is a bending force constant, I_x is a reduced moment of inertia about whichever of the three axes is appropriate, and r_e is a radius of extension of the vibrating groups from their pivot, and is numerically not very different from the magnitude of the length which is included in I_x. Dimensionally, these (lengths)^2 cancel, so that the wagging frequencies as well are proportional to $(k_b/<\mu>)^{1/2}$, where $<\mu>$ is a properly averaged mass. Hence

$$\Delta S^0{}_v/R \cong \text{constant} - \frac{1}{2} \ln \overset{6}{\underset{i=1}{\pi}} k_i + 3 \ln <\mu> + \frac{1}{24}\left(\frac{h}{2\pi kT}\right) \sum_{i=1}^{6} \frac{k_i}{<\mu>} + \ldots.$$

It follows that when ΔS^0_v is plotted against log μ, a straight line with slope 13.7 would result, provided (a) k_i did not vary from one molecule to the next; (b) the simple reduced masses were equal to the properly averaged masses; and (c) the magnitudes of the remaining terms in the expansion are negligible. In Fig. 1, group 2 has roughly a slope of 14, while group 1 has roughly a slope 5.5.

Analyses of other bimolecular association reactions in this manner will be of interest, particularly where the vibrational spectra are unknown, or have not been worked out. We are currently investigating the tri-aryl methyl radical dimers.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Computations of Entropy Increments in Gaseous Bimolecular Associations. II. The Dimerization of Carboxylic Acids, and the Addition of Fluorine to Halogen Fluorides

BY LEON SLUTSKY AND S. H. BAUER

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The procedures described in the preceding paper (I)[6] have been extended to two groups of reactions, the dimerization of carboxylic acids and the addition of fluorine to three halogen fluorides. For the first group, the magnitude of $\Delta S^0{}_{vib}$ has been cited as an argument for describing the dimers as consisting of weakly coupled monomers, according to the principle discussed in paper I. A highly simplified model for the structure of the dimers permitted a normal coördinate treatment which led to the six new fundamental frequencies ascribed to each dimeric species (formic, acetic, trifluoroacetic acids), as a consequence of the association process. The fact that the computed entropy increments check the reported values to better than one entropy unit lends strong quantitative support to the model proposed. Since the addition of fluorine to the three halogen fluorides involves the rupture of one bond, the formation of two new bonds, and extensive rearrangements of the original structures, the magnitudes of the entropy increments do not have a simple interpretation. They are useful in the making of estimates of average bond energies. Interesting differences between the several central halogen atoms appear when their fluorine ligancies go up by two. Arguments are presented for selecting the "higher" of the two possible values for the heats of dissociation of ClF, BrF and IF.

The Carboxylic Acids.—That the equilibrium constants for the dimerization of carboxylic acids differ appreciably, depending on the group substituted into the carboxyl carbon atom has been known for some time. Recently[1] speculations have appeared as to whether such differences are due primarily to enthalpy or entropy factors. The literature is replete with reports of experimental results regarding these systems, from which one may select values to prove either conclusion. Where available we prefer the data by Taylor and Bruton[2,3] since these investigators worked in the low pressure region where corrections for higher degrees of polymerization and deviation from ideal behavior are unnecessary. In the case of trifluoroacetic acid, Nash[1] computed equilibrium constants after he had extrapolated isothermal density curves to zero pressure. Reference to Table I shows that small differences appear both in the enthalpy and entropy terms, and that due to the rather close balance between them, appreciable variations in the magnitudes of the equilibrium constants result. Indeed, closer inspection of the reported entropy increments raises the question why these should be so nearly alike, since the masses and moments of inertia of the molecular species vary over a considerable range. The computations described below permitted the unscrambling of the effects due to mass, moments of inertia, internal rotations and molecular vibrations.

TABLE I

	$\Delta H^0{}_{433}$, kcal./mole	$\Delta S^0{}_{433}$, e.u.	$K_p(433)$, atm.$^{-1}$	Ref.
HCOOH	−14.1	−35.98	0.299	2
H_3CCOOH	−15.3	−36.84	.474	3
F_3CCOOH	−14.0	−36.30	.135	1
CH_3H_2CCOOH	−15.2	−36.39	.503	2

The structures for which the moments of inertia were computed are those given by Karle and Brockway,[4] *cf.* Table II. From these and the known molecular weights, one may readily compute $\Delta S^0{}_{tr.+r.}$ (rigid molecules). These are summarized in Table III.

The deduced values for $\Delta S^0{}_{(rigid)}$ first must be corrected for contributions due to restricted internal rotation. For simplicity we have assumed that the heights of the barriers hindering free rotation about C–C bonds remain unaltered due to the association process, and that both in acetic and trifluoroacetic acids the magnitude is 2500 cal./mole, with three equal minima in the angular potential function. Although these are not valid assumptions, the errors introduced thereby are of the order of one entropy unit, which is within other limitations to be introduced later. For acetic acid

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(1) R. E. Lundin, F. E. Harris and L. K. Nash, THIS JOURNAL, **74**, 4654 (1952).

