TABLE VIII. β-CAROTENE STEREOISOMERS IN FRESH ALFALFA AND IN VARIOUS ALFALFA PRODUCTS

	Stereoisomer Ratio, %		
Sample	Neo-B	All-trans	Neo-U
Fresh alfalfa	4.6	90.0	5.4
Sun-cured meal	12.3	76.6	11.1
Dehydrated meals			
E	32.8	55.7	11.5
A	33.3	56.8	9.9
B	31.8	57.0	11.2
D	41.8	43.8	14.4
F	41.2	45.7	13.0
G[a]	42.7	40.0	17.3
C	42.2	43.8	14.0

[a] Low-temperature dehydrator.

DISCUSSION

The foregoing experiments showed that the principal factor responsible for the formation of cis isomers of β-carotene during drying of alfalfa is increased temperature. The interpretation of the effect of light in the reisomerization is more difficult since no means of identification of the separate molecules is possible. However, the over-all results show a conversion of neo-B to all-trans and neo-U. The decrease of neo-B to 8.0% in the extract (Table IV) by irradiation is similar to the results of Zechmeister (*8*) who found pure neo-B transformed by sunlight (45 minutes) into 60% all-trans, 27% neo-U, and 10.5% neo-B + neo-C,D, etc. The other pure isomers when tested in a similar way were more stable. Perhaps the ease of oxidation is also concerned with this phenomenon since the neo-B was more labile during storage.

The presence of lower amounts of cis isomers in sun-cured alfalfa is explained by these studies. With the moderate temperature of drying, only small amounts of cis isomers are formed while the presence of light tends to reisomerize neo-B to the other forms.

The irradiation of dehydrated alfalfa meal to increase its vitamin A potency would be a simple means of enhancing the nutritive value of the product. However, the ever present dust coats irradiating equipment and reduces its efficiency. Also, initial cost and power requirements of this equipment may be prohibitive.

SUMMARY

High temperature during dehydration promotes the formation of cis isomers of β-carotene in alfalfa.

Irradiation of alfalfa meal with visible light decreases the amount of neo-B and increases the all-trans and neo-U in solution or in meal, resulting in an increased vitamin A potency.

Neo-B is destroyed more rapidly than the other isomers during storage.

LITERATURE CITED

(1) Bailey, G. F., Atkins, M., and Bickoff, E. M., IND. ENG. CHEM., **41**, 2033 (1949).

(2) Bickoff, E. M., Atkins, M., Bailey, G. F., and Stitt, F., *J. Assoc. Offic. Agr. Chemists*, **32**, 766 (1949).

(3) Bickoff, E. M., and Thompson, C. R., *Ibid.*, **32**, 755 (1949).

(4) Deuel, H. J., Jr., Johnston, C., Meserve, E. R., Polgár, A., and Zechmeister, L., *Arch. Biochem.*, **7**, 247 (1945).

(5) Deuel, H. J., Jr., Johnston, C., Sumner, E., Polgár, A., and Zechmeister, L., *Ibid.*, **5**, 107 (1944).

(6) Johnson, R. M., Swick, R. W., and Baumann, C. A., *Ibid.*, **22**, 122 (1949).

(7) Kemmerer, A. R., and Fraps, G. S., *J. Biol. Chem.*, **161**, 305 (1945).

(8) Zechmeister, L., *Chem. Revs.*, 34, 267 (1944).

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Methane Chlorination Using Hydrogen Chloride and Oxygen

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Using hydrogen chloride and oxygen, with either steam or nitrogen as inert, methane was chlorinated over a copper chloride catalyst in a 1-inch inside diameter tube at temperatures around 400° to 550° C. The product consisted of the four chloromethanes, whose proportions could be varied considerably by adjustment of feed gas composition. Conditions were found at which almost complete conversion of hydrogen chloride to chlorinated product could be attained. Methane conversion varied from 10 to 40% per pass, with about half again as much burned. Using elemental chlorine and air, methane was chlorinated under the same conditions with high utilization of the by-product hydrogen chloride formed, in that 70% to over 90% per pass of the chlorine fed was converted to chlorinated product. Considerable control over product analysis was again attainable. Methane conversion to product likewise varied between 10 and 40%, with half again as much burned.

CHLORINATION of hydrocarbons with hydrogen chloride represents a possible outlet for by-product hydrogen chloride produced in industry. Of further interest would be the chlorination of hydrocarbons simultaneously with elemental chlorine and with the hydrogen chloride evolved as a by-product. The chlorination of methane in operations of this type is discussed herein.

