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Molecular Structures of Acetyl Chloride and Acetyl Bromide as Determined by Gas Electron Diffraction

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The molecular structures of acetyl chloride and acetyl bromide have been investigated by the sector-microphotometer method of gas-phase electron diffraction. The thermal average distances, r_g, and the valence angles, φ_α, have been determined, with estimated limits of error, to be as follows: for acetyl chloride, $r_g(\text{C=O})=1.187\pm0.003$ Å, $r_g(\text{C–Cl})=1.798\pm0.003$ Å, $r_g(\text{C–C})=1.508\pm0.005$ Å, $\varphi_\alpha(\text{OCCl})=120.3°\pm0.6°$, $\varphi_\alpha(\text{CCCl})=112.2°\pm0.9°$, and $\varphi_\alpha(\text{CCO})=127.5°\pm0.9°$; and for acetyl bromide, $r_g(\text{C=O})=1.184\pm0.004$ Å, $r_g(\text{C–Br})=1.975\pm0.004$ Å, $r_g(\text{C–C})=1.518\pm0.008$ Å, $\varphi_\alpha(\text{OCBr})=120.8°\pm0.9°$, $\varphi_\alpha(\text{CCBr})=109.5°\pm1.2°$, and $\varphi_\alpha(\text{CCO})=129.7°\pm1.1°$. The C=O distances in these molecules are shorter than those in acetaldehyde and acetone by about 0.02 Å. This may be attributed to the effect of a highly electronegative halogen atom adjacent to the carbonyl group.

The interatomic distances of acetyl chloride and acetyl bromide were first investigated by the visual method of electron diffraction.[1–3] The purpose of the present study is to determine more accurate structure parameters of these molecules by the sector-microphotometer method.[4] Sinnott observed the microwave spectra of ten isotopic species of acetyl chloride and determined the r_s structure parameters from the rotational constants.[5] He showed further that, at the equilibrium conformation, a methyl hydrogen atom is eclipsed to the oxygen atom. The microwave spectrum of acetyl bromide was investigated by Krisher,[6] but the interatomic distances were not determined. These rotational constants are being used in our laboratory as additional information in a more complete and more accurate analysis of the structure parameters and the barrier to internal rotation. The results will be reported in a forthcoming paper.

Experimental

The samples of acetyl chloride and acetyl bromide were special-grade and extra-pure reagents respectively, obtained from commercial sources. The unit used in the present study has been reported elsewhere.[7] Both short (109.3 mm) and long camera lengths (244.3 mm) were used. Diffraction photographs were taken at room temperature (~16°C) with an r^3-sector. The experimental conditions were as follows: accelerating voltage, about 42 kV; sample pressure, about 60 Torr; exposure times, 25—35 sec; electron-beam current, 0.1—0.3 μA. The developing and photometric process were described in a previous work.[8] In order to calibrate the wavelength of the electron beam, carbon disulfide was used as the reference material.

Analysis

Reduction of the Molecular Intensity. The relation between the optical desity, D, and the scattering intensity, I, was previously estimated to be $I=D(1+0.03D)$ for the plates used in the present study (Fuji Process Hard).[9] The observed intensities were obtained from the optical densities by the use of this relation. The data adopted for analysis covered the range of $q=30$—130 for the short camera length and that of $q=10$—60 for the long camera length. After correction for the deviation of the sector shape from an ideal r^3-curve, the leveled total intensities, I_T, were obtained by dividing I by the theoretical background.[10] The experimental background was obtained by Karles' non-negativity criterion for the radial distribution curve.[11] The molecular intensity curves, $qM(q)^{obs}$, derived in this way and the experimental radial distribution curves for the short camera length are shown in Figs. 1 and 2.

Least-squares Analysis. The molecular parameters were determined by applying the least-squares method to the $qM(q)^{obs}$ with a conventional weight function.[9] The molecular model for the least-squares fitting was assumed as follows:

(i) An eclipse conformation for the H and O atoms;

(ii) $r_a(\text{C–H})=1.1070$ Å (a value observed for ethane)[12] and the nonbonded distances related to the H atoms were fixed at calculated values, and

(iii) $\angle\text{CCH}=110°21'$ (Sinnott's r_s value) and the tilt angle of the methyl group$=0°$.

In addition to these assumptions, all the mean amplitudes were fixed at the values calculated from the spectroscopic data, since it was impossible to adjust the distances and the mean amplitudes simultaneously. The asymmetry parameters, κ, were estimated according to the equation given by Kuchitsu,[13] while the Morse parameters were assumed to be 2.0 Å^{-1} for the bonded atom pairs and zero for the nonbonded pairs. The elastic and inelastic scattering factors were obtained from the sources cited in a previous work.[9] It is not clear whether or not the H atom is eclipsed to the O atom in acetyl bromide. However, this ambiguity is not relevant to the present work, because the molecular intensity

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[1] R. W. Dornte, *J. Amer. Chem. Soc.*, **55**, 4126 (1933).

