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Interaction of Low-Energy Electrons with Conjugated Cyclic Perchlorocarbons[1a]

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Abstract: The interactions of low-energy (<10 eV) electrons with 1,2,3,4,5-pentachlorocyclopentadiene and the conjugated cyclic C_5, C_6, C_7, and C_8 perchlorocarbons have been studied. The gas-phase nonbenzenoid aromatic cyclopentadienide anion ($C_5Cl_5^-$) has been generated from hexachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene in a mass spectrometer with electron energies of <4 eV. $C_8Cl_6^-$ and $C_6Cl_6^-$ were the two major carbon-containing anionic species produced from the interaction of low-energy electrons with octachlorocyclooctatetraene and hexachlorobenzene, respectively. Only traces of anions containing carbons were observed from octachlorocycloheptatriene. Ionization efficiency curves for most of the more abundant anions, indicating the resonance capture maxima and showing the overall relationship between the electron energy and the corresponding anion intensities, have been obtained.

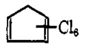
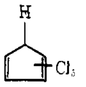
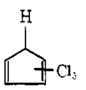
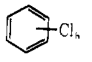
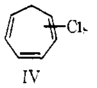
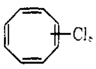
When low-energy electrons come in contact with organic molecules in a mass spectrometer, several events may occur. If the electron energies are below the appearance potential of the respective molecule, none of these events may be observed in the conventional positive ion mode of a mass spectrometer. Because of this, very little is known about these low-energy (i.e., <10 eV) electron interactions with organic molecules. In contrast, there are numerous studies in the literature on the ionization, fragmentation, and rearrangements that occur in organic molecules under electron impact at higher energies.

In a continuing effort to better understand these low-energy interactions, we have utilized negative ion mass spectrometry in a study of five compounds: hexachlorocyclopentadiene (I), 1,2,3,4,5-pentachlorocyclopentadiene (II), hexachlorobenzene (III), octachlorocycloheptatriene (IV), and octachlorocyclooctatetraene (V).

Generation of the Pentachlorocyclopentadienide Anion ($C_5Cl_5^-$) from C_5Cl_6. The solution chemistry of the pentachlorocyclopentadienide anion has been studied extensively by several investigators.[2,3] The anion has six π electrons, is considered to be aromatic, and, therefore, should possess some degree of stability. Wulfsberg and West have prepared several salts of the pentachlorocyclopentadienide anion, all of which are thermally unstable at room temperature.[2] They also found the anion to be unstable in solution at temperatures above −30 °C. To our knowledge, there are no previously reported gas phase studies on the cyclopentadienide anion.

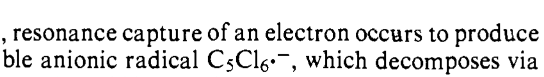
We have found that the gas phase pentachlorocyclopentadienide anion ($C_5Cl_5^-$) can be generated from hexachlorocyclopentadiene with low-energy electrons in a mass spectrometer. And, except for Cl^-, it is the major anion produced from hexachlorocyclopentadiene (see Table I). Two distinct

Table I. Low-Energy Negative Ion Spectra of Compounds I, II, III, IV, and V[a]

