with CN, reaction 3′ is more like a reaction between two radicals and a low activation energy can be expected. It should be noted that if N_2^+ is formed directly in a three-fragment decomposition of $CH_3N_2CH_3^+$, the thermochemistry remains the same and there is no way to distinguish between a two-fragment and a three-fragment formation of N_2^+.

Potential Functions and the Bonding in the XCO Free Radicals

James S. Shirk and George C. Pimentel

Contribution from the Chemistry Department, University of California, Berkeley, California 94720. Received January 3, 1968

Abstract: Careful normal coordinate analysis for the free radicals HCO, FCO, and ClCO reveals carbonyl stretching force constants of 13.7 ± 0.5, 14.3 ± 0.1, and 14.5 ± 0.5 mdyn/Å, respectively. These force constants suggest carbonyl bond orders near 2.3. This result and its relative insensitivity to the electronegativity of the attached atom contrast with the force constants in the XNO and XOO molecules. The bonding is discussed in terms of the Linnett quartet scheme and the $(p-\pi^*)$ bond idea. An improved estimate of the HCO molecular geometry is derived: $r_{CH} = 1.16$ Å, $r_{CO} = 1.17$ Å, and $\angle HCO = 123.8°$.

The vibrational spectra of three triatomic carbonyl free radicals have been reported, HCO,[1,2] FCO,[3] and ClCO.[4] We have recently measured the carbonyl stretching frequency of the acetyl radical.[5] Normal coordinate analyses which fully exploit the wealth of isotopic data have not been reported earlier and are presented here. The resulting potential functions permit a consideration of the bonding in these related molecules.

Normal Coordinate Analyses

All available frequencies were considered in the least-squares determination of the best-fit potential function.[6] For each of the XCO molecules (X = H, F, Cl) a variety of valence bond potential functions was derived, extending from the most general, with six potential constants, to the simplest, with all off-diagonal force constants set equal to zero. In each case, the fit was evaluated in terms of average discrepancy $\bar\epsilon$ between calculated and observed frequencies.

FCO and ClCO. Normal coordinate analyses on FCO and ClCO were straightforward. In the absence of structural data, we follow Milligan, *et al.*,[3,4] who used bond lengths from the stable prototypes HFCO (C-F, 1.36 Å and C-O, 1.18 Å) and Cl_2CO (C-Cl, 1.75 Å and C-O, 1.18 Å) and two possible bond angles, 120° (in analogy with HCO) and 135° (in analogy with the isoelectronic NO_2).

(1) G. E. Ewing, W. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, **32**, 927 (1960).
(2) D. E. Milligan and M. E. Jacox, *ibid.*, **41**, 3032 (1964).
(3) D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, *ibid.*, **42**, 3187 (1965).
(4) D. E. Milligan and M. E. Jacox, *ibid.*, **43**, 866 (1965).
(5) See J. S. Shirk, Ph.D. Thesis, University of California, Berkeley, 1966.
(6) The calculations were based upon the computer program by J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules, V and VI," Technical Report No. 231-64, Shell Development Co., Emeryville, Calif., 1964.

Table I shows calculations for FCO using three principal force constants only, one off-diagonal constant, and three off-diagonal constants. With a single

Table I. Force Constant Calculations for FCO. Eight Observed Frequencies

	Isotopes		Frequencies,[3] cm⁻¹		
F	C	O	ν_1	ν_2	ν_3
19	12	16	1855	1018	626
19	13	16	1814	995	620
19	12	18	1813	1016	...