[2] P. W. Allen and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 236 (1951).

[3] Y. Morino, K. Kuchitsu, M. Iwasaki, K. Arakawa, and A. Takahashi, *Nippon Kagaku Zasshi*, **75**, 647 (1954).

[4] The study by this method was once carried out by G. A. Boulet, Dissert. Abstract (Univ. of Michigan), **25**, 3283 (1964), but the accuracy of the results was unsatisfactory.

[5] K. M. Sinnott, *J. Chem. Phys.*, **34**, 851 (1961).

[6] L. C. Krisher, *ibid.*, **33**, 1237 (1960).

[7] Y. Murata, K. Kuchitsu, and M. Kimura, *Oyo Butsuri*, **9**, 591 (1970).

[8] H. Fujii and M. Kimura, This Bulletin, **43**, 1933 (1970).

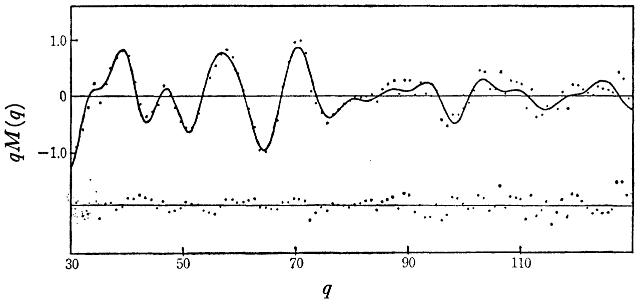
[9] S. Konaka and M. Kimura, *ibid.*, **43**, 1693 (1970).

[10] The experimental data of the leveled total intensity have been filed with the Chemical Society of Japan. A copy may be secured by citing the document number (Document No. 7201) and by remitting, in advance, ¥300 for photoprints. Payment may be made by check or money order payable to the Society.

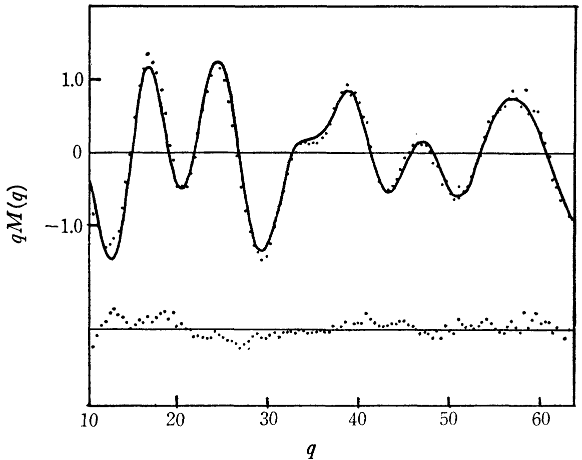
[11] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

[12] L. S. Bartell and H. K. Higginbotham, *ibid.*, **42**, 851 (1965).

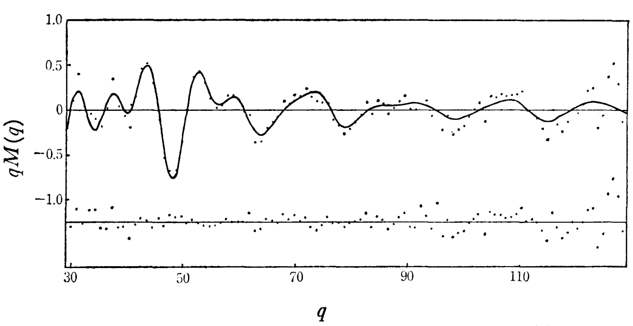
[13] K. Kuchitsu, This Bulletin, **40**, 498 (1967).



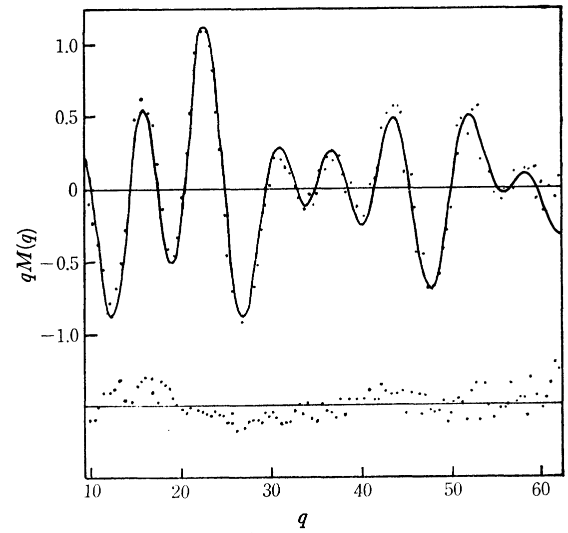
(a) Acetyl chloride (for the short camera length)



