Green Sulfur, A New Allotropic Form

BY FRANCIS OWEN RICE AND JEROME DITTER

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In a previous publication,[1] it was shown that if sulfur vapor in a flowing system at a pressure of about 0.2 mm. and a temperature of about 500°, is suddenly cooled to liquid nitrogen temperatures, a purple solid, probably S_2, condenses out. During the course of this work, a green modification sometimes appeared but the authors[1] did not study this form beyond showing that it was not, as they originally thought, a mixture of yellow and purple sulfur. This hypothesis was disproved by grinding together, under liquid nitrogen, mixtures of purple and ordinary yellow sulfur and showing that there was no formation of green sulfur. In this note we shall give an account of a study of the preparation and properties of green sulfur.

When sulfur, below its melting point, is sublimed in a vacuum onto a liquid nitrogen-cooled surface, only yellow sulfur is obtained. If, however, the sulfur is melted, a green form mixed with yellow condenses on the liquid nitrogen-cooled surface. In order to determine if the green form can be prepared by condensing sulfur vapor in equilibrium with liquid sulfur, we constructed the apparatus shown in Fig. 1. The bulb, A, containing sulfur was evacuated with a separate line which was sealed off before making a run. The temperature of the bath was slowly raised to 200° but at no time did the deposit on the liquid nitrogen-cooled finger have a color other than that of yellow sulfur. Deposition was sufficiently slow to ensure near equilibrium conditions in the vapor in the bulb A since even at 200°, where the vapor pressure of sulfur is 2.12 mm., a visible deposit on the cold finger was obtained only after several minutes.

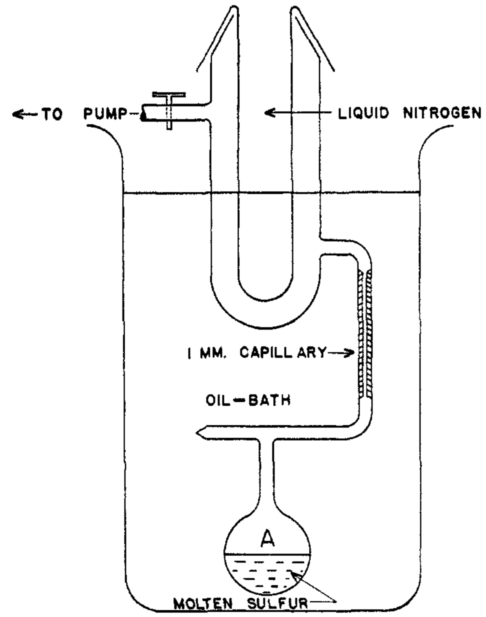

Fig. 1.

A series of experiments was then performed in an apparatus (see Fig. 2) which enabled us to determine the best conditions for preparing green sulfur by condensing the vapor under non-equilibrium conditions. The furnace used in this apparatus was much shorter than that used in the preparation of purple sulfur and therefore, in this experiment, the conditions were not such as to favor the attainment of equilibrium. As might be expected from our preliminary experiment with green sulfur, this form appears even when the furnace is not heated provided the oil-bath is kept above the melting point of sulfur. If the sulfur is maintained below its melting point by keeping the oil-bath in the range 80–110°, only yellow sulfur appears on the cold finger if the furnace is at room temperature but, if its temperature is raised to about 200°, a slightly greenish deposit is obtained which gradually changed to a very deep green as the furnace temperature is raised to about 400°. When the furnace temperature approaches 450°, purple sulfur begins to form as in the experiments previously reported.[1] These results with solid sulfur are obtained both with amorphous and crystalline sulfur.

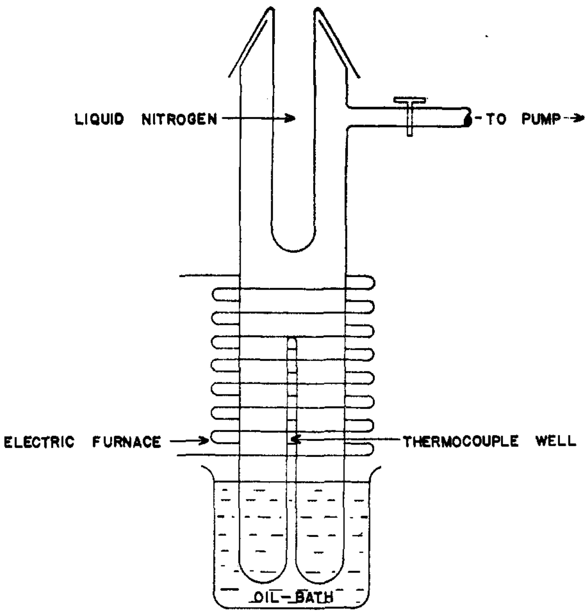

Fig. 2.

