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Electron Affinities of Perfluorobenzene and Perfluorophenyl Compounds

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Abstract: The electron affinities of C_6F_6 (0.52 eV), C_6F_5CN (1.1 eV), C_6F_5–C_6F_5 (0.91 eV), $C_6F_5CF_3$ (0.94 eV), $C_6F_5COCH_3$ (0.94 eV), $(C_6F_5)_2CO$ (1.61 eV), and 1,4-$(CN)_2C_6F_4$ (1.89 eV), estimated error ±0.1 eV, were determined by measuring gas-phase electron-transfer equilibria, $A^- + B = A + B^-$ (eq 1), with a pulsed electron high-pressure mass spectrometer. A represents the perfluoro compounds, while B represents standards, i.e., compounds like nitrobenzenes and quinones whose electron affinity had been determined earlier in this laboratory. The determinations for C_6F_6 and C_6F_5CN are based on the determination of the temperature dependence of K_1 and $\Delta H_1°$ values from van't Hoff plots. For the other compounds the assumption $\Delta H_1° \approx \Delta G_1°$ was made. The EA(C_6F_6) = 0.52 eV value is much lower than the literature value of Lifshitz and Tiernan, EA(C_6F_6) ≥ 1.8 eV. It was found that electron-transfer equilibrium 1 to C_6F_6 and from $C_6F_6^-$, when exothermic, proceeds at near collision limit, i.e., near ADO rates. This indicates that $(C_6F_6^-)^*$ of geometry equal to C_6F_6 is not of much higher energy than the vibrational ground state of $C_6F_6^-$. The measured entropy change $S°(C_6F_6^-) - S°(C_6F_6) = 7.4$ cal/(deg mol) is probably largely due to a change of symmetry between C_6F_6 (rotational symmetry number $\sigma = 12$) and $C_6F_6^-$ ($\sigma = 1$ or 2).

The electron affinity of hexafluorobenzene is of special interest in connection with the perfluoro effect.[1] Studies of the photoelectron spectra and the energies of occupied molecular orbitals of unsaturated and aromatic compounds have indicated that perfluoro substitution decreases the energy of the π orbitals only slightly but lowers significantly the energy of σ-type orbitals.[1,2] The perfluoro effect can be explained on the basis of the well-known substituent effects. The fluorine atom is strongly electron withdrawing by the field-inductive effect and weakly electron pair donating (π donation). Thus, fluorine substitution can be expected to be strongly stabilizing to σ-type orbitals, while the combined field effect stabilization and opposing π donation can have only a moderately net stabilizing effect on π-type orbitals.

The benzene radical anion is of interest in experimental organic chemistry as the species formed in the first stage of the Birch[3] reduction of benzene by solvated electrons in ammonia solution. It is also of theoretical interest since addition of an electron to benzene leads to a typical Jahn-Teller situation. Examination of the π molecular orbitals in benzene shows that the added electron can be accommodated in either one of the pair of degenerate e_{2u} (π^*) orbitals. The system distorts under such circumstances, splitting into two components, ^2A_u and ^2B_u, for which structures of lower symmetry (D_{2h}) are predicted by molecular orbital calculations.[4,5] In the gas phase benzene does not form a stable negative ion on electron capture,[6] and therefore the symmetry of that ion is not easily determined by experiment. On the other hand, C_6F_6 does form a stable $C_6F_6^-$ ion, and if the electron is in a π^* type of orbital, one would expect a Jahn–Teller distortion. This would lead to a loss of symmetry which could be detected experimentally.

According to Radom,[4,5] single fluorine substitution in benzene lowers the energy of the lowest unoccupied π^* orbital and increases the electron affinity by ~6 kcal/mol, the structure of the ring in the negative ion remaining distorted as in $C_6H_6^-$ (D_{2h}). Unfortunately Radom's calculations were not of sufficient accuracy to provide absolute electron affinities. Electron transmission spectroscopy measurements have shown that the $C_6H_6^-$ ion is unstable in the gas phase, i.e., has a negative electron affinity of −1.15 eV. The electron affinity for C_6H_5F was found to be −0.89 eV.[6b] The predicted increase of EA with single fluorine substitution is thus 0.26 eV or ~6 kcal/mol in agreement with Radom's[4,5] result.

Increased fluorine substitution in benzene increases the electron affinity[6d,7] such that at some high fluorine content the electron affinity becomes positive. Stable $C_6F_6^-$ have been observed in the gas phase, and electron affinity determinations have been performed.[8,9] The most recent determination,[9] which is generally quoted in the literature, is EA(C_6F_6) ≥ 1.8 eV (41.5 kcal/mol). This value is much higher than the value that one could deduce by the naive assumption that each fluorine increases the electron affinity by the same amount (0.26 eV) so that six F would increase the electron affinity by 1.56 eV, i.e., from EA(C_6H_6) ≈ −1.15 eV to EA(C_6F_6) ≈ +0.41 eV.

