the molecular volume of the liquid. The values secured were as follows: cyclohexane, 70.6; ethyl alcohol, 129.4.

It is apparent from a comparison of the dielectric constants of the liquids as well as of the internal pressures that in pure liquid alcohol the attractive forces between the molecules are much greater than in pure cyclohexane. In dilute solutions of ethyl alcohol in cyclohexane the ethyl alcohol molecules are widely separated by the interspersed cyclohexane molecules. As a result the attractive forces between the ethyl alcohol molecules are negligible as compared with that in pure ethyl alcohol and the relative escaping tendency of the ethyl alcohol is much greater than in pure ethyl alcohol. As a result the vapor pressure of ethyl alcohol in such solutions exhibits wide deviations from Raoult's law. Since the ethyl alcohol molecules are too far apart to attract each other appreciably, they exert little squeezing out effect on the cyclohexane molecules and consequently the cyclohexane vapor pressure deviates but slightly from ideal behavior in solutions dilute in ethyl alcohol. In solutions concentrated in ethyl alcohol, the ethyl alcohol molecules are but slightly separated by the cyclohexane molecules. The separation, however, is not sufficient to alter appreciably the attractive forces between the alcohol molecules. Therefore, the effect of the added cyclohexane is merely that of reducing the number of molecules per unit volume and the result is only a slight deviation from Raoult's law. However, in such solutions cyclohexane exhibits large deviations from Raoult's law because of the squeezing out effect produced by the ethyl alcohol molecules, whose attraction for each other is much greater than the attraction of the cyclohexane molecules for each other or for the alcohol molecules. At intermediate concentrations the deviations of each component from ideal behavior are intermediate between their respective deviations in dilute and concentrated solutions, as would be expected on the basis of the explanation given.

Summary

1. A modification of the dynamic method for measuring vapor pressures devised by Pearce and Snow has been adapted to the determination of the total vapor pressure, and the partial vapor pressures of the components of binary solutions of ethyl alcohol and cyclohexane, ranging in concentration from pure alcohol to pure cyclohexane, at 25°.

2. The data have been used to calculate the activity coefficients, which indicate the deviations from Raoult's law.

3. Deviations from ideal behavior have been discussed and explained on the basis of the difference in polarity and internal pressure of the two components.

The Photo-oxidation of Liquid Carbon Tetrachloride

By Ernest H. Lyons, Jr., and Roscoe G. Dickinson

When liquid carbon tetrachloride is illuminated in an open quartz vessel by a quartz mercury arc, reaction occurs; the main reaction has been supposed[1] to be given by the equation $2CCl_4 \longrightarrow C_2Cl_6 + Cl_2$. The use of carbon tetrachloride as an actinometric substance for use in therapeutic work has been considered.[2]

We have found, in preliminary experiments, that carbon tetrachloride irradiated in the above manner develops a strong odor of phosgene; and if the liquid is then shaken with water, an acid solution results which oxidizes potassium iodide. Evidently, when carbon tetrachloride is irradiated in the presence of oxygen, some oxidation occurs; moreover, since the total amount of reaction is ordinarily not large, further complication may arise from the presence of traces of water. Consequently we have undertaken to exclude water and to determine the effect of ultraviolet light on carbon tetrachloride first in the absence of oxygen, and second, in its presence.

The photochemical procedure we have used has

(1) See, for example, Benrath and Hertel, Z. wiss. Phot., 23, 30 (1924); Morton, "Radiation in Chemistry," D. Van Nostrand Co., New York, 1928, pp. 55, 119.

(2) Mackenzie and King, "Practical Ultraviolet Therapy," Benn, 1926; Hymas, Quart. J. Pharm., 2, 281 (1929).

been to illuminate simultaneously a sample of carbon tetrachloride and an actinometer solution each filling a small quartz flask. The radiation was that from a water-cooled quartz mercury arc provided with a magnet to deflect the arc against the lamp wall; the radiation was filtered through 8 mm. of 10% sodium acetate solution. Liquid carbon tetrachloride has been found[3] readily to absorb radiation shorter than about 2600 Å. and to be substantially transparent to radiations longer than about 2650 to 2700 Å. The sodium acetate solution transmits the mercury line 2537 Å. but absorbs most of the shorter wavelength lines. Since in a cooled mercury arc the line 2537 Å. is strong and there are no strong lines in its neighborhood, it follows that, with the arrangement we have used, the primary effect on carbon tetrachloride is due to this radiation.
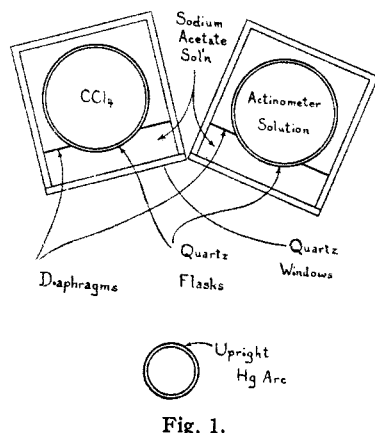

Fig. 1.

