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# Study of Charge Transfer in Back-Bonding to Carbonyl and Nitrosyl Groups

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The carbon 1s, nitrogen 1s, and oxygen 1s binding energies of a wide variety of transition-metal carbonyl and nitrosyl compounds are subjected to correlative analysis. The carbon 1s and oxygen 1s binding energies of the carbonyls are linearly related to the C–O stretching force constants, and the nitrogen 1s and oxygen 1s binding energies of the nitrosyls are linearly related to the N–O stretching force constants. The data indicate that transfer of electron density to the CO and NO groups is accompanied by weakening of the C–O and N–O bonds. From the relative binding energy shifts it is calculated that, in back-bonding to CO groups, more charge is transferred to the carbon atoms than to the oxygen atoms, and, in back-bonding to NO groups, similar amounts of charge are transferred to the nitrogen and oxygen atoms.

## Introduction

It has been established that the carbon 1s and oxygen 1s binding energies of metal carbonyl compounds are at least approximately linearly correlated with the corresponding C–O stretching force constants. Such correlations, for solid-state binding energies, have been observed by Barber et al.[1] for eight compounds and by Willemen et al.[2] for four compounds. In a recent paper we have shown that the oxygen 1s binding energies of 19 metal carbonyl compounds in the gas phase are linearly correlated with the degeneracy-weighted average C–O stretching frequencies.[3] (The average frequencies were used as convenient stand-ins for C–O force constants.) In that paper we did not discuss carbon 1s binding energies because then we had measured only a few such energies and we feared that the binding energies of carbon atoms directly bonded to a variety of metal atoms might not be as well correlated with average stretching frequencies as the binding energies of the relatively isolated, terminal oxygen atoms. However, now we have both carbon 1s and oxygen 1s data for almost three times as many carbonyl compounds as were involved in our first study, including better data for several of the compounds studied earlier. Having both C 1s and O 1s binding energies, we can determine the relative amounts of electronic charge transferred to the carbon and oxygen atoms in $d\pi \rightarrow \pi^*$ back-bonding. We also now have nitrogen 1s and oxygen 1s binding energies for 15 metal nitrosyl compounds; with these data the relative charge transferred to the nitrogen and oxygen atoms can be determined, and the back-bonding in nitrosyl compounds can be compared with that in carbonyl compounds. We have calculated the C–O and N–O stretching force constants for all the carbonyl and nitrosyl compounds which we have studied and for which the necessary vibrational frequencies are known.

## Results and Discussion

In Table I are listed the carbon 1s and oxygen 1s binding energies determined for 55 metal carbonyl compounds in the gas phase. For those compounds for which the necessary vibrational spectroscopic data are available, we have listed the degeneracy-weighted C–O stretching frequencies and the corresponding weighted C–O stretching force constants, calculated by the Cotton–Kraihanzel (CK) method.[4] In Figure 1 the carbon 1s binding energies are plotted vs. the C–O force constants, and in Figure 2 the oxygen 1s binding energies are plotted vs. the same force constants (correlation coefficients 0.95 and 0.94, respectively). The linear correlations shown by these plots confirm the fact that transfer of electron density to the carbon and oxygen atoms of a CO group is accompanied by a weakening of the C–O bond. The data strongly suggest that the carbon and oxygen core binding energies can be taken as measures of $d\pi \rightarrow \pi^*$ back-bonding in transition-metal carbonyl compounds. From Figures 1 and 2 it is obvious that the carbon 1s and oxygen 1s binding energies are linearly correlated with each other. Figure 3 is a plot of the oxygen 1s binding energies vs. the carbon 1s binding energies (correlation coefficient 0.97). The justifications for presenting this otherwise superfluous plot are that it includes points for five more compounds than are in Figures 1 and 2 and that it shows a significantly better linear correlation than shown in Figures 1 and 2. At least two explanations can be offered for the poorer correlations in Figures 1 and 2. First, the carbon 1s and oxygen 1s binding energies are not *solely* determined by the degree of back-bonding (which is presumably manifested as changes in atomic charge). On going from one compound to another there are changes in the electronic relaxation energy associated with core ionization and changes in the electrostatic potential due to the metal atom and other ligands.[5] Although these changes in relaxation energy and potential are roughly linerly correlated with the changes in atomic charge,[5] parts of these changes are unsystematic, that is, not so correlated. The unsystematic parts of the changes in relaxation energy and potential contribute to the scatter in the plots of binding energy vs. force constant. However, in the correlation of the 1s binding energies of carbon and oxygen atoms *in the same carbonyl groups*, the unsystematic parts of the changes in relaxation energy and potential would be expected to have about the same magnitude and sign and would be largely canceled. In addition, errors in spectrometer calibration cause scatter in the points of Figures 1 and 2 but tend to cancel when carbon 1s binding energies and oxygen 1s binding energies which were determined in the same runs are correlated. Even if we ascribe all the scatter of the points in Figures 1 and 2 to unsystematic changes in relaxation energy and potential, we conclude from the standard deviations that the average unsystematic change in the sum of these quantities on going from one compound to another is less than about 0.2 eV. This conclusion is important because it indicates that shifts in core binding energies greater than 0.2 eV in compounds of this type can be interpreted in terms of changes in atomic charge. In fact, the data suggest that even smaller shifts can be thus interpreted within sets of structurally similar molecules. For

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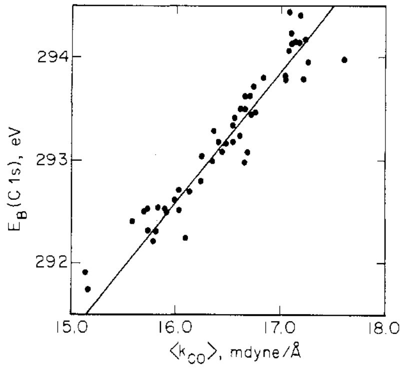

**Figure 1.** Plot of carbon 1s binding energies for gas-phase metal carbonyl compounds vs. C–O stretching force constants. Correlation coefficient = 0.951; standard deviation = 0.23 eV.