(b) Acetyl chloride (for the long camera length)

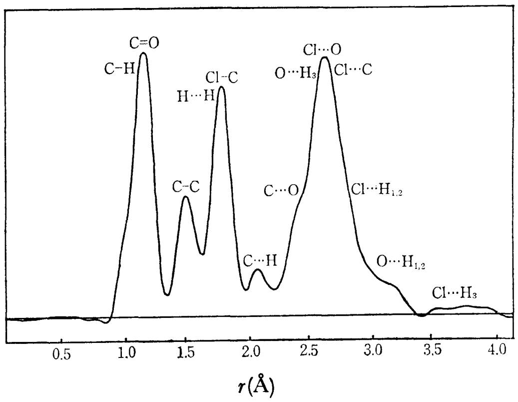


(c) Acetyl bromide (for the short camera length)

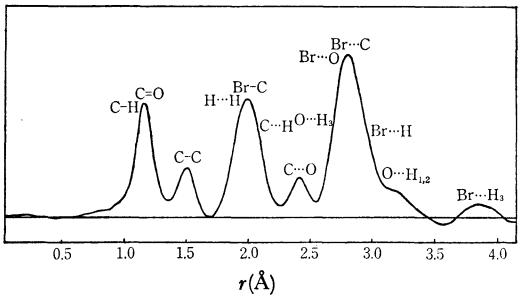


(d) Acetyl bromide (for the long camera length)

Fig. 1. Molecular intensity curves. The dots and the solid curves show the observed and best-fit theoretical values, respectively.



(a) Acetyl chloride



(b) Acetyl bromide

Fig. 2. Experimental radial distribution curves for the short camera length data.

curves for the eclipsed and staggered models are indistinguishable from each other.

Four plates for each of the two camera distances were used for analysis. The averages of the parameters were taken using weights inversely proportional to the squares of the standard deviations obtained by the least-squares fitting. The

TABLE 1. RESULTS OF THE LEAST SQUARES ADJUSTMENT (IN Å UNITS)

(a) Acetyl chloride

		σ_1	σ_2
r_a(Cl–C)	1.7968	0.0011	0.0003
r_a(Cl···C)	2.7440	0.0024	0.0006
r_a(Cl···O)	2.6031	0.0016	0.0005
r_a(C–C)	1.5058	0.0021	0.0005
r_a(C=O)	1.1862	0.0010	0.0007
r_a(C···O)	2.4153	0.0033	0.0008
$k^{b)}$	0.917	0.009	0.003

(b) Acetyl bromide

		σ_1	σ_2
r_a(Br–C)	1.9736	0.0015	0.0014
r_a(Br···C)	2.8594	0.0043	0.0017
r_a(Br···O)	2.7691	0.0028	0.0023
r_a(C–C)	1.5158	0.0032	0.0011
r_a(C=O)	1.1828	0.0016	0.0009
r_a(C···O)	2.4430	0.0050	0.0029
$k^{b)}$	0.849	0.008	0.006

a) Weighted averages of the results for eight plates (four from the long camera length and four from the short camera length). The definitions of σ_1 and σ_2 are given in Ref. 14.

b) Index of resolution (dimensionless).

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14) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

Table 2. Error matrices[a] (in 10^{-4} Å units)

(a) Acetyl chloride

	Cl–C	Cl···C	Cl···O	C–C	C=O	C···O	k
Cl–C	28	11	0	0	0	11	20
Cl···C		80	47	−11	0	39	53
Cl···O			45	−11	0	41	11
C–C				52	0	0	0
C=O					23	0	28
C···O						87	70
k[b]							293

(b) Acetyl bromide

	Br–C	Br···C	Br···O	C–C	C=O	C···O	k
Br–C	68	36	26	−30	13	−46	24
Br···C		132	24	−26	18	−63	150
Br···O			74	−9	−9	−37	−98
C–C				97	−13	26	79
C=O					41	−9	60
C···O						158	72
k[b]							516

a) $\sigma_{ij}=\mathrm{sgn}\,[(B^{-1})_{ij}]\cdot[|(B^{-1})_{ij}|\cdot V^{*}PV/(n-m)]^{1/2}$, where the notations follows Ref. 14.

b) Index of resolution k is dimensionless.

structure parameters and the standard errors, σ_1 and σ_2,[14] derived are shown in Table 1. Table 2 shows the error matrices which were computed for the best-fit models, corresponding to the theoretical intensity curves for the short camera length depicted in Figs. 1(a) and 1(c).

