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The Mercury-6($^3P_1$)-Photosensitized Decomposition of Methylmercuric Chloride Vapor: A New Methyl Radical Source[1]

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A study has been made of the mercury-6($^3P_1$)-photosensitized decomposition of methylmercuric chloride vapor at 200° under static conditions. The principal gaseous products of the reaction are ethane and methane. The calomel by-product plays no part in the reaction. The over-all quantum yield of substrate consumption is 1.0, and the primary quantum yield of methyl radical formation is at least 0.95. For ethane and methane the quantum yields are 0.44 and 0.05, respectively. In the proposed mechanism, the formation of ethane is explained by methyl radical recombination, and methane, by an abstraction reaction with the substrate. Small amounts of higher hydrocarbons were found, and these are attributed to the interaction of methyl and methylene radicals, with the latter species arising from the thermal decomposition of CH_2HgCl. The reaction should have considerable value as a methyl radical source in mercury-photosensitization studies.

Introduction

Interest in the present investigation arose from studies on the reaction of ^{202}Hg 6($^3P_1$) atoms, photoexcited in natural mercury vapor, with methyl chloride.[3] In this latter study, it was concluded that a major portion of the calomel product must form in the primary process, since the calomel was found to be highly enriched in ^{202}Hg. With a similar primary process operative in the reaction of CH_3HgCl vapor with Hg 6 ($^3P_1$) atoms, methyl radicals and calomel would form, and mercury would be regenerated, since CH_3Hg radicals are unstable.[4] The reaction appeared, therefore, to be of considerable interest as a potential method for generating methyl radicals in mercury-photosensitization. In addition, if the postulated mechanism should prove correct, the reaction would also be of interest in mono-isotopic mercury-photosensitization studies. Thus, in the reaction of a photoexcited isotopic species ($^iHg^*$), in natural mercury vapor (^NHg), with the substrate, it would be possible to distinguish between these primary processes

$$CH_3{}^NHgCl + {}^iHg^* \longrightarrow CH_3 + {}^NHg + {}^iHgCl \text{ and}$$

$$CH_3{}^NHgCl + {}^iHg^* \longrightarrow CH_3 + {}^iHg + {}^NHgCl$$

since, in the first process, the calomel product would be enriched in the mercury isotope present in the lamp. The details of the investigation are given.

Experimental

Methyl mercuric chloride was prepared by the addition of dilute hydrochloric acid to a 40% aqueous solution of methyl mercuric hydroxide. The precipitated product was filtered, washed with distilled water and taken up in a minimum of hot ethanol. The crystalline material was obtained by cooling the ethanol solution in an ice-bath. The crystals, as thin plates, were washed in distilled water, air-dried and stored over phosphorus pentoxide. Final purification was done by vacuum sublimation, which also served to reduce the crystals to a fine powder, convenient for sample preparation. Since the material sublimes readily, sealed tube melting points were made. For the vacuum-sublimed material the m.p. found was 172.4–172.6°. The literature values[5,6] are 167 and 170°.

Since the vapor pressure of the compound had only been reported[7] for the range − 6 to 12°, vapor pressure measurements were made on the sublimed material from 30–150°, using a tensimeter similar in design to that described by Sanderson.[8]

The vacuum system was of conventional design for static experiments in mercury-photosensitization. Two cylindrical quartz cells were used, both 3 cm. in length and 5 cm. in diameter. The desired pressure of methyl mercuric chloride vapor was achieved by inserting the appropriate weight of solid, contained in a small, evacuated ampoule, into the reaction cell. The ampoule terminated in a thin tip, which could be broken *in vacuo*, by shaking the cell.

After insertion of the ampoule, the cell was connected to the vacuum manifold. The stem of the cell was provided with a quartz-to-Pyrex graded seal to which were attached, after insertion of the ampoule, a break-tip and the capillary side-arm for connection to the vacuum system. Upon evacuation, the cell was allowed to equilibrate in mercury vapor, by connecting to a mercury saturator for 2 hr., after which it was flame-cut from the manifold.

After the ampoule had been cracked open by shaking, the cell was rigidly positioned in a furnace, the temperature of which was automatically controlled to ±0.5°. One end of the furnace was provided with a window of Vycor 7910 glass, 3 mm. thick, which admitted to the cell only radiation of wave length exceeding 2200 Å.

For the photosensitization experiments, the mercury resonance radiation source was a Biosteritron lamp, and for the photolyses, a Utility Model, quartz, high-pressure arc was used. Both sources are products of the Hanovia Chemical and Mfg. Co., East Rutherford, N. J. Photosensitization tests with the quartz arc showed the 2537 Å. resonance line to be completely reversed.

