I. The Rate of Hydration of Methyl Vinyl Ketone.
II. The Hydrolysis of Optically Active 2-octanol Acetal.
III. Electron Diffraction Investigations of the Structures of Certain Organic Compounds.

Thesis by

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THE RATE OF HYDRATION OF METHYL VINYL KETONE

Introduction

This investigation is the fourteenth in a series[1] conducted in These Laboratories to determine the effect of various substituents on the kinetics and the thermochemistry of the hydration of the ethylenic double bond. The present study concerns the reversible hydronium ion catalyzed hydration of methyl vinyl ketone to 3-ketobutanol-1 and the corresponding dehydration.

The dehydration reaction is a common method of preparing methyl vinyl ketone. Various dehydrating agents and catalysts have been used, such as zinc chloride[2,3], potassium carbonate solution[4], iodine[5], and hydronium ions, with or without the additional presence of calcium chloride[6]. The hydration reaction has received scant attention, but has been mentioned as occurring in the presence of aqueous potassium carbonate[4]. Neither the equilibrium nor the kinetics have been discussed in these references, however.

In the present work, the kinetics have been determined for the acid catalyzed reaction in dilute aqueous solution, the heat of hydration has been calculated from equilibrium values at different temperatures, and the heats of activation for the forward and reverse reactions have been calculated from the equilibria and kinetic constants of the hydration.

Preparation of Materials

Methyl Vinyl Ketone. This was prepared by dehydrating a crude sample of 3-ketobutanol-1 produced by a modification of the method described in D. R. P. 223, 207. One kilogram of acetone was stirred overnight with 150 gms. of paraformaldehyde and 20 ml. of 30% aqueous potassium carbonate.

The resulting solution was neutralized to litmus with dilute sulfuric acid, and the precipitated potassium sulfate filtered out. The bulk of the excess acetone was removed by distilling from a steam bath and the remainder fractionated off free through an efficient column. The ketobutanol was not further purified before dehydration. 5 ml. of 85% phosphoric acid was added to the material in the still, and the aqueous azeotrope (bp. 78° uncorr.) of methyl vinyl ketone was distilled off very slowly through the column and dried over magnesium sulfate. Yield 35 gms. (10% of theory). After this synthesis had been worked out, a substantially identical one was published by White and Heyward[6].

The methyl vinyl ketone was redistilled under vacuum through a short column immediately before use (bp. 31.5° $C_{120\ mm.}$ η_D^{22} 1.4080). Determination of unsaturation by the method used in this investigation showed 1.003 double bonds per mole.

Attempts were also made to prepare methyl vinyl ketone by brominating methyl ethyl ketone to methyl-1-bromoethyl ketone, preparing a cyclic acetal with ethylene glycol, dehydrobrominating with potassium hydroxide and hydrolyzing the acetal. This resulted in tars at the dehydrobromination step, and consequently this method of preparation was abandoned.

<u>3-ketobutanol-1</u>. Attempts to prepare pure ketobutanol by fractionating the crude material invariably yielded a product giving an appreciable positive test for unsaturation. Apparently spontaneous dehydration occurred upon heating. Distillations at reduced pressures were not satisfactory, since the viscosity of the material made bumping and flooding of packed columns extremely troublesome. Because of these factors, the unsaturated compound was used as the starting material for all experiments.

Reagent grade perchloric acid and sodium hydroxide were used to prepare the solutions of constant ionic strength.

Analysis

Methyl vinyl ketone would not absorb bromine rapidly and quantitively from a dilute aqueous solution in the absence of a catalyst. Even in the presence of a 200% excess of bromine for five minutes the absorption was not more than 95% of theory. Quantitative bromination in thirty seconds could be achieved, however, by the mercuric ion catalysis procedure of Lucas and Pressman[7]. Substitution was negligible, amounting to only 2% in thirty minutes.

Experimental Procedure

For the rate experiments, the reactions were carried out in ordinary 500 ml. volumetric flasks. Preliminary experiments indicated that the rates would be most conveniently measured in solutions with hydronium ion concentrations of the order of a few tenths molar.

Enough perchloric acid was added to each of the three flasks used at each temperature to make a 0.2 M solution and to one of them was added enough solid sodium hydroxide to neutralize one half the acid. The flasks were made up to volume with distilled water and their exact acidity determined by titration. All three flasks were thus of 0.2 M ionic strength, two of them being 0.2 M in hydronium ions and the other 0.1 M.

This made it possible to determine the order of the reaction with respect to both the methyl vinyl ketone and the hydronium ion by measuring rates at each temperature in two solutions of the same acidity but having different concentrations of the unsaturated compound and at the same time in two solutions having the same concentration of methyl vinyl ketone, but with acidities differing by a factor of two.

Even with vigorous shaking, it was not found possible to accomplish sufficiently rapid and complete mixing of the unstaurated compound with the solution in the volumetric flasks when they were filled to the mark. This difficulty was overcome by withdrawing exactly 100 ml. of solution from the flask before commencing the hydration experiment.

Before each run, the acid solutions were placed in a thermostat, which held the desired temperature within ± 0.05° C., until thermal equilibrium was established. They were removed, the proper amount of methyl vinyl ketone added, and the stopper~~r~~ed flask vigorously shaken and swirled to achieve a homogeneous solution. A sample was immediately taken and analyzed, and the flask returned to the thermostat. Samples were thereafter taken and analyzed at appropriate intervals, the progress of the reaction being followed by the decrease in unsaturation.

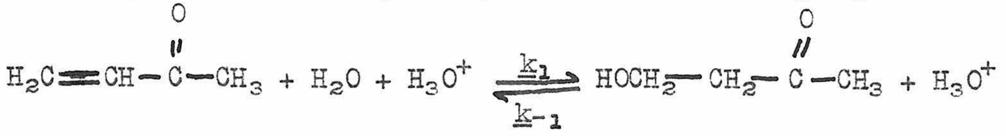
The procedure was as follows: Into a special vacuum flask of a type previously employed in these investigations[1a], was measured enough standard bromate-bromide solution (BrO_3^-/Br^- ratio $= 1/15$) to correspond to an approximately 25% excess of bromine, based on the estimated strength of the solution. The flask was then evacuated with an aspirator. Next, 5 ml. of six normal sulfuric acid was added through the stopcock to release the bromine, and five minutes were allowed to elapse in order to insure complete liberation. This waiting period was essential for accurate results. Enough 0.2 M mercuric sulfate solution which was 2 M in sulfuric acid to prevent the precipitation of basic salts, was next added to bring the ratio of mercuric ion to bromide ion in the flask above unity. The flask was wrapped in black cloth to prevent any photochemical side-effects, and the sample was introduced by means of a special wash-out pipette, calibrated to contain and deliver a definite sample[1a]. The flask was vigorously shaken for thirty seconds, following which 10 ml. of saturated sodium chloride solution and 5 ml. of 20% potassium iodide solution was added, the vacuum broken, and the stopper removed. The liberated iodine was immediately titrated with standard thiosulfate solution. If this titration was delayed, increasingly troublesome fading of the end point resulted. A delay of ten minutes would result in an uncertainty of about 1 ml. in a titration corresponding to the absorption of the bromine liberated by 20 ml. of the standard bromate-bromide solution. This was probably due to iodine substitution in the organic molecule, which is a slow reaction.

The equilibrium values for the hydration were determined separately from the rates, to avoid cumulative errors due to repeated sampling. In these determinations, 1000 ml. volumetric flasks containing 800 ml. of solution were used, since the equilibrium lies so far on the side of the hydrated compound that large samples were necessary to get an accurate analysis.

After the analysis of the original sample, these flasks were left undisturbed until adequate time for attaining equilibrium had elapsed, as indicated by the rate determinations. The equilibrium titrations were then made, and then the temperature of the thermostat was lowered until the reaction had been driven considerably further towards hydration. Next the equilibrium temperature was restored, and, after a suitable interval, the equilibrium titration repeated. The stability of this reaction system was indicated by the fact that identical equilibrium values were obtained when the equilibrium was approached from either side in this manner, even when the total time elapsed was very considerable, on the order of a week. The equilibrium data are summarized in Table I.

Data and Discussion

The hydration of methyl vinyl ketone is shown by Equation I.



$$H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + H_2O + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + H_3O^+ \qquad (I)$$

Table I

Equilibrium Data for the Hydration of Methyl Vinyl Ketone

Temp. °C	μ, M	$[H_3O^+]$ N	initial m.v.k. concentration M	K
15	0.2	0.201	0.0312	44.4
15	0.2	0.201	0.0319	44.4
15	0.2	0.099	0.0152	44.2
			Av.	44.4
25	0.2	0.200	0.0310	33.5
25	0.2	0.204	0.0308	33.3
25	0.2	0.110	0.0160	33.6
			Av.	33.5
35	0.2	0.199	0.0313	27.3
35	0.2	0.202	0.0302	27.6
35	0.2	0.100	0.0146	27.6
			Av.	27.5

At a given hydronium ion concentration in dilute equeous solution the hydration is first order with respect to the unsaturated compound, as shown by the fact that plots of $\log_{10}\frac{\epsilon}{\epsilon-x}$ against t (Figures I, II, and III), described below, are identical even when the initial concentrations of methyl vinyl ketone varies by a factor of two. So closely does this relation hold that it is impossible to distinguish the points for these two plots on the graph. This fact, plus the fact that this plot is a straight line as required by integrated Equation II, representing two opposed first order reactions coming to equilibrium, shows also that the dehydration reaction is first order with respect to the ketobutanol.

$$\log_{10}\frac{\epsilon}{\epsilon-x} = \underline{t}\ (\underline{k}_1 + \underline{k}_{-1}) \ / \ 2.303 \qquad \text{(II)}$$

In this equation, x is the fraction of the original unsaturated compound hydrated at time t, ϵ is the fraction hydrated at equilibrium, and $\underline{k}_1$ and $\underline{k}_{-1}$ are the specific first order rate constants for the hydration and dehydration, respectively, at a given temperature.

Both reactions are first order with respect to hydronium ion, as shown by the fact that, at constant ionic strength, a decrease by half in the hydronium ion concentration results in a decrease by one half in the rate constants.

The possibility that an equilibrium might be simultaneously set up between the ketobutanol on one hand and formaldehyde and acetone on the other was also considered. The presence of formaldehyde in the equilibrium mixture was tested for by Leach's procedure[8]. It was found that the equilibrium mixture gave a negative result, whereas a solution with a concentration of formaldehyde corresponding to 1/2 of 1% of the ketobutanol present at equilibrium gave a positive reaction. Hence the decomposition of ketobutanol in this way cannot have been a significant factor.