(2) M. D. Taylor and J. Bruton, *ibid.*, **74**, 4151 (1952).

(3) M. D. Taylor, *ibid.*, **73**, 315 (1951).

(4) J. Karle and L. O. Brockway, *ibid.*, **66**, 574 (1944).

TABLE II

	$I_aI_bI_c \times 10^{114}$ (g. cm.^{2})^3 Monomer	Dimer
Formic	0.0776	30.02
Acetic	1.209	177.7
Tri-F-acetic	28.88	4999
Propionic	5.327	808.5

TABLE III

Ideal gas, at one atm.

	S^0_{433} (tr. + r.), e.u. monomer (σ = 1)	S^0_{433} (tr. + r.), e.u. dimer (σ = 2)	ΔS^0(rigid), e.u.
Formic	61.19	67.85	−54.53
Acetic	64.79	70.39	−59.18
Tri-F-acetic	69.84	75.66	−64.02
Propionic	67.35	73.03	−61.67

the entropy associated with rotation of the methyl groups with respect to the rest of the molecule may be deduced from the barrier assumed and the reduced moments of inertia.[5] For trifluoroacetic acid, the entropy contribution for free internal rotation was calculated by means of the relation

$$S_{\text{f.i.r.}} = 2.287(\log T + \log I_m - 2 \log n) + 89.93$$

and the increment due to restricted rotation was read from the available tables.[5] Thus we found (at 160°) the values listed in Table IV.

TABLE IV

	$S_{\text{r.i.r.}}$ (dimer), e.u.	$2S_{\text{r.i.r.}}$ (monomer), e.u.	$\Delta S_{\text{r.i.r.}}$ e.u.
Formic	0	0	0
Acetic	5.62	5.55	0.07
Tri-F-acetic	10.44	9.12	1.32
Propionic	(calculations not performed)		
	Estimated		1

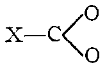
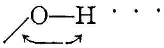
We are now in a position to deduce the increment in entropy arising from the vibrational contributions. These are given in Table V. The fact that the increment in vibrational entropy is so large is significant[6]; the conclusion is inevitable that in the association process the monomer units become only weakly bonded to each other. Then the six new vibrational frequencies to be associated with the dimer ring may be considered as arising from the relative vibrations of two massive subsystems; consequently they are very low. The naive assumption that the ring can be treated as a single unit vibrationally is indeed unsatisfactory since this not only would argue for ΔS_{vib} of about one-half that observed, but also would require that the entropy increment associated with the dimer ring be about the same for all four acids. It is difficult to see how the 8 e.u. difference between formic and trifluoroacetic acids could be accounted for by postulating a sufficiently extensive loosening of the bonds upon dimerization of the latter.[7] On the other hand, if our conclusion regarding the proper description of the dimers is correct, a simple model should not only lead to vibrational entropy increments of the magnitudes observed, but should also account for their correct sequence. The following model is treated briefly in the appendix. In it we have assumed that the vibrational contributions to the entropy in the monomer units remain essentially unaltered upon dimer formation. Further, that insofar as the six new vibrations are concerned, the units  remain rigid, and that the quadrilateral formed by the four oxygen atoms is a rectangle symmetric about a line joining the opposite carbon atoms. The force constants for the O–H · · · · O stretching motions were obtained by assuming an inverse power type of potential matched for the observed O · · · · O separation and half of the heats of dissociation. The force constants for the  bending were taken to be $(0.97/1.08)k_{\text{O-H bend}}$, recorded for various monomers[8,9,10] both for the in-plane and out-of-plane motions. Six frequencies were thus deduced for each of three acid dimers. These are listed in Table VI, while a comparison

TABLE V

	ΔS^0(exp), e.u.	ΔS^0(rigid+ r.r.), e.u.	ΔS^0(vib-x), e.u.
Formic	−35.98	−54.53	+18.55
Acetic	−36.84	−59.11	+22.27
Tri-F-acetic	−36.30	−62.70	+26.40
Propionic	−36.39	−60.67	+24.28

TABLE VI

	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$\tilde{\nu}_4$	$\tilde{\nu}_5$	$\tilde{\nu}_6$
Formic	172	348	124	481	145	96
Acetic	165	332	114	215	143	35
Tri-F-acetic	126	286	54	127	89	16

TABLE VII

	$\Delta S^0_{\text{vib-x}}$, e.u.	$\Delta S^0_{\text{ring-c}}$, e.u.	Difference, e.u.
Formic	18.55	17.68	0.87
Acetic	22.27	21.47	.80
Tri-F-acetic	26.40	27.37	− .93

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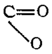
(5) H. S. Taylor and S. Glasstone, "Treatise on Physical Chemistry," Vol. I, D. Van Nostrand Co., New York, N. Y., 1942, p. 661.