Compd	*m/e*	%	Species
	70	8.0	$(Cl_2)^-$
	72	4.6	
	74	1.2	
I	235	62	$(C_5Cl_5)^-$
(2.08 eV)	237	100	
	239	58	
	241	21	
	243	4,0	
	245	0.6	
	70	21	$(Cl_2)^-$
	72	13	
	74	2.5	
	82	1.9	$(CCl_2)^-$
	84	1.3	
	86	*b*	
	201	71	$(C_5HCl_4)^-$
	203	100	
	205	52	
	207	8.2	
	209	1.0	
II	235	35	$(C_5Cl_5)^-$
(2.40 eV)	237	52	
	239	38	
	241	12	
	243	2.1	
	245	*b*	
	70	7.1	$(Cl_2)^-$
	72	4.1	
	74	0.9	
	82	1.3	$(CCl_2)^-$
	84	0.8	
	86	*b*	
	201	79	$(C_5HCl_4)^-$
II	203	100	
(3.80 eV)	205	52	
	207	9.0	
	209	1.0	
	235	7.0	$(C_5Cl_5)^-$
	237	12	
	239	7.5	
	241	2.9	
	243	0.5	
	245	*b*	
	70	61	$(Cl_2)^-$
	72	38	
	74	13	
	212	47	$(C_6Cl_4)^-$
	214	60	
	216	36	
	218	15	
	220	3.4	
	222	*b*	
	282	61	$(C_6Cl_6)^-$
III	284	100	
(11.0 eV)	286	72	
	288	25	
	290	6.1	
	292	0.9	
	294	*b*	
	70	100	$(Cl_2)^-$
	72	58	
	74	8	
	294, 296, 298	0.2	$(C_7Cl_6)^{-c}$
	329, 331, 333	0.2	$(C_7Cl_7)^{-c}$
IV	364	0.6	$(C_7Cl_8)^{-c}$
(1.9 eV)	366	1.5	
	368	0.9	
	370	0.8	
	70	100	$(Cl_2)^-$
	72	63	
	74	11	
	271	0.6	$(C_8Cl_5)^-$
	273	0.6	
	275	0.5	
	306	14	$(C_8Cl_6)^-$
V	308	25	
(0.15 eV)	310	18	
	312	6	
	314	1.5	
	316	0.2	
	318	*b*	

[a] Cl^- has not been included in the data. [b] A relative percentage value of 0.1. [c] The signal to noise ratio was too small at this level of sensitivity to obtain accurate measurements for the relative intensities of these ions.

maxima are observed at 2.08 and 3.80 eV in the ionization efficiency (IE) curve for $C_5Cl_5^-$ from hexachlorocyclopentadiene (Figure 1). The occurrence of IE maxima in this low electron energy range indicates that this anion is being formed by a dissociative resonance capture process.[4] This is illustrated in eq 1.



$$C_5Cl_6 + \xrightarrow{e^-} C_5Cl_6^- \begin{cases} \xrightarrow{a} C_5Cl_5^- + Cl \\ \xrightarrow{b} C_5Cl_5 + Cl^- \end{cases} \qquad (1)$$

In eq 1, resonance capture of an electron occurs to produce the unstable anionic radical $C_5Cl_6\cdot^-$, which decomposes via two pathways (a and b). The electronic nature of the proposed anion-radical intermediate ($C_5Cl_6\cdot^-$) is not known. However, the fact that two maxima are observed may indicate that two different high-energy electronic states of this species are being formed. Two of the maxima observed in the IE curve for Cl^- (Figure 2) from hexachlorocyclopentadiene are consistent with the proposed mechanism in eq 1. Both the 1.75 and 3.75 eV maxima in Figure 2 are the same within experimental error as the two maxima observed in the IE curve for the formation of $C_5Cl_5^-$ from hexachlorocyclopentadiene (Figure 1).

Cl_2^- is the only other anion produced from hexachlorocyclopentadiene, whose IE curve could be obtained (<1% of $C_5Cl_4^-$ is also observed). The IE curve for Cl_2^- from C_5Cl_6 (Figure 3) showed a maximum at 5.7 eV. This maximum is very close to the value observed for the maximum at 6.0 eV in the previously discussed IE curve for Cl^- from hexachlorocyclopentadiene (Figure 2), and could represent the formation of Cl^- from Cl_2^- as shown in eq 2.[5]

$$C_5Cl_6 + \xrightarrow{e^-} C_5Cl_4\cdot + Cl_2^- \longrightarrow Cl\cdot + Cl^- \qquad (2)$$

From C_5HCl_5. The pentachlorocyclopentadienide anion was also formed from 1,2,3,4,5-pentachlorocyclopentadiene (II). It is possible, however, to generate another stable aromatic anion ($C_5HCl_4^-$) by cleavage of the C-Cl bond (as in b in eq 3). In fact, the relative intensity of this anion ($C_5HCl_4^-$) was found to be much larger than the $C_5Cl_5^-$ ion at all electron voltages investigated. The $C_5HCl_4^-$ is several times more intense than $C_5Cl_5^-$ even at 3.85 eV, which is the resonance capture maximum for formation of $C_5Cl_5^-$ from C_5HCl_5 (see Table I). In other words, cleavage of the C-Cl bond (process b, eq 3) is highly favored over cleavage of the C-H bond (process a). First-order approximation of the dissociation

