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

The Schönberg Rearrangement. Kinetics of the Rearrangement of Bis-(4-chlorophenyl) Thioncarbonate to the Thiolcarbonate[1]

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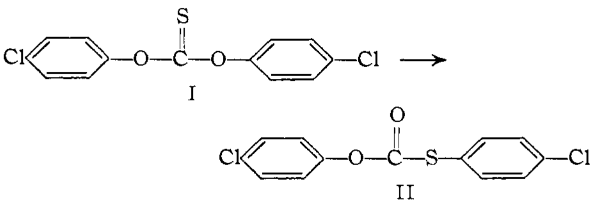
The rate of the rearrangement of bis-(4-chlorophenyl) thioncarbonate (I) to bis-(4-chlorophenyl) thiolcarbonate (II) without solvent has been measured at a number of temperatures around 250°. The reaction is first order, the energy of activation is 38.2 kcal./mole, and the entropy of activation at 263.8° is −12.6 cal./deg./mole. Isolation experiments show that the reaction is essentially quantitative. The kinetics are in agreement with the idea that the reaction involves a four-membered cyclic transition state.

In a recent study[2] of the Schönberg rearrangement of diaryl thioncarbonates to diaryl thiolcarbonates, it was found that the reaction was favored by electron-withdrawing groups in the *ortho* and *para* positions. The present paper reports a kinetic study of the rearrangement of the 4-chloro compound (I → II); it is found that the reaction is strictly first order, and that the kinetics are in agreement with the idea that the reaction is a nucleophilic displacement by sulfur, with a four-membered cyclic transition state.[2]



I

II

Experimental

Bis-(4-chlorophenyl) thioncarbonate (I) was prepared by the action of thiophosgene on 4-chlorophenol,[2] and was recrystallized from alcohol until there was no change in the ultraviolet absorption spectrum on further crystallization; the m.p. was 158.0–159.0°.

Analytic Method.—The reaction was followed spectrophotometrically; since the absorption curves for I and II were not markedly different (Fig. 1), it was found advisable to use the optical density at 244 mμ, and construct an optical density–composition plot[1] in the manner described by Carlin and Odioso[3] using a total concentration of the two components I and II of 0.0160 g./l. in 95% ethanol. The composition of unknown mixtures could then be determined by making up a solution of total concentration 0.0160 g./l., determining the optical density at 244 mμ, and reading the composition from the plot. Optical densities were determined with a Beckman DU spectrophotometer.

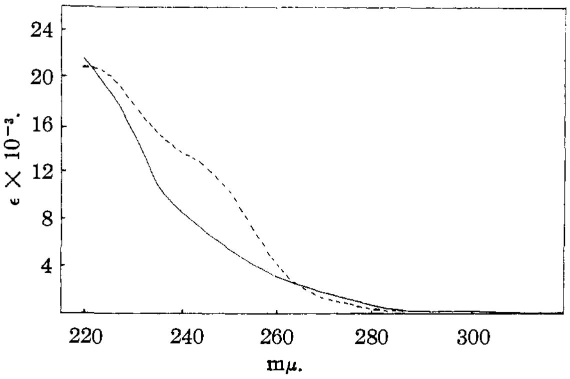


Fig. 1.—The ultraviolet absorption spectra of: —, bis-(*p*-chlorophenyl) thioncarbonate (I); -----, bis-(*p*-chlorophenyl) thiolcarbonate (II).

Procedure.—The measurements were run in a thermostat containing Fisher bath wax, held in a tall beaker which was heated by a Glas-Col mantle. This was regulated to keep the bath about 15° below the desired temperature; the fine heating control was provided by an immersion heater, controlled by mercury regulator and a relay. The temperature of the bath, which was constant within ±0.1°, was measured by an Anschütz thermometer.

Ten 1-cc. samples of a solution containing 0.2000 g. of bis-(4-chlorophenyl) thioncarbonate (I) in 25 cc. of benzene were pipetted into ten test-tubes (12 × 75 mm.). The benzene was evaporated at reduced pressure and the test-tubes were sealed; the tubes, in a wire basket, were then placed in the thermostat. To counteract the lag in the attainment of the thermostat temperature by the tubes, and the cooling effect of the tubes on the thermostat, the temperature of the thermostat was raised about 5° above that desired for the run before the basket was put in; the temperature dropped at once to the desired point. The tubes for short reaction times (300 and 600 sec.) were put in singly to minimize the temperature drop in the bath. No correction was applied for the heating lag. At appropriate intervals, test-tubes were removed and cooled by immersion in chloroform. The tubes were broken, the solid was dissolved in alcohol and the solution was made up to 50 cc. The solutions were diluted to a total concentration of 0.0160 g./l. by making a 5-cc. sample up to 50 cc. The optical densities were determined at 244 mμ and the compositions obtained from the plot.