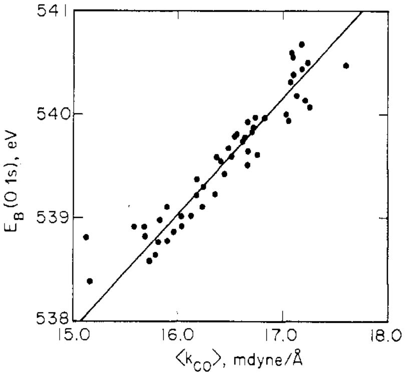

**Figure 2.** Plot of oxygen 1s binding energies for gas-phase metal carbonyl compounds vs. C–O stretching force constants. Correlation coefficient = 0.944; standard deviation = 0.22 eV.

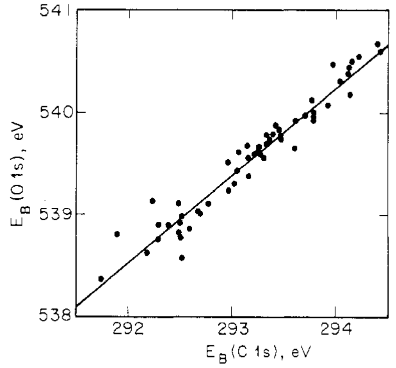

**Figure 3.** Plot of oxygen 1s binding energies vs. carbon 1s binding energies for gas-phase metal carbonyl compounds. Correlation coefficient = 0.970; standard deviations = 0.14 eV for $E_B$(O 1s) and 0.17 eV for $E_B$(C 1s).

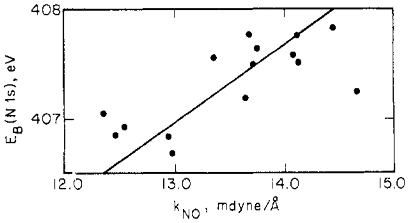

**Figure 4.** Plot of nitrogen 1s binding energies for gas-phase metal nitrosyl compounds vs. N–O stretching force constants. Correlation coefficient = 0.73; standard deviation = 0.37 eV.

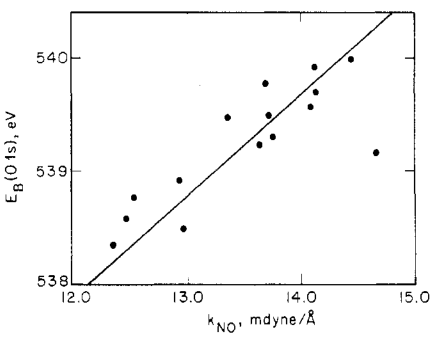

**Figure 5.** Plot of oxygen 1s binding energies for gas-phase metal nitrosyl compounds vs. N–O stretching force constants. Correlation coefficient = 0.81; standard deviation = 0.39 eV.

example, in the correlations of the C 1s and O 1s binding energies with C–O force constants for the 12 pentacarbonylmanganese compounds, $RMn(CO)_5$, the standard deviations are only 0.18 and 0.13 eV, respectively. Because a considerable part of these standard deviations is due to random experimental error, it seems reasonable to conclude that the average unsystematic changes in relaxation energy and potential in this set of compounds are no greater than about 0.1 eV.

From the slope of Figure 3 we can calculate the average relative amounts of electronic charge transferred to or from the oxygen and carbon atoms of carbonyl groups on going from one carbonyl compound to another. If we ignore changes in relaxation energy and potential, we can write $\Delta Q = \Delta E/k$, where $\Delta Q$ and $\Delta E$ are the changes in atomic charge and core binding energy and $k$ is a constant inversely proportional to the radial distance of the valence electrons.[6,7] Hence the ratio of the charge transferred to the oxygen and carbon atoms is calculated as

$$\frac{\Delta Q_O}{\Delta Q_C} = \frac{\Delta E_B(\mathrm{O\ 1s})}{\Delta E_B(\mathrm{C\ 1s})}\frac{k_C}{k_O} = 0.849\left(\frac{23.0}{32.5}\right) = 0.601$$

In other words, on going from one carbonyl compound to another, most of the change in charge of a CO group occurs at the carbon atom. Now because of the close correlation of the binding energies with C–O force constants and the fact that changes in C–O force constants are usually interpreted in terms of changes in back-bonding,[8-10] we believe that our data measure the relative atomic orbital contributions to the $\pi^*$ orbitals of a coordinated CO group. Various high-quality molecular orbital calculations are in agreement that the CO groups of metal carbonyls are negatively charged;[11-13] in other words, considerably less negative charge is transferred from the CO to the metal by $\sigma$ bonding than is transferred from the metal to the CO by $\pi$ bonding. There is little question that the $\pi^*$ orbitals of a *free* CO molecule reside more on the carbon atom than on the oxygen atom. Our results indicate that the same is true for a coordinated CO: as the interaction of the metal d$\pi$ orbitals with the CO $\pi^*$ orbitals increases, the shift of electron density to the carbon atoms is greater than that to the oxygen atoms. There are calculations in accord with this result. Schreiner and Brown[9] have calculated that

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(6) Values of $\langle 1/r \rangle$ for carbon, nitrogen, and oxygen were taken from ref 7. For carbon and nitrogen, the value for an $sp^3$ hybrid orbital was used. For oxygen, the value for an orbital with 20% s character was used. The rounded $k$ values in units of electronic charge per electronvolt are 23.0, 27.9, and 32.5, respectively.

