were identified: phenol, benzyl alcohol, ξ-hydroxybenzaldehyde, phenyl benzoate, and a second isomer of ξ-benzoylbenzaldehyde. However, we were only able to detect one isomer of ξ-phenylbenzaldehyde instead of the two encountered before.

The formation of phenol as an intermediate in the production of ξ-benzoylphenol was predicted earlier. Phenyl benzoate may be a product of the reaction of phenol and benzoic acid.

Tolualdehydes

The affinity of benzaldehyde for electrons is due to its specific conjugated structure, which allows the formation of a stable molecular ion. The substitution of a methyl group on the benzene ring does not markedly affect the electron affinity of the molecule, but the position of the substituent can play an important role in the course of the reactions.

Table I. Relative yields of benzophenone and benzil from benzaldehyde in the presence of various gases. Also given are the recovery of organic material after extraction (%R) and the overall conversion yield (%C)

Gas	PhCO·Ph	PhCO·CO·Ph	%R	%C
Ar	100	100	38	27
Ar/0.2% N₂O	93	77	36	21
Ar/5% CH₄	28	32	40	11
N₂	33	32	36	10
Air	< 0.1	< 0.1	49	2

Table II. Relative yields of products from benzaldehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
Phenol	3	PhOH
Benzyl alcohol	0.5	PhCH₂·OH
ξ-Hydroxybenzaldehyde	0.3	HOC₆H₄·CHO
Biphenyl	4	PhPh
Benzophenone	52	PhCO·Ph
Phenyl benzoate	3	PhCO·OPh
ξ-Phenylbenzaldehyde	2	PhC₆H₄·CHO
ξ-Benzoylphenol	6	PhCO·C₆H₄·OH
Benzil	100	PhCO·CO·Ph
ξ-Benzoylbenzaldehyde	1	PhCO·C₆H₄·CHO
ξ-Benzoylbenzaldehyde	20	PhCO·C₆H₄·CHO

Table III. Relative yields of products from tolualdehydes

Reaction conditions	ortho	meta	para
Substrate mass (mg)	20	20	20
Nitrogen flow (ml · min^{-1})	10	10	10
Current (μA)	40	80	50
Voltage (kV)	10	9	10
Reaction time (hr)	4	2	3
%R	60	44	54
%C	14	21	27

Relative yields of products from o-, m-, and p-tolualdehyde are shown in Table III. Longer reaction times than for benzaldehyde were required to obtain sufficient amounts of products for analysis. This is probably because the boiling point of benzaldehyde (178.1°C) is lower than those of tolualdehydes (199–205°C) [10], so there is less material in the vapor phase. The major reaction products were 2,2'-, 3,3'- and 4,4'-dimethylbenzil, respectively (Tables IV—VI).

The two unidentified products of molecular weight 134 formed from o-tolualdehyde (Table IV) have similar spectra and are apparently isomers. The base peak in each spectrum is at m/z 105 (corresponding to PhCO$^+$), and there are abundant ions at m/z 77 (Ph$^+$) and m/z 51 (C$_4$H$_3^+$). Possible identities are phenylglyoxal (PhCO · CHO) and phthaldialdehyde [C$_6$H$_4$(CHO)CHO], but no reference compounds were available to us and the mode of formation of such compounds is unclear. The unidentified compound of molecular weight 226 affords a base peak of m/z 119 [C$_6$H$_4$(CHO)CH$_2^+$?] and an abundant tropylium ion at m/z 91 (C$_7$H$_7^+$). The base peak is formed by a loss of 107 a.m.u. (PhCH$_2$O$^+$?) from the molecular ion, so the unidentified compound could be any one of several isomers with molecular formula C$_{15}$H$_{14}$O$_2$.

Analogs of these unidentified compounds are not formed from m- or p-tolualdehyde, although the latter affords an unidentified minor product of molecular weight 136 which may be p-anisaldehyde (CH$_3$O · C$_6$H$_4$ · CHO) or an isomer.

Chlorobenzaldehydes

The boiling points of chlorobenzaldehydes (212–214°C) [10] are even higher than those of the tolualdehydes, yet adequate amounts of products are obtained in as little as 90 minutes (Table VII).