FCO bond angle, deg	k_1, mdyn/Å	k_2, mdyn/Å	k_α, ergs/rad²	k_{12}, mdyn/Å	$k_{2\alpha}$, mdyn	$k_{1\alpha}$, mdyn	$\bar\epsilon$, cm⁻¹
120	13.3	3.55	1.77	...	...	...	3.8
120	14.1	3.18	2.30	0.91	...	...	1.5
120	13.1	4.83	1.54	...	0.21	...	1.4
120	14.2	4.51	1.81	...	...	1.07	0.7
120	14.3	5.09	1.42	0.61	0.30	0.27	0.3
135	12.8	4.61	1.48	...	...	...	1.9
135	13.0	4.0	1.68	...	−0.37	...	2.0
135	14.3	4.51	1.40	0.79	...	...	0.6
135	14.2	5.13	1.34	1.16	0.10	−0.31	0.4

off-diagonal force constant and a 120° angle, $k_{1\alpha}$ gives the best fit to the observed frequencies, whereas with a 135° angle k_{12} is the most effective term. With either angle, the fit is better than the experimental error in the frequencies (± 1 cm⁻¹). With six parameters, there was further and about the same improvement at 120 and 135° bond angles. Three conclusions can be drawn from Table I: (a) The data do not provide a basis for fixing the bond angle in the range 120–135°. (b) Without an accurate bond angle, the data do not suffice to determine the off-diagonal force constants. (c) Despite conclusions a and b, reasonable and useful limits can be placed on the principal force constants.

Table II. Force Constant Calculations for ClCO. Five Observed Frequencies

	Isotopes		Frequencies,[4] cm^{-1}		
Cl	C	O	ν_1	ν_2	ν_3
35	12	16	1880	570	281
35	13	16	1839	554	...

ClCO bond angle, deg	k_1, mdyn/Å	k_2, mdyn/Å	k_α, erg/rad^2	k_{12}, mdyn/Å	$k_{2\alpha}$, mdyn	$k_{1\alpha}$, mdyn	$\bar{\epsilon}$, cm^{-1}
120	14.11	1.54	0.50	...	...	...	0.6
120	14.73	1.60	0.48	0.59	...	...	0.3
120	14.06	1.84	0.42	...	...	0.06	0.4
135	13.93	1.94	0.36	...	...	...	0.7
135	15.00	1.94	0.36	0.67	...	...	0.2
135	14.01	1.56	0.45	...	...	−0.06	0.5

Table III. Force-Constant Calculations for HCO. Eleven Observed Frequencies

	Isotopes		Frequencies, cm^{-1}		
H	C	O	ν_1	ν_2	ν_3
1	12	16	2488	1861	1090
1	13	16		1821	1084
2	12	16	1937^a	1800^a	852
2	13	16	1910^a	1780^a	845

r_{CH}, Å	r_{CO}, Å	HCO bond angle, deg	k_1, mdyn/Å	k_2, mdyn/Å	k_α, erg/rad^2	k_{12}, mdyn/Å	$k_{2\alpha}$, mdyn	$k_{1\alpha}$, mdyn	$\bar{\epsilon}$, cm^{-1}
(1.08)	1.19	119.5	14.1	3.34	0.67	...	...	...	10.3
(1.08)	1.19	119.5	14.4	3.21	0.88	...	0.39	...	5.5
1.16	1.17	123.8	14.2	3.33	0.76	...	...	...	2.1
1.16	1.17	123.8	14.3	3.32	0.77	...	0.14	...	0.6
1.16	1.17	123.8	13.2	3.34	0.77	...	...	0.24	0.4

^{a} Not included in normal coordinate analysis.

Accepting only those calculations with $\bar{\epsilon}$ less than 1 cm^{-1} (the experimental uncertainty), the carbonyl force constant, k_{CO}, is 14.3 ± 0.1 mdyn/Å, the C–F force constant, k_{CF}, is 4.8 ± 0.3 mdyn/Å, and the bending force constant, k_α, is 1.5 ± 0.3 ergs/rad^2.

Table II shows similar calculations for ClCO. Since only five frequencies are known, only three- and four-parameter potential functions were employed. As in the more well-determined case of FCO, only the principal force constants can be considered to be determined, but these are usefully defined: k_{CO} is 14.5 ± 0.5 mdyn/Å, k_{CCl} is 1.7 ± 0.2 mdyn/Å, and k_α is 0.43 ± 0.07 erg/rad^2.

