Reactions between Electron Absorbing Organic Compounds and Electrons at Near Thermal Energies

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Abstract: A corona discharge cell has been designed for the generation of near thermal electrons and their reaction with electron absorbing compounds. Benzaldehyde, diethyl maleate, *cis*-stilbene, chlorobenzene, and benzyl chloride have been reacted in this cell and the products were identified by gas chromatography–mass spectrometry. The mechanism of the reaction for the attachment of electrons was confirmed as dissociative for chlorobenzene and benzyl chloride and nondissociative for benzaldehyde, diethyl maleate, and *cis*-stilbene.

The attachment of near thermal energy electrons (0.01–1 eV) to molecules has been investigated by several techniques.[1-4] These methods generally involve electronically monitoring electron concentrations. Few studies have been made where the final neutral products of an electron–molecule reaction were identified. Lovelock[5] reported that thermal electrons from a point discharge react with water-saturated diethyl fumarate in a liquid organic phase to produce succinate, malate, and oxalacetate. About 30 molecules of fumarate were removed for every electron added. Stockdale and Hurst,[1] using a swarm technique to study electron attachment to chlorobenzene and bromobenzene, observed Cl^- and Br^- in a negative ion time-of-flight mass spectrometer. This paper describes an apparatus for the generation of near thermal electrons and a study of their reactions with some electron absorbing organic compounds. The potential of this technique for the confirmation of electron attachment mechanisms is indicated.

The process of attachment of electrons to molecules is generally considered to occur by one of four possible mechanisms represented by the chemical equations 1–4.

$$AB + e^- \rightleftharpoons AB^- \qquad (1)$$

$$AB + e^- \longrightarrow A\cdot + B^- \qquad (2)$$

$$AB^- \longrightarrow A\cdot + B^- \qquad (3)$$

$$AB^- \longrightarrow A^- + B\cdot \qquad (4)$$

The first reaction is referred to as nondissociative attachment, while the last three are called dissociative attachment. The rate of the reactions can be related to the coefficient for electron capture, K, of molecule AB. Wentworth and Chen,[6] using the pulse-sampling technique,[7] have shown that $\ln KT^{3/2}$ is linearly related to $1/T$ and the plots are characteristic of the various mechanisms. Also, they listed several compounds which undergo electron attachment by the various mechanisms.

Lovelock[8] and Zlatkis and Lovelock[9] have discussed electron capturing compounds in terms of simple and conjugate electrophores. Simple electrophores are those compounds which contain halogen or nitro substituents while conjugate electrophores contain two specific groups which are not necessarily electron absorbing, but when linked by specific bridges confer electron absorbing properties on the molecule. Comparison of these investigations shows that the conjugate electrophores attach electrons *via* nondissociation (eq 1), while the simple electrophores react *via* the dissociative mechanism (eq 2–4).

Radicals from the four mechanisms react further to form more radicals and neutral products. In certain cases the nature of the neutral product can be used to identify the mechanism by which the electron reacted.

In the case where a stable radical anion is formed (eq 1), it may undergo a number of reactions. However, only in the case of associative detachment will the molecular structure of the original molecule be retained. If the concentration of AB is maintained in large excess so that the associative detachment occurs between AB^- and AB then the reactions can be represented by the following. The predominance of

$$AB^- + AB \longrightarrow ABAB + e^- \qquad (5)$$

$$AB^- + AB \longrightarrow ABA + B^- \qquad (6)$$

$$AB^- + AB \longrightarrow ABB + A^- \qquad (7)$$

products in the form of ABAB, ABA, and/or ABB would indicate that nondissociative electron attachment had occurred to form a stable anion radical.

The negative species A^- and B^- can transfer their electrons to another AB by the following reactions. The

$$A^- + AB \longrightarrow AB^- + A\cdot \qquad (8)$$

$$B^- + AB \longrightarrow AB^- + B\cdot \qquad (9)$$

radicals $A\cdot$ and $B\cdot$ can then react with AB as follows.

$$A\cdot + AB \longrightarrow A_2 + B\cdot \qquad (10)$$

$$B\cdot + AB \longrightarrow B_2 + A\cdot \qquad (11)$$

The radicals produced from dissociative electron attachment (eq 2, 3, and 4) react according to eq 10 and 11. Therefore, the predominance of products of the type A_2 and B_2 indicates that dissociative electron attachment was the initial step. Furthermore, from

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[1] J. A. Stockdale and G. S. Hurst, *J. Chem. Phys.*, **41**, 255 (1964).