We then made a new series of experiments in which the furnace temperature was kept constant at about 200° and the temperature of the sulfur was raised from about 80 to about 170°. As mentioned previously a deposit, colored slightly greenish, was obtained in the lower range of temperature of the oil-bath but as its temperature was raised, the color deepened until in the range of 150–170° an intensely green sublimate formed on the cold finger.

We offer the following tentative hypothesis to account for these phenomena. We think that the molecule of green sulfur is S_8, in which the eight-membered ring of ordinary stable sulfur has opened to form an S_8 chain. This would explain why subliming solid sulfur does not give the green form but subliming liquid sulfur does, since[2] liquid sulfur in the range 30–40° above its melting point appears to be predominantly S_8 chains. The behavior of S_8 rings in the vapor may be understood if we assume that the speed of decomposition of the S_8 chain molecules into smaller molecules is smaller than the speed of the rupture of the S_8 ring molecules into S_8 chain molecules.

We have no conclusive single piece of evidence for this view but it is in agreement with several properties of the green form. This form is stable indefinitely at liquid nitrogen temperatures but changes into yellow sulfur at a measurable rate above −100°. At room temperature the change occurs in a few seconds. When the yellow sulfur formed by transition from the green variety is analyzed by extraction with carbon disulfide in a Soxhlet extractor, the composition is approximately

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[1] F. O. Rice and C. N. Sparrow, THIS JOURNAL, **75**, 848 (1953).

[2] G. Gee, *Trans. Faraday Soc.*, **48**, 315 (1952).

10% amorphous sulfur and 90% crystalline sulfur, suggesting that the change from green to yellow simply consists of closing the ring.

If green sulfur consists of diradical chains, it would be expected to be paramagnetic in virtue of the unpaired electrons. A qualitative test using a powerful electromagnet showed that green sulfur is very slightly paramagnetic and becomes diamagnetic when it changes to yellow sulfur.

Rate measurements of the transition from green to yellow sulfur were conducted using the method previously described for purple sulfur. We repeated the rate measurements for purple sulfur and confirmed the previous result that there is an initial rapid reaction followed by a slower change at almost constant speed. In the present work we estimated the speed of the initial change for purple sulfur at the four temperatures: −107, −102, −98 and −88° and by plotting the logarithm of the rate against the reciprocal of the time obtained an activation energy of 2.0 kcal. as compared with the previously reported value of 3.1 kcal. for purple sulfur. Using the same method for green sulfur we obtained the value 3.9 kcal. for the activation energy of the change green → yellow sulfur.

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The Isolation of Diosgenin from Solanum Xanthocarpum[1]

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During the course of isolation of solasodine from the dried fruits of *Solanum xanthocarpum* we have encountered a persistent impurity which has now been identified as diosgenin.

Although Gupta and Dutt[2] have reported the isolation of a sterol, carpesterol, $C_{36}H_{54}O_4$, m.p. 248°, and a $\Delta^{\alpha,\beta}$-unsaturated lactone (solanocarpone) $C_{28}H_{42}O_7$, m.p. 78°, the presence of the sapogenin, diosgenin, had been undetected hitherto.

The occurrence of small amounts of diosgenin along with solasodine provokes an interesting speculation as to the possible mode of biogenesis of solasodine. This finding is also of interest in view of the recent report of Briggs and O'Shea[3] who obtained small amounts of diosgenin by treating N-nitrososolasodine with boiling aqueous acetic acid. The main product of this reaction was an isomer of diosgenin.