(6) A. Shepp and S. H. Bauer, THIS JOURNAL, **76**, 265 (1954).

(7) The extent of weakening of the vibrations which are characteristic of the monomer molecule as a consequence of dimerization is illustrated by the following table, for trifluoroacetic acid.[8]

Assignment	Monomer $\tilde{\nu}$, cm.$^{-1}$	Dimer $\tilde{\nu}$, cm.$^{-1}$
OH stretching	3587	3248–2700
C=O stretching	1826	1788
C–O deformation	1465	1465
C–O stretching	1300	1203
C–F stretching	1244	1244
OH bending (in plane)	1130	1203
C–F stretching (asymm).	1182	1182 (e)
OH bending (out pl.)	904	1123
C–C stretching	825	825
C=O bending 	708	708

The frequencies tabulated above account for 11 of the 18 vibrational degrees of freedom of CF_3COOH. Restricted internal rotation about C–C accounts for a twelfth. Three of the remaining frequencies are associated with C–F bending modes; by analogy with the C–F stretching modes these should not be much affected by association. There remain three low frequencies, two CF_3 wagging, and one carboxyl group wagging, appreciable changes in which could contribute significantly to ΔS^0. We estimate an upper limit of five units if such a loosening were to occur.

(8) W. Fuson, M. Josien, E. A. Jones and J. A. Lawson, *J. Chem. Phys.*, **20**, 1627 (1952).

(9) V. Z. Williams, *ibid.*, **15**, 243 (1947).

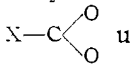
(10) R. C. Herman and R. Hofstadter, *ibid.*, **6**, 534 (1938).

between $\Delta S^0_{\text{vib-x}}$ and the entropy contribution deduced from each set of frequencies ($\Delta S^0_{\text{ring-c}}$ is presented in Table VII.

A considerable number of Raman frequencies in this range have been recorded[11] for the dimers; we were not successful in matching a set of six computed values with those reported for a given acid. However, this is not surprising in view of the crudeness of our model and the absence of detailed information on intensities and polarizations of the Raman lines. A careful reinvestigation of a series of acids may prove worthwhile. In the meanwhile we believe that a rational treatment for the dimerization process may be presented in terms of the formation of weak bonds between monomers, with the latter practically maintaining their identity. This is consistent with the model assumed in the theoretical computation of heats of association for the aliphatic acids.[12] Furthermore, one may argue that the order of decreasing hydrogen bond strengths is

$$\left.\begin{matrix}\text{acetic}\\ \text{propionic}\end{matrix}\right\} > \left\{\begin{matrix}\text{formic}\\ \text{trifluoroacetic}\end{matrix}\right.$$

as is reflected by the experimental values for the heats of association (Table I); it is not distributed according to the magnitudes of the equilibrium constants. The latter sequence is confused by the effect of mass on the vibrational entropy decrement.

The difference between the calculated ring-vibrational entropies and those deduced from experiment are probably due to: (a) the assumption of rigidity of the  $X{-}C\begin{smallmatrix}O\\O\end{smallmatrix}$ unit, which would tend to make the computed value low; (b) a small amount of weakening of the original bonds due to dimerization; and (c) the neglect of anharmonicity in the ring vibrations. In the case of trifluoroacetic acid the calculated value was too high; and this might be explained as being due to an underestimation of the bending force constants for this acid, the correct values being probably closer to those assigned for the other two (see Table IX).

The Fluorination of Halogen Fluorides.—The entropy increment for the reaction ($IF_5 + F_2 = IF_7$) was computed for various combinations of models, assuming the symmetries C_{4v} and C_{5v} for the pentafluoride and the symmetries D_{5h} and D_{7h} for the heptafluoride. Preliminary electron diffraction results[13] on the structures of IF_7 and the vibrational frequency assignments reported by Lord, *et al.*,[14] for both fluorides were used. The lengths of I–F bonds were assumed to be equivalent and equal to 1.88 Å. in the C_{5v} and D_{7h} configurations; in the C_{4v} and D_{5h} configurations the I–F bonds along the principal rotation axis were taken to be 1.93 Å., while the I–F bonds extending to the girdle were assigned lengths of 1.83 Å. The latter two values are those which appear in the radial distribution curve for IF_7, roughly with a $^2/_5$ weighing. The ideal gas entropy increments for the above reaction, at 400°K., for four combinations of symmetries are given below. The spectroscopic data[14]

IF_5 ↓	D_{5h}	D_{7h} ← IF_7
C_{4v}	$\underline{-42.51}$	−43.80
C_{5v}	−43.13	−43.18

favor the C_{4v}–D_{5h} combination (the underlined value). From the variation of the equilibrium constant for the above reaction with temperature, Bernstein and Katz[15] reported −43.5 ± 3 e.u. Since the D_{7h} structure is most implausible, the problem of distinguishing by means of thermochemical data between the two possible configurations for IF_5 reduces to checking predicted entropy increments which are 0.6 e.u. apart. For a series of eleven measurements taken at regular intervals between 600–400°K., the ideal gas equilibrium constants will have to be determined to an accuracy of 4% (equivalent to 0.04 mm.).