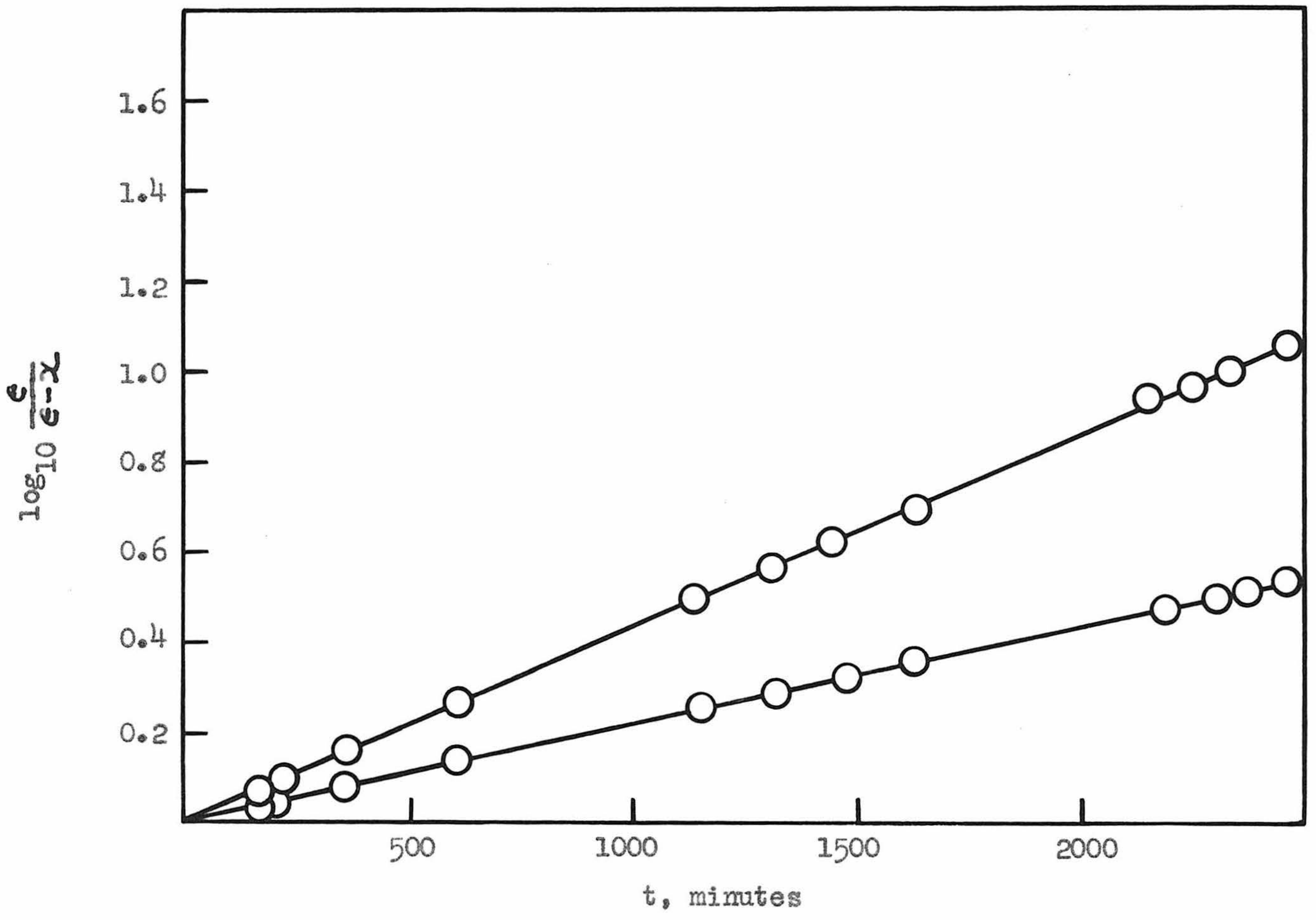


Figure I

Hydration data at 15° C

Upper curve $[H_3O^+] = 0.2$ M; lower curve $[H_3O^+] = 0.1$ M

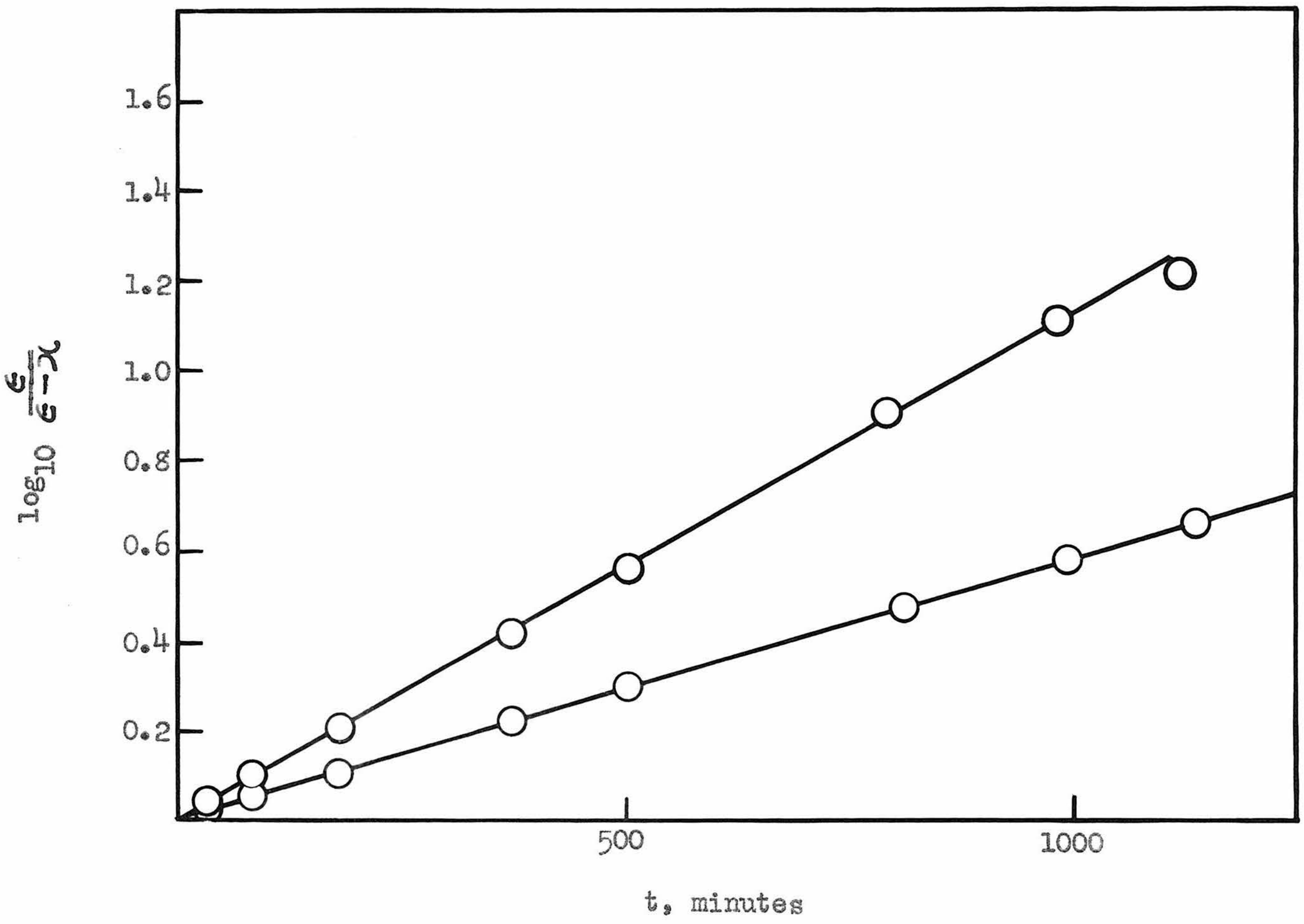


Figure II

Hydration data at 25° C

Upper curve $[H_3O^+]$ = 0.2 M; lower curve $[H_3O^+]$ = 0.1 M

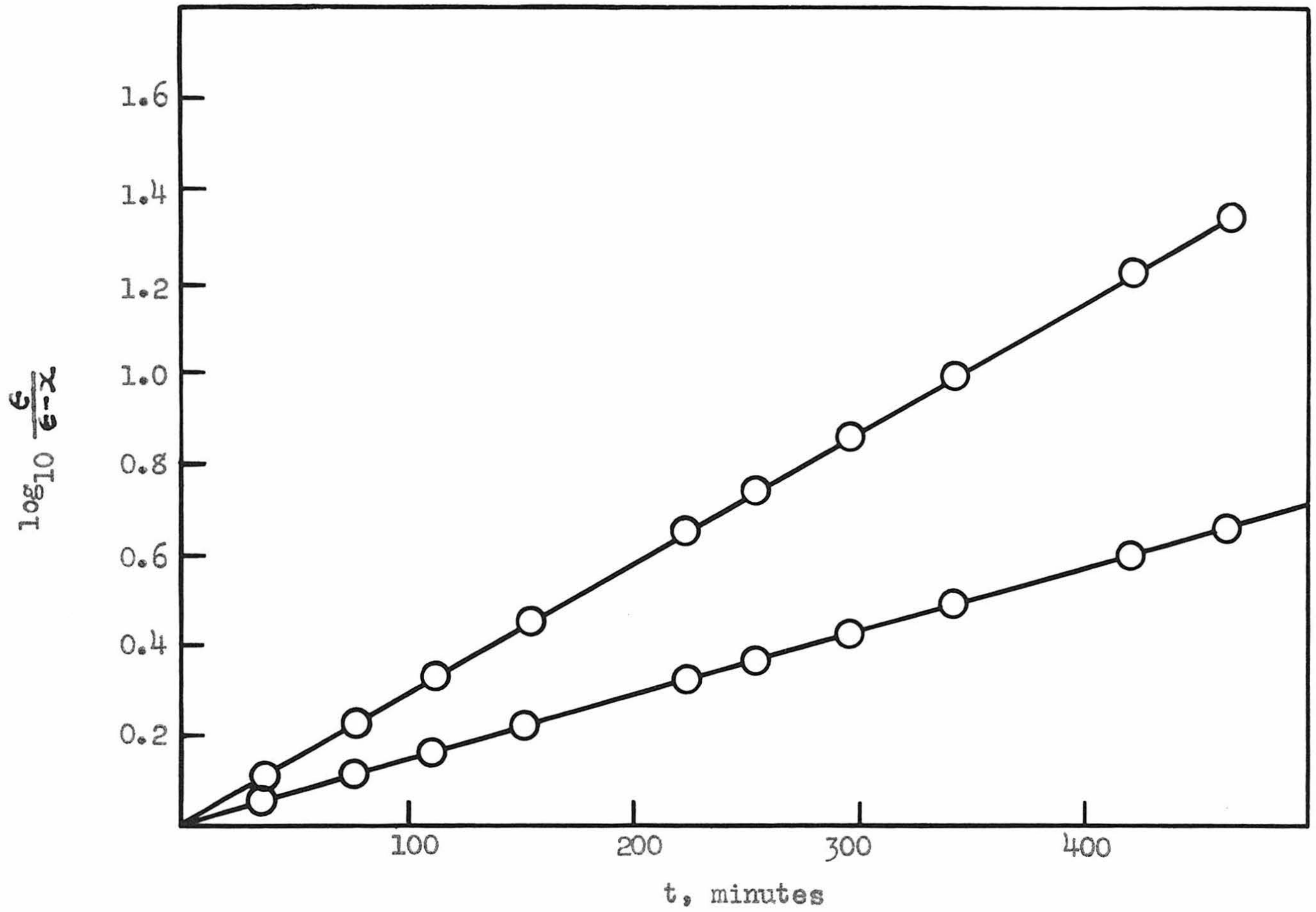


Figure III

Hydration data at 35° C

Upper curve $[H_3O^+]$ = 0.2 M; lower curve $[H_3O^+]$ = 0.1 M

The values of $\underline{k}_1$ and $\underline{k}_{-1}$, the specific velocity constants for the forward and reverse reactions, were calculated from the equilibrium constant and the integrated expression for a first order reversible reaction approaching equilibrium.

$$K = \frac{\underline{k}_1}{\underline{k}_{-1}} = \frac{\epsilon}{1-\epsilon}$$

$$\log_{10} \frac{\epsilon}{\epsilon - x} = \frac{(\underline{k}_1 + \underline{k}_{-1})t}{2.303}$$

Thus the slopes of the straight lines in Figures I, II, and III are equal to $\frac{\underline{k}_1 + \underline{k}_{-1}}{2.303}$. The kinetic data are summarized in Table II.

The "salt effect" which in general throughout these investigations has caused the equilibrium to shift towards the hydrated compound when sodium ions replace hydronium ions in solutions of constant ionic strength was not detected in this case. This is due, no doubt, to the fact that the ionic strength is much lower than was used with most of the other compounds.

The heats of activation of the forward and reverse reactions respectively were calculated from the plots of $\log_{10} \frac{\underline{k}_1}{H_3O^+}$ and $\log_{10} \frac{\underline{k}_{-1}}{H_3O^+}$ against the reciprocal of the absolute temperature (Figure V). This gives Q_1 = 16.50 kcal and Q_2 = 20.75 kcal.

The value of ΔH for the reaction was calculated from the slope of the plot of $\log_{10} K_{eq}$ against the reciprocal of the absolute temperature and gave the value -4.2 kcal.

In conclusion, the data of this determination may be compared with the results of the other two ketones studied in this series.

25° C

unsaturated substance	K	$\frac{\underline{k}_1}{H_3O^+}$ hr^{-1}	$\frac{\underline{k}_{-1}}{H_3O^+}$ hr^{-1}	Q_1 kcal	Q_2 kcal	ΔH kcal
methyl vinyl ketone	33.5	.76	.023	16.5	20.7	-4.2
methyl propenyl ketone	6.0	.20	.035	16.3	20.3	-4.2
mesityl oxide	15.0	.30	.02	12.8	20.4	-7.5

Table II

Kinetic Data Concerning the Reversible Hydration of Methyl Vinyl Ketone

Temp. °C	$[H_3O^+]$, M	μ, M	initial m.v.k. M		$\frac{k_1}{[H_3O^+]}$	$\frac{k_{-1}}{[H_3O^+]}$
15	0.200	0.2	0.0298		0.292	6.56×10^{-3}
15	0.201	0.2	0.0160		0.290	6.56×10^{-3}
15	0.097	0.2	0.0290		0.290	6.53×10^{-3}
				Av.	0.291	6.55×10^{-3}
25	0.212	0.2	0.0301		0.760	2.28×10^{-2}
25	0.204	0.2	0.0155		0.760	2.28×10^{-2}
25	0.110	0.2	0.0291		0.760	2.26×10^{-2}
				Av.	0.760	2.28×10^{-2}
35	0.202	0.2	0.0307		1.90	6.95×10^{-2}
35	0.202	0.2	0.0163		1.93	6.98×10^{-2}
35	0.102	0.2	0.0303		1.91	6.94×10^{-2}
				Av.	1.91	6.96×10^{-2}

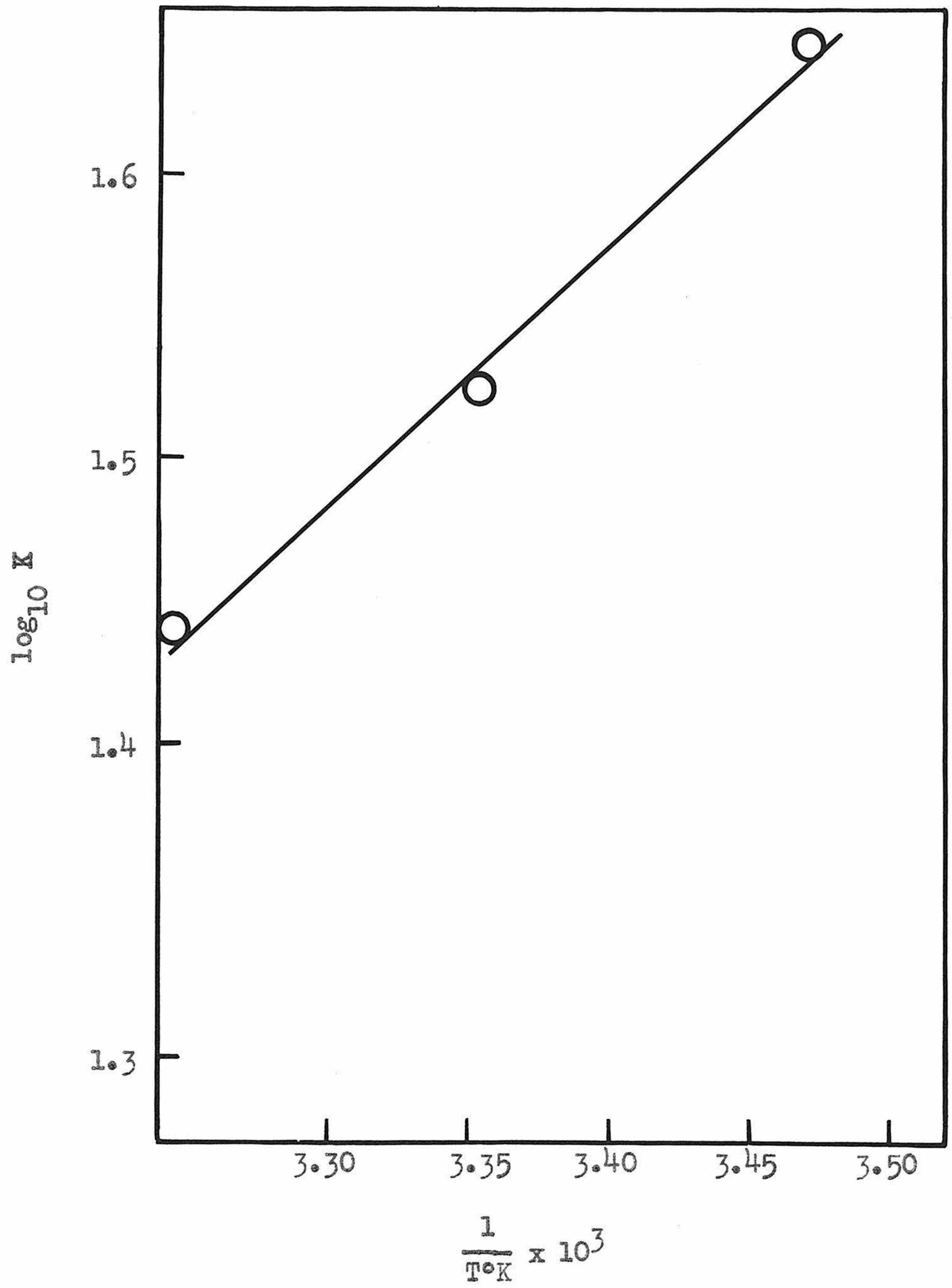


Figure IV

Plot of $\log_{10}$ K against $\frac{1}{T°K}$

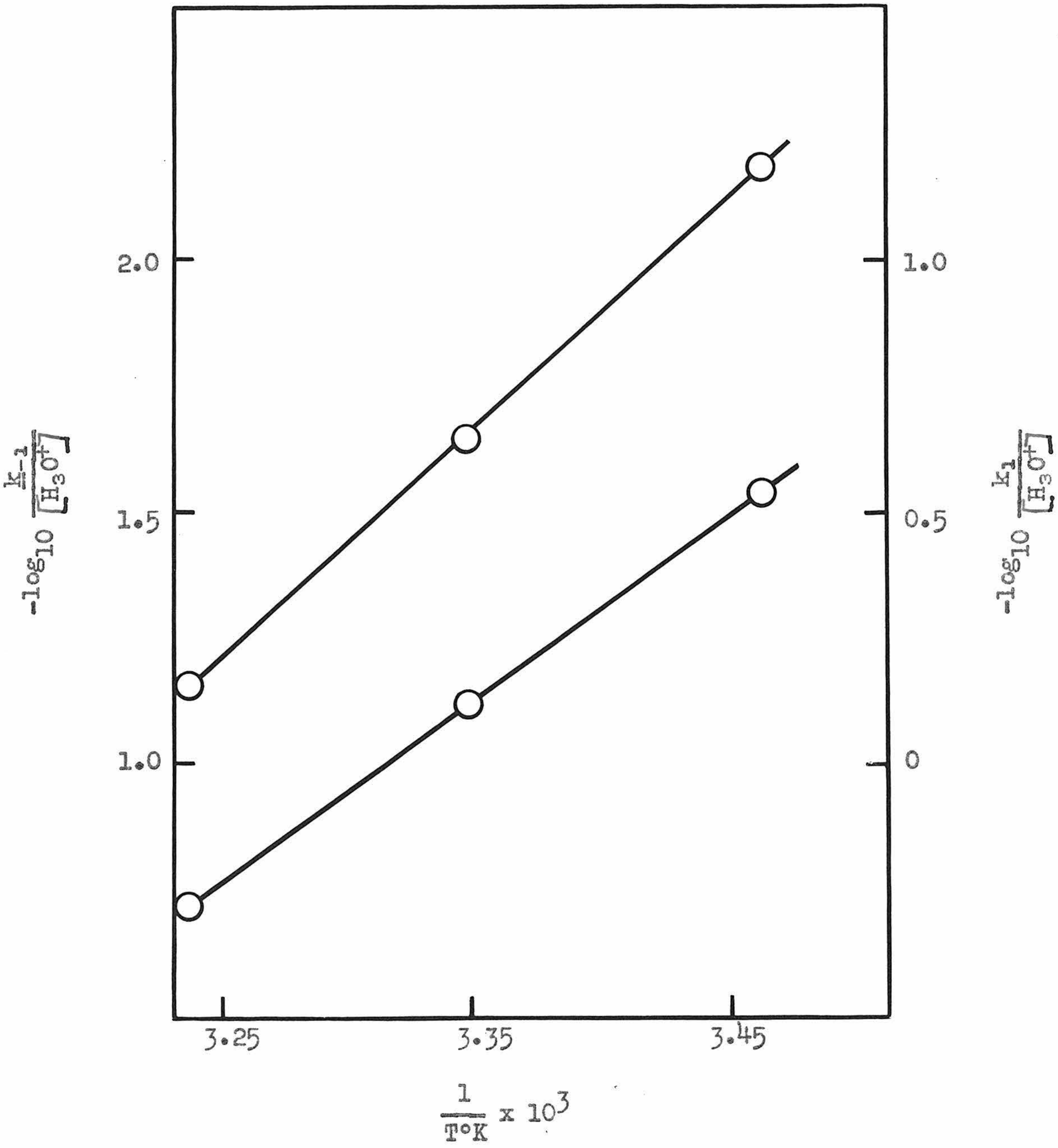


Figure V

Plot of $-\log_{10}$ $\underline{k}_1$ (lower curve) and $-\log_{10}$ $\underline{k}_{-1}$ (upper curve) against $\frac{1}{T°K}$

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this is again an analogy upon which it would be dangerous to rely very heavily.

Hammett made no reference to the results of Hermans[3], who found that cyclic 1,2 glycols formed acetals which, upon hydrolysis, yielded principally the cis or trans form identical with the original starting material. Hermans considered his work to prove conclusively that the alkyl oxygen bond was not broken in acetal hydrolysis, but the cyclic compounds have certain restraints against inversion that might be partly responsible for his results even if the mechanism were of the type he considered disproven.

Several experimental approaches to the problem of testing Hammett's mechanism are possible. If the hydrolysis were carried out in water enriched in the oxygen isotope of atomic weight eighteen, and the alcohol product pyrolyzed to give water, the water thus obtained could be analyzed by the mass spectrometer, or by py~~n~~cnometry or the falling drop method of determining density, to ascertain whether the oxygen of the alcohol had originated in the acetal or the water.

On the assumption that the hydrolysis is merely a specific example of a general solvolysis reaction, methanolysis could be carried out and the products analyzed by fractionation for the presence of methyl ethers.