An essential step in any such utilization of hydrogen chloride is usually the Deacon reaction, which was developed originally to provide a means of oxidizing hydrogen chloride to elemental chlorine, as follows:

$$2HCl(g) + {}^{1}/_{2}O_2 = H_2O(g) + Cl_2 \tag{1}$$

The reaction as written is exothermal, with $\Delta H^\circ = -14$ kg.-cal., hence the equilibrium becomes less favorable with increasing temperature. Using the data of Lewis and Radash (*3*) equilibrium conversions of hydrogen chloride to elemental chlorine were calculated to be 73 and 65.9% at 450° and 500° K., respectively, given a feed composition of 80% air and 20% hydrogen chloride.

This reaction proceeds slowly without a catalyst, but Deacon found that copper chloride accelerated rates sufficiently so that operations became possible at 500° C. or thereabouts, at which

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TABLE I. HYDROGEN CHLORIDE RUNS[a]

I. HYDROGEN CHLORIDE–AIR-METHANE RUNS

Run No.	Gas Feed				HCl Converted	CH_4		X[b]	R[c]	M[d]
	N_2	O_2	CH_4	HCl		Burned	Converted			
At 450° C.										
3	1.42	0.377	0.393	0.327	0.306	0.062	0.112	2.74	0.78	0.81
15	1.87	0.494	0.50	0.50	0.333	0.101	0.143	2.33	0.67	0.67
17	1.72	0.457	0.91	0.475	0.359	0.096	0.222	1.61	0.395	0.785
18	1.18	0.313	0.61	1.09	0.271	0.059	0.152	1.78	0.445	0.865
19	1.58	0.42	1.01	0.39	0.333	0.085	0.218	1.53	0.33	0.79
21	2.28	0.61	1.24	0.65	0.374	0.166	0.259	1.44	0.30	0.61
22	0.78	0.205	0.415	0.215	0.118	0.032	0.093	1.27	0.285	0.575
139	2.1	0.560	0.407	0.217	0.228[e]	0.052	0.124	1.84	0.56	0.405[e]
At 500° C.										
12	1.50	0.40	0.74	0.74	0.353	0.085	0.175	1.99	0.48	0.88

II. HYDROGEN CHLORIDE–OXYGEN-STEAM-METHANE RUNS

Run No.	Gas Feed				HCl Converted	CH_4		X[b]	R[c]	% HCl Converted
	H_2O	O_2	CH_4	HCl		Burned	Converted			
At 450° C.										
130	1.78	0.420	0.413	0.248	0.174	0.06	0.094	1.85	0.42	70
134	1.63	0.463	0.214	0.197	0.142	0.076	0.055	2.58	0.66	72
136	2.43	0.422	0.420	0.303	0.200	0.079	0.097	1.97	0.476	66
137a	1.88	0.208	0.410	0.192	0.148	0.047	0.089	1.66	0.360	77
138	1.78	0.313	0.420	0.202	0.161	0.241	0.095	1.70	0.375	79

[a] Values in columns 2 to 8, inclusive, are in gram moles per hour.
[b] X = column 6/column 8.
[c] R = column 6/column 4.
[d] M = column 6/column 3; moles of HCl converted per mole of oxygen fed.
[e] 100% conversion of HCl explains low value of M.

temperature the equilibrium is still reasonably favorable. Reaction 1 was not a commercial success, however, because of the high cost of recovering the chlorine and the unreacted hydrogen chloride from the product gases, because of catalyst loss through volatilization, and because the catalyst becomes less active at higher hydrogen chloride concentrations. In an attempt to improve the operation, a number of other materials have been investigated as catalysts, as for example, a mixture of thorium oxide, rare earths, and cuprous chloride (*4*). The Germans reportedly had good success in operating the Deacon process using as catalyst a molten bath of 7 parts of ferric chloride to 3 parts of potassium chloride at 450° C. (*5*).

Roka (*9*) was the first to introduce methane into the Deacon reaction. He found that chlorination proceeded with a copper catalyst to yield all four chloromethanes simultaneously, and without excessive combustion of the methane present, as follows:

$$CH_4 + HCl + {}^1/_2\,O_2 \longrightarrow CH_3Cl(g) + H_2O(g) \tag{2a}$$

$$CH_3Cl + HCl + {}^1/_2\,O_2 \longrightarrow CH_2Cl_2(g) + H_2O(g) \tag{2b}$$

$$CH_2Cl_2 + HCl + {}^1/_2\,O_2 \longrightarrow CHCl_3(g) + H_2O(g) \tag{2c}$$

$$CH_3Cl + HCl + {}^1/_2\,O_2 \longrightarrow CCl_4(g) + H_2O(g) \tag{2d}$$

Roka's findings were confirmed by Tomasik (*10*) and by Chu (*1*). More recently, Riblett (*8*) described methane chlorination in two stages, first by direct use of chlorine, followed by condensation of the chlorinated products, and addition of air to react with the by-product hydrogen chloride present. No study, however, has been made of the possibility of chlorinating methane simultaneously with elemental chlorine and with the hydrogen chloride evolved as by-product, with net reactions as follows:

$$ {}^1/_2\,Cl_2 + CH_4 + {}^1/_4\,O_2 \longrightarrow CH_3Cl(g) + {}^1/_2\,H_2O(g) \tag{3a}$$

$$ {}^1/_2\,Cl_2 + CH_3Cl + {}^1/_4\,O_2 \longrightarrow CH_2Cl_2(g) + {}^1/_2\,H_2O(g) \tag{3b}$$

$$ {}^1/_2\,Cl_2 + CH_2Cl_2 + {}^1/_4\,O_2 \longrightarrow CHCl_3(g) + {}^1/_2\,H_2O(g) \tag{3c}$$

$$ {}^1/_2\,Cl_2 + CHCl_3 + {}^1/_4\,O_2 \longrightarrow CCl_4(g) + {}^1/_2\,H_2O(g) \tag{3d}$$

Reactions of classes 2 and 3 are all strongly exothermal; for example, the value of ΔH°_{298} for Reaction 2a is −37 kg.-cal. and for Reaction 3a is −27 kg.-cal. Equilibrium constants are very favorable over the probable range of operating temperature—for example, K_p is of the order of 10^8 at 500° C. for Reaction 2a and 10^{29} for Reaction 3a. However, two important operating problems involve control of chlorinated product composition and of side reactions. Possible side reactions might be of several varieties, such as combustion, hydrolysis of the chloromethanes, interaction between chloromethanes as follows:

$$CH_3Cl + CHCl_3 \longrightarrow 2CH_2Cl_2 \tag{4a}$$

$$CH_2Cl_2 + CCl_4 \longrightarrow 2CHCl_3 \tag{4b}$$

and the formation of compounds of more than one carbon atom.

The only hydrocarbon chlorination of this type operated on an industrial scale appears to be the Raschig phenol process (*6, 7*). Here, benzene is chlorinated with hydrogen chloride and air to the intermediate monochlorobenzene for subsequent hydrolysis to phenol. Side reactions are minimized because of the low temperature of operations (about 200° C.) while chlorination is halted at the monochloro stage by use of a large excess of benzene.

VARIABLES STUDIED

In the work described below, three separate types of runs were made depending upon the components present in the feed gas.

I. Hydrogen chloride–air–methane
II. Hydrogen chloride–oxygen-steam-methane
III. Chlorine-air-methane

The variables studied were the velocity and contact time of the reacting gases with the catalyst, feed gas composition, and temperature in the catalyst bed. The catalyst used was always copper chloride deposited on pumice of about 10 mesh, though in a few runs a "diluted" catalyst was used, comprising 1 part of standard catalyst and 5 parts of plain pumice. The total pressure likewise was not varied, but was maintained at a trifle above 1 atmosphere in all runs. Nominal catalyst bed temperature was 450° C. and also 500° C. in type I runs, 450° C. in type II runs, while type III runs were made at 400°, 450°, 500°, and 550° C. Velocities were varied from 1.62 to 4.78 total gram moles entering per hour in type I runs, 2.5 to 4.72 gram moles per hour in type II runs, and 3.16 to 6.13 gram moles in type III runs. Catalyst bed length was usually 26 inches, but was on occasion considerably reduced. Ranges of inlet gas composition are discussed below, and shown in Tables I and II.

EXPERIMENTAL PROCEDURE

The feed gas was prepared by metering the component gases separately, allowing these to mix, and delivering the mixture to the reaction tube. This tube, 1 inch in inside diameter, was located in an electric furnace, and contained the heated catalyst bed. Temperature traverses could be made by moving a thermocouple through a small tube running lengthwise through the center of this catalyst bed. This catalyst was prepared by soaking 10-mesh pumice granules in copper chloride solution, followed by oven drying at 110° C. The diluted catalyst was prepared by thorough mixing of 1 part of these coated granules with 5 parts of uncoated pumice granules. In all cases, the apparatus was operated for 1 hour before a run, to ensure attainment of steady state conditions. In this way, equilibrium was reached by the copper chloride, which absorbs large amounts of hydrogen chloride.