Some structural information on $C_6F_6^-$ is available from ESR measurements in solution and from theoretical calculations. Symons,[10] on the basis of ESR coupling constant magnitudes, has suggested that $C_6F_6^-$ has a highly distorted structure, the carbon skeleton being similar to the chair form of cyclohexane. It was also suggested[10] that the extra electron resides in a σ^*-type orbital in line with the perfluoro effect and earlier arguments by Yim and Wood.[11] However, a more recent and more detailed theoretical examination by Shchegoleva[12] points out a structure that leads to better agreement with the coupling constants. This is a planar carbon structure containing out-of-plane C–F bonds. The extra electron occupies a π^*,σ^* combination orbital in which the π^* component prevails.[12]

Recently, we were able to determine the electron affinities of a large number of molecules by means of electron-transfer equilibria (eq 1) measurements.[13-15] Determination of the

$$A^- + B = A + B^- \qquad (1)$$

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Table I. Results from Electron-Transfer Equilibria[a] at 150 °C (Reaction 1)

A[b]	$\Delta G_1°$	$-\Delta G_4°$(A)	$-\Delta G_4°$(B)
B = $(C_6F_5)_2CO$			
4-CNNB	+1.3	38.7	37.4
3-NO_2NB	−0.2	36.9	37.1
3-CNNB	−2.1	34.8	36.9
3-CF_3NB	−5.3	31.6	36.9
$-\Delta G_4°((C_6F_5)_iCO$			37.1
B = $C_6H_5COCH_3$			
4-FNB	+3.0	25.0	22.0
NB	+1.0	22.8	21.8
2-MeNB	−1.0	20.7	21.7
4-MeONB	−0.9	20.3	21.2
2,3-$(CH_3)_2$NB	−2.3	19.4	21.7
$-\Delta G_4°(C_6F_5COCH_3)$			21.7
B = $C_6F_5CF_3$			
2-FNB	+2.2	24.2	22.0
NB	+1.5	22.8	21.3
2,3-$(CH_3)_2$NB	−2.0	19.4	21.4
$-\Delta G_4°(C_6F_5CF_3)$			21.6
B = $(C_6F_5)_2$			
3-MeNB	+1.3	22.1	20.8
2-MeNB	−0.2	20.7	20.9
2,3-$(CH_3)_2$MeNB	−1.6	19.4	21.0
$-\Delta G_4°(C_6F_5)_2$			20.9

[a] All numerical results in kcal/mol, at 150 °C (423 K), $\Delta G_4°$(B) is free energy change for reaction 4. Stationary electron convention and neglect of spin multiplicity of electron lead to $\Delta S_4°(B) = S°(B^-) - S°(B)$. [b] Reference compounds whose $\Delta G_4°$(A) was determined in previous work.[13,15] NB stands for nitrobenzene.

equilibrium constant K_1 is obtained with a pulsed electron high-pressure mass spectrometer. Capture of secondary electrons produced by the ionizing pulse leads to formation of A^- and B^-. These then engage in electron-transfer reaction 1 which reaches equilibrium 1. Determination of K_1 leads to $\Delta G_1°$; see eq 2. In

$$\Delta G_1° = -RT \ln K_1$$

$$\Delta G_1° = \Delta H_1° - T\Delta S_1°$$

$$\Delta H_1° = \mathrm{EA(A)} - \mathrm{EA(B)} \qquad (2)$$

favorable cases the temperature dependence of K_1 can be determined also and $\Delta H_1°$ and $\Delta S_1°$ can be obtained from van't Hoff plots. When a number of equilibria as in eq 1 are measured, a ladder (scale) of relative EA can be established which is then calibrated by anchoring it at one point to the known electron affinity of one compound (SO_2).

The $\Delta S_1°$ values, when available, provide information on the geometry changes attendant in the formation of the negative ions. Thus equilibria measurements (eq 1) involving C_6F_6 could yield not only the electron affinity of this compound but also indicate geometry changes on formation of $C_6F_6^-$.

In the present work, determinations involving several substituted perfluorobenzenes were performed also. These provide the changes of the electron affinity on perfluorination of substituted benzenes. Since some of the trends in the EA changes can be predicted on the basis of expected substituent effects, these data, while interesting in their own right, provide an additional confirmation of the C_6F_6 electron affinity determination.

Experimental Section

The present and earlier measurements[13-15] were performed with the same instrument. A mixture of gases with suitable composition flows slowly through the thermostated ion source–reaction chamber. A short pulse (10–50 μs) of 2000-V electrons produces positive ions and secondary electrons. At the ~4-torr gas pressure used, carrier gas CH_4 (~4 torr), thermalization of the secondary electrons is rapid. Near thermal electrons are captured by the compounds A and B present at millitorr partial pressures in the ion source. Collisional deactivation of the resulting $(A^-)^*$ and $(B^-)^*$ by the major gas leads to thermal A^- and B^-. These engage in the electron-transfer reaction (1). The number densities of the ions are low such that the dominant loss of charge is due to the diffusion to the wall. Ambipolar positive–negative ion diffusion to the wall is established ~100 μs after the electron pulse. Within a similar time the fundamental diffusion mode is established also. The ion intensities in the ion source are determined by measuring the wall current, i.e., bleeding the gas mixture through a narrow slit into an evacuated region where the ions are mass analyzed and detected and time analyzed with a multiscaler.

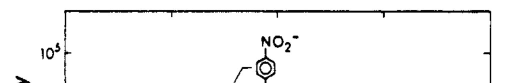

Figure 1. Time dependence of intensities of major ions observed after ionizing electron pulse. The ion source at 150 °C contains 3-torr CH_4 bath gas, 0.5-mtorr 4-cyanonitrobenzene gas, and 11.9-mtorr C_6F_5CN gas. Rapid disappearance of the $C_6F_5CN^-$ ion is due to the reaction $C_6F_5CN^- + 4\text{-CNNB} = C_6F_5CN + 4\text{-CNNB}^-$. The slope of the logarithmic plot of $C_6F_5CN^-$ gives the reaction frequency (pseudo-first-order rate constant) $\nu_1 = k_1[4\text{-CNNB}]$.