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(13) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

**Table I.** Carbon 1s and Oxygen 1s Binding Energies, Degeneracy-Weighted Average C–O Stretching Frequencies, and Number-Weighted Average C–O Force Constants[a]

| carbonyl compd | $E_B$(C 1s), eV | $E_B$(O 1s), eV | ⟨$\nu_{CO}$⟩, cm$^{-1}$ | ⟨$k_{CO}$⟩, mdyn/Å |
|---|---|---|---|---|
| $C_6H_6Cr(CO)_3$ | 291.74 | 538.37 | 1938[b] | 15.18 |
| $C_7H_7V(CO)_3$ | 291.9[c,d] | 538.8[c,d] | 1935[e] | 15.14 |
| $Mo(CO)_5P(NMe_2)_3$ | 292.2 | 538.62 | 1977 | 15.80 |
| $C_5H_5Cr(CO)_2NS$ | 292.24 | 539.12 | 1996 | 16.10 |
| $C_5H_5Mn(CO)_3$ | 292.30 | 538.90 | 1974[f] | 15.75 |
| $Mo(CO)_5PMe_3$ | 292.30 | 538.75 | 1978[g] | 15.82 |
| $C_5H_5V(CO)_4$ | 292.4[c,d] | 538.8[c,d] | 1963[h] | 15.58 |
| $C_5H_5(Me)Mo(CO)_3$ | 292.5 | 538.8[i] | 1971[j] | 15.70 |
| $Me(OMe)CCr(CO)_5$ | 292.5[d,k] | 539.1[d,k] | 1984[l] | 15.91 |
| $C_5H_5Cr(CO)_2NO$ | 292.51 | 538.91 | 1986[m] | 15.94 |
| $C_5H_5Mo(CO)_2NO$ | 292.52 | 538.77 | 1984 | 15.91 |
| $C_5H_5W(CO)_2NO$ | 292.52 | 538.57 | 1974 | 15.75 |
| $C_5H_5Mn(CO)_2CS$ | 292.53 | 538.97 | 1980[n] | 15.85 |
| $Mo(CO)_5P(OEt)_3$ | 292.6 | 538.85 | 1989[o] | 15.99 |
| $C_5H_5Co(CO)_2$ | 292.68 | 539.01 | 1998 | 16.14 |
| $Mo(CO)_5P(OMe)_3$ | 292.7 | 539.0 | 1992[o] | 16.04 |
| $C_7H_8Fe(CO)_3$ | 292.79 | 539.09[i] | 2004[p] | 16.23 |
| $W(CO)_5CS$ | 292.97 | 539.50 | 2030[q] | 16.66 |
| $C_3H_5Fe(CO)_2NO$ | 292.98 | 539.22 | 2012 | 16.36 |
| $C_4H_6Fe(CO)_3$ | 293.03[r] | 539.29[r] | 2005[s] | 16.25 |
| $Mo(CO)_5PCl_3$ | 293.06 | 539.41 | 2017[o] | 16.45 |
| $Cr(CO)_5CS$ | 293.07 | 539.60 | 2034[q] | 16.72 |
| $Cr(CO)_6$ | 293.16 | 539.66[i] | 2026[t] | 16.59 |
| $W(CO)_6$ | 293.17 | 539.54 | 2024[t] | 16.56 |
| $C(CH_2)_3Fe(CO)_3$ | 293.17[r] | 539.17[r] | 2016[u] | 16.43 |
| $Mo(CO)_6$ | 293.22 | 539.58 | 2028[t] | 16.63 |
| $HCCo_3(CO)_9$ | 293.26 | 539.63 | | |
| $BrCCo_3(CO)_9$ | 293.28 | 539.66 | | |
| $Mn_2(CO)_{10}$ | 293.28[v] | 539.57[v] | 2017[f] | 16.45 |
| $MeCCo_3(CO)_9$ | 293.32 | 539.56 | | |
| $ClCCo_3(CO)_9$ | 293.34 | 539.67 | | |
| $Mo(CO)_5PF_3$ | 293.34 | 539.77 | 2024[g] | 16.56 |
| $Cr(CO)_5PF_3$ | 293.37 | 539.72 | | |
| $Co_2(CO)_8$ | 293.40[v] | 539.78[v] | 2025[x] | 16.58 |
| $MeCOMn(CO)_5$ | 293.44 | 539.86 | 2035[y] | 16.74 |
| $C_3H_5Mn(CO)_5$ | 293.47 | 539.82 | 2036[z] | 16.76 |
| *cis*-$Mo(CO)_3(PF_3)_3$ | 293.49 | 539.73 | 2030[t] | 16.66 |
| $Mn(CO)_4NO$ | 293.49[aa] | 539.77[aa] | 2026[aa] | 16.59 |
| $MeRe(CO)_5$ | 293.62 | 539.64[i] | 2033[bb] | 16.71 |
| $MeMn(CO)_5$ | 293.62 | 539.91 | 2032[cc] | 16.69 |
| $Fe(CO)_5$ | 293.71[v] | 539.96[v] | 2036[f] | 16.76 |
| $Ni(CO)_4$ | 293.78[v] | 540.11[v] | 2066[dd] | 17.25 |
| $Fe(CO)_2(NO)_2$ | 293.79[aa] | 539.91[aa] | 2059[dd] | 17.14 |
| $HMn(CO)_5$ | 293.80[v] | 539.95[v] | 2039[ee] | 16.81 |
| $Co(CO)_3NO$ | 293.81[aa] | 539.99[aa] | 2056[dd] | 17.09 |
| $HCo(CO)_4$ | 293.94[v] | 540.06[v] | 2068[ff] | 17.29 |
| $Mn(NO)_3CO$ | 293.98[aa] | 540.47[aa] | 2088[dd] | 17.62 |
| $IMn(CO)_5$ | 294.05 | 540.30 | 2057[cc] | 17.10 |
| $SiCl_3Mn(CO)_5$ | 294.12 | 540.37 | 2058[gg] | 17.12 |
| $BrMn(CO)_5$ | 294.14 | 540.43 | 2063[cc] | 17.20 |
| $H_2Fe(CO)_4$ | 294.15[v] | 540.17[v] | 2060[hh] | 17.15 |
| $ClMn(CO)_5$ | 294.16 | 540.49 | 2066[cc] | 17.25 |
| $CF_3COMn(CO)_5$ | 294.22 | 540.54 | | 17.11[w] |
| $CF_3Mn(CO)_5$ | 294.40 | 540.67 | 2062[ii] | 17.19 |
| $SiF_3Mn(CO)_5$ | 294.43 | 540.59 | 2056[jj] | 17.09 |