Mean Amplitudes. The mean amplitudes of vibration used for the analysis were calculated by the normal coordinate treatment.[15] The force constants for the Urey-Bradley force field determined by Overend *et al.* were used for acetyl chloride.[16] The force constants for acetylbromide were transferred from those for acetyl chloride and methyl bromide, and adjusted by a trial-and-error method so as to reproduce the vibrational frequencies obtained from the infrared spectra.[17] The force constants thus determined and the vibrational frequencies of acetyl bromide are shown in Tables 3 and 4 respectively. Evans and Overend estimated[19] the out-of-plane bending force constant for acetyl bromide to be 0.39 mdyn·Å[20] from Taft's inductive and resonance substituent constants. This value is slightly smaller than the constant, Θ, listed in Table 3. The calculated mean-square amplitudes, l, are shown in Table 5.

Table 3. Force constants for acetyl bromide (K, H, and F in mdyn/Å; Y and Θ in mdyn·Å)

K(C–H)	4.62	H(O–C–Br)	0.105
K(C–C)	2.93	F(H···C)	0.445
K(C=O)	12.05	F(H···H)	0.064
K(C–Br)	1.45	F(C···O)	0.360
H(H–C–C)	0.240	F(C···Br)	0.419
H(H–C–H)	0.398	F(O···Br)	0.560
H(C–C–O)	0.270	Y[a]	0.014
H(C–C–Br)	0.247	Θ[a]	0.455

a) Y and Θ are the force constants of the torsional and out-of-plane bending modes respectively.

Table 4. Vibrational frequencies of acetyl bromide (in cm^{-1} units)[a]

		Obs.[b]	Calc.			Obs.	Calc.
A′	ν_1	3017	3017		ν_9	335	344
	ν_2	2945	2946		ν_{10}	305	313
	ν_3	1826	1826				
	ν_4	1426	1419	A″	ν_{11}	3029	3017
	ν_5	1363	1397		ν_{12}	1426	1420
	ν_6	1089	1079		ν_{13}	1005	1045
	ν_7	945	946		ν_{14}	490	490
	ν_8	563	575		ν_{15}	150[c]	151

a) The numbering of the modes follows Ref. 16.

b) Ref. 17.

c) Ref. 18.

Table 5. Mean amplitudes of acetyl chloride and acetyl bromide calculated by the normal coordinate treatment at 289°K (in Å units)

	CH_3COCl	CH_3COBr
C–X	0.0512	0.0547
C···X	0.0666	0.0713
X···O	0.0565	0.0638
X···$H_{1,2}$[a]	0.1322	0.1359
X···H_3[a]	0.1012	0.1012
C–C	0.0506	0.0505
C=O	0.0376	0.0371
C···H	0.1060	0.1054
C···O	0.0584	0.0604
C–H	0.0780	0.0779
O···$H_{1,2}$	0.1092	0.1112
O···H_3	0.1359	0.1367
H···H	0.1274	0.1276

a) The hydrogen atom on the symmetry plane is numbered 3.

Estimation of Errors. The limits of error were estimated from 2.5 times σ_1 and from the systematic errors. The error due to the uncertainties in the fixed structure parameters was taken into consideration as one of the systematic errors. Yokozeki and Kuchitsu[21] treated this error by a Monte-Carlo technique. However, the present authors have dealt with it by a different and simpler method as follows:

(a) *Procedure*: It was assumed that a variation in one of the fixed parameters, Δ, caused a displacement in each adjusted parameter, δ, linearly proportional to the variation, and that such displacements were simply additive. A least-squares adjustment was carried out by varying only one of the fixed parameters at a time as much as its uncertainty. This procedure was applied to all the fixed parameters.

(b) *Uncertainties in the Fixed Parameters*: The uncertainties in the C–H and C···H distances were assumed to be 0.010 Å, while those for the other nonbonded distances related to the hydrogen atoms were assumed to be; r(O···H): 0.010 Å, and r(Cl···H): 0.010 Å for acetyl chloride, r(O···H): 0.010 Å and r(Br···H): 0.015 Å for acetyl bromide. The uncertainties in the mean amplitudes were assumed to be 10%.

By analogy with the estimation of errors in a previous work,[9] the uncertainties in the asymmetry parameters,

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[15] S. J. Cyvin, "Molecular Vibration and Mean Square Amplitudes," Elsevier Publishing Co., Amsterdam (1970).

[16] J. Overend, R. A. Nyquist, J. C. Evans, and W. J. Potts, *Spectrochim. Acta*, **17**, 1205 (1961).

[17] J. A. Ramsey and J. A. Ladd, *J. Chem. Soc., B*, **1968**, 118.

[18] L. C. Hall and J. Overend, *Spectrochim. Acta*, **23A**, 2535 (1967).

[19] J. C. Evans and J. Overend, *ibid.*, **19**, 701 (1963).

[20] The original value 0.39×10^{-5} dyn/rad should read 0.39 mdyn·Å.

[21] A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 2356 **(1971)**.

