Reactions of Selected Molecular Anions with Oxygen

W. B. Knighton, J. A. Bognar and E. P. Grimsrud†

Department of Chemistry, Montana State University, Bozeman, Montana 59717, USA

An investigation of the gas-phase reactions of molecular oxygen with the molecular anions of 17 compounds formed by resonance electron capture was undertaken using a pulsed e-beam high-pressure mass spectrometer. The molecular anions of sulphur hexafluoride, perfluromethylcyclohexane, cis- and trans-perfluorodecalin, m-chloronitrobenzene, o-, m-and p-fluoronitrobenzene and o-, m- and p-dinitrobenzene were found to be unreactive towards oxygen. Those of o- and p-chloronitrobenzene, penta- and perchlorobenzene, perfluorobenzene, and perfluorotoluene were found to react readily with oxygen. The second-order rate constants for these reactions are shown to bear an inverse dependence on temperature. The reactions involving o- and p-chloronitrobenezene and penta-and perchlorobenzene proceed via a branched mechanism by which an ion of the type [M + O − Cl] $^-$ and Cl$^-$ ion are simultaneously produced. A greater variety of negative ions are formed in the reactions of the molecular anions of perfluorobenzene and perfluorotoluene with oxygen. The electron affinities of pentachlorobenzene (0.7 eV) and perchlorobenzene (1.0 eV) are also reported for the first time.

INTRODUCTION

Electron-capture mass spectrometry (ECMS) offers extraordinarily high sensitivity and chemical specificity for trace analyses for numerous compounds of environment and biomedical interest.[1–6] In ECMS, molecular anions, M$^-$, of the compound of interest, M, are often provided by the resonance electron-capture (EC) mechanism:[7,8]

$$e + M \xrightarrow{\quad\quad} M^{-*} \xrightarrow{\;B\;} M^- \qquad (1)$$
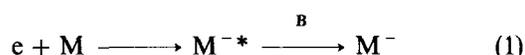
in which an intermediate, M^{-*}, is initially formed with relatively high internal energy (assuming M has a relatively large electron affinity (EA)). If M is a polyatomic species, the lifetime of M^{-*} against either electron detachment or dissociation will often be sufficiently long that M^{-*} can be stabilized[8,9] by collisions with the buffer gas molecules, B, at the pressures commonly used for ECMS (about 1 Torr; 1 Torr = 133.3 Pa). If the EA of M is about 1 eV or greater, the stabilized ion, M$^-$, will also be stable against thermal electron detachment[10,11] at the ion source temperatures commonly used for ECMS (about 200 °C or less). Since the first step in reaction sequence (1) is usually rate determining,[8] the overall rate constants for the resonance EC reaction of most polyatomic molecules of EA > 1.0 eV are expected to be very fast and independent of changes in pressure for pressures in excess of 1 Torr. Therefore, resonance EC reactions have provided efficient means of ionization under both chemical ionization (CI) and atmospheric pressure ionization (API) conditions.

A problem frequently encountered in practical applications of ECMS, however, is that a variety of additional and unexpected negative ions are sometimes

formed along with or instead of the expected M$^-$ ion.[1,6,12–23] One cause of unexpected ions is thought to be associated with side-reactions of the analyte with trace levels of molecular oxygen that are invariable present in even purified buffer gases.[12] For example, in the EC mass spectra of certain aromatic halogenated compounds, M = RX, ions of the type [M + O − X]$^-$ (that is, an oxygen atom has replaced a halogen atom) have been observed.[1,4,12,24,25] Isotopic labelling studies have shown[12] that the oxygen atom incorporated into the [M + O − X]$^-$ ion does, indeed, come from trace levels of molecular oxygen and not from trace levels of water present in the ion source. It has been suggested[12] that the oxygen-derived unexpected ions are formed by either of the following two gas-phase reactions:

$$O_2^- + M \to \text{products} \qquad (2)$$

$$M^- + O_2 \to \text{products} \qquad (3)$$

in which the reactant ion, either O_2^- or M$^-$, is formed first by resonance EC, reaction (1). The possibility that oxygen-derived ions are formed by reactions occuring on the surface of the ion source[6] should also not be ruled out.

