showing a tendency to decompose on standing. The samples, sealed in thin-walled tubes, were allowed to warm up very gradually in an alcohol bath contained in a large transparent Dewar tube; a calibrated toluene thermometer was used to read the temperature.

Summary

Three new fluorobromides of silicon, $SiFBr_3$, SiF_2Br_2 and SiF_3Br, have been prepared, analogous to the previously known fluorochlorides, and their chief physical properties have been determined.

The cleavage of Si_2F_6 with bromine yields SiF_3Br and SiF_2Br_2, together with SiF_4. The fluorination of silicon tetrabromide with antimony trifluoride (without a catalyst) yields all three mixed halides. Suitable experimental conditions for the preparation of these compounds are given.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF BRITISH COLUMBIA]

Systems of Sulfur Dioxide and Monolefins. I. Caprylene and Sulfur Dioxide

BY W. F. SEYER AND LISLE HODNETT

A series of investigations has been carried out on the relationships existing between sulfur dioxide and normal paraffin hydrocarbons. It was found that the critical solution temperature was a function of molecular weight.[1] It then became desirable to know whether similar conditions were true for the unsaturated derivatives of the normal paraffins having one double bond, *i. e.*, monolefins. In the case of cetene ($C_{16}H_{32}$) and sulfur dioxide, the curve defining the limits of the coexistence of the two liquid phases has the same general shape as that of any two partially miscible liquids.[2] Freezing point measurements carried out on mixtures of sulfur dioxide and amylenes in this Laboratory indicated that these substances were miscible in all proportions, hence it was estimated that partial miscibility ought to begin at about a chain length of eight carbon atoms. F. de Carli has stated that caprylene was only slightly soluble in liquid sulfur dioxide and formed a yellow solution, which he regarded as a sign of compound formation.[3]

Experimental

The general procedure in determining the freezing and miscibility points was the same as that already described when dealing with the normal hydrocarbons. A difficulty, however, was encountered in the purification of the olefin that was not met with in the case of $C_{16}H_{32}$, nor in the case of the normal hydrocarbons, but was similar to that which was experienced when dealing with cyclohexene. When ordinary caprylene is mixed with sulfur dioxide it takes on a deep red color. A small amount of this red compound dissolves in the sulfur dioxide layer giving it a yellow tinge. In a previous experiment[4] it was found that the presence of minute quantities of air in cyclohexene–sulfur dioxide mixtures, caused immediate condensation of the cyclohexene and sulfur dioxide[4] producing a reddish colored compound, whose composition has been established by Marvel and coworkers.[5]

In this particular case oxygen was found to be the catalyst that induced reaction which was absent when all work was done in an inert atmosphere of nitrogen. From the work of I. L. Ryden and C. S. Marvel it would appear that the coloration of the caprylene–sulfur dioxide mixtures is due to the formation of polysulfones.[6]

The course of the reaction was undoubtedly due to the presence of peroxides in the caprylene because much coloration took place upon refluxing it over metallic sodium and formation of a red amorphous compound continued as long as a positive test for peroxides was obtained. The test employed was that recommended by Conant and Peterson[7] in which a solution of ferrous ammonium sulfate and ammonium thiocyanate is used. The original material gave a deep red color with this reagent even after it had been distilled, but after it had been refluxed over sodium in an inert atmosphere for six or seven hours no color developed.

Materials

The caprylene used was obtained from the Eastman Kodak Co. It had a boiling point lying between 124–126° which could not be changed materially by the ordinary laboratory rectification methods. The material was very similar to that used by Brühl,[8] who claimed that caprylene was a mixture of the two isomeric compounds of 1- and 2-octene and reported the refractive index as n^{20}D 1.4132. Our own had slightly higher value, n^{20}D 1.4137, after purification.

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[1] Seyer and Todd, *Ind. Eng. Chem.*, **23**, 325–327 (1931).

[2] Seyer and Hugget, *Trans. Roy. Soc. Canada*, **18**, Sec. III, 209 (1924).

[3] F. de Carli, *Gazz. chim. ital.*, **57**, 347–355 (1926).

[4] Seyer and King, THIS JOURNAL, **55**, 3140 (1933).

[5] D. S. Frederick, H. D. Cogan and C. S. Marvel, *ibid.*, **56**, 1815 (1934).

[6] L. L. Ryden and C. S. Marvel, *ibid.*, **57**, 2311 (1935).

[7] J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932).

[8] J. W. Brühl, *Ann.*, **235**, 11 (1886).