Table IV. Relative yields of products from o-tolualdehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
o-Cresol	11	HOC$_6$H$_4$ · CH$_3$
2-Methylbenzyl alcohol	7	CH$_3$ · C$_6$H$_4$ · CH$_2$ · OH
Unknown (M.Wt. = 134)	15	
Unknown (M.Wt. = 134)	53	
ξ-(2-Tolyl)-2-methylbenzaldehyde	21	CH$_3$ · C$_6$H$_4$ · C$_6$H$_3$(CH$_3$)CHO
Unknown (M.Wt. = 226)	9	
ξ-(2-Tolyl)-2-methylbenzoic acid	5	CH$_3$ · C$_6$H$_4$ · C$_6$H$_3$(CH$_3$)COOH
2,2'-Dimethylbenzil	100	CH$_3$ · C$_6$H$_4$ · CO · CO · C$_6$H$_4$ · CH$_3$
ξ-(2-Methylbenzoyl)-2-methylbenzaldehyde	3	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_3$(CH$_3$)CHO

Table V. Relative yields of products from m-tolualdehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
m-Cresol	2	HOC$_6$H$_4$ · CH$_3$
ξ-Hydroxy-m-tolualdehyde	2	CH$_3$ · C$_6$H$_3$(OH)CHO
3,3'-Dimethylbiphenyl	2	CH$_3$ · C$_6$H$_4$ · C$_6$H$_4$ · CH$_3$
ξ-(3-Tolyl)-3-methylbenzaldehyde	3	CH$_3$ · C$_6$H$_4$ · C$_6$H$_3$(CH$_3$)CHO
3,3'-Dimethylbenzophenone	65	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_4$ · CH$_3$
ξ-(3-Tolyl)-3-methylbenzaldehyde	3	CH$_3$ · C$_6$H$_4$ · C$_6$H$_3$(CH$_3$)CHO
ξ-(3-Methylbenzoyl)-ξ-methylphenol	5	CH$_3$C$_6$H$_4$ · CO · C$_6$H$_3$(CH$_3$)OH
3,3'-Dimethylbenzil	100	CH$_3$ · C$_6$H$_4$ · CO · CO · C$_6$H$_4$ · CH$_3$
ξ-(3-Methylbenzoyl)-3-methylbenzaldehyde	3	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_3$(CH$_3$)CHO
ξ-(3-Methylbenzoyl)-3-methylbenzaldehyde	39	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_3$(CH$_3$)CHO

Table VI. Relative yields of products from p-tolualdehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
p-Cresol	0.2	HOC$_6$H$_4$ · CH$_3$
4-Methylacetophenone	0.5	CH$_3$ · CO · C$_6$H$_4$ · CH$_3$
Unknown (M.Wt. = 136)	7	
3,ξ-Dimethylbenzophenone	2	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_4$ · CH$_3$
3,ξ-Dimethylbenzophenone	8	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_4$ · CH$_3$
3,ξ-Dimethylbenzophenone	21	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_4$ · CH$_3$
ξ-(4-Methylbenzoyl)-4-methylbenzaldehyde	10	CH$_3$ · C$_6$H$_4$ · CO · C$_6$H$_3$(CH$_3$)CHO
4,4'-Dimethylbenzil	100	CH$_3$ · C$_6$H$_4$ · CO · CO · C$_6$H$_4$ · CH$_3$

Table VII. Relative yields of products from chlorobenzaldehydes

Reaction conditions	ortho	meta
Substrate mass (mg)	20	20
Nitrogen flow (ml · min^{-1})	10	10
Current (μA)	100	80
Voltage (kV)	10	9
Reaction time (hr)	1.5	1.5
%R	40	75
%C	24	26

Previously, we identified four products of 3-chlorobenzaldehyde, with a conversion yield of 22% [9]. We have now identified 13 products with a conversion yield of 26% (Table IX). The newly identified products are 3-chlorosalicylaldehyde, 3-chloroacetophenone, 3-chlorobenzyl alcohol, 5-chlorosalicylaldehyde, 3-chloro-4-hydroxybenzaldehyde, 3-chlorobenzamide, 3-chlorobenzophenone, 3-chlorobenzil, ξ-(3-chlorobenzoyl)benzaldehyde, and ξ-(3-chlorobenzoyl)-3-chlorobenzaldehyde. We did not find dichlorodeoxybenzoin among the reaction products of the current study. The product previously reported as 4,4'-dichlorobenzophenone was, of course, 3,3'-dichlorobenzophenone.