[a] Unreferenced data in this table were determined in this study by methods described in the Experimental Section. [b] Davidson, G.; Riley, E. M. *Spectrochim. Acta, Part A* 1971, *27a,* 1649. [c] Rietz, R. R.; Schaaf, T. F.; Jolly, W. L. *Inorg. Chem.* 1975, *14,* 2818. [d] The data differ from the published data because of a spectrometer recalibration and a change to the use of 248.62 eV for the Ar $2p_{3/2}$ reference and 870.37 eV for the Ne 1s reference. See: Johansson, G.; Hedman, J.; Berndtsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc. Relat. Phenom.* 1973, *2,* 295. [e] Werner, R. P. M.; Manastyraskyj, S. A. *J. Am. Chem. Soc.* 1961, *83,* 2023. [f] Haas, H.; Sheline, R. K. *J. Chem. Phys.* 1967, *47,* 2996. [g] Dalton, J.; Paul, I.; Smith, J. G.; Stone, F. G. A. *J. Chem. Soc. A* 1968, 1199. [h] Durig, J. R.; Marston, A. L.; King, R. B.; Houk, L. W. *J. Organomet. Chem.* 1969, *16,* 425. [i] Reference 3. [j] King, R. B.; Houk, L. W. *Can. J. Chem.* 1969, *47,* 2959. [k] Perry, W. B.; Schaaf, T. F.; Jolly, W. L.; Todd, L. J.; Cronin, D. L. *Inorg. Chem.* 1974, *13,* 2038. [l] Kreiter, C. G.; Fischer, E. O. *Chem. Ber.* 1970, *103,* 1561. [m] Herberhold, M.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* 1979, *18,* 631. [n] Andrews, M. A. *Inorg. Chem.* 1977, *16,* 496. [o] Reference 38. [p] Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* 1965, *3,* 341. [q] Butler, I. S.; Garcia-Rodriguez, A.; Plowman, K. R.; Shaw, C. F. *Inorg. Chem.* 1976, *15,* 2602. [r] Koepke, J. W.; Jolly, W. L.; Bancroft, G. M.; Malmquist, P. A.; Siegbahn, K. *Ibid.* 1977, *16,* 2659. [s] Davidson, G. *Inorg. Chim. Acta* 1969, *3,* 596. [t] Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Radiochem.* 1966, *8,* 1. [u] Andrews, D. C.; Davidson, G.; Duce, D. A. *J. Organomet. Chem.* 1975, *97,* 95. [v] Reference 17. [w] Graham, W. A. G. *Inorg. Chem.* 1968, *7,* 315. [x] Sweany, R. L.; Brown, T. L. *Ibid.* 1977, *16,* 415. [y] Noack, K. *J. Organomet. Chem.* 1968, *12,* 181. [z] Clarke, H. L.; Fitzpatrick, N. J. *Ibid.* 1972, *40,* 379. [aa] Chen, H. W.; Jolly, W. L. *Inorg. Chem.* 1979, *18,* 2548. [bb] Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* 1960, *93,* 901. [cc] Reference 27. [dd] Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* 1966, *5,* 1960. [ee] Braterman, P. S.; Harrill, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* 1967, *89,* 2851. [ff] Edgell, W. F.; Magee, C.; Gallup, G. *Ibid.* 1956, *78,* 4185. [gg] Onaka, S. *Bull. Chem. Soc. Jpn.* 1973, *46,* 2444. [hh] Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* 1968, 2162. [ii] Edgar, K.; Lewis, J.; Manning, A. R.; Miller, J. R. *Ibid.* 1968, 1217. [jj] Reference 32.

the carbon p$\pi$ atomic orbitals contain more charge when CO is bonded to chromium, whereas the oxygen p$\pi$ charge is nearly unaffected. Electron density difference plots of Ziegler and Rauk[13] indicate that, when $Ni(CO)_3$ bonds to CO, most of the electron density is transferred from the carbons of the $Ni(CO)_3$ to the carbon of the entering CO.

In Table II are listed the nitrogen 1s and oxygen 1s binding energies determined for 15 metal nitrosyl compounds in the gas phase. In all these compounds the nitrosyl groups are of the terminal, linear type, isostructural with terminal carbonyl groups. We know of no compounds with bent nitrosyl groups that have sufficient volatility for study in our spectrometer. In the table we have listed the degeneracy-weighted N–O stretching frequencies and the CK N–O stretching force constants. In Figure 4 the nitrogen 1s binding energies are plotted vs. the N–O force constants, and in Figure 5 the oxygen 1s binding energies are plotted vs. the same force constants. Although these plots show more scatter than those of Figures 1 and 2, they indicate that the nitrogen and oxygen core binding energies can be taken as measures of d$\pi \rightarrow \pi^*$ back-bonding in metal nitrosyl compounds. As in the case of the carbonyl compounds, the plot of the binding energies

**Table II.** Nitrogen 1s and Oxygen 1s Binding Energies, Degeneracy-Weighted Average N–O Stretching Frequencies, and N–O Force Constants[a]

| nitrosyl compd | $E_B$(N 1s), eV | $E_B$(O 1s), eV | ⟨$\nu_{NO}$⟩, cm$^{-1}$ | $k_{NO}$, mdyn/Å |
|---|---|---|---|---|
| $Mn(NO)_3PMe_3$ | 406.69 | 538.48 | 1717 | 12.97 |
| $C_5H_5Cr(CO)_2NO$ | 406.84 | 538.91 | 1715 | 12.94 |
| $C_5H_5W(CO)_2NO$ | 406.85 | 538.57 | 1683 | 12.46 |
| $C_5H_5Mo(CO)_2NO$ | 406.93 | 538.77 | 1688 | 12.54 |
| $C_5H_5W(NO)_2H$ | 407.05 | 538.33 | 1675[b] | 12.35 |
| $C_3H_5Fe(CO)_2NO$ | 407.19 | 539.22 | 1760 | 13.63 |
| $C_5H_5NiNO$ | 407.25 | 539.15 | 1825 | 14.66 |
| $C_5H_5Cr(NO)_2Cl$ | 407.47 | 539.45 | 1764[c] | 13.69 |
| $Fe_2(NO)_4Br_2$ | 407.51 | 539.68 | 1792 | 14.13 |
| $Cr(NO)_4$ | 407.56[d] | 539.46[d] | 1742[d] | 13.35 |
| $Fe_2(NO)_4I_2$ | 407.58 | 539.55 | 1789 | 14.08 |
| $Mn(NO)_3CO$ | 407.65[d] | 539.28[d] | 1764[e] | 13.69 |
| $Fe(CO)_2(NO)_2$ | 407.76[d] | 539.91[d] | 1788[e] | 14.07 |
| $Mn(CO)_4NO$ | 407.77[d] | 539.77[d] | 1764[e] | 13.69 |
| $Co(CO)_3NO$ | 407.83[d] | 539.99[d] | 1806[e] | 14.35 |

[a] Unreferenced data in this table were determined in this study by methods described in the Experimental Section. [b] Legzdins, P.; Martin, D. T. *Inorg. Chem.* 1979, *18,* 1250. [c] Reference 47. [d] Chen, H. W.; Jolly, W. L. *Inorg. Chem.* 1979, *18,* 2548. [e] Van Hecke, G. R.; Horrocks, W. D., Jr. *Ibid.* 1966, *5,* 1960.

