The Electronic Structures of Several Aliphatic Carbonyls. The Effects of Polar Substituents

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The electronic structures of several aliphatic carbonyls, X_2CO, CH_3COX, and $(XCO)_2$ (X=H, F, CN, CH_3), have been investigated by the INDO method. Variations in the calculated electron density, the $n\pi^*$-excitation energy, the electron affinity, and the ionization potential with α-X substitution are explained qualitatively in terms of the σ-attracting and π-donating character of F, the π-attracting nature of CN and XCO, and the σ,π-donating property of CH_3. The lowest $^3n\pi^*$ excitation energies and ionization potentials calculated by the UHF method are in reasonable agreement with the experimental values in most cases. The partitioning of the total energy suggests that the C–O bonds of X_2CO compounds in the lowest $^3n\pi^*$ state and the radical anions derived from them are somewhat longer than those of the parent molecules, primarily because of the decrease in the electron-core attraction. The C–C bonds in some $(XCO)_2$ compounds appear to be cloven as easily as the C–X one on thermal activation and electron impact.

The structural and photochemical properties of aliphatic carbonyls in the excited state have already received considerable attention.[1,2] However, no all-valence-electron study of the electronic structure has yet been carried out. We thus applied the INDO method to several aliphatic carbonyls, X_2CO, CH_3COX, and $(XCO)_2$ (X=H, F, CN, CH_3), in the ground and excited states, as well as to the radical anions and cations derived from them. The total energies were partitioned into one- and two-atom terms,[3,4] and we tried to determine how the interatomic interactions influence the electronic excitation, ionization, and electron attachment.

Method of Calculation

The INDO calculations of the closed- and open-shell configurations were carried out by the usual procedure.[3] The total energy of the molecule is written as a sum of one- and two-atom terms:[3,4]

$$E_{\rm total} = \sum_{\rm A} E_{\rm A} + \sum\sum_{\rm A<B} E_{\rm A-B} \tag{1}$$

$$E_{\rm A-B} = E^1_{\rm A-B} + E^2_{\rm A-B} + E^3_{\rm A-B} \tag{2}$$

where the two-atom terms are given by:

$$E^1_{\rm A-B} = 2\sum_{\rm r}^{\rm A}\sum_{\rm s}^{\rm B} P_{\rm rs} S_{\rm rs} \beta^\circ_{\rm AB} \tag{3}$$

$$E^2_{\rm A-B} = -\frac{1}{2}\sum_{\rm r}^{\rm A}\sum_{\rm s}^{\rm B} P^2_{\rm rs} \gamma_{\rm AB} \tag{4}$$

$$E^3_{\rm A-B} = (P_{\rm AA}P_{\rm BB} - P_{\rm AA}Z_{\rm B} - P_{\rm BB}Z_{\rm A})\gamma_{\rm AB} + Z_{\rm A}Z_{\rm B}/R_{\rm AB} \tag{5}$$

Here, $P_{\rm rs}$ and $S_{\rm rs}$ are the bond order and the overlap integral between the r and s atomic orbitals; $\beta^\circ_{\rm AB}$, $\gamma_{\rm AB}$, and $R_{\rm AB}$ are the empirical bonding parameter, the two-center repulsion integral, and the distance between the A and B atoms respectively, and $P_{\rm AA}$ and $Z_{\rm A}$ are the electron density and the core charge at the atom A respectively. When wavefunctions of the unrestricted Hartree-Fock (UHF) type are used, Eq. (4) takes this form:

$$E^2_{\rm A-B} = -\sum_{\rm r}^{\rm A}\sum_{\rm s}^{\rm B}[(P^\alpha_{\rm rs})^2 + (P^\beta_{\rm rs})^2]\gamma_{\rm AB} \tag{6}$$

where $P^\alpha_{\rm rs}$ ($P^\beta_{\rm rs}$) is the bond order between the r and s atomic orbitals of the α- (β-) spin electron. We have used the original INDO parameters of Pople *et al.*[3] throughout this work.