After irradiation, the cell was connected, *via* its breakseal, to an analytical system. The total number of moles of gaseous products was determined by transferring all gaseous products, by means of a Toepler pump, to a calibrated gas buret. The products then were pumped into a sample tube and analyzed on a mass spectrometer (Consolidated Engineering Corp., Type 21–103). For representative runs, the solids remaining after reaction were examined by the X-ray powder method. For this purpose, the G. E. XRD-1, diffraction unit with Cu target, was used.

The intensity of 2537 Å. resonance radiation, incident upon the cell from the Biosteritron source, was determined by solution actinometry, with the potassium ferrioxalate method, developed by Parker[9] and Hatchard and Parker.[10]

Results

The Vapor Pressure of Methyl Mercuric Chloride.—Four sets of data were obtained on samples of vacuum-sublimed methyl mercuric chloride, over the temperature range 30–150°. Readings were taken, on the average, at 5°-intervals in tem-

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(1) Requests for reprints should be addressed to the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. A portion of this work was presented at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

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perature. By the method of least squares, the following vapor pressure equation was obtained

$$\log P_{\text{mm.}} = 9.6794 - (3396.6/T)$$

From measurements over the range −6 to 12°, Charnley and Skinner[7] found

$$\log P_{\text{mm.}} = 9.48 - (3385/T)$$

The values obtained by these authors, in the low temperature range of their measurements, are slightly lower than those predicted by our equation. Thus, at 10°, Charnley and Skinner found the vapor pressure to be 0.0033_4 mm. The value calculated from our equation at this temperature would be 0.0048_4 mm. The agreement is considered satisfactory, when allowance is made for the markedly different temperature ranges of the two sets of measurements.

Thermal Reaction.—Since the photosensitization experiments were to be carried out at 200°, a few measurements were made to assess the importance of the thermal reaction. It was found that the decomposition of methyl mercuric chloride could not be detected below 260°. At this temperature, and a substrate pressure of 152 mm., 1.23% decomposition was found to occur after 35 hr. Mass spectrometric analysis of the gaseous products from the run gave, in mole per cent.: H_2 = 2.1; CH_4 = 16.5; C_2H_6 = 7.7; C_3H_8 = 1.0; and CH_3Cl = 67.3. Hence methyl chloride would appear to be the major product of the thermal reaction. At 200°, the thermal decomposition is negligible.

Photolytic Reaction.—Absorption spectra obtained for ethanol solutions of methylmercuric chloride, using a Cary, Model 14, recording spectrophotometer, indicated 2600 Å. as the upper wave length limit of absorption. Since it was therefore possible that some photolysis could occur at 2537 Å., measurements were made with a Hanovia Utility Model quartz arc, in which the resonance line is reversed. The relative intensities of the quartz arc and Biosteritron resonance lamp were determined, in the 2200–3000 Å. region, with a Westinghouse WL-775 phototube, which is insensitive above 3000 Å. The phototube output was measured with a Beckman Ultrohmeter. A Vycor, 7910, filter served to remove radiation below 2200 Å. In the 2200–3000 Å. region it was found that the Biosteritron source was five times as intense as the quartz arc. In the direct photolysis, sufficient products could be obtained for analysis in a 5 hr. exposure. In a representative run, at a substrate pressure of 122.5 mm., 7.6% decomposition occurred in 5 hr. Analysis of the gaseous products, in mole per cent., gave: H_2 = 0.1; CH_4 = 37.0; C_2H_6 = 49.5; C_3H_8 = 1.9; $n\text{-}C_4H_{10}$ = 0.3; $i\text{-}C_4H_{10}$ = 0.2; C_2H_4 = 2.8; C_4H_8 = 0.1; C_4H_6 = 0.1; and CH_3Cl = 7.2. Thus, in contrast to the thermal reaction, methane and ethane are the major products of the photolytic reaction, rather than methyl chloride. From the absorption spectrum of the substrate, and the spectral distribution of the Biosteritron source, it was estimated that the direct photolytic reaction could not contribute more than 0.5% to the photosensitized decomposition. When the large absorption coefficient of mercury for its own resonance radiation is taken into account, the partitioning of the 2537 Å. radiation to the direct molecular absorption can be considered negligible.

