was therefore concluded that CH_2HgCl radicals at 200° undergo unimolecular decomposition to methylene radicals and calomel

$$CH_2HgCl \longrightarrow CH_2 + HgCl \quad (8)$$

Presumably the small amounts of ethylene, butene and butanes arise from the interaction of methyl and methylene radicals. Since these are very minor reaction products, it would appear unwise to attempt to write specific reactions for their formation from the data available in this initial study.

The small quantum yield of methyl chloride formation was a surprising result of this investigation. There seems little doubt that it arises by the chain step

$$CH_3 + CH_3HgCl \longrightarrow CH_3Cl + CH_3 + Hg \quad (9)$$

The intermediate CH_3Hg has been shown by Gowenlock and Trotman[12] to be unstable above $-10°$. Charnley and Skinner[7] have estimated $D(CH_3\text{–}HgCl)$ to be 63.8 ± 2.9 kcal./mole. However, $D(CH_3Hg\text{–}Cl)$ has not been determined. For $D(ClHg\text{–}Cl)$, Wieland[13] considers 80 kcal./mole to be a probable value. It is likely that $D(CH_3Hg\text{–}Cl)$ would be somewhat lower than the $HgCl_2$-value. Cottrell[14] assigns $D(CH_3\text{–}Cl)$ the value 80 kcal./mole. Hence reaction (9) could be slightly exothermic. The small yield of methyl chloride would suggest that the reaction has an appreciable activation energy.

It is apparent from the data in the tables that the quantum yield of propane formation becomes very small as the extent of substrate decomposition is reduced. This would suggest that propane is not a primary product of the reaction. On this basis it could be explained by the recombination of primary methyls with the ethyl radicals formed in (4)

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \quad (10)$$

By correcting for the small amount of ethane consumed in the formation of propane, the primary quantum yield of ethane formation is estimated from Table III to be 0.44. Now, if the over-all quantum yield of substrate consumption is taken as 1.0 and allowance is made for the substrate consumed in step (5), in the formation of methane, at a quantum yield of 0.05, the primary quantum yield should be at least 0.95, indicating that the reaction shows almost perfect primary efficiency. It should finally be noted that the over-all efficiency of the methyl mercuric chloride reaction is largely due to the absence of substrate reformation by recombination of the primary fragments

$$CH_3 + HgCl \longrightarrow CH_3HgCl \quad (11)$$

Such behavior arises from the fact that HgCl shows little free radical-character in the gas phase.

Conclusions.—As a result of this investigation, it has been shown that the mercury-photosensitized decomposition of gaseous methylmercuric chloride, at 200°, leads to the formation of methyl radicals with a primary quantum yield of at least 0.95. The reaction should prove of considerable value as a methyl radical source in mercury-photosensitization studies.

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An Electron Diffraction Investigation of the Molecular Structure of Trichloroacetonitrile[1]

BY R. L. LIVINGSTON, W. L. PAGE AND C. N. R. RAO[2]

RECEIVED DECEMBER 21, 1959

The molecular structure of trichloroacetonitrile has been studied by electron diffraction by the visual interpretation of sectored photographs. These parameters were obtained: C–N = 1.165 ± 0.025, C–C = 1.465 ± 0.025, C–Cl = 1.765 ± 0.01 Å., and $\angle CCCl = 109.5 \pm 1°$.

In a number of compounds containing a single C–C bond adjacent to a triple bond, the single bond distance has been found to be considerably shorter than the "normal" value of about 1.54Å. Molecules studied in this Laboratory include CH_3CN,[3] CF_3CN[3] and $C(CH_3)_3CN$.[4] In the case of CH_3CN, this shortening can be explained by hyperconjugation, but this does not seem to be a good explanation for the shortening observed in CF_3CN. At least part of the contractions in all of these molecules has been attributed to hybridization effects.[5]

We now have made a study of the molecular structure of trichloroacetonitrile, Cl_3CCN, as a member of this series of molecules, with a particular interest in the C–C distance. Although trichloroacetonitrile has been studied by microwave spectroscopy,[6,7] a unique structure was not obtained by this method. It seemed desirable to attempt to obtain all of the interatomic distances in this molecule