[2] R. E. Fox, *ibid.*, **26**, 1281 (1957).

[3] L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, *ibid.*, **43**, 4273 (1965).

[4] W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966).

[5] J. E. Lovelock, *Nature* (London), **195**, 488 (1962).

[6] W. E. Wentworth and E. Chen, *J. Gas Chromatogr.*, **4**, 170 (1967).

[7] J. E. Lovelock, *Anal. Chem.*, **35**, 474 (1963).

[8] J. E. Lovelock, "Physical Processes in Radiation Biology," Academic Press, New York, N. Y., 1964, p 183.

[9] A. Zlatkis and J. E. Lovelock, *Clin. Chem.*, **11**, 259 (1965).

Table I. Product Distribution of Benzaldehyde Reaction

Product	Structure	Actual yield, % wt		Relative yield (biphenyl = 1.00)	
		I[a]	II[b]	I[a]	II[b]
Acetophenone	$C_6H_5—CO—CH_3$	0.62	0.054	0.054	0.018
Benzyl alcohol	$C_6H_5—CH_2OH$	2.2	0.45	0.19	0.15
Phenol	$C_6H_5—OH$	3.3	0.43	0.29	0.15
Biphenyl	$C_6H_5—C_6H_5$	11.4	2.96	1.00	1.00
Component 6	(mol wt 198)	0.69	0.090	0.061	0.031
Benzophenone	$C_6H_5—CO—C_6H_5$	18.0	1.85	1.58	0.63
Component 8	(mol wt 198)	0.75	0.036	0.066	0.012
Benzil	$C_6H_5—CO—CO—C_6H_5$	45.3	2.27	3.98	0.77

[a] Charge, 0.540 C; gas, argon + 2% CO_2; *H* value, 90 molecules/electron. [b] Charge, 0.442 C; gas, argon; *H* value, 9 molecules/electron.

the above reactions several molecules of AB may be removed by the addition of a single electron. The above equations are strictly true only where molecule AB is diatomic. In this work AB represents a polyatomic molecule which can be separated into two distinct radicals. For example, chlorobenzene may be separated into a phenyl radical corresponding to A, and a chlorine atom corresponding to B. Using the above equations, the mechanisms of electron attachment for some representative compounds were investigated.

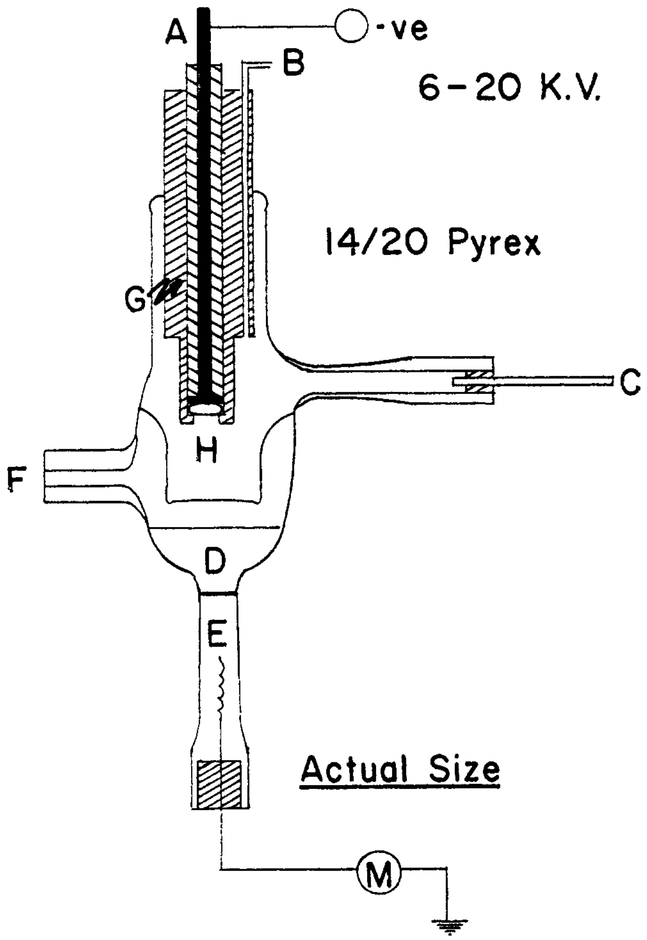

Figure 1. Generator for near thermal energy electrons: A, stainless steel rod; B, argon gas inlet; C, CO_2 gas inlet; D, test material; E, 1.0 *M* CsCl solution containing a silver–silver chloride electrode; F, gas outlet; G, Teflon jacket; H, quartz lens; M, 0–100 μA meter.