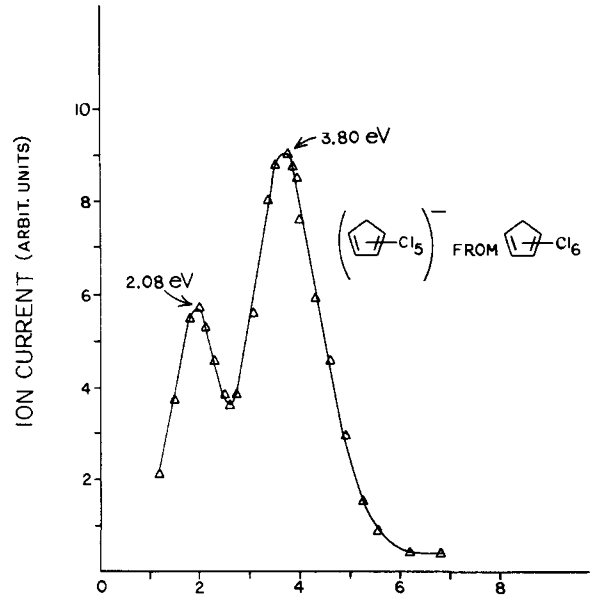
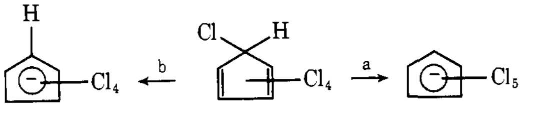


Figure 1. Ionization efficiency curve for $C_5Cl_5^-$ from C_5Cl_6.



(3)

energies of the allylic C-H and the allylic C-Cl bond indicate that the C-H value is 20 kcal/mol greater than the value for the C-Cl bond.[6] This is consistent with the preferential cleavage of the C-Cl bond which is observed. The IE curve maxima for the formation of both ions $C_5Cl_5^-$ and $C_5HCl_4^-$ is also consistent with these data. The IE maximum for the formation of $C_5Cl_5^-$ and $C_5HCl_4^-$ from C_5HCl_5 occurs at 3.8 and 2.4 eV, respectively.

1,2,3,4-Tetrachlorocyclopentadiene. No negative ions containing carbons were observed from 1,2,3,4-tetrachlorocyclopentadiene at either low or high voltages. Yet, when there is a chlorine atom at C(5), as in 1,2,3,4,5-pentachlorocyclopentadiene, both $C_5Cl_5^-$ and $C_5HCl_4^-$ are easily observed. This would seem to indicate that the presence of at least one chlorine atom at C(5) in this system is a necessary condition for the formation of an aromatic or carbon-containing anion in any significant amount.[7]

Hexachlorobenzene (III). Hexachlorobenzene was the only one of the four perchlorocarbons investigated which gave abundant molecular ion peaks.[8] The IE curve for the negative molecular ion[9] from hexachlorobenzene was not complex and contained only one maximum at 11 eV. When the complete spectrum was obtained at 11 eV, only two ions ($C_6Cl_6\cdot^-$ and $C_6Cl_4\cdot^-$) containing carbon were observed (Table I). The fact that the molecular anion $C_6Cl_6\cdot^-$ is observed is interesting from both a mechanistic and theoretical point of view. The hexachlorobenzene molecule is already aromatic with six π-electron resonance stabilization. This means that the additional electron must enter one of the antibonding orbitals. Apparently, the six chlorine substituents inductively distribute the negative charge, thereby stabilizing $C_6Cl_6\cdot^-$, giving it a lifetime long enough to allow its observation in the mass spectrometer. This seems more probable since all attempts to observe negative ions from benzene under similar conditions gave no molecular anion.

The relative intensity of $C_6Cl_4\cdot^-$ from hexachlorobenzene was too small to obtain an accurate IE curve; however, the Cl^- and Cl_2^- from hexachlorobenzene had maxima at 6.3 and 5.7 eV, respectively (see Figure 3 for Cl_2^-).