The actinometer contained a half-normal solution of monochloroacetic acid whose photochemical hydrolysis has been measured by Rudberg.[4] The hydrolysis is found to proceed according to the equation $CH_2ClCOOH + H_2O \longrightarrow CH_2OH-COOH + HCl$. Rudberg found a quantum yield within 7% of unity. Like the carbon tetrachloride, the monochloroacetic acid solution absorbs 2537 Å. fairly strongly but does not absorb any strong mercury lines of longer wave length. Hence the same radiation has been supposed to be effective in the actinometer as in the carbon tetrachloride.

Materials.—Consistent results could not be obtained unless the carbon tetrachloride was first subjected to rigorous treatment. Starting with c. p. material, the treatment found most satisfactory was to saturate with chlo-

rine dioxide and illuminate strongly with white light. As the chlorine dioxide was destroyed the saturation and illumination were repeated a number of times. Finally the carbon tetrachloride was washed with potash solution, then with water, distilled and dried over calcium chloride.

The monochloroacetic acid was Kahlbaum technical preparation. It was distilled three times in an all-glass still; the fraction retained boiled between 184 and 187°. The acid was kept in a desiccator and made up in 0.5 n aqueous solution immediately before use.

Apparatus.—The arrangement of the photochemical apparatus is shown in plan in Fig. 1. The spherical quartz flasks holding the carbon tetrachloride and actinometer solution were 38 mm. in diameter. The neck of the carbon tetrachloride flask had a Pyrex extension; this was fastened to the quartz by means of a fused silver chloride joint, the quartz and Pyrex surfaces at the joint being previously platinized. The Pyrex extension facilitated sealing the flask. For experiments in the presence of oxygen, a gas reservoir, a Pyrex bulb of several hundred cc. capacity, was attached to the extension. The carbon tetrachloride could then be kept saturated with oxygen by frequently flowing the liquid into the gas reservoir. Each quartz flask was placed in a small tank of sodium acetate solution with a polished quartz window; a diaphragm with a 25-mm. opening was placed just in front of each flask. All parts were mounted in reproducible positions.

A magnet (not shown) was placed so as to deflect the arc toward the line of contact of the two tanks. In spite of the symmetrical arrangement, the amount of light received by the two flasks was not quite the same. A number of runs made with monochloroacetic acid solution in each flask agreed to about 1% in giving 1.21 as the ratio of light received by the actinometer flask to that received by the carbon tetrachloride flask. This ratio was used in the calculation of quantum yields.

After illumination the actinometer solution was analyzed for chloride by potentiometric titration with silver nitrate following essentially the procedure described by Rudberg.[4] Since the chloroacetic acid underwent a slow thermal hydrolysis, an unilluminated portion of the actinometer solution was likewise titrated and the difference between the two titers attributed to photohydrolysis.

The carbon tetrachloride was analyzed ordinarily by shaking it with water, adding potassium iodide, and titrating with thiosulfate. This gave a measure of the oxidizing power (presumably free chlorine) developed by the illumination. The solution was then boiled to remove any carbon dioxide from hydrolysis of phosgene, cooled and potassium iodate added. After ten minutes, the solution was again titrated with thiosulfate to determine the acid present. The validity of this titration under the conditions prevailing was checked by carrying it out with known amounts of hydrochloric acid comparable to those appearing in the experiments.

In some cases the sample was split into two portions. The first portion was analyzed for oxidizing agent and acid as described and the second for chloride as follows. The oxidizing agent, assumed to be chlorine, was destroyed by adding ammonia, boiling and acidifying. The total chloride was then determined by potentiometric titration just as with the actinometer solutions. From the analysis

(3) Massol and Fauçon. Compt. rend., 189, 314 (1914); Melville and Wallo. Trans. Faraday Soc., 29, 1255 (1933).

(4) Rudberg. Z. Physik. 24, 247 (1924).

of the first portion, the amount of chloride resulting from the chlorine was calculated, and subtracted from the total found in the potentiometric titration.

The Effect of λ 2537 in the Absence of Oxygen.—A number of experiments were made without adequate exclusion of both oxygen and water. These gave erratic amounts of acid and chlorine. With improvements in experimental arrangement, however. it became clear that pure carbon tetrachloride underwent substantially no reaction on illumination with λ 2537.
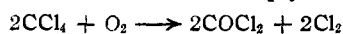
In these experiments the carbon tetrachloride was freed from oxygen by boiling it and at the same time bubbling nitrogen through it. The nitrogen had been taken from a tank and bubbled through a cuprous ammonia solution which was continuously regenerated by being flowed over metallic copper. The nitrogen was then washed in a permanganate solution and bubbled through concentrated sulfuric acid before being passed into the carbon tetrachloride. The flask containing the carbon tetrachloride was sealed off without interrupting the stream of nitrogen. In some experiments, anhydrone was present in the carbon tetrachloride flask during illumination; in others calcium chloride and in some cases no dryer.

