kcal./mole for the heat of isomerization and ±0.038 kcal./mole for the heat of vaporization.

The simplified equations

$$-\Delta H_i = 0.16\Delta t + 0.02\Delta p$$
$$\Delta H_{v_n} - \Delta H_v = 0.05\Delta t - 0.08\Delta p$$

relate the heats of combustion and of vaporization of the paraffins to their boiling points.

Predicted values of thermochemical properties for the 35 nonanes are given.

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An Electron Diffraction Investigation of Formic Acid Monomer

BY VERNER SCHOMAKER AND JOHN MICHAEL O'GORMAN[1]

In the course of an investigation of the structure of some simple esters,[1a] 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.[2] It seemed unlikely that replacement of the acid hydrogen atom 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.

The present study has confirmed our doubts as to the validity of the earlier investigation, and shows that formic acid monomer, actually in close agreement with the simple esters, has a carbon-oxygen double bond distance only a trifle greater than normal, a carbon-oxygen single bond distance considerably less than normal (presumably due to resonance), and an O—C=O bond angle only slightly less than the angle $125^1/_4°$ of the classical tetrahedral model. It appears that Karle and Brockway misinterpreted their photographs and greatly overstated the reliability of their work; the possibility of an important discrepancy between the two sets of photographs may be ruled out of consideration inasmuch as the experimental procedures, although differing somewhat in the means employed for obtaining monomeric molecules of formic acid, both appear to be satisfactory.

Experimental

Formic acid is largely in the form of dimer at temperatures where its vapor pressure is suitable for use in the usual electron diffraction apparatus. 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°, to give the proper pressure (*ca.* 300 mm.), and then to admit the vapor into the camera through a stopcock and a special nozzle separately heated to approximately 250°. This scheme is different from that adopted by Karle and Brockway[2] and has the advantages of simplicity and convenience and of not requiring that the substance under investigation be maintained in contact with stopcock grease or other materials at high temperatures for relatively long periods of time. Its obvious possible disadvantage—that the rate of dissociation might not be sufficient for substantial attainment of equilibrium in the moment required for gas to pass through the heated portion of the nozzle—has been allowed for in the operating procedure, and, moreover, has been shown to be of no consequence in the case of formic acid. (The rate of dissociation of formic acid dimer would be very rapid indeed, if, as seems likely, the energy of activation for the reaction of breaking the hydrogen bonds in the dimer is equal merely to the bond energy of these bonds.)

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 of entrance of the glass tubing into the camera 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 free 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 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°. By repeating

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[1a] J. M. O'Gorman, W. Shand, Jr., and V. Schomaker, to be published.

[2] J. Karle and L. O. Brockway, THIS JOURNAL, 66, 574 (1944).

the process, a product was obtained which melted very sharply at 8.4°.

Extrapolation of the data of Coolidge[3] indicated that a vapor temperature of about 200° 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°. The pictures at 50° were characteristic of the dimer,[2] having inner features very different from those made at higher temperatures. At 125° 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°.

The investigation was carried out in the apparatus described by Brockway.[4] The photographs were taken at a camera distance of 10.84 cm. with electrons of wave length 0.0609 Å. (corrected for film expansion), as determined by standardization against zinc oxide.[5]

Interpretation of the Photographs

The appearance of the pictures is represented by curve V in Fig. 3 except for an eleventh ring just beyond $q = 100$, whose diameter was measured but which could not be seen clearly enough to make it worthwhile for use in the structure determination. This visual curve[6] was drawn for $q > 18$ before any theoretical curves had been examined, and the dotted portion was filled in subsequently from a preliminary theoretical intensity curve. Reëxamination of the photographs during the course of the investigation showed that the third minimum may well be slightly deeper, the fourth maximum is appreciably stronger, and the eighth minimum is considerably deeper than shown, but otherwise confirmed curve V as being everywhere correct within the limits of our ability to see the features of the photographs and to interpret them in terms of our theoretical intensity curves. The eighth minimum, although not represented deep enough in curve V, is nevertheless shown in correct qualitative relation to the adjoining much stronger seventh and somewhat stronger ninth minima. Reëxamination of the photographs suggested also that the eighth maximum may be considerably stronger than shown by V and the seventh maximum somewhat so, but unfortunately it was not possible to make a sharp decision on these points (which would have been most useful in narrowing the final range of acceptable models), because the tenth and eleventh maxima, the outer members of the group of neighboring rings needed for comparison in making such a sharp decision, are not very distinct. It will be noticed that four more rings were measured than were reported by Karle and Brockway.[2]