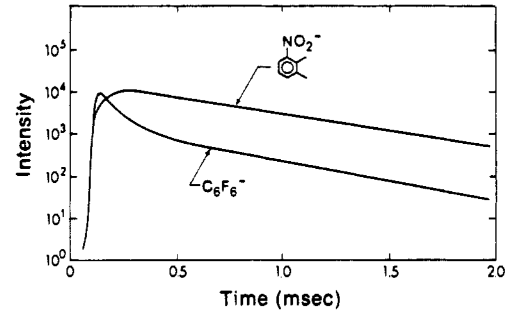

Figure 2. Time dependence of intensities observed after ionizing pulse. The ion source at 116 °C contains 4.5-torr CH_4, 0.12-mtorr 2,3-$(CH_3)_2$NB, and 14-mtorr C_6F_6 gases. After a short kinetic stage where some of the $C_6F_6^-$ is involved in net electron transfer to 2,3-$(CH_3)_2$NB, the reaction $C_6F_6^- + 2,3\text{-}(CH_3)_2NB = C_6F_6 + 2,3\text{-}(CH_3)_2NB^-$ reaches equilibrium. The constant intensity ratio of the two ions in equilibrium appears as a constant distance between the curves in the logarithmic plot used.

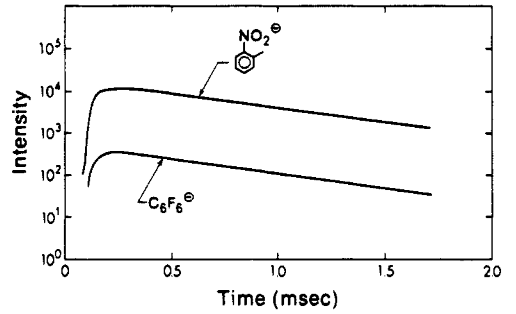

Figure 3. Time dependence of ion intensities observed after ionizing pulse. Ion source temperature = 152 °C, bath gas CH_4 = 4 torr, C_6F_6 = 49 mtorr, 2-MeNB = 4.8 mtorr. Ions reach equilibrium more rapidly than in Figure 2 due to the higher concentration of neutral reactants.

Measurements and Results

The measured $\Delta G_1°$ values at 150 °C for equilibrium I involving all C_6F_5X except C_6F_6 and C_6F_5CN are summarized in Table I. The temperature 150 °C, at which also the earlier

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Table II. Rate Contants for Exothermic Electron-Transfer Reactions (1) Involving Perfluorophenyl Compounds[a]

	A	B	$-\Delta G_1°$	10^9k
1.	C_6F_6	2,3-$(CH_3)_2$NB	4.6	2.0
2.	C_6F_5CN	4-CNNB	11.7	1.4
3.	C_6F_5CN	3-CF_3NB	4.6	2.6
4.	C_6F_5CN	3-ClNB	1.8	1.3
5.	C_6F_5CN	4-ClNB	1.2	1.0
6.	2-ClNB	C_6F_5CN	1.3	1.9
7.	C_6F_5CN	3-FNB	1.0	0.9

[a] Free energy change for reaction 1 in kcal/mol. Rate constant in cm^3 molecule^{-1} s^{-1}. Abbreviation NB stands for nitrobenzene.

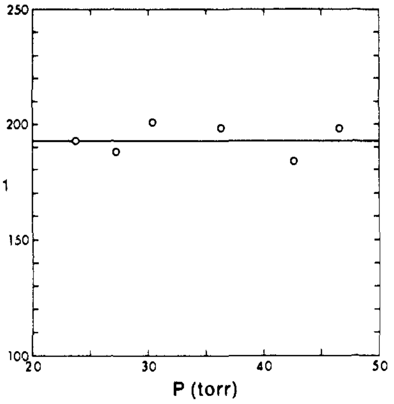

Figure 4. Independence of equilibrium constant K_1 for the reaction $C_6F_6^-$ + 2,3-$(CH_3)_2$NB = C_6F_6 + 2,3-$(CH_3)_2NB^-$. Total ion source pressure changed at constant $P(C_6F_6)/P$(2,3-$(CH_3)_2$NB) = 5.8. Ion source temperature, 150 °C.

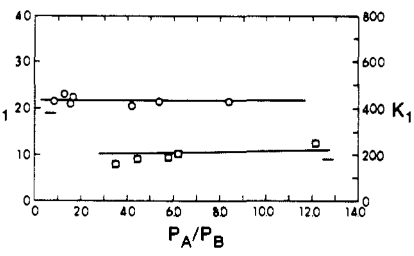

Figure 5. Independence of equilibrium constant K_1 for reaction 1 with P_A/P_B ratios (○) C_6F_5CN and 3-FNB, (□) C_6F_6 and 2,3-$(CH_3)_2$NB.

experiments[13] were performed, was used because at lower temperatures, adducts $(A{\cdot}B)^-$, $(AA)^-$, or $(BB)^-$ form and interfere with the measurements. Some examples of the time dependence of the reactions (eq 1) are given in Figures 1–3.

