assumption of triply excited vibrations. All the overtone and combination assignments may be chosen to fit the selection rules.

Table II gives no assignment for the torsional vibrations due to internal rotation of the methyl groups. They are inactive for compounds having the symmetry T_d. Since all existing data can be reasonably explained as due to other vibrations, it seems highly dubious that it would be worthwhile at the present stage of investigation to attempt to derive the torsional frequencies from overtone or combination bands.

The calculations made by Silver[11] for the A_1 and E frequencies are in the main concordant with the assignment proposed here as may be seen by reference to his paper. That the calculations of Silver are not in closer agreement with observed data is probably to be ascribed to the fact that a simple valence force potential is not very satisfactory for the tetramethyl compounds for the same reasons that such a potential field does not adequately describe the methyl halides.

The assignments suggested here must certainly be considered tentative in many respects, but they may have the merit of suggesting further investigations of the Raman and infrared spectra of this interesting series of compounds, particularly in attempts to find those fundamental frequencies which in a number of cases are undoubtedly missing as yet.

Acknowledgments.—The authors wish to thank Professor J. G. Aston and Dr. L. D. McGraw for furnishing the samples of tetramethylmethane and tetramethylsilicon, respectively. The assistance of Dr. C. E. Leberknight in putting the grating spectrometer in working order is greatly appreciated. Thanks are also due to Dr. R. A. Friedel for discussion of several features of the tetramethylmethane spectrum.

Summary

The infrared absorption spectra of tetramethylsilicon and tetramethylgermanium from 1 to 15μ obtained on a rock salt prism spectrometer, are presented.

With the aid of a grating spectrometer, the nature of the spectra of the above two compounds and of tetramethylmethane has been investigated in the 3μ region under high resolution.

An assignment of all known Raman and infrared frequencies of the tetramethyl compounds of C, Si, Ge, Sn and Pb, and of tetramethylammonium ion is proposed on the basis of a molecular model having the symmetry of the point group T_d.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Filters for the Isolation of the 3130 Å. Spectral Group of the Mercury Arc

BY ROY E. HUNT[1] AND WALLACE DAVIS, JR.[1]

A number of filters have been suggested[1a-4] for the isolation of the mercury arc triplet near 3130 Å. However, no systematic data have been reported correlating spectroscopic purity of this wave length with filter concentration and resultant loss of intensity in the region of 1% total extraneous radiation.

The purpose of the present work was primarily to determine the impurities in the 3130 Å. triplet when nickel chloride, potassium chromate and potassium biphthalate solutions are used as filters. The source was intended for use in the photolysis of certain ketones, hence, only solutions expected to give high purity were tested. The investigation was extended to obtain semi-quantitative data on the relative effectiveness of several of the filter components suggested in the literature for removing specific impurities in the desired group.

In view of the nature of the filters available, extraneous radiation was divided into five categories: 1, ultraviolet radiation below 3000 Å.; 2, 3020 Å.; 3, 3342 Å.; 4, 3660 Å.; 5, all radiation above 3660 Å., including the visible and near infrared.

An additional region, the infrared of wave length longer than 1.2μ would be absorbed by 10 cm. of water in any of the liquid filter solutions.[5]

Bowen,[1a] testing solutions in 10-cm. spherical quartz flasks, which served also to condense the radiation, proposed the use of nickel chloride in hydrochloric acid, potassium chromate in sodium hydroxide, and potassium biphthalate. He found impurities amounting to 4–6% in the ultraviolet using a photoelectric cell to measure the various individual lines as dispersed through a quartz prism. He observed further that the biphthalate solution required continued renewal by means of a flow system.

The use of a solution containing cobaltous sulfate and nickel sulfate, mixed, was proposed by Bäckstrom[2] to eliminate the visible as well as most of the 3660 Å. line. He used biphthalate to remove the wave lengths below 3130 Å. and also

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[1] National Research Council Pre-Doctoral Fellows.

[1a] E. J. Bowen, *J. Chem. Soc.*, 2236 (1932).

[2] H. J. L. Bäckstrom, *Naturwissenschaftan*, **21**, 251 (1933).