HCO. The normal coordinate analysis of formyl radical presented a more challenging problem. Johns, Priddle, and Ramsay[7] obtained two inertial moments for HCO from its electronic spectrum. Assuming a normal sp^2 CH bond length, 1.08 Å, they calculated r_{CO} = 1.19 Å and $\angle$HCO = 119.5°. Using this geometry and all known isotopic frequencies, we found excessively large average errors: $\bar{\epsilon}$ = 27 cm^{-1} with a three-parameter potential function and $\bar{\epsilon}$ = 12.2 cm^{-1} with a full, six-parameter calculation. This poor fit was noted by Milligan and Jacox[2] and ascribed to Fermi resonance. Though $2\nu_3$ for the deuterated molecules does fall in the neighborhood of ν_2, it is distant by almost 100 cm^{-1}, and no intensification of $2\nu_3$ is noted. Another likely

(7) J. W. C. Johns, S. H. Priddle, and D. A. Ramsay, *Discussions Faraday Soc.*, 35, 90 (1963).

contributor is anharmonicity in the C–H stretching frequency. Such anharmonicity would make it difficult to fit either the CD or the CO stretching frequencies in DCO because of their substantial mechanical mixing.

Fortunately, enough frequencies are known to escape either or both of these difficulties. Our interest focuses on the carbonyl stretching force constant, so we can omit both ν_1 and ν_2 for deuterated molecules. There remain seven frequencies, an ample number to fix four force constants, and the carbon–hydrogen force constant will absorb the C–H anharmonicity. Table III shows these calculations, in the first two lines, again with the molecular geometry assumed by Johns, et al.[7] The four-parameter value of $\bar{\epsilon}$ still is too large, since the likely disturbances (Fermi resonance and/or anharmonicity) cannot now be responsible.

Clearly the assumption of a normal C–H bond length in formyl is inappropriate. The frequency is abnormally low and the H–CO dissociation energy, 28 kcal,[8] also signals a weak C–H bond. A better estimate of r_{CH} is provided by the value of k_2, 3.3 mdyn/Å, and the plot of CH bond length vs. force constant given by Andrews and Pimentel.[9] This plot, based upon force constants that incorporate anharmonicity (as does ours), gives r_{CH} = 1.16 Å. Now the inertial constants fix r_{CO} = 1.174 Å and the HCO angle of 123.8°. With this more realistic geometry, it is now possible to fit the seven frequencies very well, as shown in the last three lines of Table III.[10] The new geometry of HCO is verified and the principal force constants are seen to have the values k_{CO} = 13.7 ± 0.5 mdyn/Å, k_{CH} = 3.3 ± 0.1 mdyn/Å, and k_α = 0.77 ± 0.05 erg/rad^2.

Summary. Potential Constants and Bonding of XCO Molecules

Potential Constants. Table IV contrasts the potential constants with those of stable, prototype molecules. Though the potential function of acetyl radical

(8) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958.

(9) L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 47, 3637 (1967).

(10) Ogilvie [*Spectrochim. Acta*, 23A, 737 (1967)] has recently made a similar argument, that r_{CH} = 1.08 Å is too low, on the basis of the C–H stretching frequency alone (rather than using the force constant and the improved normal coordinate fit). He then deduced an alternate geometry close to that obtained here (r_{CO} = 1.1765 Å, r_{CH} = 1.148 Å, and $\angle$HCO = 123.3°) from the inertial data alone.