Most of the molecular geometries employed were taken from the literature.[5,6] No experimental data are available for the geometries of carbonyl cyanide and oxalyl cyanide;[7] the former was assumed to be $\overline{\rm CO}$=1.20 Å, $\overline{\rm CC}$=1.47 Å, $\overline{\rm CN}$=1.16 Å, and ∢CCC=120°, and the latter, to be $\overline{\rm CO}$=1.22 Å, $\overline{\rm C(CN)}$=1.47 Å, $\overline{\rm CC}$=1.50 Å, $\overline{\rm CN}$=1.16 Å, ∢CCC=120°, and ∢OCC=123°. The same geometries were employed for $^3n\pi^*$ molecules and for radical ions. All the oxalyl compounds were assumed to be in the *s-trans* conformation.

Results and Discussion

Ground State. The electron densities on the carbonyl group of X_2CO compounds are given in Table 1. It is expected, from the values of the Hammett's substituent constants, that the F atom has a σ-attracting and π-donating character, that the CN and XCO groups have σ,π-attracting nature, and that the CH_3 group has a σ,π-donating property.[8] As to the electron density at the carbonyl oxygen, it is noticeable that the population of the 2pz atomic orbital (perpendicular to the molecular plane) increases

TABLE 1. ELECTRON DENSITIES ON THE CARBONYL GROUP OF THE GROUND-STATE X_2CO MOLECULES

Molecule	Atom	Electron densities				
		Total	2s	$2p_x$	$2p_y$	$2p_z$
H_2CO	C	3.66	1.09	0.87	0.90	0.80
	O	6.23	1.76	1.37	1.90	1.20
F_2CO	C	3.18	0.97	0.76	0.69	0.76
	O	6.33	1.75	1.33	1.85	1.40
$(CN)_2CO$	C	3.66	1.00	0.87	0.94	0.85
	O	6.24	1.76	1.36	1.94	1.18
$(CH_3)_2CO$	C	3.69	1.04	0.88	0.96	0.81
	O	6.31	1.78	1.33	1.95	1.25

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Table 2. Orbital energies,[a] total energies and dipole moments of the ground-state molecules

Molecule	Orbital energy (eV) E_n	Orbital energy (eV) E_{π^*}	Total energy (eV) E_{total}	Dipole moment (D) Calcd	Dipole moment (D) Obsd
H_2CO	−13.69	4.42	−700.35	1.88	2.31[b]
F_2CO	−16.59	4.03	−2098.71	0.77	0.95[c]
$(CN)_2CO$	−13.57	1.69	−1626.10	0.02	—
$(CH_3)_2CO$	−12.28	4.04	−1160.07	2.84	2.90[d]
CH_3COH	−12.83	4.41	−930.09	2.31	2.70[e]
CH_3COF	−14.14	4.31	−1628.89	2.61	2.96[e]
CH_3COCN	−12.98	2.71	−1393.33	3.12	3.45[e]
$(HCO)_2$	−12.45	1.76	−1361.80	0.0	—
$(FCO)_2$	−13.55	1.51	−2758.80	0.0	—
$(CNCO)_2$	−12.75	0.45	−2287.86	0.0	—
$(CH_3CO)_2$	−11.29	2.22	−1821.36	0.0	1.05[f]

a) The symbols E_n and E_{π^*} denote the highest occupied n and lowest vacant π^* orbital energies respectively. b) J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951). c) V. W. Laurie and D. T. Pense, *J. Chem. Phys.*, **37**, 2995 (1962). d) J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959). e) L. C. Krisher and E. B. Wilson, Jr., *ibid.*, **31**, 882 (1959). f) At 328.45 K, G. I. M. Bloom and L. E. Sutton, *J. Chem. Soc.*, **1941**, 727.

with an increase in the π-donating ability of the substituents.

The frontier orbital energies, total energies, and dipole moments are summarized in Table 2. The calculated dipole moments show a good agreement with the experimental values except for the oxalyl compounds, which will take both *cis* and *trans* conformations under the present experimental conditions.

The orbital energies of the highest occupied and lowest vacant levels are correlated with the first ionization potential and the electron affinity respectively. The highest occupied orbital of each molecule is an n orbital localized almost completely at the carbonyl oxygen, *i.e.*, the $2p_y$ atomic orbital (perpendicular to the molecular axis). The energy levels of this orbital rise in this order: F$\ll$H, CN$<$$CH_3$, XCO. The F substituent lowers this level because of its σ-attracting character. On the other hand, the lowest vacant orbital is essentially a π^* orbital. The energy levels rise in this order: CN, XCO$\ll$F, $CH_3$$<$H. The CN and XCO substituents lower the π^* level because of their π-attracting nature.

