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REACTIONS OF THERMAL-ENERGY ELECTRONS WITH ORGANIC COMPOUNDS

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SUMMARY

The products resulting from the reaction between electrons of thermal energy and several electron-absorbing organic compounds have been studied. Thermal electrons were generated by maintaining a glow discharge between a stainless-steel electrode and a silver–silver chloride electrode in a nitrogen atmosphere.

The organic compounds investigated fell into two principal classes whose structures contained either simple or conjugated electrophores. The identification of the reaction products by gas chromatography–mass spectrometry showed that simple electrophores, such as nitrobenzene and *o*-dichlorobenzene, react predominantly by a dissociative mechanism while conjugated electrophores, such as benzaldehyde and *trans*-cinnamaldehyde, react predominantly by a non-dissociative mechanism. *m*-Chlorobenzaldehyde, containing both a simple electrophore (chlorine substituent) and a conjugated electrophore (carboxaldehyde moiety), was found to react primarily by a non-dissociative mechanism. *trans*-Cinnamaldehyde, even though possessing a more extensive system of conjugation than benzaldehyde, was found to be less reactive than the latter. Reaction mechanisms consistent with possible pathways of the major products of representative compounds studied are also presented.

INTRODUCTION

In order to provide an adequate theory for the operation of the electron-capture detector (ECD) and to predict its sensitivity to different compounds, the principal problem has always been a lack of knowledge concerning the products formed in the detector by electron attachment. Such products are expected to include neutral molecules, radicals and positive and negative ions.

Several methods have been described that attempt to identify these products. One of them uses a column interposed between two electron-capture detectors for the separation and detection of these products[1,2]. However, only limited information is obtained and failure of the second detector to register products is no proof that they

do not exist in the first; they may have been totally consumed or they may not have been able to pass through the interposed column. An alternative possibility is that the products with weak electron-capturing properties will not be seen by the second detector.

Another technique for studies of this type is plasma chromatography[3]. Using nitrogen as a carrier gas, the plasma chromatograph creates the negative reactant species of low-energy electrons to react with the gas chromatographic peak component and form characteristic product ions.

In 1970, Durbin et al.[4] developed a procedure first introduced by Lovelock in 1962[5]. They studied the products formed by exposing certain compounds to electrons of near-thermal energy generated in a glow discharge. The products formed were identified by gas chromatography–mass spectrometry.

This study is a continuation of these investigations. The identification of the reaction products could help in the understanding of the response of the ECD to different classes of compounds and also, in consequence, aid in the selection of electrophores for the development of new derivatizing agents.

EXPERIMENTAL

A schematic diagram of the apparatus used in this work is shown in Fig. 1.

Nitrogen of ultra-high-purity grade (Iweco, Houston, TX, U.S.A.) was used as the carrier gas and passed through a cartridge packed with molecular sieve, charcoal and calcium sulfate. All of the tubing in the system was made of PTFE to minimize chemical contamination. The flow was controlled by a micro-metering valve to deliver a total flow of 50–60 ml min^{-1}.

The electrical circuit consisted of a high-voltage d.c. voltage supply (Model 230-2P, Sorenson, South Norwalk, CT, U.S.A.) connected in series, first to the discharge cell and then to a microammeter (Model 177 microvolt DMM, Keithly Instruments, Cleveland, OH, U.S.A.) as shown in Fig. 1.
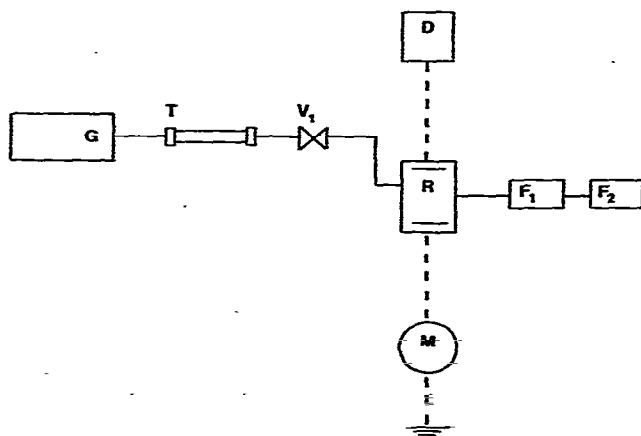

Fig. 1. Diagram of experimental apparatus. ———, Gas circuit; —, electrical circuit. R = Thermal-electron generator and reaction vessel; D = high-voltage d.c. source; G = gas tank; T = drying tube; V$_1$ = micrometering valve; F$_1$ = ball-type flow meter; F$_2$ = bubble-type flow meter; M = μA meter.