Recovery of reaction products was accomplished by passing the gas from the catalyst bed through two scrubbers and then through three cold traps cooled in dry ice–ethyl alcohol baths. The first scrubber contained water to dissolve hydrogen chloride, while the second contained sulfuric acid to dry the gas. The first cold trap condensed the chloroform, carbon tetrachloride, and part of the two lighter chloromethanes. The last two traps contained an equivolume mixture of chloroform and carbon tetrachloride, through which the gas was bubbled to capture the remaining methylene chloride and methyl chloride, plus any unreacted chlorine. After a run was completed, production of hydrogen

TABLE II. CHLORINE-AIR-METHANE RUNS[a]

Run No.	Gas Feed				Cl_2 Converted to Chlorinated Product	CH_4		X[b]	R[c]	% Cl_2 Converted[d]
	N_2	O_2	CH_4	Cl_2		Burned	Converted			
At 450° C.										
32a	1.76	0.469	0.940	0.160	0.128	0.130	0.188	1.36	0.28	80
36	1.72	0.454	0.90	0.252	0.171	0.139	0.217	1.57	0.38	68
37	2.08	0.554	0.547	0.158	0.133	0.097	0.164	1.61	0.48	84.5
39	2.00	0.535	0.527	0.337	0.180	0.261	0.148	2.42	0.68	53.5
40	2.06	0.547	0.540	0.190	0.160	0.091	0.184	1.74	0.60	89.5
46	1.92	0.507	0.740	0.154	0.145	0.075	0.183	1.56	0.40	94
48	3.74	0.99	1.00	0.280	0.240	0.133	0.293	1.63	0.48	86
101	2.06	0.547	0.414	0.243	0.197	0.105	0.160	2.45	0.96	81
103	2.08	0.555	0.40	0.129	0.116	0.149	0.131	1.78	0.58	90
104a	2.1	0.555	0.428	0.159	0.129	0.112	0.134	1.91	0.60	81
106	2.05	0.547	0.414	0.259	0.244	0.080	0.184	2.65	1.18	91
107	2.14	0.573	0.294	0.263	0.229	0.127	0.124	3.67	1.56	87
109	2.08	0.555	0.294	0.251	0.233	0.100	0.160	2.92	1.58	93
110	2.95	0.780	0.60	0.244	0.191	0.118	0.197	1.94	0.64	78
111	2.95	0.790	0.41	0.302	0.271	0.083	0.197	2.75	1.32	90
116[e]	2.14	0.573	0.294	0.282	0.256	0.073	0.155	3.29	1.74	91
At 400° C.										
112	0.212	0.56	0.427	0.235	0.182	0.092	0.160	2.26	0.86	79
At 550° C.										
49[f]	0.191	0.506	0.734	0.137	0.130	0.052	0.174	1.50	0.36	95

[a] Values in columns 2 to 8, inclusive, in gram moles per hour.
[b] $X = 2 \times$ column 6/column 8.
[c] $R = 2 \times$ column 6/column 4.
[d] Column 6/column 5.
[e] Diluted catalyst run.
[f] Bed length of 4 inches.

TABLE III. EXIT GAS ANALYSES FOR SELECTED RUNS

Run No.	CO_2	CO	CH_4	O_2	N_2
Hydrogen Chloride–Air-Methane Runs					
15	2.3	2.1	10.2	3.8	81.6
18	0.6	3	23.8	1.5	71.1
21	1.9	3.2	22.1	2.6	70.2
139	1.4	0.8	10.0	11.4	76.4
Hydrogen Chloride–Oxygen-Steam-Methane Runs					
137a	9.4	4.4	80.2	6	0
134	19.4	2.0	23	55.6	0
Chlorine-Air-Methane Runs					
32a	3	2	22.4	5.2	67.4
36	2.6	3.5	22.1	3	68.8
39	2.9	8.5	4.5	1.4	82.7
40	2.3	1.3	10.8	8.9	76.7
46	2.6	0.4	17.7	8.9	67.7
49	1.0	1.3	19.9	11.7	66.1
107	4.3	0.9	1.8	6.2	86.8
116	2.1	0.7	4.2	11.1	81.3

chloride was determined by titration of the solution in the first scrubber. The product in the three cold traps was subjected first to low temperature fractionation to separate chlorine (if any) and methyl chloride, then fractionated further for the high boiling components. The results as reported in Table IV are probably accurate to ±5% of the value reported for components present in excess of 20%, but accuracy is probably only about 10% of the value reported for components present in 5% quantities, or thereabouts. The solvent-free exit gas was sampled and analyzed with an Orsat apparatus. Independent material balances were made on carbon, nitrogen, and chlorine, and each usually closed within 5%.