The time dependence of the ion intensities of $C_6F_5CN^-$ and $4\text{-}CNC_6H_4NO_2^-$ (4-$CNNB^-$) shown in Figure 1 demonstrates the rapid electron transfer from the perfluoro negative ion to 4-CNNB. A rate constant of $k_1 = 1.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} can be deduced[13,14] from these data, for this obviously exothermic reaction. An electron-transfer equilibrium is not reached in this experiment.

$$C_6F_5CN^- + 4\text{-CNNB} = C_6F_5CN + 4\text{-CNNB}^-$$

Several rate constants obtained from runs similar to that shown in Figure 1 and determined by using procedures described previously[13,14] are shown in Table II.

Runs in which electron-transfer equilibria were achieved are shown in Figures 2 and 3. The electron transfer between C_6F_6 and 2,3-$(CH_3)_2$NB is shown in Figure 2. The initial change of intensities is due to net electron transfer from $C_6F_6^-$ to 2,3-$(CH_3)_2$NB. The system reaches equilibrium after some 0.4 ms. At equilibrium the nitrobenzene anion is seen to be dominant over $C_6F_6^-$ even though the neutral C_6F_6 is present at a 100-fold excess over the neutral nitrobenzene. Obviously the EA of C_6F_6 must be considerably lower than EA(2,3-$(CH_3)_2$NB) = 19.8 kcal/mol.[13,15] The electron-transfer equilibrium in Figure 3 is achieved faster than that in Figure 2 due to the higher concentrations of the reactants, C_6F_6 and 2-MeNB. The observed relative ion intensities and the given neutrals concentrations lead to the requirement EA(C_6F_6) < EA(2-MeNB) = 21.3 kcal/mol.[13,15] The $\Delta G_1°$ values evaluated from K_1 obtained in runs like those shown in Figures 2 and 3 are given in Table I.

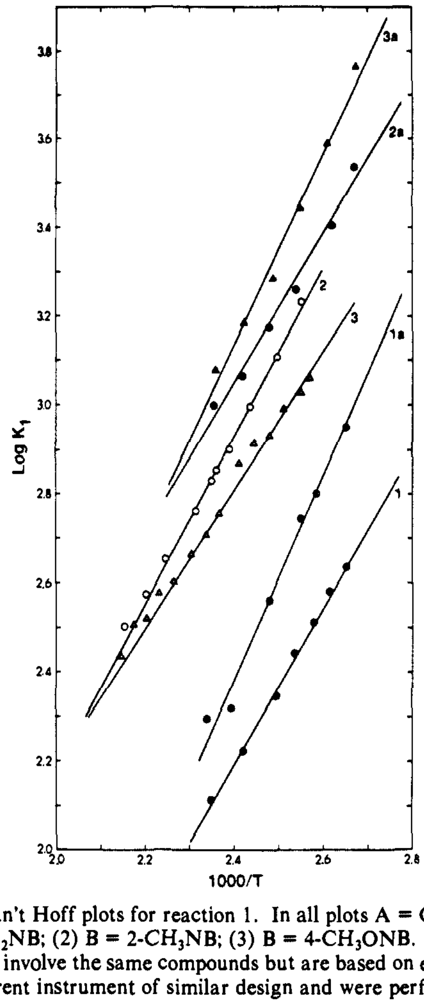

Figure 6. van't Hoff plots for reaction 1. In all plots A = C_6F_6. (1) B = 2,3-$(CH_3)_2$NB; (2) B = 2-CH_3NB; (3) B = 4-CH_3ONB. The 1a, 2a, and 3a plots involve the same compounds but are based on experiments with a different instrument of similar design and were performed by a different investigator. Agreement between two sets of determinations is much poorer than that commonly obtained with systems not involving C_6F_6. $\Delta H°$, $\Delta S°$, and $\Delta G°$ values from these plots are given in Figure 8.

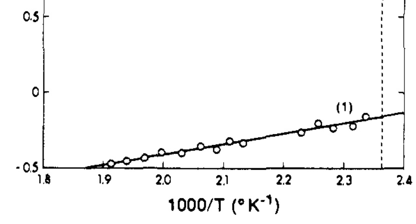

Figure 7. van't Hoff plots for reaction 1. (1) A = C_6F_5CN, B = 3-FNB; (2) A = 4-FNB, B = C_6F_5CN; (3) A = NB, B = C_6F_5CN. $\Delta H°$, $\Delta S°$, and $\Delta G°$ values from these plots are given in Figure 9.

For some systems, it was examined whether the equilibrium constant K_1 remains invariant with the changing total pressure and changing partial pressure ratio P_B/P_A. Examples of such

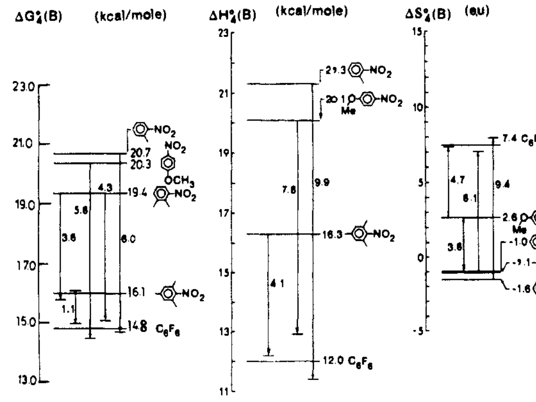

Figure 8. Summary of results obtained from van't Hoff plots of equilibria involving C_6F_6; see Figure 6. The data from two additional van't Hoff plots not shown in Figure 6 are also included. Values given beside the arrows correspond to $\Delta G_1°$, $\Delta H_1°$, $\Delta S_1°$ results obtained for equilibria between compounds shown and C_6F_6. The values of the ordinates correspond to $-\Delta G_4°$, $-\Delta H_4°$, and $\Delta S_4°$ for the compounds B involved in reaction 4. The value given beside C_6F_6 is the average for reaction 4 based on all the measurements shown.

