pounds given by Franklin and Field[8] in the form of values of ΔH_f for propyl ions shows that all but two of the values lie in the range 188–195 kcal./mole regardless of whether the ions were formed from n-C_3H_7 or sec-C_3H_7 derivatives. These data suggest further that only one species of $C_3H_7{}^+$ ion is formed in these dissociative ionization processes. On the basis of the ionization potentials of n- and sec-propyl radicals measured in this work, it seems clear that a heat of formation of 188–195 kcal./mole is much too low to correspond to a n-$C_3H_7{}^+$ ion. On the assumption that this is the sec-$C_3H_7{}^+$ ion, taking an average gives $\Delta H(sec$-$C_3H_7{}^+) = 193$ kcal./mole. Using $I(sec$-$C_3H_7) = 7.90$ v. (182 kcal./mole), then ΔH_f $(sec$-$C_3H_7)$ would be 11 kcal./mole. Since $\Delta H_f(C_3H_8) = -24.8$ kcal./mole[26] and $\Delta H_f(H) = 52.1$ kcal./mole,[27] one is led to a value of $D(sec$-C_3H_7—$H) = 88$ kcal./mole. This result is about 6 kcal./mole lower than the indirect electron impact value.[6] It should be emphasized that owing to the uncertainty as to the identity and heat of formation of the $C_3H_7{}^+$ ion formed in the dissociative ionization processes, the 88 kcal./mole value derived above should be considered as having no validity whatever and is cited only to illustrate the difficulties encountered in the interpretation of the data.
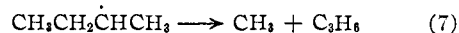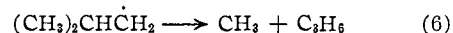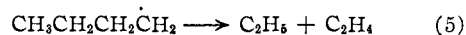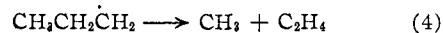
The available appearance potential data for butyl ions also have been summarized and recalculated as ionic heats of formation by Field and Franklin.[8] These values range from 165 kcal./mole to about 200 kcal./mole. Although the butyl ions from t-butyl derivatives tend, on the average, to have lower heats of formation than those from derivatives of the other butyl radicals, they are by no means consistent in this respect. In other compounds it is also not evident which butyl ion may be formed. In such circumstances it is apparent that values for bond dissociation energies derived using the $A(R^+) - I(R)$ relation, and the existing appearance potential data would be quite unreliable.

(26) F. D. Rossini, et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(27) F. D. Rossini, et al., "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular 500 (1952).

Thermal Decomposition of Propyl and Butyl Radicals.

—Very little information is available from the literature on the modes of dissociation of the isomeric propyl and butyl radicals. As pointed out by Trotman-Dickenson,[28] even when rates of decomposition for propyl and butyl radicals have been measured, it is in most instances not known which of the isomeric radical species was involved. If the products of decomposition of each radical species were known, the identification would be greatly facilitated.

In the present work some qualitative observations on the modes of decomposition of the n-propyl and the four butyl radicals have been made. Using low energy electrons to identify the products, reactions (4) to (8) were found to occur

$$CH_3CH_2\dot{C}H_2 \longrightarrow CH_3 + C_2H_4 \qquad (4)$$

$$CH_3CH_2CH_2\dot{C}H_2 \longrightarrow C_2H_5 + C_2H_4 \qquad (5)$$

$$(CH_3)_2CH\dot{C}H_2 \longrightarrow CH_3 + C_3H_6 \qquad (6)$$

$$CH_3CH_2\dot{C}HCH_3 \longrightarrow CH_3 + C_3H_6 \qquad (7)$$

$$(CH_3)_3\dot{C} \longrightarrow H + (CH_3)_2C{:}CH_2 \qquad (8)$$

The sensitivity for detection using this method was rather low, and it is estimated that an alternative dissociation amounting to 5% of the total would not have been detected. Within this limit, however, only one mode of dissociation was observed for each of the radicals, as given above. None of the radicals decomposed by way of a hydrogen migration. Reactions 5 and 7 are in agreement with the conclusions of McNesby, Drew and Gordon[29] that intramolecular hydrogen shifts do not occur in the thermal decomposition of the n-butyl and sec-butyl radicals. It is interesting to note that the decomposition of the t-butyl radical proceeds by a C–H split, even though an alternative mode of dissociation into CH_3 and C_3H_6 by way of an intramolecular H atom shift is less endothermic by about 11 kcal./mole.