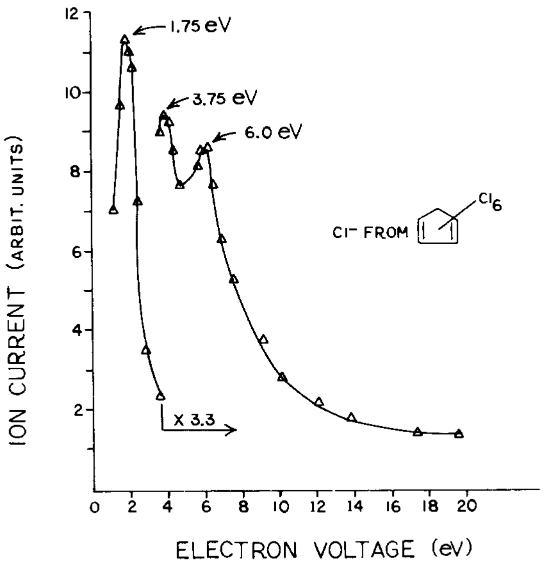


Figure 2. Ionization efficiency curve for Cl^- from C_5Cl_6.

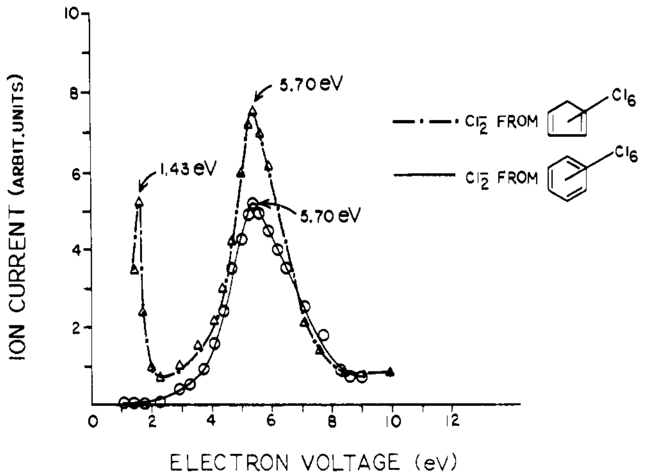


Figure 3. Ionization efficiency curve for Cl_2^- from C_5Cl_6 and C_6Cl_6.

Octachlorocycloheptatriene (C_7Cl_8). Electron bombardment of C_7Cl_8 with 1.9-eV electrons gave mainly Cl^- and Cl_2^- with only trace amounts of $(C_7Cl_6)^-$, $(C_7Cl_7)^-$, and $(C_7Cl_8)^-$ being produced (see Table I). No anions containing carbon were observed in a relative abundance greater than 2% of the Cl_2^- ion over the wide range of electron energies that were investigated (0-30 eV).

The dominating influence of aromaticity on the relative abundance of the anion produced is clearly illustrated by a comparison of these results with those discussed above for the analogous hexachlorocyclopentadiene.

The addition of an electron to each molecule (C_5Cl_6 and C_7Cl_8) and the loss of a chlorine atom from each would produce $C_5Cl_5^-$ and $C_7Cl_7^-$, respectively. The nonaromatic eight π-electron species $(C_7Cl_7)^-$ from C_7Cl_8 was formed in only trace amounts (0.29% of Cl_2^-), whereas the aromatic anion $(C_5Cl_5)^-$ from C_5Cl_6 was 12 times more intense than Cl_2^- and represents over 90% of the total ion current if Cl^- is excluded.

Octachlorocyclooctatetraene (C_8Cl_8). The negative molecular ion of octachlorocyclooctatetraene could not be obtained. Four ions, two containing carbon, were observed: $C_8Cl_6\cdot^-$, $C_8Cl_5^-$, Cl_2^-, and Cl^-. The most intense ion other than Cl^- was $C_8Cl_6^-$ (ion cluster at *m/e* 308 in Table I). The IE curve for this ion (Figure 4) was quite complex and contained four distinct and reproducible maxima at 0.15, 1.40, 4.7, and 8.3