A third method, which is the one adopted in this investigation, consists of hydrolyzing the optically active acetal of some alcohol whose asymmetric center is the carbinol carbon atom. If the mechanism proposed by Hammett were the correct one, considerable racemization might be expected to take place in the process of forming and hydrolyzing the acetal. If no racemization takes place, either the alkyl oxygen bond is unaffected, or the asymmetric center is completely inverted at the time of forming and again at the time of hydrolyzing the acetal.

Experimental

d- and l- 2-octanol. Eastman White Label 2-octanol, which is a racemic mixture, was resolved by the method of Kenyon[4]. The alcohol was converted to the acid phthalate by reaction with an equimolar amount of phthalic anhydride. The half-ester was then converted to its brucine salt and this was crystallized from acetone, giving about a 90% resolution. The crystals and the mother liquor were separately freed from brucine by treatment with aqueous hydrochloric acid, and the half-esters thus recovered were separately crystallized twice from glacial acetic acid, yielding the two enantiamorphs in optically pure form. The hydrogen phthalates were then hydrolyzed by aqueous sodium hydroxide and the alcohols were steam distilled, separated from water, and redistilled under vacuum (bp. 73° C.$_{10 \text{ mm.}}$).

d- and l- 2-butanol. Attempts to resolve this substance by the method given above were unsuccessful. When the partially resolved acid phthalates were crystallized, mixed crystals were obtained. The solubility of the racemic crystal is less than that of the pure enantiamorphs.

Acetaldehyde. This was freshly prepared when needed by the acid catalyzed depolymerization of Merck C. P. paraldehyde. It was fractionated through a forty centimeter column packed with glass helices and used immediately.

Preparation of acetal. To forty grams of (+)octanol-2 (α_D^{24} = +7.93° (1 dcm.)) was added six grams of anhydrous calcium chloride, one drop of concentrated aqueous hydrochloric acid, and twelve milliliters of freshly distilled acetaldehyde. This mixture was allowed to stand for two days, during which time the calcium chloride gradually assumed a mushy consistency. The mixture was filtered and drierite was added to the filtrate, causing a considerable evolution of heat. After filtration, the liquid was distilled, yielding sixteen grams of 2-octanol acetal (bp. 115° C.$_{1.5\ \mathrm{mm.}}$ $\alpha_{23°\ \mathrm{C.}}$ = 18.5).

Hydrolysis of acetal. To twenty grams of a five percent solution of phosphoric acid, eight grams of 2-octanol acetal were added and the mixture refluxed for one hour. The organic phase was separated and, after drying with magnesium sulfate, was distilled. The entire product distilled in the range 72 - 73° C.$_{10\ \mathrm{mm.}}$ and had an observed rotation in a one decimeter tube of +7.91° at 24.5° C. Within the limit of accuracy of the instrument, this shows complete retention of configuration.

Summary

Pure optically active 2-octanol acetal has been prepared and hydrolyzed. The alcohol retains its optical activity completely in the process. This is evidence that the alkyl oxygen bond is not broken, contrary to the supposition of Hammett.

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ELECTRON DIFFRACTION INVESTIGATIONS OF THE STRUCTURES OF CERTAIN ORGANIC COMPOUNDS

The apparatus used in this investigation has been described by Brockway[1]. The wave length of the electrons was determined for each investigation by calibration with zinc oxide smoke[2].

Both the radial distribution and the correlation methods were used in interpreting the photographs. The radial distribution was calculated with the equation

$$rD(r) = \sum_{q=1}^{q=100} I(q)\, e^{-aq^2} \sin\left(\frac{\pi}{10} rq\right)$$

where a is selected to give e^{-aq^2} the value 0.1 at q=100. The values of I(q) were taken from the visual curves, labelled V in all drawings. The dotted portion of the visual curves in the central region where observation is unreliable were obtained by calculation of a reasonable model.

The theoretical intensity curves used in the correlation treatment were calculated from the equation

$$I(q) = \sum_{ij} (Z_i \quad F_i)(Z_j \quad F_j)\, e^{-b_{ij}q^2} \sin\left(\frac{\pi}{10} r_{ij}q\right)$$

where Z is the atomic number of atom i, F_i the atomic scattering function of the same atom[3], and r_{ij} is the distance between atoms i and j. The temperature factor b is given the value 0.00016 for bonded C—H terms and zero for all others unless particularly noted.

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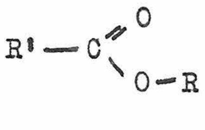
AN ELECTRON DIFFRACTION INVESTIGATION OF THE STRUCTURES OF METHYL FORMATE, METHYL ACETATE, AND METHYL CHLOROFORMATE

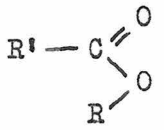
Introduction

The structure of simple carboxylic esters has received considerable elucidation from studies of dipole moments[1,2,3]. This work is summarized and discussed in the fifth chapter of Wheland's book, The Theory of Resonance.[4] These studies lead to the general conclusion that all simple aliphatic esters are planar, with no free rotation about the single bond between the carbonyl carbon and the ether link oxygen. This planarity is presumably due to resonance between the single and double carbon oxygen bonds. Combustion studies show a resonance energy for simple esters of approximately 20 kcal per mole.

There are two possible planar configurations, I and II:



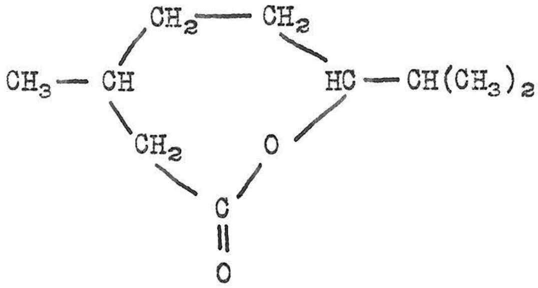
(I)



(II)

From simple arguments based on the dipole moments of acetone and ether, the predicted moment of configuration I, which we shall call cis, is 1.53 Debye. That of form II is 3.53 D. The dipole moments of all simple saturated aliphatic esters are experimentally found to lie in the range 1.7 - 1.9 D. This is strong evidence that configuration I is dominant, and the fact that the experimental values are constant over a temperature range of several hundred degrees indicates that essentially no rotation at all occurs. The predicted dipole moments receive support from the data for γ-butyrolactone which is constrained in the configuration II by the five membered ring and has for its measured moment 4.12 D, in fair agreement with prediction.

That this planarity is due to resonance, and not to some strong attraction for the alkyl radical by the carbonyl oxygen is shown by the dipole moment of an ε-lactone, III.



(III)

This seven membered ring is large enough so that although it will not allow configuration I, it does not necessarily hold the molecule in configuration II or even very close to it. If a powerful attraction existed between carbonyl oxygen and the alkyl group, calculation shows that this molecule might be expected to have a dipole moment of 2.7 D or less. Since the observed moment is 4.33 D, practically the same as γ-butyrolactone, it seems certain that the ester linkages are all planar, and that resonance can be the only explanation.

It was to check these conclusions from an entirely different point of view that the present study was undertaken. The electron diffraction investigation lead to the same results, except that instead of absolute planarity in configuration I, all three esters gave indication of a twist of the methyl oxygen bond out of the plane by about 20 or 30°.

Methyl formate has six shape parameters, and methyl acetate and chloroformate have seven each. No molecules of such complexity have previously been investigated by electron diffraction, presumably because a truly exhaustive investigation of all parameters would involve the calculation of the theoretical scattering curves for many hundreds of possible models. *A priori*, it seemed likely that, at least for some parameters, a considerable range of possible values would be found which could not be definitely excluded by the data and that the precision of the determination would necessarily be less than had been achieved in the case of simpler molecules. Early in this work it became apparent that, on the contrary, the theoretical scattering curves were unusually sensitive to slight changes in any of the principal parameters. This may be due to the fact that any such change affects several of the distances in the molecule and hence the corresponding scattering terms.

Interpretation

In calculating the theoretical curves, the atomic numbers were used for coefficients except that hydrogens were given the weight 1.25. A C—H bond distance of 1.09 Å was assumed, and unbonded C...H and O...H terms were given a temperature factor of 0.0004. The C—H bonds were assumed to be tetrahedral.

To study the effects of parameter changes without actually calculating the models in each case, as well as to predict the parameter changes necessary to improve the fit of certain features of the visual and theoretical curves, use was made of a simple graph of a type not previously mentioned in the literature. When q is plotted aginst r_{ij} on log log paper, the loci of maxima and minima of the scattering function used in this work are straight lines. Using this graph, it is easy to see which changes in interatomic distances would bring about a desired change in the amplitude of the scattering function at any given point, and furthermore to select among these possibilities the changes least likely to disturb the pattern at other structure-sensitive regions of the curve.

Before this method of approaching a satisfactory model can be applied, it is necessary to be very close to the correct parameter region, because of the great sensitivity of the theoretical curves which has been mentioned. Hit and miss models, based on reasonable conjectures, failed completely even to approach the desired scattering pattern. In order to obtain a model even roughly satisfactory, it was necessary to refine the interpretation of the complex peaks in the radial distribution functions to an extent which would not heretofore have been considered justifiable.

For each distance in the molecule, a peak was plotted with its width at half height equal to 0.14 Å in agreement with theory and its height proportional to its coefficient in the scattering equation. From these individual peaks the complex features in the radial distribution function were synthesized, taking care that the models should be geometrically possible. In some cases this synthesis was exact, but in others, particularly for the features representing the unbonded distances, the area under the radial distribution feature was not the same as the combined areas of the peaks going to make it up. In such cases the best results were obtained by synthesizing a feature with the same width and shape, making any necessary compromises in height alone.

Methyl Acetate

This is the first of the three molecules for which a satisfactory structure was found. The radial distribution function RD (Figure I) shows two complicated peaks, the first representing the bonded distances in the molecule, of which there are five, and the second representing distances

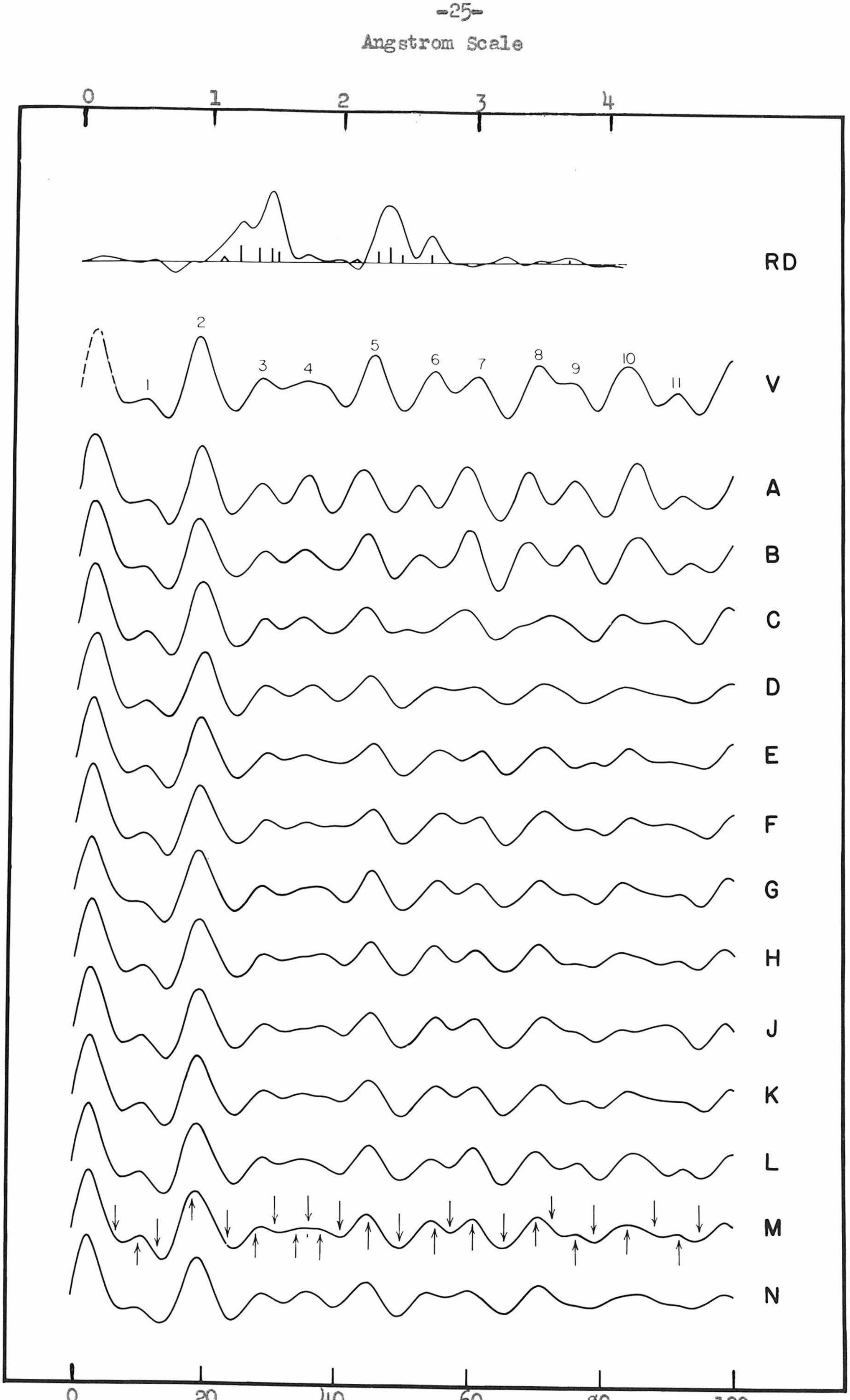
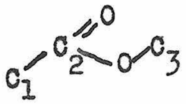


Figure I

Theoretical Curves for Methyl Acetate

Table 1

Methyl Acetate Parameter Chart



$\angle\alpha$ is the angle between the C—O—C plane and the O=C—O plane

Model	C=O	C—C	C_2—O	C_3—O	$\angle$C—C—O	$\angle$O=C—O	$\angle$C—O—C	$\angle\alpha$
A	1.24 Å	1.54 Å	1.43 Å	1.43 Å	110°	130°	111°	180°
B	1.24	1.54	1.43	1.43	115	120	111	0
C	1.23	1.51	1.38	1.46	113	120	110	0
D	1.23	1.52	1.37	1.46	116	123	110	free
E	1.23	1.52	1.37	1.46	116	123	110	33
F	1.21	1.52	1.37	1.46	116	123	110	33
G	1.23	1.52	1.37	1.46		to fit RD		
H	1.22	1.52	1.35	1.46	117	124	113	20
J	1.21	1.52	1.37	1.45	117	124	113	23
K	1.21	1.52	1.37	1.45	117	124	113	29
L	1.23	1.50	1.37	1.45	116	122	115	23
M	1.22	1.51	1.36	1.46	117	124	114	20
N	1.22	1.51	1.36	1.46	117	124	114	free

between atoms bonded to a common atom, of which there are three if we ignore hydrogen terms. In addition there are single peaks at 2.68, 3.26, and 3.73 Å. The well defined nature of the first of these is a strong argument against free rotation, because it represents one of the distances to which free rotation would give a rather wide range of values. For the peak at 3.26 Å, no corresponding distance could be found in any reasonable model, hence it must be regarded as a chance fluctuation. The peak at 3.73 Å is rather important in confirming the configuration finally selected.

In applying the correlation treatment, models were first calculated, using reasonable assumptions based on the structure of acetic acid monomer as determined by Karle and Brockway.[5] Model A is the trans form and Model B the cis form based on these assumptions. Their defects are obvious. Ten more models were calculated using variations intended to cover all reasonable possibilities based on chemical intuition rather than a rigorous interpretation of the radial distribution function. None of these were at all satisfactory. Model C will serve as an example. It scarcely resembles the visual curve at all, and yet it can be seen (Table I) that its parameters differ from those of the final model (model M) only by amounts often considered as within reasonable limits of error for electron diffraction investigations. This emphasizes the extreme parameter sensitivity of the theoretical curves for this molecule.

Model E was selected with a more careful interpretation of the radial distribution function. The improvement in the region of the third and fourth rings as well as the sixth and seventh rings is immediately obvious. Model D was the same as model E except that the long terms which are important in deciding whether the molecule is planar or not have been omitted as a crude approximation of free rotation. The importance of these long terms is illustrated by the great difference between models D and E. Model F differs from model D by 0.02 Å in one parameter only. This has resulted in a change in the nature of the fifth minimum and a noticeable lowering of the seventh maximum.

Since greater attention to the radial distribution function had resulted in such a great improvement, model G was calculated on the basis of rigidly adhering to the distances obtained by analysing the complex parts of the radial distribution in the manner that has been described, even though the model is geometrically impossible. It will be seen that this model is practically an exact fit, which confirms the accuracy of the analysis, leaving the fact that the model is not geometrically possible to be explained on the basis of imperfections in drawing the visual curve.

Model H is a geometrically possible configuration adhering as closely as possible to the distances of model G. It is satisfactory except for the virtual disappearance of the ninth maximum and the weakness of the tenth. By the use of the chart of loci of maxima and minima corresponding to given interatomic distances, models J, K, L, and M were calculated in an attempt to improve the fit or to maintain it while varying parameters. Model J fits well until the region beyond q = 80; model L was planned to fit exactly in the region of the last four peaks, but is seen to disagree seriously at the sixth and seventh. Between models K and M there is little to choose; the range of possible values must certainly include both of them. Model N is a recalculation of model M, assuming free rotation.

