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Addition Compounds of Thiourea

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Solid complexes of thiourea with hydrocarbons have been discovered by Fetterly[1a] and by Angla.[1b] They are in some respects very similar to the complexes of urea. Thiourea, however, forms complexes with more or less "compact" molecules while organic urea complexes are formed only by molecules containing a fairly long hydrocarbon chain. Thus urea and thiourea appear to offer possibilities of complementary applications.

The methods, definitions and notation of the preceding paper on urea complexes are used also for the thiourea complexes. The dew point method has been found to be useful for the more volatile substances. The "non-aqueous reaction" method can hardly be used because the approach to equilibrium is too slow. For the "aqueous reaction" method the activity of thiourea in aqueous solution is required.

Activity of Thiourea in Aqueous Solution.—The only available data for deriving the activity in the desired temperature range appear to be two freezing point depressions.[2] In order to obtain additional information for 25 and 50° we examined the equilibrium of a few complexes by means of both methods (dew point and aqueous reaction). The results were used for calculating the activity of thiourea.

For interpolation the relation

$$\log a' = \log x + B(1 - x)^2 \qquad (1)$$

was assumed to hold, where a' is the activity of thiourea referred to the pure supercooled liquid, x the mole fraction of thiourea and B an interaction coefficient. Since eqn. (1) does not furnish a good representation of the data for urea, it cannot be expected to give accurate results for thiourea, but the approximation will be sufficient for the present purpose.

The activity a of thiourea referred to the solid can be expressed by means of the mole fraction $\bar{x}$ of the saturated solution[3] and the degree of saturation

$$s = x/\bar{x} \qquad (2)$$

From (1) and (2) we obtain

$$\log a = \log s + B\bar{x}(1 - s)(2 - \bar{x} - s\bar{x}) \qquad (3)$$

The results from equilibrium determinations and the activity curves for B = 2.4 (25°), B = 0.9 (50°) are shown in Fig. 1. For 0° the value B = 4.2 was derived from Roth's freezing point of a 0.3933 M solution.

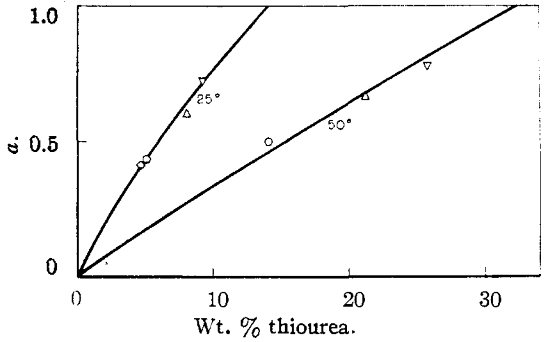

Fig. 1.—Activity of thiourea in aqueous solution (from equilibrium with triptane O, methylcyclopentane △, cyclohexane ▽, methylcyclohexane ◇).

Results

The compositions of eleven thiourea complexes[4] are given in Table I. The molal ratios of both isoparaffins and naphthenes increase fairly regularly with the number of carbons. The molal ratios of the naphthenes are slightly higher than those of the isoparaffins of equal carbon number. The weight ratios do not sensibly depend on the size (2.25 ± 0.15 for isoparaffins, 2.5 ± 0.2 for naphthenes).

TABLE I

COMPOSITION OF THIOUREA COMPLEXES AND INCREASE OF HEAT CONTENT ON DECOMPOSITION

	Molal ratio thiourea/ reactant	Weight ratio thiourea/ reactant	ΔH, kcal./ mole
2,2-Dimethylbutane	2.6	2.3	4.4
2,3-Dimethylbutane	2.4	2.1	...
2,2,3-Trimethylbutane	2.9	2.2	3.7
2,2,4-Trimethylpentane	3.3	2.2	3.4
2,2,4,4-Tetramethylpentane	4.0	2.4	...
Cyclopentane	2.4	2.6	2.2
Methylcyclopentane	2.9	2.6	...
Cyclohexane	3.0	2.7	...
Methylcyclohexane	2.9	2.3	...
Isopropylcyclohexane	4.1	2.5	1.5
Carbon tetrachloride	3.0	1.5	...

Weight ratios as well as molal ratios are considerably lower than the ratios for urea complexes. Isoparaffins occupy almost one half of the total complex volume while n-paraffins occupy little more than one-third.

cis-Decalin reacts with thiourea but the reaction proceeds so slowly that no reliable data

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[1] (a) L. C. Fetterly, unpublished results, Shell Oil Company, Inc., Wilmington, California; (b) B. Angla, *Compt. rend.*, **224**, 402 (1947).