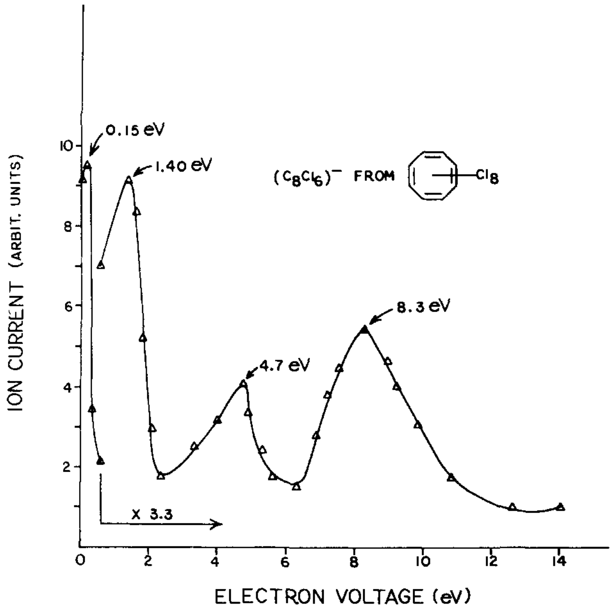


Figure 4. Ionization efficiency curve for $C_8Cl_6^-$ from C_8Cl_8.

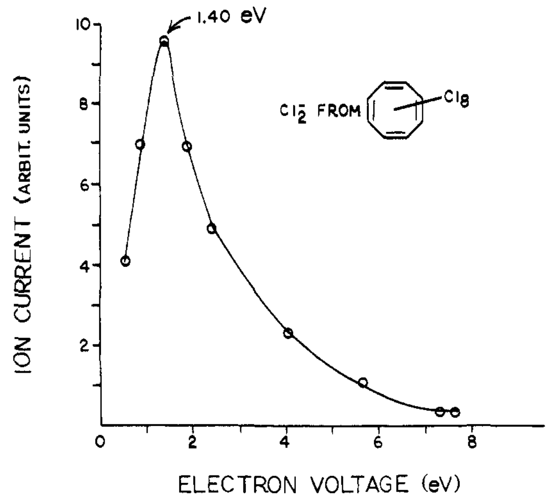


Figure 5. Ionization efficiency curve for Cl_2^- from C_8Cl_8.

eV. The complexity of this IE curve indicates that the formation of $C_8Cl_6^-$ from C_8Cl_8 is quite involved. The mechanism or process represented by these maxima is not known. The maximum in the IE curve for the formation of Cl_2^- from C_8Cl_8 (Figure 5) at 1.4 eV is the same as one of the maxima in the IE curve for $C_8Cl_6\cdot^-$ from C_8Cl_8. This indicates that at least one of the pathways for formation of $C_8Cl_6^-$ has the same energy requirements as that found for the formation of Cl_2^- and implies that both may be formed by the same process as shown in eq 4.

$$C_8Cl_8 + 2e^- \xrightarrow{1.4\ \mathrm{eV}} C_8Cl_6\cdot^- + Cl_2^- \qquad (4)$$

The aromatic anion ($C_8H_8^{2-}$) containing ten π electrons has been observed in solution.[10] All efforts to observe the corresponding $C_8Cl_8^{2-}$ in the gas phase were fruitless. However, an interesting explanation for the above relationship between the Cl_2^- and $C_8Cl_6\cdot^-$ would be to postulate the intermediate formation of $C_8Cl_8^{2-}$, which decomposes very rapidly as shown below in eq 5. This would be consistent with the observed IE curves. The gas-phase dianion $(C_8Cl_8)^{2-}$ would have severe electronic interactions and would not have any enhanced contribution to its stability by solvation and counterion effects, as is the case with the analogous $C_8H_8^{2-}$ in solution.[10]