RESULTS

CHLORINE CONVERSION. In all three types of runs made, chlorine appeared in the exit gas only as hydrogen chloride or as chloromethanes, never in free molecular form. In runs of type I, the conversion of the hydrogen chloride to chlorinated product remained at 0.73 ± 0.16 moles of hydrogen chloride per mole of oxygen fed, as shown by the value of M reported in column 11 of Table I. When this ratio of moles of hydrogen chloride fed to moles of oxygen fed was less than 0.73 ± 0.16, as in run 139, then all the hydrogen chloride present was converted to chlorinated product. In type II runs, 73 ± 7% of the hydrogen chloride present was converted to chlorinated product, independent of the amount of oxygen present, as is again evident from an inspection of column 11 of Table I. Finally, in runs of type III, 86 ± 8% of the chlorine fed was converted to chlorinated product, as shown in column 11 of Table II. Two exceptions here were runs 36 and 39, whose conversions of only 68 and 53.5%, respectively, appear attributable to an oxygen deficiency, since the oxygen concentrations in the exit gas were at the unusually low levels of 3 and 1.4% according to Table III. Within wide composition limits, however, the fraction of the chlorine fed which was converted to chlorinated product remained relatively constant.

Further inspection of Tables I and II shows that the foregoing generalizations are independent of the gas velocity, the temperature, and the concentration of the methane in the feed gas, over the range of variables explored. Therefore, it is evident that in all three types of runs, the operator can exercise wide control over the quantity R, defined as the ratio of the gram atoms of chlorine converted to chlorinated product divided by the gram moles of methane fed.

PRODUCT COMPOSITION. Extensive similarities were found to exist between the three types of runs made. All four chloromethanes were always present, though their proportions varied widely, as shown in Table IV for selected runs. An average formula for the combined chlorinated product may be written as $CH_{4-X}Cl_X$, where X is the gram atoms of chlorine present per gram mole of combined product. The value of X clearly cannot be smaller than unity or greater than 4.

The distribution of the chloromethanes in the chlorinated product was found to be a unique function of the average chlorine content, X, and this function was the same for all three types of runs. This is evident from an inspection of the analytical data of Table IV as presented in Figure 1, where the mole percentages of each component in the product are plotted against X, the average chlorine content. The value of X can, in turn, be controlled by suitable adjustment of the feed gas composition. This is a consequence of finding that X appears to be a function only of the ratio, R. This relation is shown in Figure 2, which presents values of X and R from columns 9 and 10 of Tables I and II. Inspection shows that the data points of type I and type II runs fall on a single line—namely, curve a—while the points of type III runs fall on a separate but similar curve, b.

METHANE UTILIZATION. It is clear, from the definitions of X and R, that the fractional conversion of methane fed to chlorinated product is equal to the ratio R/X. If methane conversion had been constant in these runs, then the data points plotted in Figure 2 would have fallen on straight lines of slope X/R passing through the origin. Inspection shows that this is not the case, but that the fraction of methane converted becomes larger for increasing values of X and R, ranging from about 0.22 to 0.28 in runs of types I and II, and from 0.22 to 0.52 in runs of type III.

The ratio of moles of methane burned to moles of methane converted to chlorinated product can be determined by contrasting

TABLE IV. PRODUCT COMPOSITION

Run No.	Average X	Mole %			
		CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Hydrogen Chloride–Air-Methane Runs					
3	2.74	7	32	39.5	21.5
15	2.33	27.5	34.5	28	10
17	1.61	57.5	27.5	9	6
18	1.78	52	24	17	7
19	1.53	65	22	7	6
Hydrogen Chloride–Oxygen-Steam-Methane Runs					
130	1.85	45.5	31	16	7.5
134	2.58	17	30.5	32	21
136	1.97	41	28	23	8
137a	1.66	56	26	14	4
Chlorine-Air-Methane Runs					
32a	1.36	73	21	3.5	2.5
36	1.57	60	28	7	5
46	1.56	60	27	7.5	5.5
48	1.63	56	29	10	5
49	1.5	65	24	8	3
103	1.78	47	36	9.5	7.5
106	2.65	18	25	32	25
107	3.67	2	2.5	21.5	74
110	1.94	40	31	23.5	5.5
112	2.26	23	34	33	10
116	3.29	7	11	28.5	54

