order dependence on chloride ion. A more detailed dependence on chloride can be made at lower and higher Cl/Cu ratios than we employed. There is, however, a disadvantage to working with high ratios in that acetone is readily salted out of water by chloride, and in order to operate in solutions of high chloride to cupric ratios and still maintain measureable cupric concentrations a sensitive method of detecting cupric concentration must be found. The ambiguity of the spectral method of determining cupric complexes[15] makes the use of this possibility of following low copper concentration changes dubious at the present time.

Other mechanisms not involving acetone (in large excess), or involving a combination of other cupric chloride complexes may also be formulated which are consistent with the results. At present we are not able to distinguish among these processes. Indications from the behavior of the spectrum of cupric chloride in acetone with changing acid and salt concentrations disfavor either $CuCl_3^-$ or $CuCl_4^{=}$ as active intermediates. It seems reasonable that in media of such low dielectric constant as acetone and acetone–water solutions such neutral species as $CuCl_2$ and its dimer would predominate.

The results from the benzoquinone experiment indicate that a free radical process for the reduction of cupric chloride by acetone is unlikely. For example, we can write

$$CuCl_3^- + CH_3COCH_3 \xrightarrow{\text{slow}} CuCl_2^- + HCl + CH_3COCH_2$$

$$CH_3COCH_2\cdot + CuCl_2 \xrightarrow{\text{fast}} CH_3COCH_2Cl + CuCl$$

This possibility, however, cannot be entirely eliminated on the basis of the evidence on hand.

Acknowledgment.—I would like to thank Dr. J. Kumamoto for many illuminating discussions.

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[CONTRIBUTION NO. 1993 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Molecular Structure of Formyl Fluoride

BY MORTON E. JONES, KENNETH HEDBERG AND VERNER SCHOMAKER

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The structure of HCOF has been investigated by electron diffraction in the gas phase. The parameters were refined by a least squares technique based upon the observations and calculated intensity curves. The parameter values and limits of error (taken as 2σ) are C–F = 1.351 ± 0.013 Å., C=O = 1.192 ± 0.011 Å., O...F = 2.225 ± 0.019 Å., C–F/C=O = 1.134 ± 0.005 and ∠O–C–F = 121.9 ± 0.9°.

Carbon–halogen bond lengths show interesting variations. For example, the distances in methylene fluoride, fluoroform, carbon tetrafluoride, carbonyl fluoride and acetyl fluoride (1.358,[1] 1.332,[2] 1.323,[3] 1.32[4] and 1.37 Å.,[5] respectively) are all shorter than the distance in methyl fluoride (1.391 Å.[3]), but, while the chloro- and bromomethanes show similar but less marked distance variations (the data for the iodomethanes are incomplete), the carbon–chlorine, –bromine, and –iodine distances in the acetyl halides (1.82, 2.00 and 2.21 Å.)[5] are all considerably longer than is found in the corresponding methyl halides (1.781, 1.939, and 2.139 Å.).[6] We therefore felt it would be worth while to study the structure of formyl fluoride.

Experimental

Formyl fluoride was prepared from formic acid, sodium fluoride and benzoyl chloride,[7] collected in a Dry Ice trap, vacuum distilled at −40 and −35° and passed over sodium fluoride to remove hydrogen chloride. The resulting product boiled at −24°.

The methods used for obtaining photographs and for calculating radial distribution and theoretical intensity curves have been outlined in recent reports from this Laboratory.[8] Visual interpretations of the photographs were made independently by two authors. Comparisons were made with photographs of formic acid,[9] which are very similar to those of formyl fluoride, in order to help with the interpretations. Our two visual curves are in excellent agreement on all points except the relative depths of minima 5, 7 and 8, where re-examination of the photographs showed curve K.H. is to be preferred (Fig. 1).

Results

The radial distribution curve (Fig. 1) has strong peaks centered at 1.27 and 2.22 Å., corresponding to ∠O–C–F ~ 122°. Theoretical intensity curves were therefore calculated with $Z_{\mathrm{H}}^{eff} = 1.25$ for C–H = 1.09 Å., $1.072 \leqslant$ C–F/C=O $\leqslant 1.197$, $117° \leqslant$ ∠O–C–F $\leqslant 127°$, and $a_{\mathrm{C-H}} = 0.0016$ $(a_{ij} = {}^1/_2(\overline{\delta r^2}_{ij} - \overline{\delta r^2}_{\mathrm{C=O}}))$; for most of the curves the O . . . H and F . . . H terms were omitted and $a_{\mathrm{C-F}}$ and $a_{\mathrm{O\ldots F}}$ were set equal to zero.