Table 6. Displacements, δr, of the adjusted parameters due to the uncertainties of the fixed parameters (in 10^{-4} Å units)

Fixed parameter	Acetyl chloride			Acetyl bromide	
	δr (C···Cl)	δr (O···Cl)	δr (C···O)	δr (C···Br)	δr (O···Br)
l(C···X)	+15	+11	+1	−2	+40
l(O···X)	−32	−22	−59	−77	−9
l(C···O)	+31	+23	+23	0	0
$r(O\cdots H_3)$	−1	−1	+1	+4	+1
$l(O\cdots H_3)$	−6	−2	+2	+2	−3
$r(X\cdots H_{1,2})$	+7	+3	−2	+4	+6
$l(X\cdots H_{1,2})$	−5	−5	0	+15	+2
$(\sum\delta_i^2)^{1/2}$	48	34	64	79	41
$\sum\lvert\delta_i\rvert$	97	67	88	104	61

Fixed parameter	Acetyl chloride δr(C=O)	Acetyl bromide δr(C=O)
l(C=O)	0	+6
r(C–H)	+5	−10
l(C–H)	−12	−10
$(\sum\delta_i^2)^{1/2}$	13	15
$\sum\lvert\delta_i\rvert$	17	26

a) Assumed uncertainties in the fixed parameters are described in text. The plus and minus signs indicate the directions of the displacements δ, when the variations $\Delta>0$.

κ, for the bonded atom pairs were considered to be insignificant. The κ of a nonbonded atom pair was estimated by Kuchitsu to be nearly equal to or less than that of a bonded atom pair.[22] Even if a large value of 100×10^{-7} Å^3 is used for the κ's of the nonbonded atom pairs, the resulting changes in the distances amount to only 0.0004 Å. Therefore, the errors due to the uncertainties in the κ values were ignored.

The results of the calculations are shown in Table 6, where only significant contributors to the error-estimation are presented. In general, the error in an adjusted distance due to the uncertainty in a fixed parameter is significant only if the adjusted distance and the fixed parameter are involved in the same peak in the radial distribution curve. The C=O distance was sensitive to only the uncertainties in the distance and mean amplitude of the C–H bond and in the mean amplitude of the C=O bond. For the C···O distance in acetyl bromide and the C–C and C–X distances, which have no close-by distances except for those which make very small contributions to the molecular intensity, the effect of the uncertainties in the fixed parameters was negligible. It is to be noted that more than about 80% of each error for the nonbonded distances comes from the uncertainties in the mean amplitudes for the C···X, C···O, and O···X pairs.

(c) *Error Estimation*: The last two entries, $(\sum\delta_i^2)^{1/2}$ and $\sum\lvert\delta_i\rvert$, in Table 6 are two possible estimates of the uncertainty in an adjusted parameter due to the uncertainties in the fixed parametes, where δ_i is the displacement due to the variation in the ith fixed parameter. Of the two estimates, $\sum\lvert\delta_i\rvert$ has been adopted as the systematic error to be included in the limits of error. Were the uncertainties in these fixed parameters perfectly random and mutually independent,—in other words, were the law of propagation of error valid in this case, then $(\sum\delta_i^2)^{1/2}$ instead of $\sum\lvert\delta_i\rvert$ might have been taken. However, it seems proper to adopt the latter larger value, unless the nature of the error is clear. The errors due to the uncertainties in the fixed parameters for r(C···X), r(O···X), and r(C···O in chloride) were four times as large as that of the scale factor and were nearly equal to 2.5 σ_1.

The errors in the scale factor were estimated to be 0.05% for acetyl chloride and 0.06% for acetyl bromide. Systematic errors due to the other sources were not included in the limits of error, for they were considered to be insignificant.[9]

Results and Discussion

The parameter, r_α, determined by the least-squares refinement was transformed to the thermal average distance, r_g, by the relation $r_g=r_\alpha+l_\alpha^2/r_\alpha$.[23] The r_α parameter was evaluated by subtracting the harmonic and the centrifugal contributions from r_g, following the equation $r_\alpha=r_g-(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)/2r_e-\delta r$.[24] Here, the third term, δr, was neglected. The angle, φ_α, composed of the thermal-average nuclear position[25] was calculated from the r_α parameters. The final r_g distances and the φ_α angles are listed in Table 7, together with the limits of error. The sums of the φ_α(OCX), φ_α(CCX), and φ_α(CCO) angles for acetyl chloride and acetyl bromide equal 359°56′ and 359°57′ respectively. These values are consistent with the planar structure of the CCOX skeleton. For a comparison of these results for acetyl chloride and acetyl bromide with those reported by Sinnott[5] and Krisher[6] respectively, it is necessary to take into consideration the corrections for the molecular vibrations, including internal rotation. The procedure for dealing with these systems and the results obtained will be reported in forthcoming papers.