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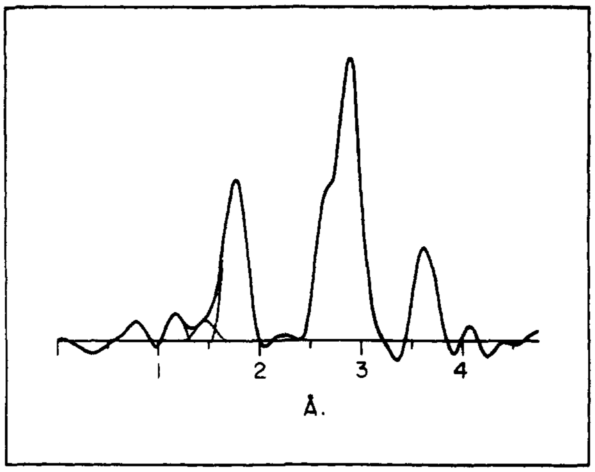

Fig. 1.—Radial distribution curve for trichloroacetonitrile.

by electron diffraction and to compare these results with the "best model" obtained by microwave spectroscopy.

Experimental

The compound was synthesized according to directions given by McBee, *et al.*[8] After several vacuum distillations, an infrared spectrum of the substance showed strong peaks for C≡N and CCl_3 and did not show any carbonyl absorption band. An elemental analysis was run.

Anal. Calcd.: C, 16.63; N, 9.72; Cl, 73.67. Found: C, 16.88; N, 9.46; Cl, 73.35.

Electron diffraction patterns of the compound were photographed using an r^3 sector and Kodak Lantern Slide Contrast Plates. The wave length of the electrons was 0.05452Å. (corresponding to an accelerating potential of 48,322 v.). The pressure of the sample was about 20 mm. and the best exposure times were between 15 and 30 sec. Five of the patterns were chosen for the visual measurement of the diffraction ring diameters and the estimation of the relative intensities of the rings. The visual data from the sectored plates extended from $q = 16$ to $q = 92$. A plot of the relative intensities of the features against their q values is shown in Fig. 3.

A radial distribution curve was calculated from the sector visual intensity curve using the equation[9]

$$rD(r) = \sum_{q\,\min}^{q\,\max} I_0 \exp{(-bq)^2} \sin\left(\frac{\pi q r}{10}\right)$$

and setting $\exp(-bq^2) = 0.1$ at $q = 90$. The data for the range $q = 0$ to $q = 16$ were supplied from a theoretical intensity curve calculated with the equation[10]

$$I(q) = k \sum_i{}' \sum_j{}' A \exp{[-\alpha(r_{ij} - r_{e\,ij})^2]} \sin\left(\frac{\pi q r}{10}\right)$$

and based on a model which employed the results of Baker, *et al.*[6]

Results and Discussion

The radial distribution curve (Fig. 1) shows four peaks. The first peak, observed at 1.17Å., was due to the C–N distance and was fitted with a root mean square amplitude of vibration, Δr_{ij}, of zero. The second peak was decomposed by the Karles'[11] method to give 1.465Å. for C–C and 1.765Å. for C–Cl; Δr_{ij} values for the two atom pairs were 0.05 and 0.053, respectively. The third peak was due to Cl· · ·Cl, C· · ·Cl and C· · ·N; no attempt was made to decompose it, although a rough estimate, 2.88Å., of the Cl· · ·Cl distance was made. The fourth peak at 3.62 was due to N· · ·Cl; it was fitted with a Δr_{ij} of 0.07. The results of the radial distribution curve are summarized in Table I.

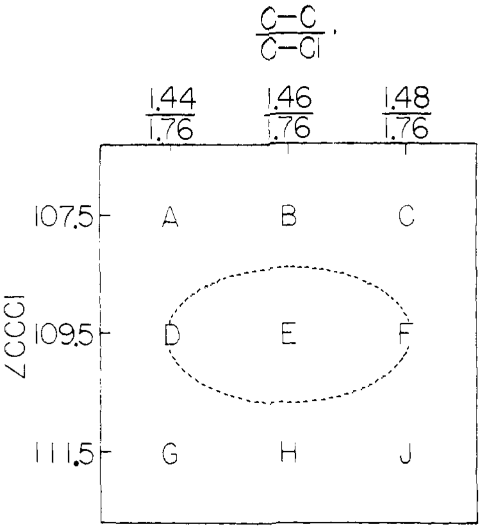

Fig. 2.—Parameter field for trichloroacetonitrile in the plane C–N = 1.16Å.