Besides the calculation of these models, much time and thought was put into studying the changes that would be brought about by changing any one of the parameters, or any two of them simultaneously in order to seek possibilities for structures giving essentially the desired pattern but having

Table II

Methyl Acetate

max	min	q_{obs}	q_M	q_M/q_{obs}
1		6.90	8.0	(1.160)
	1	10.36	10.5	(1.014)
2		13.31	14.0	(1.052)
	2	18.44	18.9	(1.025)
3		23.86	24.3	1.018
	3	28.06	28.8	1.026
4		30.92	31.6	1.022
	4	34.18		
4a		35.98		
	4a	37.77		
5		40.71	41.1	1.010
	5	45.15	44.8	0.992
6		49.61	49.9	1.006
	6	55.18	54.5	0.998
7		57.30	57.5	1.003
	7	60.84	60.8	0.999
8		65.53	54.2	.995
	8	70.30	70.4	1.001
9		72.79	74.2	1.019
	9	76.26	76.0	0.997
10		79.08	79.3	1.003
	10	84.10	84.3	1.002
11		88.18	90.0	1.021
	11	91.89	91.7	0.998
12		95.07	95.4	1.003
	12	99.98	98.9	0.988

Average (19 measurements) 1.005

Average deviation 0.008

different parameters. This search was unsuccessful.

A quantitative comparison of observed and calculated maxima and minima for model M is shown in Table II.

It is not easy to set limits of error in a study of this kind, but the considerations which have been discussed lead to the following parameters: C—H = 1.09 Å (assumed), C=O = 1.22 ± 0.03 Å, C—C = 1.51 ± 0.03 Å, C—O (carboxyl) = 1.36 ± 0.04 Å, C—O (methoxyl) = 1.46 ± 0.04 Å, ∠C—C—O = 116 ± 3°, ∠C—O—C = 113 ± 3°, ∠O=C—O = 124 ± 4°, and for the angle of the C—O—C plane with the plane of the carboxyl group 25 ± 8° out of the cis planar configuration.

Methyl Formate

The radial distribution function, RD in Figure II, shows a complicated feature representing the four bonded distances in the molecule, an unresolved peak at 2.28 Å which represents the unbonded O ···· O and C ···· C distances, and a single peak at 2.68 Å which is the long C ···· O distance and shows that the molecule is planar and largely if not entirely in the cis configuration.

In applying the correlation procedure, models were first calculated based on the parameters taken from the structure of formic acid monomer as determined by Karle and Brockway.[5] Models A and B are the cis and trans forms respectively, and they both differ very seriously from the visual curve. Model C has the same distances as A and B, but the methoxyl bond is twisted 30° out of the planar cis configuration. This causes a remarkable improvement. Except for the nature of the fourth peak and the bad quantitative fit in the region around q = 50, it is an acceptable model. It differs from the model finally chosen in a somewhat smaller O—C—O angle

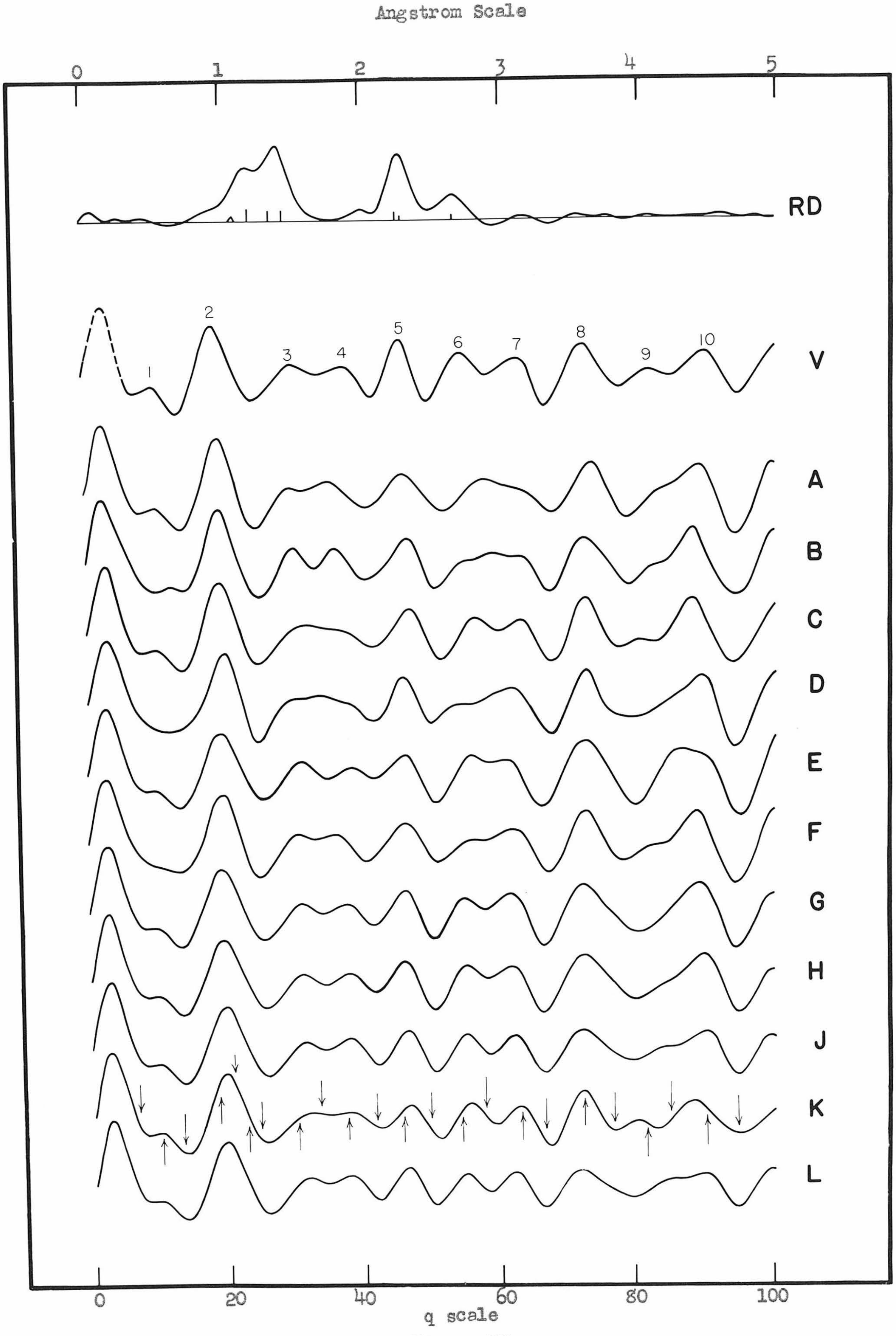
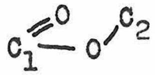


Figure II

Theoretical Curves for Methyl Formate

Table III

Methyl Formate Parameter Chart

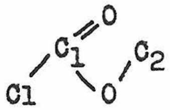


$\angle\alpha$ is the angle between the C—O—C plane and the O=C—O plane

Model	C=O	C_1—O	C_2—O	$\angle$O=C—O	$\angle$C—O—C	$\angle\alpha$
A	1.24 Å	1.42 Å	1.42 Å	117°	111°	0°
B	1.24	1.42	1.42	117	111	180
C	1.24	1.42	1.42	117	111	30
D	1.24	1.42	1.42	117	111	106
E	1.21	1.42	1.45	117	111	51
F	1.24	1.42	1.42	117	111	free
G	1.21	1.39	1.45	122	110	37
H	1.20	1.38	1.46	123	111	36
J	1.21	1.36	1.46	124	112	32
K	1.21	1.36	1.46	124	112	0
L	1.22	1.36	1.46	124	114	20

Table IV

Methyl Chloroformate Parameter Chart



$\angle\alpha$ is the angle of the C—O—C plane with the O=C—O plane

Model	C=O	C_1—O	C_2—O	Cl—C	$\angle$Cl—C—O	$\angle$O=C—O	$\angle$C—O—C	$\angle\alpha$
A	1.18Å	1.40Å	1.40Å	1.73Å	112°	122°	110°	0°
B	1.18	1.40	1.40	1.73	112	122	110	180
C	1.18	1.40	1.40	1.73	112	122	110	free
D	1.21	1.35	1.46	1.74	113	125	112	23
E	1.18	1.35	1.46	1.72	112	126	111	20
F	1.18	1.35	1.46	1.74	112	126	111	free

Table V

Methyl Formate

min	max	q_{obs}	q_J	Q_j/Q_{obs}
1		6.83	8.3	(1.215)
	1	10.05	9.9	0.985
2		13.35	13.6	1.019
	2	18.63	18.6	0.998
2a		20.87	20.9	1.001
	2a	22.66		
3		24.56		
	3	30.11	31.0	1.029
4		33.52	34.1	1.017
	4	37.48	37.7	1.006
5		41.56	41.9	1.008
	5	45.56	46.0	1.010
6		49.78	50.4	1.012
	6	54.38	54.8	1.008
7		57.86	58.2	1.006
	7	63.00	61.9	0.983
8		66.62	66.4	.997
	8	72.25	71.6	.991
9		76.58	79.0	1.032
	9	81.38	83.0	1.020
10		84.98	85.4	1.005
	10	90.24	89.5	0.992
11		94.70	89.9	(.850)

Average (19 measurements) 1.009

Average deviation 0.011

and in making both C—O bonds identical at the average of the values finally determined. Models D and E are included as examples of hit and miss trials in the region of the values finally determined, and their rejection is easily justified. Model F is a free rotation model based on Karle and Brockway's distances. Besides quantitative disagreements, the nature of the sixth and seventh rings is completely inacceptable. Models G, H, J, and K are examples of models chosen after application of the strict interpretation of the radial distribution function, followed by variations as indicated by the chart of maxima and minima for given interatomic distances. In Model G, the seventh maximum is too high, and the ninth maximum has disappeared. Models H, J, and K are all acceptable and although the measurement arrows have been drawn on model K, there is little to choose between the three. Model L was calculated to correspond closely with the structure finally selected for methyl acetate. It is acceptable, and lies within the limits of the determination, although perhaps not quite as good a fit as models J or K.

A quantitative comparison of maxima and minima for model J is given in Table V.

The results of this determination may be summarized as follows: C—H = 1.09 Å (assumed), C=O = 1.21 ± 0.03 Å, C—O (carboxyl) = 1.36 ± 0.04 Å, C—O (methoxyl) 1.46 ± 0.04 Å, $\angle$O=C—O = 124 ± 4°, $\angle$C—O—C = 112 ± 3°, and for the angle of the C—O—C plane with the plane of the carboxyl group, 30 ± 10° out of the cis planar configuration.

Methyl Chloroformate

The radial distribution function in Figure III shows a complicated first feature representing the bonds between carbon and hydrogen or oxygen,

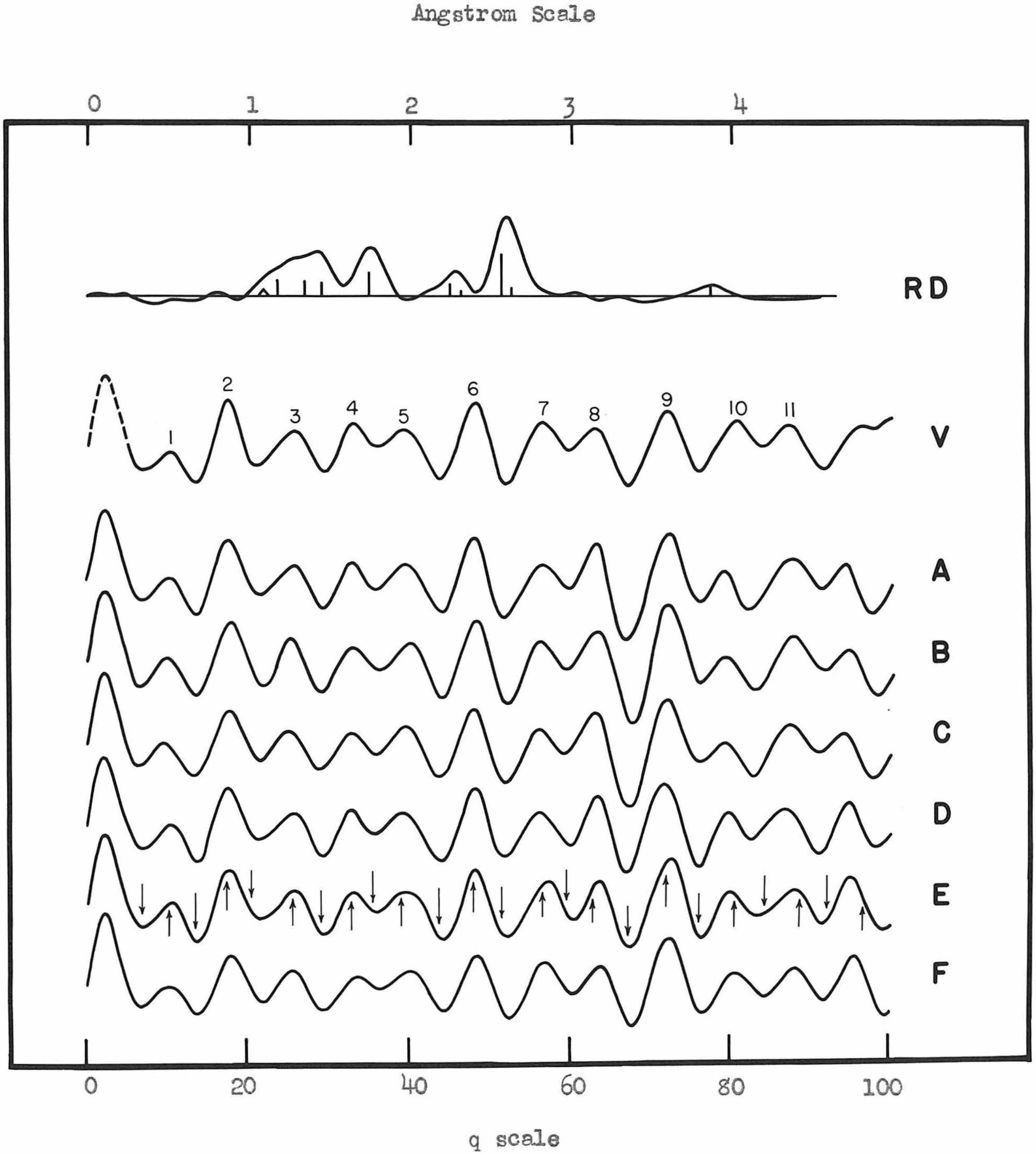


Figure III

Theoretical Curves for Methyl Chloroformate a single well resolved peak at 1.74 Å representing the C—Cl bond, a peak at 2.28 Å which contains the O ···· O and C ···· C distances, a very prominent peak at 2.59 Å representing the Cl ···· O and C ···· O distances, and a small peak at 3.87 Å which represents the distance between the chlorine and the methyl carbon. The radial distribution method thus leads again to an essentially planar model in the cis configuration.

In applying the correlation method, models A, B, and C were calculated from a loose interpretation of the radial distribution function to represent cis, trans, and free rotation models respectively. They are not at all satisfactory. Model D was calculated on the basis of a rigid analysis of the radial distribution function. Except that the eighth maximum is too strong, it is quite satisfactory. This flaw is corrected in model E by shortening the C═O bond, a change indicated by the type of analysis previously discussed in this series of compounds. Model F is a free rotation version of model E, from which it differs only very slightly. This is because the chlorine distances dominate the pattern for this molecule, and only the longest and least heavily weighted of these varies with free rotation. The argument against free rotation for this molecule, then, depends on the presence of the small peak in the radial distribution function at 3.87 Å, as predicted for the cis configuration. Parameters not involving the chlorine atom are not determined for this molecule with the same precision that was possible in the case of methyl formate and acetate.

A quantitative comparison of measured maxima and minima with those calculated for model E is to be found in Table VI.

The final results of this determination may be summarized as follows: C—H=1.09 (assumed), C═O = 1.19 ± 0.03 Å, C—O (carboxyl) = 1.35 ± 0.04 Å,

Table VI

Methyl Chloroformate

min	max	q_{obs}	Q_E	Q_E/Q_{obs}
1		6.80	7.0	(1.029)
	1	10.16	10.4	(1.024)
2		13.42	13.6	1.013
	2	17.27	17.4	1.007
3		20.35	21.7	1.066
	3	25.49	25.8	1.012
4		29.02	29.6	1.020
	4	32.77	32.9	1.004
5		35.35	35.8	1.013
	5	38.84	39.5	1.017
6		43.53	44.3	1.018
	6	47.78	48.0	1.005
7		51.37	52.1	1.014
	7	56.28	57.0	1.013
8		59.29	60.1	1.014
	8	62.53	63.2	1.011
9		66.87	67.2	1.005
	9	71.80	72.2	1.006
10		75.79	76.2	1.005
	10	80.24	79.8	0.995
11		83.93	83.3	.992
	11	88.41	88.0	.995
12		91.85	91.2	.993
	12	96.34	94.7	.983

Average (22 measurements) 1.009

Average deviation 0.009

C — O (methoxyl) = 1.46 ± 0.04 Å, C — Cl = 1.74 ± 0.02 Å, ∠O ═ C — O = 126 ± 4°, ∠C — O — C = 111 ± 4°, ∠Cl— C—O = 112 ± 2°, angle of the C—O — C plane with the plane of the carboxyl group = 20 ± 10°.