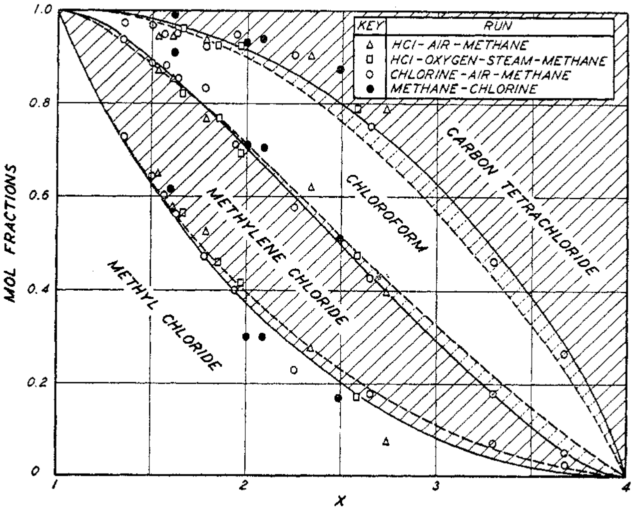

Figure 1. Proportions of the Four Chlorinated Methanes in Product

Data points for methane-chlorine runs are from Wilson and Howland (*11*). Solid curves computed by solving Equations 5 through 8, simultaneously. Dotted lines computed by solving Equations 5, 6, and 9 to 12 simultaneouly

columns 7 and 8 of Tables I and II. This ratio was roughly 0.5 for runs of types I and II, and averaged somewhat higher in type III runs, but significantly exceeded unity only in run 39. The products of combustion in all cases were water, carbon monoxide, and carbon dioxide; typical exit gas analyses for a few selected runs are presented in Table III on a dry, solvent-free basis. Inspection shows that these analyses varied considerably and that both unburned methane and molecular oxygen existed in the exit gas. No free hydrogen was ever found.

TEMPERATURE. When using an "undiluted" catalyst, exploration lengthwise with a traveling thermocouple always showed the presence of "hot spots" in runs of types I and III, but not in runs of type II. These hot spots were zones 1 to 2 inches long located near the inlet end of the bed, in which the temperature rose quite steeply to a peak of 600° C. and over. Operations were not completely isothermal, since temperature varied considerably outside the hot spots. The temperatures reported in Tables I and II are the average temperatures (outside the hot spots) at which these runs were made. Hot spots were not found with the traveling thermocouple in runs of types I and III when using a diluted catalyst, but it is possible here that at least some of the coated grains could have been substantially above nominal bed temperatures without detection.

Performances in all cases appeared relatively unaffected by temperature in the ranges explored, and for this reason no closer temperature control was attempted. For example, in the hydrogen chloride–air-methane runs, chloride and methane conversions and also product composition for run 12 at 500° C. follow the correlations established for the other runs, which were made at 450° C. Similarly, chlorine runs number 49 and 112, respectively, at 550° and 400° C. follow the same correlations as the other chlorine runs, which were at 450° C.

The results suggest that the reaction occurs largely in the hot spots when these develop. For example, run 46 involved a catalyst bed of standard length of 26 inches with a hot spot of 550° C. and a nominal temperature of 450° C., while run 49 was made with a 4-inch bed maintained at 550° C. The exit gas compositions shown in Table III, as well as product compositions shown in Table IV, were very similar for these two runs. However, reaction appears to occur as extensively with a diluted catalyst, which shows no detectable hot spots, as with an undiluted catalyst. This is shown by run 116, in which a diluted catalyst bed of normal length was used, and no hot spot developed. Results were in substantial agreement with run 107 using an undiluted catalyst, in which a 550° C. hot spot developed.

DISCUSSION

PRODUCT DISTRIBUTION. It is evident from the foregoing that the operator can exercise considerable control over operations. He can control the inlet composition in all three types of runs to secure any desired value of R, which in turn fixes X and the distribution of the individual components in the chlorinated product. This product distribution relationship is the same in all three types of runs, as shown in Figure 1, regardless of the temperature and gas velocity. Inspection of the plotted points shows further that product distribution is similar to that reported by Wilson and Howland (*11*) for the chlorination of methane with molecular chlorine by the method of Haas and McBee. One possible explanation for this somewhat surprising finding is that equilibrium is always attained for Reactions 4a and 4b. The curves drawn in Figure 1 show reasonably good agreement with the experimental points; these curves were drawn to represent the product distribution under equilibrium conditions as calculated from the following four simultaneous equations:

$$A + B + C + D = 1.0 \tag{5}$$

$$A + 2B + 3C + 4D = X \tag{6}$$

$$B^2/AC = 1.5 \tag{7}$$

$$C^2/BD = 1.5 \tag{8}$$

Here A, B, C, and D represent, respectively, the mole fraction of the mono-, di-, tri-, and tetrachloromethanes present in the chlorinated product. Equation 5 states that the mole fractions sum up to unity; Equation 6 is the analytical definition of X (which was arbitrarily assigned various values in solving these equations); and Equations 7 and 8, respectively, present the equilibrium constants for Reactions 4a and 4b. Because of the limitations of precision of the entropy and enthalpy data available on the reaction partners involved, only a range of magnitudes for the equilibrium constants for Reaction 4a and 4b could be calculated, and the value of 1.5 used in Equations 7 and 8 lies within this range. Since these reactions show only a very small enthalpy change, little variation in their equilibrium constants is to be expected with temperature.