The amounts of light used in these experiments were from 2 to 4 × 10^{-5} einsteins of λ2537. The amounts of chlorine or acid produced were less than 2 × 10^{-7} equivalents. Hence the quantum yields were less than about 0.01 equivalent of chlorine or acid per einstein absorbed.

The Effect of λ 2537 in the Presence of Oxygen.—A considerable number of experiments were performed using various techniques for the introduction of dry carbon tetrachloride and oxygen into the reaction vessel. These experiments yielded variable and unequal amounts of chlorine and acid; since we now regard the procedures as faulty in various respects, they will not be described. The following procedure always gave reproducible and intelligible results. A distilling flask was provided with a delivery arm with a sealed tip which would extend through the gas reservoir into the quartz flask. The flask was charged with carbon tetrachloride and anhydrone, sealed and allowed to stand for several hours. Then the tip of the delivery arm was broken and the arm quickly inserted into the reaction flask which previously had been carefully dried. A temporary ring seal was made by wiring on a short piece

of rubber tubing. A vacuum pump was connected through a calcium chloride tube to a side arm on the gas reservoir and the pressure reduced until the carbon tetrachloride boiled gently at 35–40°. It then distilled into the reaction flask, about half of the tetrachloride being lost to the pump. After the distillation, a stream of dried oxygen was run through the liquid without removing the distilling flask. The gas reservoir was then sealed up. The results obtained with this procedure are given in Table I.

The number of einsteins given is the number entering the carbon tetrachloride. It appears from the table that under the conditions of these experiments, the numbers of equivalents of chlorine, of acid resulting from hydrolysis, and of chloride are equal. This would be the case if the photochemical reaction were simply

$$2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2$$

The quantum yields in these experiments lie very close to one molecule of carbon tetrachloride oxidized per quantum absorbed. The intensity (in einsteins absorbed per unit time) was varied more than four-fold in this series.

Discussion.—Only continuous and no discrete absorption has been found with gaseous carbon tetrachloride in the ultraviolet.[5] This indicates that the primary absorption process is a dissociation, presumably into $CCl_3 + Cl$. The failure of pure carbon tetrachloride to decompose might then be attributed to a much higher specific rate for the process $Cl + CCl_3 \longrightarrow CCl_4$ than for either of the processes $2Cl \longrightarrow Cl_2$ and $2CCl_3 \longrightarrow C_2Cl_6$. An alternative would be to suppose that on illumination with λ2537 a small concentration of Cl_2 is built up but that the process $CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl$ occurs with a high specific rate so that little net decomposition results.

For the oxidation, mechanisms leading to the oxidation of one CCl_4 per quantum may readily be devised. For example, if a peroxide intermediate be assumed we may write: $CCl_3 + O_2 \longrightarrow CCl_3O_2$ followed by $2CCl_3O_2 \longrightarrow 2COCl_2 + O_2 + Cl_2$. However, before taking any particular mechanism too seriously it would be desirable to determine whether the quantum yield we have found is preserved under varying conditions, for example of temperature or oxygen concentration.

Summary

Contrary to previous suppositions, it has been found that pure liquid carbon tetrachloride is not decomposed when irradiated with light of wave

(5) Henrici. Z. Physik. **77**. 35–51 (1932); Leifson, Astrophys. J., **63**. 73 (1926).

TABLE I

IRRADIATION OF CARBON TETRACHLORIDE AND OXYGEN WITH λ 2537

Time, min.	Einsteins × 10^5	Equiv. chlorine × 10^5	Equiv. acid × 10^5	Equiv. chloride × 10^5	Equiv. chlorine per einstein	Equiv. acid per einstein
360	48.2	92.1	93.2	93.0	1.91	1.94
270	38.1	85.1	85.4	85.4	2.23	2.24
300	24.1	47.6	48.0	48.0	1.98	1.99
360	50.3	112.0	110.3	109.9	2.23	2.19
400	12.1	23.5	23.7	21.3	1.94	1.96
360	17.7	36.5	37.6		2.06	2.12
500	19.9	38.8	38.2		1.95	1.92
360	24.6	49.5	49.1		2.01	2.00
210	9.6	19.0	18.9		1.98	1.97
240	11.1	21.0	21.5		1.89	1.94
240	11.4	22.9	22.3		2.01	1.96
120	10.0	20.0	19.7		2.00	1.97

length 2537 Å. In the presence of oxygen, this irradiation has been found to produce reaction such that on subsequent hydrolysis equal numbers of equivalents of chloride, acid and oxidizing agent are found; the reaction is assumed to be

$2CCl_4 + O_2 \longrightarrow 2COCl_2 + 2Cl_2$. Using a monochloroacetic acid actinometer, quantum yields of one carbon tetrachloride oxidized per quantum absorbed have been found.