TABLE I

RESULTS OF THE RADIAL DISTRIBUTION CURVE FOR TRICHLOROACETONITRILE

Distance	Peak position	Δr_{ij}	Area	nZ_iZ_j/r_{ij}
C–N	1.17	0.00[b]	11.8	20.8
C–C	1.465[a]	.05	10.3	14.2
C–Cl	1.765[a]	.053	100	100
C· · ·N	. . .	. .	250	248.9
C· · ·Cl	. . .	. .		
Cl· · ·Cl	2.88[b]	. .		
N· · ·Cl	3.62	.07[b]	57.3	56.7

[a] Peak position obtained by fitting the peaks by the Karles' method. [b] Rough estimate.

In order to determine the range of uncertainties in the various parameters, a correlation procedure was carried out using the equation given above. Keeping the C–N distance fixed at 1.16Å., nine models were calculated, varying the C–C distance from 1.44 to 1.48Å. and the CCCl angle from 107.5 to 111.5°. The C–Cl distance was kept constant at 1.76Å. This parameter field is shown in Fig. 2. Two additional parameter fields were calculated assuming C–N distances of 1.14 (plane X1) and 1.18Å. (plane X2). The relevant amplitudes of vibration for the different atom pairs were based on the radial distribution results.

Curves for models A, B, B1, B2 and C fail to reproduce the observed curve in that they all show maximum 7 as a separate and distinct peak rather than as a shoulder on the inside of maximum 8; the curve for model B1 is shown in Fig. 3. Models G, H, H1, H2 and J give rise to curves which do not possess a shoulder on the eighth maximum and instead give an intense peak in this region; these curves also do not have a tenth maximum. The tenth maximum appears as a shoulder on the eleventh maximum in curves J and H2 and as a

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TABLE II

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR TRICHLOROACETONITRILE

Feature max.	Feature min.	$q_{obsd.}$	D	E	F	qc/q_0 E1	F1	E2	D2
3		15.83	1.013	1.011	1.011	1.009	1.008	1.013	1.015
	3	19.85	0.999	0.997	0.995	0.998	0.996	0.996	0.998
4		23.04	1.019	1.016	1.019	1.017	1.018	1.017	1.019
	4	26.46	1.006	1.005	1.003	1.006	1.005	1.003	1.005
5		29.23	1.005	1.005	1.004	1.006	1.006	1.004	1.005
	5	32.43	1.001	1.002	1.002	1.002	1.003	1.001	1.000
6		35.63	1.018	1.022	1.026	1.022	1.024	1.024	1.019
	6	43.09	0.983	0.976	0.968	0.978	0.972	0.970	0.978
8		50.12	0.992	0.993	0.995	0.993	0.995	0.994	0.992
	8	53.09	1.008	1.007	1.007	1.008	1.008	1.007	1.008
9		56.50	1.012	1.011	1.009	1.013	1.012	1.007	1.011
	9	59.90	1.008	1.006	1.004	1.007	1.006	1.004	1.007
10		63.73	0.988	0.981	0.981	0.984	0.982	0.984	0.987
	10	66.92	0.995	0.993	0.991	0.993	0.992	0.992	0.994
11		70.53	1.010	1.006	1.007	1.006	1.005	1.007	1.009
	11	74.36	1.014	1.011	1.009	1.011	1.009	1.011	1.013
12		77.96	1.007	1.005	1.003	1.006	1.005	1.004	1.007
	12	81.36	1.003	1.000	0.997	1.002	1.000	0.998	1.002
13		84.96	1.001	0.997	0.995	0.997	0.995	0.996	1.000
	13	88.14	1.004	1.003	1.001	1.003	1.002	1.003	1.005
14		91.95	1.012	1.008	1.008	1.010	1.009	1.009	1.011
Mean qc/q_0			1.005	1.003	1.002	1.003	1.002	1.002	1.004
Av. dev. from mean			0.007	0.008	0.009	0.008	0.008	0.008	0.008

shoulder on the ninth maximum in curves G and H1. Model D1 gives rise to a curve which does not reproduce the shoulder on the eighth maximum nor is the sixth minimum deep enough. Qualitatively models E, E1, E2, F1 and D2 are best but D and F must be accepted as borderline cases. In curve D the sixth maximum is ill defined and the ninth minimum is not deep enough; in curve F the shoulder on the eighth maximum is a little too well defined and the ninth minimum is not deep enough. The acceptable parameter field is enclosed by the dotted line in Fig. 2.

