

tem.^{9,10} Moreover, since $K_4 = K_3K_{1h}/K_{2h}$, it follows that $k_{-4}'/k_{-3} = k_4/K_{1h}k_3$. The values of k_3 and k_4 have been determined in the present study and $K_{1h} = 1.28 \times 10^{-3} M$ at 25.0° and ionic strength 3.0 M.¹¹ Consequently $k_{-4}'/k_{-3} = 1.9 \times 10^3$ under the above conditions. This ratio may be compared with 1.1×10^3 for the ratio of the rates of the $Fe^{2+}-FeOH^{2+}$ and $Fe^{2+}-Fe^{3+}$ reactions,⁹ and 1.4×10^3 for the ratio of the rates of the $Cr^{2+}-FeOH^{2+}$ and $Cr^{2+}-Fe^{3+}$ reactions.¹² The similarity of the ratios is quite striking and their magnitude provides further evidence for the view that the $FeCl^{2+}-FeOH^{2+}$, $Fe^{2+}-FeOH^{2+}$, and $Cr^{2+}-FeOH^{2+}$ reactions proceed *via* inner-sphere, hydroxide-bridged transition states.

Finally, regardless of the detailed mechanisms of reactions 6 and 7, these studies have important implications for the mechanism of the chloride-catalyzed

(9) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(10) B. Baker and N. Sutin, to be published.

(11) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(12) G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964).

iron(II)-iron(III) exchange reaction. The results obtained in this work are in agreement with the conclusion reached previously, namely, that the chloride-bridged path provides the major pathway for the $FeCl^{2+}-Fe^{2+}$ reaction.^{2,13} A new feature provided by the present studies is that the rate law for the iron(II)-iron(III) exchange reaction in the presence of chloride ions should contain an additional term of the form $k(FeCl^{2+})(Fe^{2+})/(H^+)$ arising from reaction 6. This term should be revealed by studies of the chloride dependence of the iron(II)-iron(III) exchange reaction as a function of acidity.¹⁴

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(13) The rate constant for the chloride-bridged $FeCl^{2+}-Fe^{2+}$ reaction determined in the present studies is $28.8 M^{-1} sec^{-1}$ at 25.0° and ionic strength 3.0 M, in good agreement with the value previously reported.²

(14) This term did not show up in previous studies⁹ of the iron(II)-iron(III) exchange reaction because the acid dependence of the exchange reaction was determined in the absence of chloride ions, while the chloride dependence was determined at constant acidity.

Correspondence

Correlation of Force Constants with Bonding in the Dichalcogenides of Carbon¹

Sir:

There are ten possible species in the series of linear XCY molecules with X, Y = O, S, Se, Te. For the mixed species with X ≠ Y, there are four general quadratic valence force constants to be determined from only three fundamental frequencies. Therefore, one must have more information than the three frequencies to solve the normal coordinate problem for a general quadratic valence force field. As noted by Wentink² there is a remarkable constancy of the CO and CS distances in the molecules CO₂, OCS, OCSe, CS₂, SCSe, and SCTe. This implies that the CX and CY bonding is similar in structure in all ten XCY species. Hopefully we can use this constancy of bond structure to evaluate the force constants.

Wentink³ has observed the vibrational spectra of some of the more unusual of these compounds and has discussed² the fundamental frequencies and force constants. He showed that the data could be explained by a Lennard-Jones type of potential for essentially van der Waals interaction of the two end atoms as developed by Duchesne and Monfils.⁴

It is the opinion of this author that, in contrast to the above, the van der Waals forces should be relatively small between the end atoms of a linear triatomic

molecule and that so-called resonance effects⁵ are much more important in contributing to the interaction constant. For CO₂ the carbon atom π bonds to the two oxygens, sharing its two valence π orbitals with four oxygen π orbitals. If one CO bond is stretched, its CO π bonding is weakened. This makes the carbon π orbitals more available to π bond with the other oxygen tending to shorten its CO bond. We can define an interaction displacement coordinate, $(S_{CO})_{CO}$, = $-\beta$, as the change in length of one CO bond to minimize the energy after unit positive change in length of the other CO bond.⁶ It is easily shown^{5,7} that

$$F_{CO,CO'} = -(S_{CO})_{CO} F_{CO} = \beta F_{CO} \quad (1)$$

With the similarity in bonding mentioned in paragraph 1 in mind, the following hypotheses are reasonable.