For the reaction ($BrF_3 + F_2 = BrF_5$) sufficient data are not available to permit relating the symmetry number of the trifluoride to that of the pentafluoride. Spectroscopic data[16] favor the assignment of the latter to C_{5v}. On this basis, and with the further assumption that the Br–F distances are equivalent and equal to the sum of the covalent radii, Stephenson and Jones[16] tabulated the thermodynamic properties of the pentafluoride. A third law entropy is available for bromine trifluoride.[17] The value for the gas at the normal boiling point was corrected to 300°K. Thus the entropy decrement for the addition of fluorine to bromine trifluoride was deduced to be $\Delta S^0_{300} = -42.21$ e.u. Further, by combining the above values with the available data for BrF and Br_2[18] the entropy change for the reaction ($8BrF = 3Br_2 + BrF_3 + BrF_5$) was estimated to be $\Delta S^0 = -114$ e.u. (ideal gas value).

The entropy decrement computed for the reaction ($ClF + F_2 = ClF_3$) on the basis of the accepted structure of the product[19] and the published spectroscopic data for the reactants and product[18,20] check with the value deduced from the observed variation of the equilibrium constant with temperature,[15] $\Delta S^0 = -32.6$ e.u.

With the aid of the above values, we found it possible to solve for a rational set of *average bond energies* (a.b.e.) based upon various heats of formation, dissociation energies from spectroscopic studies and minimum values for ΔF^0's. These are summarized in Table VIII. For the dissociation energies of F_2, Br_2 and I_2 we used 37.7,[21] 45.5,[22] 35.5[22] kcal./mole, respectively. Then, the a.b.e. for IF_5 follows from the heat of formation of the gaseous compound as reported by Wolf,[23] $Q^f = 194.6$ kcal./mole, and the

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(11) Summary of Conference on Recent Research on the Hydrogen Bond in the Soviet Union, ONRL Report 106-52 (1952).

(12) M. M. Jones, W. R. Gilkerson and G. A. Gallop, *J. Chem. Phys.*, **20**, 1048 (1952).

(13) S. H. Bauer, unpublished data.

(14) R. C. Lord, M. A. Lynch, Jr., W. C. Schumb and E. J. Slowinski, This Journal, **72**, 522 (1950).

(15) R. Bernstein and J. J. Katz, *J. Phys. Chem.*, **56**, 885 (1952).

(16) C. V. Stephenson and E. A. Jones, *J. Chem. Phys.*, **20**, 1830 (1952).

(17) G. D. Oliver and J. W. Grisard, This Journal, **74**, 2705 (1952).

(18) G. Herzberg, "The Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1950.

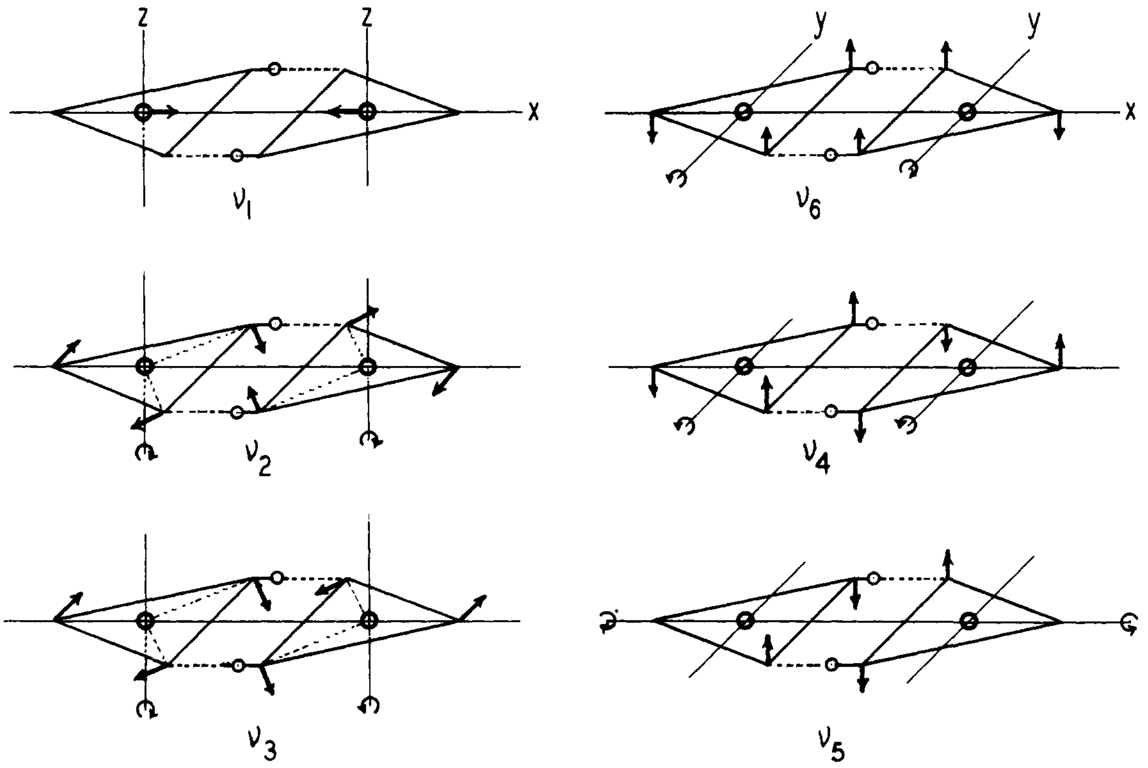
(19) (a) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **21**, 602 (1953); (b) D. F. Smith, *ibid.*, **21**, 609 (1953).