A diagram of the discharge cell is shown in Fig. 2. The system of the electrodes designed yields currents up to 250 μA. The flow discharge is maintained by application of a negative potential of 5–15 kV to the stainless-steel electrode in the gas atmosphere; the inner glass tube allows limited diffusion of vapor molecules from the test substance to the region of ionization around the stainless-steel electrode. It is very important that the surface of this electrode remains perfectly smooth and does not present any sharp edges where the electric field is enhanced, or it will induce arcing. The silver–silver chloride in 1.0 M cesium chloride served as a well defined electrode which avoided the possibility of anodic reactions.
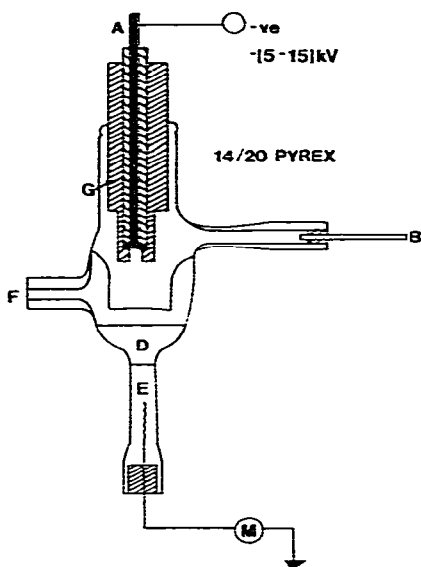

Fig. 2. Generator of free thermal-energy electrons. A = Stainless-steel rod; B = gas inlet; D = test material; E = 1.0 M cesium chloride solution containing a silver–silver chloride electrode; F = gas outlet; G = PTFE jacket; M = 0–300 μA meter.

After the reaction had been allowed to proceed for 4 h, the products remaining in the organic layer were analyzed by gas chromatography–mass spectrometry. A Finnigan 1020/OWA instrument was equipped with a 30 m × 0.32 mm I.D. DB-5 bonded-phase fused-silica capillary column (J & W Scientific) programmed from 90 to 300°C at 4°C min^{-1}. The outlet of this column was connected directly into the ion source of the mass spectrometer.

RESULTS AND DISCUSSION

Simple electrophores
    Nitrobenzene. Although nitrobenzene has a high relative electron-capture coefficient of 390 (ref. 6), only 15.5% of the starting material reacted. The quantitative distribution of the major products is given in Table I.
    The major products formed in this reaction indicate that dissociative capture is the process taking place. When attachment of an electron occurs, a nitro anion

TABLE I

MAJOR REACTION PRODUCTS WITH NITROBENZENE

Molecular weight	Compound	Yield (%)
94	Phenol	2.5
139	2-Nitrophenol	4.2
139	3-Nitrophenol	3.2
139	4-Nitrophenol	1.7
168	Mixture of 1,3-dinitrobenzene and	
	1,4-dinitrobenzene	1.9

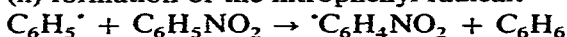dissociates from the nitrobenzene molecule, leaving a phenyl radical:

$$C_6H_5NO_2 + e^- \rightarrow C_6H_5^{\cdot} + NO_2^-$$
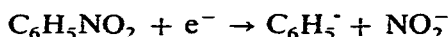
Possible chain-propagating steps include the following:

(i) reaction of the phenyl radical with water:

$$C_6H_5^{\cdot} + H_2O \rightarrow C_6H_5OH + H^{\cdot}$$
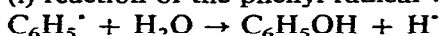
(ii) formation of the nitrophenyl radical:

$$C_6H_5^{\cdot} + C_6H_5NO_2 \rightarrow {}^{\cdot}C_6H_4NO_2 + C_6H_6$$

(iii) reaction of the nitrophenyl radical with water:

$${}^{\cdot}C_6H_4NO_2 + H_2O \rightarrow HOC_6H_4NO_2 + H^{\cdot}$$
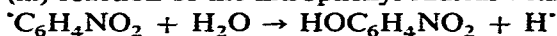
(iv) reaction of the nitrophenyl radical with nitrobenzene:

$${}^{\cdot}C_6H_4NO_2 + C_6H_5NO_2 \rightarrow O_2NC_6H_4NO_2 + C_6H_5^{\cdot}$$
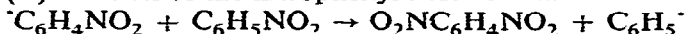
The low overall yield of the reaction could be explained by the fact that the initial step could be reversible.