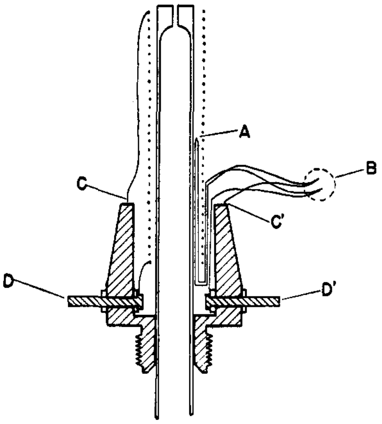

Fig. 1.—A, Thermocouple; B, thermocouple "cold junction" where the thermocouple elements are joined to copper wires; C,C', grounded connections; D,D', insulated lead-ins. Electrical and thermal insulation is provided by a layer of asbestos cord wound between the thermocouple and the heating coil, and by another layer enclosing the entire nozzle.

Curve V was used in the evaluation of the radial distribution function[4] by the approximation[6]

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

with $q_i = 1,2,3,\cdots,100$, $q = (10/\pi)s = (40/\lambda) \sin \varphi/2$, and $\exp[-a'(100)^2] = 0.10$. The resulting curve, RD in Fig. 3, has main peaks at 1.27 and 2.27 Å., in fair agreement with that of Karle and Brockway,[2] which has main peaks at 1.33 and 2.27 Å. The second peak represents the unbonded O···O distance, and the first peak, which is notably broad, is an unresolved representation of the singly and doubly bonded carbon–oxygen distances with an inside shoulder representing the C–H and O–H distances. If allowance is made for this shoulder and for the unequal weights ($1/r_1$ and $1/r_2$) 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,[6] most of which are shown in Fig. 3, were drawn for the preferred model of Karle and Brockway[2] (C—O = 1.42 Å., C═O = 1.24 Å., ∠ O—C═O = 117°) and for seventeen other models in which the ratio of the longer to the shorter carbon–oxygen distance was varied from 1.33/1.25 Å. to 1.41/1.17 Å., keeping the average of the two distances constant at 1.29 Å., and the angle O—C═O was varied from 121 to 129°, as indicated by the plot of C—O/

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[3] A. S. Coolidge, THIS JOURNAL, **50**, 2166 (1928).

[4] L. O. Brockway, *Revs. Modern Phys.*, **8**, 231 (1936).

[5] C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943).

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

C=O *vs.* ∠ O—C=O in Fig. 2. For all curves the assumed C–H (1.09 Å.) and O—H (0.97 Å.) terms were multiplied by the 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 a direct indication of their maximum possible effect, which is quite small; moreover, interpolation between CB and CBH according to a reasonable temperature factor shows that the actual effect of these terms is negligible except in the neighborhood of the first and third maxima.

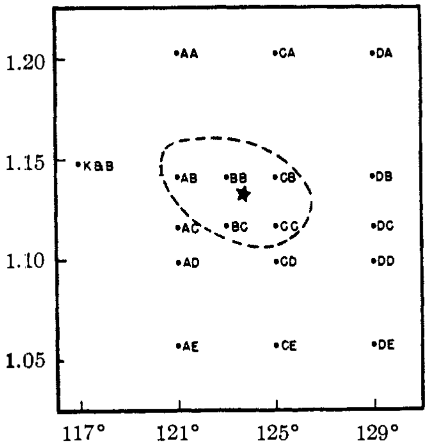

Fig. 2.—Models for which theoretical curves were calculated. The star represents the most satisfactory model and the dotted line indicates the limits of uncertainty.