[3] E. J. Bowen, *J. Chem. Soc.*, 76 (1935).

[4] R. Spence and W. Wild, *ibid.*, 352 (1937).

[5] J. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1945, p. 370.

experimented with a 0.0012 M sodium cinnamate solution. The latter in a 1-cm. cell gave a purity of 96% 3130 Å. with most of the extraneous radiation due to 3340 Å. The cinnamate solution was photochemically unstable, however.

In the present investigation these filters were tested in various combinations, to determine their relative effectiveness in removing each of the five groups of 3130 Å. impurities. The Corning Red Purple Corex glass, used by many recent workers,[6] was also tested. The specific purposes assumed for each filter appear in Table I, in which the numbers refer to the regions of radiation tabulated above.

Table I

Assumed Useful Absorption Regions for Filters Tested

Filter	Primary region	Other regions
Nickel solution	4	5
Cobalt solution	5	(3)
Potassium biphthalate solution	2	1
Potassium chromate solution	3	1, (5)
Red Purple Corex glass	5	. . .

Experimental

The solution filters were made up from stock solutions of 0.01 M potassium chromate, 2 M cobaltous chloride and 1.78 M nickel chloride. For these, Merck "reagent" and Baker C. P. "analyzed" salts were used without purification.[7] The filters were tested in cylindrical quartz cells, of 1 in. diameter with optically plane parallel windows. The first three were used in 50 mm. thicknesses and the potassium biphthalate (0.0245 M) in a thickness of 10 mm.

In all tests the chromate solution was placed between the source and the biphthalate, since the former as well as the latter is an effective absorber for most of the wave length region below 3000 Å. Thus the chromate served to protect the biphthalate which otherwise tended to decompose under the full ultraviolet radiation of the arc, whereas the chromate was unaffected. In several tests the chromate and nickel solutions were mixed in the same cell. Although the results appeared unchanged, it seemed advisable to keep the solutions separated in the subsequent tests to prevent possible complications.

The glass filter was a Corning Red Purple Corex No. 9863, 5 mm. thick with polished surfaces. To determine what fraction of the galvanometer deflection was due to radiation in region 5 (above 3660 Å.) a Corning Greenish Nultra glass No. 3850, 5 mm. thick, was inserted in the light path after each set of measurements. This filter transmits about 5% of 3660 Å. and less than 0.01% of the ultraviolet below 3500 Å. The resulting deflections were further broken down into "blue-green" and "yellow-red-infrared" by the addition of a 5 mm. thickness of Corning H. R. Lantern Blue glass No. 5543. Radiation passed by this latter combination would fall at 3600–5000 Å., and the light absorbed would be between 5000 and 12,000 Å.

A cesium oxide photocell with plane quartz window was used to measure relative intensities of λ3130 Å. with various filter combinations. It was possible also to measure the visible and infrared radiation using the Corning glasses described above. Due to the small percentages of this extraneous light, deflections were not corrected for varying spectral response of the photocell. Cell currents were read on a scale at two meters from a sensitive Leeds and Northrup Type 2500 galvanometer. An Ayrton shunt allowed full-scale deflection over a 100-fold intensity range.

The optical set-up consisted of a 150-watt Hanovia Type U A 30 A2 mercury arc in a brass housing. The radiation passed directly through the successive quartz filter cells, the one nearest to the arc having a water-cooled jacket. The emergent beam then passed through the glass filters and was focused by a quartz lens onto the photocell. The cell could be easily removed from the light path, allowing the beam to be converged by a second lens onto the slit of a small Bausch and Lomb Littrow-type spectrograph with quartz prism. Using Eastman Kodak 1-F plates, this instrument had a sensitivity extending from about 2000 to 6000 Å., with a dispersion at 3130 Å. of 15 Å. per mm.

