

range, but toward saturation the affinity of polyvinyl alcohol for water becomes greatest. Using the integral free energy equation (9) over the range of its validity and graphically integrating the differential free energy curve at higher partial pressures of water, integral free energies have been calculated and are tabulated in Table II.

The  $-\overline{\Delta H}$  values are shown in Fig. 7, from which the integral net heats listed in Table II were obtained.

As long as the sorption follows a linear sorption isotherm at both upper and lower temperatures the differential heats are constant with polymer composition; the curves for cellulose acetate, polyvinyl butyral and alcohol illustrate this behavior. The unusually large  $-\overline{\Delta H}$  value for cellophane is noteworthy as it is a rather clear indication that the structure or internal configuration of the water-attracting polar groups must have a considerable influence on the heat of hydration, otherwise  $-\overline{\Delta H}$  for cellophane would be no larger than that for polyvinyl alcohol, or cellulose itself. The increased water affinity and heat of hydration of regenerated cellulose over that for cellulose or cellulose acetate were pointed out some time ago by Sheppard and Newsome.<sup>19</sup> Note the slight rise in  $-\overline{\Delta H}$  for polyvinyl alcohol at high partial pressures of the water vapor.

In conclusion one of us (M.D.) wishes to acknowledge (1) the help received in several stimulating discussions with Professor Bull and (2) a grant from E. I. du Pont de Nemours and Co. which defrayed part of the expense of preparing this manuscript.

(19) S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **36**, 930 (1932) and earlier papers. The  $\overline{\Delta F}$  and  $\overline{\Delta H}$  curves of Simril and Smith<sup>2</sup> for cellophane are entirely similar to ours.

### Summary

1. Equations for the free energy of adsorption or sorption of any substance in terms of the constants of the linear, Langmuir and Brunauer, Emmett and Teller adsorption isotherm equations have been derived for both the differential and integral free energies.

2. Similar equations for the differential net heats (isosteric heats) are also given.

3. Data of Bull on the amount of water sorbed by proteins and nylon have been recalculated to yield differential free energies and differential and integral net heats of sorption different from those discussed by Bull, but, in the case of the integrated free energy data, equal to the previously published values of Bull.

4. The average differential heats over the first layer graphically computed from Bull's data are much higher than calculated from the constant  $c$  of the BET theory assuming  $a_1b_2/a_2b_1$  to be unity (this assumption is undoubtedly not valid).

5. The fraction of polar groups associated with one water molecule at saturation is shown to be equal to the fraction of amorphous polymer in unstretched and stretched nylon. The significance of this observation is not clear.

6. As the initial differential heats vary widely for sorption on chemically similar polar groups, the structural configuration of the groups must be considered.

7. Differential and integral free energies and heats of hydration are graphed or tabulated for five polymers, cellophane, cellulose acetate, polyvinyl alcohol, polyvinyl butyral and vinylidene chloride-acrylonitrile co-polymer.

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## Cuprous Chloride Derivatives of C<sub>5</sub> Diolefins

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Studies on the formation of cuprous chloride compounds with butadiene and isoprene have been reported by Gilliland and his co-workers.<sup>2</sup> The butadiene-cuprous chloride was found to have the formula, C<sub>4</sub>H<sub>6</sub>·2CuCl, and that reported for the compound with isoprene was C<sub>5</sub>H<sub>8</sub>·3CuCl. However, the authors expressed considerable doubt as to the latter formula, suggesting that the reaction may not have been complete in their experiments.

In addition a cuprous chloride complex of piperylene, formed by reaction with CuNH<sub>4</sub>Cl<sub>2</sub> solution, has been reported by Lur'ye and co-

workers,<sup>3</sup> and a similar solution was used by Craig<sup>4</sup> to separate the geometrical isomers of piperylene from contaminating olefins by formation and subsequent dissociation of the cuprous chloride compounds. The complex salts were formed at room temperature and decomposed at 60 to 100°. In this study by Craig it was observed that the *cis* isomer formed a more stable derivative than the *trans* isomer.

In the present research, vapor pressure curves for the cuprous chloride complexes of isoprene and a mixture of the piperylene isomers have been

(1) Present address: Copolymer Corporation, Baton Rouge, Louisiana.

(2) Gilliland, Bliss and Kip, *THIS JOURNAL*, **68**, 2088 (1941).