Experimental[4]

The finely ground dry fruits (2.62 kg.) of *Solanum xanthocarpum* were extracted in a Soxhlet extractor with petroleum ether (4 l., 65–75°) for 44 hours, then with methanol (3.5 l.) for 140 hours. The methanol extract was evaporated to dryness on the water-bath and the semi-solid mass taken up in 10% acetic acid, treated with charcoal at boiling temperature and filtered through Filter-cel. The filtrate was made basic with ammonia and the glycoside collected. After several triturations with petroleum ether the crude, partially solid material was dissolved in hot methanol and hydrochloric acid (2 *N* with respect to methanol), refluxed for 2.5 hours, an additional half-hour with charcoal, and finally filtered through Filter-cel. The precipitated, crude solasodine hydrochloride was collected. Further dilution of the mother liquor with ether yielded more of the same substance. The hydrochloride was dissolved in hot methanol, water added to incipient turbidity, and made alkaline with ammonia gas. The solasodine (24.23 g.) was collected after standing overnight. Eight grams of the above crude, dry solasodine was dissolved in 1200 cc. of dry ether and 140 cc. of 1% ethereal hydrogen chloride was added with agitation. After cooling in ice-water for one-half hour the solasodine hydrochloride was collected and washed with cold dry ether. The ethereal filtrate was washed with Na_2CO_3 solution, water and dried over Na_2SO_4. Evaporation of the solvent yielded 50 mg. of crude diosgenin which after chromatography and recrystallization from acetone afforded 8 mg. of needles, m.p. 194–198°. Its infrared spectrum was identical with that of an authentic specimen of diosgenin.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 77.71; H, 10.00.

In another experiment the crude diosgenin was directly acetylated in the usual manner with acetic anhydride–pyridine and chromatographed over alumina. Crystallization from acetone and recrystallization from methanol yielded flat rods, m.p. 194.5–196°. Its infrared absorption spectrum likewise was identical with that of an authentic specimen of diosgenin acetate.

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[1] The *Solanum xanthocarpum* was obtained from the Institute of Agriculture, Anand, through the generous coöperation of the American Consul General, Bombay, India.

[2] M. P. Gupta and S. Dutt, *J. Ind. Chem. Soc.*, **15**, 95 (1938).

[3] L. H. Briggs and T. O'Shea, *J. Chem. Soc.*, 1654 (1952).

[4] The melting points are uncorrected and taken on the Kofler block.

Some Alkyl Thiocarbamates Prepared from Alkyl Thiocyanates by Riemschneider's Reaction

BY K. SCHMIDT AND P. KOLLEK-BÖS

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As was shown by Riemschneider and coworkers,[1a] the melting points of the primary aliphatic thiocarbamates differ only slightly from one another. On the basis of this observation the melting points of the hitherto unknown thiocarbamates, *n*-$C_{13}H_{27}$–, *n*-$C_{15}H_{31}$–, *n*-$C_{17}H_{35}$– and *n*-$C_{19}H_{39}$–$SCONH_2$, were predicted.

Since we had in connection with other investigations the thiocyanates *n*-$C_{13}H_{27}$–, *n*-$C_{15}H_{31}$–, *n*-$C_{17}H_{35}$– and *n*-$C_{19}H_{39}$–SCN at our disposal, we converted them by Riemschneider's reaction[1b,c] into the corresponding thiocarbamates and determined the melting points of the latter. The procedure followed was analogous to that given for the preparation of myristyl thiocarbamate.[1c] As is evident from the following table, there is good agreement between the predicted and the observed melting points of the four thiocarbamates.

	M.p., °C.	
	Predicted	Obsd.
n-$C_{13}H_{27}SCONH_2$	110	109.5–110
n-$C_{15}H_{31}SCONH_2$	111–111.5	111.5
n-$C_{17}H_{35}SCONH_2$	111.5–112	111–112
n-$C_{19}H_{39}SCONH_2$	113	113.5

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[1] R. Riemschneider and co-workers, (a) *Angew. Chem.*, **64**, 420 (1952); (b) THIS JOURNAL, **73**, 5905 (1951); *Pharmazie*, **4**, 460 (1949); *Chimica e industria (Milan)*, **34**, 353 (1952); *Z. Naturforsch.*, **7b**, 277 (1952); (c) *Monatsh.*, **84**, 316 (1953).