

Electron Affinities of Di- and Tetracyanoethylene and Cyanobenzenes Based on Measurements of Gas-Phase Electron-Transfer Equilibria

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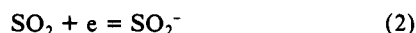
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Abstract: The electron affinities of tetracyanoethylene, *trans*-1,2-dicyanoethylene, and eleven substituted benzonitriles as well as two naphthonitriles were determined by measurement of the electron-transfer equilibria $A^- + B = A + B^-$ with a pulsed electron high ion source pressure mass spectrometer. Rate constants for exothermic electron transfer involving the cyano compounds were found to be near unit collision efficiency. The EA (tetracyanoethylene) = 3.17 eV obtained in the present work is considerably higher than the 2.3 eV photodetachment value of Palmer and Lyons. The electron affinities of benzene and benzonitrile substituted by CN, CHO, and NO₂ increase in the given order, while the order for nitrobenzene is CHO, CN, NO₂. This reversal of order is explained on the basis of a larger attenuation of the π -withdrawing effect relative to the field effect of substituents when the electron density in the π^* single-electron orbital is decreased.

Recently we reported¹⁻⁴ electron-affinity determinations of some 50 compounds: substituted nitrobenzenes and quinones,^{1,3} SF₆ and perfluorocyclohexanes,² perfluorobenzenes,⁴ SO₂, NO₂, and benzophenones.¹ The determinations were based on measurement of the electron-transfer equilibria 1 observed in the high-pressure



ion source reaction chamber of a pulsed electron mass spectrometer. Determinations of the equilibrium constants K_1 and their temperature dependence³ led to ΔG°_1 , ΔH°_1 , and ΔS°_1 . Absolute electron affinities are obtained¹⁻⁴ by anchoring the above data to the known electron-attachment energies ΔH°_2 and ΔS°_2 of SO₂ (external standard).⁵⁻⁷



While the above group of compounds included some cyano-substituted nitrobenzenes, a systematic study of cyano compounds was not made. The present work presents such a study. The electron affinities of cyano compounds in solution have been investigated by polarographic half-wave potential measurements⁸ and charge transfer spectra.^{9,10} Some gas-phase determinations with the magnetron method¹¹ and the electron capture detector method¹² also have been reported. Recently Lyons and Palmer¹³ published an electron-photodetachment determination of the electron affinity of tetracyanoethylene.

Mirek and Buda¹⁴ have calculated electron affinities of polycyano compounds using the MNDO method. The MNDO calculations do not provide reliable absolute electron affinities; however, the authors¹⁴ found that a calibration of the MNDO values to experimental results can be used for extrapolation of the calculations to predict unknown EA values.

Polycyano compounds like tetracyanoethylene C₂(CN)₄ and tetracyanoquinodimethane have very high electron affinities and form charge-transfer complexes with unusual properties. For example, crystals of the complex tetrathiofulvalene and tetracyanoquinodimethane have unusually high ionic conductivity.¹⁵

Experimental Section

The measurements were performed with a pulsed-electron high-pressure ion source mass spectrometer which has been described previously.¹⁶ The techniques used for the equilibria 1 determinations have been reported in previous work.¹⁻⁵

Results and Discussion

(1) Measurement of the Kinetics and Equilibria of the Electron-Transfer Reactions. By proper selection of the composition of the reaction mixtures one can measure the electron-transfer equilibria or the kinetics of the electron transfer 1. Shown in

Figure 1 is the time dependence of the ion intensities of a reaction mixture containing, 4-methoxynitrobenzene and 4-(trifluoromethyl)benzonitrile. The concentrations of the two compounds are sufficiently high and the electron affinities are relatively close, within 1.8 kcal/mol, so that equilibrium is established very soon, i.e., after some 0.2 ms, as indicated by the constant concentration ratio of the corresponding negative ions observed in Figure 1. This represents a typical run with good conditions for the determination of the equilibrium.

The results shown in Figure 2 illustrate conditions favorable for rate constant determination. 3-CF₃C₆H₄CN has an electron affinity which is 10.8 kcal/mol lower than that of 4-CNC₆H₄CN. The fluoro compound, present at a large concentration (9.2 mTorr), captures initially more of the electrons and then transfers these to the higher EA dicyano compound. The pseudo-first-order rate constant $v_1 = k_1[B]$ is obtained from the slope of the logarithmic decay of the $A^- = 3\text{-CF}_3\text{C}_6\text{H}_4\text{CN}^-$ and then k_1 is determined with use of the known $B = 4\text{-CNC}_6\text{H}_4\text{CN}$ concentration.

The results in Figure 3 illustrate an experiment which provides both a rate constant k_1 for the electron transfer and the equilibrium

(1) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627

(2) (a) Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 1059. (b) Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3983.

(3) Chowdhury, S.; Heinis, T.; Grimsrud, E. P.; Kebarle, P. *J. Phys. Chem.* **1986**, *90*, 2747.

(4) (a) Chowdhury, S.; Nicol, G.; Kebarle, P. *Chem. Phys. Lett.* **1986**, *127*, 130. (b) Chowdhury, S.; Grimsrud, E. P.; Heinis, T.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 3630.

(5) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.

(6) There are four other determinations (ref 7) for SO₂ by different physical measurements, which are within 0.1 eV of the Hall's (ref 5) value.

(7) (a) Hughes, B. M.; Lifshitz, C.; Tiernan, T. O. *J. Chem. Phys.* **1973**, *59*, 3162. (b) Feldman, D. *Z. Naturforsch.* **1970**, *A25*, 621. (c) Rothe, E. W.; Tang, S. Y.; Reck, G. P. *J. Chem. Phys.* **1972**, *62*, 3829. (d) Refaey, K. M. A.; Franklin, J. L. *J. Chem. Phys.* **1976**, *65*, 1994.

(8) Rieger, P. H.; Bernal, Z.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683.

(9) Bately, M.; Lyons, L. C. *Nature (London)* **1962**, *196*, 573.

(10) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: London, 1969.

(11) Farragher, A. L.; Page, F. M. *Trans. Faraday Soc.* **1967**, *63*, 2369.

(12) Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.

(13) Lyons, L. E.; Palmer, L. D. *Aust. J. Chem.* **1976**, *29*, 1919.

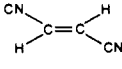
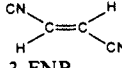
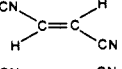
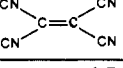
(14) Mirek, J.; Buda, A. *Z. Naturforsch.* **1984**, *39*, 386.

(15) Farraris, J. P.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 945.