(20) Z. K. Schäfer and E. Wicke, *Z. Elektrochem.*, **52**, 206 (1948).

(21) R. N. Doescher, *J. Chem. Phys.*, **20**, 330 (1952).

(22) R. A. Durie and A. G. Gaydon, *J. Phys. Chem.*, **56**, 316 (1952).

(23) A. A. Woolf, *J. Chem. Soc.*, 231 (1951).



In-plane

Out-of-plane.

Fig. 1.—Schematic representation of the six normal modes of vibration. The identification of ν_1, ν_2, ν_3, ν_4, with the frequencies listed in Table VI is certain; ν_5 and ν_6 cannot be represented as simply as indicated, the normal modes being combinations of the motions shown.

TABLE VIII

AVERAGE BOND ENERGIES (IN KCAL.) FOR THE ATOMIZATION OF VARIOUS FLUORIDES

Central atom	1	3	5	7 Fn
Cl	60.4	41.4	..	..
Br	59.6	[52.6][a]	[48.3][a]	..
I	66.3	..	62.2	53.9

[a] [ ] indicate minimum values.

heat of sublimation of iodine (ΔH_s = 14.88 kcal./mole). The a.b.e. for the heptafluoride may be deduced from these data plus the additional fact that the enthalpy increment for the addition of one mole of fluorine to the pentafluoride is 28.5 kcal. at 500°K.[15] The latter value has been corrected to room temperature. We are now in a position to argue for the *higher* of the two possible values reported for the dissociation energy of IF by Durie and Gaydon.[22] It would be most surprising if the dissociation energy of the diatomic molecule were of the order of 18 kcal. less than the a.b.e. in the pentacoördinated compound; however, the decreasing magnitude with increasing ligancy is to expected. Two admittedly weak arguments have been advanced by these authors[22,24] in favor of the lower value: A. The fact that IF is not a stable chemical species where IF_5 may be readily accounted for if the heat of reaction for

$$5I_2(g) + 5F_2(g) = 4I_2(g) + 2IF_5(g) \qquad \Delta H_2$$

s greater than the heat of reaction for

$$5I_2(g) + 5F_2(g) = 10IF(g) \qquad \Delta H_1$$

Regrettably, an arithmetic error misled these authors to state that ΔH_1 lies *between* the two possible values for ΔH_2. Hence they selected the lower dissociation energy for IF. Actually, $\Delta H_1 = -404$ kcal. (rather than −167), and hence is numerically greater than $\Delta H_2 = -297$ kcal. computed for the higher value. B. The higher value suggests that IF is somewhat more stable than BrF and ClF; and if the higher values are accepted for all three diatoms, there is an increasing progression in the ratio (dissociation energy/force constant) for the sequence with increasing atomic weight. We believe that these effects are just those to anticipate for a sequence with increasing polarity of the bond, due to greater differences between the electronegativity of the bonded atoms.

Bernstein and Katz[15] investigated the thermal dissociation of BrF_5, and could detect no decomposition of the pentafluoride to the trifluoride and fluorine. Hence they concluded that the minimum value (numerically) for the reaction ($BrF_3 + F_2 = BrF_5$), $-\Delta F^0 \leqslant 18.0$ kcal., at 670°K. Upon combining this with the above estimated value for the entropy increment, one may deduce that for this reaction, $-\Delta H^0 \leqslant 46.0$ kcal. Further, Ruff and Braida[25] observed that the conversion of BrF into Br_2, BrF_3 and BrF_5 goes practically to completion at 50°, and thus we deduced a minimum value