(3) Lur'ye, Marushkin, Chistov and Shlossberg, *C. A.*, **32**, 6099 (1938); *Sintet. Kauchuk*, **3**, No. 6, 13 (1934).

(4) Craig, Geometric Isomers of Piperylene, Abstract of Papers for American Chemical Society Meeting, September, 1942, Buffalo, N. Y.

determined. So far as the equilibrium pressure curve of the isoprene compound is concerned, the results obtained in this Laboratory are in agreement with the findings of Gilliland.<sup>2</sup> However, it has been demonstrated with a high degree of assurance that the formula for the isoprene compound is  $C_5H_8 \cdot 2CuCl$ , completely analogous to the formula for the butadiene compound. The formula for the piperylene complex was also found to be  $C_5H_8 \cdot 2CuCl$ .

### Experimental

**Preparation of Piperylene and Isoprene.**—Piperylene and isoprene were both obtained from the pyrolysis products of petroleum by a combination of fractional distillation and reaction with cuprous chloride, the method described by Lur'ye and co-workers<sup>5</sup> being employed.

A piperylene fraction composed of 70% diene and 30% olefins was treated with a molar excess of cuprous chloride in a modified type of autoclave described by Lur'ye.<sup>5</sup> After a reaction period of one to two hours at temperature between  $-5$  and  $+5^\circ$  the unreacted hydrocarbon was removed at 100 mm. pressure and 25 to  $35^\circ$ . The diene fractions were then obtained by heating to a maximum temperature of  $135^\circ$  at pressures as low as 20 mm. Twelve reactions of this type with different samples gave diene products with the following ranges of physical properties:  $n_D^{20}$  1.4291–1.4308;  $d_4^{20}$ , 0.6790–0.6809; refractivity intercept ( $n_D^{20} - 1/d_4^{20}$ ) 1.0896–1.0909; per cent. of diene by gravimetric maleic anhydride method as modified by Farmer and Warren,<sup>6</sup> 93.7–97.6.

From the known properties of piperylene and isoprene it was apparent that the latter material was present as an impurity in these samples and also that a mixture of the isomeric pipervlenes was present, with the *trans* isomer predominating.

These partially purified samples were combined and fractionated through a 48-inch by one inch distilling column packed with  $3/4$  by  $1 1/4$  turn glass helices, for which the estimated efficiency was 20 theoretical plates. A blend of three fractions obtained from this distillation having the following ranges of physical properties was employed for the equilibrium pressure studies of the piperylene-cuprous chloride complex:  $n_D^{20}$  1.4295–1.4306;  $d_4^{20}$ , 0.6775–0.6796; refractivity intercept, 1.0906–1.0908. Comparison of these physical properties, particularly the refractivity intercept,<sup>7</sup> with those for piperylene published by Craig<sup>4</sup> indicates that, although the liquid was principally *trans*-piperylene, some isoprene was apparently present. The properties of the final fraction also indicated the presence of some *cis* isomer.

Despite the lack of complete purity the piperylene was considered suitable for use. The previous measurements of Craig<sup>4</sup> and Gilliland<sup>2</sup> had indicated that the isoprene complex was less stable than that of piperylene and hence it was believed that the isoprene present would be substantially eliminated during the removal of unreacted hydrocarbons prior to the equilibrium pressure measurements.

An isoprene fraction containing approximately 70% diene and 30% olefins and pentanes was purified in the same way as the crude piperylene fraction. No attempt was made to remove piperylene possibly present, which may be the cause of the slight differences between the equilibrium pressures observed in this research and those given by Gilliland.<sup>2</sup>

**Determination of Equilibrium Vapor Pressures.**—Dissociation pressures of the cuprous chloride compounds were determined in an apparatus similar to that

described by Gilliland and co-workers.<sup>5</sup> Pressure readings were accurate to 1 mm. and temperature readings to  $0.2^\circ$ .

Approximately 1.5 moles of the diene was added to 0.17 mole of cuprous chloride which was dispersed on 80 g. of powdered pumice. The mixture was allowed to react for about twelve hours at  $0^\circ$  and then the excess hydrocarbon was removed by evacuation to 100 mm. pressure at the same temperature. The boiling points of the hydrocarbons concerned are all below  $0^\circ$  at this pressure. After several hours of evacuation, the pressure was reduced as rapidly as possible to less than 1 mm. and then the system was closed off and connected to a manometer. Equilibrium was assumed to have been established at a given temperature when no further change in the pressure reading occurred for a minimum period of one hour.

