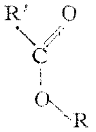
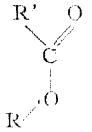
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1401]

# An Electron Diffraction Investigation of Methyl Formate, Methyl Acetate and Methyl Chloroformate

BY JOHN MICHAEL O'GORMAN,[1] WILLIAM SHAND, JR., AND VERNER SCHOMAKER

The structures of simple carboxylic esters have received considerable elucidation from studies of dipole moments.[2,3,4,5] This work is summarized and discussed in the fourth and fifth chapters of Wheland's book,[6] "The Theory of Resonance." The conclusion from these studies is that simple aliphatic esters do not have free rotation about the carbonyl carbon–ether oxygen bond, but are planar with the configuration I, which we shall call *cis*.


I


II

The configuration II was found in an ε-lactone[4] where the ring makes the *cis* configuration impossible, but does not, of itself, compel planarity. The general preference for the *cis* configuration suggests that there is an attraction between the carbonyl oxygen and the alkyl group R; however, resonance energies (about 20 kcal. per mole[6,7]) of the simple esters and the results for the ε-lactone in Marsden and Sutton's work indicate that the conjugation of the carbonyl double bond with the unshared pairs of the ether oxygen atom must also be important.

No structure determination of a simple ester in the gas phase has been reported. General interest, therefore, as well as the desire to check by an independent experimental method the results drawn from the dipole moment studies have led to the present investigation of three of the simplest esters by electron diffraction.

Good diffraction patterns were obtained in the apparatus described by Brockway[8] with vapor from liquid samples held at or slightly below room temperature. The visual curves V (Figs. 1, 2, 3) were then drawn[9] and the radial distribution functions[1] calculated from them by the approximation[9]

$$rD(r) = \sum_{q_i} V(q_i)\exp(-aq_i^2)\sin\left(\frac{\pi}{10}q_i r\right)$$

with $q_i = 1,2,3,\ldots,100$, $q = \frac{\pi}{10}s = \left(\frac{40}{\lambda}\right)\sin\phi/2$, and $\exp(-aq^2_{max}) = 0.15$ and $0.03$ for two separate computations for methyl acetate and 0.10 for the other two esters. The visual curves for $q > 10$ were drawn before any theoretical curves had been calculated, but the dotted portions in the central region were taken from a curve calculated for a reasonable model.[9]

The theoretical intensity curves used in the correlation treatment were calculated from the equation[9]

$$I(q) = {\sum_{ij}}' \frac{Z_iZ_j}{r_{ij}}\exp(-b_{ij}q^2)\sin\left(\frac{\pi}{10}r_{ij}q\right)$$

where $r_{ij}$ is the distance between atoms $i$ and $j$ and $Z_i$ is the atomic number of atom $i$ except that for hydrogen the value 1.25 was used. The coefficient $b_{ij}$ was given the value 0.00016 for bonded hydrogen terms, 0.0004 for unbonded hydrogen terms, and zero for all others. Hydrogen-hydrogen terms and all terms for unbonded distances between hydrogen and atoms not bonded to the same carbon atom were omitted.

In applying the correlation treatment, it soon became apparent that the intensity curves were extremely sensitive to slight parameter changes, a circumstance which appears to be related to the large number of distances which are not quite resolved in the radial distribution functions. Numerous hit or miss models based on reasonable conjectures with comparatively little regard for the radial distribution functions were first tried, but they failed completely to reproduce some of the major features and most of the finer details of the observed patterns. In order to obtain a model even roughly satisfactory, it was necessary to refine the interpretation of the complex peaks of the radial distribution functions to an extent which is not usual and, at least in this laboratory, had not previously been considered worth while. For each of the complex peaks a trial and error synthesis was made by adding together a set of peaks each representing the ideal contribution from one of the component distances. The ideal simple peak was approximated by a Gaussian curve of suitable half-width (*e. g.*, 0.07 Å. at half-height for the first methyl acetate radial distribution curve) and an area proportional to the coefficient $Z_iZ_j/r_{ij}$ of the intensity equation. In some cases a very good fit was obtained in this way, but

---

(1) University of California, Santa Barbara, Calif.

(2) A. Eucken and L. Meyer, *Physik. Z.*, **30**, 397 (1929).

(3) C. T. Zahn, *ibid.*, **33**, 730 (1932).

(4) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

(5) S. Mizushima and M. Kubo, *Bull. Chem. Soc. Japan*, **13**, 174 (1938).