The Lowest Excited State. The lowest nπ^* singlet and triplet excitation energies, $\Delta E^V(^1n\pi^*)$ and $\Delta E^V(^3n\pi^*)$, as calculated by the virtual-orbital approximation without configuration interaction, are given in Table 3. These energies are expressed by:

$$\Delta E^V(^1n\pi^*) = (E_{\pi^*}-E_n) - J_{n\pi^*} + 2K_{n\pi^*} \tag{7}$$

and;

$$\Delta E^V(^3n\pi^*) = (E_{\pi^*}-E_n) - J_{n\pi^*} \tag{8}$$

where $(E_{\pi^*}-E_n)$ is the frontier orbital energy gap and where $J_{n\pi^*}$ and $K_{n\pi^*}$ are the interorbital Coulomb and exchange integrals respectively. $J_{n\pi^*}$ decreases with the replacement of the H atom by the CH_3, CN, and XCO groups as a result of the expansion of the π^* orbital of the carbonyl group. $K_{n\pi^*}$ is small because of the different symmetries of the n and π^* orbitals.

The nπ^* energy change caused by α-X substitution will be discussed qualitatively on the basis of the orbital energies alone, because the variation in $(E_{\pi^*}-E_n)$ with the substituents is generally greater than the changes in $J_{n\pi^*}$ and $K_{n\pi^*}$. Thus, an inspection of the relative heights of the frontier orbitals as discussed in the preceding section suggests that the nπ^* excitation energies increase in this order: XCO$<$CN, $CH_3$$<H<$F. Such energy shifts show a reasonable agreement with the experimental data (Table 3).

The nπ^* excitation energies from Eqs. (7) and (8) are 1—2 eV greater than experimental values. Although there are some obvious ways to improve the

Table 3. The lowest singlet and triplet nπ^* excitation energies (eV)

Molecule	Singlet transition Calcd $\Delta E^V(^1n\pi^*)$	Singlet transition Obsd	Triplet transition[a] Calcd $\Delta E^V(^3n\pi^*)$	Triplet transition[a] Calcd $\Delta E^U(^3n\pi^*)$	Triplet transition[a] Obsd
H_2CO	4.98	3.54—5.43[b]	4.50	3.43	3.15—3.47[b]
F_2CO	8.01	—	7.60	6.06	—
$(CN)_2CO$	5.55	2.92—4.77[c]	5.16	2.74	—
$(CH_3)_2CO$	5.34	3.54—4.45[d]	4.92	2.77	3.39[b]
CH_3COH	5.47	3.54—5.28[d]	5.05	3.30	2.48—3.65[d]
CH_3COF	7.39	6.04[e]	7.00	4.98	—
CH_3COCN	5.32	4.01[f]	4.90	2.40	—
$(HCO)_2$	4.34	2.72[g]	3.99	3.08	2.42[g]
$(FCO)_2$	5.40	4.02[h]	5.05	4.17	3.71[h]
$(CNCO)_2$	4.60	—	4.30	2.86	—
$(CH_3CO)_2$	4.35	2.83[i]	4.05	3.02	2.45[i]

a) ΔE^V and ΔE^U obtained from Eqs. (7), (8), and (9), respectively. b) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, New York, N.Y. (1966), Appendix. c) J. Prochorow, A. Tramer, and K. L. Wierzchowski, *J. Mol. Spectrosc.*, **19**, 45 (1966). d) Ref. 1. e) K. Yates, S. L. Klemenko, and I. G. Csizmadia, *Spectrochim. Acta*, **25A**, 765 (1969). f) B. E. Tate and P. D. Bartlett, *J. Amer. Chem. Soc.*, **78**, 5575 (1956). g) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957). h) W. J. Balfour and G. W. King, *J. Mol. Spectrosc.*, **25**, 132 (1968). i) H. Shimada and Y. Kanda, This Bulletin, **40**, 2742 (1967).

correlation, we did not attempt to do so. Instead, we dealt with the lowest $^3n\pi^*$ excited state by the UHF method, retaining the original INDO parametrization.

The triplet excitation energies, $\Delta E^U(^3n\pi^*)$, in the UHF method are defined as:

$$\Delta E^U(^3n\pi^*) = E^U_{total}(^3n\pi^*) - E_{total}(\text{ground}) \quad (9)$$

These values are generally in better agreement with the experimental values than $\Delta E^V(^3n\pi^*)$.