The spectrograph was used to determine relative intensities of the extraneous lines lying close to 3130 Å., with different filter combinations. Intensities were obtained from density tracings made with a small recording microdensitometer employing a Kipp and Zonen (Delft, Holland) galvanometer. The nine exposures on each plate, covering a variation of filter concentrations, were taken at times inversely proportional to the corresponding galvanometer deflection. Thus the integrated intensity of 3130 Å., assuming the reciprocity law, should be equal for each exposure, to within a few per cent. The varying densities of the 3340 and 3022 Å. lines allowed a determination of the relative purity of the 3130 Å. line under each condition. In measuring the photometer tracings, line densities were used; *i. e.*, the ratio of intensities in two weak lines was taken as the reciprocal of the ratios of I_t, the light transmitted by the emulsion.

The per cent. transmission for the different concentrations of solutions was obtained from the photocell intensity measurements and extrapolations to zero concentrations. Potassium chromate, nickel chloride, and cobalt chloride (less than 1 molar) were found to obey Beer's law within 1–2%.

Results

The results of this work are summarized in Table II.

The function of the cobaltous chloride solution was chiefly to remove certain components of the visible spectrum. A similar purpose was served by Red Purple Corex. While the latter absorbs most of the visible light, it transmits freely below 4000 Å. and deep into the ultraviolet. It also has several absorption minima in the red and infrared. Nickel chloride solution possesses absorption maxima which coincide almost exactly with the minima in the Corex curve.[8] In addition, nickel chloride exhibits an extremely sharp cut-off at about 3500 Å., transmitting almost completely the 3340 Å. line and absorbing nearly all of the 3660 Å. line.

The measured transmission of Red Purple Corex at 3130 Å. was about 85%. From Table II it is seen that 5 mm. of Red Purple Corex is over 10 times as efficient in removing the visible components as is cobaltous chloride. Hence, the Red Purple Corex was substituted for cobalt in all subsequent tests.

A proper combination of Red Purple Corex and

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(6) See, for example, Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).

(7) Work conducted by the Institute of Optics at the University of Rochester has indicated that the impurities usually present in nickel chloride, while very detrimental to the transmission at short wave lengths, had almost no effect on the long wave length cut-off at 3600 Å. In fact, the presence of slight amounts of iron in some instances improved the isolation of 3130 from 3660 Å.

(8) Institute of Optics, University of Rochester.

TABLE II

EFFECT OF FILTER CONCENTRATIONS ON INTENSITY AND SPECTRAL PURITY

Potassium biphthalate 0.0245 *M* in 10 mm. cell; ultraviolet below 3100 Å. less than 0.01%

K_2CrO_4 in 50 mm. cell, *M*	$NiCl_2$ in 50 mm. cell, *M*	$CoCl_2$ in 50 mm. cell, *M*	Red Purple Corex, mm.	Intensity in cm. galvanometer deflection			Max. % at 3342 Å.	% 3130 Å. transmitted
				Ultra-violet	3600–5000 Å.	5000–12000 Å.		
0.00000	0.178	..	5.0	177	..	...	..	100
.00025	.178	..	5.0	81.8	0.00	0.24	0.4	46.2
.0005	.178	..	5.0	60.4	.00	.24	.01	34.1
.001	.178	..	5.0	20.3	.00	.24	.01	11.5
.002	.178	..	5.0	2.13	.00	.14	.01	1.20
.0005	.000	..	5.0	71	..	(.33)	(.01)	100
.0005	.178	..	5.0	60.4	.00	.24	.01	85.1
.0005	.356	..	5.0	48.6	.00	.10	.01	68.5
.0005	.890	..	5.0	28.6	.00	.01	.01	40.3
.0005	1.78	..	5.0	12.9	.00	.00	.01	18.2
.0005	0.178	0.00	...	67	..	...	..	100
.0005	.178	.02	...	65.6	.9	44.5	.03	98
.0005	.178	.2	...	55.7	.1	11.0	.03	83.2
.0005	.178	.5	...	40.6	.02	2.9	.03	60.6
.0005	.178	1.0	...	22.6	.02	1.0	.02	33.7
.0005	.178	2.0	...	4.6	.00	0.23	.01	6.86