[2] W. A. Roth, *Z. physik. Chem.*, **43**, 557 (1903).

[3] A. Seidell, "Solubilities," 3rd ed., Vol. 2, D. Van Nostrand and Co., New York, N. Y., 1941, p. 41.

[4] After this paper had been submitted, we learned that Angla in a recent communication (*Ann. chim.*, [12] **4**, 639 (1949)) reported a molal ratio m = 3 not only for cyclohexane and carbon tetrachloride but also for other compounds, including cyclopentane. Using Angla's method we obtain m = 2.5 for cyclopentane.

could be obtained. No addition compound was obtained at 0° or at room temperature from the dimethylpentanes (2,2 or 2,3 or 2,4), 2-methyl-2-butene, isopropyl alcohol, secondary or tertiary butyl alcohol, 2-methyl-2,4-pentanediol, isopropyl ether, methyl isobutyl ketone, or dimethylsulfolane (2,4-dimethylthiolane 1,1-dioxide).

The equilibrium constants for the decomposition of the complexes are shown in Figs. 2 and 3. The increase of heat content on decomposition or the heat of formation ΔH (kcal./mole reactant) is given in Table I for those complexes for which the equilibrium has been determined over a range of 30° or more. A comparison with the equilibrium constants of urea complexes reveals considerable differences.

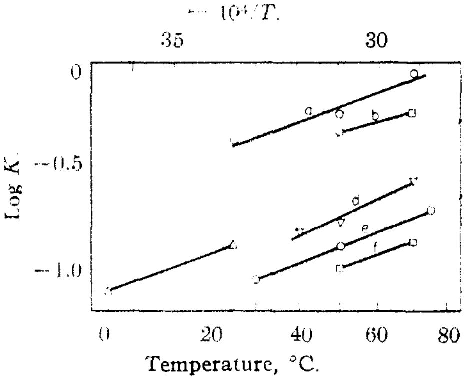

Fig. 2.—Equilibrium constants (isoparaffins and carbon tetrachloride): a, 2,2,4-trimethylpentane; b, 2,3-dimethylbutane; c, 2,2,4,4-tetramethylpentane; d, 2,2-dimethylbutane; e, triptane; f, carbon tetrachloride.

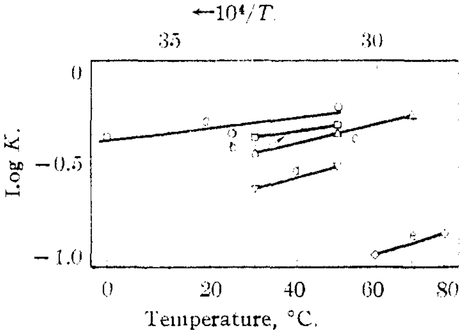

Fig. 3.—Equilibrium constants (naphthenes): a, isopropylcyclohexane; b, methylcyclohexane; c, cyclopentane; d, methylcyclopentane; e, cyclohexane.

Firstly, the stability of the thiourea–hydrocarbon complexes is relatively low. Even at 0° the values of K are greater than 0.05. This corresponds approximately to the urea complex of *n*-octane. The high stability of urea complexes of the longer *n*-paraffins has no parallel in thiourea complexes of hydrocarbons.

Secondly, the temperature coefficient of K and therefore the heat of formation of the thiourea complexes is low. Consequently the stability of the thiourea complexes decreases much less rapidly and the decomposition temperatures are comparatively high.

Thirdly, no relation between the free energy, the heat of formation and the molal ratio appears to exist.

The relation between structure and stability of thiourea complexes is by no means simple. Quite obviously "compact" molecules form more stable complexes but no more definite relation is apparent. The difference in stability of 2,3-dimethylbutane and its 2,2-isomer is remarkable. The dimethylpentanes do not form stable complexes, 2,2,4-trimethylpentane one of low stability, 2,2,4,4-tetramethylpentane a much stabler one. The introduction of a methyl group influences cyclopentane and cyclohexane strongly but in opposite directions.

Summary

The composition and the equilibrium constants for the decomposition of the thiourea complexes of five isoparaffins, five naphthenes and carbon tetrachloride have been determined. Compared with urea complexes, free energy and heat of formation as well as the molal ratio (thiourea/reactant) are low. Approximate values for the activity of thiourea in aqueous solution are presented.

Emeryville, California Received January 10, 1950