(6) G. W. Wheland, "The Theory of Resonance," Wiley and Sons, New York, N. Y. 1944.

(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(8) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936). Camera distance 10.91 cm.; electron wave length 0.0613 kX., calibrated with respect to zinc oxide smoke (C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.*, **14**, 271 (1943)). Corrections were made for film expansion.

(9) (a) R. A. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942); (b) P. A. Shaffer, Jr., V. Shomaker, and L. Pauling, *J. Chem. Phys.*, **14** 659 (1946).

usually it was necessary to change the scale of areas for different complex peaks of the same radial distribution curve by as much as 25%. Except for terms involving hydrogen, no account was taken of the likely differences in ideal peak width and in the preliminary work no requirement of geometrical consistency was imposed on the distances.

Comparison of calculated theoretical curves with the visual curves was used to refine the parameters obtained from the radial distribution function. The full correlation treatment, however, was not applied, because it would have been impracticable to calculate theoretical curves for the customary minimal network of models, which for the acetate and chloroformate esters would have numbered about $3^7$. Instead, extensive use was made of a log–log plot of the positions of the maxima and minima of sin $(\pi/10)rq$ as a function of $r$ in order to study the effect of parameter variations without actually calculating the intensity functions in each case. This procedure was very effective in predicting parameter changes which would improve particular aspects of a theoretical curve without spoiling others.

### Methyl Acetate

Methyl acetate is the first of the three molecules for which a satisfactory structure was found. The radial distribution function *RD* (Fig. 1) shows two complicated peaks, the first representing the five bonded distances and the second representing the three distances between heavy atoms bonded to a common atom. 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 can only represent the methoxy carbon—carbonyl oxygen distance, to which free rotation would give a rather wide range of values. The peak at 3.26 Å. was regarded as a false peak, but that at 3.73 Å., which must be interpreted as the methyl–methyl distance, is rather important in confirming the configuration finally selected. To be sure, the 3.26 Å. peak is almost as strong, and it is possible, though unlikely, that it corresponds to a small fraction of molecules with a configuration about midway between *cis* and *trans*.

Models A, B, and C, based in part upon the structure of acetic acid monomer as determined by Karle and Brockway,[10] are typical of the models calculated before the careful interpretation of the radial distribution function. They are not at all satisfactory, even though some of the later ones, such as C, have parameters (Table I) only slightly different from the model, M, finally selected. Model E was selected by the more careful interpretation of the radial distribution function. The improvement, especially in the region of the sixth and seventh rings, is obvious. Model D is the same as Model E except that the long terms,

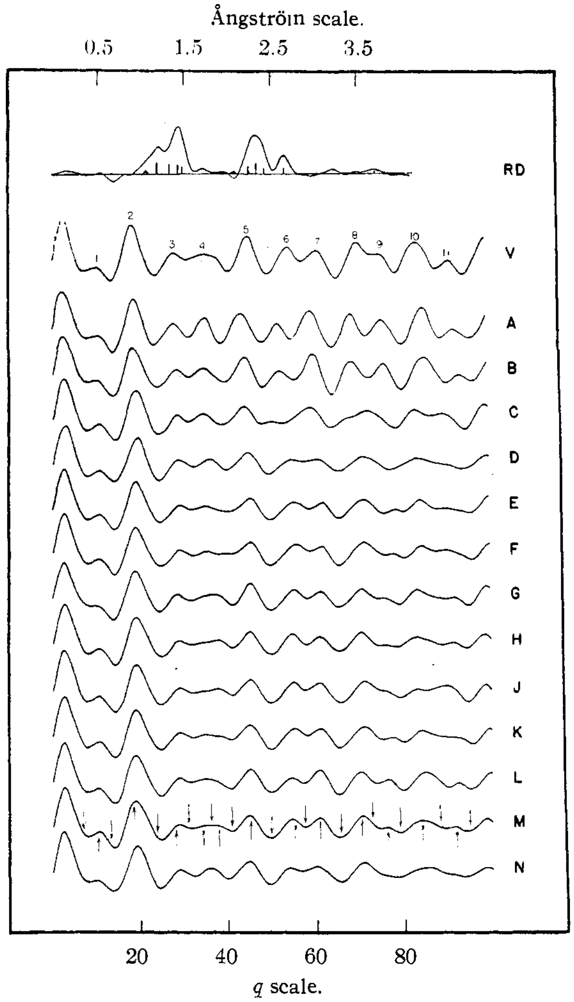
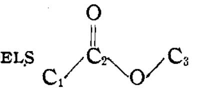


Fig. 1.—Methyl acetate.