(28) A. F. Trotman–Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955.

(29) J. R. McNesby, C. M. Drew and A. S. Gordon, J. Chem. Phys., 24, 1260 (1956).

ONTARIO, CANADA

The Molecular Structure of Carbon Suboxide[1]

BY R. L. LIVINGSTON AND C. N. RAMACHANDRA RAO[2]

The molecular structure of carbon suboxide has been studied by electron diffraction by the visual interpretation of sectored plates. The bond distances obtained were C–C = 1.28 ± 0.01₅ Å. and C–O = 1.16 ± 0.01₅ Å. The diffraction data are consistent with a linear symmetric structure but small deviations from linearity cannot be excluded.

Introduction

Previous electron diffraction investigations[3]–[5] of the molecular structure of carbon suboxide em-

ployed the visual method with non-sectored plates and hence did not yield highly accurate interatomic

(3) L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci., 19, 860 (1933).

(4) H. Boersch, Monatsh., 65, 311 (1935).

(5) H. Mackle and L. E. Sutton, Trans. Faraday Soc., 47, 937 (1951).

distances. The objective of the present investigation was to provide more accurate values for the interatomic distances and perhaps yield some data on the question of linearity of the molecule.[6-7]

Experimental

Carbon suboxide was prepared by the method of Hurd and Pilgrim[8] and was purified by the method of Long, et al.[7]

Electron diffraction patterns were taken using an r^3-sector employing electrons of wave length 0.05452 Å. Kodak Lantern Slide Contrast Plates were used. The photographs were taken both at short (10.19 cm.) and long (25.04 cm.) camera distances.

A visual intensity curve was constructed making use of five patterns, two taken at the long camera distance and three at the short camera distances. The curve extended from $q = 14$ to $q = 110$.

A radial distribution curve was calculated[9] from the sector-visual data setting exp $(-bq^2) = 0.10$ at $q = 100$. The data for the range $q = 0$ to $q = 13$ were interpolated from a theoretical curve. The radial distribution curve thus calculated showed some negative areas and other extraneous features. These extraneous features were treated as intensity data and a Fourier inversion was carried out. This provided the information as to the regions and approximate changes in the intensity data necessary to obtain an acceptable radial distribution curve. After obtaining this information the visual intensity estimates of the particular features were examined to see whether such changes in intensity were justified. Intensity changes were made wherever it was found justified and another radial distribution curve calculated. (Such modifications of intensity estimates do not change the positions of the major peaks to any appreciable extent but do change the peak areas.) This procedure was repeated a second time and the third radial distribution curve thus obtained is shown in Fig. 1. It still showed some extraneous features but was regarded as an acceptable curve for this type of procedure.[10]
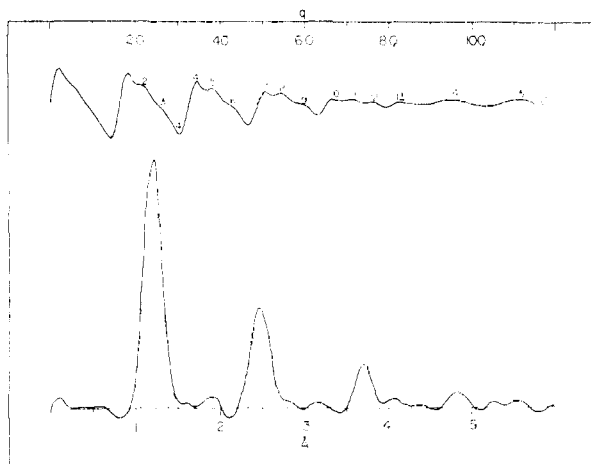

Fig. 1.—The theoretical intensity curve for model 2 and the radial distribution curve for carbon suboxide.

(6) H. D. Rix, J. Chem. Phys., 22, 429 (1954).

(7) D. A. Long, F. S. Murfin and R. L. Williams, Proc. Roy. Soc. (London), A223, 251 (1954).

(8) C. D. Hurd and F. D. Pilgrim, THIS JOURNAL, 55, 757 (1933).