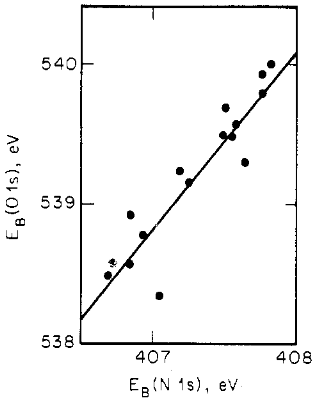

**Figure 6.** Plot of oxygen 1s binding energies vs. nitrogen 1s binding energies for gas-phase metal nitrosyl compounds. Correlation coefficient = 0.914; standard deviations = 0.22 eV for $E_B$(O 1s) and 0.18 eV for $E_B$(N 1s).

against one another, shown in Figure 6, shows a better correlation. The results can be interpreted in essentially the same way as in the case of the carbonyl compounds. From the slope of Figure 6 we can calculate the average relative amounts of charge transferred to the oxygen and nitrogen atoms of nitrosyl groups on going from one nitrosyl compound to another:

$$\frac{\Delta Q_O}{\Delta Q_N} = \frac{\Delta E_B(\text{O 1s})}{\Delta E_B(\text{N 1s})}\frac{k_N}{k_O} = 1.257\left(\frac{27.9}{32.5}\right) = 1.08$$

Apparently the oxygen and nitrogen atoms undergo comparable changes in charge, with perhaps slightly more change in charge occurring at the oxygen atom. To some extent this result is expected. An increase in the electronegativity of one atom in a diatomic molecule causes the contribution of that atom to the $\pi^*$ MO to *decrease*. Thus, because nitrogen is more electronegative than carbon, one would expect that $d\pi \rightarrow \pi^*$ bonding would transfer relatively more charge to the oxygen atoms of NO groups than to the oxygen atoms of CO groups. However, in free NO$^+$, the $\pi^*$ orbital is located more on the nitrogen atom than on the oxygen atom,[14] and thus it is at first sight surprising that a greater (or at least comparable) amount of charge is transferred to the oxygen atom of a coordinated NO$^+$ group than to the nitrogen atom. The explanation probably is to be found in the fact that the effective electronegativity of the nitrogen atom in a coordinated NO$^+$ group is much higher than it is in free NO$^+$; indeed it would not appear unreasonable if the nitrogen atom had a greater electronegativity than that of the oxygen atom. These changes in electronegativity can be understood in terms of the changes in *formal* charge. An increase in positive formal charge corresponds to an increase in electronegativity.[15] In free NO$^+$, the nitrogen atom has zero formal charge and the oxygen atom has a positive formal charge:

$$:N{\equiv}O{:}^{+}$$

In coordinated NO$^+$, the nitrogen atom has a positive formal charge, and the oxygen atom loses its positive formal charge in proportion to the extent of back-bonding:

$$^{-}M{-}\overset{+}{N}{\equiv}O{:}^{+} \leftrightarrow M{=}\overset{+}{N}{=}O$$

In a carbonyl compound, even with strong back-bonding, the formal charge of the oxygen atom is never more negative than that of the carbon atom, so the effective electronegativity of the oxygen atom is always greater than that of the carbon atom.

$$^{-}M{-}C{\equiv}O{:}^{+} \leftrightarrow M{=}C{=}\underset{\cdot}{\dot{O}}{:}$$

Su and Faller[16] observed that the difference between the oxygen 1s and the nitrogen 1s binding energies for crystalline complexes containing linear nitrosyl groups was 132 ± 1 eV, i.e.

$$E_B(\text{O 1s}) \approx E_B(\text{N 1s}) + 132$$

The equation of the least-squares line through the points in Figure 6 is

$$E_B(\text{O 1s}) = 1.257E_B(\text{N 1s}) + 27.06$$

However the standard deviation of the slope (1.257) is 0.16, and the data only marginally justify fitting to an equation with two adjustable parameters rather than to a one-parameter equation. Indeed, the average difference between $E_B$(O 1s) and $E_B$(N 1s) in Table II is 131.91 eV, with a standard deviation of 0.24 eV, and therefore our gaseous nitrosyl data are consistent with the solid-state data of Su and Faller.[16] It would be of considerable interest to obtain gas-phase data for bent nitrosyls to see if the $E_B$(O 1s) − $E_B$(N 1s) difference for these compounds is significantly lower than 132 eV, as was found for the crystalline compounds. The standard deviation of the slope (0.849) of the line in the plot of $E_B$(O 1s) vs. $E_B$(C 1s) (Figure 3) is only 0.03; in this case the data strongly justify fitting to a two-parameter equation rather than a one-parameter equation.

## Experimental Section

The unreferenced binding energies in Tables I and II were determined by using procedures previously described.[17] A few of the data are redeterminations of values reported earlier.[3] In general, the binding energies given to two decimal places are known to ±0.05 eV; those given to one decimal place have uncertainties of ±0.1 eV. It was not possible to resolve the oxygen 1s spectra of the carbonyl nitrosyl compounds, except Mn(NO)$_3$CO, into separate peaks. In these cases the full widths at half-maximum for the O 1s lines were significantly greater (1.60-eV average) than those of the other nitrosyl compounds (1.40-eV average), and the reported O 1s binding energies are weighted averages for the NO and CO oxygens. Therefore we believe the reported nitrosyl O 1s binding energies of the carbonyl nitrosyl compounds are uncertain by 0.2–0.3 eV. If the points involving these data are deleted from Figure 6, the slope of the least-squares line is increased only from 1.257 to 1.321, and our conclusions are not changed significantly.