TABLE I

METHYL ACETATE MODELS 

∠α is the angle between the C—O—C plane and the O═C—O plane

| | C═O, Å. | C—C, Å. | $C_2$—O, Å. | $C_3$—O, Å. | ∠C—C—O | ∠O═C—O | ∠$C_2$—O—$C_3$ | ∠α |
|---|---|---|---|---|---|---|---|---|
| A | 1.24 | 1.54 | 1.43 | 1.43 | 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 | | See text | | |
| 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 |

For all models C–H = 1.09 Å., ∠H–C–H = $109^1/_2$°. Acetate skeleton planar.

---

(10) J. Karle and L. O. Brockway, THIS JOURNAL, 66, 574 (1944).

which are important in determining whether or not the molecule is planar, have been omitted as a crude approximation to free rotation. The great differences between Models D and E illustrate the importance of these long terms. Model F differs from Model E by 0.02 Å. in one parameter only. The nature of the fifth minimum and of the ninth feature are changed and the seventh maximum is noticeably lowered.

Since greater attention to the radial distribution had resulted in such a great improvement, Curve G was calculated with the distances obtained by analyzing the radial distribution curve in the manner which has been described. It will be seen that the curve provides practically an exact fit, confirming the analysis. The distances used are not perfectly consistent with any geometrical model, but the discrepancies are in no case greater than a few hundredths of an ångström, and may be attributed to errors in the visual curve or in the analysis of the radial distribution features. 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 feature and the weakness of the tenth. Using the maxima-minima chart already described, Models J, K, L, and M were chosen for calculation in an attempt to improve the fit or to maintain it while varying parameters. Model J fits well out to $q = 80$. 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. Reference to the free rotation Curve, N, shows that the rotation-dependent terms may be very considerably attenuated at large $q$ without greatly changing the agreement; accordingly, it is not possible to make a precise estimate of the amplitude of oscillation of the dihedral angle about the average value.

The quantitative comparison of observed and calculated maxima for Model M is shown in Table II.

TABLE II

METHYL ACETATE

Values in parentheses were omitted and values in square brackets given double weight in computing averages

| Min. | Max. | $q_{obs.}$ | $q_M/q_{obs.}$ |
|---|---|---|---|
| 1 | | 6.90 | (1.160) |
| | 1 | 10.36 | (1.014) |
| 2 | | 13.31 | (1.052) |
| | 2 | 18.44 | (1.025) |
| 3 | | 23.86 | 1.018 |
| | 3 | 28.06 | 1.026 |
| 4 | | 30.92 | 1.022 |
| | 4 | 34.18 | |
| 4a | | 35.98 | |
| | 4a | 37.77 | |
| 5 | | 40.71 | [1.010] |
| | 5 | 45.15 | [0.992] |
| 6 | | 49.61 | [1.006] |
| | 6 | 55.18 | 0.998 |
| 7 | | 57.30 | [1.003] |
| | 7 | 60.84 | 0.999 |
| 8 | | 65.53 | [1.995] |
| | 8 | 70.30 | [1.001] |
| 9 | | 72.79 | 1.019 |
| | 9 | 76.26 | 0.997 |
| 10 | | 79.08 | 1.003 |
| | 10 | 84.10 | 1.002 |
| 11 | | 88.18 | 1.021 |
| | 11 | 91.89 | 0.998 |
| 12 | | 95.07 | 1.003 |
| | 12 | 99.98 | 0.988 |
| | | Average | 1.005 |
| | | Average deviation | 0.008 |

Besides the calculation of these models, much time and thought were put into studying the changes that would be brought about by changing any parameter or any two of them simultaneously in order further to investigate the error of the determination, particularly with regard to the possible existence of simultaneous variations of several of the parameters by comparatively large amounts which would leave an acceptable intensity curve. Because no such comparative indeterminateness of the problem could be found, we have based our estimated limits of error on the range of acceptability found for the models which were actually considered and we present these estimates with some confidence that they represent fairly the reliability of the determination. Our results may be summarized as follows: C=O = 1.22 ± 0.03 Å., C—C = 1.52 ± 0.04 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°, configuration approximately *cis* (Structure I) with average dihedral angle 25° (limiting values for the average, 0° and 35°).