Table IV. Force Constants for HCO, FCO, ClCO, and Other Carbonyl Molecules

Molecule	k_{CO}, mdyn/A	k_{CF}, mdyn/Å	k_{CCl}, mdyn/Å	k_{CH}, mdyn/Å	k_α, erg/rad^2	Ref
C≡O	18.5					a
H$_2$C=C=O	16.1 ± 0.5					b
ClCO	14.5 ± 0.5		1.7 ± 0.2		0.43 ± 0.07	This work
FCO	14.3 ± 0.1	4.8 ± 0.3			1.5 ± 0.3	This work
HCO	13.7 ± 0.5			3.3 ± 0.1	0.77 ± 0.05	This work
F$_2$CO^f	12.8	4.5				c
Cl$_2$CO^f	12.6		1.99			c
H$_2$CO	12.6 ± 0.2			4.4		d
HFCO	11.3	4.76		4.80		e

^{a} G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945. ^{b} C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **38**, 2816 (1963). ^{c} J. Overend and J. R. Scherer, *ibid.*, **32**, 1296 (1960). ^{d} T. Shimanouchi and I. Suzuki, *ibid.*, **42**, 296 (1965). ^{e} H. W. Morgan, P. A. Staats, and J. H. Goldstein, *ibid.*, **25**, 33 (1956). ^{f} Urey–Bradley force field used.

cannot be fixed, its C–O stretching frequency of 1844 (CH$_3$CO) and 1836 cm^{-1} (CD$_3$CO)[5] is close to those of FCO and HCO, so its k_{CO} must also be near 14 mdyn/Å. We see that all of the XCO free radicals have carbonyl stretching frequencies distinctly higher than their fully bonded prototypes. Furthermore, the values of k_{CO} depend only slightly upon X. The value of k_{CH} is lower in HCO than in formaldehyde, whereas the k_{CCl} and k_{CF} constants seem to be about the same as in the stable molecules Cl$_2$CO, F$_2$CO, and HFCO.

Bonding. The relative constancy of k_{CO} in the XCO radicals differs markedly from the behavior of the X–NO and X–OO counterparts. In these molecules k_{NO} and k_{OO} are markedly lower in HNO and HOO than in the halogenated counterparts.[11]

Linnett[12] has discussed this trend in the nitrosyl series HNO, FNO, ClNO, and BrNO within the framework of his "double quartet" scheme. In this system the ease with which the adduct, X, accepts a negative formal charge influences markedly the contribution of the various possible resonance forms for XNO and hence the NO bond order.

A similar argument explains the analogous bond orders in the XOO compounds.

Within the "double quartet" description, the only likely structure for X–CO radicals is

$$X—C\overset{\cdot}{=}O—$$
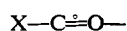
Since there is only one likely structure, the electro-

(11) See R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, **88**, 2394 (1966).
(12) J. W. Linnett, "The Electronic Structure of Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964.

negativity of the X atom will have much less influence upon the CO bond order. The predicted CO bond order, 2.5, is close to, though above, the observed 2.3. Thus the "double quartet" scheme provides a consistent rationale for the bonding in the X–OO, X–NO, and X–CO compounds.

An alternate way of discussing the XNO and XOO compounds, in terms of a [p–π*] or [s–π*] bond, has been proposed by Spratley and Pimentel.[11] In this view, electron sharing can link a sufficiently electronegative X atom weakly to NO or to OO without substantially changing the electron occupancy of the half-occupied π* orbitals. The extension of this scheme to CO adducts would treat the X–C bond formation as an overlapping of the half-filled X-atom orbital with the vacant π* orbital of CO. Since the π* orbital is empty, the X atom can only inject electron occupancy into it, and, inevitably, the CO bond must be weakened. A full sharing of the lone bonding electron should give a one-half order X–C bond and a two and one-half order C–O bond. This situation would be expected when X is a hydrogen atom, and, as X is made more electronegative, the CO bond should become stronger. Qualitatively, these expectations are realized, but the trend is very much smaller than was anticipated on the basis of the XNO and XOO molecules. In addition, there is no obvious way to accommodate the fact that the bond orders are below 2.5, a difficulty shared with the Linnett scheme.