(1) For XCY any change in CX bond order⁸ gives rise to a proportional change of opposite sign for CY bond order, independent of Y. The proportionality constant, γ , is the same for all X.

(2) A small change in bond order causes a proportional change of opposite sign in bond length and vice versa. The proportionality constant, P_{CX} , depends on the atoms involved.

Using these hypotheses (or approximations) we can

(5) C. A. Coulson, J. Duchesne, and C. Manneback, "Victor Henri Memorial Volume," Maison Desoer, Liege, 1948, p 33.

(6) The work of S. F. A. Kettle [*Spectrochim. Acta*, 1388 (1966)] indicates that changes in σ bonding are relatively negligible for this system.

(7) L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962).

(8) By bond order is meant a measure of the degree of bonding. The bond order can range continuously from 0 to 3.

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) T. Wentink, Jr., *J. Chem. Phys.*, **30**, 105 (1959).

(3) T. Wentink, Jr., *ibid.*, **29**, 188 (1958).

(4) J. Duchesne and A. Monfils, *ibid.*, **17**, 586 (1949).

derive a general expression for the interaction constants in terms of the primary force constants.

Let $\Delta r_{CX} = +1$. From hypothesis 2, the CX bond order decreases by $\alpha_{CX} = -1/P_{CX}$. This leads to an increase in CY bond order of $-\gamma\alpha_{CX}$ and a corresponding decrease in CY distance of $\Delta r_{CY} = \gamma\alpha_{CX}P_{CY}$. Combining these relations

$$\frac{\Delta r_{CY}}{\Delta r_{CX}} = (S_{CY})_{CX} = -\gamma \frac{P_{CY}}{P_{CX}}$$

With eq 1 this shows that $\gamma = \beta$ and

$$F_{CX,CY} = +\beta \frac{P_{CY}}{P_{CX}} F_{CY} = +\beta \frac{P_{CX}}{P_{CY}} F_{CX}$$

The last equality arises because by symmetry $F_{CX,CY} = F_{CY,CX}$, and leads to the relation $P_{CY}/P_{CX} = (F_{CX}/F_{CY})^{1/2}$. We then find

$$F_{CX,CY} = +\beta(F_{CX}F_{CY})^{1/2} \quad (2)$$

Thus, from eq 2 if we know approximate values for F_{CX} and F_{CY} and a value for β , which by hypothesis 1 is constant for all X and Y, we can calculate $F_{CX,CY}$ for the ten molecules we are considering.

The fundamental harmonic frequencies for CO_2 are known^{9,10} much better than those for the other nine molecules. Therefore they have been used to calculate the CO_2 force constants from which β was evaluated as 0.0788 using eq 1. Approximate values for F_{CS} and F_{CSe} were calculated from the frequencies of CS_2 and CSe_2 . Since frequencies were not available for CTe_2 , an approximate value of 4.6 mdynes/A, given by Wentink,² was used for F_{CTe} . Because of the noted similarity in bonding, it is reasonable to assume these primary force constants do not change appreciably