o-Dichlorobenzene. Fifty-five percent of the starting material reacted. The quantitative distribution of the major products is given in Table II. It appears that *o*-dichlorobenzene reacts via a dissociative mechanism. Possible propagating steps include the following:
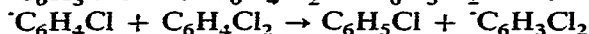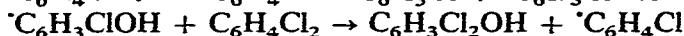
$$ClC_6H_4Cl + e^- \rightarrow {}^{\cdot}C_6H_4Cl + Cl^-$$
$${}^{\cdot}C_6H_4Cl + H_2O \rightarrow HOC_6H_4Cl + H^{\cdot}$$
$${}^{\cdot}C_6H_4Cl + HOC_6H_4Cl \rightarrow C_6H_5Cl + {}^{\cdot}C_6H_3ClOH$$
$${}^{\cdot}C_6H_3ClOH + C_6H_4Cl_2 \rightarrow C_6H_3Cl_2OH + {}^{\cdot}C_6H_4Cl$$
$${}^{\cdot}C_6H_4Cl + C_6H_4Cl_2 \rightarrow C_6H_5Cl + {}^{\cdot}C_6H_3Cl_2$$
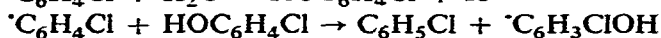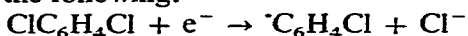
TABLE II

MAJOR REACTION PRODUCTS WITH *o*-DICHLOROBENZENE

Molecular weight	Compound	Yield (%)
112	Chlorobenzene	10.6
180	Trichlorobenzene	21.6
162	2,4-Dichlorophenol	0.9
162	2,6-Dichlorophenol	8.8
162	2,3-Dichlorophenol	0.8
162	3,5-Dichlorophenol	5.0
128	3-Chlorophenol	1.5
222 }	Dichloro-1,1'-biphenyl }	
222 }	(two isomers) }	2.1
256 }	Trichloro-1,1'-biphenyl }	
256 }	(two isomers) }	2.6

$$\cdot C_6H_3Cl_2 + C_6H_4Cl_2 \rightarrow C_6H_3Cl_3 + \cdot C_6H_4Cl$$
$$\cdot C_6H_4Cl + C_6H_4Cl_2 \rightarrow C_6H_4Cl\text{-}C_6H_4Cl + Cl\cdot$$
$$\cdot C_6H_4Cl + C_6H_3Cl_3 \rightarrow C_6H_4Cl\text{-}C_6H_3Cl_2 + Cl\cdot$$
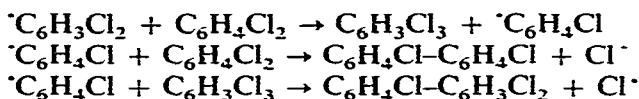
Comparing the overall yield for the reaction with *o*-dichlorobenzene with the one obtained by Durbin *et al.*[4] with chlorobenzene, it appears that the presence of a second chlorine atom on the benzene ring enhances the reactivity towards electron capture.

Conjugate electrophores

Benzaldehyde. Forty percent of the starting material reacted. The quantitative distribution of the major products is given in Table III. It shows that non-dissociative electron capture is the predominant mechanism, as indicated by the following:

$$C_6H_5CHO + e^- \rightarrow [C_6H_5CHO]^-$$
$$[C_6H_5CHO]^- + C_6H_5CHO \rightarrow [C_6H_5CO]^- + C_6H_5\overset{\cdot}{C}O + H_2$$
$$C_6H_5\overset{\cdot}{C}O + [C_6H_5CO]^- \rightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5 + e^-$$

$$C_6H_5\overset{\cdot}{C}O + C_6H_5CHO \rightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5 + \cdot CHO$$

$$H\overset{\cdot}{C}O + C_6H_5CHO \rightarrow (CHO)_2 + C_6H_5\cdot$$
$$C_6H_5\cdot + C_6H_5CHO \rightarrow C_6H_5\text{-}C_6H_5 + \cdot CHO$$
$$C_6H_5\cdot + C_6H_5CHO \rightarrow \cdot C_6H_5\text{-}C_6H_5CHO + H\cdot$$
$$C_6H_5\cdot + H_2O \rightarrow C_6H_5OH + H\cdot$$
$$C_6H_5\overset{\cdot}{C}O + C_6H_5OH \rightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4OH + H\cdot$$