The C–O and N–O stretching frequencies are from the literature in those cases in which the infrared measurements were carried out by using nonpolar hydrocarbon solvents. The unreferenced values are based on our measurements, using either hexane or pentane solvent.

The force constants are those obtained by the CK procedure,[4] which, although approximate, gives reasonable relative force constants for comparing bond strengths.[18] Even though more accurate force constants have been calculated for some of the compounds, we have not used these because we believe it is important that all the constants used in a correlation be calculated by a consistent procedure. It can be easily shown, by using the "exact" secular equations involved in the CK method, that a force constant can be simply obtained from the familar equation

$$k = 4\pi^2 c^2 \mu \nu^2$$

if one uses the degeneracy-weighted stretching frequency, $\langle\nu\rangle$, for $\nu$. For example, the degeneracy-weighted C–O stretching force

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(14) The $\pi^*$ orbital of CO is localized 68% on the carbon atom and 32% on the oxygen atom. (See: Snyder, L. C.; Basch, H. "Molecular Wave Functions and Properties"; Wiley-Interscience: New York, 1972.) The $\pi^*$ orbital of $O_2^{2+}$ is symmetrically distributed between the two atoms. Undoubtedly the delocalization of the $\pi^*$ orbital of the intermediate isoelectronic species NO$^+$ is intermediate between that of CO and $O_2^{2+}$.

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constant[19] of an octahedral carbonyl $M(CO)_6$ is evaluated as $\langle \nu_{CO} \rangle = {}^1/_6\nu_{A_{1g}} + {}^2/_6\nu_{E_g} + {}^3/_6\nu_{T_{1u}}$. For calculating the C–O and N–O stretching force constants, we used the relations

$$k_{CO} = 4.0423 \times 10^{-6}\langle \nu_{CO} \rangle^2 \qquad k_{NO} = 4.4004 \times 10^{-6}\langle \nu_{NO} \rangle^2$$

In the case of carbonyls having more than one structural type of CO group, we calculated the overall weighted average $k_{CO}$ values.

Dicarbonyl($\eta^5$-cyclopentadienyl)cobalt was obtained from Pressure Chemical Co. The compound was twice purified by chromatography in petroleum ether on a silica gel column. After solvent removal, the compound was purified on the vacuum line; the pure compound was collected in a −30 °C trap. The infrared data were in precise agreement with the literature values[20] ($\nu_{CO}$ = 2028 and 1967 cm$^{-1}$).

Methylidynetricobalt nonacarbonyl, prepared by the method of Nestle et al.,[21] melted at 105–106 °C (lit. mp 105–106 °C) and showed infrared absorptions (pentane solution) at 2028, 2042, 2058, and 2100 cm$^{-1}$ (C–O stretching) (lit.[21] IR ($CCl_4$ solution): $\nu_{CO}$ = 2025, 2045, 2060, 2105 cm$^{-1}$).

(Chloromethylidyne)tricobalt nonacarbonyl, prepared by the method of Nivert et al.,[22] melted at 131–133 °C (lit. mp 131–133 °C) and showed infrared absorptions (pentane solution) at 2112, 2064, 2048, 2032, and 1993 cm$^{-1}$ (lit.[22] IR ($CCl_4$ solution): $\nu_{CO}$ = 2112, 2065, 2045, 2020, 1985 cm$^{-1}$).

(Methylmethylidyne)tricobalt nonacarbonyl was kindly provided by L. Stuhl. The compound was sublimed just prior to use.

(Bromomethylidyne)tricobalt nonacarbonyl, prepared by the method of Ercoli et al.,[23] melted at 119–120 °C (lit. mp 130–132 °C) and showed infrared absorptions (pentane solution) at 2108, 2061, 2045, and 2032 cm$^{-1}$ (C–O stretching) (lit.[24] IR (hexane solution): $\nu_{CO}$ = 2108.7, 2064.4, 2046.6, 2031 cm$^{-1}$).

Dicarbonyl($\eta^5$-cyclopentadienyl)(thiocarbonyl)manganese, prepared by the method of Fenster and Butler,[25] melted at 51–52 °C (lit. mp 51–53 °C) and showed infrared absorptions (pentane solution) at 2010 and 1965 cm$^{-1}$ (C–O stretching) and 1275 cm$^{-1}$ (C–S stretching) (lit.[25] IR ($CS_2$ solution): $\nu_{CO}$ = 2006, 1954 cm$^{-1}$; $\nu_{CS}$ = 1266 cm$^{-1}$).

Dicarbonyl($\eta^5$-cyclopentadienyl)(thionitrosyl)chromium, prepared by the method of Kolthammer and Legzdins,[26] melted at 68.5–69.5 °C (lit. mp 68–69 °C) and showed infrared absorption (pentane solution) at 2025 and 1966 cm$^{-1}$ (C–O stretching) and 1180 cm$^{-1}$ (N–S stretching). (lit.[26] IR (hexane solution): $\nu_{CO}$ = 2033, 1962 cm$^{-1}$; $\nu_{NS}$ = 1180 cm$^{-1}$).

Manganese pentacarbonyl iodide was prepared by the addition of $I_2$ to a solution of $NaMn(CO)_5$ in tetrahydrofuran at room temperature. After removal of the solvent, the product was obtained by sublimation at room temperature to a 0 °C trap. The infrared spectrum of $IMn(CO)_5$ agreed with the literature.[27]

Manganese pentacarbonyl chloride was prepared by the method of Abel and Wilkinson.[28] Many attempts were made to characterize this compound by its infrared spectrum in cyclohexane solution,[27] but peaks attributable to $Mn_2(CO)_8Cl_2$ were always present, along with the bands from the monomer. This is consistent with the findings of Bamford et al.[29] that $Mn(CO)_5Cl$ easily undergoes conversion to $Mn_2(CO)_8Cl_2$ in solution with loss of CO. Consequently, the $Mn(CO)_5Cl$ sample was characterized by means of its mass spectrum,[30,31] from which any sign of $Mn_2(CO)_8Cl_2$ impurity was absent.