Models having the extreme bond ratios C—O/C=O of 1.064 and 1.205, such as CA and CE, are easily eliminated because of the absence of even rough qualitative agreement; see Fig. 3. Similarly, but not to the same degree, models such as DB and K&B with the greatest or least bond angles considered by us are not at all satisfactory.

The Evidence against Karle and Brockway's Model.—These statements are illustrated by the curves themselves; however, the case against Karle and Brockway's model will now be separately described, as an example and because of its obvious importance:

(1) The aspects of the photographs which are most obvious and most important in forcing us to reject this model[7] are the pronounced doublet character of the fifth and sixth maxima and the similar but less pronounced association of the sixth and seventh maxima. Curve K&B utterly fails to reproduce these characteristics, which may also be stated in terms of the concomitant relative depths of the fifth, sixth, seventh, eighth and ninth minima as described above and shown by our visual curve.

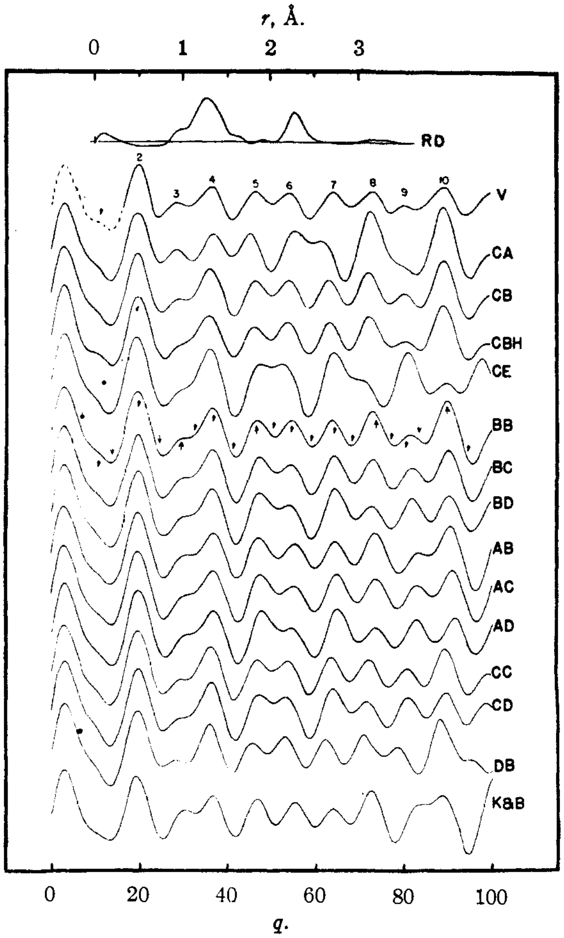

Fig. 3.—Formic acid monomer. Radial distribution curve, visual intensity curve, and theoretical intensity curves for models defined by the coördinates of the corresponding labelled points in Fig. 2.

(2) The ninth ring, which is weak and lies just to the outside of the center of the broad minimum comprising the ninth maximum and the ninth and tenth minima, is completely misrepresented by curve K&B, which places it so far up the side of the tenth maximum as to make of the whole affair a slightly unsymmetrical double maximum instead of a slightly unsymmetrical double minimum. We do not rate this relatively enormous change as more important than the changes listed under (1) because the interpretation of the appearance of the ninth and tenth rings, which are near the edge of the photographs and not so strong as to be visible without some difficulty, must be made more liberally than that of the observationally more favored parts of the pattern.