The purpose of this study was to gain an increased understanding of the detailed mechanism by which oxygen-derived unexpected ions are formed under the conditions commonly existing in an ECMS ion source. This study was performed with a pulsed e-beam high-pressure mass spectrometer (PHMS) by which mechanistic information and rate constants can be revealed by measurements of the intensity–time relationships of the ions involved.[26] It will be shown here that the gas-phase reactions of molecular anions with molecular oxygen [reaction (3)] does, indeed, account for the unexpected ions commonly observed under EC conditions. In addition, the rate constants and the ionic product distributions for several of these reactions will be reported. The molecules selected for study here are all relatively

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† Author to whom correspondence should be addressed.
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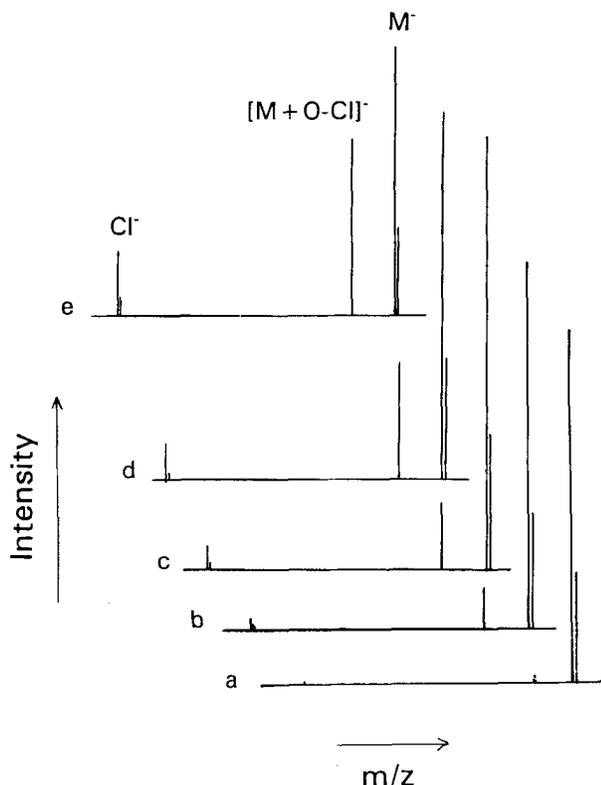
Figure 1. Mass spectral scans showing the three negative ions formed by electron-capture and ion–molecule reactions under the following conditions of the PHPMS ion source: 150 °C, 3 Torr methane buffer gas, 0.010 mTorr p-chloronitrobenzene and (a) 0.0, (b) 0.76, (c) 1.31, (d) 2.43 and (e) 4.77 mTorr oxygen.

Figure 3. Observed frequency, v_{obs}, for the reaction of the molecular anion of p-chloronitrobenzene with oxygen as a function of oxygen concentration at 150 °C. Obtained from the slopes of M⁻ decay curves, such as those shown in Fig. 2 ($v_{obs} = 2.303d(\log$ M⁻ abundance)/dt).

benzene and perchlorobenzene have not been previously reported, EA determinations of these moleculer are also reported.

EXPERIMENTAL

The pulse electron-beam high-pressure mass spectrometer (PHPMS) used has been described in detail previously.[27,28] A gaseous mixture of interest was prepared in high-purity methane buffer gas in an associated gas-handling plant (GHP) and was passed into the ion source at a rate sufficient to maintain a pressure of 3.0 Torr. Pure oxgyen was added to the GHP with a gas-tight syringe.