Experimental Section

The apparatus employed in this study is shown in Figure 1. A corona discharge of 100–200 μA is maintained by the application of a negative potential of between 10 and 20 kV to the stainless steel electrode in an argon atmosphere. A quartz dielectric is placed in front of the electrode allowing only incomplete breakdown of the ionized argon molecules. The quartz dielectric acts as an insulating barrier so that no arc develops. The barrier interrupts the conductive path and, instead of a hot localized arc, there is a cooler, diffused glow between the electrodes. Due to a positive space charge which accumulates around the cathode, the high coulomb field is practically neutralized at a distance of a few millimeters from the cathode. The electrons are brought to near thermal energies through elastic collisions with carbon dioxide. If carbon dioxide is absent, the electrons remain well above thermal energy. The inner glass tube allows limited diffusion of the vapor of the test substance to the ionization area near the stainless steel electrode. The silver–silver chloride in 1.0 *M* cesium chloride serves as a well-defined electrode which avoids the possibility of anode reactions. The weight of test substance taken was 0.05–0.20 g. The products remaining in the organic layer were subjected to gas chromatographic and mass spectral analyses. A Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector was employed. Mass spectrometric data were obtained with the LKB Model 9000 mass spectrometer–gas chromatograph.

The quantitative results are given in terms of *H* values, where *H* is the number of molecules of reactant removed per electron added. These values are calculated from the following equation, where

$$H = \frac{WD}{MIT} \tag{12}$$

W = weight of material removed, grams, M = molecular weight of the reactant, I = current, amps, T = time, seconds, and D = constant = 96,500 [(coulombs molecules)/(mole electron)].

The *H* value is a measure of a compound's ability to react with electrons, while the actual product yield is determined by the total number of electrons exposed to the substance, namely, the product *IT* in eq 12. Consequently, the importance of a reaction product is found by comparing its yield to that of the other products of the reaction.

Results and Discussion

Benzaldehyde. Benzaldehyde is a conjugate electrophore with 48 as an electron capture coefficient.[9] A chromatogram of the products obtained with benzaldehyde is shown in Figure 2. Component 1 is the starting material. The identified products are acetophenone (component 2), benzyl alcohol (component 3), phenol (component 4), biphenyl (component 5), benzophenone (component 7), and benzil (component 9). Components 6 and 8, being minor products, were not identified. Table I shows the product distribution obtained in both the presence and absence of carbon dioxide. In each case, the three compounds, biphenyl, benzophenone, and benzil, account for more than 87% of the total yield. The *H* value for the reaction using carbon dioxide is 90 molecules/electron. When the reaction was carried out in the absence of the energy-moderating gas, carbon dioxide, the H value dropped to 9 molecules/electron. With the CO_2 added to the argon, the distribution of electron energies should be drastically lowered, and in the presence of 2% CO_2, the electron energy distribution should be thermal or near thermal. Evidence for a thermal or near thermal distribution is given by electron capture (EC) studies with different gas mixtures and compositions.[4,10] The EC results are highly dependent on the presence of the substance added to argon, *e.g.*, CH_4, CO_2, or H_2. With CH_4 and CO_2 similar results are obtained when the concentrations are 10 and 1.5%, respectively.

Since the electron energy distribution should be considerably lowered with CO_2 present, the mechanism for reaction with electrons could be different. Apparently, this is the case since different product distributions are obtained when CO_2 is absent or present. However, it is quite surprising that the same products are obtained in both cases and only the distribution of products is altered. The following proposed mechanisms for reaction with and without CO_2 take this fact into account. The mechanisms also consider the difference in H values from 90 to 9 molecules/electron.