(16) Cunningham, A. J.; Payzant, J.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7627.

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Table I. Rate Constants k_1 for Electron Transfer Reaction $A^- + B = A + B^-$

A ^a	B ^a	$-\Delta G_1$, kcal/mol	$k_1 + 10^9$ (exptl), cm ³ molecule ⁻¹ s ⁻¹	$k_1 \times 10^9$ (ADO), cm ³ molecule ⁻¹ s ⁻¹	<i>t</i> , °C
4-CNBN	4-CNNB	12.9	1.2	1.1	150
2-CNBN	3-CNNB	12.5	1.4	1.8	150
3-CNBN	3-CNNB	9.0	1.6	1.8	
3-CNBN	2-CNNB	14.8	2.1	2.4	150
2,3-(CH ₃) ₂ NB	4-CNBN	6.4	1.5	1.1	150
3-CNBN	3-FNB	7.0	2.5	1.9	150
2,6-Cl ₂ BN	4-CH ₃ NB	4.5	1.7		100
4-CF ₃ BN	4-CNNB	20.1	1.2	1.0	100
4-CF ₃ BN	3-CNNB	16.2	1.9		100
	4-CNNB	10.2	1.9	1.0	150
	2-NO ₂ NB	8.4	2.7	2.4	150
3-FNB		0.6	0.5	0.9	150
F ₄ BQ		12.0	0.8		150

^aBN = benzonitrile, NB = nitrobenzene, and BQ = benzoquinone.

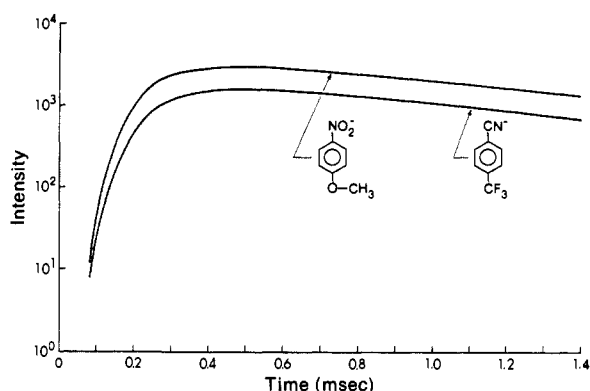
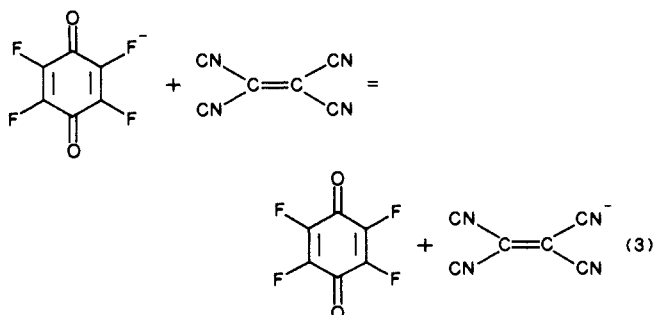


Figure 1. Time dependence of ion intensities after electron pulse. Reaction mixture: CH₄ (bath gas) 3.4 Torr; 4-(trifluoromethyl)nitrobenzene 2.4 mTorr; 4-methoxynitrobenzene 0.53 mTorr. Temperature 150 °C. Negative ions formed by electron capture rapidly reach equilibrium. Constant ion ratio corresponds to constant distance between intensities in a logarithmic plot.

constant K_1 . The reaction mixture of Figure 3 contains 40.5 mTorr of tetrafluorobenzoquinone and 0.17 mTorr of tetracyanoethylene in a 3.4 Torr of SF₆ bath gas. Since the tetrafluorobenzoquinone is present at much larger concentration, it captures electrons rapidly and is observed as the dominant ion at short times after



the electron pulse. The observed decrease of the benzoquinone negative ion and a corresponding increase of the cyanoethylene negative ion are in accordance with reaction 3, and this reaction reaches equilibrium after about 2.5 ms.

The logarithmic decay of the tetrafluoroquinone ion between 0.3 and 0.9 ms provides the rate constant for the transfer reaction 3 while the constant ion concentrations ratio at $t > 3$ ms is used to obtain the equilibrium constant. The experiment of Figure 3

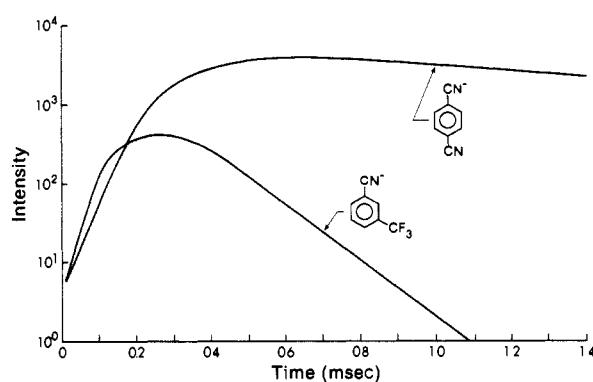


Figure 2. Time dependence of ion intensities. The 3-(trifluoromethyl)benzonitrile with linear logarithmic decay is transferring electrons to the higher electron affinity 4-cyanobenzonitrile. Reaction mixture: CH₄, 3.9 Torr; 4-cyanobenzonitrile, 0.11 mTorr; 3-(trifluoromethyl)benzonitrile, 9.2 mTorr; 150 °C.

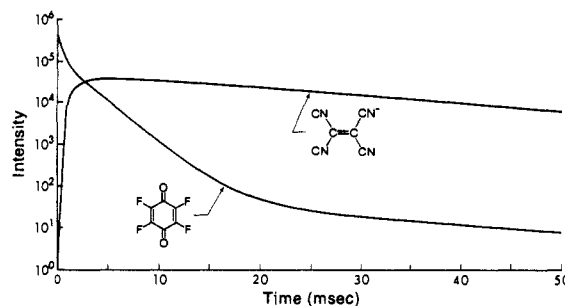


Figure 3. Initial linear logarithmic decay of fluoranil anion due to electron transfer to tetracyanoethylene. Reaction reaches equilibrium after ~3 ms: 3.4-Torr SF₆ bath gas, 40.5 mTorr of fluoranil, 0.17 mTorr of tetracyanoethylene; 235 °C.

is unusual in so far that the electron-affinity difference between the cyanoethylene and the quinone is very large, i.e., 12 kcal/mol. This requires as large a concentration ratio $[A]/[B]$ as experimentally possible (ratio used ≈ 240) which could be achieved only by using low B concentrations. The low $[B]$ slows down the achievement of equilibrium. A longer ion residence time was achieved by using SF₆ as the bath gas. Its high mass slows the dominant ion loss process, diffusion to the wall, and permits observation over a longer time interval (5 ms). These conditions had to be used since reference compounds with electron affinity closer to the cyanoethylene affinity were not available.