All halogenated compounds were obtained from commercial suppliers. These were dissolved in toluene to a concentration of about 10 mg ml⁻¹. About 1 μl of this

simple halogenated compounds that are known to undergo EC very rapidly by the resonance mechanism. These include perfluorinated alkanes and benzenes, fluoro- and chloro-substituted nitrobenzenes and highly chlorinated benzenes. From the behavior of the prototype molecular anions to be reported here, predictions of oxygens's reactivity towards many other, more complex EC-active compounds should also be made possible. Because the electron affinities of pentachloro-

Figure 2. Intensity of the molecular anion peak of p-chloronitrobenzene as a function of time after the e-beam pulse under the same conditions as described in Fig. 1

Figure 4. Illustration of the determination of the equilibrium constant for the electron transfer reaction, $C_6Cl_6^- + p$-FNB = $C_6Cl_6 + p$-FNB⁻. Ion source contained 0.053 mTorr C_6Cl_6 and 0.014 mTorr p-FNB in 3.0 Torr methane at 35 °C.

solution was then syringe injected into the GHP. Ion-ization with the ECMS ion source was initiated by an electron gun that provided ten pulses per second of 3 kV electrons to the ion source. The negative ions then produced by EC and subsequent ion–molecule reactions were individually detected by a quadrupole mass filter (Extrel, Model C-50) and an ion-counting channeltron electron multiplier detector (Galileo Electro-optics, Model 487OE). The time dependence of the intensity of each ion was determined by use of multi-channel scaler (Ortec, Model 913) that was synchronized with the pulsed e-beam. Illustrations of typical measurements are provided below.

In Fig. 1, a determination of the ionic products of reaction (3) for the case of p-chloronitrobenzene is illustrated. A series of mass spectral scans is shown where the concentration of O_2 in the methane buffer gas at 3 Torr pressure was progressively increased. It is noted that the abundances two ions, Cl^- and $[M + O - Cl]^-$, are continuously increased by added oxygen. The fact that the relative abundances of these two ions are constant for all oxygen concentrations suggests that these two ions are formed from a single, branched reaction.

In Fig. 2, the means by which rate constants for reaction (3) were determined is illustrated again for the case of p-chloronitrobenzene. It is seen that the rate at which the abundance of M^- decreases with time after each e-beam pulse is increased by added oxygen. In Fig. 3, the reaction frequency, $v_{obs} = 2.303d(\log [M^-]/dt$, is plotted against $[O_2]$. A straight line is obtained, in agreement with the expectation that $v_{obs} = k_3[O_2] + v_d$, where v_d is the first-order rate constant for diffusion of the M^- ion to the walls of the ion source. Therefore, k_3 is obtained from the slope of the line in Fig. 3.

In Fig. 4, the means by which electron affinities were determined is illustrated for the case of perchloro-benzene (C_6Cl_6) where p-fluoronitrobenezene (p-FNB) was also added to the ion source. Under the conditions shown, a state of chemical equilibrium for the electron-transfer reaction, $C_6Cl_6^- + p$-FNB $= C_6Cl_6 + p$-FNB$^-$; is reached at about 10 ms following the e-beam pulse. After 10 ms, the abundance ratio of the two ions observed is held constant by this reaction. From this abundance ratio and the known concentrations of neutral species within the ion source, the equilibrium constant, $K = [C_6Cl_6][p$-FNB$^-]/[C_6Cl_6^-][p$-FNB], for the electron-transfer reaction was obtained.[26]

RESULTS AND DISCUSSION

Electron capture by oxygen

In the PHPMS measurements described here, the O_2^- ion was not of significant relative abundance even though as much as 2000 ppm of O_2 was added to the buffer gas in some of the experiments. Therefore, it seems unlikely that reaction (2) contributes significantly to the production of unexpected ions in EC mass spectra under CI conditions. An explanation for the unimportance of O_2^- and reaction (2) under the present CI conditions can be obtained by consideration of known thermodynamic and kinetic characteristics of oxygen's EC reaction.

Oxygen's EC mechanism is more appropriately represented by reaction (4) rather than reaction (1):

$$e + O_2 \underset{B}{\overset{B}{\rightleftharpoons}} O_2^- \qquad (4)$$
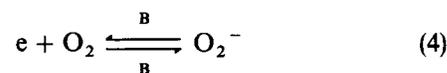
Molecular oxygen has an electron affinity [about 0.44 eV (Ref. 29)] that is significantly lower than that of most compounds for which the ECMS technique is used. Therefore, the destruction rate of collisionally stabilized O_2^- by thermal electron deteachment [the reverse of reaction (4)] can be of significant magnitude, especially at elevated ion source temperatures. The maximum concentration ratio, $[O_2^-]/[e]$, that can be created within an ion source will be determined by the equilibrium constant, K_4:[30,31]