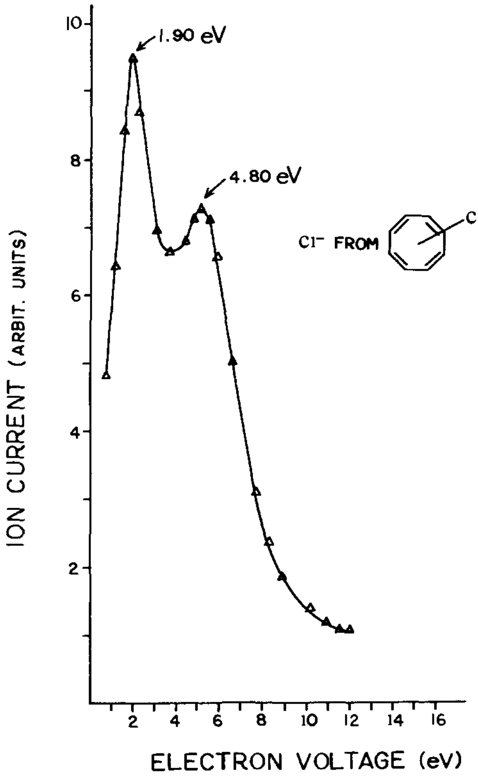


Figure 6. Ionization efficiency curve for Cl^- from C_8Cl_8.

$$C_8Cl_8 + 2e^- \xrightarrow{1.4\ \mathrm{eV}} C_8Cl_8^{2-} \xrightarrow{\mathrm{fast}} C_8Cl_6\cdot^- + Cl_2^- \qquad (5)$$

The IE curve for the Cl^- ion from C_8Cl_8 (Figure 6) showed two maxima at 1.9 and 4.8 eV. One of these (4.8 eV) is the same (within experimental error) as the 4.7 eV maximum seen in Figure 4 for $C_8Cl_6\cdot^-$ from C_8Cl_8. This would seem to indicate that another pathway or process in addition to that shown above for formation of $C_8Cl_6\cdot^-$ from C_8Cl_8, which involves the formation of Cl^-, may be important when 4.7–4.8 eV electrons are used. The maxima at 0.15 and 8.3 eV in the IE curve for $C_8Cl_6\cdot^-$ (Figure 4) do not coincide with any other maxima.

Conclusion

These studies have shown that low-energy electrons do indeed interact with cyclic perchlorocarbons to produce gas-phase anions in a mass spectrometer and that aromaticity plays an important role in determining the relative abundance of the anions observed. Furthermore, the IE curves indicate that the specific low-electron energy used is one of the more important factors for the efficient generation of a given anion from a molecule.

Experimental Section

Hexachlorocyclopentadiene and hexachlorobenzene were obtained from Aldrich Chemical Co. and further purified by vacuum distillation and sublimation, respectively. 1,2,3,4,5-Pentachlorocycntadiene and 1,2,3,4-tetrachlorocyclopentadiene were prepared from hexachlorocyclopentadiene by procedures of McBee et al.[11]

All mass spectra were recorded on a Varian CH-5 mass spectrometer with an on-line Varian 620i data system. Modification of the emission control circuits by Mr. Mike Schmidt and Mr. Heinz Runger of Varian MAT were made to enable the use of electron energies below 5 eV (with a regulated emission up to 30 μA). The IE curves were obtained by manually scanning the electron voltage and recording the particular ion current on a potentiometric recorder. The electron energies were calibrated using the known literature values for the m/e 16 peak (O^-) maxima from CO_2 (4.4, 8.2 eV), N_2O (2.2 eV), NO (8.15 eV), and m/e 35 from Cl^-/CCl_4 (0.6 eV) and are accurate to ±0.2 eV.[12] Samples were run at source pressures of 1-3 × 10^{-6} Torr, and at source temperatures ranging from 200 to 230 °C with an accelerating voltage of 3 kV.

Note Added in Proof. Christophorou has found that a large number of molecules,[13a] including some mono- and disubstituted halogenated benzene derivatives,[13b] form parent negative ions in the gas phase by capturing thermal or near thermal electrons. He has also obtained "threshold-electron-excitation spectra" of some mono-substituted benzene derivatives.[13c] One could postulate some type of electron excitation of hexachlorobenzene, prior to formation of the molecular anion radical, perhaps by elastic and inelastic electron collisions with the molecule. This would provide a partial explanation for the relatively high 11-eV maximum observed in the IE curves for the formation of the molecular anion radical of hexachlorobenzene.