The Mercury-6($^3P_1$)-Photosensitized Decomposition.—In order that the rate data might be reported as quantum yields, the light intensity, at 2537 Å., incident upon the cell from the Biosteritron source was determined repeatedly throughout the course of the measurements on the photosensitized reaction. The source showed a very steady light output. The absorbed intensity was found to be 6.4 ± 0.2 × 10^{-6} einsteins/minute.

In Table I, the quantum yield data are reported for exposures of 30-minutes duration, as a function of substrate pressure. It should be noted that, at 200°—the reaction temperature for the experiments—the vapor pressure of the substrate is 317 mm. In addition to ethane, methane and propane—the principal products of the reaction—smaller amounts of hydrogen, *n*-butane, *i*-butane, pentanes, hexanes, ethylene, propylene, butenes, pentenes, hexenes, acetylene and methyl chloride were detected. The quantum yields for these minor products did not exceed 0.015, even for extents of substrate decomposition exceeding 90%. With decreasing extent of decomposition, these products became progressively less important. It should be noted that the quantum yield of methyl chloride formation did not exceed 0.002. From Table I, it can be seen that the quantum yield of substrate disappearance is 0.95 ± 0.01, for substrate decompositions as high as 83%. With decreasing extent of reaction, ethane increases at the expense of methane.

TABLE I

THE REACTION OF METHYL MERCURIC CHLORIDE VAPOR WITH Hg 6($^3P_1$) ATOMS: QUANTUM YIELD DATA FOR RUNS OF 30-MINUTES DURATION

		Quantum yields				
P, mm.	% decomp.	CH_3-HgCl	CH_4	C_2H_6	C_3H_8	CH_4/C_2H_6
60.6	94	0.72	0.17	0.18	0.023	0.94
75.4	86	.89	.13	.27	.037	.48
82.8	82	.94	.16	.29	.038	.55
96.8	79	.96	.12	.33	.040	.36
106.2	71	.96	.098	.34	.034	.29
127.9	53	.94	.073	.38	.025	.19

In Table II, the data are presented for runs of 15-minutes duration. It is here clearly evident that the quantum yield of substrate disappearance is independent of reaction pressure. The mean value is 0.99 ± 0.03 over the pressure range 60–128

TABLE II

THE REACTION OF METHYLMERCURIC CHLORIDE VAPOR WITH Hg 6($^3P_1$) ATOMS: QUANTUM YIELD DATA FOR RUNS OF 15-MINUTES DURATION

		Quantum yields				
P, mm.	% decomp.	CH_3-HgCl	CH_4	C_2H_6	C_3H_8	CH_4/C_2H_6
50.3	77	0.98	0.13	0.33	0.039	0.39
51.4	75	.97	.11	.36	.033	.30
57.4	62	.97	.089	.38	.030	.23
82.1	44	.97	.062	.41	.022	.15
91.6	41	.94	.053	.41	.019	.13
124.1	30	.99	.065	.40	.020	.16
126.5	30	1.03	.056	.44	.017	.13
130.2	30	1.08	.059	.46	.018	.13

mm. Furthermore the quantum yield remains constant for conversions as high as 77%. When less than 50% of the substrate is decomposed, the CH_4/C_2H_6 ratio in the products is constant at 0.14 ± 0.01, and the quantum yields of formation of ethane, methane and propane are 0.42 ± 0.02, 0.059 ± 0.004, and 0.019 ± 0.0015, respectively. From Tables I and II, it is to be noted that the quantum yields of methane and ethane approach each other with increasing extent of decomposition of the substrate.

In Table III, the results are given for four runs, at a mean pressure of 128.5 ± 1.0 mm., and exposure of 5 to 20 minutes. Here it can again be seen that the quantum yield of substrate disappearance is 1.0, within the experimental error of the light-intensity determinations. The limiting value of the CH_4/C_2H_6 ratio is 0.12 ± 0.02. The quantum yield of ethane formation is the same, within the experimental error, as in the 15-minute runs, at 0.41 ± 0.02, while the methane and propane values are slightly lower than in the 15-minute runs, at 0.049 ± 0.006 and 0.012 ± 0.003, respectively. Thus, in the absence of secondary quenching reactions, the quantum yields are as follows: $CH_3HgCl = 1.0$, $C_2H_6 = 0.41$, $CH_4 = 0.05$ and $C_3H_8 = 0.01$. The minor products detected in the runs shown in Table III were CH_3Cl (0.01), C_2H_4-(0.002), C_4H_8 (0.002), n-C_4H_{10} (0.0006) and i-C_4H_{10} (0.0006). The numbers in parentheses are the quantum yields for the run of 5-minutes duration. Hydrogen was not detected in the 5-minute run. For the longer runs, the quantum yield of hydrogen formation was 0.001 to 0.002.