$$K_4(\text{cm}^3) = [O_2^-]/[e][O_2] = 2.6 \times 10^{-16}T^{-3/2}e^{4990/T}$$

$$(5)$$

where T is absolute temperature. Under standard CI conditions where the buffer gas at about 1 Torr total pressure contains about 1.0 ppm of O_2, the maximum $[O_2^-]/[e]$ equilibrium ratio that can be achieved will only be about 7×10^{-3}, 9×10^{-5} and 6×10^{-6} at 50, 150 and 250 °C, respectively [from Eqn (5)].

Kinetic details of reaction (4) should also be considered. Unlike the second-order EC reactions of typical EC-active molecules, M, summarized above (reaction (1)), EC by O_2 is third order and dependent on the total pressure of the buffer gas, B, at the pressures of interest here. The second-order rate constant for the reverse of reaction (4) has been measured in nitrogen buffer gas[30] and is given by

$$k_{-4}(\text{cm}^3 \text{ s}^{-1}) = 3.6 \times 10^{-15}T^{3/2}e^{-4990/T} \qquad (6)$$

From the relationship $K_4 = k_4/k_{-4}$ and Eqns (5) and (6), the third-order rate constant for electron capture by oxygen is therefore expected to be independent of temperature and is given by

$$k_4(\text{cm}^6 \text{ s}^{-1}) = 9.4 \times 10^{-31} \qquad (7)$$

While this expectation for k_4 strictly applies to nitrogen buffer gas, it should also provide a good estimate of k_4 in methane buffer gas. From Eqn (7), the pseudo-second-order rate constant ($k_4' = k_4[B]$) for EC by O_2 under CI conditions (1 Torr) is expected to be about 3×10^{-14} cm^3 s^{-1}. This second-order rate constant is approximately 6–7 orders of magnitude smaller than those of most EC-active compounds[7] and indicates that the production of O_2^- by the forward direction of reaction (4) will be relatively slow under normal CI conditions at all temperatures. These kinetic considerations therefore provide an additional reason why consecutive reactions (4) and (2) are probably not important in influencing the EC mass spectra obtained under typical CI conditions.

Rate constants for reactions of molecular anions with oxygen

Of the 17 EC-active compounds studied here, the molecular anions of 11 of these were found to be unreactive towards O_2 under the present experimental conditions, where up to 5 mTorr O_2 were added to the ion source. An upper limit of about $k_3 < 1 \times 10^{-13}$ cm^3

s^{-1} was thereby deduced for these unreactive compounds, which included sulfur hexafluoride (SF$_6$), perfluoromethylcyclohexane (C$_7$F$_{14}$), cis- and trans-perfluorodecaline (C$_{10}$F$_{18}$), m-chloronitrobenzene, o-, m- and p-fluoronitrobenzene and o-, m- and p-dinitrobenzene. The six compounds whose molecular anions were found to be reactive towards oxygen are listed in Table 1 along with the rate constant, k_3, for each. m-Chloronitrobenzene is also included in Table 1 in order to represent the maximum estimated reactivities of the non-reactive molecular anions. The reaction efficiency (the percentage of M$^-$–O$_2$ collisions that result in reaction) for each reaction is also indicated. As expected,[12,25] o- and p-chloronitrobenzene do react with O$_2$, but with relatively low efficiency (<1%). The reactions of perchlorobenezene (C$_6$Cl$_6$), pentachlorobenzene (C$_6$Cl$_5$H), perfluorobenzene (C$_6$F$_6$) and perfluorotoluene (C$_6$F$_5$CF$_3$) are significantly faster with reaction efficiencies ranging from 5% to 21%.

It is noted in Table 1 that for those reactions that were studied at two temperatures (150 and 35 °C), k_3 is consistently about twice as great at the lower temperature. More extensive measurements of the temperature dependence of the reactions of C$_6$Cl$_6$$^-$ with O$_2$ were also made and these data are shown in Fig. 5 in the form of an Arrhenius plot (which assumes that the temperature dependence of a rate constant will take the form $k = A\exp(-E_a/RT)$, where A is a constant and E_a is the activation energy). By least-squares treatment of the data shown in Fig. 5, a negative activation energy of $E_a = -1.4$ kcal mol^{-1} was obtained (1 kcal = 4.184 kJ).