Discussion of Results

The configuration assigned to simple esters from studies of dipole moments has been confirmed by electron diffraction for the case of methyl acetate, methyl formate, and methyl chloroformate. The bulk of the evidence that these molecules are almost planar, with the methyl group cis with respect to the carbonyl carbon comes from the radial distribution treatment of the data, although the correlation method confirms it, especially in the case of the first two compounds studied. For methyl chloroformate the correlation method cannot be said to have offered any evidence against free rotation. There seems little doubt that resonance is the explanation of this almost planar structure. The determination does not show any noticeable lengthening of the C ═ O bond, but a considerable shortening of the carboxyl C — O bond, and, perhaps somewhat surprisingly, a corresponding lengthening of the methoxyl C — O bond are necessary to get theoretical curves which fit the data. In the case of methyl chloroformate, both the C ═ O and C — Cl bond seem shorter than the commonly accepted values, although these do lie within the limits of error.

The cis configuration involves the approach of the methyl carbon to a distance of about 2.65 Å from the carbonyl oxygen. This is so close that it suggests, that steric effects may be responsible for the 20-30° angle of the C — O — C plane out of the plane of the carboxyl group which seemed called for by the radial distribution treatment of all three molecules.

Since in the case of methyl formate the molecule could be completely planar in the trans position, the greater stability of the cis configuration probably involves some attraction of a hydrogen bond type in addition to resonance.

It must be mentioned that the fact that it was possible to get almost perfect fits which were disturbed by any considerable shift in any parameter does not have as great a significance in the case of a seven parameter problem as it would in a simpler molecule. With seven parameters to vary, it would probably have been possible to get quite as satisfactory an agreement with a visual curve with considerable inaccuracies in the drawing. In a problem as complicated as this, it is very important to get the visual curve right the first time, since it is less likely that failure to get agreement will lead to reexamination of the photographs than in a simpler case. This investigation indicates that by refinements of method it may be possible to investigate the structures of more complicated molecules than were formerly considered suitable for investigation by electron diffraction.

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FORMIC ACID MONOMER

Introduction

In the course of the investigation of the structure of some simple esters, it was found in the case of methyl formate that no satisfactory theoretical intensity curves could be obtained without deviating considerably in the formate radical from the structure assigned to formic acid monomer by Karle and Brockway.[1] It seemed unlikely that replacement of a proton by a methyl group would lead to any considerable change in the structure of the formate group. In the case of the ester the investigation of possible models could not be exhaustive, due to the large number of parameters, and the possibility existed that some overlooked model might have given a satisfactory theoretical intensity curve. These two considerations made it seem worthwhile to reinvestigate the structure of formic acid monomer.

Experimental

At temperatures where its vapor pressure is suitable for use in the usual electron diffraction apparatus, formic acid is largely in the form of dimer. In order to obtain a vapor which was essentially pure monomer, it was decided to heat the liquid sample outside the apparatus to about 50° C., to give the proper pressure (ca. 300 mm. Hg) and then to admit the vapor into the camera through a stopcock and a special nozzle separately heated to approximately 250° C.

The nozzle (Fig. 1) was made of 7-mm. pyrex tubing, and was packed with 1/16" nichrome helices for a distance of 70 mm. from the capillary end. The packing was held in place by a wad of nichrome wire. The point

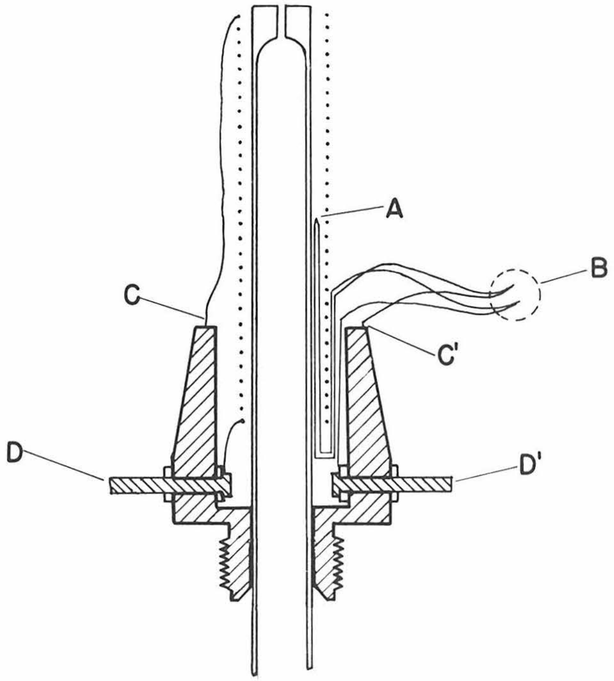

Figure I

A	Thermocouple
B	Thermocouple "cold junction" where the thermocouple elements are joined to copper wires
C,C'	Grounded connections
D,D'	Insulated lead-ins. Electrical and thermal insulation is provided by a layer of asbestos cord wound between the thermocouple and the heating coil, and by another layer enclosing the entire nozzle.

of entrance of the glass tubing was sealed with a rubber gasket held in place by a compression nut. "Creeping" of the glass nozzle up into the camera had to be prevented by a metal band, clamped around the glass tubing and bearing against the compression nut. The cold junction, where the thermocouple elements were joined to copper wires, was allowed to stand freely in the evacuated camera chamber at a distance of about 10 cm. from the nozzle and was presumed to be at room temperature. The uncertainty of the exact cold junction temperature was unimportant, since it was only necessary to know the nozzle temperature within 5 or 10 degrees.

The formic acid used was obtained by crystallizing the 98-100% product of the Eastman Kodak Company. The acid was converted to a crystalline slush by chilling, and the crystals were dried by centrifuging. This operation was carried out in a cold room maintained at 6° C. By repeating the process, a product was obtained which melted very sharply at 8.4° C.

Extrapolation of the data of Coolidge[2] indicated that a vapor temperature of about 200° C. would give an equilibrium concentration of 95% monomer, even at atmospheric pressure. This suggested a nozzle temperature in this neighborhood. In order to determine the conditions actually needed for the study of the monomer, pictures were taken with nozzle temperatures of approximately 50°, 125°, 175°, 200°, and 250° C. The pictures at 50° were characteristic of the dimer,[1] having inner features very different from those made at higher temperatures. At 125° C. the pictures were already chiefly characteristic of the monomer, but many features were indistinct due to interference of the dimer pattern. The pictures taken at 175°, 200°, and 250° showed the monomer pattern and were essentially indistinguishable from each other. All the pictures used in the final structure determination were taken with a nozzle temperature of 240°-250° and a sample temperature of 45°-50°.

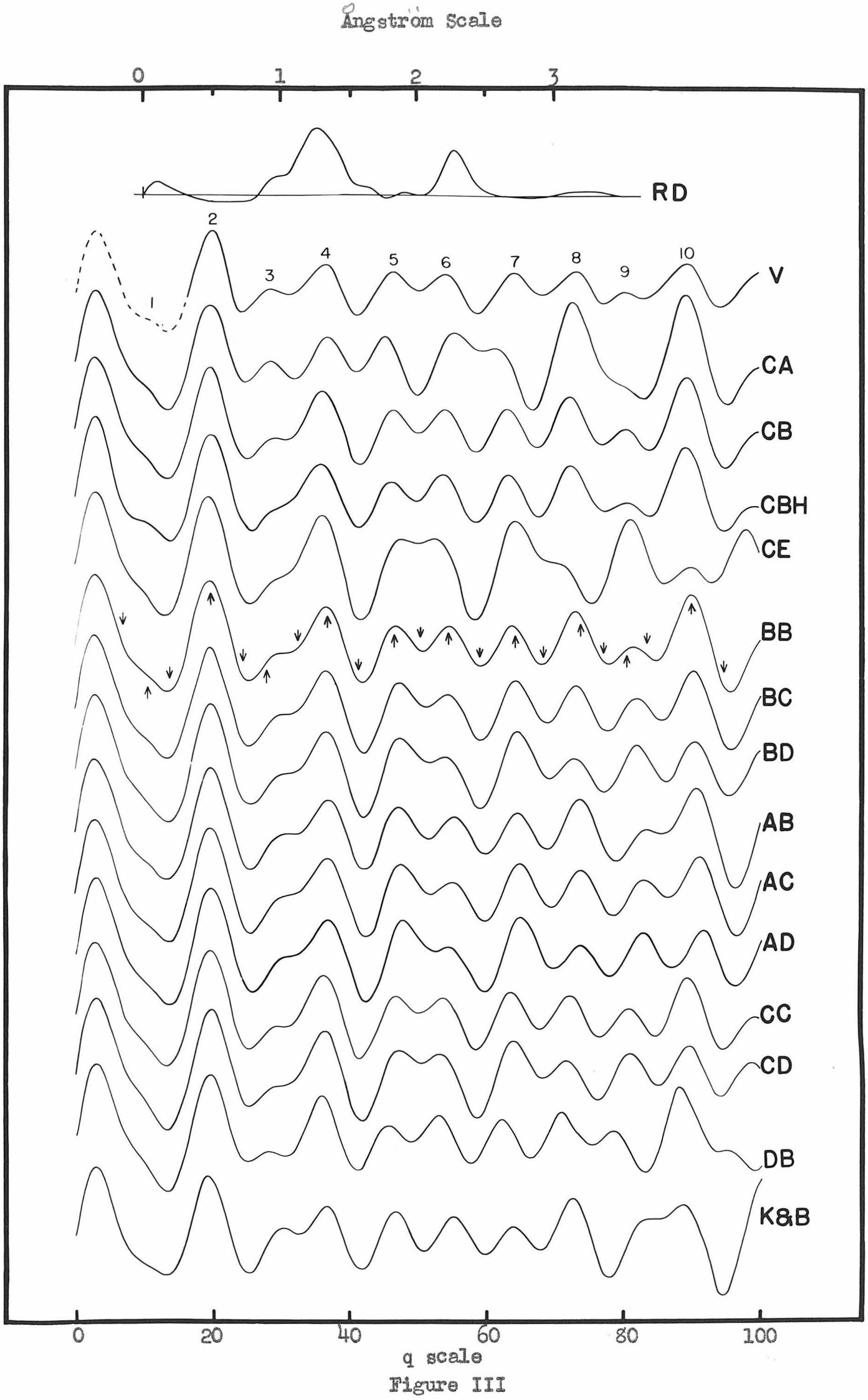

Figure III

Theoretical Curves for Formic Acid Monomer

The investigation was carried out in the apparatus described by Brockway.[3] The photographs were taken at a camera distance of 10.84 cm. with electrons of wavelength 0.0609 Å. (corrected for film expansion), as determined by standardization against zinc oxide.[4]

The appearance of the pictures, which show features out to about $q = 100$, is represented by curve V in Figure III. It will be noticed that four more rings were measured than were reported by Karle and Brockway.[1]

The radial distribution function, RD in Figure III, shows main peaks at 1.27 Å. and 2.27 Å., in agreement with that of Karle and Brockway.[1] The second peak represents the unbonded O...O distance, and the first peak is an unresolved representation of the singly and doubly bonded carbon-oxygen distances with a shoulder on the left representing the C—H and O—H distances. If allowance be made for this shoulder and for the unequal weights ($\frac{1}{r_1}$ and $\frac{1}{r_2}$) of the two carbon-oxygen distances, an average carbon-oxygen distance of 1.29 Å., corresponding to an O=C—O bond angle of 123°, is indicated.

Theoretical intensity curves were drawn for eighteen models, keeping the average of the two carbon-oxygen constants at 1.29 Å., as well as for the preferred model of Karle and Brockway[1] (C—O = 1.42 Å., C=O = 1.24 Å., ∠O—C=O = 117°). The longer carbon-oxygen distance was varied from 1.33 Å. to 1.41 Å. and the shorter from 1.17 Å. to 1.25 Å. The angle O=C—O was varied from 121° to 129°. Figure II is a plot of the ratio C—O/C=O against the O=C—O angle. For all curves the assumed C—H (1.09 Å.) and O—H (0.97 Å.) terms were multiplied by a temperature factor, $\exp(-0.00015\ q^2)$. The long unbonded hydrogen distances were ignored, except in the case of curve CBH, where they have been added to curve CB without a temperature factor. This gives an indication of their maximum possible effect, and it will be seen that this is quite small.

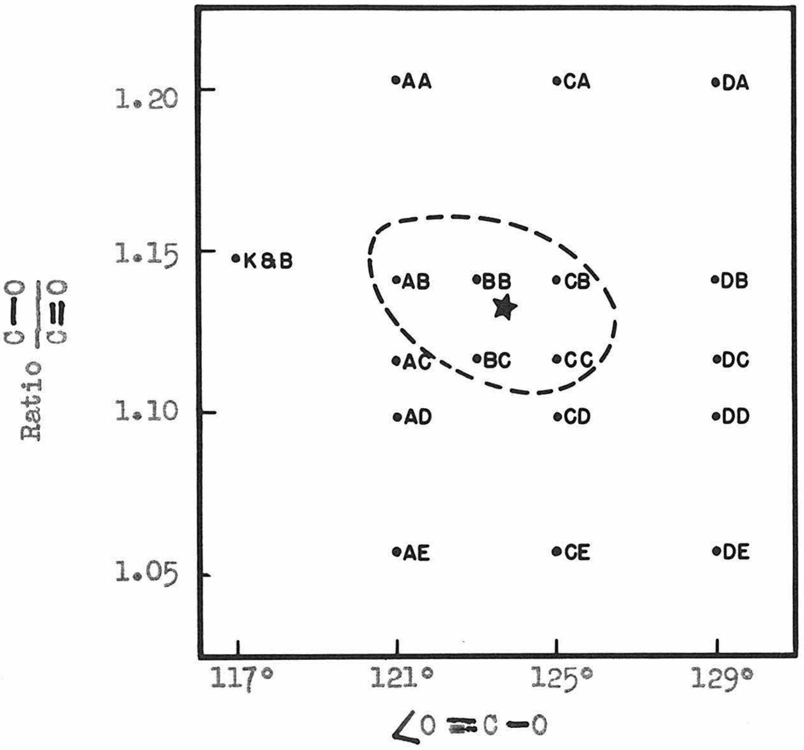

Figure II

Parameter Plot for Formic Acid Monomer

The star represents the most satisfactory model and the dotted line shows the limits of uncertainty.

Discussion

Models having the extreme bond ratios C—O/C=O of 1.063 and 1.205, such as CA and CE, are easily eliminated because of the absence of even rough qualitative agreement. Among the most important features of the photographs may be mentioned the sixth and seventh maxima, which are weaker than the fifth and eighth, and the seventh minimum, which is deeper than the minima on either side of it. Reexamination of the photographs during the course of the investigation showed that the third minimum is deeper and the fourth and eighth maxima are somewhat stronger than shown on curve V, but otherwise confirmed the visual curve as originally drawn.

Curve BB has been selected as the best, although from considerations to be discussed later we feel certain that the ideal model has a slightly larger angle and a slightly lower bond ratio, lying approximately one quarter of the way along a line joining models BB and CC in Figure II. The three models with the bond ratio 1.133 which most closely resemble curve V have been subjected to quantitative comparison in Table I. Although the differences are slight, it will be seen that the average deviation is least for model BB, followed by CB and AB, in that order. This is confirmed by an inspection of the qualitative features. In AB the nature of the ninth ring is incorrect and the fourth maximum is too weak. In model CB the minima on either side of the ninth feature are again in incorrect relationship; the fifth maximum is too weak, and the third minimum not deep enough. This evidence cannot be considered sufficient to eliminate CB and AB from consideration entirely, but rather as setting the limits of the determination. If the angle is increased to 129°, as in model DB, the disagreement becomes so striking as to indicate that the limit of accuracy has been greatly exceeded.

All the models of bond ratio 1.133 suffer from some defects in common. In particular, the eighth and ninth minima are too deep compared to the seventh, and the fifth maximum is not strong enough compared to the sixth, while the eighth is too strong compared to the seventh. It will be seen that by changing to bond ratio 1.115, as in models AC, BC, and CC, these defects are not merely diminished, but in most cases strongly reversed. This indicates that the true bond ratio lies between 1.133 and 1.115, but considerably closer to 1.133. Model AC differs so greatly from V in almost all features that it may be considered as eliminated from consideration. In model BC the fifth and seventh maxima are much too strong compared to the adjacent features. Model CC agrees best of those with bond ratio 1.115, but is considerably inferior to AB, BB, and CB. The third maximum is not deep enough, the seventh maximum too strong, the eighth minimum too deep, and the ninth feature too strong. It may be considered as representing the limit of accuracy, with the ideal model lying closer to BB on a line between them. Model K and B shows extreme disagreement in the region of the ninth and tenth rings; furthermore, the eighth maximum is too strong, the seventh too weak, and the third too strong.

The considerations mentioned above lead to the selection of the following model: $C{-}O = 1.36 \pm 0.02$ Å., $C{=}O = 1.21 \pm 0.02$ Å., $\angle O{=}C{-}O = 123\ 1/2 \pm 3°$. The O...O distance is 2.27 ± 0.02 Å.