TABLE III

THE REACTION OF METHYL MERCURIC CHLORIDE VAPOR WITH Hg $6(^3P_1)$ ATOMS: QUANTUM YIELD DATA FOR RUNS OF VARIABLE DURATION

			Quantum yields				
P, mm.	Duration, min.	% decomp.	CH_3-HgCl	CH_4	C_2H_6	C_3H_8	CH_4/C_2H_6
127.4	5	9	0.98	0.061	0.43	0.008	0.14
128.1	10	18	.94	.042	.42	.011	.10
128.0	20	33	.87	.046	.38	.015	.12
130.5	20	33	.90	.048	.39	.015	.12

The solid residue, remaining after reaction, was divided into two fractions by sublimation at 50 and 100°. The fraction subliming at 50° was shown, by X-ray analysis, to be unreacted methyl mercuric chloride, and the 100°-fraction proved to be pure calomel. X-Ray patterns were made of ethyl mercuric chloride and mercuric chloride. No evidence for these compounds could be found in the solid products.

Discussion

From the nature of the products and the photochemical behavior of the system, the following primary process is postulated for the photosensitized reaction

$$CH_3HgCl + Hg\,6(^3P_1) \longrightarrow CH_3 + Hg + HgCl \quad (1)$$

By analogy with the methyl chloride reaction,[5] it would be expected that the mercury in the calomel product would come from the photoexcited mercury, rather than from the substrate. In the Introduction to this paper, it was pointed out that this question can best be settled by mono-isotopic photosensitization studies. To this end, an investigation is in progress in the laboratories of one of us (HEG), on the reaction of gaseous CH_3HgCl with $^{202}Hg\ 6(^3P_1)$ atoms, in natural mercury vapor.

The absence of hydrogen, as a significant reaction product, precludes C–H bond scission as a primary process. Similarly, there is no evidence for the formation of free chlorine atoms in the quenching reaction, since hydrogen chloride was not detected in any of the runs. It may be argued that the chlorine atoms would be consumed rapidly by reaction with mercury at the wall. Such a reaction undoubtedly would occur. However, the mercury vapor concentration is too low to account for a quantitative removal of the chlorine atoms. Thus, Masson and Steacie,[11] in their study of the reaction of methyl chloride with Hg $6(^3P_1)$ atoms, over the temperature range 72–328°, found hydrogen chloride to be a major reaction product, which they attribute to the reaction

$$CH_3Cl + Cl \longrightarrow HCl + CH_2Cl \quad (2)$$

It should further be noted that no trace of hydrogen chloride could be detected even when 94% of the substrate was decomposed, under which conditions ethane would be the major gas-phase component in the reaction cell. Chlorine atoms are known to undergo a rapid abstraction reaction with ethane.

Since quantum yield of substrate consumption is unity, and that of ethane, the major product, is slightly less than 0.5, there seems little doubt that ethane arises by the recombination of the methyl radicals formed in (1)

$$2CH_3 \longrightarrow C_2H_6 \quad (3)$$

From a study of Tables I to III, it can be seen that the methane yield rises at the expense of ethane with increasing extent of reaction, suggesting the reaction

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \quad (4)$$

Since methyl mercuric chloride is a solid at ordinary temperatures, it was necessary to confine the entire reaction system in the furnace to prevent sublimation. As a result, the volume of the reaction system was, perforce, small, and it proved difficult to obtain accurate data for low extents of conversion. From the constancy of the quantum yield of methane formation for extents of reaction less than 30%, it would appear that reaction 4 is not important under such conditions. From Table III, the limiting quantum yield for methane would appear to be 0.05. This value is ascribed mainly to the reaction

$$CH_3 + CH_3HgCl \longrightarrow CH_4 + CH_2HgCl \quad (5)$$

The fate of CH_2HgCl was of particular interest in this investigation. It was expected that this radical would undergo recombination reactions such as

$$CH_3 + CH_2HgCl \longrightarrow CH_3CH_2HgCl \quad (6)$$

and

$$2CH_2HgCl \longrightarrow ClHgCH_2CH_2HgCl \quad (7)$$

However, X-ray powder patterns of the solid residues of the reaction showed only calomel lines. It

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[11] C. R. Masson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 183 (1951).

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

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

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)

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

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

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

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]

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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 ∠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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[1] Contains material from the M.S. Thesis of W. L. Page.

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