We have identified 22 products from 2-chlorobenzaldehyde with a conversion yield of 24% (Table VIII). The unidentified compound of molecular weight 232 affords a base peak [M-35]$^{+}$ of m/z 197 which does not contain a chlorine atom. Thus, the molecule contains only one chlorine atom. It apparently has a molecular formula $C_{13}H_9O_2Cl$, and may be a hydroxylation product of 2-chlorobenzophenone.

Dichlorobenzenes

The dichlorobenzenes do not possess a conjugated substituent, and react via a dissociative mechanism [9].

The boiling point of o-dichlorobenzene (180.5°C) [10] is comparable to that of benzaldehyde, yet a reaction time of 6hr was needed to obtain sufficient quantities

Table VIII. Relative yields of products from 2-chlorobenzaldehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
2-Chlorophenol	0.4	$ClC_6H_4 \cdot OH$
Benzoic acid	3	$PhCOOH$
2-Chloroacetophenone	1	$ClC_6H_4 \cdot CO \cdot CH_3$
2-Chlorobenzyl alcohol	3	$ClC_6H_4 \cdot CH_2 \cdot OH$
ξ-Hydroxy-2-chlorobenzaldehyde	2	$ClC_6H_3(OH)CHO$
2-Chlorobenzoyl chloride	0.3	$ClC_6H_4 \cdot CO \cdot Cl$
Salicylic acid	2	$HOC_6H_4 \cdot COOH$
2-Chlorobenzamide	0.4	$ClC_6H_4 \cdot CO \cdot NH_2$
ξ-Hydroxy-2-chlorobenzaldehyde	1	$ClC_6H_3(OH)CHO$
2,2'-Dichlorobiphenyl	1	$ClC_6H_4 \cdot C_6H_4 \cdot Cl$
ξ-Phenylbenzaldehyde	2	$PhC_6H_4 \cdot CHO$
2-Chlorobenzophenone	10	$PhCO \cdot C_6H_4 \cdot Cl$
Unknown (M.Wt. = 232)	3	
2,2'-Dichlorobenzophenone	18	$ClC_6H_4 \cdot CO \cdot C_6H_4 \cdot Cl$
2,ξ-Dichlorobenzophenone	3	$ClC_6H_4 \cdot CO \cdot C_6H_4 \cdot Cl$
2-Chlorobenzil	27	$PhCO \cdot CO \cdot C_6H_4 \cdot Cl$
ξ-(2-Formylphenyl)-2-chlorobenzaldehyde	20	$C_6H_4(CHO)C_6H_3(Cl)CHO$
ξ-Chlorobenzil	15	$PhCO \cdot CO \cdot C_6H_4 \cdot Cl$
2,2'-Dichlorobenzil	100	$ClC_6H_4 \cdot CO \cdot CO \cdot C_6H_4 \cdot Cl$
ξ-(2-Chlorobenzoyl)-2-chlorobenzaldehyde	11	$C_6H_4(CHO)C_6H_3(Cl)CHO$
ξ-(2-Chlorobenzoyl)-2-chlorobenzaldehyde	22	$C_6H_4(CHO)C_6H_3(Cl)CHO$
ξ-(ξ-Formyl-ξ-chloro)-2-chlorobenzaldehyde	2	$ClC_6H_3(CHO)C_6H_3(Cl)CHO$

Table IX. Relative yields of products from 3-chlorobenzaldehyde, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
3-Chlorosalicylaldehyde	8	$ClC_6H_3(OH)CHO$
3-Chlorophenol	5	$ClC_6H_4 \cdot OH$
3-Chloroacetophenone	1	$ClC_6H_4 \cdot CO \cdot CH_3$
3-Chlorobenzyl alcohol	0.2	$ClC_6H_4 \cdot CH_2 \cdot OH$
5-Chlorosalicylaldehyde	1	$ClC_6H_3(OH)CHO$
3-Chloro-4-hydroxybenzaldehyde	0.2	$ClC_6H_3(OH)CHO$
3-Chlorobenzamide	0.5	$ClC_6H_4 \cdot CO \cdot NH_2$
3-Chlorobenzophenone	7	$PhCO \cdot C_6H_4 \cdot Cl$
3,3'-Dichlorobenzophenone	16	$ClC_6H_4 \cdot CO \cdot C_6H_4 \cdot Cl$
3-Chlorobenzil	15	$PhCO \cdot CO \cdot C_6H_4 \cdot Cl$
ξ-(3-Chlorobenzoyl)benzaldehyde	12	$ClC_6H_4CO \cdot C_6H_4 \cdot CHO$
3,3'-Dichlorobenzil	100	$ClC_6H_4 \cdot CO \cdot CO \cdot C_6H_4 \cdot Cl$
ξ-(3-Chlorobenzoyl)3-chlorobenzaldehyde	8	$C_6H_4(CHO)C_6H_3(Cl)CHO$