(3) The third ring very definitely appears as indicated by curve V, forming part of a steeply sloping but still somewhat shelf-like formation that begins with the third minimum and culmi-

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(7) There are no features of the diffraction pattern of formic acid monomer which are in a general way of outstanding importance for the choice of the most satisfactory model; however, any particular parameter variation does affect some of the features more strongly than the others, and, as is always true except in certain resolution problems, the appearance of the outer rings is generally the most sensitive to small parameter variations.

nates in the fourth maximum, and decidedly does not correspond to curve K&B, which would require that the third minimum appear sharp and deep compared to the fourth and that the third and fourth maxima together appear as an unsymmetrical doublet.[8]

We should not care to press this last point, which we regard as only barely sufficient to eliminate curve K&B and by far the least important of the three here described, except that it appears to be the only significant point of differentiation according to which Karle and Brockway based the rejection, in favor of their Model B, of their Models C, D, and M, the approximately correct models considered by them. We make this inference, in the absence of any indication by Karle and Brockway as to their reasons for rejecting their Models C, D and M, because the crucially important fifth to eighth rings lie partly beyond the range of their observations and calculations and partly just at the edge of that range (where, as we have emphasized above, it is never possible in the visual method to make reliable decisions about any other than rather great differences among theoretical intensity curves) and because the only other notable difference in common between their accepted curves B, A, K and L and their rejected curves C, D and M is in the relative depths of the first and second minima, a difference which is clearly evident in the theoretical curves but, involving a weak inner ring, is of a sort that is well known to be virtually incapable of reliable determination by visual inspection of the photographs.

It is our conclusion, then, that model K&B is incorrect, being incompatible with our photographs, and that its selection by Karle and Brockway probably was the result mainly of an incorrect interpretation of the appearance of the photographs in the neighborhood of the third ring. We believe it is highly unlikely that in the same circumstances we might have made the same error, which corresponds, according to our final results, to an error of $-5^1/_2°$ in the O—C=O bond angle, but the uncertainty of the interpretation of the third ring is such that the possibility of an only slightly smaller error could not be ruled out. Accordingly, the estimated limit of error, ±2°, placed by Karle and Brockway on their determination of this bond angle seems unreasonably small; with over two times the number of usefully sensitive features at our disposal, and with much more sensitive features at that, we have found it to be impossible to assign a narrower limit of error[9] than ±3° to our value for the same angle.

Choice of Best Model (Determination of the Shape Parameters by the Correlation Procedure Qualitative Comparisons).—In regard to qualitative representation of the observed pattern curve BB is the most satisfactory of the curves which were actually plotted, but it seems clear that the best model has a slightly larger angle ($123^1/_2°$) and a slightly lower bond ratio, corresponding to a point approximately one quarter of the way along a line from BB to CC in Fig. 2. We base this conclusion mainly on aspects of the pattern which are obvious in curve V and have already been mentioned, but there is one not altogether obvious characteristic of the pattern (and of curve V) which has not entered the argument heretofore and needs to be separately emphasized. This characteristic, one consequence of which is that the average height of the sixth and seventh maxima is less than that of the fifth and eighth, may be better described in terms of the smooth, concave-upward nature of the envelope that may be drawn to these maxima.

In regard to this characteristic each of the moderately satisfactory curves AB, BB and CB, of bond ratio 1.132, is fully satisfactory. Among these curves BB is definitely to be preferred, since in AB the nature of the ninth ring is incorrect and the fourth maximum is too weak relative to the fifth maximum, while in CB the minima on either side of the ninth feature are again in incorrect relationship (now in the opposite sense), the fourth maximum is too strong relative to the fifth, and the third minimum seems to be not deep enough. This evidence cannot be considered sufficient to eliminate CB and AB from consideration entirely, but rather serves together with the evidence on curves K&B and DB for setting the limits of the determination in the neighborhood of AB and CB, as shown in Fig. 2.