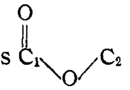
## Methyl Formate

The radial distribution curve, RD in Fig. 2, shows a complicated feature representing the four bonded distances, an unresolved peak at 2.28 Å. representing the unbonded O . . . O and C . . . C distances, and a single peak at 2.68 Å., representing the long C. . . O distance. This last peak indicates that most of the molecules must be approximately planar in the *cis* configuration

In applying the correlation procedure, Curves A to F were first calculated using the bond distances and angles reported by Karle and Brockway[10] for formic acid monomer, normal values for the methoxyl C—O distance and C—O—C angle, and various angles of rotation about the carboxyl C—O bond. These curves, which except for E differ only in the long C . . . O distance, illustrate the perhaps surprisingly great importance of this distance and confirm (Curve C) the radial distribution value of 2.68 Å. Curve C is notably unsatisfactory in the spacing of the features (Table IV)

TABLE III

METHYL FORMATE MODELS



$O{=}C_1{-}O{-}C_2$

∠α is the angle between the C—O—C plane and the O—C—O plane

| | C=O, Å. | C₁—O, Å. | C₂—O, Å. | ∠O=C—O | ∠C—O—C | ∠α |
|---|---|---|---|---|---|---|
| A | 1.24 | 1.42 | 1.42 | 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 |

For all models C-H = 1.09 Å., ∠H-C-H = 109½°, ∠O-C-H = 109½°. Formate radical planar.

and in the depths of the fourth and fifth minima, the latter especially being too shallow.

TABLE IV

METHYL FORMATE

Values in parentheses were omitted and values in square brackets given double weight in computing averages

| Min. | Max. | $q_{\mathrm{obs.}}$ | $q/q_{\mathrm{obs.}}$ | $q_c/q_{\mathrm{obs.}}$ |
|---|---|---|---|---|
| 1 | | 6.83 | (1.215) | (1.215) |
| | 1 | 10.05 | (0.985) | (1.005) |
| 2 | | 13.35 | (1.019) | (1.041) |
| | 2 | 18.63 | (1.052) | (1.031) |
| 2a | | 20.87 | | |
| | 2a | 22.66 | | |
| 3 | | 24.56 | 1.054 | 1.018 |
| | 3 | 30.11 | 1.029 | 1.049 |
| 4 | | 33.52 | 1.017 | 1.023 |
| | 4 | 37.48 | 1.006 | 1.006 |
| 5 | | 41.56 | [1.008] | [0.999] |
| | 5 | 45.56 | [1.010] | [1.025] |
| 6 | | 49.78 | [1.012] | [1.037] |
| | 6 | 54.38 | 1.008 | 0.986 |
| 7 | | 57.86 | [1.006] | [1.030] |
| | 7 | 63.00 | 0.983 | 0.997 |
| 8 | | 66.62 | [ .997] | [1.015] |
| | 8 | 72.25 | [ .991] | [1.001] |
| 9 | | 76.58 | 1.032 | 1.009 |
| | 9 | 81.38 | 1.020 | 0.987 |
| 10 | | 84.98 | 1.005 | 0.971 |
| | 10 | 90.24 | 0.992 | 0.973 |
| 11 | | 94.70 | 1.001 | 0.989 |
| | Average | | 1.008 | 1.010 |
| | Average deviation | | 0.010 | 0.017 |

Of the remaining models, G was based on the careful interpretation of the radial distribution function and H and J were steps in the search for improved agreement while K represents a further test of the 2.68 Å. distance and L is based on the results for methyl acetate. None of these is entirely satisfactory in regard to all the relations required by the visual curve for the features from the second to the eighth maximum, but in view of the large number of parameters and the high sensitivity to small parameter variations shown by these curves we feel that the correct parameters lie close to the following values, well within the indicated limits of error: C=O = 1.22 ± 0.03 Å., C—O (carboxyl) = 1.37 ± 0.04 Å., C—O (methoxyl) = 1.47 ± 0.04 A., ∠ O=C—O = 123 ± 4°, ∠ C—O—C = 112 ± 4°, configuration approximately *cis* with an average dihedral angle of 25° (limiting values, for the average, 0 and 40°). We have found that both the complete absence of the ninth maximum in curves like G or H and the bad quantitative disagreement in this region in Curve J can be relieved either by small changes in the long C . . . O distance (K, with a distance of 2.61 Å., is an extreme example, too far from J to justify simple interpolation beyond $q$ = 70) or by attentuating the long term for large scattering angles, as would in fact be the result of a moderate amplitude of oscillation of the dihedral angle about the value given above. Since it does not seem possible to make a reliable estimate of this amplitude, we present, in Table IV, the quantitative comparison of observed and calculated $q$ values for the rigid Model J. It will be noted in Table IV that there is bad disagreement for the