Summary

The structure of formic acid monomer has been reinvestigated by electron diffraction, using a new type of heated nozzle to introduce the sample into the camera. The parameter values found are $C{-}O = 1.36 \pm 0.02$ Å., $C{=}O = 1.21 \pm 0.02$ Å., and $\angle O{=}C{-}O = 123\ 1/2 \pm 3°$, in disagreement with the results of Karle and Brockway.[I]

Table I

Comparison of Observed and Calculated Maxima and Minima

			MODEL AB		MODEL BB		MODEL CB	
min	max	q_o	q_c	q_c/q_o	q_c	q_c/q_o	q_c	q_c/q_o
2		14.0	13.4	(0.957)	13.5	(0.964)	13.8	(0.986)
	2	20.0	20.2	1.010	20.1	1.005	20.1	1.005
3		24.6	25.9	(1.053)	25.9	(1.053)	25.9	(1.053)
	3	28.1	30.4	(1.082)	30.2	(1.075)	29.6	(1.053)
4		32.6	31.1	(0.954)	31.2	(0.957)	31.3	(0.960)
	4	36.9	37.0	1.002	36.6	.992	36.3	.984
5		41.4	42.3	1.021	41.9	1.012	41.7	1.007
	5	46.7	47.4	1.015	46.9	1.004	46.8	1.002
6		50.3	52.1	1.035	50.9	1.012	50.3	1.000
	6	54.5	55.5	1.018	54.8	1.006	54.1	0.993
7		59.0	60.0	1.017	59.2	1.003	58.8	.997
	7	64.1	64.7	1.009	63.8	0.995	63.2	.986
8		68.2	69.2	1.015	68.1	.998	67.5	.990
	8	73.6	73.7	1.001	72.9	.991	72.4	.984
9		76.9	79.0	1.027	78.0	1.014	77.1	1.002
	9	80.4	83.2	1.035	81.5	1.014	80.4	1.000
10		83.3	85.7	1.029	84.6	1.015	84.1	1.009
	10	89.8	90.8	1.011	89.9	1.021	89.3	1.014
	Av. of 15			1.018		1.006		0.999
	Av. dev.			0.0101		0.0073		.0077

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AN ELECTRON DIFFRACTION INVESTIGATION OF THE STRUCTURES OF CYCLOPROPYL CHLORIDE, 1,1-DICHLOROCYCLOPROPANE, AND 2,2-DICHLOROPROPANE

Introduction

This investigation was undertaken at the suggestion of Dr. J. D. Roberts, who furnished samples of the cyclic compounds. It was hoped that some correlation might be found between the structure of cyclopropyl chloride and its extreme resistance to solvolysis. The other two compounds were undertaken because of their availability and obvious analogies with each other and with the compound of principal interest.

Electrons of wavelength 0.0609 Å were used and the camera distance from diffracting center to film was 10.91 cm. for all photographs used.

Cyclopropyl Chloride

Good photographs of the diffraction pattern of this substance were readily obtained, using sample temperatures ranging from -30° C. to 0° C. The usual appearance of the photographs is represented by curve V in Figure I. The radial distribution curve RD shows principal peaks at 1.52 Å, 1.76 Å, and 2.83 Å, representing the C—C, C—Cl, and unbonded C...Cl distances respectively. This would indicate that the C—Cl bond is 56-1/2° out of the plane of the cyclopropane ring.

In applying the correlation method, the usual scattering function was multiplied by $\frac{k}{(Z-F)_C\,(Z-F)_{Cl}}$ in order to simplify the calculation of theoretical curves. Where the terms $\frac{(Z-F)_H}{(Z-F)_{Cl}}$ or $\frac{(Z-F)_H}{(Z-F)_C}$ occur as coef-

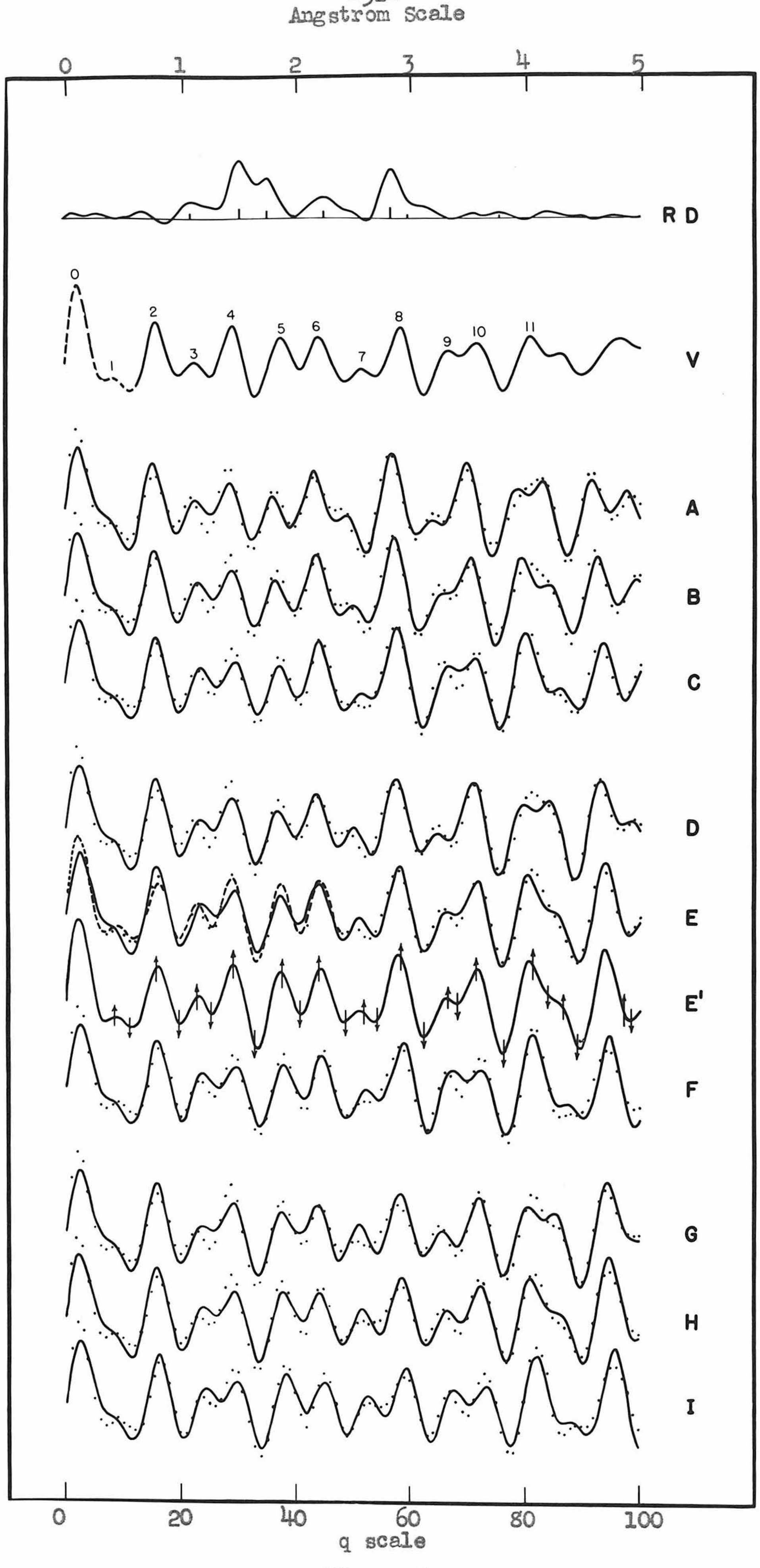

Figure I

Theoretical Curves for Cyclopropyl Chloride

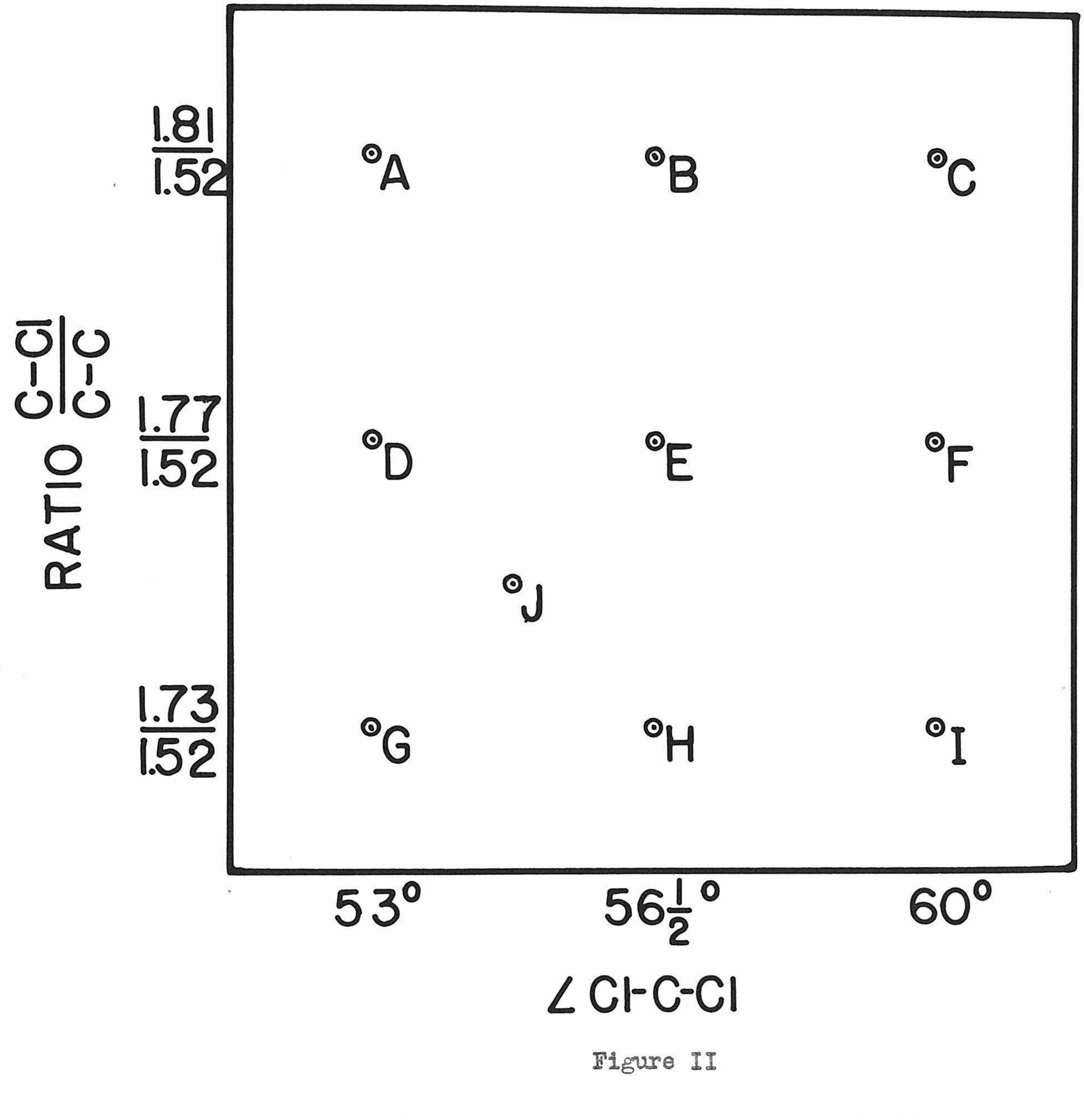

Figure II

Parameter Plot for Cyclopropyl Chloride
and 1,1-dichlorocyclopropane

(Model J was not calculated for cyclopropyl chloride.)

ficients, they were taken as constant at 0.208 and 0.089 respectively. The C—H bond was assumed to be 1.09 Å, 55° out of the plane of the ring and in a plane bisecting the corner of the triangle. No account was taken of the scattering due to hydrogen atoms with each other.

The solid curves in Figure I were calculated ignoring the unbonded hydrogen distances. In the dotted curves, these terms were inserted without temperature factors. This means that the dotted curves have full weight at the origin, becoming less significant with increase in q.

All the models with the C—Cl distance of 1.81 Å may be eliminated from several considerations. The most prominent of these is perhaps the great strength of the sixth peak compared to the fourth and fifth. All the models with the 60° angle have the common defect that the fourth peak is not strong enough compared to the fifth and sixth. In model H the order of strength of the fifth and sixth peak is reversed and the ninth minimum is too shallow. Model E fits best of the calculated curves. The dashed curve uses the same terms as the dotted curve, except that the amplitudes were calculated from the atomic numbers alone, ignoring the shape factors. This indicates that the use of shape factors was perhaps an unnecessary refinement in this case.

Model E' uses the same distances as model E, but the long hydrogen terms have been temperature factored with an exponential coefficient of 0.0004. It will be seen that this corresponds very closely to the visual curve. The nature of the third and ninth features is not quite satisfactory, and the eleventh minimum seems too deep. This last point may reasonably be assigned to observational error. Reexamination of the films showed that the third feature occurred on all of them at point of very rapid change of background, making its exact shape hard to state positively. Model D agrees better with curve V in this one respect if almost full weight is given to the hydrogen terms.

Model D, however, has several defects. The nature of the seventh and ninth features and the weakness of the eleventh taken together seem to eliminate it. Shortening the C—Cl bond distance to model H does not improve the third feature and causes other incompatibilities to arise. These changes, for example in the relative strengths of the fourth, fifth, and sixth maxima and in the nature of the seventh maximum, will in general be seen to be opposite to the effects of shortening the angle (model D). This suggests that simultaneously reducing the angle and shortening the bond might preserve and perhaps improve the features of the best model. This involves a shift on the parameter plot towards model G. This model does agree very well out to the ninth feature, which seems too low, the tenth, which is too strong, compared to the eighth, and eleventh, which is too weak. It seems, therefore, that the preferred model lies between model E and model G, close to model E but with a slightly shorted C—Cl bond and a somewhat smaller angle.

It is true that an increase of angle would bring the ninth peak in model E into closer agreement with the visual curve, but this leads to such extreme disagreements at other parts of the pattern that is seems impossible to justify such a variation. Reexamination of the films did not suggest any error in drawing curve V at this point, and it does not appear possible, therefore, to give any entirely satisfactory explanation of the disagreement concerning the ninth feature.

The considerations which have been detailed above lead to the values C—C = 1.52 ± 0.02, C—Cl = 1.76 ± 0.02, and for the angle of the C—Cl bond with the plane of the cyclopropane ring 56° ± 2°.

Table I gives the quantitative comparison of the observed maxima and minima with those calculated for model E'.

Table I

Cyclopropyl Chloride

min	max	q_{obs}	$q_{E'}$	$q_{E'}/q_{obs}$
1		5.6	6.8	(1.214)
	1	8.5	8.7	(1.024)
2		11.2	11.5	(1.027)
	2	15.7	16.0	1.019
3		19.7	19.9	1.010
	3	22.7	23.0	1.013
4		25.3	25.3	1.000
	4	29.2	29.1	0.997
5		33.0	33.4	1.012
	5	37.6	37.6	1.000
6		40.8	40.9	1.002
	6	44.0	44.3	1.007
7		48.7	48.2	0.990
	7	51.9	51.0	0.983
8		54.2	54.6	1.007
	8	58.4	58.1	0.995
9		62.3	62.4	1.002
	9	66.5	66.1	0.994
10		68.8	68.2	0.991
	10	71.4	71.7	1.004
11		76.1	76.1	1.000
	11	81.1	80.5	0.993
12		83.8	84.0	1.002
	12	86.5	86.0	0.994
13		89.2	89.3	1.001
	13	97.1	93.6	(0.964)

Average (22 measurements) 1.001

Average deviation 0.006

1,1-dichlorocyclopropane

Excellent photographs of the diffraction pattern of this substance were obtained, using sample temperatures ranging from 0° C. to room temperature. The visual appearance of the photographs is represented by curve V in Figure III. The radial distribution function RD was calculated from curve V. It shows main peaks at 1.50 Å, 1.76 Å, and 2.86 Å, representing the C—C, C—Cl, and the unresolved C...Cl and Cl...Cl distances respectively.

In applying the correlation method, the same treatment of the coefficients of the scattering terms was used as in cyclopropyl chloride, and the same assumptions for C—H and C—C bonds were used. Models were again calculated for C—Cl distances of 1.73 Å, 1.77 Å, and 1.81 Å and for angles of these bonds out of the plane of the ring of 53°, 56-1/2° and 60°. One additional model (J in Figure II) with C—Cl = 1.75 Å and an angle of 55° was also calculated. The solid and dotted curves have the same significance as in the curves of cyclopropyl chloride.

One of the most remarkable features of these curves is the extreme structure sensitivity of the ninth ring. Only model E comes very close to duplicating the visual curve in this regard.

All the models with the 60° angle differ so widely from the visual curve that their complete exclusion is easily decided upon.

In considering the other curves, it becomes apparent that the complicated eleventh feature in curve V represents perhaps an excessively optimistic attempt to see detail in this very faint part of the pattern.