The proposed mechanism when CO_2 is present involves a nondissociative electron attachment to benzaldehyde to initiate the reaction sequence. This is consistent with the electron attachment mechanism as deduced from the temperature dependence of the EC responses.[6,8] The proposed mechanism for reaction in the presence of CO_2 is as follows.

$$C_6H_5CHO + e^- \rightleftharpoons [C_6H_5CHO]^- \qquad (13)$$

$$[C_6H_5CHO]^- + C_6H_5CHO \longrightarrow [C_6H_5CO]^- + C_6H_5\dot{C}O + H_2 \qquad (14)$$

$$[C_6H_5CO]^- + C_6H_5\dot{C}O \longrightarrow (C_6H_5CO)_2 + e^- \qquad (15)$$

$$C_6H_5\dot{C}O + C_6H_5CHO \longrightarrow (C_6H_5)_2CO + H\dot{C}O \qquad (16)$$

$$H\dot{C}O + C_6H_5CHO \longrightarrow \begin{cases} H_2CO + C_6H_5\dot{C}O & (17) \\ (CHO)_2 + C_6H_5\cdot & (18) \end{cases}$$

$$C_6H_5\cdot + C_6H_5CHO \longrightarrow C_6H_5\text{–}C_6H_5 + H\dot{C}O \qquad (19)$$

Note the chain mechanism which is set up for the production of the major product, benzil (45%), in reaction steps 13–15. The $C_6H_5\dot{C}O$ radical is also produced in the chain mechanism reaction step 14. The $C_6H_5\dot{C}O$ radical is the precursor to the formation of another major product, $(C_6H_5)_2CO$ (18%). The phenyl radical, $C_6H_5\cdot$, is produced from a subsequent reaction step 18 and the third major product, $C_6H_5\text{–}C_6H_5$ (11%), is produced from $C_6H_5\cdot$ in reaction step 19. The chain mechanism to produce $C_6H_5\dot{C}O$ and $C_6H_5\cdot$ occurs by reactions 17 and 18. The mechanism properly accounts qualitatively for the relative yields of $(C_6H_5CO)_2 > (C_6H_5)_2CO > (C_6H_5)_2$.

No attempt was made to account for the minor constituents, but presumably the phenol and benzyl alcohol are formed by reaction of the radicals with water.

Reaction 14 involves the formation of $[C_6H_5\dot{C}O]^-$ and the reaction should be favorable from an energy standpoint. The electron affinity of C_6H_5CHO has been measured experimentally[11] and found to be 10.3 kcal. The electron affinity of $C_6H_5\dot{C}O$ is 55 ± 3 kcal.[12] The bond dissociation energy for C_6H_5CHO is reported to be 74 kcal.[13] However, this value may be slightly low since results from thermal electron attachment at high temperatures[12] give a lower limit to bond dissociation energy, $D_{C_6H_5CHO} \geq 78 \pm 3$ kcal. Assuming $D_{C_6H_5CHO}$ to be 74 kcal, the ΔE for reaction 14 is then estimated at

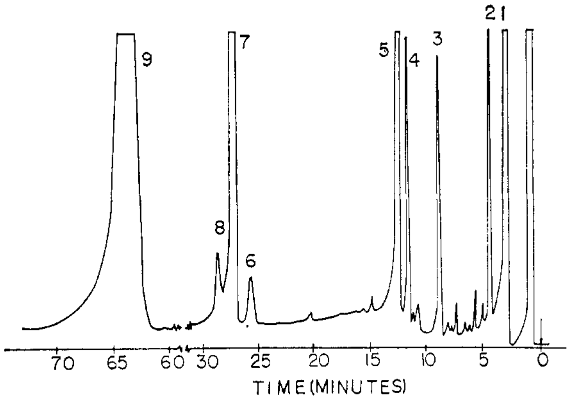

Figure 2. Chromatogram of products from the benzaldehyde reaction: column, 100 ft × 0.02 in. i.d. stainless steel capillary coated with Igepal CO-990. Column temperature was programmed from 100 to 150° at 3°/min. Carrier gas was nitrogen at 8 psi.

$$\begin{aligned} \Delta E &= EA_{C_6H_5CHO} + 2D_{C_6H_5CHO} - EA_{C_6H_5\dot{C}O} - D_{H\text{–}H} \\ &= 10.3 \quad + 2(74) \quad - 55 \quad - 104.2 \\ \Delta E &= -0.9 \pm 3 \text{ kcal} \end{aligned}$$

Since ΔE is not highly endothermic, the activation energy for reaction step 14 may not be unreasonably large and the reaction is at least feasible.