However, all the models of bond ratio 1.132 suffer from some defects in common. In particular, the eighth minimum is distinctly too deep compared to the seventh, as is the ninth to a lesser and less certainly detectable extent, and the fifth maximum appears to be 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 1.114, as in models AC, BC and CC, these defects invariably are diminished, and in most cases (the depth of the eighth minimum is an exception) reversed. Furthermore, the

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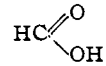
(8) In order to secure checks on our interpretation of the third ring in addition to that already provided by the present structure determination, of which the fine points depend on the outer rings of the pattern, we have made direct comparison with the photographs and curves for VCl_4 (W. N. Lipscomb and A. G. Whittaker, THIS JOURNAL, **67**, 2019 (1945)), As_4O_4 (G. C. Hampson and A. J. Stosick, *ibid.*, **60**, 1814 (1938)), and PSF_3 (D. P. Stevenson and H. Russell, Jr., *ibid.*, **61**, 3264 (1939)), which happen to show similar features. These comparisons fully confirm our interpretation but do not justify its use in a more restrictive way than described above, the third ring of the formic acid photographs not being nearly enough identical in appearance and situation to any of the similar rings of the comparison photographs.

(9) Since Karle and Brockway make frequent use[3] of the words "acceptable" and "inacceptable" with apparently the usual connotation, we assume that it was their intention to assign estimates of error in the sense that has been customary in this work; namely, as *limits of error* equal to the greatest errors which, in view of the common knowledge of the method and the judgment of the investigator, might be feared as results of the normal uncertainties of the work. (Excepting simple mistakes and other totally unrecognized circumstances, such estimated limits of error would be exceeded by the actual errors only very rarely.)

smoothness and upward-concavity of the envelope of the fifth to eighth maxima is destroyed and the ninth maximum becomes too strong, probably to a significant extent. All this indicates that the true bond ratio lies between 1.132 and 1.114, but closer to 1.132.

Curve AC differs so greatly from V in almost all features that it may be considered as eliminated from consideration, and curve BC, differing in the same ways (fifth and seventh maxima much too strong compared to their adjacent maxima, third maximum too far up the side of the fourth maximum) but not to the same degree, lies near the limit of acceptability. Curve CC is the best of those with bond ratio 1.114, but in agreement with the conclusion of the last paragraph it is considerably less satisfactory than BB, having the seventh maximum too strong, the eighth minimum too weak, and the ninth ring too strong. It may be seen that the limit of acceptability must lie very close to CC in the direction of CD, but that in the direction of increasing bond angle a greater tolerance needs to be allowed.

These considerations, then, along with many others which are certainly not independent of them but no doubt have significance in view of the complex relation between our actual observations and the theoretical curves, lead to our selection of the limits of uncertainty and best model plotted in Fig. 2. Such considerations have been made not only for the models for which curves were calculated as indicated in Fig. 2 but also, by visual interpolation, for all models lying among these. (The radial distribution curve provides adequate assurance that no other even remotely reasonable models corresponding to the formula  $\mathrm{HC}\genfrac{}{}{0pt}{}{/\!\!/\mathrm{O}}{\diagdown\mathrm{OH}}$ could be found to agree with the photographs.) It should be noted as an example of this process that the curve for the best model as estimated by interpolation between curves BB and CC shows none of the deficiencies of either curve BB or CC and gives a completely satisfactory representation of the appearance of the photographs and of curve V. (The evident slight discrepancy in regard to the exact depth of the eighth maximum has already been discussed at the beginning of this section.) If it were justifiable to make a statistical internal estimate of error for this determination of molecular shape, our success in obtaining with a two-parameter function an essentially perfect fit of such a relatively complicated curve as V would no doubt find expression in small standard errors—for example, of perhaps a half or three quarters of a degree in the bond angle—and these would be consistent with the extent to which we have been able to utilize fine points of interpretation for deciding precisely on our best model. But it does not now seem justifiable in the visual method to attempt either such internal estimates of standard error, or external estimates of standard error (except, perhaps, in regard to the over-all size determination, see below); we must be content with the essentially different statement of limits of error.[9] These limits usually have to be placed considerably beyond the range of the distribution function corresponding to guesses, such as the above, as to the standard errors.