Table X. Relative yields of products from dichlorobenzenes

Reaction conditions	ortho	meta
Substrate mass (mg)	20	20
Nitrogen flow (ml·min^{-1})	10	10
Current (μA)	15	90
Voltage (kV)	12	9
Reaction time (hr)	6.0	1.3
%R	60	8
%C	5	7

Table XI. Relative yields of products from o-dichlorobenzene, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
2-Chlorophenol	28	ClC$_6$H$_4$·OH
2,3-Dichlorophenol	86	Cl$_2$C$_6$H$_3$·OH
ξ-Chlorophenol	9	ClC$_6$H$_4$·OH
3,4-Dichlorophenol	47	Cl$_2$C$_6$H$_3$·OH
2-Chlorobiphenyl	10	PhC$_6$H$_4$Cl
2,2'-Dichlorobiphenyl	91	ClC$_6$H$_4$·C$_6$H$_4$·Cl
ξ,ξ'-Dichlorobiphenyl	16	ClC$_6$H$_4$·C$_6$H$_4$·Cl
ξ-(ξ-Chlorophenyl)-1,2-dichlorobenzene	7	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,2-dichlorobenzene	100	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,2-dichlorobenzene	32	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,2-dichlorobenzene	11	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,2-dichlorobenzene	62	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ,ξ-Dichlorophenyl)-1,2-dichlorobenzene	9	Cl$_2$C$_6$H$_3$·C$_6$H$_3$·Cl$_2$

Table XII. Relative yields of products from m-dichlorobenzene, listed in their order of elution from a DB-5 column

Compound	Yield	Structure
2-Chlorophenol	5	ClC$_6$H$_4$·OH
2,6-Dichlorophenol	98	Cl$_2$C$_6$H$_3$·OH
2,4-Dichlorophenol	89	Cl$_2$C$_6$H$_3$·OH
3-Chlorophenol	100	ClC$_6$H$_4$·OH
1,3-Dichloro-ξ-nitrobenzene	13	Cl$_2$C$_6$H$_3$·NO$_2$
3,5-Dichlorophenol	3	Cl$_2$C$_6$H$_3$·OH
ξ-Chlorobiphenyl	3	PhC$_6$H$_4$·Cl
ξ,ξ'-Dichlorobiphenyl	49	ClC$_6$H$_4$·C$_6$H$_4$·Cl
ξ-(ξ-Chlorophenyl)-1,3-dichlorobenzene	10	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,3-dichlorobenzene	8	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chlorophenyl)-1,3-dichlorobenzene	17	ClC$_6$H$_4$·C$_6$H$_3$·Cl$_2$
ξ-(ξ-Chloro-ξ-hydroxy-phenyl)-ξ-chlorophenol	31	ClC$_6$H$_3$(OH)C$_6$H$_3$(OH)Cl
ξ-(ξ-Chloro-ξ-hydroxy-phenyl)-ξ-chlorophenol	22	ClC$_6$H$_3$(OH)C$_6$H$_3$(OH)Cl

of products (Table X). A conversion yield of only 5% was observed, compared with 55% earlier [9]. The major products reported previously were chlorobenzene (10.6%) and trichlorobenzene (21.6%). Only chlorobenzene was detected in the current study when the effluent from the reaction cell was passed through methylene chloride to trap any reaction products swept from the reactor. Nevertheless, 13 products other than chlorobenzene were identified (Table XI), compared with 10 previously.

Curiously, m-dichlorobenzene (with a boiling point of 173°C [10]) afforded adequate amounts of products after a reaction time of 1.3hr. No products were trapped from the reactor effluent when bubbled through methylene chloride. A total of 13 products were identified (Table XII).

Conclusions

The modified reactor has allowed us to produce milligram quantities of products obtained from the interactions between organic substances and thermal-energy electrons. Most of the products have been identified or, at least, partially characterized. It will now be possible to initiate studies of the mechanism of formation of these products.

References

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