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THE ANALYSIS OF IMPURITIES
IN VARIOUS STAGES OF RECYCLED CARBON TETRACHLORIDE
AND CORRELATION WITH CHLORINATION PROPERTIES

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ABSTRACT

When recycling of carbon tetrachloride was suggested as a Beta plant procedure it was thought advisable to check it at various stages of the proposed purification process. Appropriate samples were obtained and the chlorination reactions were run and the products analyzed. The results showed a consistent decrease in the quality of the product in going from new, distilled, caustic wash and used carbon tetrachloride. The same samples were then submitted for analysis by infrared absorption spectra. The impurities present were discovered to arise from the use of the Celvacene lubricant. The main impurity, which was found in all of the recycle stages, was found to be an aldehyde. This impurity was proven to inhibit the reaction and its presence may be correlated with the chlorination properties of the recycled carbon tetrachloride.

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EXPERIMENTAL

The problem of recycled carbon tetrachloride was first considered by the liquid phase development group in relation to the Alpha plant procedure for the chlorination of TiO_2 to TiCl_4 .⁽¹⁾ These early results indicated that the practice of recycling the carbon tetrachloride might be undesirable. Later, conflicting results were obtained, when duplication was attempted. That is, according to the analysis of the products, recycling the carbon tetrachloride seemed a perfectly satisfactory procedure. However, judging from the appearance of the product, it was an undesirable procedure.⁽¹⁾ Subsequently the practice of recycling the carbon tetrachloride was successfully applied consistently in the Alpha chlorination process.

When recycling the carbon tetrachloride was suggested as a Beta plant procedure, it was thought advisable to check it at various stages of the proposed purification process. Mr. D. J. Shrecengost submitted appropriate samples to be tested. The reactions were run in a one liter beta type stainless steel reactor with a 35 rpm stirrer. A standard pentachloride reaction was carried out using 1000 ml of carbon tetrachloride and 250 gm of UO_2 . Either Dow (unused) carbon tetrachloride, Shrecengost (recycled), or a mixture of the two were employed. Both Bulk Treatment and Mallinckrodt oxide were used. The changes and product analyses are tabulated below.

(1) CD485 J. V. Hubbard

TABLE I

A*

Experiment No.	Type and Amount of CCl_4	Fine Material		Lumped Material	
		% Cl	% Chlorination	% Cl	% Chlorination
B225	1000 ml Dow	41.41	97.02		
B239	300 ml S-7 dist. and 700 ml Dow	40.65	95.24		
B236	700 ml S-7 dist. and 300 ml Dow	40.40	94.66		
B219	1000 ml S-7 dist.	40.01	93.74		
B221	"	40.19	94.17		
B235	1000 ml S-8 dist.	39.13	91.68		
B222	1000 ml NaOH treated S-7	38.44	90.07	28.23	66.14
B226	1000 ml untreated S-7	39.91	93.50	35.64	83.51

B**

D203	1000 ml Dow	42.77	100.21		
D200	"	41.97	98.34		
B231	1000 ml distilled S-7	40.76	95.50		
B230	1000 ml untreated S-7	39.44	93.58	25.82	60.50

* A, Bulk Treatment TO_3 Used.

** B, Mallinckrodt TO_3 Used.

As may be seen from the tables of data, which were arranged with new carbon tetrachloride at the top, diluted redistilled next, down to untreated carbon tetrachloride at the bottom, a definite decrease in quality of the product is observed in going from the top to the bottom of the tables. In other words, as the treatment of the carbon tetrachloride progressed the product improved in quality. However, the distilled carbon tetrachloride was still inferior to the Dow new carbon tetrachloride indicating that some impurity was not sufficiently removed by the recycle process. It was therefore desirable to determine the nature and source of the impurities in the various stages of the recycled carbon tetrachloride.

INFRARED ABSORPTION ANALYSIS

The concentration of the impurities in the carbon tetrachloride were known to be very low and chemical analysis appeared to be inadvisable. Samples of the recycled carbon tetrachloride were therefore submitted to the infrared laboratory to identify the impurities present and to correlate the presence of these impurities with the known chlorination properties of each sample.

The samples were run on the infrared spectrometer obtaining the absorption spectrum from 15μ to 1μ using several thicknesses of absorption cells (1.5 mm, .203 mm and .05 mm). The purpose of using the various thicknesses in the absorption path was to obtain both weak and strong absorption bands which could be thoroughly examined. The bands which appeared because of impurities in the various stages of the recycled carbon tetrachloride were determined by comparison with Dow new, methane derived, carbon tetrachloride. The results of the analyses are tabulated in the following table.