Treatment of Data.—The first-order rate constants were derived from the slopes of the straight lines obtained by plotting 2.303 log $(100/100 - x)$ against time in sec., where x = per cent. reaction at time t. The Arrhenius energy of activation was obtained in the usual way from the plot (Fig. 2) of log k against the reciprocal of the absolute temperature. The entropy of activation, $\Delta S^{\ddagger}$ was calculated in the usual way.[4]

Isolation of Products.—Most of the rate runs were not carried much beyond 50% reaction, because there appeared to be some slight decomposition indicated by discoloring in the samples heated a longer time, which interfered with the determination of the optical density. Isolation experiments were therefore carried out. Several test-tubes containing bis-(4-chlorophenyl) thioncarbonate made up in the same way as those used in the rate runs were heated at 260–270° for 210 min. The solid obtained on cooling melted, without purification, at 92–94°; the pure rearrangement product melts[2] at 96–97°, and the starting material at 158°. The material isolated gave no depression on mixed m.p. with the authentic rearrangement product.

Discussion of Results.—It is apparent that the rearrangement follows good first-order kinetics, a typical run being shown in Table I; there does not seem to be the upward drift in rate constants

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] H. R. Al-Kazimi, D. S. Tarbell and D. Plant, THIS JOURNAL, **77**, 2479 (1955).

[3] *Cf.* R. B. Carlin and R. C. Odioso, *ibid.*, **76**, 2345 (1954).

[4] H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

which was noted[5] when allyl aryl ethers were rearranged to allylphenols without solvent.

TABLE I

REARRANGEMENT OF BIS-(4-CHLOROPHENYL) THIONCARBONATE AT 268.7°

Time, sec.	Optical density, 244 mμ	Reacn., %	$k \times 10^4$, sec.$^{-1}$
300	0.414	6.0	2.07
600	.439	13.4	2.40
900	.456	18.6	2.28
1200	.462	20.5	1.91
1500	.491	29.2	2.30
1800	.503	32.7	2.20
2100	.516	36.6	2.17
2400	.521	38.0	1.99
2700	.535	42.4	2.04
3000	.548	46.4	2.08

TABLE II

FIRST-ORDER RATE CONSTANTS AT DIFFERENT TEMPERATURES

Temp., °C.	$k \times 10^4$, sec.$^{-1}$
251.4	0.62
259.6	1.11
263.8	1.46
268.7	2.04
269.3	2.08

The reaction appears to be similar to the rearrangement of arylimino ethers.[6] The entropy of activation found in our work, −12.6 cal./deg./mole, is similar to that observed in the rearrangement of allyl aryl ethers,[5] the three-carbon allyl rearrangement,[7] and of allyl vinyl ethers[8]; all of these are reactions which almost certainly involve a cyclic transition state of six atoms. Furthermore, the entropies of activation obtained for the arylimino ether rearrangement,[6] which is regarded as having a four-membered ring transition state, are in the same range. The present results, therefore, support the suggestion advanced in the previous paper[2] that the Schönberg rearrangement involves a nucleophilic attack of sulfur on the aromatic ring, with a four-membered ring transition state.

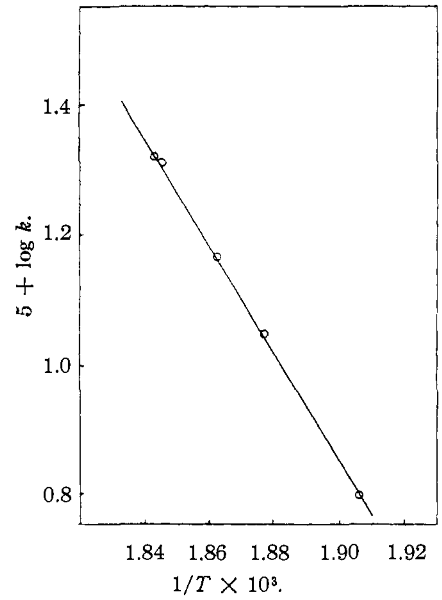

Fig. 2.—Arrhenius plot of log k vs. $1/T$.

It was noted[2] that in the case of the unsymmetrical compound, phenyl 2-naphthylthioncarbonate, there was an interchange of aryl groups to give the symmetrical compounds, which was more rapid than the rearrangement. It is possible, therefore, that the bis-(4-chlorophenyl) thioncarbonate may rearrange by an intermolecular reaction. However, the first-order kinetics and the value of $\Delta S^{\ddagger}$ indicate that the intramolecular mechanism is more probable.

Acknowledgment.—We are indebted to Dr. H. R. Al-Kazimi and Dr. Derek Plant for preliminary kinetic measurements.

ROCHESTER, N. Y.

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[5] (a) J. F. Kincaid and D. S. Tarbell, THIS JOURNAL, **61**, 3085 (1939); (b) D. S. Tarbell and J. F. Kincaid, *ibid.*, **62**, 728 (1940).

[6] K. B. Wiberg and B. I. Rowland, *ibid.*, **77**, 2205 (1955); in view of this comprehensive study, we have not thought it necessary to pursue our kinetic measurements on a variety of compounds.

[7] E. G. Foster, A. C. Cope and F. Daniels, *ibid.*, **69**, 1893 (1947).

[8] F. W. Schuler and G. W. Murphy, *ibid.*, **72**, 3155 (1950); L. Stein and G. W. Murphy, *ibid.*, **74**, 1041 (1952).