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References and Notes

(1) (a) Portions of this work were presented at the ASMS 23rd Annual Conference on Mass Spectrometry and Allied Topics, May 1975, Houston, Texas. (b) NIH Career Development Awardee, 1975-1980.
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(5) The formation of Cl_2^- is not well understood, and it may indeed be much more complex than shown in eq 2. We cannot completely rule out some type of ion molecule reaction to produce Cl_2^-, however, even at low source pressure (1 × 10^{-6} Torr) the ion is still observed. Furthermore, no Cl_2^- was observed even at high source pressure when pure Cl_2 was run in the mass spectrometer under similar conditions.
(6) (a) T. L. Cottrell in "The Strength of Chemical Bonds", Butterworths London, 1956; (b) J. Roberts and M. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, p 86.
(7) It is possible that these ions are being formed at abundance levels below the minimum detection capabilities of the instrument.
(8) Trace amounts of molecular anion peaks for C_7Cl_8 were observed (see Table I).
(9) The molecular ion is really a cluster of ions due to the isotopes olorine. The most intense peak in the cluster (*m/e* 284 in this compound) was used to obtain the IE curve, which for reasons of brevity is not shown.
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Energy Transfer from Exciplexes to Hydrocarbon Quenchers in Polar Solvents

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Abstract: Electrochemical techniques were used to generate the radical cation of tri-*p*-tolylamine (TPTA) and the radical anions of benzophenone (BP) and 1,4-dicyanobenzene (DCB). Redox processes involving these ions are chemiluminescent. The systems TPTA(+)/DCB(−) in benzonitrile and TPTA(+)/BP(−) in acetonitrile emit in bands assigned to the exciplexes $^1(DCB^-TPTA^+)^*$ and $^1(BP^-TPTA^+)^*$, respectively. Aromatic hydrocarbons (R) can be added without interference in the radical-ion chemistry. When anthracene or one of its phenyl or methyl derivatives is added to the TPTA(+)/DCB(−) system, a blue emission from the singlet $^1R^*$ appears and the exciplex band is slightly quenched. Fluoranthene, pyrene, and *trans*-stilbene exert no such effects. These results are consistent with energy transfer, in energetically favorable cases, from an exciplex state to R with the resulting formation of the triplet $^3R^*$. The blue bands may arise from triplet-triplet annihilation. Similar results are seen in the TPTA(+)/BP(−) system. The chemiluminescence efficiency (Φ_{ecl}) for the TPTA(+)/DCB(−) system is 1.4 × 10^{-5}. The fluorescence efficiency (Φ_f') of the exciplex $^1(DCB^-TPTA^+)^*$ is placed in the range $10^{-5} \leq \Phi_f' \leq 1$ and the exciplex yield of radical-ion annihilation (Φ_e) is between the limits $10^{-5} \leq \Phi_e \leq 1$.

Theories of excited-state production in electron-transfer processes usually do not take into account the possible participation of intermediate complexes.[1-7] For example, the reaction between the radical ions A^- and D^+ is regarded as proceeding directly to the ground states A and D or to locally excited states A* and D*. An intervening complex state, such as the singlet or triplet exciplex $^{1,3}(A^-D^+)^*$, is not considered. As Weller and Zachariasse have demonstrated, this assumption does not hold for radical-ion annihilations in media of low polarity, where processes such as

$$A^- + D^+ \rightarrow {}^{1,3}(A^-D^+)^* \qquad (1)$$

can proceed with fairly high yields.[5,8-10] Even so, it has been widely held that direct exciplex formation is not important for polar media, which strongly solvate the ions and destabilize the exciplex. Comparisons between experimental product-state distributions and theoretical predictions have accordingly had an emphasis on data obtained in polar solvents.[6,7]

Recently, Bard and Park have shown that exciplexes actually do arise from radical-ion reactions in polar solvents[11,12] and their work raises doubt about the assumed unimportance of the exciplex pathway in such media. In addition, they and Hemingway have indicated that the benzophenone/tri-*p*-tolylamine exciplex $^1(BP^-TPTA^+)^*$ can engage in energy transfer to the metal complex $Eu(DBM)_3{\cdot}pip$ with high apparent efficiency; that is,

$$^1(BP^-TPTA^+)^* + Eu(DBM)_3{\cdot}pip \rightarrow Eu(DBM)_3{\cdot}pip^* + BP + TPTA \qquad (2)$$

where DBM is dibenzoylmethide and pip is piperidine.[13]

Their work stimulated our experiments in this area. We have used aromatic hydrocarbon interceptors to explore further the