$Mn(CO)_5Br$ (Strem) was shown to be pure by its infrared spectrum.[27]

$F_3SiMn(CO)_5$ was prepared and characterized as described in the literature.[32]

$CF_3COMn(CO)_5$ was prepared by the reaction of trifluoroacetic anhydride with $NaMn(CO)_5$ in tetrahydrofuran; the melting point agreed with the literature.[20] $CF_3Mn(CO)_5$ was made by the decarbonylation of the trifluoroacetyl derivative.[20]

($\sigma$-Allyl)manganese pentacarbonyl was prepared according to the literature[33] and purified by fractional condensation in vacuo. The product was trapped at 0 °C; volatile impurities and solvent were trapped (along with a small amount of product) at −196 °C, and nonvolatile impurities remained in the original flask at 20 °C. The product was shown to be pure by its NMR spectrum, using $CDCl_3$ solvent.

All the $Cr(CO)_5PX_3$ and $Mo(CO)_5PX_3$ complexes were prepared by the same general procedure,[34] which involves the reaction of the iodopentacarbonylmetalate $M(CO)_5I^-$ with an equimolar amount of the ligand in the presence of a Lewis acid. The complex [$n$-$Bu_4N$][$Mo(CO)_5I$][35] and the Lewis acid $Et_3OBF_4$[36] were prepared by literature methods. The complexes were purified by vacuum distillation ($Mo(CO)_5PF_3$, mp 4.5–5.5 °C (lit.[37] mp 5 °C)), sublimation ($Mo(CO)_5PCl_3$, mp 31 °C (lit.[38] mp 30 °C); $Mo(CO)_5PMe_3$; $Mo(CO)_5P(NMe_2)_3$, mp 150–153 °C dec (lit.[39] mp 152–154 °C dec)), or recrystallization ($Mo(CO)_5P(OMe)_3$, mp 7–8 °C (lit.[40] mp 8 °C); $Mo(CO)_5P(OEt)_3$).

The complex $cis$-$Mo(CO)_3(PF_3)_3$ was prepared by reaction of $\pi$-$C_9H_{12}Mo(CO)_3$ with $PF_3$ at an elevated temperature and pressure.[41] Sublimation of the crude product yielded a pure sample, mp 63–64 °C (lit.[37] mp 64 °C).

$Cr(CO)_5CS$ and $W(CO)_5CS$ were prepared by treating the reduced carbonyls (prepared from the hexacarbonyls and sodium amalgam in refluxing tetrahydrofuran) with thiophosgene at room temperature.[42] Pure (>95%) $Cr(CO)_5CS$ was obtained from the $Cr(CO)_6$/$Cr(CO)_5CS$ product mixture by repeated recrystallization from hexane. Pure (>95%) $W(CO)_5CS$ was obtained by converting the $W(CO)_6$/$W(CO)_5CS$ product mixture to $W(CO)_6$/$trans$-$W(CO)_4CSI^-$, isolating the thiocarbonyl salt and then substituting $I^-$ with CO in the presence of a $Ag^+$ salt. Purity was established by comparison of the experimental and published infrared spectra and by GLC using a 10% SE-30 column.

($\eta^5$-Cyclopentadienyl)nitrosylnickel, prepared by the method of King,[20] melted at −40 to −39 °C (lit. mp −41 °C) and showed an infrared absorption (pentane solution) at 1825 cm$^{-1}$ (N–O stretching) (lit.[43] IR (liquid): $\nu_{NO}$ = 1810 cm$^{-1}$).

($\eta^3$-Allyl)dicarbonylnitrosyliron, prepared by the method of Chaudhari et al.,[44] melted at −19 to −18 °C and showed infrared absorptions (pentane solution) at 2040 and 1984 cm$^{-1}$ (C–O stretching) and 1760 cm$^{-1}$ (N–O stretching) (lit.[45] IR (petroleum ether): $\nu_{CO}$ = 2038, 1983 cm$^{-1}$; $\nu_{NO}$ = 1761 cm$^{-1}$).

Dicarbonyl($\eta^5$-cyclopentadienyl)nitrosylchromium, prepared by the method of Crease and Legzdins,[46] melted at 66–67 °C and showed infrared absorptions at 2024 and 1960 cm$^{-1}$ (C–O stretching) and 1715 cm$^{-1}$ (N–O stretching) (lit.[47] IR ($CH_2Cl_2$ solution): $\nu_{CO}$ = 2020, 1945, cm$^{-1}$; $\nu_{NO}$ = 1680 cm$^{-1}$). Dicarbonyl($\eta^5$-cyclopentadienyl)nitrosylmolybdenum, prepared by the method of Seddon et al.,[48] melted

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at 83–84.5 °C and showed infrared absorptions (pentane solution) at 2018 and 1950 $cm^{-1}$ (C–O stretching) and 1688 $cm^{-1}$ (N–O stretching) (lit.[47] IR ($CH_2Cl_2$ solution): $\nu_{CO} = 2020, 1937$; $\nu_{NO} = 1663$).

Dicarbonyl($\eta^5$-cyclopentadienyl)nitrosyltungsten, prepared by the method of Crease and Legzdins,[46] melted at 107–108.5 °C and showed infrared absorptions at 2010 and 1938 $cm^{-1}$ (C–O stretching) and 1683 $cm^{-1}$ (N–O stretching) (lit.[47] IR ($CH_2Cl_2$ solution): $\nu_{CO} = 2010, 1925\ cm^{-1}$; $\nu_{NO} = 1655\ cm^{-1}$).

Trinitrosyl(trimethylphosphine)manganese was prepared by the reaction of $Mn(NO)_3CO$[49] and trimethylphosphine in xylene solution. After the reaction, the solvent was removed in vacuo. The green residue was sublimed at 50 °C to obtain dark green crystals. The infrared spectrum (pentane solution) showed nitrosyl bands at 1792 and 1680 $cm^{-1}$.

$W(Cp)(NO)_2H$ was kindly furnished by Prof. Legzdins of the University of British Columbia.

Chloro($\eta^5$-cyclopentadienyl)dinitrosylchromium, prepared by the method of Hoyano et al.,[47] melted and decomposed at 144–145 °C (lit. mp 144 °C).