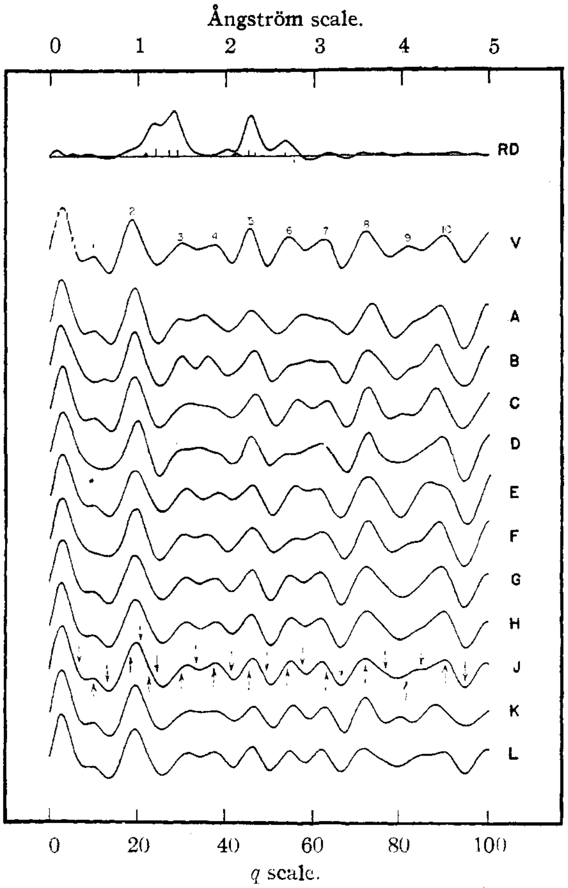


Fig. 2.—Methyl formate.

second maximum and third minimum. When the films were reëxamined it appeared that the original measurements might well have been in error, for it was found possible in good conscience to make measurements compatible with the theoretical curves; only the original values, however, are given in Table IV. Feature 2a, finally, can be perceived readily enough on the photographs, but its weakness and general nature are such as to correspond only to some such slight irregularity in slope on the outside of the second maximum as is shown, for example, by Curve J.

## Methyl Chloroformate

The radial distribution curve (RD in Fig. 3) shows a complicated first feature representing the bond distances between carbon and hydrogen or oxygen, 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, broad peak at 3.87 Å. which represents the distance between the chlorine and the methyl carbon atoms and corresponds to an almost planar molecule in the *cis* configuration.

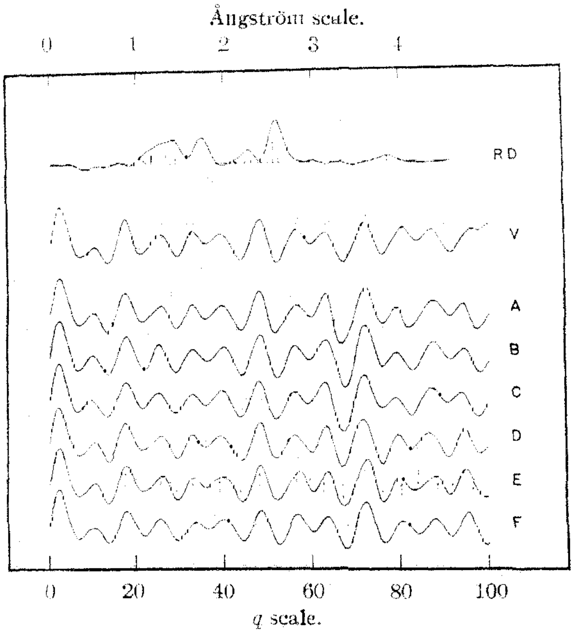
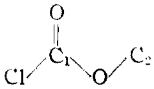


Fig. 3.—Methyl chloroformate.