Qualitative comparisons of these curves and our observations led to C–F/C=O = 1.136 ± 0.009 and ∠O–C–F = 121.7 ± 1.7° for the shape of the molecule. We decided, however, to verify and refine the results by least squares.[10] The parame-

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[8] See K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

[9] J. M. O'Gorman and V. Schomaker, *ibid.*, **69**, 2638 (1947).

[10] W. Hamilton and V. Schomaker have discussed the use of least squares with visual electron diffraction data and have treated bicyclo(2,2,1)heptadiene and bicyclo(2,2,2)octane as examples, and O. Bastiansen, L. Hedberg and K. Hedberg have applied least squares to sector-microphotometer data for 1,3,5,7-cycloöctatetraene, refining simultaneously five distance parameters and six vibration parameters. In anticipation of the publication of these more typical applications of the method (its advantages are especially important for many-parameter problems) we here only sketch its use for formyl fluoride.

TABLE I

ELECTRON DIFFRACTION DATA

	Threefold intensity comparisons						Positional comparisons			
No.[a]	Δ[b]	$\partial/\partial R$[c]	$\partial/\partial T$[c]	$W^{1/2}$	No.	Δ[d]	$\partial q_i/\partial R$	$\partial q_i/\partial T$	$\partial q_i/\partial S$	$W^{1/2}$
	Maxima						Maxima			
2,4-3	−0.4	−0.4	+0.5	2	2	+0.3	+0.1	0.0	−0.2	8
2,5-4	−1.2	+0.1	−0.3	7	3	+ .2	.0	−0.1	− .3	0
4,6-5	+0.3	+ .1	+ .4	10	4	+ .7	.0	− .1	− .4	16
5,7-6	−1.0	−1.0	−0.1	10	5	+ .7	−0.2	− .2	− .5	8
6,8-7	+0.6	+1.1	.0	7	6	+ .7	+ .1	− .4	− .6	8
7,9-8	+ .7	−1.6	.0	3	7	+ .6	− .2	− .3	− .7	24
8,10-9	−2.4	+1.7	+0.4	3	8	+ .4	.0	− .2	− .7	40
					9	+ .3	+0.3	− .6	− .8	12
					10	+1.0	− .2	− .3	− .9	8
	Minima						Minima			
2,5-3	−1.7	+0.1	0.0	4	3	−0.5	−0.1	−0.1	−0.3	8
3,5-3	+1.0	+ .2	+0.1	2	4	+ .6	− .4	− .3	− .3	0
3,6-5	+1.2	+ .4	.0	4	5	+ .4	− .1	− .1	− .4	40
5,7-6	−0.8	+ .8	−0.1	4	6	.0	− .1	− .3	− .5	24
6,8-7	+ .5	−1.1	.0	5	7	+0.7	+ .2	− .2	− .6	32
7,9-8	− .1	+0.3	+0.4	10	8	+ .5	− .2	− .3	− .7	32
8,10-9	+0.5	+ .7	−1.0	4	9	− .3	+ .3	− .5	− .8	12
9,11-10	+1.3	− .2	+0.7	3	10	+ .7	− .2	− .4	− .9	4
					11	+ .9	+ .1	− .3	−1.0	4

Av. dev. $q/q_0 = 0.004$

[a] See text. [b] The intensity combinations (on an arbitrary scale) deduced from a model with C–F/C═O = 1.133, F...O/S = 2.240, C–H/C═O = 0.9046, ∠H–C–F = 110°, $a_{\mathrm{C-H}}(s) = 0.0016$, and $a_{\mathrm{H\ldots F}} = a_{\mathrm{H\ldots O}} = 0.0030$ were subtracted from those deduced from the visual curve. The visual intensity scale, which might better have been regarded as one of the parameters of the least-squares adjustment, was instead fixed once and for all by a comparison with the theoretical curves. [c] Partial derivative of the theoretical intensity combinations. [d] $q_{\mathrm{obs.}} - q_{\mathrm{calc.}}$

ters were chosen, for convenience in using the existing curves, as R = C–F/C═O, S = (C–F + C═O)/2.57, and T = F . . . O/S. Thirty-three observational equations were written, based upon eighteen measurements of positions of maxima and minima and thirteen threefold comparisons of intensity, which were put into suitable form by subtracting the intensity of the middle feature from the average of the outer features as recorded in the visual curve K.H. The desired adjustments and the derivatives for the parameters R and T were obtained by differencing the observations and similarly obtained quantities from appropriate theoretical intensity curves; the derivatives for S, the scale parameter, were calculated directly. Weights were assigned in the ways described by Hamilton and Schomaker[10] and Ibers and Schomaker.[11] Table I summarizes these data.