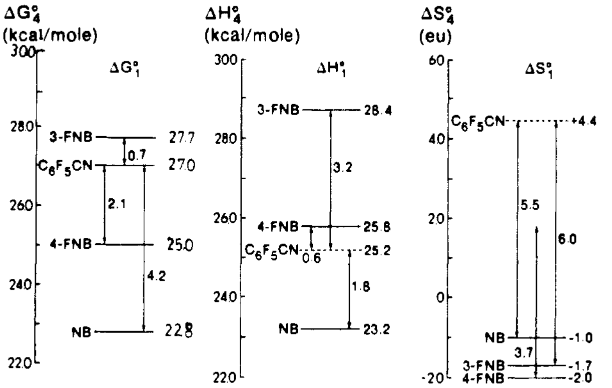

Figure 9. Summary of results from the van't Hoff plots of equilibria involving C_6F_5CN. For explanation of notation, see Figure 8.

measurements are given in Figures 4 and 5.

The temperature dependence of the equilibrium constant K_1 involving equilibria of C_6F_6 and C_6F_5CN with reference compounds was measured in a series of experiments. The resulting van't Hoff plots are shown in Figures 6 and 7. The $\Delta G_1°$, $\Delta H_1°$, and $\Delta S_1°$ values deduced for C_6F_6 are given in Figure 8, while those for C_6F_5CN are in Figure 9.

The available $\Delta G_1°$ data can be converted to $\Delta G_3°$ values for electron transfer from the major reference compound SO_2, and the $\Delta G_3°$ values can be converted to $\Delta G_4°(B)$ values since $\Delta G_4°(SO_2)$ is available.[15] Since $\Delta H_1°$ and $\Delta S_1°$ data were

$$SO_2^- + B = SO_2 + B^- \qquad (3)$$

$$B + e = B^- \qquad (4)$$

determined for C_6F_6 and C_6F_5CN, Figures 6 and 7, one can evaluate $\Delta H_4°$ and $\Delta S_4°$ for these compounds from the known[15] corresponding values for SO_2. The stationary electron convention was used for reaction 4; furthermore, the spin of the free electron was not considered.[15] Therefore $\Delta S_4°(B) = S°(B^-) - S°(B)$.

The electron detachment energy $-\Delta H_4°(C_6F_6)$ deduced from Figure 8 is 12.0 kcal/mol (0.52 eV). This is a very small value, and thermal electron detachment from $C_6F_6^-$, i.e., the reverse of reaction 4, can be expected at temperatures above ~150 °C. A study of the thermal electron detachment rates of the azulene negative ion Az^- was reported recently from this laboratory.[16] The time dependence of $C_6F_6^-$ observed in experiments where only C_6F_6 and the carrier gas were present in the ion source is shown in Figure 10. At short times $C_6F_6^-$ is by far the major ion. Its intensity decreases with time more rapidly than the decrease expected due to diffusion to the wall. Thus, the k_D due to diffusion expected at this temperature[16] is 1100 s^{-1}, while the observed decay rate constant for the initial linear log portion in Figure 10 is 4300 s^{-1}. Material balance considerations show that conversion of $C_6F_6^-$ by ion-molecule reactions into the minor ions m/z 310 $(C_{10}F_{10})^-$, 205 $(C_6F_6{\cdot}F^-)$, 183 $(C_6F_5O^-)$, and other low intensity ions not shown in Figure 10 are only a minor sink for $C_6F_6^-$. This means that the major sink must be thermal electron detachment. This supposition is confirmed by the unusual shape of the intensity curves observed in Figure 10. The linear, logarithmic decay of $C_6F_6^-$ quite suddenly converts to a much bigger negative slope at residence times of ~1.2 ms. In the same conversion region the intensities of the other negative ions are observed to suddenly increase. The very same type of behavior was encountered in the thermal detachment study of Az^- (see Figure 6b, ref 16), and an explanation for it was given in terms of the breakdown of a positive space charge field at low electron detachment rates, i.e., at ~1.2 ms for the conditions in Figure 10. Therefore, the results in Figure 10 positively identify the occurrence of electron detachment from $C_6F_6^-$ at temperatures of 150 °C and above. These results are an independent confirmation of the *low* electron affinity of C_6F_6 deduced from the electron-transfer equilibria measurements: see Figure 8. Had C_6F_6 had a high electron affinity in the 1.7-eV range[9], thermal electron detachment would have been observed[16] only at temperatures several hundreds of degrees higher than 150 °C.

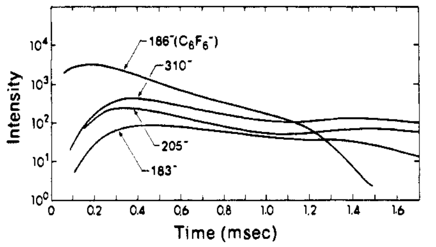

Figure 10. Time dependence of intensities of major ions observed after electron pulse with CH_4, 3 torr, containing C_6F_6, 1.8 mtorr. Temperature, 149 °C. The major $C_6F_6^-$ ion decreases more rapidly than expected since diffusion to the wall and conversion to minor ions m/e 310, etc., are the only loss mechanisms. The major cause for decrease is thermal electron detachment, $C_6F_6^- = C_6F_6 + e$. Due to rapid loss of electrons to the wall, weak positive field is present which traps the negative ions. At ~1.2 ms this field collapses since production of the electrons by detachment is insufficient to maintain it.