Table 7. Thermal average distances r_g and φ_α angles of acetyl chloride and acetyl bromide (distances in Å units)

	CH_3COCl		CH_3COBr	
r_g(C=O)	1.1874	0.0028[a]	1.1840	0.0044[a]
r_g(C–X)	1.7983	0.0029	1.9751	0.0039
r_g(C–C)	1.5075	0.0053	1.5175	0.0080
r_g(C···X)	2.7456	0.0112	2.8612	0.0150
r_g(O···X)	2.6043	0.0077	2.7706	0.0093
r_g(C···O)	2.4167	0.0119	2.4445	0.0126
φ_α(OCX)	120°19′	38′	120°48′	54′
φ_α(CCX)	112°10′	51′	109°29′	1°12′
φ_α(CCO)	127°27′	53′	129°40′	1°6′

a) Limits of error.

The interatomic distances, the stretching vibrational frequencies, and the force constants for carbonyl bonds in various compounds are compared in Table 8. The r_g distances were chosen as the interatomic distances except for the CH_3COF, COF_2, $COCl_2$, and CH_3COCN molecules, for which the r_g distances are not known. The r_g distance may be larger, by as much as about 0.01 Å, than the corresponding r_s (or r_0) value. Even so, it is evident that molecules with at least one halogen

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22) K. Kuchitsu, *ibid.*, **40**, 505 (1967).

23) K. Kuchitsu and L.S. Bartell, *J. Chem. Phys.*, **35**, 1945 (1961).

24) Y. Morino, K. Kuchitsu, and T. Oka, *ibid.*, **36**, 1108 (1962).

25) K. Kuchitsu, This Bulletin, **44**, 96 (1971).

Table 8. Interatomic distances, stretching frequencies and force constants of carbonyl groups in the gas state (r in Å, ν in cm^{-1}, and K in mdyn/Å)

No.	Compound	r(C=O)[a)]		Ref.	ν(C=O)	Ref.	K(C=O)	Ref.
1	CH_3COF	1.181 (10)	r_s	26	1867	17	12.13	44
2	CH_3COCl	1.187 (3)	r_g	c)	1820	17	11.23	16
3	CH_3COBr	1.184 (4)	r_g	c)	1826	17	12.05	c)
4	CH_3COI				1808	17		
5	COF_2	1.174 (10)	r_0	27	1928	37	12.61	44
6	$COCl_2$	1.166 (2)	r_0	28	1827	38	12.54	44
7	HCHO	1.209 (3)	r_g	29	1744	39	11.07	39
8	CH_3CHO	1.209 (3)	r_g	29	1743	39	10.61	39
9	OCH-CHO	1.212 (2)	r_g	30	1745	40	10.60	45
10	H_2C=CH-CHO	1.217 (3)	r_g	30	1724	40	10.30	46
11	C_6H_5-CHO	1.210 (5)	r_g	31	1725	41		
12	CH_3COCH_3	1.211 (4)	r_g	29	1738	39	10.32	47
13	HCOOH[b)]	1.217 (3)	r_g	32	1794	41	11.20	48
14	CH_3COOH[b)]	1.214 (3)	r_g	33	1788	42	10.90	48
15	CH_3CH_2COOH[b)]	1.211 (3)	r_g	34	1787	41		
16	$(COOH)_2$	1.208 (1)	r_g	35	1756[b)]	43		
17	CH_3COCN	1.226 (5)	r_s	36	1740	36	10.90	44

a) Expermimental errors quoted in references are shown in parentheses.
b) Monomer.
c) The present work.
d) α-Oxalic acid.

atom attached to a carbonyl group have shorter r(C=O)'s and higher ν(C=O)'s than do molecules containing no halogen atom, as may be seen in Table 8. Since the carbonyl-stretching frequencies are relatively insensitive to variations in the masses of atoms or groups attached to the carbonyl groups, a relation between the stretching frequency and the distance was frequently discussed in the past by assuming the carbonyl frequency to be one of the characteristics of the carbonyl bond. Margoshes *et al.*,[49)] for example, plotted the bond distances *versus* the stretching frequencies for the carbonyl groups and mentioned that the points lie on a smooth curve with average deviations of 0.013 Å from the curve, with the largest error being 0.05 Å. They adopted the distances of not only simple molecules in the gas state, but also complex molecules such as amino acids in the crystalline state. However, now that we have more accurate structures in the gas state, a similar plot may

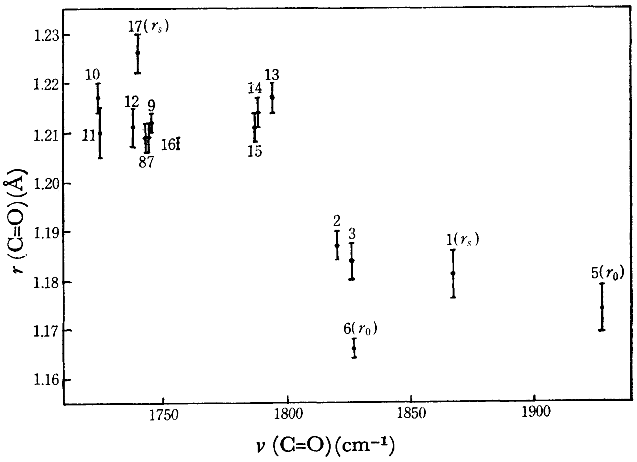

Fig. 3. Relation between bond length and stretching frequency for carbonyl groups. The numbers correspond to the compound numbers listed in Table 8 and the distances are entered in r_g unless remarked as r_s (or r_0). The vertical bars show the errors quoted in references.