nickel chloride solution can be used to remove almost completely the Hg arc radiation above 3500 Å. The total visible intensity transmitted by a standard thickness of Corex (3 mm.) and the weakest nickel chloride solution (0.178 *M*) was insignificant on a percentage basis. It was also too small to be recorded conveniently on the spectrograph; hence, visual methods were used to obtain an almost totally dark beam. It was found impossible to increase the glass thickness and the nickel chloride concentration to a point where the source would be invisible when viewed directly from in front of the filter train. Most objects, including the cornea, fluoresce to varying degrees under ultraviolet radiation, with a pale blue glow easily mistaken for visible blue light. However, a true image of the beam as viewed on a non-fluorescing screen of magnesium oxide freshly deposited on aluminum was made to vanish entirely using 0.356 *M* nickel chloride and 0.0005 *M* potassium chromate, each in a 50 mm. cell, 10 mm. of 0.0245 *M* potassium biphthalate, and two 5-mm. thicknesses Red Purple Corex.

Since potassium chromate absorbs more strongly at 3340 than at 3130 Å. it can be used to remove the former mercury line completely. Its absorption, however, of the 3130 Å. is quite pronounced, as seen in Table II. Hence, an increase in the purity of this line brought about by increasing the potassium chromate concentration will necessarily be at the expense of 3130 Å. intensity. For most purposes a concentration of 0.0005 *M* potassium chromate in a 50-mm. layer, with a resulting 50% decrease in the desired intensity gives about the limit of practicable purification. The extraneous line is reduced then to less than 0.1% of the total.

Potassium chromate also absorbs nearly completely below 2900 Å., transmitting, however, several per cent. of 3020 and 2967 Å. To remove these lines potassium biphthalate was used. Although somewhat light-sensitive, it exhibited an amazingly sharp spectral cut-off just below 3100 Å. At a concentration of 0.0245 *M*, the biphthalate removed light below 3050 Å. to the extent that no radiation of wave length shorter than this appeared on the spectrographic plates, even at exposures ten thousand times greater than needed to produce a 3130 Å. image. At half this biphthalate concentration, the 3020 and 2967 Å. lines taken together are about 1% as intense as the 3130 Å. group.

The biphthalate tended in some experiments to become opaque to the desired wave lengths. The photochemical nature of the process is not clear, since it would be expected that if benzoic acid derivatives were the products the transmission would increase with exposure. At the intensities used—approximately 10^{13}–10^{14} quanta per second—and with the protecting layer of potassium chromate to remove the shorter ultraviolet, approximately 20% decrease in transmission resulted after twenty-four hours of exposure.

One final point should be noted concerning the selectivity of the solutions tested: they eliminate light above about 3300 Å. and below about 3050 Å. If medium or high pressure mercury arcs are used as light sources, the pressure broadening of the mercury triplet near 3130 Å. is considerable, in the order of 50 to 150 Å. Thus, the light isolated may extend from 3050 Å. to 3200 or 3300 Å.

The authors wish to thank Dr. F. W. Paul of the Institute of Optics for his advice and assistance on several aspects of the problem and for the loan of filter materials and measuring apparatus. The aid of Dr. A. B. F. Duncan and Mr. R. Holdsworth of the Department of Chemistry is also gratefully acknowledged.

Summary

Five filters commonly used to isolate λ 3130 Å. from the mercury arc spectrum have been critically evaluated over a range of concentrations. Cobaltous chloride was found to be of doubtful value. The combination of a 50-mm. length of 0.178 *M* nickel chloride, 50 mm. of 0.0005 *M* potassium chromate, 10 mm. of 0.0245 *M* potassium biphthalate, and 5 mm. of Red Purple Corex glass (Corning No. 9863), reduces extraneous ultraviolet radiation to less than 0.01%. About 25% of the 3130 Å group is transmitted. With a high-pressure arc, in which the desired triplet is broadened, the above filters restrict the radiation to the region 3100–3300 Å.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Catalysis of the Reaction of Chlorine and Oxalic Acid. Complexes of Trivalent Manganese in Solutions Containing Oxalic Acid

BY HENRY TAUBE

In the present study observations on the catalysis by manganic ion of the reaction

$$H_2C_2O_4 + Cl_2 = 2H^+ + 2Cl^- + 2CO_2$$

are reported. Analysis of the rate data accumulated in the study of this case of homogeneous catalysis has led to conclusions about the stability of complexes of trivalent manganese and oxalate in solutions containing hydrochloric acid and about the mechanism of the relatively slow net disappearance of the catalyst in the system.