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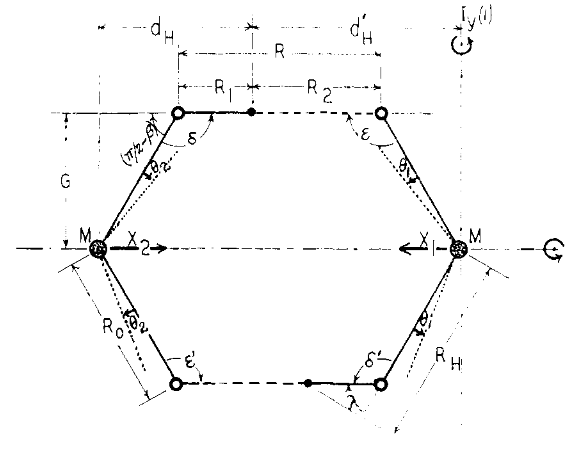
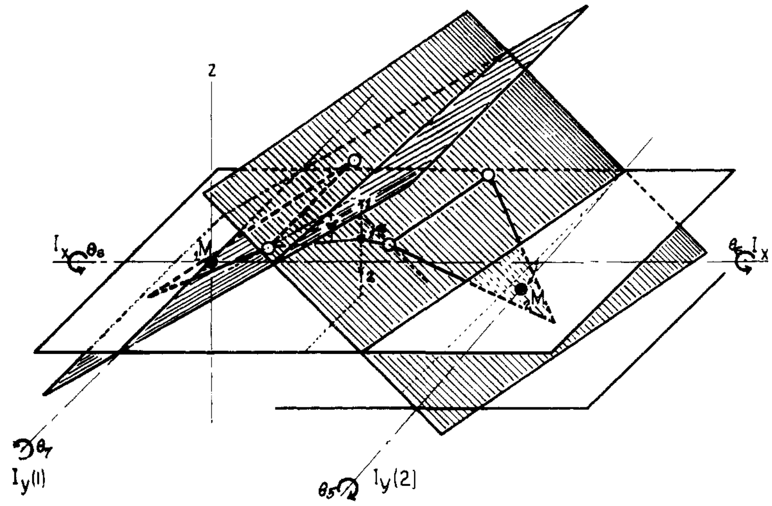
(24) R. A. Durie, *Proc. Roy. Soc.* (*London*), **207A**, 388 (1951).

(25) O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **214**, 81 (1933).



(a) In-plane parameters.



(b) Out-of-plane parameters.

Fig. 2.—Definition of the structural parameters for (a) the in-plane motions, and (b) the out-of-plane motions.

for the free energy change ($-\Delta F^0 \leqslant 22$ kcal. at 50°). Since we have an estimate of the entropy change for this interconversion, we have deduced a minimum value for the enthalpy

$$8BrF = 3Br_2 + BrF_3 + BrF_5 \quad -\Delta H^0 \leqslant 59.0$$

These minimum values may be combined with the *higher* value for the dissociation energy of BrF to obtain the number given in Table VIII. If the lower value (50.1) were adopted for the dissociation energy of BrF, the minimum a.b.e.'s deduced for the bromine trifluoride and pentafluoride would be 39.9 and 40.7. These certainly do not fit the orderly progression which is evident when the higher value is chosen. It is interesting to note that the unexpected observation regarding the stability of BrF_5 relative to BrF_3 which seems to have startled some investigators, and which is a consequence of the rather large heat for the association reaction, is nevertheless consistent with the trends which appear in the table. Perhaps more striking is the fact that because of the large a.b.e. value for IF_5, the a.b.e. in IF_7 is quite high in spite of the relatively low heat of fluorination for the former.

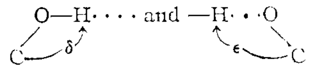
The enthalpy change for the reaction ($ClF + F_2 = ClF_3$) is $\Delta H^0_{310} = -25.0$ kcal.[15] Upon combining this with the higher value for the heat of dissociation of ClF, one may readily deduce the a.b.e. in ClF_3 to be 41.4 kcal.

The fact that the maximum ligancy to fluorine is lower, the smaller the atomic weight of the halogen, and that the a.b.e. follow a roughly parallel correlation may be explained in terms of non-bonded F–F repulsion, which clearly increases with decreasing radius of the central atom. The large internuclear distance and low dissociation energy in fluorine has been explained[26] in terms of non-bonding electron interaction.

Appendix

Outline of the Normal Coördinate Treatment for the Mutual Vibrations of the Monomer Units, as Present in the Dimer

The form of the potential function postulated for the interaction between the oxygen atoms, O–H····O, was $V(r) = Q(R/r)^6 - 2Q(R/r)^3$, wherein Q was assigned half the magnitude of the ΔH^0 of dissociation of the corresponding dimer, and R is the equilibrium O···O separation. From this it follows that the force constant for stretching is $k_{st} = 18Q/R^2$. The force constants for the bending motions at the oxygen atoms



were taken to be about the same as those computed from the observed O–H bending vibrations in the corresponding monomers, corrected for the larger O–H distances present in the dimer; *i.e.*, multiplied by the ratios (0.97/1.08) and (0.97/1.68) for Δδ and Δε, respectively. Typical values are listed in Table IX. A schematic representation of the normal vibrations is given in Fig. 1. The structural parameters which appear in the expression for the potential energy are defined in Fig. 2.