Products of reactions of molecular anions with oxygen

The ionic products produced by reaction (3) are also listed in Table 1. For o- and p-chloronitrobenzene, the ion [M + O − Cl]$^-$ is observed, as expected.[12,25] The neutral product simultaneously formed with this ion can be assumed to be molecular ClO,[12] since the production of O and Cl atoms would be prohibitively endothermic. The present investigation also reveals, however, that the Cl$^-$ ion is formed in the reactions of o-ClNB$^-$ and p-ClNB$^-$ with O$_2$. The measurements for p-ClNB indicate that the relative amount of Cl$^-$ ion formed is greatly increased with increased temperature.

Table 1. Rate constants and products in the reactions of various molecular anions with molecular oxygen, M$^-$ + O$_2$ → products

Compound (EA)[a]	T (°C)	$k_3 \times 10^{11}$ [b]	Efficiency[c] (%)	Product ions[d]
o-ClNB[e] (1.2)	150	0.12	0.21	Cl$^-$ (63%)
				[M + O − Cl]$^-$ (37%)
m-ClNB (1.3)	150	<0.01[f]	<0.02	None detected
p-ClNB (1.3)	150	0.14	0.24	[M + O − Cl]$^-$ (66%)
				Cl$^-$ (34%)
	35	0.28	0.49	[M + O − Cl]$^-$ (95%)
				Cl$^-$ (5%)
C$_6$Cl$_6$ (1.0)	150	3.1	5.3	[M + O − Cl]$^-$ (94%)
				Cl$^-$ (6%)
	35	5.3	9.8	[M + O − Cl]$^-$ (94%)
				Cl$^-$ (6%)
C$_6$Cl$_5$H (0.7)	35	12	21	[M + O − Cl]$^-$ (79%)
				Cl$^-$ (21%)
	150	—[g]	—[g]	[M + O − Cl]$^-$ (64%)
				Cl$^-$ (36%)
C$_6$F$_6$ (0.52)	35	10	17	F$^-$ (42%)
				[M − C$_2$F$_2$]$^-$ (29%)
				[M + O − CF$_2$]$^-$ (15%)
				[M − C$_2$F$_4$]$^-$ (10%)
				[M + O − CF]$^-$ (4%)
C$_6$F$_5$CF$_3$ (0.94)	150	3.5	6.0	[M + O − CF$_2$]$^-$ (75%)
				[M + 2O − CF$_3$]$^-$ (10%)
				[M + O − CF]$^-$ (10%)
	35	5.5	9.5	[M + O − CF$_2$]$^-$ (75%)
				[M + 2O − CF$_3$]$^-$ (10%)
				[M + O − CF]$^-$ (10%)

[a] The electron affinities listed here were obtained from Ref. 33, except for those of C$_6$Cl$_5$H and C$_6$Cl$_6$, which were determined here.
[b] Rate constants determined here for reaction (3).
[c] The reaction efficiency (Eff) was determined by Eff = $100k_3/k_c$, where k_c is the calculated collision rate constant.[34] For all reaction (3)s studied here, $k_c = 5.8 \times 10^{-10}$ cm^3 s^{-1}.
[d] For the cases of perfluorobenzene and perfluorotoluene, several additional ions of minor relative abundance were also observed.
[e] NB = nitrobenzene.
[f] No reaction was detected. The value indicated is an estimate of the detection limit for determination of k_3.
[g] This rate constant could not be reliably measured at 150 °C because thermal electron detachment[32] is the dominant means of C$_6$Cl$_5$H$^-$ loss at this temperature.

Figure 5. Rate constant measured for reaction of $C_6Cl_6^-$ with O_2 a function of inverse temperature. From these data, a negative activation energy $E_a = -1.4\ \text{kcal mol}^{-1}$ is deduced.