Determination of the Interatomic Distances by the Correlation Procedure Quantitative Comparison.—Values of $q_{\text{calc.}}/q_o$ are shown in Table I for models AB, BB, CB, CC and (BB + CC/2), an interpolated model half way between BB and CC. The values for the interatomic distances C=O, C—O, and O···O which result from the assumption of each of these models are shown as calculated from the average of $q_{\text{calc.}}/q_o$ for the eleven most reliably measurable features of the pattern and the interatomic distances actually assumed in the calculation of the curves. (Being rounded to even hundredths of an ångström, by mistake not always in the correct direction, the assumed O···O distance sometimes differs from that corresponding to the nominal bond angle (Fig. 2) by as much as 0.006 Å.) Two other sets of averages of $q_{\text{calc.}}/q_o$ are shown in order to illustrate the stability of the results with respect to other possibly reasonable schemes for weighting the measurements, which are of recognized inferior reliability, of the weak or strongly asymmetric features.

These comparisons, when interpolated to the best model selected in the qualitative considerations, lead to our final results for formic acid monomer: C=O = 1.213 ± 0.026 Å., C—O = 1.368 ± 0.034 Å., O···O = 2.275 ± 0.025 Å., and, directly from the qualitative comparison, ∠ O—C=O = $123^1/_2°$ ± 3° and C—O/C=O = 1.127 ± 0.018. It is our belief that neither the distance values themselves nor their quoted limits of uncertainty would suffer any significant loss of meaning if they were rounded to even hundredths of an ångström in either direction; however, it must be remembered that possible errors compatible with the determination are contingent in ways that cannot be expressed by simple statements, such as these, of separate limits of uncertainty for each of the measured quantities. This is obvious so far as the shape determination is concerned, and for the distances can be seen already in Table I without reproducing the maps of distance values which were prepared (by extrapolation) for the determination of the distance limits. Each of these limits is the sum of a term representing the greatest uncertainty so determined as resulting from the limits of error of the shape determination (Fig. 2) and of a term proportional to the distance, to allow for the effect of the estimated possible error of the size determination for any particular assumed shape of model. This term was taken as 0.018 Å. for the O···O distance in order to allow for the 0.010 Å. limit of error observed in These Laboratories in a series of checks[10] on diatomic mole-

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(10) V. Schomaker and D. P. Stevenson, unpublished investigations. The results of these checks could of course also be expressed in terms of a standard error.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED POSITIONS OF MAXIMA AND MINIMA

Min.	Max.	q_0	AB	BB	$q_{\text{calc.}}/q_0$ CB	CC	$\frac{BB + CC}{2}$
2		14.1	(0.950)	(0.957)	(0.979)	(0.965)	(0.961)
	2	20.0	1.010	1.005	1.005	.990	.998
3		24.6	(1.053)	(1.053)	(1.053)	(1.037)	(1.045)
	3	29.5	(1.030)	(1.024)	(1.003)	(0.986)	(1.005)
4		32.6	(0.954)	(0.957)	(0.960)	(.963)	(0.960)
	4	36.9	1.003	.992	.984	.986	.989
5		41.4	1.022	1.012	1.007	1.007	1.010
	5	46.7	1.015	1.004	1.002	1.004	1.004
6		50.3	1.036	1.012	1.000	1.000	1.006
	6	54.3	1.022	1.009	0.996	0.991	0.995
7		59.0	1.017	1.003	.997	.993	.998
	7	64.1	1.009	0.995	.986	.992	.994
8		68.2	1.015	.998	.990	.996	.997
	8	73.6	1.001	.990	.984	.981	.986
9		76.9	(1.027)	(1.014)	(1.003)	(.986)	(1.005)
	9	80.4	(1.035)	(1.014)	(1.000)	(1.005)	(1.010)
10		83.3	(1.029)	(1.016)	(1.010)	(1.016)	(1.016)
	10	89.8	1.011	1.001	0.994	0.994	0.998
Av. 17 features[a]			1.017	1.006	.998	.996	1.001
Av. deviation			0.014	0.013	.011	.011	0.011
Av., 14 features[a,b]			1.018	1.005	.997	.996	1.000
Av. deviation			0.0090	0.0071	.0077	.0069	0.0069
Av., 11 features[a,b,c]			1.015	1.002	.995	.994	.998
Av. deviation			0.0071	0.0061	.0067	.0056	.0050
C=O, Å.			1.228	1.212	1.204	1.213	1.213
C—O, Å.			1.391	1.373	1.363	1.352	1.362
O···O, Å.			2.274	2.275	2.279	2.276	2.275