(9) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, J. Chem. Phys., 14, 659 (1946).

(10) The procedure described here, namely, the visual treatment of sectored diffraction photographs, has been used in this Laboratory for several molecules. Sufficient experience has been gained with the method to regard it as being reliable. Most significant, perhaps, is the fact that four molecules have been studied by three methods: the visual treatment of non-sectored plates, the visual treatment of sectored plates and the microphotometer treatment of sectored plates. In each case the visual-sector method yielded results in excellent agreement with and only slightly less accurate than the results obtained by the microphotometer method. Detailed comparisons of these methods will be published soon.

Results and Discussion

The radial distribution curve shows four peaks. The first peak was decomposed by the Karles' method[11] to yield the C–C and C–O distances. The second peak was decomposed to give the long C——C and the intermediate C——O distances. The third and fourth peaks were due to the long C——O distance and the O——O distance, respectively, and could be fitted[12,13] approximately with mean amplitudes of vibration Δr_{ij}, of about 0.10 and 0.14.

The areas of the major peaks of the radial distribution curve agree well with the calculated values of $n Z_i Z_j / r_{ij}$. The areas of the third and the fourth peaks however do not show good agreement with the $n Z_i Z_j / r_{ij}$ values. This is probably because very small oscillations in the zero line of the radial distribution curve can change the shape of such small peaks considerably. The results of the radial distribution curve are summarized in Table I.

TABLE I

RADIAL DISTRIBUTION RESULTS FOR CARBON SUBOXIDE

Distance	r_{ij}, Å.	Δr_{ij}	Area	$n Z_i Z_j / r_{ij}$
C–O	1.16	0.05	100	100
C–C	1.28	.04	63.2	67.5
C–C (long)	2.56	.08	19.5	16.9
C–O (intermediate)	2.44	.08	49.6	47.0
C–O (long)	3.70	.10[a]	27.1	31.3
O——O	4.82	.14[a]	10.4	16.0

[a] Rough estimates.

Since the long C–C and intermediate C–O distances obtained by the decomposition of the second composite peak of the radial distribution curve exactly correspond to the appropriate sums of the C–C and C–O distances obtained by the decomposition of the first peak of the radial distribution curve, any deviations from linearity must be small. It is not possible, for example, to eliminate the C_{2h} and C_{2v} models discussed by Herzberg[14] provided each angle is within 5 or 10° of 180°; deviations appreciably larger than these would not be consistent with the radial distribution results.

It is possible that the decomposition of the composite peaks by the Karles' method[11] may not be very accurate since the radial distribution curve was calculated from the sector-visual intensity data. In order to make certain of the parameters obtained by the radial distribution method and to determine the uncertainties on the parameters, a correlation procedure was carried out. Three models were calculated assuming linear geometry with C–O distances of 1.14, 1.16 and 1.18 Å. (models 1, 2 and 3) keeping the C–C distance constant at 1.28 Å. The model with C–O = 1.16 Å. showed excellent agreement with the experimental curve and is shown in Fig. 1. The other two models showed deviations in the shapes and amplitudes of several features, in particular, minima 11, 13 and 14 and maxima 12, 13, 14. Since there is some general agreement in the qualitative aspects and since the

(11) I. L. Karle and J. Karle, J. Chem. Phys., 18, 963 (1950).

(12) J. Karle and I. L. Karle, ibid., 17, 1052 (1949).

(13) J. Karle and I. L. Karle, ibid., 18, 957 (1950).

(14) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

TABLE II

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR CARBON SUBOXIDE

Feature Max.	Min.	q_0	q_c/q_0 1	2	3
	1	14.08	1.010	0.999	0.983
1		18.38	1.004	1.001	.998
	4	30.50	1.003	0.995	.982
4		34.61	1.004	.998	.995
5		37.86	1.011	.999	.998
	7	47.04	0.995	.992	.981
7		50.75	1.008	1.001	.998
8		54.52	1.007	0.995	.988
	10	63.15	1.006	0.994	.987
10		66.66	1.003	1.000	1.002
12		75.81	1.016	1.004	0.983
	13	79.80	. . .	0.994	0.983
14		92.65	1.026	1.020	. . .
15		108.80	1.029	1.025	1.016
	Mean		1.009	1.001	0.992
Av. dev. from the mean			0.007	0.006	0.009