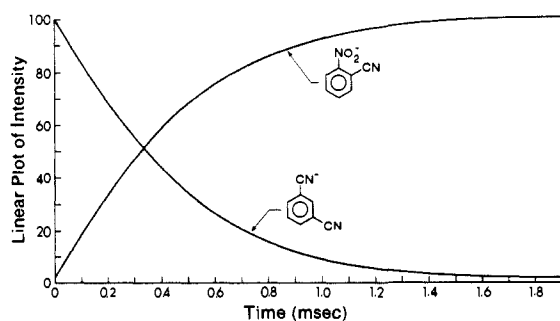


Figure 4. Time dependence of ion intensities in percent of total ion current. Reversible electron transfer leading slowly to equilibrium. 3.5 Torr of CH_4 , 1 mTorr of 3-cyanobenzonitrile, 0.06 mTorr of 2-cyanobenzonitrile; 101 °C.

Table II. Data from van't Hoff plots of K_1 for $\text{A}^- + \text{B} = \text{A} + \text{B}^-$ Equilibria

A	B	ΔS_1 , cal/deg	ΔH_1 , kcal/mol	$\Delta G_1(250^\circ\text{C})$, kcal/mol
1 NB	4-CNBN	+2.04	-2.1	-2.9
2 4-CNBN	3-FNB	-2.5	-3.2	-2.1
3 4-CF ₃ BN	2-CH ₃ NB	-4.2	-3.8	-2.1
4 4-CF ₃ BN	2,3-(CH ₃) ₂ NB	-3.8	-2.2	-0.7
5 2-CH ₃ NB	2-CNBN	+1.4	-1.0	-1.2
6 2-CNBN	NB	-2.1	-1.4	-0.5
7 NB	4-COCH ₃ NB	-2.1	-3.3	-2.3
8 4-COCH ₃ BN	3-FNB	-1.0	-3.2	-2.8
9 3-FNB		+0.7	-0.4	-0.7

The rate constants k_1 for a number of exothermic electron transfer reactions are given in Table I. The determinations, where the exothermicity was large, were based on the linear log plots as in Figure 2 or 3. For low exothermicities, where the system rapidly approached equilibrium, the rate constant was obtained by computer fitting of the observed time dependence to the theoretical (pseudo) first-order reversible rate expressions. The assumption of equal diffusion loss rates for both ions is made in these cases. An example of the ion intensities in such a determination is given in Figure 4.

The rate constants given in Table I are compared to the ADO¹⁷ orbiting collisions rate expressions. The experimental rate constants are seen to be close to the collision rates. The accuracy of the experimental constants is estimated as $\pm 0.5 \times 10^{-9}$ molecules⁻¹ cm³ s⁻¹. The presence of net molecular dipole in B leads to experimental and ADO rate constants around 2×10^{-9} molecules⁻¹ cm³ s⁻¹. Molecules B, which have no net dipole and have low polarizability, have the lowest rate constants, e.g., *trans*-1,2-dicyanoethylene.

Exothermic electron-transfer reactions generally proceed at near collision rates.¹⁻⁴ Thus, the cyanobenzenes and cyanoethylenes are similar to the other systems measured so far. Only in cases where the geometries of A and A⁻ or B and B⁻ are drastically different (SF₆, perfluorocyclohexanes)^{2a} does one observe electron-transfer rates which are orders of magnitude lower than the collision rates.

The equilibrium constants K_1 determined from experiments like those shown in Figures 1 and 3 were used to evaluate ΔG_1° via eq 4. The ΔG_1° obtained from a number of interconnecting

$$-\Delta G_1^\circ = RT \ln K_1 \quad (4)$$

equilibria are shown in the ΔG_1° scale (ladder) given in Figure 5. For all reactions measured, checks were made of the invariance of K_1 with total pressure of the gas mixture (constant P_A to P_B ratio). Such results are shown for three reactions in Figure 6. Checks where the P_A/P_B ratio was changed were also performed.