[a,b,c] Averages taken with the omission of the $q_{\text{calc.}}/q_0$ values for: (a), the very unreliable (*i. e.*, on a percentage basis) measurement of the second minimum; (b), the unsymmetrical and weak third and fourth minima and third maximum; and (c), the similarly difficulty ninth and tenth minima and ninth maximum.

cules with a considerable range of internuclear distances and for an additional 0.008 Å. which we believe is sufficient to account for any additional uncertainty that arises from the slight instability of the $q_{\text{calc.}}/q_0$ averages with respect to systematic rejection of the two groups of unreliable features. Our standard allowance of 0.010 Å. was assigned to the O···O distance inasmuch as it evidently is the distance which in this relatively simple problem characteristically determines the number and, generally, the positions of the measured rings.

The average deviations of the quantitative comparisons are all satisfactorily small, particularly the more important eleven-feature averages, that for the best model being definitely significantly smaller (0.0050) than the corresponding value 0.0110 for Karle and Brockway's best model and the corresponding selection (rejection of third minimum and maximum) of their data; however, the average deviations show a trend, which we have noticed in other cases as well, that in a general way supports the qualitative-comparison choice of model. The indications of the eleven-feature average deviations actually agree almost precisely with the qualitative comparisons, but in general the trends seem to suggest a slight increase in the bond angle, possibly to a value greater than 124°. Although this indication may possibly be significant, we decided to give it no weight in our final results as quoted above.

It is interesting that for our data the 2.275 Å. contour or *isotel* for the resulting O···O distance (see above) passes close to the point representing Karle and Brockway's model. Accordingly, it is not surprising that although their results (C=O = 1.24 ± 0.03 Å., C—O = 1.42 ± 0.03 Å., ∠ O—C=O = 117 ± 2°, $C{\cdot\cdot}O_{\text{av.}}$ = 1.33 Å. (*vs.* our 1.29 Å.), and O···O = 2.27 Å.) are generally in considerable or great disagreement with ours, in this one respect the agreement is essentially perfect. This observation suggests that the experimental *s* (or *q*) scales of the two sets of data must be in agreement. Direct comparison shows that they indeed are so: the average algebraic deviation for the seven features which were used in the final comparisons of both investigations is only 0.27%, our measured *s* values being generally the smaller. This is true even though the average absolute deviation between the two sets of measurements is very much greater (1.8% for the same selection of features), as is natural since differences in interpretation of the finer details of the pictures were obviously involved and since the accuracy of the individual s_0 values may be inferred from the average deviations of the s/s_0 averages to be certainly not much better than 0.5% for our measurements nor than 1.0% for Karle and Brockway's. (It would be entirely misleading to include the very widely deviating measurements of the third minimum and third maximum in this consideration of the respective s_0 scales because it is obvious that these deviations are simply representations of the extremely different qualitative interpretations made of these features in the two investigations.) To express this matter in still another way, Karle and Brockway's measurements for the second maximum and the consecutive features from the fourth maximum to the seventh minimum lead with our model BB to an average $q_{\text{calc.}}/q_0$ of 1.002, in excellent agreement with our averages.