Solution of the normal equations gave the results $R = 1.1337$, $T = 2.2485$, and $S = 0.9896$, or, in terms of interatomic distances, C═O = 1.192 Å., C–F = 1.351 Å., and O . . . F = 2.225 Å., corresponding to ∠ O–C–F = 121°57′. In order to estimate the limits of error we calculated the error matrix $M = B^{-1}$, where B is the matrix of the coefficients of the normal equations, and added to the diagonal scale parameter term the quantity $(0.004)^2$, which seems to be a fair estimate of the additional independent scale factor error arising from uncertainties in wave length calibration, film expansion correction, and measurement of camera distance. (B was normalized by dividing by the usual factor $\sum_i W_i V_i^2/n - m$), in which W_i is the weight assigned to an observation and V_i is its residual, n is the number of observations, and m is the number of parameters being fitted—in this case three.) The estimated error matrix for the interatomic distances and the two interesting shape parameters is then

$$M_r = \{\mu_{ij}\} = AB^{-1}\tilde{A} = \begin{array}{ccccc} \mathrm{C{=}O} & \mathrm{C{-}F} & \mathrm{O\ldots F} & \angle\mathrm{O{-}C{-}F},\ \mathrm{deg.} & \mathrm{C{-}F/C{=}O} \\ \end{array}$$
$$\begin{pmatrix} +31.0 & +31.2 & +44.5 & -894.6 & -3.3 \\ +31.2 & +39.4 & +49.6 & -1099.6 & +3.3 \\ +44.5 & +49.6 & +85.5 & +313.7 & -0.7 \\ -894.6 & -1099.6 & +313.7 & +3289.0 & -1.2 \\ -3.3 & +3.3 & -0.7 & -1.2 & +5.8 \end{pmatrix} \times 10^{-6}$$

where the element μ_{ij} is the average value of the product of the two errors ϵ_i and ϵ_j and A is the matrix of coefficients in the transformation equations relating these parameters and the parameters R, T and S. It has been estimated (W. Hamilton and V. Schomaker, ref. 10) that 2σ provides a satisfactory limit of error. Our final results are, then, C–F = 1.351 ± 0.013 Å., C═O = 1.192 ± 0.011 Å., O . . . F = 2.225 ± 0.019 Å., C–F/C═O = 1.134 ± 0.005, ∠O–C–F = 121.9 ± 0.9°.[12]

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(11) J. A. Ibers and V. Schomaker, *J. Phys. Chem.*, **57**, 699 (1953).

(12) It must be emphasized that our least squares adjustment has been made for a molecule of rigid heavy atom structure, and it is possible that the amount by which a proper inclusion of vibration factors could change our results would be a substantial fraction of our shape parameter error limits. We have not studied this quantitatively, but a qualitative examination of appropriate curves shows that inclusion of vibration factors would probably lead to somewhat smaller values for C–F/C═O and ∠O–C–F.

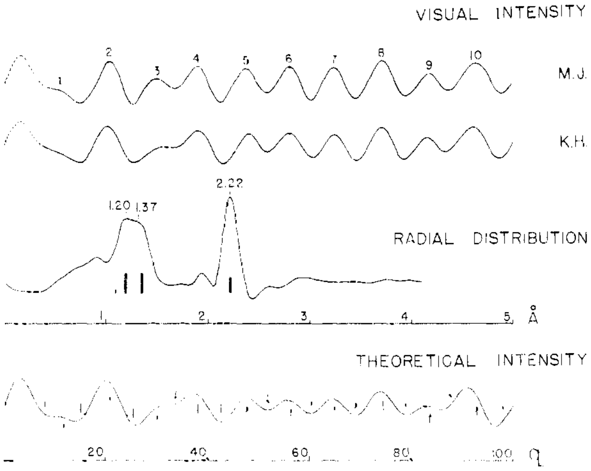

Fig. 1.—Electron diffraction curves for formyl fluoride. The theoretical intensity curve is for C–F/C=O = 1.133 and ∠F—C=O = 121°.