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26) L. Pierce and L. C. Krisher, *J. Chem. Phys.*, **31**, 875 (1959).
27) V. W. Laurie and D. T. Pence, *ibid.*, **37**, 2995 (1962).
28) G. W. Robinson, *ibid.*, **21**, 1741 (1953).
29) C. Kato, S. Konaka, T. Iijima, and M. Kimura, This Bulletin, **42**, 2148 (1969).
30) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **4**, 41 (1969).
31) M. Ogasawara, The 23rd Annual Meeting of the Chemical Society of Japan, Tokyo (1970).
32) A. Almenningen, O. Bastiansen, and T. Motzfeldt, *Acta Chem. Scand.*, **23**, 2848 (1969).
33) J. L. Derissen, *J. Mol. Structure*, **7**, 67 (1971).
34) J. L. Derissen, *ibid.*, **7**, 81 (1971).
35) Z. Náhlovská, B. Náhlovský, and T. G. Strand, *Acta Chem. Scand.*, **24**, 2617 (1970).
36) L. C. Krisher and E. B. Wilson, Jr., *J. Chem., Phys.*, **31**, 882 (1959).
37) A. H. Nielsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, *ibid.*, **20**, 596 (1952).
38) J. Overend and J. C. Evans, *Trans. Faraday Soc.*, **55**, 1817 (1959).
39) P. Cossee and J. H. Schachtschneider, *J. Chem. Phys.*, **44**, 97 (1966). The force constant with the least errors was selected among those reported by the authors.
40) R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).
41) E. J. Hartwell, R. E. Richards, and H. W. Thompson, *J. Chem. Soc.*, **1948**, 1436.
42) M. Haurie and A. Novak, *J. Chim. Phys.*, **62**, 137 (1965).
43) L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **19**, 435 (1963).
44) J. Overend and J. R. Scherer, *ibid.*, **16**, 773 (1960).
45) T. Fukuyama, K. Kuchitsu, and Y. Morino, This Bulletin, **41**, 3019 (1968).
46) T. Fukuyama, K. Kuchitsu, and Y. Morino, *ibid.*, **41**, 3021 (1968).
47) G. Dellepiane and J. Overend, *Spectrochim. Acta*, **22**, 593 (1966).
48) K. Nakamoto and S. Kishida, *J. Chem. Phys.*, **41**, 1554 (1964).
49) M. Margoshes, F. Fillwalk, V. A. Fassel, and R. E. Rundle, *ibid.*, **22**, 381 (1954).

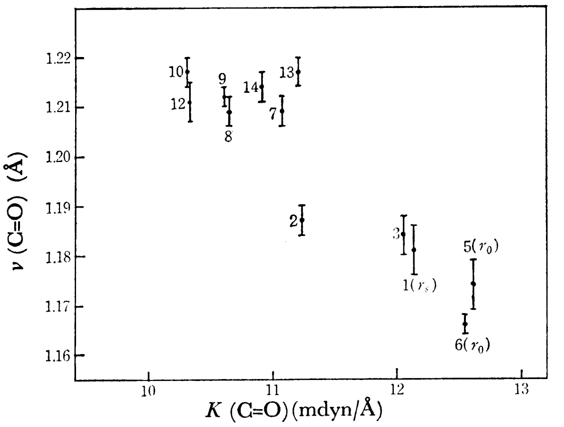

Fig. 4. Relation between bond length and force constant for carbonyl groups.

be made with the latest data (shown in Fig. 3). Roughly speaking, there exists a tendency for a molecule with a shorter r(C=O) to have a higher ν(C=O), as was pointed out by Margoshes *et al.* However, the plotted points can hardly be said to fall on a smooth curve in view of the accuracy of the current distance data.