The occurrence of electron detachment from $C_6F_6^-$ presents a problem for the measurements of the temperature dependence of electron-transfer equilibria involving C_6F_6. Thus of necessity, the van't Hoff plots cannot be extended to high temperatures where the detachment becomes much more rapid than the electron-transfer equilibria. In the present equilibria measurements, the detachment problem was partially overcome by using reference compounds whose electron affinity was larger than that of C_6F_6. This minimized electron detachment from the reference compound. The equilibria were also operated for neutral ratios, where $C_6F_6^-$ was the minor ion and the reference negative ion the major ion. Furthermore, because of the higher EA of the reference compound, a large pressure ratio of C_6F_6 to the reference compound could be used, and this combined with a deliberate use of relatively large partial pressures for both compounds leads to efficient recapture of detached electrons by reattachment to C_6F_6 and the reference compound. Results obtained under such conditions were shown in Figure 3.

A detailed kinetic analysis combining the electron-transfer kinetics with the electron detachment-attachment and ion diffusion loss kinetics (see azulene[16]) is possible but was not performed.

The van't Hoff plots involving C_6F_6, see Figure 6, include data where a given equilibrium system was remeasured on a different apparatus of similar design and by a different researcher in our laboratory. The reproducibility of the data for C_6F_6 seen in Figure 7 by the two measurements is considerably worse than that

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[16] Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3983.

Table III. Summary[a] of Thermochemical Data for $C_6F_5X^-$

B	$-\Delta G_4°$(B), kcal/mol	$-\Delta H_4°$(B), kcal/mol	$\Delta S_1°$(B), cal/deg
1,4-$(C_N)_2C_6H_4$	43.5 ± 1		
$(C_6F_5)_2CO$	37.1 ± 1		
C_6F_5CN	27.0 ± 1	25.0 ± 1	+4.4 ± 2
$C_6F_5COCH_3$	21.7 ± 1		
$C_6H_5CF_3$	21.6 ± 1		
$(C_6F_5)_2$	20.9 ± 1		
C_6F_6	14.8 ± 1	12.0 ± 2[b] 11.7 ± 2[c]	+7.4 ± 2

[a] From Table I and Figures 7 and 8. [b] From average $\Delta H_4°$, Figure 7. [c] From $\Delta H_4° = \Delta G_4° + T\Delta S_4°$ where $\Delta S_4°$ and $\Delta G_4°$ are the average values from Figure 8.

Table IV. Substituent Effect[a] of X in $C_6H_5NO_2$ and C_6F_6

X	XNB	XC_6F_5
H resp. F	22.8 (0)	14.8 (0)
4-CN	38.7 (15.9)	27.0 (12.2)
3-CN	34.8 (12.0)	
3-CF_3	31.6 (6.8)	21.6 (6.8)
3-$COCH_3$	29.3 (~6.5)	21.7 (6.9)

[a] All values relate to $-\Delta G_4°(B) \approx EA(B)$ in kcal/mol, where B are the substituted nitrobenzenes and perfluorobenzenes. The values in parentheses give the difference between $\Delta G_4°(NB) - \Delta G_4°(XNB)$ in the left column and $\Delta G_4°(C_6F_6) - \Delta G_4°(XC_6F_5)$ in the right column.

Table V. Comparison of Electron Affinities of Hydrogen and Perfluorophenyl X Compounds

EA, kcal/mol[a]		ΔEA, kcal/mol[b] tot ΔE	ΔEA, kcal/mol[b] tot ΔE/no. of F
C_6H_6, ~ −26.4[c]	C_6F_6, 14.8	41.2	6.9 (6)[d]
C_6H_5CN, ~5.5[e]	C_6F_5CN, 27.0	21.5	4.3
$C_6H_5COCH_3$, ~7.7[e]	$C_6F_5COCH_3$, 21.7	14.0	2.8
$(C_6H_5)_2CO$, 15.3	$(C_6F_5)_2CO$, 37.1	21.8	2.2
1,3-$(CN)_2C_6H_4$, 26.7	1,4-$(CN)_2F_4$, 43.5	16.8	4.2

[a] Since electron attachment enthalpies $\Delta H_4°$ are available only for C_6F_6 and C_6F_5CN, we are using in this table the assumption $-\Delta G_4° \approx$ EA. The values for $\Delta G_4°$ are taken from Table III. [b] The numbers in the second column give the total ΔEA divided by the number of F atoms introduced on perfluorination. [c] Burrow.[6d] [d] Electron affinity difference between C_6H_6 and C_6H_5F according to Radom[4,5] and Burrow and Jordan.[6] [e] Chen and Wentworth.[18]

generally found for other systems.[15] Part of the fault probabily lies in the electron detachment problem and the careful choice of conditions required. Another difficulty was the observed occurrence of side reactions in the presence of traces of oxygen ($P_{O_2} > 5 \times 10^{-5}$ torr). Traces of O_2 led to production or increase of intensities of the following ions: *m/z* 152 ($C_5F_4O^-$), 171 ($C_5F_5O^-$), 183 ($C_6F_5O^-$), 205 ($C_6F_6{\cdot}F^-$), 272 ($C_{10}F_8^-$), 310 ($C_{10}F_{10}^-$). A minor leak in the gas handling plant of the instrument, on which the majority of the measurements were performed, led to a presence of oxygen at the 10^{-4}-torr level. While it is believed that the above reactions were still too slow to affect the results, part of the scatter in the van't Hoff data obtained with the two instruments may be due to this cause.