The production of oxygen-free hydrocarbon was carried out in the apparatus shown in Fig. 1. The material in question along with metallic sodium was introduced into the flask through the side arm (G). The outlet from the nitrogen apparatus was then connected to the flask at (G) and a steady stream of gas allowed to sweep through the apparatus while refluxing took place, which operation lasted from six to seven hours. At the conclusion of the refluxing period, the side arm (C) was bent at (D) and the parts (F) and (E) attached. The hydrocarbon was next distilled from (A) and condensed in (E) while a constant stream of nitrogen passed through the apparatus and made its exit from the side-tube. The hydrocarbon was then once more distilled through the same apparatus, after it had been cleaned and fresh sodium introduced. Three fractions were collected of which the middle portion was used for the investigation.

As the slightest trace of oxygen caused coloration when sulfur dioxide was added to the hydrocarbon it was of the utmost importance to have the nitrogen as pure as possible. The method of preparation as suggested by Mellor was found to be the most satisfactory, for the present compound.[9]

Procedure

The hydrocarbon having been purified and stored in the container had next to be introduced in the desired amounts into the glass bulbs without appreciable contamination with oxygen. The transferring operation was carried out by means of the device illustrated in Fig. 2. By closing the stopcock at (B) and opening the one at (A), nitrogen could be used to flush out the air in the bulb (D) through tube (T). The container (E) was then quickly transferred from the condenser, the tube (C) inserted through the stopper and the side-arm of (E) connected to tube (B) by means of the rubber sleeve (S). Upon closing (A) and opening (B), caprylene could be forced from (E) to (D) in any desired amounts. The bulb (d) having received the desired amounts was then disconnected at S′, stoppered, weighed, frozen and then rapidly sealed onto the sulfur dioxide filling apparatus which has already been described in a previous article. Liquid air was used as the cooling agent and the bath consisted of low-boiling petroleum ether.[1] In this case, however, the sulfur dioxide was prepared from Baker C. P. sodium bisulfite. In all over 30 bulbs were filled in this manner.

The temperatures at which crystals appeared and the two liquid phases disappeared were determined in the usual manner. To measure these temperatures a pentane thermometer was used which read to 0.2° but could be estimated to within 0.05°. It was standardized, at the freezing point temperatures of sulfur dioxide and caprylene in the pure state, against a Leeds and Northrup resistance thermometer which in turn had been standardized by the Bureau of Standards at Washington. The results of these measurements are given in Table I.

TABLE I

Weight caprylene, g.	Weight SO_2, g.	Weight %, SO_2	Mol %, SO_2	Temp. of disappearance of 2 liquid phases, °C.	F. p., °C.
		100.00	100.00		− 75.4
0.0588	6.6579	99.12	99.50		− 75.8
.0461	4.5568	98.78	99.31		− 76.2
.0707	3.5639	98.05	98.88	−62.7	− 75.6
.1734	3.6490	95.46	97.39	−36.0	
.2787	3.9589	93.42	96.13	−31.9	− 75.6
.3826	3.5519	90.30	94.22	−25.6	
.3989	2.3408	85.44	91.13	−20.5	− 75.8
.4600	1.7847	79.51	87.17	−17.3	− 75.8
.9442	2.8030	74.80	83.86	−16.9	− 75.6
.5940	1.4227	70.61	80.79	−16.4	− 75.6
.7164	1.6657	69.92	80.27	−16.7	− 75.8
.6926	1.2766	64.84	76.35	−16.9	− 76.0
1.0661	1.9310	64.43	76.01	−16.8	
0.9368	1.4487	60.73	73.02	−17.0	− 75.5
.9599	1.2572	56.70	69.62	−17.8	− 76.1
1.1335	1.1410	50.16	63.80	−18.8	
0.7039	0.6166	46.57	61.81	−20.0	− 75.8
1.5431	.9303	37.61	51.34	−25.2	
0.4026	.5709	28.93	41.61	−32.8	− 76.0
2.0771	.5234	20.13	30.63	−47.1	− 75.8
3.7764	.4998	11.69	18.81		− 88.4
3.6818	.4000	9.80	15.98		− 89.5
3.5646	.3504	8.95	14.68		− 93.2
3.7910	.3138	7.64	12.65		− 97.7
4.9809	.1093	2.15	3.71		−105.6
4.2031	.0049	0.116	0.202		−105.4
		.00	.00		−105.2

Although the caprylene as has been pointed out is not a pure octane, yet because of the great difficulty encountered in preparing pure octane it was thought worth while to determine its freezing point with some degree of care. The apparatus described in Fig. 3 was used for this purpose. A special freezing point tube (C) was constructed with an air-tight cover (F) through which passed the quartz tube of the resistance thermometer. The side arm (E) was filled with a cork packing such that the shaft through it rotated freely without air leaking by, the mercury between the layers of cork acting as an additional seal. The

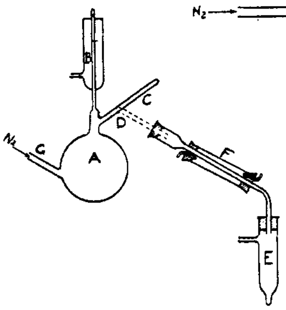

Fig. 1.