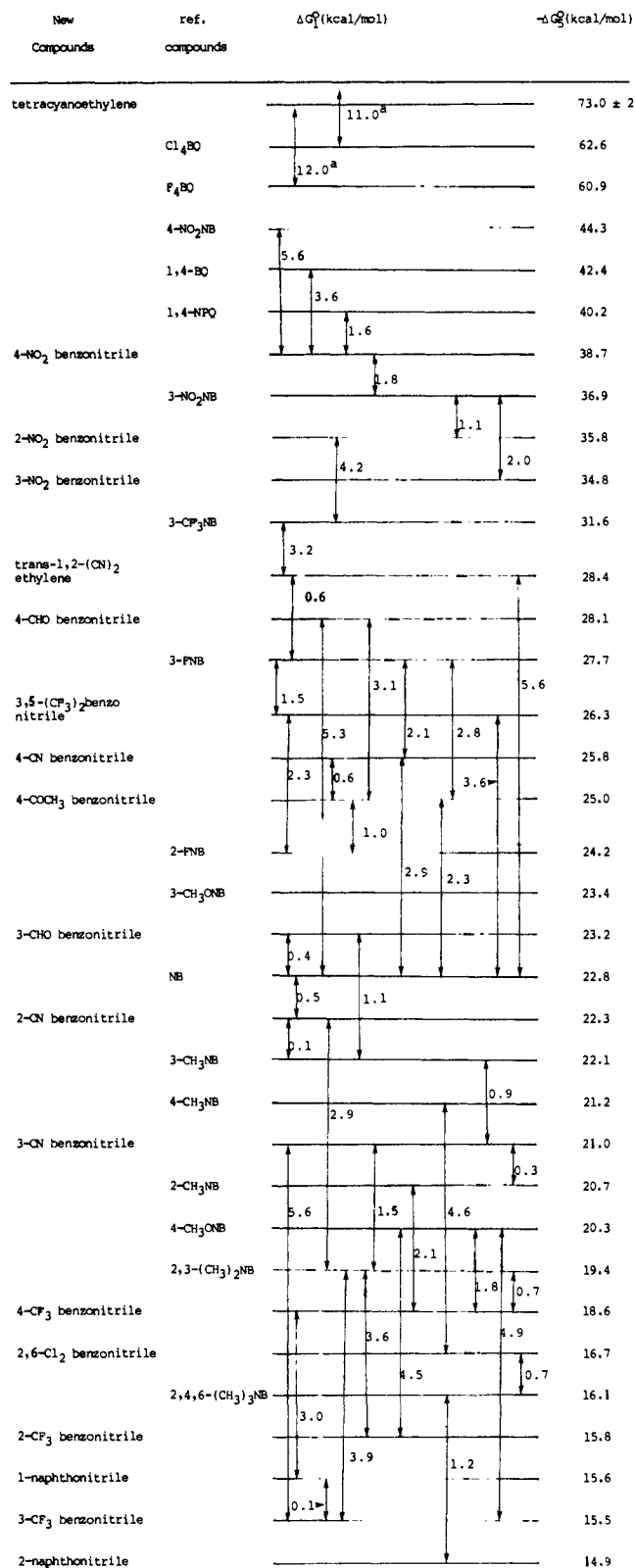


Figure 5. Ladder of free energy changes ΔG_1° at 423 K obtained from equilibrium constants K_1 for reactions 1: $\text{A}^- + \text{B} = \text{A} + \text{B}^-$. Scale giving ΔG_5° on right corresponds to free energy change for electron capture of a stationary electron: $\text{e} + \text{B} = \text{B}^-$.

Generally two or three different ratios were used, and only systems where K_1 was essentially invariant are shown in the ΔG_1° ladder Figure 5.

The ladder in Figure 5 is calibrated to the known¹⁻⁵ electron attachment free energies ΔG_5° of the reference compounds.



(17) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 211.

(18) Lyons, L. E.; Palmer, L. D. *Chem. Phys. Lett.* **1973**, *21*, 442.

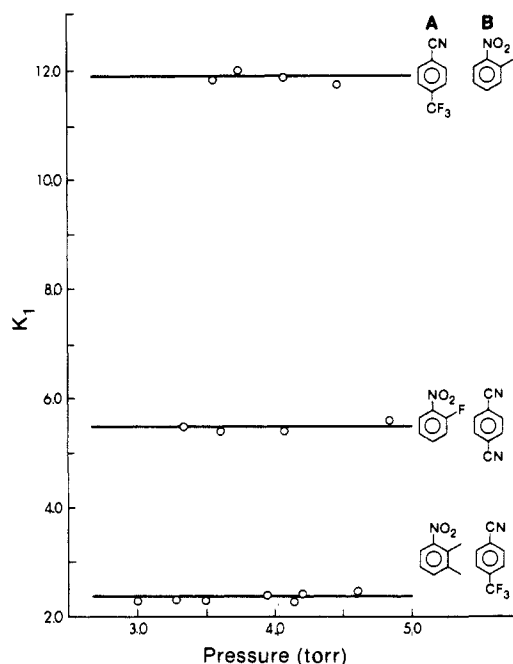


Figure 6. Tests of invariance of equilibrium constant K_1 with changing pressure of bath gas and pressure of A and B at constant P_A/P_B .

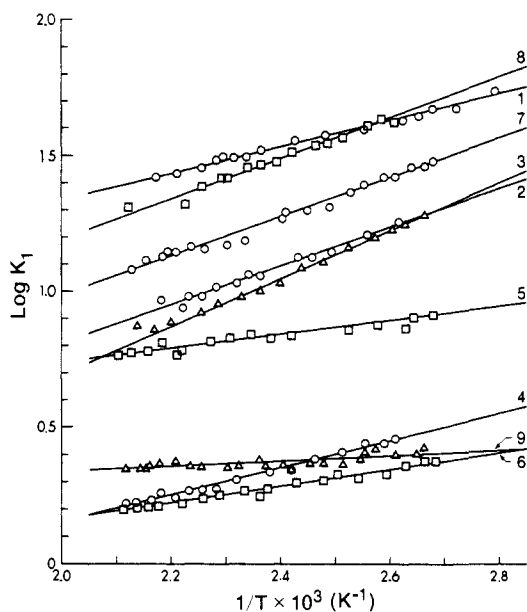


Figure 7. van't Hoff plots of equilibria $A^- + B = A + B^-$. Numbers beside plots correspond to reactions given in Table II.

In order to establish the nature of the ΔS°_1 changes of the cyano compounds, van't Hoff plots for 9 different equilibria were obtained by measuring the temperature dependence of the respective equilibrium constants K_1 . These plots are shown in Figure 7. The ΔH°_1 and ΔS°_1 values derived from these plots are given in Table II, and ladders of the ΔH°_1 and ΔS°_1 values are shown in Figures 8 and 9. The ΔH°_1 values in Figure 8 anchored to the known^{3,5} ΔH°_5 values for electron attachment to the reference compounds provide the corresponding ΔH°_5 for the cyano compounds. Some of the new ΔH°_5 can be obtained via more than one thermodynamic ΔH°_1 cycle, and these redundant cycles are indicators of the consistency of the measurements. Thus of the five cyano compounds for which ΔH values were obtained, four were determined via two cycles. These are consistent in general to less than 1 kcal/mol. The largest inconsistency (1.3 kcal/mol) occurs for 4- $\text{CH}_3\text{COC}_6\text{H}_4\text{CN}$ (see Figure 8).

The entropy changes ΔS°_1 in Figure 9 were converted to ΔS°_5 via the known³ ΔS°_5 of the reference compounds. The consistency

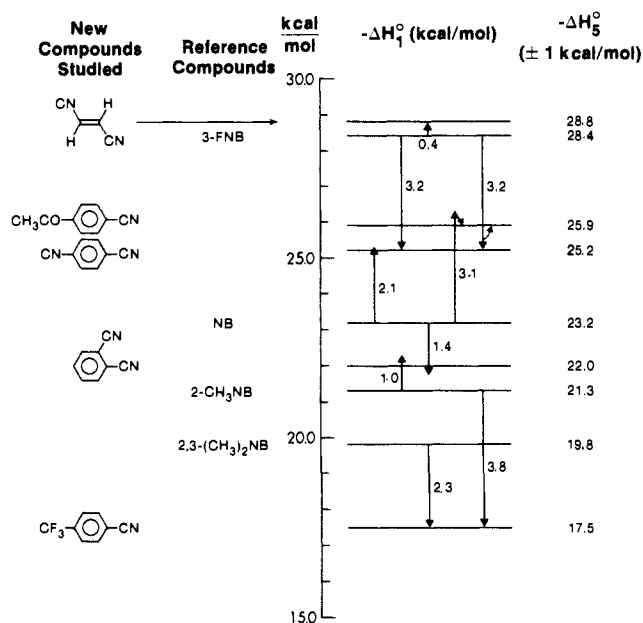


Figure 8. Ladder of ΔH°_1 values, obtained from van't Hoff plots, (see Figure 7 and Table II).