Models A, B and C are, respectively, *cis*, *trans*, and free rotation versions of a skeleton whose parameters were based on a loose interpretation of the radial distribution curve. They are unsatisfactory. Model D was derived from the more careful consideration of the radial distribution curve, E is a modification of D suggested by the analysis of details of the curves, and F is a free rotation version of E. From D and E it may be inferred that good agreement in all details could be achieved for the whole range of $q$ values by a model having a rather large amplitude of oscillation about the equilibrium dihedral angle. The effective contribution of the variable distances would be reduced by a half at about $q = 50$ and this attenuation is indicated by the width, above background, of the 3.87 Å. peak in RD. Actual calculation of such a model was not attempted, because of the difficulty of an accurate estimate of oscillation amplitude and because the pattern is so dominated by terms involving the heavy chlorine atom that over-all parameter sensitivity is somewhat less than in the other two esters. The main results of the determination may be summarized as follows: C═O = 1.19 ± 0.03 Å., C—O (carboxyl) = 1.36 ± 0.04 Å., C—O (methoxyl) = 1.47 ± 0.04 Å., C—Cl = 1.75 ± 0.02 Å., ∠ O═C—O = 126 ± 4°, ∠ C—O—C = 111 ± 4°, ∠ Cl—C—O = 112 ± 3°, configuration approximately *cis* with average dihedral angle 20° (limiting values 0° and 30°). The quantitative comparison of observed and calculated $q$ values for Model E is given in Table VI; the average deviation is satisfactorily small but would be even less if the rotation dependent terms were attenuated for large values of $q$.

TABLE V

METHYL CHLOROFORMATE MODELS



∠α is the angle of the C—O—C plane with the OC—O plane

| | C═O, Å. | C₁—O, Å. | C₂—O, Å. | Cl—C, Å. | ∠ Cl—C—O | ∠ O═C—O | ∠ C—O—C | ∠α |
|---|---|---|---|---|---|---|---|---|
| A | 1.18 | 1.40 | 1.40 | 1.73 | 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 | 1.74 | 112 | 126 | 111 | 20 |
| F | 1.18 | 1.35 | 1.46 | 1.74 | 112 | 126 | 111 | Free |

For all models C—H = 1.09 Å., ∠H—C—H = $109^1/_2$°. Chloroformate skeleton planar.

## Discussion

The *cis* configuration assigned to simple carboxylic esters from studies of dipole moments is confirmed by our results for methyl acetate, methyl formate, and methyl chloroformate and the conclusion that this configuration is due, at least in part, to resonance is supported by the marked shortening found for the carboxyl C—O bonds as well as the apparent widening of the C—O—C angles. The greater than tetrahedral value of the X—C—O angle in methyl acetate and methyl chloroformate is also suggestive of double bond character of C—O bond, the O—C═O angle in every case being close to the value 125° of the classical model. The methoxyl C—O bond appears to be longer than normal by about 0.04 Å. We can offer no suggestion about the mechanism of this effect, which may possibly be associated with the resonance, but it is noteworthy that

Bailey[11] found an even greater lengthening (to 1.51 Å.) of the corresponding bonds in the diethyl terephthalate crystal.

TABLE VI

METHYL CHLOROFORMATE

Values in parentheses were omitted and values in square brackets given double weight in computing averages

| Min. | Max. | $q_{obs.}$ | $q_E/q_{obs.}$ |
|---|---|---|---|
| 1 | | 6.80 | (1.029) |
| | 1 | 10.16 | (1.024) |
| 2 | | 13.42 | (1.013) |
| | 2 | 17.27 | (1.008) |
| 3 | | 20.35 | (1.066) |
| | 3 | 25.49 | 1.012 |
| 4 | | 29.02 | 1.020 |
| | 4 | 32.77 | 1.004 |
| 5 | | 35.35 | [1.013] |
| | 5 | 38.84 | 1.017 |
| 6 | | 43.53 | [1.018] |
| | 6 | 47.78 | [1.005] |
| 7 | | 51.37 | [1.014] |
| | 7 | 56.28 | 1.013 |
| 8 | | 59.29 | [1.014] |
| | 8 | 62.53 | 1.011 |
| 9 | | 66.87 | [1.005] |
| | 9 | 71.80 | [1.006] |
| 10 | | 75.79 | 1.005 |
| | 10 | 80.24 | 0.995 |
| 11 | | 83.93 | .992 |
| | 11 | 88.41 | .995 |
| 12 | | 91.85 | .993 |
| | 12 | 96.34 | .983 |
| | | Average | 1.007 |
| | | Average deviation | 0.007 |

The bond distances and bond angles values reported by Bailey (C=O, 1.28 Å.; C—O, 1.32 Å. and 1.51 Å.; ∠ C—O—C, 117°; ∠ O—C=O, 125°; ∠ C—C—O, 125°) can be made to seem generally consistent with our results if it is assumed that the extent of resonance is considerably greater in the terephthalate than in our simple esters, not only in the expected conjugation of the double bond with the benzene ring but also with the unshared electron pairs of the ethoxyl oxygen atom. The fact that the ester skeleton is completely planar in the crystal in contrast to the average dihedral angle of 20 or 25° in our gas molecules would of course lead to increased conjugation of the latter sort, but it is not clear that the effect should be so large or that it should not be cancelled out by the cross-conjugation with the ring.