When carbon dioxide is absent the electron distribution is higher in energy than when carbon dioxide is present. Electron energies may range as high as 10–25 V. The initial electron attachment process is quite likely predominately dissociative. When CO_2 is absent, the possible initial steps are

$$C_6H_5CHO + e^- \longrightarrow \begin{cases} C_6H_5\cdot + [COH]^- & (20) \\ (C_6H_5CO)^- + H\cdot & (21) \end{cases}$$

Nondissociative capture to form $[C_6H_5CHO]^-$ probably occurs but only to a minor extent.

Possible chain propagating steps leading to the observed products are shown in eq 22–29. No mechanism is given for the formation of benzyl alcohol. One may note, however, that benzyl alcohol is the expected product from the reduction of benzaldehyde.

$$C_6H_5\cdot + C_6H_5CHO \longrightarrow \begin{cases} C_6H_5\text{–}C_6H_5 + H\dot{C}O & (22) \\ C_6H_6 + C_6H_5\dot{C}O & (23) \end{cases}$$

$$H\cdot + C_6H_5CHO \longrightarrow \begin{cases} C_6H_5\cdot + H_2CO & (24) \\ C_6H_5\dot{C}O + H_2 & (25) \end{cases}$$

$$H\dot{C}O + C_6H_5CHO \longrightarrow \begin{cases} (CHO)_2 + C_6H_5\cdot & (26) \\ H_2CO + C_6H_5\dot{C}O & (27) \end{cases}$$

$$C_6H_5\dot{C}O + C_6H_5CHO \longrightarrow \begin{cases} (C_6H_5CO)_2 + H\cdot & (28) \\ (C_6H_5)_2CO + H\dot{C}O & (29) \end{cases}$$

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(10) W. E. Wentworth, R. S. Becker, and R. Tung, *J. Phys. Chem.*, **71**, 1652 (1967).

(11) W. E. Wentworth and E. Chen, *ibid.*, **71**, 1929 (1967).

(12) W. E. Wentworth and J. Wiley, unpublished data. Electron attachment studies to acetophenone revealed a dissociative process at higher temperatures which allows the determination of $EA_{C_6H_5CO}$.

(13) M. Szwarc and J. W. Taylor, *J. Chem. Phys.*, **22**, 270 (1954).

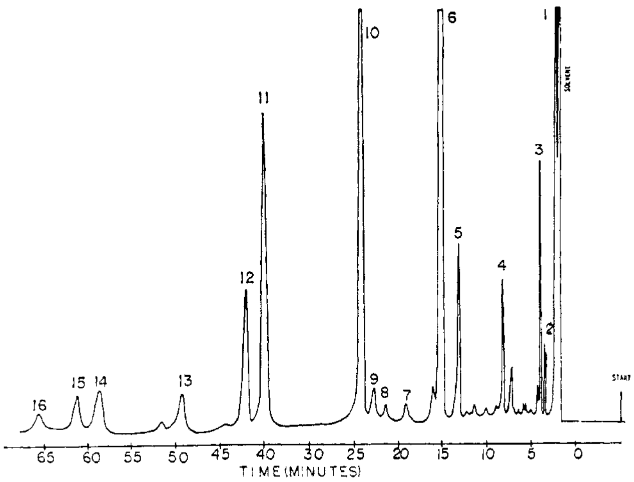

Figure 3. Chromatogram of products from the chlorobenzene reaction: column, 500 ft × 0.02 in. i.d. stainless steel capillary coated with Igepal CO–990. Column was operated isothermally at 160° and 20 psi of nitrogen as carrier gas.

Diethyl Maleate. Diethyl maleate, a conjugate electrophore, was exposed to near thermal energy electrons and the major products remaining in the organic layer were found to be diethyl succinate, diethyl malate, and two unidentified compounds (mol wt 190 and 300). Diethyl oxalacetate was not found to be present. The reaction conditions and product distribution are shown in Table II. The *H* value for the reaction was 31 molecules/electron. In the absence of CO_2, the *H* value dropped to 18 molecules/electron.