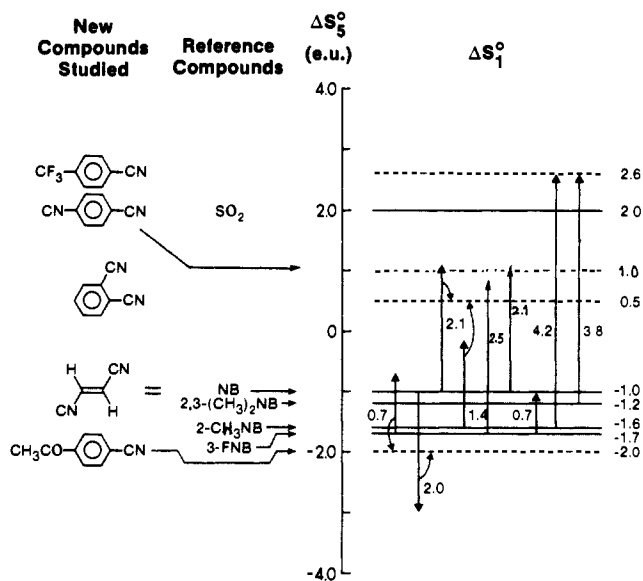


Figure 9. Ladder of ΔS°_1 values from van't Hoff plots (see Figure 7 and Table II).

of the ΔS°_5 values, where multiple cycles occur, is found to be within ± 1 eu.

(2) **Entropy Changes on Electron Capture by Cyano Compounds.** The entropy changes ΔS°_5 given in Figure 9 are for reaction 5a; however, the stationary electron convention³



$$\Delta S^{\circ}_5 = S^{\circ}(B^-) - S^{\circ}(B) \quad (5b)$$

was used and the spin multiplicity of the free electron was not considered, therefore the ΔS°_5 values are for the formal change (eq 5b). In the formal change (eq 5b) there is an entropy change due to the change from singlet B to doublet B^- of $R \ln 2 = 1.4$ eu. Therefore, the 4- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$, 4- $\text{CNC}_6\text{H}_5\text{CN}$, and 2- $\text{CNC}_6\text{H}_4\text{CN}$ for which $\Delta S^{\circ}_5 \approx 2$ eu experience only a very small loosening of the internal motions, amounting to ~ 0.5 eu, on becoming a negative ion. This is in contrast with the nitrobenzenes for which $\Delta S^{\circ}_5 \approx -1$ to -2 eu (see Figure 9). As discussed earlier,³ the stiffening of the internal motions in the nitrobenzene negative ions indicated by the negative ΔS°_5 is probably due to a stiffening of the internal rotation around the C-N bond which leads to more

Table III. Electron Affinities

compound	EA (present work)		EA (eV) lit. exptl	EA (eV) from $E_{1/2}$ data and CTS	EA (eV) theoretical	
	kcal/mol	eV/mol			MNDO ^a	others
tetracyanoethylene	73.0 ± 2	3.17 ± 0.2	2.9 ± 0.1 ^h 2.3 ± 0.3 ^g	2.90 ^b + 0.13 2.80 ^c ± 0.13	2.480	3.06 ^e 3.05 ^f
<i>trans</i> -1,2-dicyanoethylene ^d	28.8	1.24			0.870	
4-(oxomethyl)benzotrile	28.1	1.22				
4-(1-oxoethyl)benzotrile ^d	25.9	1.13				
4-cyanobenzotrile ^d	25.4	1.10		1.10 ^b 1.07 ^b	1.096	
3,5-dimethylbenzotrile	26.3	1.14				
2-cyanobenzotrile ^d	22.0	0.95		0.95 ^b	0.973	
3-(oxomethyl)benzotrile	23.2	1.00				
3-cyanobenzotrile	21.0	0.91		0.90 ^b	0.895	
4-methylbenzotrile ^d	17.5	0.76				
2,6-dichlorobenzotrile	16.1	0.72				
2-methylbenzotrile	16.1	0.70				
1-naphthotrile	15.6	0.68				
3-(trifluoromethyl)benzotrile	15.5	0.67				
2-naphthotrile	14.9	0.65				

^aBuda,¹³ obtained¹³ by subtracting 0.575 eV, from MNDO result. ^bWentworth.¹² ^cMastori, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6781. ^dEA from van't Hoff plot. ^eCompton.²⁶ ^fRezpa.²⁵ ^gPalmer.¹³ ^hPage.¹¹

than 1-eu loss, and a possible stiffening of the O–N–O and C–N–O bending vibrations, with a ~1-eu loss. The loss of rotation and possibly some of the other stiffening is caused by increased conjugation of the NO₂ group and the benzene ring in the negative ion and by the presence of negative charge on the NO₂ group due to its electron-withdrawing field and resonance effect. Considering the cyanobenzenes we note that there is no internal rotation around the cyanobenzene bond; furthermore, the π -withdrawing effect of this group is smaller and the group has less vibrations. Thus the absence of entropy loss on the formation of the negative ion of cyanobenzenes is not surprising. The 4-CH₃COC₆H₄CN has a negative ΔS°_5 , similar to that for the nitrobenzenes. This entropy loss is probably due to factors similar to those operating in the nitrobenzene; i.e., the internal rotation around the C–C bond joining the aceto group to the benzene becomes much more hindered in the negative ion due to increased conjugation and negative charge on the O atom. Also, bending vibrations involving the aceto group could be expected to stiffen due to increased electron density in the aceto group.

(3) **The Electron Affinities of the Cyano Compounds and Specifically Tetracyanoethylene.** The electron affinities EA(B) of the cyano compounds B are listed in Table III. The values given for some of the compounds are based on the $\Delta H^\circ_5(B)$ determinations (see Figure 5), and these correspond to the stationary electron capture enthalpies at ~298 K. Since, generally $\Delta H^\circ_5(0\text{ K}) \approx \Delta H^\circ_5(300\text{ K})$ within less than 1 kcal/mol,³ these values should be very close also to the adiabatic electron affinities at 0 K. The remaining electron affinities quoted are based on the assumption $\Delta H_5(B) \approx \Delta G^\circ_5(B)$ i.e., $\Delta S^\circ_5 \approx 0$. The $\Delta G^\circ_5(B)$ values were taken from Figure 5. These values are less accurate since ΔS°_5 changes within the range of -2 to +2 eu (see Figure 9). However, 4 eu at 400 K amounts only 1.6 kcal/mol so that these data should be within ± 1 kcal/mol of $\Delta H^\circ_5(B)$. van't Hoff plots for all compounds B were not obtained because this would have been a very time consuming procedure.