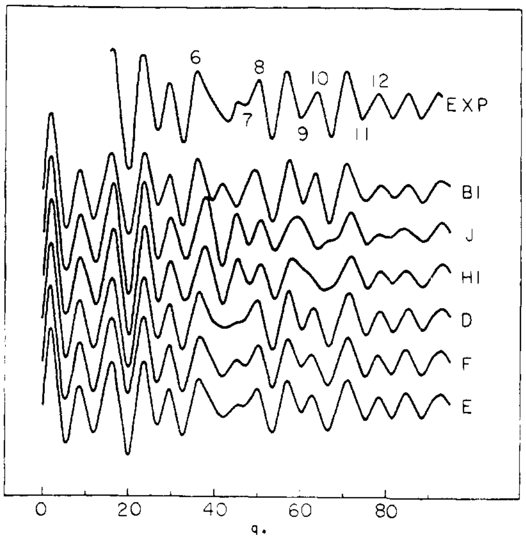

Fig. 3.—Experimental and theoretical intensity curves for trichloroacetonitrile.

In Table II the experimentally determined q values are listed along with the q_c/q_0 ratios for the acceptable models. Maximum 7 and minimum 7 were not included since the measurements of their positions were not considered reliable. The parameters calculated from these models are collected in Table III. The final parameters, based on the radial distribution curve and the correlation procedure, are:

C–N	$1.16_5 \pm 0.02_5$ A.
C–C	$1.46_5 \pm 0.02_5$ Å.
C–Cl	$1.76_5 \pm 0.01$ Å.
<CCCl	109.5 ± 1°

The results of this study are in agreement with the microwave results of Baker, *et al.*,[6] whose best model had C–N = 1.158, C–C = 1.460 and C–Cl = 1.770Å., and ∠CCCl = 109°56′.

TABLE III

PARAMETERS FROM ACCEPTABLE MODELS OF TRICHLOROACETONITRILE

	D	E	F	E1	F1	E2	D2
C–Cl	1.76_9	1.76_5	1.76_4	1.76_5	1.76_4	1.76_4	1.76_7
C–C	1.44_7	1.46_4	1.48_3	1.46_4	1.48_3	1.46_3	1.44_6
C–N	1.16_6	1.16_3	1.16_2	1.14_3	1.14_2	1.18_2	1.18_5
Cl···Cl	2.89_4	2.88_9	2.88_6	2.88_9	2.88_6	2.88_6	2.89_2
C···Cl	2.63_3	2.64_8	2.65_5	2.64_8	2.65_5	2.64_5	2.63_0

The C–C distance of 1.46_5Å. in trichloroacetonitrile may be compared with that in similar molecules: CH_3CN,[3] 1.46_5, CF_3CN,[3] 1.47, and $C(CH_3)_3CN$,[4] 1.46Å. Hyperconjugation does not seem to be a good explanation for all of these short C–C distances. It seems possible that hybridization effects may be responsible for the entire C–C shortening in such molecules. The C–N distance (1.16_5Å.) is in conformity with that in CH_3CN[3] (1.15_5Å.) and $C(CH_3)_3CN$[4] (1.16_0Å). The C–Cl distance in trichloroacetonitrile, 1.765Å., is comparable to that in carbon tetrachloride,[12] 1.766Å., and in chloroform, 1.77Å.[13]

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The Chemisorption of Carbon Monoxide on Metals[1]

BY R. A. GARDNER[2] AND R. H. PETRUCCI

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The adsorbed species resulting from the chemisorption of carbon monoxide on copper oxide, nickel and cobalt were studied by infrared spectroscopy. An infrared technique developed by Eischens was used to obtain the spectra. The observations made in this investigation serve to support and extend the Wolkenstein hypothesis of the mechanism of chemisorption. Surface atoms can act as strong or weak electron donors and acceptors; the adsorbed species assume the opposite role. Adsorbed carbon monoxide species displayed vibration frequencies corresponding to the possession of non-integral numbers of electrons ranging from $(CO)^{+0.70}$ to $(CO)^{-1.30}$ with absorption bands from 2173 to 2000 cm.$^{-1}$.