Although the formation of Cl^- ion was noted in previous studies of these reactions, its origin was not known and was suggested to be by a subsequent electron-capture reaction involving the neutral product, ClO.[12] The present study clearly indicates, however, that the complete reaction (3) for o- and p-chloronitrobenzene is the following:

$$M^- + O_2 \rightarrow [MO_2]^- \begin{cases} \rightarrow [M + O - Cl]^- + ClO & (8a) \\ \rightarrow Cl^- + [M + 2O - Cl] & (8b) \end{cases}$$
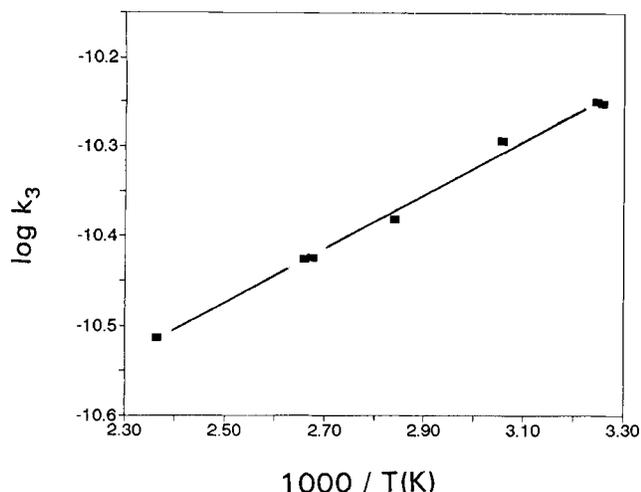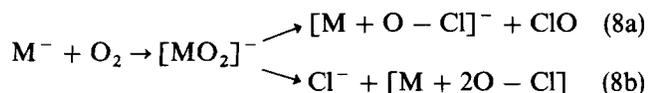
The intermediate species, $[MO_2]^-$, in reaction (8) has been envisioned[12] to result from a nucleophilic attach by O_2 on the carbon atom to which the chlorine atom is attached resulting in the following structure (shown for the case of p-ClNB):
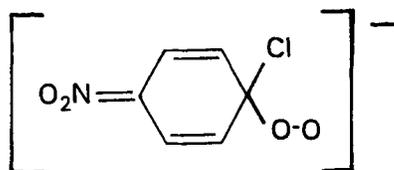
The fact that this type of structure cannot be written for the *meta* isomer of chloronitrobenzene probably accounts for the nonreactivity of m-ClNB$^-$ with oxygen. The most likely structure envisioned for the odd-electron neutral product shown in reaction (8b), $[M + 2O - Cl]$, would be the following (again shown for the case of p-ClNB), in which the O_2 moiety has bridged the benzene ring:
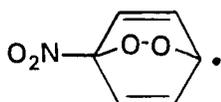
The fact that the Cl^- ion is the major ionic product observed for the case of o-ClNB at 150 °C might be explained by a greater stability of the $[M + 2O - Cl]$ species for this isomer where the O_2 moiety would be expected to bridge across the 2- and 5-positions of nitrobenzene instead of the 1- and 4-positions, as shown for the case of the *para* isomer.

The two ionic products formed in the more efficient reactions of $C_6Cl_6^-$ and $C_6Cl_5H^-$ with O_2 are also ions of the types $[M + O - Cl]^-$ and Cl^- (Table 1). Therefore, the mechanism of these reactions appears to be the same as the branched reaction (8a/8b) discussed above for the cases o- and p-chloronitrobenzene.

The molecular anions of perfluorobenzene and perfluorotoluene react very efficiently with oxygen to form a relatively diverse set of product ions, the major ones of which are listed in Table 1. An interesting feature of these data is that whereas F^- is the major ionic product of the reaction of $C_6F_6^-$ with O_2, F^- was not formed in the reaction of $C_6F_5CF_3^-$ with O_2. Additional experiments concerning the reaction of $C_6F_6^-$ with O_2 in carbon dioxide buffer gas have been reported previously[32] and are in good agreement with those reported here.