**Empirical Formulas for Piperylene-Cuprous Chloride and Isoprene-Cuprous Chloride Complexes.**—I. To 5.97 moles of cuprous chloride contained in an autoclave of the type described by Lur'ye<sup>3</sup> partially filled with steel balls was added 7.5 moles of piperylene having the physical constants:  $n_D^{20}$  1.4309,  $d_4^{20}$  0.6806. After the mixture had reacted for four and one-half hours at  $-5$  to  $+2.5^\circ$ , the excess hydrocarbon was distilled off at  $-3$  to  $+16.5^\circ$  and 100 mm. pressure. Since the vapor pressure of the piperylene-cuprous chloride complex is about 8 mm. at  $16^\circ$ , negligible dissociation of the complex occurred during this process. Decomposition of the compound at higher temperature up to  $114^\circ$  resulted in a recovery equivalent to 5.74 moles of diolefin having the physical constants:  $n_D^{20}$  1.4306,  $d_4^{20}$  0.6792, and analyzing 97.7% diene by hydrogenation.<sup>9</sup>

II. The experiment was repeated using cuprous chloride dispersed on powdered pumice (to prevent caking) contained in an ice-cooled flask. To 0.47 mole of cuprous chloride was added 1.63 moles of the piperylene recovered from the dissociation of the complex in the previous experiment. The mixture was allowed to react for twelve hours at  $0^\circ$  and then the excess hydrocarbon was removed as in the previous experiment. Decomposition of the complex by heating above the dissociation temperature at 100 mm. pressure allowed a recovery equivalent to 0.456 mole of piperylene.

III. Three experiments similar to the second experiment with piperylene were conducted using isoprene with the properties:  $n_D^{20}$  1.4200;  $d_4^{20}$  0.6798. In each a molar excess of diene was mixed with cuprous chloride dispersed on pumice and the mixture was allowed to react for twelve to fourteen hours. The excess hydrocarbon was removed and the complex formed decomposed as in the previous experiments.

### Results and Discussion

The measured dissociation pressures at various temperatures for the piperylene-cuprous chloride complex and the isoprene-cuprous chloride complex are shown in Tables I and II, respectively. In Fig. 1 the logarithms of the dissociation pressures have been plotted against the reciprocal of the absolute temperature. The dissociation curve for the isoprene-cuprous chloride complex as determined by Gilliland<sup>2</sup> is also presented. The difference between Gilliland's data and those of the present research is attributed to the possible presence of piperylene in the isoprene employed in these experiments.

The stability of the piperylene-cuprous chloride complex (dissociation temperature at  $760$  mm.,  $68.4^\circ$ ) is much the same as that of the butadiene-cuprous chloride compound (dissociation

(5) Lur'ye, Marushkin, Afanas'yev and Pimenov, *Sintet. Kauchuk*, **3**, No. 6, 19 (1934).

(6) Farmer and Warren, *J. Chem. Soc.*, 3234 (1931).

(7) Kurtz and Headington, *Ind. Eng. Chem., Anal. Ed.*, **9**, 21 (1937); Ward and Kurtz, *ibid.*, **10**, 559 (1938).

(8) Gilliland, Seebold, Fitzhugh and Morgan, *This Journal*, **61**, 1960 (1939).

(9) Robey and Morrell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 880 (1942).

TABLE I  
DISSOCIATION PRESSURES OF THE PIPERYLENE-CUPROUS  
CHLORIDE COMPLEX

Temp., °C.	Pressure of complex, mm.	Temp., °C.	Pressure of complex, mm.
6.0	2.5	42.0	84
25.5	21	45.0	98
35.0	53	50.0	206
40.0	77	55.0	315
41.0	82	68.0	756

TABLE II  
DISSOCIATION PRESSURES OF ISOPRENE-CUPROUS CHLORIDE

Temp., °C.	Pressure of complex, mm.
6.7	34
15.0	40
26.0	107
35.0	261

temperature at 760 mm., 63.5°) whereas the isoprene-cuprous chloride compound is much less stable (dissociation temperature at 760 mm., 46°). The difference in stability observed with the isoprene complex may be caused by the branching of the hydrocarbon chain.