TABLE IX

	k_{st}, dynes/cm.	$k_{bip}(\delta)$, bend in-plane in dynes/radian	$k_{bop}(\alpha)$, bend out-of-plane in dynes/radian
Formic	1.158×10^4	7.094×10^{-12}	5.523×10^{-12}
Acetic	1.281×10^4	6.929×10^{-12}	5.608×10^{-12}
Tri-F-acetic	1.150×10^4	6.395×10^{-12}	4.093×10^{-12}

The In-plane Vibrations.—Let x_1, x_2 designate the displacements of the centers of mass of the monomer units from their equilibrium positions, and θ_1, θ_2 be the instantaneous angles of rotation of the rigid portions about axes (z) passing through their respective centers of mass perpendicular to the plane of Fig. 2a. M is the mass of a monomer unit, and I_z is the moment of inertia about that axis. The stretching terms in the potential energy are

$$2V_{st(ip)} = k_{st}[2(x_1 + x_2)^2 + 2R^2_0(\theta_1 + \theta_2)^2\cos^2\beta]$$

while the bending terms are

$$2V_{b(ip)} = k_{bip}(\delta)[(\Delta\delta)^2 + (\Delta\delta')^2] + k_{bip}(\epsilon)[(\Delta\epsilon)^2 + (\Delta\epsilon')^2]$$

The latter expression may be considerably simplified if we make the further approximation that $\Delta\delta/\Delta\epsilon \doteq R_1/R_2$ for an arbitrary relative displacement of the two units; further, we have noted above that $k_{bip}(\epsilon)/k_{bip}(\delta) \doteq R_1/R_2$. Hence, to this approximation

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(26) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

$$2V_{\mathrm{b(ip)}} = k_{\mathrm{bip}}(\delta)\,\frac{R_1}{R_2}\left(1 + \frac{R_1}{R_2}\right)[(\Delta\epsilon)^2 + (\Delta\epsilon')^2]$$

From Fig. 2a

$$\Delta\epsilon\left(1 - \frac{R_1^2}{R_2^2}\right) = \theta_2\left(1 - \frac{R_0}{R_2}\sin\beta\right) - \theta_1\,\frac{R_{\mathrm{H}}}{R_2}\sin\lambda$$

with a similar expression for $\Delta\epsilon'$, except that θ_1, θ_2 are transposed. When these are squared, combined, and the potential function differentiated, the following components appear in the potential energy matrix

$$V_{X_1,X_1} = V_{X_2,X_2} = V_{X_1,X_2} = V_{X_2,X_1} = 2k_{\mathrm{st}}$$

$$V_{\theta_1,\theta_1} = V_{\theta_1,\theta_2} = A\left[\left(1 - \frac{R_0}{R_2}\sin\beta\right)^2 + \frac{R^2{}_{\mathrm{H}}}{R^2{}_2}\sin^2\lambda\right] + 2k_{\mathrm{bip}}(\delta)\,R_0^2\cos^2\beta$$

$$V_{\theta_1,\theta_2} = V_{\theta_2,\theta_1} = -2A\left[\left(1 - \frac{R_0}{R_2}\sin\beta\right)\frac{R_{\mathrm{H}}}{R_2}\sin\lambda\right] + 2k_{\mathrm{bip}}(\delta)\,R_0^2\cos^2\beta$$

where we have set

$$k_{\mathrm{bip}}(\delta)\,\frac{R_1}{R_2}\left[1 + \frac{R_1}{R_2}\right]\left[1 - \frac{R_1^2}{R_2^2}\right]^{-2} = A$$

The secular determinant is therefore

$$\begin{vmatrix} 2k_{\mathrm{st}} - M\omega^2 & 2k_{\mathrm{st}} & 0 & 0 \\ 2k_{\mathrm{st}} & 2k_{\mathrm{st}} - M\omega^2 & 0 & 0 \\ 0 & 0 & V_{\theta_1\theta_1} - I_z\omega^2 & V_{\theta_1\theta_2} \\ 0 & 0 & V_{\theta_2\theta_1} & V_{\theta_2\theta_2} - I_z\omega^2 \end{vmatrix}$$

for which the roots are

$$\omega = 0 \qquad \omega_1 = 2\sqrt{k_{\mathrm{st}}/M}$$

$$\omega_2 = \sqrt{(V_{\theta_1\theta_1} + V_{\theta_1\theta_2})/I_z} \qquad \omega_3 = \sqrt{(V_{\theta_1\theta_1} - V_{\theta_1\theta_2})/I_z}$$

These correspond to the frequencies listed in Table VI.