The frequency-distance curve will serve for diagnostic purposes, but it is inappropriate for use in discussing the nature of the carbonyl bond, because the effect of the coupling between different normal modes of vibration is neglected. This has been particularly stressed by Overend *et al.*[16,44,50] A more physically significant quantity may be the force constant for the C=O bond. In Fig. 4, the r(C=O) values are plotted against the force constants, K(C=O), which, except for acetyl chloride, were calculated on the basis of the simple or a modified Urey-Bradley force field, with certain approximations where necessary. The value for acetyl chloride (Compound 2) is only an estimate made by Overend *et al.* by the use of the corresponding values for acetone and phosgene.[16] Since the calculated C=O stretching frequency for acetyl chloride is about 40 cm^{-1} smaller than the observed value, the best-fit force constant must be larger than this value, probably close to the force constants for acetyl bromide (Compound 3). The force constants for acids fall in the same region as those for the other compounds with no halogen atom. This is encouraging for the purpose of finding a relation between the force constant and bond length. However, the force constants listed in Table 8 have fairly large uncertainties, presumably ± 0.5 mdyn/Å on the average, and the r(C=O) values for the carbonyl halides cannot be compared directly with those for the other compounds. Nevertheless, it is clear, in surveying Table 8 and Fig. 4, that the halogen-containing compounds have the larger C=O force constants and the shorter bond lengths.

The shortening in the C=O bond length mentioned above may be considered to be partly due to the "*inductive effect*" and, perhaps, partly to the "*dipolar field effect*."[51] Kagarise pointed out a linear relation between the sum of the electro-negativity values, χ_X and χ_Y, of the substituents, X and Y, and the carbonyl stretching frequencies for molecules of the X.CO.Y type, not including acids; *i.e.*, the higher the sum of the electronegativity values, the higher the frequency.[52] A plot of the sum of the electronegativity values against the r(C=O) bond length is shown in Fig. 5. The χ's for the $-CH_2CH_3$ and $-OH$ groups were estimated to be 2.36 and 2.83 respectively, according to Kagarise's idea. The data for glyoxal, acrolein, benzaldehyde, oxalic acid, and acetyl cyanide were not plotted, since estimations of the χ's of the substituents, $-CH=CH_2$, $-C_6H_5$, and $-C\equiv N$, were difficult. However, since the χ's of the vinyl and phenyl groups are supposed to be similar to that of the H atom,[54] the data for acrolein and benzaldehyde would be in the region representing aldehydes, ketones, and acids on the electronegativity-distance map. It should be noticed that the sums of the electronegativity values for acids are nearly equal to those for acetyl chloride and bromide, while the r(C=O) distances for acids are much longer than those for the halides. This suggests that the C=O bonds in the halogen-containing compounds have partly a triple-bond character.[55]

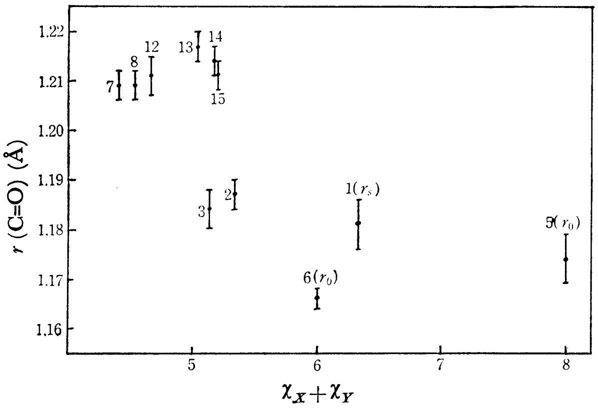

Fig. 5. Relation between the bond length of a carbonyl group and the sum of the electronegativity values of substituents for gaseous carbonyl-containing compounds. The electronegativity values of atoms are on the Gordy-Thomas scale[53] and those of the atomic groups, $-CH_3$, $-CH_2CH_3$, and $-OH$ were evaluated by Kagarise's method.[52]

Empirical relations between the bond lengths and the force constants for very simple molecules have been proposed by several workers.[56-58] Among them, Ladd *et al.*[58] have applied the relation for the carbonyl bond to amide molecules as well as to some of the molecules listed in Table 8, and have predicted the C=O stretching force constants. Their predicted values are generally reasonable. However, since the data of the bond

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50) J. Overend and J. R. Scherer, *ibid.*, **32**, 1296 (1960).

51) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, **1957**, 4294.

52) R. E. Kagarise, *J. Amer. Chem. Soc.*, **77**, 1377 (1955).

53) W. Gordy and W. J. Orville-Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

54) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall Inc., U. S. A. (1963).

55) See, *e.g.*, S. Bratož and S. Besnainou, *J. Chem. Phys.*, **34**, 1142 (1961).

56) R. M. Badger, *ibid.*, **2**, 128 (1934); **3**, 710 (1935).

57) C. H. Douglas Clark, *Phil. Mag.*, **18**, 459 (1934).

58) J. A. Ladd, W. J. Orville-Thomas, and B. C. Cox, *Spectrochim. Acta*, **20**, 1771 (1964).

lengths and the force constants are as yet incomplete, it is not possible for the time being to proceed to an unequivocal discussion of the relation between the bond length, the force constant, and the nature of the carbonyl bond.

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