The limits of error for C–F/C=O and ∠O–C–F are surprisingly small compared to the values ±0.009 and ±1.7° first derived for these parameters by the correlation procedure. It appears that one important reason for this difference is the inclusion of the measurements of positions of features in the least squares equations. In ordinary practice of the correlation procedure the contribution of such measurements is often neglected in the determination of shape parameters. A least squares determination of the shape parameters for formyl fluoride omitting the measurement of positions of features leads to the results C–F/C=O = 1.135 ± 0.006 and ∠O–C–F = 121.5 ± 1.3°.

Discussion

Our C–F and C=O bond lengths for formyl fluoride are consistent with the corresponding lengths in many other molecules in that each bond is somewhat shortened relative to its length in the relevant methane where only one substituent is present (CH_3F, CH_2O). Comparison with the values reported for acetyl fluoride (1.37, 1.16 Å.)[10] is not simple, however, the substitution of methyl for hydrogen having opposite effects on C–F and C=O whereas the most natural expectation would be of lengthening for both. All in all, it seems best that further discussion should await a wider survey of the facts than is here feasible.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Interhalogen Compounds[1]

BY MAX T. ROGERS, RICHARD D. PRUETT AND JOHN L. SPEIRS

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The electric moments of bromine trifluoride, chlorine trifluoride and iodine pentafluoride have been measured in the vapor phase by the refractivity method. A planar T-configuration for bromine trifluoride, similar to that now established for chlorine trifluoride, accounts satisfactorily for the dipole moment of the molecule. The large electric moment of iodine pentafluoride excludes the trigonal bypyramidal and pentagonal planar structures. It is in satisfactory agreement with a distorted octahedral arrangement in which the iodine atom is probably below the plane of the four fluorine atoms on the side opposite the fifth fluorine atom, and the unshared pair is in the sixth position.

Introduction

The electric moments of chlorine monofluoride, bromine monofluoride and chlorine trifluoride have been found by microwave methods[2] but the only halogen fluoride studied by conventional radiofrequency techniques is bromine pentafluoride.[3] The dielectric constants and electric dipole moments of bromine trifluoride, chlorine trifluoride and iodine pentafluoride in the vapor state have, therefore, been measured at radio-frequencies. The results are reported here along with some conclusions concerning the structures of the molecules.

Experimental

Materials.—Bromine trifluoride and chlorine trifluoride (Harshaw Chemical Co.) were purified by several distillations in a Monel apparatus. The middle fraction of the final distillation was used in each case for the measurements. Iodine pentafluoride was part of a sample purified by distillation through a packed column[4]; the mole per cent. impurity indicated by freezing point lowering measurements was about 0.02 mole %.

Apparatus.—Dielectric constants were measured by the heterodyne-beat method. The fixed oscillator was crystal-controlled at 500 kc. and the variable-frequency-oscillator was of the negative-transconductance type described by Chien.[5] The beat frequency was compared with a fixed-frequency 400-cycle reference using an oscilloscope; in this way locking-in of the oscillators was prevented.

Capacitance was measured by the substitution method using a General Radio type 722-N precision capacitor (1100 $\mu\mu$f.). Introduction of the gas into the measuring cell increased the capacitance in the tank-circuit of the variable-frequency oscillator; the precision capacitor was then adjusted to restore the original beat frequency. To produce a suitably large change of scale reading on the precision capacitor from the very small capacitance changes obtained, and to have a nearly linear relationship between these, auxiliary capacitors were employed in a network arrangement. The precision capacitor and a Type 380-M General Radio mica decade (0.01 to 0.001 mf.), were placed in parallel and this combination was then used in series with a small variable air capacitor (175 $\mu\mu$f.). The measuring cell was then arranged in parallel with the above system of three capacitors in the tank circuit of the oscillator. The ranges were adjusted so that 10,000 dial units on the precision ca-

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(1) Physical Properties of the Halogen Fluorides. IV. For preceding article of this series see M. T. Rogers, M. B. Panish and J. L. Speirs, THIS JOURNAL, **77**, 5292 (1955).

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