Table II. Product Distribution for Diethyl Maleate Reaction[a]

Products	Structure	Yield, % wt
Diethyl succinate	$C_2H_5OOC—CH_2—CH_2—COOC_2H_5$	13.0
Diethyl malate	$C_2H_5OOC—CHOH—CH_2—COOC_2H_5$	20.6
Unidentified	(Mol wt 190)	12.8
products	(Mol wt 300)	25.9

[a] Reactant, diethyl maleate ($C_2H_5OOC—CH{=}CH—COOC_2H_5$); charge, 0.975 C; H = 31 molecules/electron; gas, argon + 2% CO_2.

cis-**Stilbene.** The major products obtained when *cis*-stilbene, a conjugate electrophore, was allowed to react with near thermal energy electrons were bibenzyl (C_6H_5-CH_2-CH_2-C_6H_5), deoxybenzoin (C_6H_5-CO-CH_2-C_6H_5), 1,2-diphenylethanol (C_6H_5-CHOH-CH_2-C_6H_5), and two unidentified products thought to be the *cis* and *trans* isomers of the enol form of deoxybenzoin. The products of the *cis*-stilbene reaction are quite similar in type to the products of the diethyl maleate reaction. In both reactions the products are formed from reaction at the double bond. Hydrogenation occurs forming succinate and bibenzyl; hydration occurs forming malate and 1,2-diphenylethanol. The fact that the ketone, deoxybenzoin, is formed in the *cis*-stilbene reaction indicates that oxalacetate is probably formed in the maleate reaction.

Comparison of these reaction products with eq 5 shows that *cis*-stilbene and diethyl maleate react with near thermal electrons in a nondissociative manner. The stable anion radical formed on attachment of the electron undergoes reaction with the water present to give the resultant products.

Chlorobenzene. A chromatogram of the products obtained with chlorobenzene, a simple electrophore, is shown in Figure 3. The major products are biphenyl (component 6), *m*-chlorobiphenyl (component 10), *o*-chlorobiphenyl (component 11), and *p*-chlorobiphenyl (component 12). Minor products identified are *o*- and *p*-dichlorobenzene (component 2), *m*-dichlorobenzene (component 3), *o*-chlorophenol (component 4), phenol (component 5), and *m*-chlorophenol (component 14). Components 7 and 8 are dichlorophenols while components 12, 15, and 16 are dichlorobiphenyls. Component 8 is unidentified and component 1 is the starting material, chlorobenzene.

The quantitative distribution of the four major products is given in Table III. The *H* value for the reaction was 60 molecules/electron. The *H* value for the reaction in the absence of CO_2 was 54 molecules/electron. For molecules reacting according to eq 2, the probability of the reaction normally increases to a peak value and then falls off as the electron energy increases. In the absence of carbon dioxide, the electron energy distribution would move to higher values and the *H* value would be expected to increase. The *H* value in this reaction, however, remains approximately constant apparently because the polyatomic vapors of chlorobenzene also act as an energy moderator. The vapor pressure of chlorobenzene at 30° is 15 mm, and could thus furnish a sufficient concentration of polyatomic molecules to cool the electrons to near thermal energy.

The four major products formed in this reaction indicate that dissociative capture is the process taking place. When attachment of an electron takes place, a chlorine anion dissociates from the chlorobenzene molecule, leaving a phenyl radical. The phenyl radical then reacts with a neutral chlorobenzene molecule to form biphenyl and the chlorobiphenyls. The reactions are shown below

$$C_6H_5Cl + e^- \longrightarrow C_6H_5\cdot + Cl^- \tag{30}$$

Possible chain propagating steps are

$$C_6H_5\cdot + C_6H_5Cl \begin{cases} C_6H_5\text{-}C_6H_5 + Cl\cdot & (31)\\ C_6H_6 + Cl\text{-}C_6H_4\cdot & (32) \end{cases}$$

$$Cl\text{-}C_6H_4\cdot + C_6H_5Cl \begin{cases} C_6H_5\text{-}C_6H_4\text{-}Cl + Cl\cdot & (33)\\ Cl\text{-}C_6H_4\text{-}Cl + C_6H_5\cdot & (34) \end{cases}$$

$$Cl\cdot + C_6H_5\text{-}Cl \longrightarrow Cl\text{-}C_6H_4\cdot + HCl \tag{35}$$

None of the reactions is endothermic by more than 4 kcal so reaction at thermal energies is at least feasible.

Wentworth, Chen, and Lovelock[4] have suggested that chlorobenzene may form a stable radical anion intermediate upon attachment of an electron, *i.e.*, reaction according to eq 3. Compton, Christophorou, and Huebner[14] invoke a temporary negative ion state in chlorobenzene to explain the strong electron energy loss resonance which exists in chlorobenzene near 1 eV. They have shown that the production of strong, vibrationally excited (and possibly reactive) neutral chlorobenzene molecules is in competition with the formation of Cl^- through dissociative attachment. If

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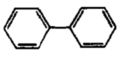
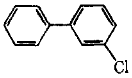
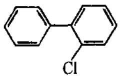
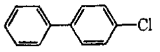
[14] R. W. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.*, **23**, 656 (1966).

