second constituent should be found by subtracting from the total current (sum of i_{d_1} and i_{d_2}) the value which the first diffusion current i_{d_1} would have at the potential at which the total current is measured. Application of equation (7) using the values of r. v. given in the last column of Table I yields satisfactory results in such mixtures.

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[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Reaction of Olefins with Solid Cuprous Halides

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Experimental results on the reaction between the olefins, ethylene, propylene, and isobutylene and solid cuprous halides have been reported by Gilliland, Seebold, FitzHugh and Morgan.[1] They found that the olefins combined mole for mole with solid cuprous halides yielding a compound which could be written empirically as $C_nH_{2n}\cdot$ CuX. The equilibrium pressure curves for the various olefin compounds with solid cuprous chloride were almost identical and it was therefore concluded that the reaction was characteristic of the unsaturated structure and not markedly influenced by molecular weight.

The work reported in this paper summarizes the results obtained on the reaction of diolefins and acetylene with solid cuprous halides.

Experimental

Procedure.—The apparatus used and the procedure followed were essentially the same as described for the low pressure studies in the previous work.[1] Pressure readings were considered accurate within 1 mm. and temperature readings within 0.5°. The low equilibrium pressures were the least accurate both because of an extremely slow rate of approach to equilibrium and because they were calculated by taking small differences between large numbers.

It was found that acetylene would not react directly with solid cuprous halides. The addition compounds however, were easily prepared in solution, following the procedure given by Chavastelon.[2] For example, with cuprous chloride, the procedure was as follows: cuprous oxide was dissolved in 38% hydrochloric acid and acetylene bubbled through the solution. Dilution with water gave a white precipitate, which was removed, washed with alcohol and ether and dried in a current of acetylene. A purple color indicated formation of the complex.

Butadiene was obtained from the Standard Oil Development Company and was estimated to be over 98% pure. Isoprene, purity about 74% (the rest being pentanes and pentenes), was obtained from the United Gas Improvement Company. It should be noted that in both cases the reaction with cuprous chloride proved to be a very simple and effective method of purification. Cyclopentadiene of a high degree of purity was prepared by depolymerization of dicyclopentadiene obtained from the United Gas Improvement Company.

Results

The results show that such solid reactions are not limited to the mono-olefins. One mole of butadiene reacts with two moles of cuprous chloride (CuCl) yielding a compound which may be empirically represented as $C_4H_6\cdot 2CuCl$. Isoprene forms a compound with cuprous chloride, but the maximum reaction observed was 0.336 mole of isoprene per mole of cuprous chloride. This ratio would correspond approximately to the formula $C_5H_8\cdot 3CuCl$, although the low isoprene content may be due to the fact that reaction was not complete. From the similarity of the unsaturated structure of isoprene and butadiene and from the heat of reaction data it seems probable that the compound may be $C_5H_8\cdot 2CuCl$. This behavior is similar to that of isobutylene reported in the previous work,[1] where it was found that only 0.62 mole of isobutylene reacted per mole of salt while both ethylene and propylene reacted practically mole for mole. No reaction of cyclopentadiene with cuprous chloride at 0° could be detected, and this may also be due to steric hindrance.

Koblyanskii, Shul'ts, and Piotrovskii[3] have investigated the composition of the complex compounds formed by the reaction between CuCl and butadiene. They report the preparation of the compound $C_4H_6\cdot 2CuCl\cdot 4H_2O$ from aqueous solution as a finely crystalline, yellow precipitate. From an anhydrous medium or by washing the hydrate with alcohol an anhydrous compound $C_4H_6\cdot 2CuCl$ was obtained.

Christgau[4] studied the reaction of butadiene

(1) Gilliland, Seebold, FitzHugh and Morgan, THIS JOURNAL, **61**, 1960 (1939).

(2) Chavastelon, *Compt. rend.*, **126**, 1810 (1898).

(3) Koblyanskii, Shul'ts and Piotrovskii, *Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka*, Litera B, IV; *Synthetic Rubber*, 20–23 (1935).