$$C_6H_5\overset{\cdot}{C}O + C_6H_5CHO \rightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4CHO + H\cdot$$
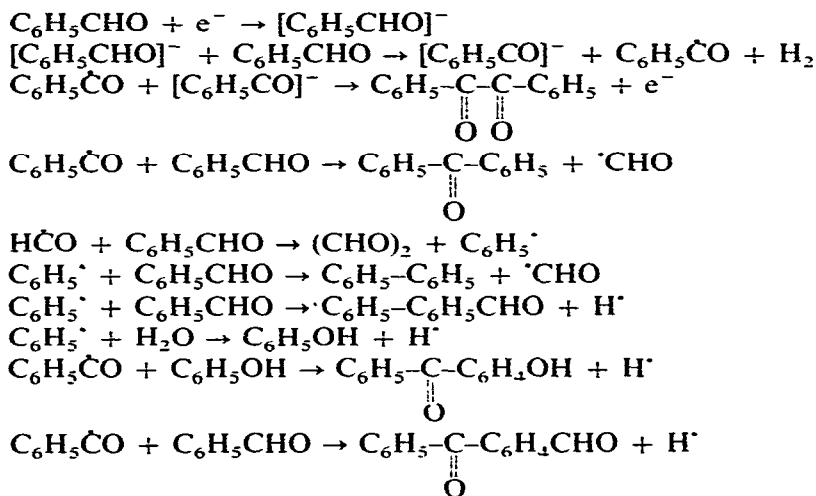
m-Chlorobenzaldehyde. After studying, successively, simple electrophores and conjugate electrophores, and noticing that they reacted via dissociative and non-dissociative mechanisms, respectively, it was of interest to study how a compound containing both would react.

In the reaction with *m*-chlorobenzaldehyde, 22% of the starting material reacted. The quantitative distribution of the major products is given in Table IV.

The overall reactivity of *m*-chlorobenzaldehyde towards electron capture is lower than that of benzaldehyde. From the identified products, it appears that non-

TABLE III

MAJOR REACTIONS PRODUCTS WITH BENZALDEHYDE

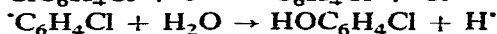| Molecular weight	Compound	Yield (%)
154	Biphenyl	4.2
182	Benzophenone	8.0
182 } 182 }	Biphenyl carboxaldehyde } (two isomers) }	4.7
198	Hydroxybenzophenone	3.4
210	Benzil	9.0
210	Benzophenone carboxaldehyde	5.1

TABLE IV

MAJOR REACTION PRODUCTS WITH m-CHLOROBENZALDEHYDE

Molecular weight	Compound	Yield (%)
128	Chlorophenol	5.1
250	4,4'-Dichlorobenzophenone	1.5
278	Dichlorobenzil	1.3
264	Chlorodeoxybenzoin	1.8

dissociative electron capture is the predominant mechanism (formation of dichloro-benzophenone and dichlorobenzil).

trans-Cinnamaldehyde. The overall yield of the reaction with *trans*-cinnamaldehyde was 23 %, and the quantitative distribution of the major products is given in Table V.

TABLE V

MAJOR REACTION PRODUCTS WITH *trans*-CINNAMALDEHYDE

Molecular weight	Compound	Yield (%)
134	Phenylpropanal	2.9
162	Phenylpropanoic acid	2.3
248	4-Benzyl-2-carboxy-1-hydronaphthalene	6.8
266	1,6-Diphenyl-3,4-hexanedione and another isomer	1.9

As the major product formed is a hydrogenated dimer of cinnamaldehyde, the predominate mechanism is non-dissociative. Two hydrogenation reactions occur: formation of phenylpropanal by hydrogenation of cinnamaldehyde and formation of phenylpropanoic acid by hydrogenation of phenylpropenoic acid (impurity in the starting material).

The overall yield of the reaction is lower than that of benzaldehyde. This indicates that, even though there is a more extensive conjugated system in the reaction with *trans*-cinnamaldehyde, more conjugation does not imply higher reactivity towards electron capture.

CONCLUSION

The glow discharge is a simple, straightforward method of studying the reactions of thermal-energy electrons with organic compounds. The main advantage over methods previously described[2] is that the products of the reaction are produced in sufficient yield to be recovered and characterized. Thus, the different mechanisms involved were determined.

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