For the crystal structure of pentaerythritol tetraacetate, Goodwin and Hardy[12] reported results that, on the whole, might be interpreted as indicating no resonance, in contradiction to all the other evidence which has been cited here. Doubt is cast on their determination, however, by the astonishingly large (1.33 Å.) C=O distance, which is altogether inconsistent with this interpretation, and by an improbable lack of planarity of the acetate skeleton, amounting to a displacement of the carboxyl carbon atom relative to the plane of the acetate group of about 0.20 Å.

Our average dihedral angle of 20 or 25°, and the indications of a considerable amplitude of oscillation about these averages are compatible with various possibilities, including, for example, a rather wide oscillation about the completely planar *cis* configuration or an actual failure, perhaps due to steric influences, to attain true planarity coupled with considerable variability of the long unbonded interatomic distances due to dihedral oscillation and to other vibrations of the molecule. In this regard the exact configuration cannot be considered as established by our work.

Finally, it remains to mention that the possibly somewhat shortened C=O and C—Cl distances in methyl chloroformate are similar to those determined[13] for phosgene, which gave 1.18 Å. for C=O and 1.74 for C—Cl.

## Summary

The structures of the methyl formate, methyl acetate, and methyl chloroformate molecules have been investigated by electron diffraction in the gas phase. They all have approximately planar heavy-atom skeletons with the ester methyl group *cis* to the carbonyl oxygen atom, in agreement with earlier evidence from dipole moment measurements and theoretical arguments. A moderate amplitude of rotatory oscillation of the methoxyl groups relative to the carboxyl groups seems to be indicated but a precise estimate of its magnitude could not be obtained. The bond distance and bond angle results for the three molecules are the following: Methyl formate, C=O, 1.22 ± 0.03 Å.; C—O (carboxyl), 1.37 ± 0.04 Å.; C—O (methoxyl), 1.47 ± 0.04 Å.; ∠ O=C—O, 123 ± 4°; ∠ C—O—C, 112 ± 4°; average dihedral angle of rotation from the planar configuration, 25° (limiting values for the average, 0° and 40°). Methyl acetate, C=O, 1.22 ± 0.03 Å.; C—C, 1.52 ± 0.04 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°; average dihedral angle of rotation from the planar configuration, 25° (limiting values for the average, 0° and 35°). Methyl chloroformate, C=O, 1.19 ± 0.03 Å.; C—O (carboxyl), 1.36 ± 0.04 Å.; C—O (methoxyl), 1.47 ± 0.04 Å.; C—Cl, 1.75 ± 0.02 Å.; ∠ O=C—O, 126 ± 4°; ∠ C—O—C, 111 ± 4°; ∠ Cl—C—O, 112 ± 3°; average dihedral angle of rotation from the planar configuration, 20° (limiting values for the average, 0° and 30°). Because of the comparatively great complexity of these molecules, it was not

---

(11) M. Bailey, *Acta Cryst.*, **2**, 123 (1949).

(12) T. H. Goodwin and R. Hardy, *Proc. Roy. Soc.* (*London*) **A164**, 360 (1938).

(13) V. Schomaker, D. P. Stevenson and J. E. LuValle, to be published.

possible to make wholly reliable assessments of the limits of error; the values given are only somewhat rough estimates.

PASADENA 4, CALIF. RECEIVED MARCH 9, 1950

---

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Electrolytic Properties of Aqueous Solutions of Polyacrylic Acid and Sodium Hydroxide. II. Diffusion Experiments Using Radioactive Sodium[1]

BY JOHN R. HUIZENGA,[2] PHILIP F. GRIEGER AND FREDERICK T. WALL

## I. Introduction

Previous work[3] on the electrical transference properties of polyacrylic acid-sodium hydroxide solutions, using radioactive sodium as a tracer, has shown that a significant fraction of the sodium ions are associated with the polymer. Kern[4] arrived at a similar conclusion, but his estimates of the fraction of associated sodium, based on osmotic pressure and conductance measurements, are in poor agreement with each other as well as with our transference results. In making his computations from conductance measurements, Kern assumed that a negligible fraction of the current was carried by polymer ion. Transference measurements, however, show this assumption to be invalid, for over the range 25 to 100% neutralization, the polymer ion carries roughly half the current. Consequently, Kern's estimate based on conductivities gives much too low a value for bound sodium. On the other hand, his osmotic pressure measurements appear to lead to values which are too high, judging from his observed osmotic pressures for pure acid solution, which are as much as 30% lower than those computed from the *p*H values of the solutions.