TABLE I
INTERACTION CONSTANTS AND HARMONIC STRETCHING
FREQUENCIES FOR LINEAR XCY

Molecule	$F_{CX,CY}$	Calcd ^a		Obsd ^b		Ref
		ω_1	ω_3	ω_1	ω_3	
CO_2	1.263	1354.6	2396.6	1354.5	2396.4	c
CS_2	0.62	671	1560	672	1559	d
CSe_2	0.48	376	1308	373 ± 6	1323 ± 10	e
CTe_2	0.36	257	1121
OCS	0.88	889	2111	876 ± 6	2091 ± 10	f
OCSe	0.77	679	2070	650 ± 6	2045 ± 10	f
OCTe	0.67	567	2042
SCSe	0.54	515	1451	516 ± 6	1457 ± 10	e
SCTe	0.47	435	1385	431 ± 6	1386 ± 10	e
SeCTe	0.41	312	1222

^a For the calculation the values $\beta = 0.0788$, $F_{CO} = 16.025$ mdynes/A, $F_{CS} = 7.86$, $F_{CSe} = 6.1$, and $F_{CTe} = 4.6$ were used. ^b Unfortunately, except for CO_2 , and perhaps CS_2 , the accuracy of the observed frequencies is poor, partially owing to Fermi resonance perturbations. The limits of error are rather arbitrary but should encompass the true values. ^c See ref 9 and 10. ^d D. Agar, E. K. Plyler, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **66A**, 259 (1962). ^e These "observed" harmonic values are calculated from the observed frequencies in ref 1 with application of approximate anharmonic corrections analogous to those for CO_2 and CS_2 . ^f See ref 2; these are approximate harmonic frequencies, accuracy unknown. For discussion of OCS see A. G. Maki, E. K. Plyler, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **66A**, 163 (1962).

(9) C. P. Courtoy, *Ann. Soc. Sci. Bruxelles, Ser. I*, **73**, 5 (1959).

(10) H. R. Gordon and T. K. McCubbin, Jr., *J. Mol. Spectry.*, **19**, 137 (1966).

among the different molecules considered. The procedure followed here was to calculate the harmonic frequencies of the ten molecules from β and the approximate values for the primary stretching force constants and to compare them with observed frequencies. Table I gives the results.

The interaction constants in Table I are not greatly different from those given by Wentink; however, the derivation behind them is more realistic chemically. The agreement is quite good considering the approximations involved. The calculated values for SCSe and SCTe are well within the experimental accuracy of the observed values. The results of Table I do indicate that F_{CO} , F_{CS} , and F_{CSe} are somewhat lower in OCS and OCSe than in CO_2 , CS_2 , and CSe_2 . It is gratifying that the 14 observed frequencies can be approximated so well using only five parameters (β , F_{CO} , F_{CS} , F_{CSe} , and F_{CTe}).

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Spin Delocalization in Substituted Anilines Complexed with Bis(2,4-pentanedionato)nickel(II)¹

Sir:

Recently it was reported that the spin delocalized in mono-N-substituted anilines octahedrally coordinated with salicylaldimine complexes is typical of that expected for delocalization involving a π -orbital mechanism.² As spin delocalized from the metal to the phenyl group by a π mechanism through an sp^3 hybridized nitrogen appeared unfeasible, these authors adopted the suggestion of LaMar that π delocalization occurs through an ionic form involving ionization of the N-H proton leaving the nitrogen with a p orbital available for π bonding with the metal.

As a part of an investigation involving the use of paramagnetic complexes to determine diamagnetic resonance positions,³ isotropic shifts of substituted aniline proton resonances due to complexing with metal 2,4-pentanedionates, $\text{M}(\text{AA})_2$, were observed. The nmr spectra of solutions containing an excess of monomethylaniline and $\text{Ni}(\text{AA})_2$ show isotropic shift ratios, Table I, similar to those previously reported for the salicylaldimine complexes.² In addition, the N-H proton resonance was observed to be broadened and shifted strongly upfield. This militates against signifi-

(1) Most of this work was carried out at Princeton University and was supported by the National Science Foundation through Grant No. GP-3397.

(2) J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, **5**, 1029 (1966).

(3) (a) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, (1966); (b) *ibid.*, **87**, 5350 (1965); (c) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 152 (1966).