Radical Ions. The radical anions and cations derived from the parent molecules were treated by the UHF method. The electron affinities, E_A, and ionization potentials, I_D, were obtained from:

$$E_A = E_{total}(\text{ground}) - E^U_{total}(\text{anion}) \quad (10)$$

$$I_D = E^U_{total}(\text{cation}) - E_{total}(\text{ground}) \quad (11)$$

and are summarized in Table 4.

The calculated electron affinities are 0.5—1.0 eV greater than the $(-E_{\pi^*})$ obtained from Table 2, but still appear to be much smaller than the experimental ones. The E_A values increase in this order: H, F$<$CH$_3$$<XCO<$CN. The oxalyl compounds might have as large electron affinities as carbonyl cyanide.

The ionization potentials calculated from Eq. (11) are 1—3 eV smaller than the $(-E_n)$ from Table 2 and compare well with the experimental values. In both the X_2CO and CH_3COX compounds, they show this ordering: CH$_3$$<XCO, H, CN<$F. It should be noted that the effects of α-X substitution on E_A and I_D given here are almost identical with those already mentioned for the π* and n orbital energies in the ground state.

Table 4. Electron affinities and ionization potentials (eV)

Molecule	Electron affinity		Ionization potential	
	Calcd	Obsd	Calcd	Obsd
H_2CO	−3.7	—	12.2	10.9[c]
F_2CO	−3.6	—	14.7	—
$(CN)_2CO$	−0.8	1.2[a]	11.9	—
$(CH_3)_2CO$	−2.9	—	9.8	9.7[c]
CH_3COH	−3.5	—	10.9	10.2[c]
CH_3COF	−3.5	—	12.4	—
CH_3COCN	−1.7	—	10.5	—
$(HCO)_2$	−1.0	—	12.0	11.4[d]
$(FCO)_2$	−1.0	—	13.0	—
$(CNCO)_2$	0.7	—	12.3	—
$(CH_3CO)_2$	−1.2	1.1[b]	10.5	9.5[e]

a) T. Fueno and Y. Yonezawa, This Bulletin, **45**, 52 (1972). b) R. N. Compton, L. G. Christophrou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966). c) K. Watanabe, *ibid.*, **26**, 542 (1957). d) Monog. Ser. Res. Instit. Appl. Elect. Hokkaido Univ., No. 4, (1954—1957), Appendix. e) H. Neuert, *Z. Naturforsch.*, **7a**, 293 (1952).

Partitioning of the Energy. The two-atom terms for several X_2CO and $(XCO)_2$ compounds in the ground state (G), and lowest $^3n\pi^*$ state (T), as well as those for radical anions (A) and cations (C) derived

Table 5. Two-atom terms in the total energies of some X_2CO and $(XCO)_2$ compounds (eV)

Molecule	State[b]	Bonded atoms			Non-bonded atoms	Sum[a]
		E_{C-O}	E_{C-X}	E_{C-C}	E_{X-X}	$\sum\sum_{A<B} E_{A-B}$
H_2CO	G	−46.06	−20.42	—	0.40	−85.55
	T	−35.95	−19.96	—	0.15	−75.86
	A	−38.23	−19.18	—	0.74	−73.43
	C	−43.01	−18.55	—	0.32	−79.44
F_2CO	G	−47.18	−29.93	—	0.83	−104.58
	T	−32.46	−28.66	—	0.60	−88.88
	A	−39.94	−26.29	—	1.38	−87.52
	C	−36.94	−30.72	—	0.32	−98.14
$(CN)_2CO$	G	−42.46	−31.17	—	−0.06	−222.26
	T	−33.78	−31.83	—	−0.51	−214.64
	A	−35.60	−32.33	—	0.15	−213.19
	C	−38.59	−30.57	—	−0.40	−217.23
$(HCO)_2$	G	−44.04	−20.07	−30.58	−0.08	−156.93
	T	−41.39	−19.60	−31.15	−0.04	−152.83
	A	−39.17	−19.40	−35.43	0.03	−148.23
	C	−46.15	−18.99	−25.80	0.03	−154.85
$(FCO)_2$	G	−44.98	−28.16	−27.76	0.21	−172.85
	T	−41.49	−27.88	−27.96	0.16	−166.96
	A	−40.58	−25.95	−33.10	0.46	−161.64
	C	−45.42	−29.30	−21.98	0.02	−171.79
$(CNCO)_2$	G	−42.25	−31.26	−29.27	−0.07	−293.41
	T	−45.54	−33.30	−29.30	−0.02	−289.95
	A	−37.54	−31.28	−33.14	0.00	−285.33
	C	−44.03	−30.70	−24.57	0.04	−291.57