The agreement between the experimental points and calculated curves of Figure 1 suggests that equilibrium for Reactions 4a and and 4b is in fact attained. On the other hand, no reactions could be made to occur in this apparatus between the chloromethanes. For example, mixtures of methyl chloride and chloroform were passed over the catalyst at 450° C. both in the presence and absence of oxygen and water vapor, but no methylene chloride was found in the product gases. This negative finding suggests that some other explanation must be found which does not postulate the occurrence of Reactions 4a and 4b.

One such alternative explanation of the data points of Figure 1

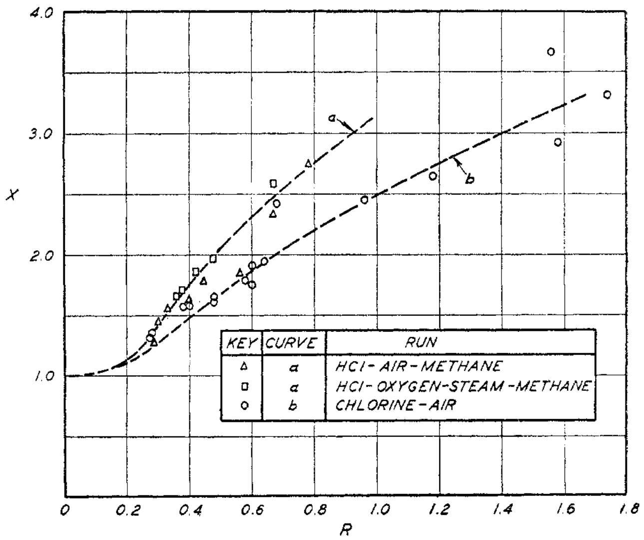

Figure 2. Average Number of Chlorine Atoms per Mole of Chlorinated Product, *X*, *vs.* Operating Ratio *R*

Plotted from experimental data in Tables I and II

follows from the assumption that chlorine or hydrogen chloride introduced into a mixture will combine by Reactions 3 or 2 in proportions determined by probability considerations. Molecular or atomic chlorine is assumed to combine with a molecule either of methane or of mono-, di-, or trichloromethane with equal readiness. These chlorination reactions further are assumed to be much more rapid than methane combustion, so that no significant methane burning occurs before chlorination is complete. Finally, it is assumed that no significant loss of chlorinated hydrocarbons occurs by combustion.

Fuoss (*2*) has presented a general solution for consecutive competing reactions which is applicable to this case.

Assume a system initially containing (among other components) 1 mole of methane, but which now (after reactions 2 or 3 but before combustion) contains y_0, y_1, y_2, y_3, and y_4 moles, respectively, of methane, mono-, di-, tri-, and tetrachloromethane. Product distribution is then:

$$y_1 = -y_0 \ln y_0 \tag{9}$$

$$y_2 = ({}^1/_2) y_0 \ln^2 y_0 \tag{10}$$

$$y_3 = (-{}^1/_6) y_0 \ln^3 y_0 \tag{11}$$

The mole fractions of the individual chloromethanes in the combined chlorinated product can be obtained by the relations:

$$A = y_1/(1 - y_0);\ B = y_2/(1 - y_0);\ C = y_3/(1 - y_0) \tag{12}$$

The value of D and X can be calculated from Equations 5 and 6, respectively.

The dotted lines of Figure 1 were computed by use of Equations 5, 6, and 9 to 12. Inspection shows that the agreement of the data points with these dotted lines is not much worse than with the solid lines computed from Equations 5 to 8. The fact that this agreement is not better may be because methane and mono-, di-, and trichloromethane do not, as assumed here, chlorinate with equal readiness, but instead have some other relative probability of chlorination, such as $1:{}^3/_4:{}^1/_2:{}^1/_4$, reflecting the hydrogen atoms in the respective molecules. Fuoss has presented equations applicable to this case also, which on the whole, however, do not correlate quite as well with the data points of this work as the dotted lines of Figure 1. Possible complications introduced by combustion appear to make further analysis of the relative probabilities of chlorination unwarranted.