In model A, the sixth and ninth maxima are too strong and the disagreement in the region beyond $q = 80$ is too extreme to be assigned to observational error. In model B, the ninth peak has disappeared and the seventh peak has changed its nature entirely. Model D disagrees at the ninth peak,

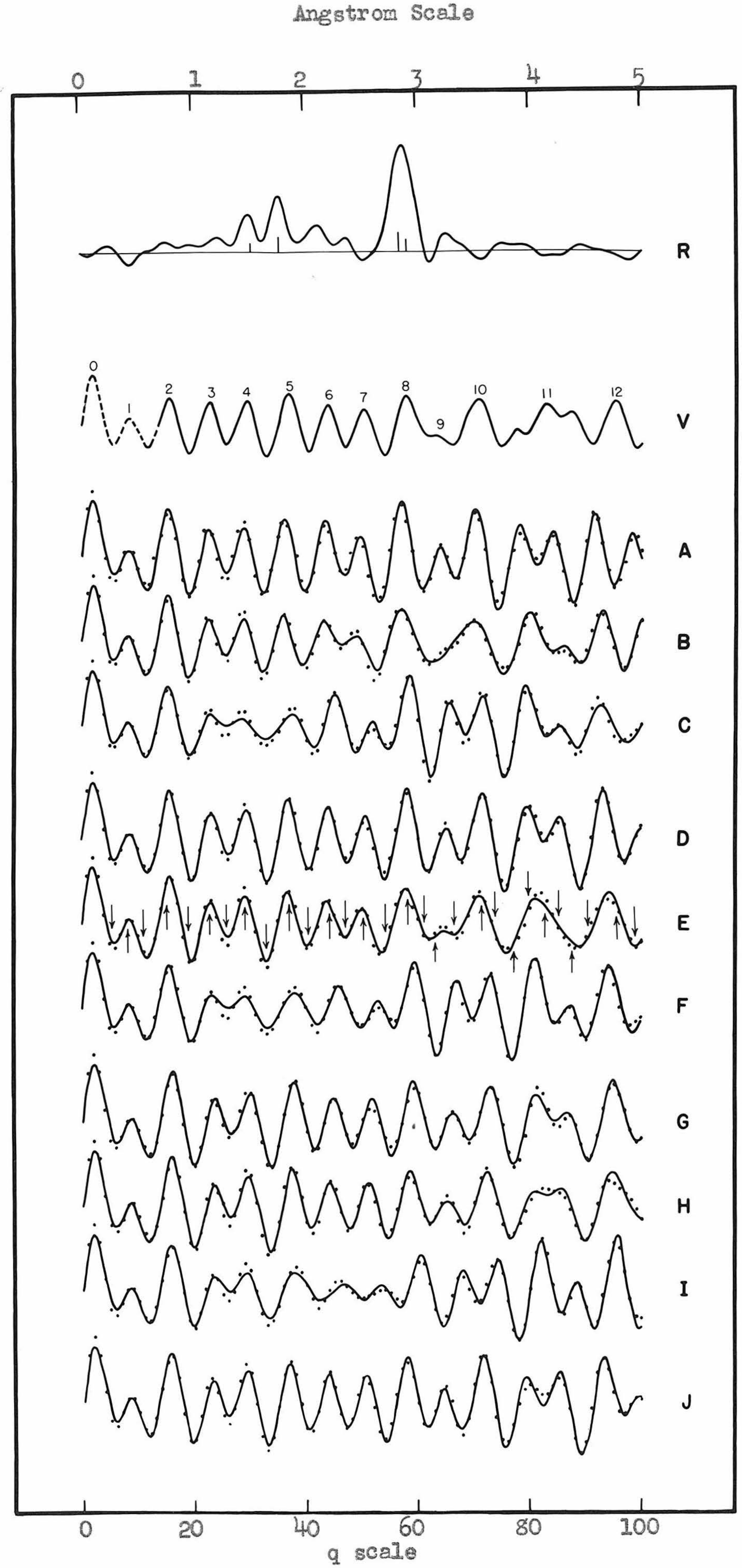

Figure III

Theoretical Curves for 1,1-dichlorocyclopropane

Table II

1,1-dichlorocyclopropane

min	max	q_{obs}	q_E	q_E/q_{obs}
1		5.56	5.8	(1.043)
	1	8.36	8.6	(1.029)
2		11.16	11.6	(1.039)
	2	15.24	15.6	1.024
3		19.17	19.4	1.012
	3	22.98	22.9	0.997
4		25.75	25.9	1.006
	4	29.27	29.1	0.994
5		33.00	32.9	.997
	5	37.01	36.7	.992
6		40.48	40.2	.993
	6	44.28	43.7	.987
7		46.93	46.9	.999
	7	50.24	49.9	.993
8		54.16	53.5	.988
	8	58.20	57.7	.991
9		61.12	62.0	1.014
	9	63.17	64.0	1.013
10		66.53	67.0	1.007
	10	71.43	70.9	0.993
11a		73.71	75.9	(1.030)
	11a	77.05		
11b		79.70		
	11b	82.72	80.9	(0.978)
11c		85.01		
	11c	87.54		
12		90.34	89.0	.985
	12	95.55	94.0	.984
13		98.98	99.0	1.000

Average (20 measurements) 0.999

Average deviation .009

and it is hard to reconcile it in the region of the eleventh peak, even by making very generous allowance for the difficulty of clear observation in this part of the pattern. In models G and H, the fourth minimum is not deep enough while the seventh minimum is too deep. The ninth feature is too strong in both these models. Model J was calculated in an attempt to set closer limits than had been done in the case of cyclopropyl chloride. It does not agree even as well as model D. The third maximum is too weak, and the sensitive ninth feature is clearly in disagreement with the photographs. These considerations lead to a model of essentially the same configuration as for cyclopropyl chloride, except for a slightly longer C—Cl bond distance. The limits of error overlap, however. The most acceptable model has the following parameters: C—C = 1.52 ± 0.02 Å; C—Cl = 1.77 ± 0.02 Å; ∠Cl—C—Cl = 112° ± 4°. Table II gives the quantitative comparison of the observed and calculated maxima and minima for model E.

2,2-dichloropropane

This substance was made by dropping acetone on phosphorus pentachloride and distilling the product through a helices-packed column having an efficiency of about eight plates. When redistilled through the same column, the entire sample came over at 68.2° C. (uncorr.). Good photographs of the diffraction pattern of this substance were obtained using sample temperatures ranging from 0° C. to room temperature. The visual appearance of the photographs is represented by curve V in Figure IV. The radial distribution function RD, calculated from curve V, shows principal peaks at 1.52 Å and 1.80 Å, as well as a very incompletely resolved pair with apparent components of approximately 2.72 Å and 2.95 Å. These represent the C—C, C—Cl, C...Cl, and Cl...Cl distances respectively.

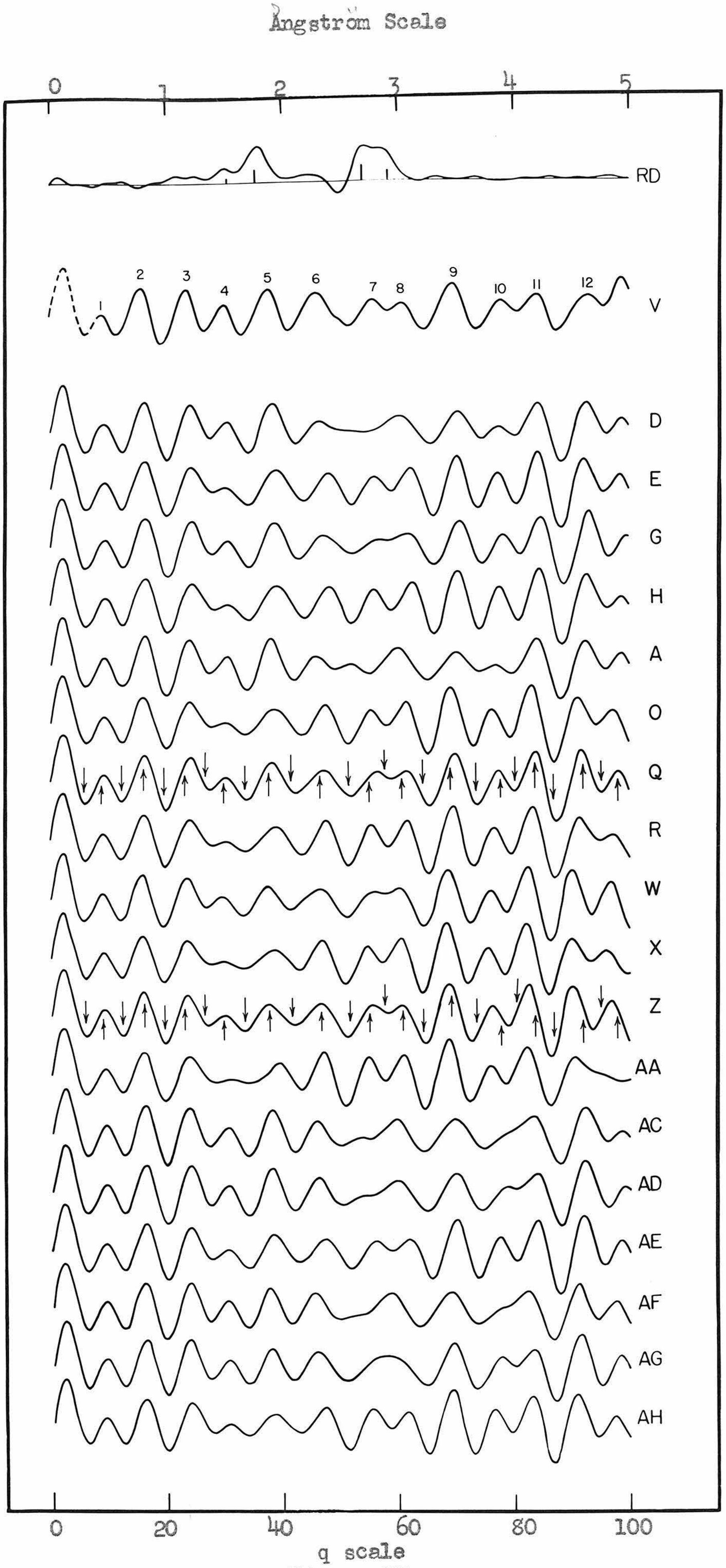

Figure IV

Theoretical Curves for 2,2-dichloropropane

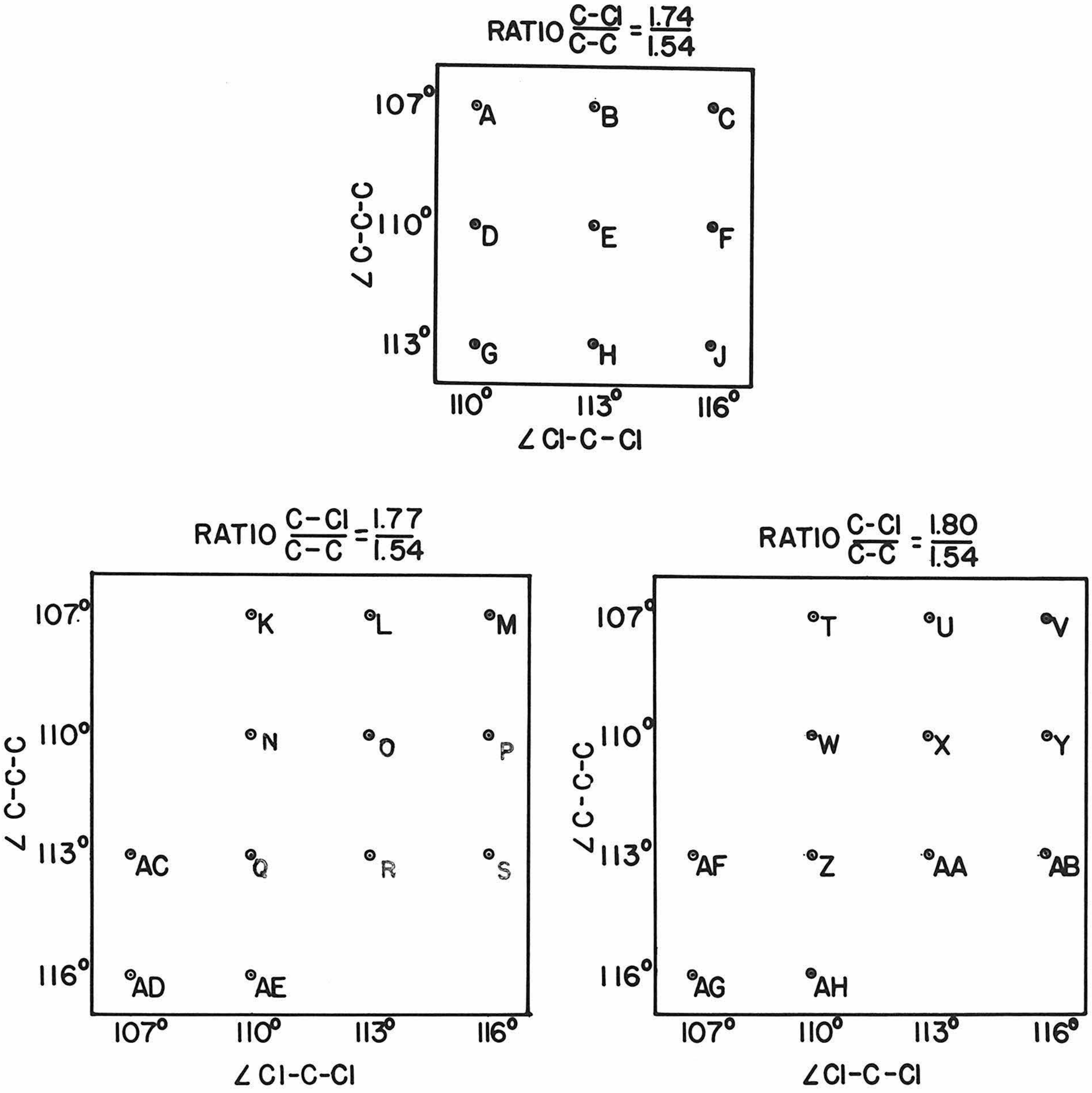

Figure V

Parameter Plot for 2,2-dichloropropane

In applying the correlation method, the same treatment of coefficients was used as for the cyclic compounds. Since the restraint imposed by the closed ring is absent, this compound has one additional shape parameter. Figure V is a parameter map showing all models calculated, the more significant of which are plotted in Figure IV. The size parameter was provisionally taken to give a C—C bond of 1.54 Å instead of 1.52 Å as in the case of the cyclic compounds. The unbonded C...H terms are included in all curves, with a temperature factor coefficient of 0.0004. The long H...Cl distances have been ignored, on the assumption that thermal vibration and presumed free rotation of the methyl groups would greatly reduce their contribution. Nevertheless, it is important to recognize that the above factors do not entirely cancel the contribution of these distances, especially at low values of q, and that they have an aggregate scattering power approximately three-quarters as great as that of the long C...Cl terms, which are the most important in the molecule. Ignoring these long H...Cl terms entirely means that at low values of q the calculated curves may be expected to show all features somewhat too far out. The quantitative comparison in Table III clearly shows this trend.

All models in the plane with $\frac{C-Cl}{C-C}$ ratio of $\frac{1.74}{1.54}$ are easily eliminated from consideration. Models E, G, and H are the best with this bond ratio but the pattern in the region of the sixth, seventh, and eighth rings is strikingly at variance with curve V. In the plane with $\frac{C-Cl}{C-C}$ ratio $\frac{1.77}{1.54}$ considerably better agreement is to be found. Model Q gives the best fit, although the angles are rather surprising. Model O, which corresponds more closely with what might have been predicted from analogies with similar molecules such as isopropyl chloride, whose structure is known, has several points of disagreement. Besides the reversal in strength of two pairs, the fifth and sixth and the seventh and eighth, there is the weakness of the fourth peak to cast doubts on this model. Model N does not appear in Figure IV, but in it the seventh peak has become a mere shoulder on the eighth peak, eliminating the eighth minimum entirely. Models AC and AD differ radically in several respects from the visual curve. Model R is a rather poor fit, as can be seen by brief inspection. Model AE, in spite of its rather improbable C—C—C angle, fits rather well. The eighth maximum is stronger than the seventh, but this is almost the only flaw in it. The present treatment must, therefore, yield a result including this model.

In the plane with $\frac{C-Cl}{C-C}$ ratio $\frac{1.80}{1.54}$, model Z gives the best fit. It is inferior to both Q and AE however. The relationship of the fifth and sixth maxima to each other and to the seventh feature is unsatisfactory.

Arrows corresponding to experimental measurements have been drawn to both curves Q and Z. It can be seen that the quantitative data is often slightly better for Z. The qualitative comparison of the pattern, however, strongly favors Q. On the basis of these considerations, a ratio between that of the two models, but somewhat closer to Q, seems indicated. Of the other models on the $\frac{1.80}{1.54}$ plane, all except W and AH differ so much from the visual curve that they need not be considered. Model W closely resembles model N and, like it, is rejected on the basis of the nature of the seventh and eighth rings. Model AH agrees perfectly in this region, but the relationship of the fourth, fifth, and sixth peaks to each other is completely inacceptable.

The quantitative comparison of the measurements with model Q is found in Table III. It exhibits the wide divergence that has already been mentioned in connection with the omission of the long H...Cl terms.