a) The value $\sum\sum_{A<B} E_{A-B}$ in Eq. (1) is given. b) The symbols G, T, A, and C denote the ground state, the lowest triplet state, radical anion, and radical cation, respectively.

from the parent molecules, are summarized in Table 5. The E_{C-X} of X_2CO changes markedly with the α-X substitution. The E_{C-C} of $(XCO)_2$ compounds also varies with the substituents and is either greater or smaller in magnitude than E_{C-X}. This must be related at least in part to the ease of thermal decomposition of both C–X and C–C bonds for oxalyl compounds.[9] The non-bonded two-atom terms, E_{X-X}, increase in this order: CN-CN<H-H<F-F. This suggests a small steric repulsion between the CN groups.

Table 6. Partitionings of the two-atom terms E_{C-O} for X_2CO and E_{C-C} for $(XCO)_2$ compounds (eV)

Molecule	State[a)]	E^1_{A-B}	E^2_{A-B}	E^3_{A-B}
		E_{C-O} Terms		
H_2CO	G	−49.91	−11.52	15.37
	T	−43.95	−8.27	16.27
	A	−45.45	−9.30	16.52
	C	−49.45	−10.86	17.30
F_2CO	G	−51.85	−10.98	15.65
	T	−43.67	−7.22	18.43
	A	−47.13	−9.16	16.35
	C	−48.44	−8.84	20.34
		E_{C-C} Terms		
$(HCO)_2$	G	−33.37	−4.85	7.64
	T	−32.90	−5.56	7.31
	A	−36.16	−6.38	7.11
	C	−29.97	−3.94	8.11
$(FCO)_2$	G	−31.70	−4.50	8.44
	T	−30.78	−5.01	7.83
	A	−34.33	−5.90	7.13
	C	−27.93	−3.53	9.48

a) The symbols G, T, A, and C denote the ground state, the lowest triplet state, radical anion, and radical cation, respectively.

The various types of two-atom terms, Eqs. (3)—(5), for the E_{C-O} values of several X_2CO compounds in the G, T, A, and C states are summarized in Table 6, together with those for the E_{C-C} of $(XCO)_2$ compounds. It has been established that formaldehyde is non-planar, with a somewhat lengthened carbonyl bond, in the lowest $^3n\pi^*$ state.[10] The E_{C-O} of X_2CO in the T state is considerably decreased in magnitude from the parent molecules. Most of the decrease originates from E^1_{C-O}, which corresponds to the off-diagonal core matrix elements, while the decreases in the electron-exchange term, E^2_{C-O}, and the electrostatic term, E^3_{C-O}, are both relatively immaterial. At any rate, the large decrease in $|E_{C-O}|$ upon excitation suggests a drastic reorganization of electrons in the carbonyl moiety. This, in turn, is probably related to the fact that these molecules have longer carbonyl bonds in the excited state. The increases in the E_{C-O} and E_{C-C} values of $(XCO)_2$ are not so great as that of the E_{C-O} of X_2CO.

As for the radical anion (A), E_{C-O} is decreased by 7—8 eV in magnitude from the parent molecules. As was true in the case of the T state, most of the decrease originates from E^1_{C-O}. Probably, these radical anions will also have a longer carbonyl bond than the parent molecules. In oxalyl compounds, the decrease in $|E_{C-O}|$ is rather small and is nearly counterbalanced by the increase in $|E_{C-C}|$.

The change in the sum of two-atom terms, $\sum\sum_{A<B} E_{A-B}$, from the parent molecule is rather small for radical cations. However, it is noticeable that the $|E_{C-C}|$ values of some oxalyl compounds are decreased by 5—6 eV upon ionization, primarily as a result of the decrease in $|E^1_{C-C}|$. Thus, it is likely that the C–C bond is cloven as easily as the C–X bond in such cases.

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