TABLE II

	Position of Absorption Band	Functional group Causing Band	Compound	New CCl ₄	Shrec. #7 Used CCl ₄	Shrec. #7 Used and Caustic Washed	Shrec. #7 Distilled	Shrec. #8 Distilled
1	3047 Cm ⁻¹	C-H	Cellulose Ester and Aldehyde	0	90	72.5	30.8	14.8
2	2311 Cm ⁻¹	C=O	Carbon Dioxide	0	80	0	0	0
3	1766 Cm ⁻¹	C=O	Acid Chloride & Aldehyde	0	100	83.3	64.0	37.5
4	1735 Cm ⁻¹	C=O	Cellulose Ester	0	40	29.2	16.2	3.5
5	1168 Cm ⁻¹	C-O	Cellulose Ester and Aldehyde	0	60	55.8	47.1	14.9
6	911 Cm ⁻¹	C-C Inorganic Band	Carbon Chain and Inorganic Impurity	0	20	23.9	0	0

7 4 1

5.

Table II

The first vertical column gives the frequency of the center of the absorption band in reciprocal centimeters. The second column indicates the functional group which causes the absorption band. The third column gives the compound to which the functional group is attached. The strongest impurity in the used carbon tetrachloride was estimated to be on the order of .1% or less for the concentration of the impurity causing the 1766 cm^{-1} band. The remaining numbers in the vertical column are estimates of the amount of these impurities present relative to the concentration of the impurity causing the 1766 cm^{-1} absorption band. Since extinction coefficients vary for different functional groups and various compounds these values may be compared with each other within an error of $\pm 100\%$. The figures in the horizontal rows may be compared with greater accuracy. These figures were calculated from the extinction of the various bands and may be compared with an accuracy of $\pm 5\%$.

Of the six absorption bands observed in the recycle carbon tetrachloride samples, the ones of special interest are the C-H bands at 3047 cm^{-1} , the C = O band at 1766 cm^{-1} , and the C = O at 1735 cm^{-1} . It was noted that the C-H band and the C = O band of the lower frequency disappear in approximately the same proportion in going from the used to the distilled carbon tetrachloride. The position of the C = O group indicates that this compound is a partially chlorinated ester. The C = O band at 1766 cm^{-1} is seen to appear in all of the recycle carbon tetrachloride and since the distilled samples were known to be inferior to the Dow new carbon tetrachloride the presence of this impurity might be correlated with the chlorination properties of these samples.

The phosgene in the used carbon tetrachloride had evidently hydrolyzed since it was not detected. Phosgene would have given an absorption band around 1800 cm^{-1} . The carbon dioxide that appeared in the used carbon tetrachloride was completely removed by the caustic work.

The presence of the impurities containing the C-H, C = O groups (2), the C - O and the C - C no doubt come from the Celvacene which was used in the packing around the stirring rod in the reactors. Celvacene is a mixture of a cellulose ester and castor oil which has been polymerized to the desired consistency by heating. A number of spectra of Celvacene were run, as well as Celvacene dissolved in carbon tetrachloride also Celvacene dissolved in carbon tetrachloride and heated in a chlorination reactor. There was no noticeable difference in the spectrum of these samples. The C = O band at 1736 cm^{-1} appeared but the C-H band was at a lower frequency than that which was found in the recycle samples. The C = O band at 1766 cm^{-1} was not present.

Several grams of Celvacene were then chlorinated by passing Cl_2 over it at 170°C . The resulting residue was dissolved in CCl_4 and the spectrum run and examined. The spectrum showed the same 1736 cm^{-1} C = O band and the C-H band now appeared at a higher frequency. It is known that the C-H frequency shift in this direction when the hydrogen occurs in halogenated compounds, (3) and this shift was evidently caused by the partial chlorination of the cellulose ester in the Celvacene. No attempt was made in this experiment to collect the more volatile fragments. Another experiment was run and the

(2) With the exception of the C = O band from CO_2 .

(3) Barnes, Gore, Liddel, Williams, Infrared Spectroscopy, Page 19, Reinhold Publishing Corporation, 1944.

volatile fragments were collected. These fragments were found to be largely water and little could be done with it in the way of infrared absorption analysis. (4) The sample was washed with carbon tetrachloride and the infrared spectrum obtained but the 1766 cm^{-1} band could not be identified. The $\text{C}=\text{O}$ band at 1736 cm^{-1} and the C-H band at 3047 cm^{-1} were not present. It therefore seemed probable that the portion of the Celvacene that chlorinates most readily and breaks up into light fragments giving off water vapor and other volatile impurities is the castor oil.

A chlorination reaction was then run using 1000 cc of carbon tetrachloride in which 5 gms of Celvacene had been dissolved and 250 gm of UO_3 . The resulting product due to the water vapor from the chlorinated castor oil was of very poor quality and could not be analyzed. The uranium chloride and the phosgene were removed from the carbon tetrachloride by washing with water and the spectrum of the carbon tetrachloride obtained. The 1736 cm^{-1} $\text{C}=\text{O}$ band and the C-H band both occurred at the proper frequencies but the 1766 cm^{-1} band was not present.