Table III. Product Distribution for Chlorobenzene Reaction

Product	Structure	Actual yield, % wt I[a]	II[b]	Rel yield, biphenyl = 1.00 I[a]	II[b]
Biphenyl		4.0	3.8	1.00	1.00
m-Chlorobiphenyl		2.0	1.2	0.50	0.32
o-Chlorobiphenyl		1.4	0.9	0.35	0.24
p-Chlorobiphenyl		0.7	0.5	0.175	0.13

[a] Reactant, chlorobenzene; charge, 0.036 C; gas, argon + 2% CO_2; *H* value, 60 molecules/electron. [b] Reactant, chlorobenzene; charge, 0.036 C; gas, argon; *H* value, 54 molecules/electron.

Table IV. Product Distribution for Benzyl Chloride Reaction

Product	Structure	Actual yield, % wt I[a]	II[b]	Rel yield, bibenzyl = 1.0 I[a]	II[b]
Benzyl alcohol	$C_6H_5—CH_2OH$	0.9	0.3	1.0	0.15
Phenol	$C_6H_5—OH$	<0.1	<0.1		
Bibenzyl	$C_6H_5—CH_2—CH_2—C_6H_5$	0.9	2.0	1.0	1.0
cis-Stilbene	$C_6H_5—CH{=}CH—C_6H_5$	0.1	0.3	0.1	0.15
trans-Stilbene	$C_6H_5—CH{=}CH—C_6H_5$	1.6	3.8	1.8	1.9

[a] Reactant, benzyl chloride; charge, 0.060 C; gas, argon + 2% CO_2; *H* value, 24 molecules/electron. [b] Reactant, benzyl chloride; charge, 0.284 C; gas, argon; *H* value, 34 molecules/electron.

either a stable radical anion or a temporary ion state is produced in chlorobenzene, then reaction according to eq 5 would result in the formation of dichlorobiphenyl. However, dichlorobiphenyls are produced in low yield (Figure 3) indicating that if a stable radical anion or a temporary negative ion state is indeed formed, it does not react according to eq 5. Reaction according to eq 6 would yield chlorobiphenyls; however, these are more likely produced from the dissociative reactions shown above.

Benzyl Chloride. Benzyl chloride, a simple electrophore, was exposed to near thermal energy electrons and the products remaining in the organic layer were found to be benzyl alcohol, phenol, bibenzyl, *cis*-stilbene, and *trans*-stilbene. The quantitative distribution of the products is shown in Table IV. The *H* value for the reaction was 24 molecules/electron. In the absence of CO_2, the *H* value increased to 34 molecules/electron. The vapor pressure of benzyl chloride is approximately 1 mm at 30°. Apparently, in the absence of CO_2, a sufficient concentration of polyatomic energy-moderating molecules is not present and the *H* value increases.

The products indicate dissociative attachment occurs in this reaction. On attachment of an electron to the benzyl chloride molecule, a chlorine anion dissociates from the molecule, leaving a benzyl radical which can react with benzyl chloride to form bibenzyl. The proposed reactions are given below.

$$C_6H_5CH_2Cl + e^- \longrightarrow C_6H_5CH_2\cdot + Cl^- \tag{36}$$

$$C_6H_5CH_2\cdot + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2\text{-}CH_2C_6H_5 + Cl\cdot \tag{37}$$

$$Cl\cdot + C_6H_5CH_2Cl \longrightarrow C_6H_5\dot{C}HCl + HCl \tag{38}$$

$$C_6H_5\dot{C}HCl + C_6H_5CH_2Cl \longrightarrow C_6H_5CH{=}CH\text{-}C_6H_5 + HCl + Cl\cdot \tag{39}$$

$$C_6H_5CHCl + C_6H_5CH_2Cl \longrightarrow C_6H_5CHCl_2 + C_6H_5CH_2\cdot \tag{40}$$

None of the above reaction steps is highly endothermic so their corresponding activation energies could be low and the reaction could proceed at ambient temperature.