The observed reactions of $C_6F_6^-$ with O_2 are of general interest and are presently under investigation.

Discussion of Results

(a) Rate Constants for Electron Transfer. The rate constants for electron transfer shown in Table II are close to the collision values predicted by the ADO theory.[17] The decrease of the calculated ADO and the observed experimental rate constant with decreasing molecular dipole of the neutral molecule B in isomers like 3-NO_2NB and 4-NO_2NB were discussed in our previous work.[13] A similar trend is observed in Table I, which shows that the rate constants decrease for B in the order 3-ClNB, 4-ClNB. This is in line with a decreasing molecular dipole due to increasing opposition of the C–Cl and C–NO_2 dipoles in the above pairs.

The rate constants for reactions involving C_6F_5–CN in Table II are arranged in order of decreasing exothermicity of the reaction. There appears to be a weak trend for the rate constant to decrease as the exothermicity decreases. For example, from ADO one might expect $k_2 \approx k_5$ (Table II), while one finds $k_2 = 1.4k_5$, which means that the reaction with the higher exothermicity is somewhat faster. Earlier rate constant measurements[13-15] showed that electron-transfer reactions (eq 1) proceed with near ADO collision rates, down to small exothermicities, when there are no significant geometry changes between A and A^- and B and B^-. This was the case for substituted nitrobenzenes and quinones.[13] However, systems for which there was a significant geometry change (SF_6, C_7F_{14})[14] and where the energy of the negative ion having a geometry equal to that of the neutral (i.e., vertical transition) was significantly larger than that for the ground-state geometry of the ion had rate constants which decreased below collision efficiency with decreasing exothermicity of the reaction. This decrease did occur already for exothermicities as large as 15 kcal/mol and lead, at low exothermicities, to rate constants many orders of magnitude lower than the collision limit.[14] Obviously C_6F_6 and C_6F_5CN, see Table II, do not fall in this class. Their behavior is consistent with small geometry changes which lead to small energy differences between the vertical and ground-state geometry of the ion.

(b) C_6F_6 and Perfluorophenyl Compounds. Electron Affinities and Entropies of Electron Attachment. Electron attachment enthalpies are available only for the compounds for which van't Hoff plots of the equilibrium constants K_1 were made, i.e., C_6F_6 and C_6F_5CN. In order to be able to extend the comparison over the other perfluoro compounds, we will consider the electron attachment free energies $\Delta G_4°$(B) which are available for all the compounds used. Because of the convention adopted in the preceding section (i.e., stationary electron and neglect of spin multiplicity of the free electron), the $\Delta G_4°$(B) differ from the $\Delta H_4°$(B) only by the term $T(S°(B^-) - S°(B))$, which is small. Therefore $\Delta H_4° \approx \Delta G_4°$ and EA(B) $\approx \Delta G_4°$(B), generally within less than 2 kcal/mol.

The $\Delta G_4°$(B) values are shown in Table III. The EA(C_6F_6) $\approx -\Delta H_4 = 12.0$ kcal/mol is very much lower than the 41.5 kcal/mol value from the literature.[9]

The electron affinities for the other C_6F_5X compounds in Table III are also very much lower than 41.5 kcal/mol[9] and are of magnitudes consistent with qualitative predictions of substituent effects. This is illustrated in Table IV which makes a comparison of $\Delta G_4°$(B) values of substituted nitrobenzenes X–NB and the perfluorophenyls C_6F_5–X. Nitrobenzene has an electron affinity of 22 kcal/mol. The extra electron is in a π^*-type orbital which extends over the aromatic and nitro group. Electron-withdrawing substituents X on nitrobenzene increase the electron affinity relative to unsubstituted NB. One might expect that such substituents will increase also the electron affinity of C_6F_6. Since the negative charge in NB^- is probably more delocalized than in $C_6F_6^-$, one might expect a larger substituent effect for the fluorinated compound, in X for hydrogen substitution. However, since in the change C_6F_6 to C_6F_5X the substitution is X for F, the loss of the electron-withdrawing effect of the removed F atom will decrease the enhancing effect of the X substituent. Therefore, the increase of EA for NB to XNB might be expected to be similar to that for C_6F_6 to C_6F_5X. This is what is found in Table IV, where the substituent effect for C_6F_6 is found to be somewhat smaller than that for NB but still of rather similar magnitude.

The increase of electron affinity on perfluorination is explored in Table V, which utilizes also some literature data.[6,18] The phenyl–X compounds are arranged in order of increasing electron affinities. Substituents X that increase the electron affinity of benzene delocalize the negative charge. Therefore, it is reasonable

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(17) Su, T.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1.

(18) Chen, E. C. M.; Wentworth, W. E. *J. Phys. Chem.* **1975**, *75*, 1161.

to expect that the increase of electron affinity in phenyl-X, occurring on perfluorination, should be smaller for the more delocalized, higher electron affinity phenyl-X compounds. This is borne out by the data in Table IV. The increase is by far the largest for the change C_6H_6 to C_6F_6, where there is also an additional boost since six rather than five fluorine atoms are introduced. The increase on perfluorination per F atom is also given in Table V. These values are seen to decrease quite regularly with increasing electron affinity of the compounds. One exception is the dicyanoperfluorobenzene for which the effect per F atom is quite large (4.2) even though this compound has the highest electron affinity. Obviously, the comparison per fluorine atom is flawed since the position of the fluorines is not taken into account. There is evidence[6d] that F substitution of four fluorine atoms in positions 2, 3, 5, and 6 is particularly effective in increasing the electron affinity of benzene, and the change from 1,4-$(CN)_2C_6H_4$ to the 1,4-$(CN)_2C_6F_4$ involves such a substitution.