Table III

2,2-dichloropropane

min	max	q_{obs}	q_Q	q_Q/q_{obs}
1		5.42	6.3	1.163
	1	8.62	9.3	1.079
2		11.68	12.4	1.062
	2	15.60	16.1	1.032
3		19.33	20.1	1.040
	3	23.28	24.2	1.039
4		26.87	27.8	1.036
	4	30.06	30.6	1.018
5		33.23	34.0	1.023
	5	37.64	38.3	1.018
6		41.19	42.8	1.039
	6	46.07	47.3	1.027
7		51.05	52.2	1.022
	7	55.42	56.5	1.019
8		58.16	58.9	1.013
	8	60.86	61.6	1.012
9		64.45	65.7	1.019
	9	69.60	69.8	1.003
10		73.36	73.9	1.007
	10	77.86	77.5	0.995
11		80.31	80.1	.997
	11	83.75	83.7	.999
12		86.81	87.8	1.011
	12	92.17	91.6	0.994
13		95.24	95.2	1.000
	13	98.15	98.1	0.999

Because of the obvious trend in the above ratio, the cause of which is discussed in the text, the usual calculation of averages would be misleading.

Although it seems that more work needs to be done before considering this structure completely and satisfactorily determined, the considerations which have been mentioned lead to the following provisional model: C—C = 1.54 ± 0.02 Å; C—Cl = 1.78 ± 0.02 Å; ∠Cl—C —Cl = 110° ± 2°; ∠C—C —C = 114° ± 4°. This would give an angle Cl—C—C of 108-1/2° ± 3°.

Discussion of Results

The C—C bond distance of 1.52 ± 0.02 Å in the cyclic compounds, although shorter than that found for saturated straight chain compounds, seems to agree with a tendency noticed in cyclopropane[1] and spiropentane[2] towards shorter bonds in the case of three-membered carbon rings. Whether the value of 1.76 ± 0.02 Å for the C —Cl bond in cyclopropyl chloride represents a real shortening corresponding to some double bond character in the bond as was predicted by Dr. J. D. Roberts[3] is not easy to state positively. Not only do the limits of error overlap the values for the normal distance of this bond as accepted in These Laboratories, but some workers in the field of structure consider 1.76 Å to be the value found in the case of carbon tetrachloride.

The interpretation of the data for 2,2-dichloropropane has obvious shortcomings. It is clear that a mistake was made in assuming that the contributions from the H...Cl terms could safely be neglected. Certain theoretical curves in the region of particular interest should be recalculated with some necessarily approximate scattering terms, heavily temperature factored, to represent the contribution of these distances. It is certain that this will improve the quantitative fit, although its effect on the qualitative aspects of the correlation treatment cannot be safely predicted, it might cause some revision of the final results.

The angles reported as a result of the treatment so far given seem strange. Previous work on such compounds as 1,1,1-trichloroethane and isopropyl chloride[4] does not indicate that a methyl group attracts or repels a chlorine attached to the same carbon any more than it does another methyl group. Any attempt to understand the bond angles in this molecule must await a more precise interpretation of the data.

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AN ACCURATE PRESSURE REGULATING DEVICE OF SIMPLE CONSTRUCTION

The type of vacuum regulator first described by Lewis[1] and modified by Warner[2] has several advantages for distillation setups, among them the lack of electrical connections, the absence of a deliberate air leak, and the constancy of regulated pressure despite moderate variations in leaks, or in evolution of gases in the system, or in the capacity of the aspirator or pump.

The device described by Lewis[1] suffers from two disadvantages: the necessity of making a sealed joint very close to a sealed-in fritted-glass disk, and the fact that, at low pressures, the gas bubbles which displace the mercury become so large that their diameters, in millimeters, are an appreciable fraction of the regulated pressure, measured in millimeters of mercury, and these large bubbles cause a surging back and forth of the mercury in the side arm. This makes regulation at less than ten millimeters' pressure very uncertain. Warner's[2] model avoids both these difficulties, but, in the author's experience, when it is used to regulate pressure in an essentially static system for long periods, mercury almost invariably falls down the inlet tube and destroys the regulation. The device shown in Figure I is free from these objections. With it, pressures as low as 2 or 3 millimeters of mercury in a reasonably tight system may be maintained for hours as closely as it is possible to read a mercury manometer.

Tube F is made from a stock (Corning 39570) pyrex tube with sealed-in fritted disk by cutting the tube on one side of the disk and grinding it flush. A 25-millimeter tube with a disk of medium porosity has been found satisfactory. Stopcock C is used to prevent surges of mercury when

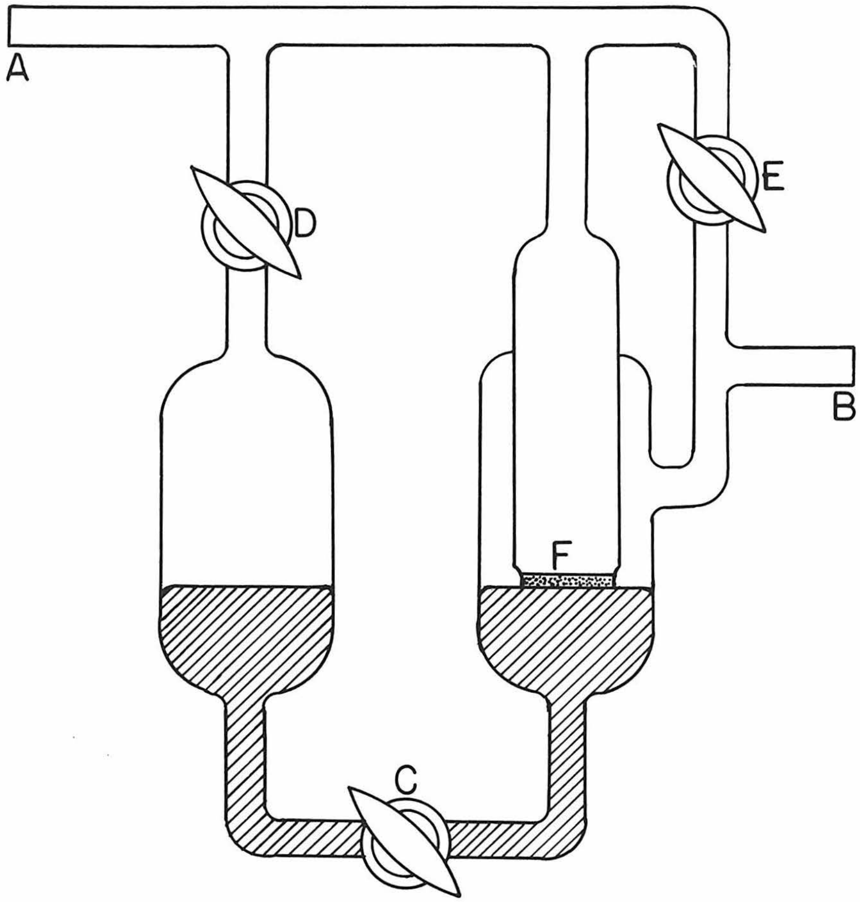

Figure I

vacuum is being established or released with consequent high rate of air flow. During these periods the mercury should be kept clear of the fritted glass by tilting the apparatus and closing C when sufficient mercury has been displaced. The pump is connected at A and the system at B. During the preliminary evacuation stopcocks D and E are both open. When the correct pressure is reached the pump is momentarily shut off to allow the system to become static, stopcocks D and E are closed, and C is opened. Minor adjustments are made by tipping the whole apparatus slightly. If the pressure in B increases it pushes the mercury out of the way, allowing the pump to act through the disk at F until the desired vacuum is again established.

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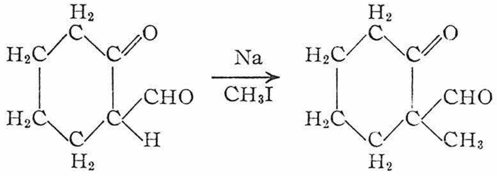
[Reprinted from the Journal of the American Chemical Society, 66, 1041 (1944).]

ATTEMPTED REPETITION OF A REPORTED TOTAL ASYMMETRIC SYNTHESIS

Sir:

In a recent letter to the editors of *Nature*, Paranjape, Phalnikar, Bhide and Nargund[1] report the synthesis of several optically active substances from inactive starting materials without the use of any asymmetric reagents or catalysts. They report that the asymmetric synthesis occurred at the following step in their series of reactions



(inactive)

$[\alpha]_D$ −26.22

The reported activity was determined on the crude material, since the methylated formylcyclohexanone was reported to be an unstable liquid, impossible to purify by distillation.

An attempt has been made in these Laboratories to repeat this extraordinary result, which would not be predicted on the basis of any known theory of optical activity.

Inactive formylcyclohexanone was prepared according to the method of Rupe and Klemm,[2] and the methylation was carried out using two different techniques.

In the first trial, formylcyclohexanone was added to a 10% ethanolic solution of sodium ethylate and refluxed with methyl iodide. This yielded, after evaporation of the solvent and washing with water, a reddish liquid, a portion of which darkened and resinified when an attempt was made to distill it. The crude material had a specific rotation of zero, with an error of ±0.7° due to the difficulty of taking readings on such a comparatively strongly colored material.

In the second synthesis, the sodium salt of the formylcyclohexanone was suspended in toluene and allowed to react with methyl iodide. This procedure yielded a much clearer product after removal of the solvent, and it was possible to determine that the material was totally inactive within the 0.01° accuracy of the Zeiss polarimeter. Readings were taken on the material itself as well as on chloroform solutions of it as reported by the Indian authors.

Considerable speculation on possible sources of their reported results has yielded no reasonable explanation.

Contribution No. 970 from the
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[1] K. D. Paranjape, N. L. Phalnikar, B. V. Bhide and K. S. Nargund, *Nature*, **153**, 141 (1944).

[2] H. Rupe and Otto Klemm, *Helv. Chim. Acta*, **21**, 1539 (1938).

Propositions submitted by John Michael O'Gorman

in partial fulfillment of the requirements for the degree

of Doctor of Philosophy, September 3, 1946.

Committee: Professors Schomaker (Chairman), Pauling, Lucas, Yost,
D.H. Campbell, Swift, Niemann, Buchman

I. Dr. Verner Schomaker has suggested that the following compound, sym. hydrindacene,  , if it could be prepared by dehydrogenating the saturated form described by Arnold,[1] would exhibit the same sort of resonance as has been postulated to explain the deep color of azuline. An attempt to repeat Arnold's synthesis failed. I propose that it might well be prepared by another method, and that unsym. hydrindacene would exhibit the same phenomenon, and from considerations of resonance, might be easier to form by dehydrogenation.

II. (a) The preparation of the compound ClO_2F has been described.[2] Analogy with chlorate ion suggests an F—Cl bond, whereas considerations of electronegativity and formal charge seem to favor an F — O bond. I propose an electron diffraction investigation to settle this interesting point.

(b) The same apparatus and techniques used to prepare ClO_2F would serve, by a simple change in starting materials, to prepare NOF and NO_2F, which should also be investigated.

III. (a) Dimethyl carbonate, which dipole moment measurements indicate is cis with respect to both methyls and the carbonyl oxygen, would have no more shape parameters than methyl formate, but some additional distances which might well lead to a more precise electron diffraction determination than seems likely for any other ester.

(b) Although dimethyl formate has possibilities similar to those of methyl chloroformate for resonance which would weaken the rigidity of the planar structure, it gives much less evidence of such free rotation than the chloro compound. This, together with the preference of esters for the cis configuration even though complete planarity is not possible as it is in the trans configuration and the very short (2.65 Å) distance between methyl carbon and carbonyl oxygen in esters studied so far, argues for the existence of some attraction of the hydrogen bond type between the methyl carbon and the carbonyl oxygen in esters.

IV. (a) I propose that the present high efficiency distilling columns are vastly overcomplicated in the matter of distilling heads and more particularly of packing and jacketing, and much simpler devices of similar efficiency may easily be devised.

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(1) Arnold, R. T., and Barnes, R. A., J. Am. Chem. Soc. 66, 960 (1944)
(2) Schmitz, H., and Schumaker, H. J., Z. Anog. Allgem. Chem., 249, 238 (1944)

(b) Mercury diffusion vacuum pumps which will operate when backed by good water aspirators have been designed and recently placed on the market. Certain advantages are obvious, but the water to run the usual type of aspirator may cost from twenty to fifty cents an hour in southern California. I propose to use a regular aspirator to bring the fore vacuum down to the required point, after which it should be disconnected and an aspirator with a tiny thread jet be used to maintain the pressure at the vapor pressure of water. This reduction in size would affect a great saving in water and not affect the vacuum if the system were reasonably free from leaks.

(c) Natelson and Zuckemann[3] have described an extremely simple process for determining the vapor pressure of a single drop of liquid at any temperature. They mention that this can be used to determine the entropy of vaporization, but apparently have overlooked the fact that their device offers a means of getting corrected boiling points accurately without the necessity for thermometer stem corrections, mathematical calculations involving assumptions as to the nature of the liquid, or even the necessity of heating the compound to within more than about fifty degrees of its boiling point.

V. (a) A simple laboratory preparation of glyoxyllic acid is not to be found in the literature. I propose that the well known quantitative analytical test for 1,2-dihydroxy compounds by cleavage with periodic acid be utilized as a preparative method, starting with tartaric acid. The very expensive periodic acid could be recovered as barium iodate and reoxidized with chlorine, either directly or after metathesis with sodium sulfate.

(b) Vinyl acetylene is another simple compound for which only a very complicated synthesis involving expensive apparatus has been described. I propose a simple arrangement of ordinary apparatus to give good yields of this compound.

VI. (a) I propose that the following modifications in the analytical scheme of Noyes and Swift be considered:

1. The present confirmatory test for arsenic often fails when used on the semi micro scale. A modified Gutzeit test would illustrate a new type of reaction and prove much more sensitive.
2. The thiocyanate test for iron can easily be rendered roughly quantitative, and yields better results than the present method.

(3) Natelson, S, and Zuckerman, Ind. Eng. Chem; Anal. Ed., 17, 739 (1945)

3. Reactions in non-aqueous systems, such as the oxidation of manganese dioxide to manganate ion in the sodium carbonate head or the formation of cobalt borate in the borax head are valuable from pedagogical considerations and might well be included in the analytical scheme.
4. The separation of zinc and aluminum is the most unsatisfactory procedure in the present scheme. Since the phenomenon of overvoltage makes it possible to electroplate zinc but not aluminum from faintly acid solutions, I propose that consideration be given to the possibility of using some simple device, perhaps powered by flashlight batteries, to accomplish this separation.
5. The use of a spectroscope should be made a part of the alkali and alkaline earth analysis, not only as an aid to correct results, but to demonstrate to the students that a spectroscope is not an analytical cure-all, capable of replacing the entire scheme of analysis.

(b) In the freshman course at the Institute, the following changes are proposed:

1. Even at the expense of wrenching the logical order of development, quantitative considerations of equilibrium should be introduced quite early in the first term, and plentiful home work problems of this type be supplied all through the balance of the year, since this concept is the most difficult of all for beginners to grasp, although practice will generally lead to comprehension.
2. The development of the equilibrium constant expression from rate considerations should be abandonned as likely to cause more misconception than clarification. Furthermore, to avoid the danger that students will be more struck by the differences than the similarities, the expressions "solubility product", "ionization constant", and "dissociation constant" should be avoided until the students are familiar with them as equilibrium constants for specific types of reactions.
3. A long range program to develop a set of large scale experiments and demonstration models, clearly visible and understandable at the back of the lecture room, should be commenced. These should be kept assembled, ready to go, between school years.

VII. The acetals of unsymmetrical secondary alcohols are often characterized in the literature as simple compounds. Beilstein is more careful, and classifies them as dl. Actually, the synthesis of the acetal has introduced a new quasi-asymmetric center, and the compounds have two meso forms in addition to the d and l.

VIII. When a dl acid has been partially resolved by crystallizing its salt with some alkaloid, often a change to a different alkaloid or to a different principal of separation is necessary to complete the resolution. A possible method of furthering a partial resolution which does not seem to have been mentioned in the literature would be to crystallize the salt the acid forms with some divalent metal ion. A divalent anion could be used in the resolving of bases.

IX. The preparation of flurochlorobromomethane has been described.[4] This is is a pentatomic asymetric molecule, and its resolution, which was not accomplished by forming its molecular compound with digotinin, would be of theoretical interest. I propose that this compound be subjected to chromatography on columns packed with optically active salts of such metals as cobalt or silver.

X. Many problems of interest to biologists and chemists may be attacked by the use of tracer atoms. No suitable radio active isomers of oxygen or nitrogen exist, although stable isotopes of unusual atomic weight are available commercially. A mass spectrometer for use principally on these two atoms would not need better than five percent resolving power, and it should be possible for the Institute to design and make one of this low accuracy for a fraction of the cost of the more precise ones available commercially. Such a device would, for example, have given an absolutely unequivocal answer to the problem of the hydrolysis of acetals.

XI. Students of mine who have been in the air corps assure me that a minute or two of breathing oxygen will cure any hangover. I propose that a simple device using water and sodium peroxide cartridges, with gauze to filter out alkaline spray, would make a fortune if marketed under some such title as the Acme Atomic Nuclear Anti-katzenjammer Fission Apparatus.

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(4) Berry, K. L. and Sturtevant, J. M., *J. Am. Chem. Soc.*, 64, 1599 (1942)