The electric field in the discharge apparatus is nonuniform, especially in the upper part of the discharge. Consequently, the maximum in the electron energy distribution would vary throughout the length of the discharge. As a result, the exact energy at which the reactions occur cannot be specified. However, by varying the carbon dioxide concentration, large changes in electron energies are effected, as evidenced by the large changes in the *H* values for the conjugate electrophoric compounds. While the initial electron attachment process may not occur at the energy of maximum probability of attachment, the mechanism, nevertheless, is the same.

For electron energies above 6 eV, O^- can be produced from CO_2 in the thermalization process,[15] while at lower values the absence of negative ions has been reported.[16]

The O^- could possibly react with the organic test material in the discharge apparatus. However, elimination of CO_2 from the discharge appartus resulted in products identical with those obtained when CO_2 was present. Only the *H* value and, therefore, the total yield and product distribution changed. This indicates that the only role CO_2 has is to thermalize the electrons.

The contribution of positive ions, excited species, and photons to the observed yield is considered neg-

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ligible. Positive ions are expected to remain in the vicinity of the discharge (upper) electrode due to its high negative field. Excited species are apparently quenched near the discharge electrode since the addition of a quenching gas (*i.e.*, CO_2) increases rather than decreases the yield in a number of reactions. Furthermore, the gas flow in the reaction vessel is such that the test vapors are carried in a direction away from the discharge electrode so that there should be little contact between the test material and positive ions and excited species.

In general, photochemical reactions have very low efficiency, thus requiring intense light sources, reflection, etc., for measurable reactions to occur. The discharge in our apparatus is a soft, diffuse glow and maintained rarely in excess of 2 hr. Consequently, the effect of photons on these reactions is considered negligible.

It was not determined whether the reactions occur in the gas phase or in the liquid phase. However, some evidence indicates that the reactions occur in the gas phase. If the reactions occur in the liquid phase, then the H value would be dependent upon the time the electrons travel through the liquid phase and this time would depend on the liquid phase thickness. Thus the H value would be a function of the sample weight. It was found, however, that the H values did not vary with the weight of reactant. This then indicates that the reactions occur in the gas phase.

Conclusions

A corona discharge is a simple, inexpensive means for the generation of near thermal energy electrons. Although the electrons are not monoenergetic, large changes in their energy can be effected through use of a polyatomic energy-moderating gas. Experiments with this discharge cell indicate that both dissociative and nondissociative electron capture can be observed. Dissociative capture was confirmed for chlorobenzene and benzyl chloride, while benzaldehyde, diethyl maleate, and *cis*-stilbene were shown to attach electrons in a nondissociative manner. Of particular significance is the fact that the products of these reactions are actually recovered and characterized by gas chromatography–mass spectrometry. This technique should find application for both organic syntheses and investigation of the role of free electrons in biological systems.[8]

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Heats of Transfer of β-Dicarbonyl Compounds from Carbon Tetrachloride to Sulfuric Acid

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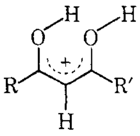
Abstract: The relative heats of transfer from carbon tetrachloride to concentrated sulfuric acid for a series of compounds containing β-carbonyl groups have been measured. A large Baker–Nathan effect has been observed on the heats of transfer of substituted β-diketones. The destabilization of protonated carbonyl compounds in H_2SO_4 when methyl is replaced by phenyl has been observed. It is suggested that the size of the organic ion may play a significant role in the substituent effects observed in this system.

The interaction of compounds containing β-carbonyl groups with Lewis and Brønsted acids has been of continuing interest. Most attention has been focused on the complexes of β-dicarbonyl compounds with various metals.[1] However quite recently Olah and Brouwer have independently reported nmr studies of mono- and diprotonated β-diketones,[2–4] alkyl acetoacetate derivatives,[2] and malonic acid derivatives.[2] Other nmr studies of protonated β-dicarbonyl compounds have been made by Deno[5] and Olah.[6] These studies indicate that the compounds are protonated cleanly, no products other than the protonated species being detected by nmr. Studies in these laboratories confirm that these reactions are completely clean within our limits of detection. In addition, a thorough study of the protonation of acetylacetone in aqueous sulfuric acid using acidity function techniques has been reported.[7]

The observation by Brouwer[2] that the ion formed by protonation of a β-dicarbonyl compound ($RC(=O)CH_2C(=O)R'$) has the structure I when R is alkyl or aryl and II when R and R′ are alkoxyl is particularly interesting. In order to compare the stabilities of I and



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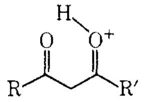

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