Electron affinity values from the literature are also given in Table III. For 3-cyanobenzotrile, 2-cyanobenzotrile, and 4-cyanobenzotrile there is agreement within less than 0.1 eV of the present values and the data of Chen and Wentworth¹² based on a correlation between experimental gas-phase determinations and solution EA's from polarographic half-wave potentials and charge transfer spectra. Good agreement between the electron-transfer equilibria EA and Chen and Wentworth correlated EA from solution data was observed also in previous work;¹ however, this does not mean that the solution derived data are not affected by differential solvation (see Figure 6, Grimsrud¹).

For tetracyanoethylene there are two experimental gas-phase literature values, one of Lyons and Palmer,¹³ 2.3 ± 0.3 eV, and the other due to Page,¹¹ 2.9 eV, and two indirect values 2.9 and 2.8 eV based on Chen and Wentworth's¹² correlation. The latter

three values are close to the present result of 3.1 ± 0.2 eV. The significantly lower value of Lyons¹³ is based on electron photodetachment from the C₂(CN)₄⁻ negative ion and might have been considered as the most reliable of the literature data. However, examination of the experimental results and the interpretation by Lyons¹³ reveals significant problems. The photodetachment curve obtained had no visible structure above the onset which occurred at 2 eV. The first report of Lyons¹⁸ gave an EA of 2.0 eV. A calibration to relative values from charge-transfer spectra⁹ showed that this value is too low and Lyons reinterpreted the onset curve.¹³ Making the reasonable assumption that the major geometry change on formation of the negative ion corresponds to a stretch of the central C=C bond, Lyons and Palmer¹³ fitted the curve to a progression of vibrational transitions involving this stretch. The fit indicated some 0.4-eV contribution due to vibrational excitation present in the ion (hot bands). This assignment moves the EA by 0.4 eV above the threshold, i.e., to 2.4 eV. The analysis, while plausible, need not be correct. The present 3.1-eV result indicates a much bigger shift due to excitation of the negative ion. The ion was produced¹³ by surface ionization of (CN)₄C₂ on a 1600 K molybdenum filament. This mode of production needs not to be the main source of vibrational excitation. In the experimental arrangement used,¹³ the ions are created at 10⁻² Torr and enter the quadrupole mass analyzer volume through a channel. The pressure at the quadrupole entrance region, where high electric fringe fields are present, might be sufficiently high to lead to collisional excitation of the negative ions. Unfortunately, electron-affinity determinations based on the photodetachment thresholds are very sensitive to the presence of excitation in the negative ion. Even when only a small fraction of the ions is excited, a tail will be observed which is difficult to analyze at low energy resolution.

The value of 2.9 eV due to Page,¹¹ which is close to the present result, was obtained by the Magnetron method. This method is not reliable.^{19,20} The major problem is the absence of identification of the negative ion, i.e., the nature of the negative ion is deduced on the basis of reagents added. Often other ions than those assumed to be present are found to be dominant.²⁰ It is interesting to note that mass spectral analysis for the case of C₂(CN)₄ has shown²⁰ that the dominant ion is C₄(CN)₄⁻. This fact lends support to the Page determination.

The uncertainty of the present determination for tetracyanoethylene given as ± 0.2 eV, see Table III, is larger than usual. The larger error was assumed in order to take into account the very large ΔG°_1 values of the equilibria involved in the determinations

(19) Kebarle, P. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972.

(20) Herron, J. T.; Rosenstock, H. M.; Shields, W. R. *Nature (London)* **1965**, *206*, 611.

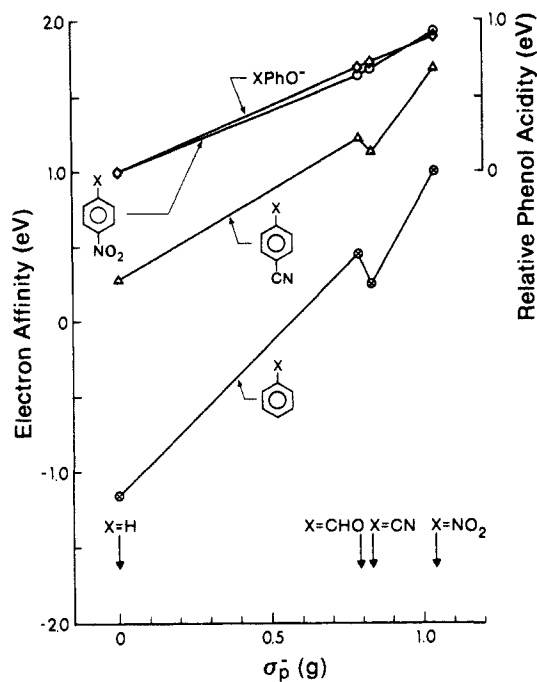


Figure 10. Plot of electron affinities of para substituted benzenes, cyanobenzenes, and nitrobenzenes with electron-withdrawing substituents X (CHO, CN, NO₂) vs. Hammett-Taft σ_p^- substituent constants based on gas-phase acidities of substituted phenols.¹⁷

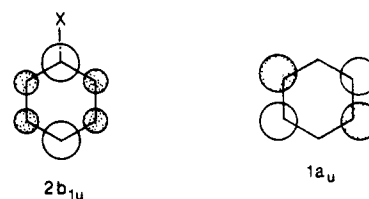
and the slow electron-transfer kinetics (see Figure 3). However, the results in Figure 3 clearly demonstrate that tetracyanoethylene has an electron affinity that is many kcal/mol above that of the reference compound tetrafluoroquinone, EA = 2.56 eV, a compound with higher EA than the 2.3-eV result of Lyons¹³ for tetracyanoethylene.

The structure of tetracyanoethylene is known from electron-diffraction measurements.²¹ The molecule is planar and symmetric with linear C—C≡N bonds. The central C=C bond is 0.017 Å longer than that of ethylene. The electron forming the negative ion enters the LUMO π^* -type orbital located mostly on the ethylene carbons whose energy is lowered by the π - and σ -electron-withdrawing effect of the CN groups. Theoretical calculations^{22,23} show the expected weakening (lengthening) of the central C=C bond, smaller weakening of the C≡N bonds, and strengthening of the C—CN bonds in the negative ion. The spin density has been calculated²⁴ to distribute itself as 0.612 on the central carbons and 0.021 and 0.077 on each C and N atom of the cyano groups. Unfortunately, no accurate modern calculations of C₂(CN)₄ and the negative ion have been made. The theoretical results^{25,26} for EA(C₂(CN)₄) given in Table III are semiempirical calculations. The agreement with the present experimental value may be fortuitous.