TABLE III

PRINCIPAL PARAMETERS FROM ACCEPTABLE MODELS

Parameter, Å.	1	2	3
C–O	1.15_0	1.16_1	1.17_1
C–C	1.29_2	1.28_1	1.27_0

experimental curve is a visual curve, they were considered as barely acceptable. The quantitative

electron diffraction data are shown in Table II. The parameters calculated from the three models are listed in Table III. The final parameters of carbon suboxide by the radial distribution curve and the correlation procedure are

$$C-O = 1.16 \pm 0.01_5 \text{ Å.}$$
$$C-C = 1.28 \pm 0.01_5 \text{ Å.}$$

It should be noted that the uncertainties determined in this investigation are much smaller than those reported in the earlier investigations[3-5] which employed the visual method with non-sectored plates with the data extending to about $q = 70$ at the most.

The C–C distance obtained in this investigation is smaller than the C–C distance in ethylenes and ketene.[15] This is possibly because of the greater multiple bonding in carbon suboxide. The C–O distance in C_3O_2 agrees very well with the C–O distances in ketene and carbonyl fluoride[15] but is less than the C–O distance in aliphatic ketones.[16]

(15) T. T. Broun and R. L. Livingston, THIS JOURNAL, 74, 6084 (1952).

(16) C. Romers and J. E. G. Creutzberg, Rec. trav. chim., 75, 331 (1956).

LAFAYETTE, INDIANA

Infrared Absorption Spectra of Inorganic Coördination Complexes. XVIII. Infrared Studies of Malonato Metal Complexes[1]

BY M. J. SCHMELZ,[2a] ICHIRO NAKAGAWA, SAN-ICHIRO MIZUSHIMA[2b] AND J. V. QUAGLIANO[2c]

RECEIVED AUGUST 1, 1958

The infrared spectra of malonic acid and simple metal malonates have been measured in the NaCl region. The observed bands are assigned by comparison with the frequencies reported for simpler molecules of similar structure for which normal vibration calculations are available. The spectra of the malonato metal complexes of Fe(III), Cr(III), Al(III), Cu(II) and Pd(II) are interpreted by correlation with the spectra of the alkali metal malonate salts. The nature of the oxygen-to-metal bonds present in these complexes can be determined indirectly from the observed values of the O–C–O stretching frequencies.

Introduction

A variety of organic chelating agents are known which involve one or more carboxylate ions as donor centers. Previous studies[3] indicate that in nickel(II), copper(II) and zinc(II) complexes with glycine the resonance structure of the carboxylate ion is essentially maintained and the bonding between the central metal and the carboxylate ion is essentially ionic in nature. Similarly, EDTA[4] and

aspartic acid complexes[5] of copper(II) show relatively small shifts in the O–C–O vibrations from those observed for the simple ionic salts of these ligands. The infrared spectra of the oxalato complexes of Fe(III), Cr(III), Al(III) Pd(II) and Cu(II),[6] however, reveal that the oxygen-to-metal bond present in these compounds is approximately 50% covalent in character.

The present investigation reports an infrared study of the complexes formed by these same metal ions with the bidentate malonate ion; the chelate malonato ligand is not rigid and planar like the oxalato group. The infrared absorption bands of malonic acid and its simple salts are assigned and the spectra of the malonato metal complexes are explained by comparison with these. Earlier work on malonate salts includes the infrared stud-

(1) Paper XVII in series, Spectrochim. Acta, in press. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. Presented before the Physical and Inorganic Division of the 132nd National Meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) (a) Sister Mary Judith, R.S.M., Mount Saint Agnes College, Maryland. (b) Visiting professor, Faculty of Science, Tokyo University. (c) To whom correspondence concerning this article should be addressed: Dept. Chemistry, Florida State Univ., Tallahassee.

(3) (a) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, 77, 211 (1955); (b) D. M. Sweeny, C. Curran and J. V. Quagliano, ibid., 77, 5508 (1955).

(4) M. L. Morris and D. H. Busch, ibid., 78, 5178 (1956).

(5) S. Kirschner, ibid., 78, 2372 (1956).

(6) M. J. Schmelz, T. Miyazawa, S. Mizushima, T. J. Lane and J. V. Quagliano, Spectrochim. Acta, 9, 51 (1957).