Our results obtained from transference experiments are roughly midway between Kern's two estimates, but in view of the poor agreement between the three methods, it appeared worthwhile to test the validity of the transference results in another way. This report gives the results of such a test, made by measuring the diffusion of radioactive sodium in otherwise uniform solutions of polyacrylic acid and sodium hydroxide, using the steady state technique.[5,6] The present work confirms the transference results.

## II. Basis of the Experiments

Radioactive tracers are particularly suitable for diffusion experiments because they can be used to follow molecular or ionic movements in systems of uniform total concentration. Consider a solution of an electrolyte, $C_{\nu_1}A_{\nu_2}$, with its corresponding tracer, $C^*_{\nu_1}A_{\nu_2}$, and let the cation charge be $e_1$ and the anion charge $e_2$. Let us denote the concentrations of the ions of C, C* and A by $n_1$, $n_1{}^*$ and $n_2$, respectively. Then in one dimension, the flow equations are[7]

$$J_1 = -kT\,\omega_1\,\partial n_1/\partial x - kTn_1\omega_1\,\partial \ln \gamma_1/\partial x + n_1\,\omega_1 e_1 E$$
$$J_1^* = -kT\,\omega_1\,\partial n_1^*/\partial x - kTn_1^*\omega_1\,\partial \ln \gamma_1/\partial x + n_1^*\,\omega_1 e_1 E$$
$$J_2 = -kT\,\omega_2\,\partial n_2/\partial x - kTn_2\omega_2\,\partial \ln \gamma_2/\partial x + n_2\,\omega_2 e_2 E$$

where $k$ is Boltzmann's constant, $\gamma_i$ the appropriate activity coefficient, $E$ the electric field intensity and $\omega_i$ the mobility of the $i^{\text{th}}$ species.

Let us now imagine a diffusion cell consisting of two compartments, only one of which originally contains tracer. In particular, if $n_2$ is constant throughout the cell, it is clear that in the absence of an external field, $E = 0$, $\partial \ln \gamma_i/\partial x = 0$, $J_2 = 0$ and $\partial n_1/\partial x + \partial n_1^*/\partial x = 0$. Then

$$J_1^* = -kT\omega_1 \partial n_1^*/\partial x$$

so a measurement of the tracer flow will enable one to calculate the corresponding ionic mobility providing the concentration gradient of tracer is known. For this particular system, the diffusion coefficient should be defined as

$$D_1^* = kT\omega_1 \qquad (1)$$

Clearly $D_1^*$ does not depend upon either $\omega_2$ or the activity coefficients.

Now let us consider a slightly different system in which $n_1$ is initially uniform throughout the diffusion cell. If tracer is now added to one of the compartments, then $n_2$, as well as $n_1{}^*$, will not be the same on both sides. Under these circumstances, $E$ and $\partial \ln \gamma_i/\partial x$ are not exactly zero, although they can be estimated as follows. To compute the order of magnitude of $E$, first neglect the activity coefficient terms. Then if we stipulate zero electric current, $e_1J_1 + e_1J_1^* + e_2J_2 = 0$, and electroneutrality, $n_1e_1 + n_1^*e_1 + n_2e_2 = 0$, it follows that

$$E = \frac{kT(\omega_2 - \omega_1)\,\partial n_2/\partial x}{(e_2\omega_2 - e_1\omega_1)n_2}$$

Putting the above expression for $E$ into the flow equations discloses that the third term of $J_1^*$ is less than the first term by a factor of the order of magnitude $n_1^*/n_1$ providing $|\partial n_1/\partial x|$ is not substantially greater than $|\partial n_1^*/\partial x|$, which is certainly true.

---

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Argonne National Laboratories Chicago, Ill.

(3) Huizenga, Grieger and Wall, THIS JOURNAL, **72**, 2636 (1950).

(4) Kern, *Z. physik. Chem.*, **A181**, 249 (1937-1938); **A181**, 283 (1937-1938); **A184**, 197 (1939); **A184**, 302 (1939).

(5) Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

(6) Brady and Salle, THIS JOURNAL, **70**, 914 (1948).

(7) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).