Mirek and Buda¹⁴ found that the MNDO calculated EA for several compounds when reduced by ~0.6 eV come in agreement with experimental electron affinities. However, the observed agreement was good only for cyano-substituted benzenes¹⁴ (see also Table III). The disagreement between the MNDO values for dicyanoethylene and tetracyanoethylene and the present experimental results probably reflects the inadequacy of the Mirek and Buda correction when compounds different from cyano-benzenes are involved.

(4) Electron Affinities of the Cyanobenzenes. The electron affinities of singly substituted benzenes C₆H₅X where X = CHO,

Scheme I



CN, and NO₂, substituted cyanobenzene 1,4-CNC₆H₄X, and nitrobenzene 2,4-NO₂C₆H₄X are shown in Figure 10, plotted vs. the Hammett-Taft σ_p^- parameter (see Table IV, Taft²⁷) based on the substituent effect on the gas-phase acidities of phenols.²⁷ Also shown in Figure 10, for comparison, are the relative gas-phase basicities of the phenols.²⁷ Literature electron affinities had to be used for benzene,²⁸ benzonitrile,²⁹ and benzaldehyde²⁹ since values for these have not been obtained in our laboratory. The following trends are observed. The increase of the electron affinity due to the electron-withdrawing substituent X, i.e., the slope ρ in Figure 10, decreases in the order C₆H₅X > CNC₆H₄X > NO₂C₆H₄X, i.e., the ρ value decreases as the electron affinity of the first member (X = H) in a given series increases. This effect is not surprising since the electron affinity increase of the first member is correlated with a progressively lower electron density in the π^* -type singly occupied molecular orbital (SOMO) extending over the aromatic ring of the negative ion. Thus, in the higher electron affinity compounds the electron-withdrawing X, attached to a ring carbon, has less SOMO electron density to operate on.

In addition to the above effect, there is an interesting reversal of the substituent effect between the CHO and CN group. For the low EA, i.e., high SOMO, ring density C₆H₅X compounds CHO leads to a significantly higher EA than CN, while for the high electron affinity compounds, nitrobenzene X the "normal" order,²⁷ CN stronger than CHO, electron-withdrawing effect is observed (see Figure 10).

The Hückel-type SOMO orbitals for the benzene negative ion are shown in Scheme I. Radom³⁰ has performed STO-3G calculations for several singly substituted benzene radical anions. He points out that electron-withdrawing substituents like CHO, CN, NO₂ will lead to preference for the 2b_{1u} π^* orbital as the SOMO orbital since this orbital has high electron density in the ipso position of the substituent. This means that the 2b_{1u} orbital can much better provide π -type electrons to feed the π -electron-withdrawing X and also nearby electron charge to interact with the dipole of X (field effect). The calculations of Radom³⁰ predict for the benzoanions C₆H₅X⁻, a higher SOMO electron density on X = CHO (0.528 e) relative to X = CN (0.160 e). The separation of Taft and co-workers²⁷ of the substituent effect (Table V, ref 27) into resonance *R* and field *I* effects, based on phenol gas-phase acidities and calculations, assigns a large electron-withdrawing *R* effect (-9.2) and a smaller electron-withdrawing *I* (-6.6) effect to the CHO group while for CN the opposite assignment of a small *R* (-4.5) and a large *I* (-12.1) is made. For NO₂ both effects are large, *R* (-8.1) and *I* (-12.8). We note that the larger *R* effect for CHO relative to CN is parallel to the Radom-calculated larger SOMO π density for the CHO group of the benzaldehyde anion relative to CN in the benzonitrile anion.

The observation that the CHO substituent has a stronger stabilizing effect relative to CN in the radical anions with large SOMO π^* electron densities in the ring, and the reversal of the effect as the density is decreased, see Figure 10, demonstrates that the π withdrawal (*R* effect) is much more strongly attenuated

(21) Hope, H. *Acta Chim Scand.* **1968**, *22*, 1059.

(22) Stanely, J.; Smith, D.; Latimer, B.; Devlin, J. P. *J. Phys. Chem.* **1966**, *70*, 2011.

(23) Rettig, M. F.; Wing, M. *Inorg. Chem.* **1969**, *8*, 2685.

(24) Reiger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2795.

(25) Dewar, M. J. S.; Rezza, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(26) Younkin, J. M.; Smith, L. J.; Compton, R. N. *Theor. Chim. Acta (Berlin)* **1976**, *41*, 157.

(27) Fujio, M.; McIver, R. T.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

(28) Jordan, K. D.; Burrow, P. D. *J. Chem. Phys.* **1979**, *71*, 5384.

(29) (a) Wentworth, W. E.; Kau, L. W.; Becker, R. S. *J. Phys. Chem.* **1975**, *79*, 1161. (b) Becker, S. R.; Chen, E. J. *J. Chem. Phys.* **1966**, *45*, 2405.

(30) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3310.

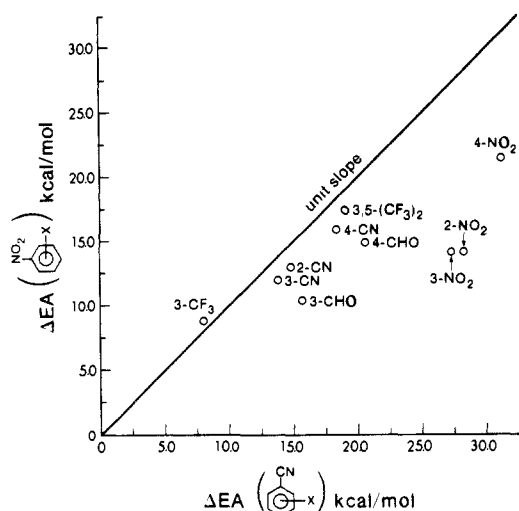


Figure 11. Relative electron affinities. Substituted cyanobenzenes vs. substituted nitrobenzenes.

with decreasing SOMO ring density than the field effect.