The Out-of-plane Vibrations.—The distances d_{H} and $d_{\mathrm{H}'}$ of Fig. 2a appear again in Fig. 2b, being the distances (in the inclined planes) from the axes $y(1)$ and $y(2)$ to the points 1 and 2, respectively. The latter are determined by the intersection of the inclined planes with the normal to the original plane, which passes through the hydrogen atom. As before

$$k_{\mathrm{bop}}(\alpha)/k_{\mathrm{bop}}(\psi) \doteq R_2/R_1 \text{ and } \alpha/\omega \doteq R_1/R_2$$

$$2V_{\mathrm{b(op)}} = k_{\mathrm{bop}}(\alpha)\left[\alpha^2 + \frac{R_1}{R_2}\psi^2\right] + \text{similar terms in } \alpha',\psi'$$

The distance

$$\overline{12} = d_{\mathrm{H}}\theta_5 - d_{\mathrm{H}'}\theta_7 + G(\theta_6 - \theta_8)$$
$$= R_1\alpha + R_2\psi$$

Hence

$$\psi = \frac{\overline{12}\cdot R_2}{R_1^2 + R_2^2}$$

Let

$$k_{\mathrm{bop}}(\alpha)\,\frac{R_2^2}{(R_1^2 + R_2^2)^2}\left(1 + \frac{R_1}{R_2}\right)\frac{R_1}{R_2} = B$$

Then, the components of the potential energy matrix are

$$V_{55} = V_{66} = B(d_{\mathrm{H}}^2 + d_{\mathrm{H}'}^2)$$
$$V_{56} = V_{65} = -2Bd_{\mathrm{H}}d_{\mathrm{H}'}$$
$$V_{57} = V_{75} = V_{68} = V_{86} = -V_{58} = -V_{85} = -V_{67} = -V_{76}$$
$$= BG(d_{\mathrm{H}} - d_{\mathrm{H}'})$$
$$V_{77} = V_{88} = -V_{78} = -V_{87} = 2BG^2$$

The secular determinant takes the form

$$\begin{vmatrix} V_{55} - I_y\omega^2 & V_{56} & V_{57} & -V_{57} \\ V_{56} & V_{55} - I_y\omega^2 & -V_{57} & V_{57} \\ V_{57} & -V_{57} & V_{77} - I_x\omega^2 & -V_{77} \\ -V_{57} & V_{57} & -V_{77} & V_{77} - I_x\omega^2 \end{vmatrix}$$

the roots of which may be expressed as

$$\omega = 0 \qquad \omega_4 = \sqrt{(V_{55} + V_{56})/I_y}$$

and

$$\begin{vmatrix} (V_{55} - V_{56}) - I_y\omega^2 & 2V_{57} \\ 2V_{57} & 2V_{77} - I_x\omega^2 \end{vmatrix} = 0$$

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NOTES

Ethyl α-(α'-Ethoxy-β'-phenylethylideneamino)-β,β-diethoxypropionate

BY HOMER ADKINS[1] AND GERALD GILBERT[2]

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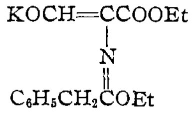
The projected synthesis of a series of substituted oxazolines required ethyl α-(α'-ethoxy-β'-phenylethylideneamino)-β,β-diethoxypropionate (I) or the corresponding aldehyde as an intermediate. However, other investigations indicate that the presence of the free aldehyde is attended by cyclization. Thus, the condensation of ethyl phenyliminoacetate with the sodium enolate of ethyl N-formyl-α-formylglycinate in the presence of hydrogen chloride has been shown to yield 2-benzyl-4-carbethoxyoxazole.[3] The substituted iminoester, II



$$\begin{array}{c} \mathrm{KOCH{=}CCOOEt} \\ | \\ \mathrm{N} \\ \| \\ \mathrm{C_6H_5CH_2COEt} \end{array}$$

II

which is stabilized by the potassium enolate, was prepared by Tiffany[4] by another route. However, several attempts to produce I from this substance in the presence of some acetal-forming reagents again yielded 2-benzyl-4-carbethoxyoxazole.

The present investigation indicates that cyclization can be avoided by preparing the acetal prior to the iminoester condensation. The reaction of ethyl β,β-diethoxyalanate with ethyl phenyliminoacetate hydrochloride proceeded readily in ethylene dichloride at room temperature and I was isolated in 70% yield.

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(1) Deceased August 10, 1949.

(2) Rohm and Haas Co., Phila., Pa.

(3) H. Adkins, R. M. Ross and D. C. Schroeder, THIS JOURNAL, 72, 5401 (1950).

(4) B. D. Tiffany, Ph.D. Thesis, University of Wisconsin, 1949; *cf.* J. W. Cornforth, E. Fawaz, L. J. Goldsworthy and R. Robinson, *J. Chem. Soc.*, 1549 (1949).