The extra electron in the perfluoro negative ions which have strongly electron-withdrawing substituents which also conjugate with the ring, like CN, NO_2, and $COCH_3$, is almost certainly in a π^*-type orbital. The consistency in the trends observed in Tables IV and V indicates that the extra electron for all the compounds involved including $C_6F_6^-$ is in a predominantly π^*-like orbital. This is in agreement with the theoretical predictions of Shchegoleva[12] for $C_6F_6^-$.

The entropy change ΔS_4° for electron attachment to C_6F_6 was found to be 7.4 cal/deg (Table III). When 1.4 cal/deg caused by the change of multiplicity (singlet to doublet)[15] is subtracted, there remains ~6 cal/deg. This change could be due to loosening of the vibrational frequencies in $C_6F_6^-$ and/or to a decrease of symmetry from C_6F_6 to $C_6F_6^-$. The kinetic data, see section a in the Results and Discussion section, showed that electron transfer to C_6F_6 occurs with near 100% collision efficiency even when the reaction is near thermoneutral. This result indicates that the energy difference between the $C_6F_6^-$ obtained by a vertical transition from C_6F_6 and the ground-state geometry of the $C_6F_6^-$ is not large.[14] This is compatible with a change of soft vibrations on formation of $C_6F_6^-$ or a change of symmetry number, since these two changes need not lead to a large energy change in the vertical transition. Thus adding of the electron may only flatten the D_{6h} minimum of the energy hypersurface and lead to a lowering of the nine out-of-plane deformations. Since these have already low frequencies in C_6F_6, further softening in $C_6F_6^-$ will be particularly effective in producing a ΔS_4° increase. Due to the high symmetry of C_6F_6, symmetry number $\sigma = 12$, a loss of symmetry in $C_6F_6^-$ resulting in $\sigma = 1$ or 2 will lead to a $\Delta S_{\text{rot,sym}}^\circ \approx 5$ cal/deg. Either of the above changes may be sufficient to lead to the observed ΔS_4° result, which itself is not very accurate.

Modern ab initio MO calculations for C_6F_6 and $C_6F_6^-$ can provide useful information on the geometry and vibrational frequency changes. We hope that the present results will encourage such theoretical work. Theoretical calculations do not perform very well for fluorine compounds particularly if polarization functions and electron correlation are not included. Therefore, abandoning the high symmetry of C_6F_6 in a geometry exploration of $C_6F_6^-$ unfortunately will be very expensive but probably worthwhile.

The present result for $EA(C_6F_6) = 0.52$ eV (12.0 kcal/mol), see Table III, is much lower than the $EA(C_6F_6) \geq 1.8$ eV obtained by Lifshitz and Tiernan[9] with the endothermic negative ion electron-transfer, tandem mass spectrometer beam method. A similar large difference is observed for perfluorotoluene, $EA(C_6F_5CF_3) = 0.94$ eV (Table III) vs. $EA(C_6F_5CF_3) \geq 1.7$ eV.[9] The consistency of the present data, Tables I–V for C_6F_6 and the substituted C_6F_5X, is very strong evidence for the reliability of the present results which makes the high values[9] almost certainly wrong. Difficulties and inconsistencies encountered in the C_6F_6 determinations were reported by Lifshitz et al.[9] Thus the thresholds obtained with I^- projectiles did not agree with the thresholds obtained with S^-, on which the determinations were based. The I^- results were rejected since the S^- results were supported by an observed decrease of the transfer cross section with energy, for O^-. This was taken to signal an exothermic electron transfer from O^- to C_6F_6 and sets the limit $EA(C_6F_6) > EA(O) = 1.47$ eV. Considering that the same publication[9] reported an electron affinity for SF_6 which was too low by some 0.4 eV,[9,14] one must conclude that the method[9] is not reliable for electron affinity determinations of perfluoro hydrocarbons and SF_6.

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Registry No. C_6F_6, 392-56-3; C_6F_5CN, 773-82-0; C_6F_5-C_6F_5, 434-90-2; $C_6F_5CF_3$, 434-64-0; $C_6F_5COCH_3$, 652-29-9; $(C_6F_5)_2CO$, 853-39-4; 1,4-$(CN)_2C_6F_4$, 1835-49-0.

Gravity-Induced Anisotropies in Chemical Waves

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Abstract: A variety of experiments are presented to illustrate that chemical wave velocities in the iron(II)–nitric acid and in the chlorite–thiosulfate reactions are profoundly affected by the convective motion of the solutions. A qualitative model is developed to interpret the—sometimes peculiar and spectacular—phenomena caused by the simultaneous cooperative effects of chemical reaction, diffusion, heat conduction, and fluid convection.

Traveling chemical waves have been observed in many chemical reactions,[1-7] all of which exhibit two common features. They are autocatalytic and they possess bistable steady states in a stirred tank reactor. Theoretical treatments, particularly of waves in the Belousov–Zhabotinskii[8-12] (BZ) and arsenite–iodate systems,[13] have yielded significant insights into the nature of these waves and how their velocities depend upon reactant concentrations.

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