A comparison between the effect of a larger variety of substituents X in positions 2, 3, and 4 on the electron affinities of cyanobenzene and nitrobenzene is given in Figure 11. The substituents which have a strong field effect and small resonance effect (CF_3 , 3,5- $(\text{CF}_3)_2$, 2-CN, 3-CN, 4-CN) fall close to the unit slope line, i.e., for these substituents the reduced SOMO density of the nitrobenzene ring, relative to the cyanobenzene ring, is of no great consequence. The strongly π withdrawing substituents

CHO and NO_2 , on the other hand, are displaced to the right, i.e., for the $\text{NO}_2\text{-C}_6\text{H}_4\text{-X}$ these substituents produce a smaller electron affinity increase relative to the $\text{CN-C}_6\text{H}_4\text{X}$. These trends are in agreement with Figure 10 and attendant discussion. Interestingly, a significant displacement is observed also for the CHO and particularly NO_2 in position 3. A plot like that in Figure 11 is somewhat misleading. For example, considering the NO_2 substituent effect on $\text{C}_6\text{H}_5\text{CN}^-$, it is obvious that the NO_2 introduction leads to a large shift of SOMO density to NO_2 which is the more powerful substituent. This will happen also when NO_2 is introduced in position 3. On the other hand, when NO_2 is introduced in position 3 of $\text{C}_5\text{H}_5\text{NO}_2^-$, the SOMO density shift to it will be considerably smaller since that substituent does not overpower the equally strong initial NO_2 . In other words a large decrease between the electron affinities of 4-dinitrobenzene and 3-dinitrobenzene is expected while for the pair 4-nitrocyanobenzene and 3-nitrocyanobenzene the decrease should be small, and these expected changes are observed in Figure 11.

Acknowledgment. This work was supported by the Canadian Natural Science and Engineering Research Council.

Registry No. 2,3- $(\text{CH}_3)_2\text{NB}$, 83-41-0; 4- CF_3NB , 455-18-5; 3-FNB, 402-67-5; F_4BQ , 527-21-9; 4-CNNB, 619-72-7; 3-CNNB, 619-24-9; 2-CNNB, 612-24-8; 4- CH_3NB , 99-99-0; 2- NO_2NB , 528-29-0; NB, 98-95-3; 2- CH_3NB , 88-72-2; tetracyanoethylene, 670-54-2; *trans*-1,2-dicyanoethylene, 764-42-1; 4-formylbenzotrile, 105-07-7; 4-acetylbenzotrile, 1443-80-7; 4-cyanobenzotrile, 623-26-7; 3,5-dimethylbenzotrile, 22445-42-7; 2-cyanobenzotrile, 91-15-6; 3-formylbenzotrile, 24964-64-5; 3-cyanobenzotrile, 626-17-5; 4-methylbenzotrile, 104-85-8; 2,6-dichlorobenzotrile, 1194-65-6; 2-methylbenzotrile, 529-19-1; 1-naphthonitrile, 86-53-3; 3-(trifluoromethyl)benzotrile, 368-77-4; 2-naphthonitrile, 613-46-7.

Kinetics of Reaction of Dodecacarbonyltriosmium with Diphenylacetylene

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Abstract: The kinetics of reaction of $\text{Os}_3(\text{CO})_{12}$ with C_2Ph_2 in decalin or tetradecane between 160 and 195 °C, and under various partial pressures of CO, have been studied. Loss of $\text{Os}_3(\text{CO})_{12}$ occurs by two main paths. One involves a very unusual bimolecular reaction between C_2Ph_2 and the cluster ($k = 5.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 170 °C; $\Delta H^\ddagger = 37.3 \pm 5.0 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = 9.7 \pm 11.5 \text{ cal K}^{-1} \text{ mol}^{-1}$). The other involves a labile preequilibrium between $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{Ph}_2)$ ($K = 2.5 \times 10^{-3}$ at 170 °C; $\Delta H^\circ = 9.4 \pm 2.9 \text{ kcal mol}^{-1}$; $\Delta S^\circ = 9.2 \pm 6.7 \text{ cal K}^{-1} \text{ mol}^{-1}$) followed by slow dissociative loss of CO ($k = 4.5 \times 10^{-4} \text{ s}^{-1}$ at 170.0 °C; $\Delta H^\ddagger = 32.4 \pm 1.8 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -1.6 \pm 4.3 \text{ cal K}^{-1} \text{ mol}^{-1}$). It is proposed that this dissociative loss of CO is accompanied by a concerted change of the $\eta^2\text{-C}_2\text{Ph}_2$ to $\mu\text{-C}_2\text{Ph}_2$ with formation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_2\text{Ph}_2)$. $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_2\text{Ph}_2)$ reacts readily with C_2Ph_2 between 80 and 95 °C in decalin to give $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ by a simple CO dissociative mechanism ($k = 6.2 \times 10^{-4} \text{ s}^{-1}$ at 85 °C; $\Delta H^\ddagger = 28.0 \pm 1.8 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = 4.6 \pm 5.1 \text{ cal K}^{-1} \text{ mol}^{-1}$). $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ fragments to form $\text{Os}_2(\text{CO})_6(\text{C}_4\text{Ph}_4)$ and $\text{Os}(\text{CO})_5$ between 50 and 70 °C at rates proportional to $[\text{CO}]$ ($k = 0.41 \text{ M}^{-1} \text{ s}^{-1}$ at 50 °C; $\Delta H^\ddagger = 8.2 \pm 1.3 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -35.3 \pm 3.9 \text{ cal K}^{-1} \text{ mol}^{-1}$). The bimolecular reaction of C_2Ph_2 with $\text{Os}_3(\text{CO})_{12}$ almost certainly leads directly to fragmentation products.

Much attention has been paid in recent years to reactions of unsaturated organic molecules with metal carbonyl clusters.¹ This has been motivated by an interest in the wide variety of bonding modes possible between such molecules and small clusters of metal atoms^{1,2} and by a desire to explore the possible uses of cluster

compounds as homogeneous or supported catalysts.^{2,3} Knowledge of the mechanisms of these reactions⁴ has not accumulated as rapidly as that of the structural nature of the products, and kinetic

(1) E.g.: *Organomet. Chem.* **1972**, *1*, et seq.
 (2) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451-470; *J. Organomet. Chem.* **1980**, *200*, 177-190; *Q. Rev. Chem. Soc.* **1982**, *11*, 283-320. (b) Lewis, J.; Johnson, B. F. G. *Gazz. Chim. Ital.* **1979**, *109*, 271-289. (c) *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980.

(3) (a) Whyman, R. Chapter 8 in ref 2c. (b) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109-148.

(4) *Inorg. React. Mech. 1971-1981, 1-7. Inorganic and Organometallic Reaction Mechanisms*; Twigg, M. V., Ed.; Plenum: New York, 1983, Vol. 1; 1984, Vol. 2; 1985, Vol. 3.

(5) Tachikawa, M. T.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172-7174.

(6) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1813-1817.