The results obtained in the experiments on the formulas of the diene-cuprous chloride compounds are shown in Table III. In both cases the formula is shown definitely to be C<sub>5</sub>H<sub>8</sub>·2CuCl, analogous to that already established for the butadiene-cuprous chloride compound. The for-

TABLE III  
FORMULAS FOR THE DIOLEFIN-CUPROUS CHLORIDE COMPLEXES

Diene taken, moles	Cu <sub>2</sub> Cl <sub>2</sub> taken, moles	Diene re-covered, moles <sup>a</sup>	Properties of recovered diene	Molar ratio Cu <sub>2</sub> Cl <sub>2</sub> /diene
			<i>n</i> <sub>D</sub> <sup>20</sup> <i>d</i> <sub>4</sub> <sup>20</sup> % diene	
A. Piperylene-Cuprous Chloride				
7.5	5.97	5.74	1.4306    0.6792    97.7 <sup>b</sup>	1.04/1.00
1.63	0.47	0.456	1.4310    .6786    ....	1.03/1.00
B. Isoprene-Cuprous Chloride				
1.53	.46	0.50	1.4212    .6802    99.0 <sup>c</sup>	0.92/1.00
1.63	.47	.39	1.4214    .6805    99.0 <sup>c</sup>	1.20/1.00 <sup>d</sup>
1.80	.47	.47	1.4216    .6806    100.0 <sup>c</sup>	1.00/1.00

<sup>a</sup> Diene recovered by dissociation of the cuprous chloride derivative after removal of excess hydrocarbon.  
<sup>b</sup> By hydrogenation. <sup>c</sup> Calculated from refractivity intercept. <sup>d</sup> The apparent discrepancy in this experiment is explained by a sudden reduction in pressure during the removal of the unreacted hydrocarbon which may have partially dissociated the cuprous chloride compound.

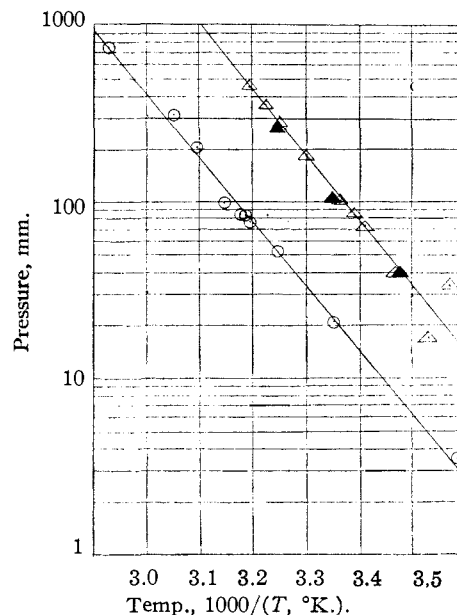


Fig. 1.—○, piperylene-Cu<sub>2</sub>Cl<sub>2</sub> complex; △, isoprene-Cu<sub>2</sub>Cl<sub>2</sub> complex; Gilliland's data (2); ▲, isoprene-Cu<sub>2</sub>Cl<sub>2</sub> complex, present paper.

mula, C<sub>5</sub>H<sub>8</sub>·3CuCl, for the isoprene complex tentatively assigned by Gilliland<sup>2</sup> has thus been shown to be incorrect, as he indicated might prove to be the case.

### Summary

1. Equilibrium dissociation pressures at various temperatures for the compound formed between piperylene and cuprous chloride have been determined and previously determined values for the compound of isoprene and cuprous chloride have been checked. The stability of the piperylene-cuprous chloride compound is about the same as that of the known butadiene-cuprous chloride compound, but the isoprene-cuprous chloride compound is considerably less stable.

2. Formulas for both the piperylene-cuprous chloride and isoprene-cuprous chloride complexes have been established as C<sub>5</sub>H<sub>8</sub>·2CuCl or C<sub>5</sub>H<sub>8</sub>·Cu<sub>2</sub>Cl<sub>2</sub>. Hence for all three diolefins, butadiene, isoprene and piperylene, the combination involves one molecule of diene to one molecule of cuprous chloride.

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