(4) Christgau, M. I. T. Thesis (1939).

with solid cuprous chloride and cuprous bromide. In both cases he found compounds containing approximately one mole of butadiene per

TABLE I

Olefin	Olefin, mole	CuCl, mole	Mole olefin per mole/CuCl	Color
Butadiene	0.0453	0.0950	0.477	Yellow
	.0167	.0359	.465	
	.0246	.0529	.465	
	.0223	.0538	.415 (CuBr)	
Isoprene	.00947	.0330	.287	Brownish-yellow
	.0231	.0688	.336	
	.00889	.0330	.269	
	.01038	.0330	.314	
	.01025	.0428	.239	
Acetylene	.0300	.0648	.462	Purple
	.0372	.0784	.475	
	.0346	.0784	.448	
	.0270	.0542	.497	
	.0481	.0900	.535	
	.0480	.0623	.770 (CuBr)	
	.0493	.0556	.886 (CuBr)	
	.0623	.0805	.774 (CuBr)	

and Figs. 1 and 2. The equilibrium data for $C_2H_2 \cdot 2CuCl$ do not agree with the results of Chavastelon,[2] but details by the latter investigator are not complete enough to attempt an explanation.

Table III presents the calculated heats of reaction for one mole of the gaseous hydrocarbon and solid cuprous chloride at a pressure corresponding to the normal boiling point of the hydrocarbons. This table also gives the latent heat of vaporization of the various hydrocarbons at their normal boiling point. The difference in these two enthalpy quantities should be the heat of reaction of the liquid hydrocarbons with solid cuprous chloride, and these differences should be more indicative of the actual heats of combination than are the heats of reaction for the gaseous olefins. These differences have been divided by the number of moles of cuprous chloride per mole of hydrocarbon, and are given in the last column of Table III. It will be noted that this heat of

TABLE II

$C_4H_6 \cdot 2CuCl$ Temp., °C.	$C_4H_6 \cdot 2CuCl$ Press., mm. abs.	$C_2H_2 \cdot 2CuCl$ Temp., °C.	$C_2H_2 \cdot 2CuCl$ Press., mm. abs.	$C_6H_5 \cdot CuCl$ Temp., °C.	$C_6H_5 \cdot CuCl$ Press., mm. abs.	$C_4H_6 \cdot 2CuBr$ Temp., °C.	$C_4H_6 \cdot 2CuBr$ Press., mm. abs.	$C_2H_2 \cdot CuBr$ Temp., °C.	$C_2H_2 \cdot CuBr$ Press., mm. abs.
17	13	0	55	10	17	0	57	−70	12
20	13	3.8	72	15	41	13	169	−60	32
24	20.5	9.8	114	20	73	25	390	..	..
25	32	14	169	22	85	40.7	766	−50	106
25	33	20	256	24	101	47	1230	..	..
30	38	24.8	377	30	186			..	..
30	43	29.8	509	34.5	286			−40	234
31	58	32	553	37	352.5			..	..
35	60	35	728	40	456			−35	314
36.5	71.5	40	982					−30	590
44	144.5	42.5	1151					−30	603
56	422.5							−25	952
58	482							−22	1661
63	679							−20	1531
64	829.5							−18	1689
66	907.5								
69	1162								

2 CuX. Christgau's equilibrium pressures for the cuprous bromide compound are given in Table II.

One mole of acetylene reacts with two moles of cuprous chloride to form the compound $C_2H_2 \cdot 2CuCl$. With cuprous bromide, however, Porter[5] found that acetylene reacted approximately mole for mole. Chavastelon[2] also reports the preparation of $C_2H_2 \cdot 2CuCl$.

The molal ratios measured are given in Table I. The equilibrium data are given in Table II

(5) Porter, M. I. T. Thesis (1939).