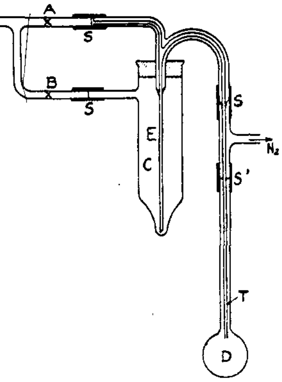

Fig. 2.

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(9) J. W. Mellor, "A Comprehensive Treatise on Theoretical and Inorganic Chemistry," Longmans, Green and Co., London, 1928, Vol. VIII, p. 48.

crank (D) was connected to a worm gear and it in turn to a small motor. It was thus possible to stir the 35 cc. of the hydrocarbon with a constant velocity by means of stirrer (S) which in turn was attached to an eccentric at (G). A Dewar tube filled with low-boiling petroleum ether served as a bath whose temperature could be regulated by forcing in liquid air through the tube (A), and by vigorous stirring. The freezing point tube was first evacuated and then caprylene, through a side arm not shown in the figure, was distilled from the special still already described. Three freezing point determinations were made, the external bath in no case falling below −106.6°, or rising above 105.6. The values are as follows: −105.01, −105.17 and −105.52° giving −105.23° as an average figure.

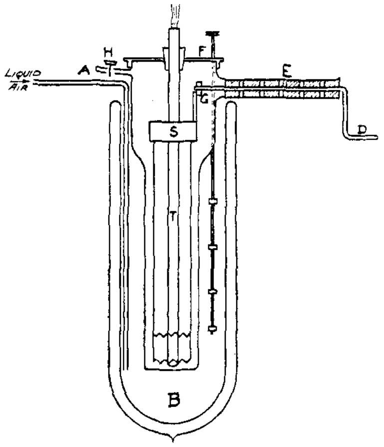

Fig. 3.

By plotting the temperatures of the freezing and miscibility points against mole per cent. of sulfur dioxide the curve of Fig. 4 was obtained. It has the familiar form of the partially miscible two-component system. Region I consists of one liquid phase; II two liquid phases; III solid sulfur dioxide and solution; IV eutectic and solid sulfur dioxide; V solid caprylene and solution. The critical solution temperature is −16.5°, while that of octane with sulfur dioxide is 26°, hence the presence of the double bond results in the lowering of the C. S. T. by as much as 42.5°.

Some days after the measurements had been made it was noticed that the contents of the tube became slightly colored. Consequently, it was thought worth while after periods of fourteen and twenty-eight days to redetermine the temperatures at which the liquid phases disappeared.

It was observed that very little reaction took place after the first fourteen days, also that the boundary temperatures had only risen from 0.2 to 0.9°. The rise, however, was quite independent of the amount of components present. The cause of the reaction was probably due to the small amount of the oxygen which found its way in during the filling operation when for a short period of time the bulbs were open to the air. In the work on cyclohexene it was pointed out that the condensation reaction ceased after the catalytic oxygen had been used up in a side reaction. It would thus appear that no reaction between sulfur dioxide and caprylene would take place at elevated room temperatures if no oxidizing agents were present.

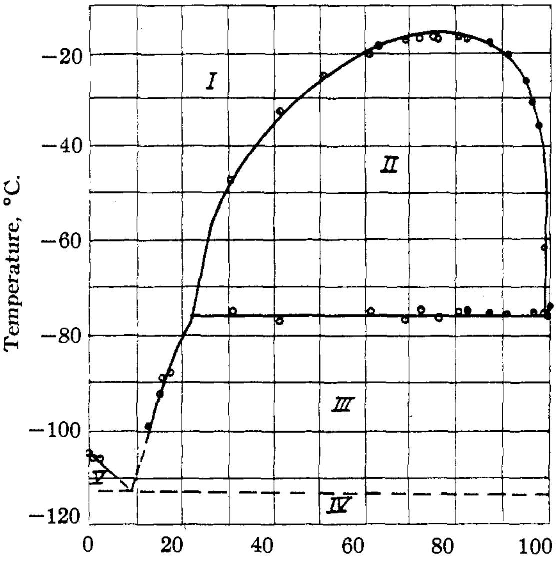

Fig. 4.—Mole percentage of sulfur dioxide.

Summary

1. Evidence has been presented that caprylene absorbs oxygen from the air to form a peroxide.

2. The freezing point and points of complete miscibility of caprylene with sulfur dioxide have been found.

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