Electron affinities of C_6Cl_6 and C_6Cl_5H

Since the electron affinities (EA) of C_6Cl_6 and C_6Cl_5H have not been previously reported, EA measurements of these two compounds were made here by the electron-transfer equilibrium method described under Experimental. For the case of C_6Cl_6, measurements of the equilibrium constant were made with p-fluoronitrobenzene (p-FNB) as a reaction partner over the temperature range from 35–150 °C ($K_{eq} = [C_6Cl_6][p\text{-}FNB^-]/[C_6Cl_6^-][p\text{-}FNB]$). In Fig. 6 these data are plotted in the form of a Van't Hoff plot. From the expected relationship, $\ln K_{eq} = -\Delta H^\circ/RT + \Delta S^\circ/R$, the standard enthalpy for this reaction, $\Delta H^\circ = 4.7\ \text{kcal}$ mol^{-1}, was obtained from the slope of the plot and and the standard entropy change of the reaction, $\Delta S^\circ = -10.7\ \text{cal K}^{-1}\ \text{mol}^{-1}$, was obtained from the intercept. Since ΔH° is expected[33] to be equal to the difference in the electron affinities of C_6Cl_6 and p-FNB, and since the EA of p-FNB is 25.8 kcal mol^{-1}, the EA of C_6Cl_6 is determined to be 21.1 kcal mol^{-1} (0.91 eV). Since the entropy of negative ionization ($M \rightarrow M^-$) for p-FNB is expected to be about -2 ± 2 cal K^{-1} mol^{-1},[33] the entropy change associated with the nega-
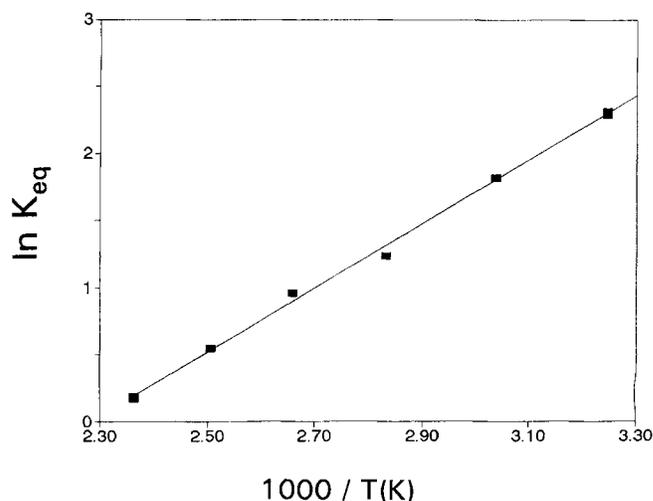
Figure 6. Equilibrium constant measured for the electron transfer reaction, $C_6Cl_6^- + p\text{-}FNB = C_6Cl_6 + p\text{-}FNB^-$, as a function of inverse temperature.

tive ionization of C_6Cl_6 is deduced to be about $+9 \pm 2$ cal K^{-1} mol^{-1}. Although this magnitude of entropy change upon negative ionization is unusually large, a similarly large entropy of negative ionization has also been observed for the closely related compound, C_6F_6 ($+8$ cal K^{-1} mol^{-1}), and was attributed to a significant loss of symmetry in the anion relative to that of the parent molecule.[33]

The EA of C_6Cl_5H was also determined here by measurement of its electron transfer equilibria using azulene as a reaction partner at $35\,°C$. Azulene was chosen because its electron affinity is near that predicted for C_6Cl_5H and it is known to undergo rapid electron transfer with a partner of similar EA.[33] Since the EA of C_6Cl_5H is relatively low, thermal electron detactment of

C_6Cl_5H was too fast as to allow accurate equilibrium measurements to be made at elevated ion source temperatures. From the measurements of $K_{eq} = 2.1$ for this reaction at $35\,°C$, $\Delta G° = -RT\ln K_{eq} = -0.44$ kcal mol^{-1} is deduced. Along with the assumption that $\Delta S° = 0$ for this reaction, and the knowledge that EA of azulene is 15.9 kcal mol^{-1},[33] the EA of C_6Cl_5H is determined here to be 16.8 kcal mol^{-1} (0.73 eV).

Acknowledgement

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