Dinitrosyliron iodide dimer, prepared by the method of Haymore and Feltham,[50] melted at 95–96 °C and showed infrared absorptions (pentane solution) at 1810 and 1768 $cm^{-1}$ (N–O stretching) (lit.[51] IR ($CCl_4$ solution): $\nu_{NO} = 1810, 1769\ cm^{-1}$).

Dinitrosyliron bromide dimer was prepared by a method analogous to that used for dinitrosyliron iodide. The compound melted at 94–96 °C and showed infrared absorptions (pentane solution) at 1817 and 1767 $cm^{-1}$ (lit.[51] IR ($CCl_4$ solution): $\nu_{NO} = 1818.5, 1767\ cm^{-1}$).

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**Registry No.** $C_6H_6Cr(CO)_3$, 12082-08-5; $C_7H_7V(CO)_3$, 12083-16-8; $Mo(CO)_5P(NMe_2)_3$, 14971-43-8; $C_5H_5Cr(CO)_2NS$, 66539-91-1; $C_5H_5Mn(CO)_3$, 12079-65-1; $Mo(CO)_5PMe_3$, 16917-96-7; $C_5H_5V(CO)_4$, 12108-04-2; $C_5H_5(Me)Mo(CO)_3$, 12082-25-6; $Me(OMe)CCr(CO)_5$, 20540-69-6; $C_5H_5Cr(CO)_2NO$, 36312-04-6; $C_5H_5Mo(CO)_2NO$, 12128-13-1; $C_5H_5W(CO)_2NO$, 12128-14-2; $C_5H_5Mn(CO)_2CS$, 31741-76-1; $Mo(CO)_5P(OEt)_3$, 15603-75-5; $C_5H_5Co(CO)_2$, 12078-25-0; $Mo(CO)_5P(OMe)_3$, 15631-20-6; $C_7H_8Fe(CO)_3$, 36343-88-1; $W(CO)_5CS$, 50358-92-4; $C_3H_5Fe(CO)_2NO$, 12071-54-4; $C_4H_6Fe(CO)_3$, 12078-32-9; $Mo(CO)_5PCl_3$, 19212-18-1; $Cr(CO)_5CS$, 50358-90-2; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $C(CH_2)_3Fe(CO)_3$, 12078-33-0; $Mo(CO)_6$, 13939-06-5; $HCCo_3(CO)_9$, 15664-75-2; $BrCCo_3(CO)_9$, 19439-14-6; $Mn_2(CO)_{10}$, 10170-69-1; $MeCCo_3(CO)_9$, 13682-04-7; $ClCCo_3(CO)_9$, 13682-02-5; $Mo(CO)_5PF_3$, 15322-05-1; $Cr(CO)_5PF_3$, 18461-42-2; $Co_2(CO)_8$, 10210-68-1; $MeCOMn(CO)_5$, 13963-91-2; $C_3H_5Mn(CO)_5$, 14057-83-1; *cis*-$Mo(CO)_3(PF_3)_3$, 15280-12-3; $Mn(CO)_4NO$, 16104-17-9; $MeRe(CO)_5$, 14524-92-6; $MeMn(CO)_5$, 13601-24-6; $Fe(CO)_5$, 13463-40-6; $Ni(CO)_4$, 13463-39-3; $Fe(CO)_2(NO)_2$, 13682-74-1; $HMn(CO)_5$, 16972-33-1; $Co(CO)_3NO$, 14096-82-3; $HCo(CO)_4$, 16842-03-8; $Mn(NO)_3CO$, 14951-98-5; $IMn(CO)_5$, 14879-42-6; $SiCl_3Mn(CO)_5$, 38194-30-8; $BrMn(CO)_5$, 14516-54-2; $H_2Fe(CO)_4$, 12002-28-7; $ClMn(CO)_5$, 14100-30-2; $CF_3COMn(CO)_5$, 14099-62-8; $CF_3Mn(CO)_5$, 13601-14-4; $SiF_3Mn(CO)_5$, 39945-25-0; $Mn(NO)_3PMe_3$, 73347-69-0; $C_5H_5W(NO)_2H$, 69532-01-0; $C_5H_5NiNO$, 12071-73-7; $C_5H_5Cr(NO)_2Cl$, 12071-51-1; $Fe_2(NO)_4Br_2$, 15696-30-7; $Cr(NO)_4$, 37355-72-9; $Fe_2(NO)_4I_2$, 15002-08-1.

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# Activation Parameters for Homogeneous Outer-Sphere Electron-Transfer Reactions. Comparisons between Self-Exchange and Cross Reactions Using Marcus' Theory

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Experimental rate constants and activation parameters for a number of outer-sphere cross reactions involving cationic transition-metal complexes are compared with the values predicted from the kinetic parameters of the corresponding self-exchange processes using the conventional Marcus treatment. The required free energies, entropies, and enthalpies of the cross reactions were obtained from electrochemical measurements using nonisothermal cells. It was found that the increasingly large disagreements seen between the experimental rate constants and the predicted values at very large thermodynamic driving forces are compatible with the presence of large unfavorable work terms required to form the binuclear collision complex prior to electron transfer. The discrepancies are especially large for reactions involving pairs of aquo complexes. Analysis of the activation parameters suggests that these discrepancies lie chiefly in the entropic component of the activation free energy. It is speculated that a major part of such entropic terms may be due to the need to reorientate solvating water molecules in order to form the highly charged collision complexes from the separated reactants, although these effects may arise partly from the presence of nonadiabatic pathways or from anharmonicity of the free energy barriers.

## Introduction

The adiabatic model of outer-sphere electron transfer developed by Marcus and others[1,2] predicts that there should be a simple relationship between the kinetics of homogeneous cross reactions and the corresponding self-exchange processes. This relationship has commonly been formulated as eq 1,

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (1)$$

$$\log f_{12} = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (1a)$$

where $k_{11}$ and $k_{22}$ are the rate constants for the two constituent self-exchange (homonuclear) reactions, $k_{12}$ and $K_{12}$ are the rate and equilibrium constants, respectively, for the corresponding cross (heteronuclear) reaction, and $Z$ is the bimolecular collision frequency in solution. A number of tests of the applicability of eq 1 to experimental kinetic data have been

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