Important conclusions can be drawn from qualitative observations which may be made on the system under study. If Mn(III), in solution as the sulfate complex, for example, is added to a solution 2 *M* in hydrochloric acid and containing also oxalic acid, the color of the trivalent manganese is discharged almost instantly. If, however, the acid solution contains also both chlorine and manganous ion, the color of trivalent manganese[1] persists for long periods of time—it has been observed up to twenty minutes—although it does eventually disappear. It is observed that chlorine does not oxidize manganous ion to the manganic state at an appreciable rate under the prevailing conditions. The persistence of manganic ion when manganous ion and chlorine are present simultaneously can therefore not be a simple equilibrium phenomenon. The direct experiment of comparing the color of a solution made up as above with one from which oxalic acid is absent, establishes that manganic ion is associated with oxalate even at 2 *M* hydrochloric acid.

Quantitative investigation of the system shows that during the time in which Mn(III) exists in the solutions described, the reaction of chlorine and oxalic acid proceeds at a greatly enhanced rate, and that manganous ion alone exerts no noticeable effect on the rate of this reaction. The rate of reaction of chlorine and oxalic acid has been measured as a function of the concentration variables, time and the temperature.

The data on the rate of reaction at zero time—when the catalyst has undergone no net decrease in concentration—are consistent with the following mechanism, and will be discussed with reference to it.[2]

Mn(III) in the solutions under investigation, usually 2 *M* in hydrochloric acid, is distributed among the ions Mn_{Cl}^{+++}, $MnC_2O_4^+$ and $Mn(C_2O_4)_2^-$.[3] Equilibrium between these species is established rapidly, and the equilibria are formulated as

$$H_2C_2O_4 + Mn_{Cl}^{+++} \underset{}{\overset{K_a}{\rightleftarrows}} MnC_2O_4^+ + 2H^+ \quad \text{(a)}$$

$$H_2C_2O_4 + MnC_2O_4^+ \overset{K_b}{\rightleftarrows} Mn(C_2O_4)_2^- + 2H^+ \quad \text{(b)}$$

The slow step in the series of reactions leading to catalysis of the reaction of chlorine and oxalic acid is the first order decomposition[2] of the ion $MnC_2O_4^+$

$$MnC_2O_4^+ \xrightarrow{k_1} Mn^{++} + C_2O_4^- \quad (1)$$

The following reactions are

$$C_2O_4^- + Cl_2 \xrightarrow{k_3} Cl + Cl^- + 2CO_2 \quad (3)$$

$$Cl + Mn^{+++} \xrightarrow{k_6} Mn^{+++} + Cl^- \quad (6)$$

Steps (3) and (6) together with the equilibria (a) and (b) account for regeneration of the catalyst.

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[1] Launer, THIS JOURNAL, **55**, 865 (1933), has shown that the net rate of decomposition of $Mn(C_2O_4)_3$ is decreased by oxygen, and that reduction of oxygen is induced by the decomposition of the complex ion.

[2] The form of the rate law agrees equally well with the slow step: $Mn^{+++} + C_2O_4^{=} \xrightarrow{k_1'} Mn^{++} + CO_2 + CO_2^-$. (1′) advanced by Launer.[5] A decision in favor of step 1 is made below (see Discussion) by arguments based on the variation of rate with temperature. No data published at present distinguish between $C_2O_4^-$ and CO_2^- as the reducing intermediate, nor, in fact, can Mn^+ be excluded as a possibility (see Discussion). The choice of $C_2O_4^-$ adopted here is quite arbitrary, and the specific rate established for the reducing intermediate may actually apply to CO_2^- or Mn^+.

[3] It is recognized that these ions associate with water, and the first at least, probably also with chloride ion. The formulas adopted are intended to imply a conclusion only about the ratio Mn(III) to $C_2O_4^{=}$ in the complex, and not to imply the absence of other interactions.