Both the probability hypothesis and the assumption of equilibrium for Reactions 4a and 4b are consistent with the findings that the proportions of the chlorinated methanes in the product are a function only of X, independent of temperature and gas velocity. Only the probability hypothesis, however, is consistent with the apparent slowness of Reactions 4a and 4b under the conditions explored. It might be noted, incidentally, that the equilibrium explanation presented is not mathematically equivalent to the probability hypothesis, in that Equation 7, but not Equation 8, can be derived from Equations 9 through 12.

SIDE REACTIONS. Contrary to Roka's work (*9*), no evidence of hydrolysis of chloromethanes was encountered, in that carbon balances checked reasonably well, and tests for alcohols, aldehydes, and ethers were negative or showed only traces. In further runs in which methyl chloride vapors were mixed with steam and hydrogen chloride and passed through the apparatus, no extensive methanol formation was found. Similarly, the hydrogen chloride-oxygen-steam-methane runs showed no evidence of extensive hydrolysis. Finally, no indication was found of the formation of compounds having more than one carbon atom, and no hydrogen formation or carbon deposition was observed.

CATALYST LIFE. When using an undiluted catalyst, the upstream end of the bed became slowly exhausted as the hot spot slowly traveled down the tube. This movement of the hot spot appeared to be due to sublimation of copper chloride, followed by deposition farther along the tube. Order of magnitude of catalyst life can be judged from the fact that the hot spot traveled 2 inches down the tube during the 200 hours of operation. The German technique of periodically reversing the direction of gas flow through these catalyst beds would presumably prolong catalyst life, while use of a diluted catalyst, or of a fluidized catalyst bed, might serve to eliminate the hot spot entirely. Use of a fluidized bed might also prevent the severe burning and cracking encountered when attempts were made to operate at substantially higher oxygen concentrations than in the runs reported.

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NOMENCLATURE

A = mole fraction of methyl chloride in chlorinated product
B = mole fraction of methylene chloride in chlorinated product
C = mole fraction of chloroform in chlorinated product
D = mole fraction of carbon tetrachloride in chlorinated product
M = moles of HCl converted per mole of O_2 fed
y_0 = $1 - y_1 - y_2 - y_3 - y_4$
y_1 = moles of methyl chloride per mole of methane fed
y_2 = moles of methylene chloride per mole of methane fed
y_3 = moles of chloroform per mole of methane fed
y_4 = moles of carbon tetrachloride per mole of methane fed
R = atoms of chlorine reacting to form chlorinated product per mole of methane fed; sometimes called the operating ratio
X = atoms of combined chlorine present in 1 mole of chlorinated product, which can then be given the average formula $CH_{4-x}Cl_x$. By definition, $X = A + 2B + 3C + 4D$.

LITERATURE CITED

(1) Chu, J. C., M.I.T. thesis, 1946.
(2) Fuoss, R. M., *J. Am. Chem. Soc.*, **65**, 2406 (1943).
(3) Lewis and Radash, "Thermodynamics," New York, McGraw-Hill Book Co., 1923.
(4) Miller, H. S., U. S. Patent 2,204,733 (1940).
(5) Murray, R. L., U. S. Dept. of Commerce, OTS, **PB 385.**
(6) Prahl, Walter (to F. Raschig G.m.b.H.), U. S. Patent 1,963,761 (June 19, 1934).
(7) Prahl, Walter, and Mathes, Wilhelm, *Ibid.*, 2,035,917 (March 31, 1936).
(8) Riblett, E. W., *Ibid.*, 2,334,033 (1943).
(9) Roka, K., Brit. Patent 186,270 (1921); Ger. Patent 478,083 (1923).
(10) Tomasik, Z., *Przemysl Chem.*, **18**, 598 (1934).
(11) Wilson, M. J. G., and Howland, A. H., *Fuel*, **28**, No. 6, 127 (1949).

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Calculation of Complex Equilibrium Relations—Correction

Edward B. Weinberger of the Gulf Research & Development Co. has kindly called to our attention the omission of a term from the first of Equations 7A in the above paper [IND. ENG. CHEM., **42**, 850 (1950)]. The term $B_a g$ should be added to the left side of this equation. The equation defining coefficient B_a may be obtained from the one given for B_j in Equations 8 by replacing B_j and v_{ij} by B_a and v_{ia}, respectively, and by deleting n_j (here only). This correction modifies only the solution by the Newton-Raphson method of those systems which contain a pure solid phase in equilibrium with a gas phase. The authors regret any inconvenience caused by this error.

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