The "Salt Error" and Normal Electrode Potential of the Quinhydrone Electrode at 25°

BY FRANK HOVORKA AND WILLIAM C. DEARING

The "salt error" of the quinhydrone electrode was recognized but neglected by Biilmann[1] in the initial study of the cell Pt/quinhydrone, H$^+$(m), H$_2$(1 atm.)/Pt at 18 and 25°. From solubility measurements Sörensen, Sörensen and Linderström-Lang[2] showed the "salt error" to be due to a change in the activity ratio of hydroquinone and quinone, the dissociation products of quinhydrone. From similar measurements Linderström-Lang[3] calculated the potential corrections for the quinhydrone electrode. He also determined by extrapolation the value of E_{KB}^0, the potential of the quinhydrone–hydrogen cell at 18° were water the experimental liquid. Kruyt and Robinson[4] confirmed the results of Linderström-Lang regarding the influence of salts on the solubilities of hydroquinone and quinone. Numerous factors which influence the potential of the quinhydrone–hydrogen cell were carefully studied by Biilmann and Jensen.[5] Tammann and Jenckel[6] and Čupr[7] determined the "salt error" of the quinhydrone electrode in a limited number of solutions, but measurements were made against the calomel electrode rather than against the hydrogen electrode in the same solutions. Harned and Wright[8] determined the normal electrode potential of the quinhydrone electrode at intervals from 0 to 40° by an indirect method which required the combining of data for two types of cells. In a similar manner Urmánczy[9] determined the "salt error" of the quinhydrone electrode against the hydrogen

electrode for solutions of various salts, but with less precision due to uncertainties of the liquid junctions involved. For further papers dealing with the quinhydrone electrode and related subjects the reader is referred to a bibliography compiled by Morgan, Lammert and Campbell.[10]

In view of the increasing importance of the quinhydrone electrode in many fields it seemed advisable to study some of the fundamental properties of the electrode in a more systematic manner and with greater precision than heretofore attained. Foremost among the objectives was a study of the quinhydrone–hydrogen cell and a determination of the "salt error" of the quinhydrone electrode in solutions of a large number of electrolytes, each over such a range of concentration as to permit definite conclusions regarding the trend of the "salt error" and the possibility of making adequate corrections. As a corollary of this was the evaluation of E_0, the normal electrode potential of the quinhydrone electrode. Several secondary objectives developed in the course of the investigation. These will be discussed later.

Apparatus and Materials

Electrolytic hydrogen from a tank was washed with concentrated potassium hydroxide solution and water, then passed over platinum at 450°. Upon reaching the thermostat the hydrogen passed through a washing bottle containing the solution being studied and thence to the electrode vessel which was similar in some respects to that used by Linderström-Lang.[3] It consisted of two tubes, C and D, of 40-cc. capacity, and E with a capacity of 20 cc. These were connected through the three-way stopcock, F. A heavy rubber cap, G, was fitted tightly over the bottom of the stopcock. This was sealed with lacquer and furnished adequate insulation from the bath.

Two hydrogen electrodes of B. & S. No. 18 platinum wire and leads were sealed into a 5-mm. tube, leaving 17 mm. of the electrode wires exposed. This was fitted into a larger tube by means of a small rubber stopper. Two

(1) Biilmann, Ann. Chim., 15, 109 (1921).

(2) Sörensen, Sörensen and Linderström-Lang, ibid., 16, 283 (1921).

(3) Linderström-Lang, Compt. rend. trav. lab. Carlsberg, 15, No. 4 (1924); 16, No. 3 (1925).

(4) Kruyt and Robinson, Verslag. Akad. Wetenschappen Amsterdam, 35, 812 (1926).

(5) Biilmann and Jensen, Bull. soc. chim., 41, 151 (1927).

(6) Tammann and Jenckel, Z. anorg. allgem. Chem., 173, 337 (1928).

(7) Čupr, Pub. Faculté Sci. Univ. Masaryk, No. 133 (1931).

(8) Harned and Wright, THIS JOURNAL, 55, 4849 (1933).

(9) Urmánczy, Magyar Chemiai Folyoirat, 39, 125 (1933).

(10) Morgan, Lammert and Campbell, Trans. Am. Electrochem. Soc., 61, 405 (1932).