NOTE ADDED OCTOBER 20, 1947.—On the basis mainly of spectroscopic data Van Zandt Williams has recently reported[11] the following complete set of structural parameters for the formic acid monomer molecule, which, he concludes, is planar

$$\text{C—H} = 1.08 \pm 0.01\ \text{Å., O—H} = 0.96 \pm 0.01\ \text{Å., C=O} = 1.225 \pm 0.02\ \text{Å., C—O} = 1.41 \pm 0.02\ \text{Å.,} \angle\text{O—C=O} = 125 \pm 1°, \angle\text{C—O—H} = 107 \pm 5°, \text{and} \angle\text{H—C=O} = 122 \pm 5°.$$

The rather poor agreement between the electron diffraction results and Williams' values can be reëxpressed significantly in terms of the principal moments of inertia, which are more directly related to the spectroscopic data. Our value for the small moment of inertia (assuming Williams' hydrogen-atom parameters) is very nearly equal to Williams' but is considerably different from Karle and Brockway's; however, the electron diffraction values for the intermediate moment of inertia, which depends essentially on the O···O distance, are in agreement and about 5% smaller than Williams'. The parameters of Williams' model which define the small moment of inertia are well confirmed by measurements on several absorption bands of HCOOH[11,12,13] and its three deuterated derivatives[11]; on the other hand, Williams' value for the intermediate moment is derived from Bauer and Badger's determination[12] of the rotational fine-spacing constant δ, which, depending on the interpretation of one incompletely band, may possibly[14] be in error by more than the original estimate of 1%, and the disagreement with our model involves just the parameter —O···O— for which (we have argued above) there is significant agreement between the two electron diffraction investigations.

Acknowledgment.—We are indebted to the International Business Machines Corporation for the loan of the equipment used in making the radial distribution function and intensity function summations.

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 = 1.213 ± 0.026 Å., C—O = 1.368 ± 0.034 Å., O···O = 2.275 ± 0.025 Å., ∠ O—C=O = 123$^1/_2$ ± 3°, and C—O/C=O = 1.127 ± 0.018. The arguments leading to these values are given in relatively great detail, and a careful effort is made to explain the probable nature of the errors that led to considerably different results in an earlier investigation.[2]

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(11) Van Zandt Williams, *J. Chem. Phys.*, **15**, 232 (1947).

(12) S. H. Bauer and R. M. Badger, *J. Chem. Phys.*, **5**, 853 (1937).

(13) H. W. Thompson, *ibid.*, **7**, 453 (1939).

(14) Private communication from Professor Badger.

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[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Reaction of Coal with Oxygen in the Presence of Aqueous Sodium Hydroxide. Effect of Methylation with Dimethyl Sulfate[1]

BY G. R. YOHE[2] AND EVA O. BLODGETT[3]

If pulverized bituminous coal is suspended in aqueous alkali and subjected to the action of oxygen at elevated temperatures and pressures, the coal substance can be converted practically completely to carbon dioxide and a mixture of relatively simple acids in which aromatic polycarboxylic acids predominate. Smith, Tomarelli and Howard subjected various coals to this type of oxidation at 100–250° with oxygen under pressures of 100–300 pounds per square inch[4]; Franke and Kiebler operated at 200–300° with total pressures of 500–1200 pounds per square inch and obtained an acid product of average equivalent weight of 80 and an average molecular weight of 250.[5] The use of much milder conditions, however, results in a much slower reaction and less far-reaching degradation of the coal substance. Smith, Tomarelli and Howard noted a very slow reaction rate below 225°[4]; other work has shown that when air is bubbled through a suspension of coal in aqueous sodium hydroxide at 95 ± 5° for three weeks, the principal product in the case of bright coals is humic acid.[6] The literature on oxidation of coal has recently been summarized by Howard.[7]

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(1) Presented before the Division of Gas and Fuel Chemistry, Atlantic City, N. J., April 17, 1947. Published with permission of the Chief, Illinois State Geological Survey.

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(4) R. C. Smith, R. C. Tomarelli and H. C. Howard, THIS JOURNAL, **61**, 2398–2402 (1939).

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(6) G. R. Yohe and C. A. Harman, *Trans. Illinois Acad. Sci.*, **32**, 134–136 (1939).

(7) H. H. Lowry, editor, "Chemistry of Coal Utilization," Vol. I, John Wiley and Sons, New York, N. Y., Chap. 9, pp. 346–376.