Since experimental attempts to duplicate the chlorination of the Celvacene in the chlorination reaction had failed to identify the compound giving rise to the 1766 cm^{-1} band it was decided to approach the problem by an empirical method. Since the impurity is found even after distillation, the boiling point of this compound should be close to that of CCl_4 , probably a few degrees higher. There is a weak C-H band that can be associated with this impurity and since the C-H band is at a high frequency it is probably a highly chlorinated compound. A chlorinated compound having

- (4) Water being very polar is practically opaque to the infrared spectrum beyond 2μ .

a terminal double bond might give an absorption band at approximately this frequency but the simplest of this type of a compound, having the $C=C$ terminal band, would be hexachloropropylene which has a boiling point of $210^{\circ}C$. which is too high. Another compound having both $C=C$ and $C=O$ groups in trichloroacrylyl chloride which has a boiling point of $159^{\circ}C$. which is still too high and besides the $C=O$ and $C=C$ bands would show a doublet instead of a single sharp band if this were the impurity present. The spectra of a number of chlorinated compounds were run including hexachloropropylene and chloroacetyl chloride. The spectra of hexachloropropylene was in no way similar to that of the impurity in question. The sample of chloroacetyl chloride was a mixture of mono, di and tri chloroacetyl chloride and the $C=O$ bands appear to be a doublet. (Though there are actually three bands, one for each compound). The lower portion of the doublet occurs at the proper frequency to account for the 1766 cm^{-1} band.

The library of curves in Barnes' book (5) were consulted for compounds having absorption frequencies at this 1766 cm^{-1} position; also the tables of absorption frequencies in T.Y.Wu's book (6) were examined. From the study of the spectra of over 400 compounds eight were found to have their strongest absorption band at this frequency. All but two of these compounds could be eliminated by the presence of other functional groups which were not found in the recycled carbon tetrachloride. The two compounds were ethyl chlorocarbonate and benzoyl chloride. The functional group which gives rise to the absorption band at 1766 cm^{-1} and also another band at 1168 cm^{-1} is $\begin{smallmatrix} Cl \\ | \\ C=O \end{smallmatrix}$.

(5) Barnes, Gore, Liddell, Williams "Infrared Spectroscopy".

(6) T.Y.Wu, "Vibrational Spectra and Structure of Polyatomic Molecules".

Thus from the above evidence of the spectrum of chloroacetyl chloride and from the examination of the spectra of a large number of compounds, the compound would appear to be a partially chlorinated acid chloride; however, since the acid chloride would be effectively removed by the caustic wash it seems probable that the absorption band is caused by two compounds having an absorption at approximately the same frequency. Since there is a weak C-H band to be associated with one or both of these compounds it seems probable that the compound which is not removed by the caustic wash is a chlorinated aldehyde. On the basis of this conclusion a chlorination reaction was run using 250 g of UO_3 and a 1000 ml solution of 1% butyl aldehyde in carbon tetrachloride. The reaction did not start until the temperature had reached 180° (40° to 50° above normal). When the reaction started it was violent and the charge was blown out. The presence of an aldehyde therefore definitely inhibits the reaction.

CONCLUSION

Referring to the analyses in table II what probably happens is this. The Celvacene which is used in the packing around the stirring rod is dissolved by the carbon tetrachloride in the chlorination reaction. (7) The cellulose ester in the Celvacene is polymerized and partially chlorinated but this impurity is almost entirely removed by the recycle purification process. The castor oil in the Celvacene is also chlorinated giving off water, which harms the quality of the product, and partially chlorinated acid chlorides and aldehydes. The acid chlorides are effectively removed

- (7) Further evidence that the Celvacene goes into the reactor is that the packing rings quickly dry out, and the material remaining on the rings does not resemble the original Celvacene but is very resinous. This is the polymerized cellulose ester.

from the carbon tetrachloride by the caustic wash but the aldehydes remain and a large portion carries through even in the distillation process. It is these aldehydes then which interfere with later chlorination reactions.

It has been definitely known for sometime that castor oil inhibits the chlorination reaction (8), what has been apparently overlooked is that Celvacene is a mixture of a cellulose ester and castor oil which has been polymerized by heating. It has been shown here that the use of Celvacene is undesirable because various organic impurities are added to the carbon tetrachloride and part of these carry through the recycle process and at least one group in particular, the aldehydes, inhibits the chlorination reaction. In view of this fact it would seem advisable to use some other lubricant in place of the Celvacene or to introduce in the purification process a method of removing the aldehydes.

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