TABLE III

Olefin	Heat of reaction[a]	Heat of vaporization[b]	Difference per CuCl
Ethylene	10,000	3320	6700
Propylene	11,000	4570	6400
Isobutylene	11,000	5370	5600
Butadiene	17,000	5530	5750
Isoprene	17,300	6430	5450
Acetylene	12,500	4020	4250

[a] Heat of reaction of gaseous olefin with solid cuprous chloride at pressure corresponding to normal boiling point of hydrocarbons—g. calories per g. mole of hydrocarbon. [b] Heat of vaporization of olefin at normal boiling point, gram calories per gram mole.[6]

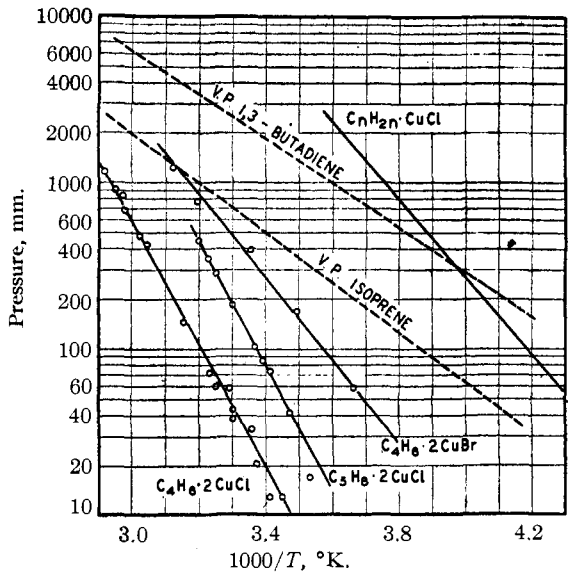

Fig. 1.

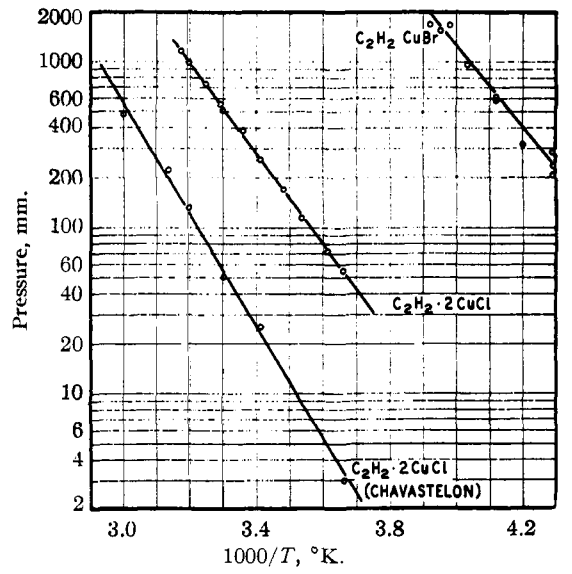

Fig. 2.

reaction per mole of cuprous chloride decreases in any given series of hydrocarbons as the molecular weight of the hydrocarbon increases, and that the values for isobutylene and butadiene are nearly the same, indicating that both double bonds in the latter compound combine with the evolution of about the same amount of heat as the double bond in isobutylene.

No reaction of amylene (2-methyl-2-butene), with solid cuprous chloride at $-65°$ could be detected. As has been pointed out,[1] a gaseous olefin cannot react with solid cuprous salts at temperatures higher than correspond to the intersection of the dissociation pressure curve with that of the vapor pressure curve of the olefin in question. Hence, if the amylene–cuprous chloride complex curve is coincident with the other mono-olefin–cuprous chloride complexes no reaction would be expected above $-70°$ (vapor pressure data of Lamb and Roper[6]). Below that temperature the pressures are too low to be accurately measured by the present apparatus.

Summary

Butadiene, isoprene, and acetylene react with solid cuprous chloride. Except for isoprene, approximately one mole of olefin reacts with two moles of cuprous chloride. No reaction of amylene and cyclopentadiene with solid CuCl could be detected.

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(6) Lamb and Roper, THIS JOURNAL, **62**, 806 (1940).