Introduction

In the past, the basic problem of chemisorption has been one of explaining the bonding between a single adsorbed species and a surface. Among the many techniques that have been used in adsorption studies are: electron microscopy,[3] mass spectrometry,[4] magnetic susceptibility,[5] field emission studies,[6] conductivity[7] and spectroscopy.[8] The vast number of experiments reported in the literature on chemisorption, while generally showing qualitative agreement, still leave many questions unanswered. Recent improvements in the sensitivity of the various experimental techniques used in the study of chemisorption have further complicated the problem—in many investigations evidence has been found for the existence of several different species resulting from chemisorption of a single gas on a single solid. The presence of several chemisorbed species also has been observed in the experiments presented in this work.

Experimental

The method used in this investigation involved "*in situ*" preparation of the adsorbent, evacuation of the infrared cell to 1×10^{-6} mm. pressure, admission of purified carbon monoxide and determination of the spectrum of the sample. This method is similar to that successfully applied by Eischens, Pliskin and Francis[9] in their pioneer work in the determination of the infrared spectra of chemisorbed molecules.

The vacuum system contained a Welch Duo Seal mechanical vacuum pump, a mercury diffusion pump and a liquid nitrogen trap. The pressure gauges used were: a Phillips cold cathode gauge type PHG-09, a McLeod gauge graduated at 0.005 microns, for calibration of the Phillips gauge, and a closed end mercury manometer. All gauges could be isolated from the system by vacuum stopcocks. Vacuums as low as 10^{-7} mm. were obtainable.

The gases used were stored in bulbs with mercury seals to prevent contamination by Apiezon N stopcock grease. The gases from commercial tanks were purified before storage. Hydrogen (99%) from the Air Reduction Corporation was further purified by passage over activated cocoanut charcoal at −195°. The charcoal had been activated at 2×10^{-5} mm. pressure at 350° for 14 hr. Carbon monoxide (95%), from the Matheson Company, was purified by passage through concentrated sulfuric acid, activated charcoal at −78° and cobaltous oxide at 25°. Oxygen from Linde Air Products Corporation was stored directly from the commercial tank.

The adsorbents were prepared from the metal nitrates in an "*in situ*" cell by the method desdribed by Eischens, Pliskin and Francis.[10] The spectra were obtained with a Perkin-Elmer Model 112 spectrometer which was modified by the installation of a vertical source unit. The spectra were recorded from 2500 to 1200 cm.$^{-1}$ with fixed monochromator slits.

The path of the infrared beam was flushed with commercial nitrogen to suppress atmospheric carbon dioxide and water vapor bands in the spectra. Several blank spectra of the sample were recorded at room temperature and at the final pressure of approximately 1×10^{-7} mm. The introduction of carbon monoxide gas was accomplished in small increments. Duplicate computed spectra were determined between the introduction of each increment.

Several experiments were performed to examine the chemisorption of CO on reflecting metal films for comparison with the results obtained for CO on supported metals. A cell was designed for the vacuum evaporation of the metal from an electrically heated tungsten wire onto the inner surface of a Pyrex tube. The tungsten wire was positioned along the longitudinal axis of the glass tube which was 1.6 cm. in diameter and 23.0 cm. in length. When the cell was placed on the diverging portion of the infrared beam (below the focus point), the beam was collimated by multiple reflections from the evaporated film. The collimated beam was directed onto the 45° angle mirror in the lower source unit and then into the monochromator. In this manner the spectra of surface chemisorbed species were obtained.

Experimental Results

To facilitate the discussion of the several systems and the numerous infrared absorption bands found for the adsorption of carbon monoxide, the experimental data are compiled in Table I; explanatory notes follow the table.

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(1) Based on the doctoral dissertation of R. A. Gardner, Western Reserve University, June, 1959. Presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 14-18 1959.

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