tivity coefficients of all in terms of electrical and non-electrical forces due to the —NH_3^+ and —COO^- groups.

8. On the basis of studies upon comparable uncharged molecules, tentative estimates have been made of the non-electrical, and therefore also of the electrostatic forces due to α-amino acids.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reactions Involving Free Alkyl Groups. I. The Photo-reaction of Methane, Chlorine and Oxygen[1]

BY LOREN T. JONES AND JOHN R. BATES

Studies of the thermal[2] and photochemical[3] chlorination of methane have shown that in both cases the reaction proceeds by a chain mechanism. Coehn and Cordes found a quantum yield of 10^4 while the work of Pease and Walz indicated a much greater chain length for higher temperatures. Both reactions are strongly inhibited by traces of oxygen. The analogy between these data and the facts of the hydrogen–chlorine reaction immediately suggests that the reaction occurs through the same intermediates which characterize the hydrogen–chlorine reaction, with methyl groups taking the place of one of the hydrogen atoms of the hydrogen molecules. If this be true, the rate should obey the expression derived by Thon[4] with substitutions

$$\frac{d[CH_3Cl]}{dt} = \frac{d[HCl]}{dt} = \frac{K\,[CH_4][Cl_2]^2}{[O_2]\,(k\,[CH_4] + [Cl_2])}$$

This would be equally true were the mechanism to follow either of the two alternative schemes

I

$$\begin{aligned} Cl_2 + h\nu &\longrightarrow Cl + Cl' \\ Cl + CH_4 &\longrightarrow HCl + CH_3 \\ CH_3 + Cl_2 &\longrightarrow CH_3Cl + Cl \\ CH_3 + O_2 &\longrightarrow \\ Cl + O_2 &\longrightarrow \end{aligned}$$

II

$$\begin{aligned} &(1) & Cl_2 + h\nu &\longrightarrow Cl + Cl' \\ &(2) & Cl + CH_4 &\longrightarrow CH_3Cl + H \\ &(3) & H + Cl_2 &\longrightarrow HCl + Cl \\ &(4) & H + O_2 &\longrightarrow \\ &(5) & Cl + O_2 &\longrightarrow \end{aligned}$$

Measurements accordingly have been made to discover if this is true, and, in addition, the verification of either I or II as the correct interpretation has been attempted.

Experimental Method

The experiments were carried out in a flow system. The rate of flow of the methane and chlorine supplied in tanks was measured by pressure flowmeters. The amount of oxygen, generated electrolytically, was regulated by the current sent through the cell. The gases were mixed and dried in a drying tower before entering the reaction unit consisting of a glass spiral illuminated by a Pyrex mercury arc. Since traces of oxygen have a very marked influence on the reaction at low oxygen concentrations, an analysis of the methane and chlorine for oxygen content was made. Approximately 3000 cc. of chlorine, when bubbled into a bulb filled with an iodide solution, gave about 30 cc. of residual gas. This was transferred to an Orsat gas analysis apparatus where the gas was first bubbled through an alkali solution to remove any traces of chlorine or other acidic gases that might be present before absorbing the oxygen in an alkaline hydrosulfite solution. There was found 0.25% oxygen in the chlorine and 0.8% in the methane. The reaction was studied by determining the amount of hydrogen chloride and unreacted chlorine in the off-gas by absorbing it in an iodide solution. The iodine liberated was titrated with a thiosulfate solution; the acid formed during the reaction was determined with alkali.

The reaction was carried out at 5, 25 and 45° at atmospheric pressure. A series of determinations was first made in which the methane–chlorine–oxygen ratio was constant, as the total rate of flow was increased from 135 cc. per minute to 370 cc. per minute.

The amount of hydrogen chloride formed after a ten-minute run remained constant within 10%, as can be seen from Table I.

Since there is a possibility of fluctuation of light intensity, a check was made at frequent intervals

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[1] The material in this paper comprises a portion of a thesis presented by Loren T. Jones to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

[2] Pease and Walz, THIS JOURNAL, **53**, 3728 (1931).

[3] Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

[4] Thon, *ibid.*, **B9**, 1 (1930).

TABLE I

CH_4, cc./min.	Cl_2, cc./min.	O_2, cc./min.	Total, cc./min.	% HCl formed	HCl formed, cc./min.
80	56	2.10	135	5.51	2.83
110	80	3.00	193	3.60	2.85
185	115	4.75	305	2.10	2.75
215	155	6.80	377	1.50	2.64

using an arbitrarily chosen concentration for each of the different series.

Experimental Results

In Fig. 1 the change in hydrogen chloride with oxygen increase is plotted for various methane–chlorine ratios at 25°. The dependence of the reaction rate on the low oxygen concentration shows up very decidedly. As would be expected if the reaction mechanism agrees with that of the hydrogen, chlorine and oxygen, the greater the chlorine concentration the greater will be the rate of formation of hydrogen chloride. The methane–chlorine concentrations were varied from a 3 to 1, to a 1 to 2 ratio.

The data are given in Tables II and III. Table II contains a typical set of measurements, the italicized values being the check run. Table III consists of a summary of all the runs for different methane–chlorine ratios and different temperatures. The first two columns give the average methane and chlorine concentrations for a number of runs (as in Table II). Next come two pairs of oxygen–hydrogen chloride values, these being minimum and maximum oxygen values with the corresponding amount of hydrogen chloride formed. Runs B at 5° were obtained using a new spiral which gave larger values for hydrogen chloride and K, but when converted on the basis of the check run (using a factor of 0.565 for K) gave good agreement with the other experiments.

TABLE II

Reaction at 25°

CH_4, cm.	Cl_2, cm.	O_2, cm.	HCl, cm.	K $k = 10$	$k = 1$	$k = 1/10$
42.5	*31.1*	*0.386*	*3.93*	*0.0163*	*0.00272*	*0.00126*
55.0	18.5	.451	1.97	.0269	.00348	.00114
54.3	18.2	1.18	0.549	.0202	.00262	.00085
53.9	18.1	1.91	.312	.0188	.00243	.00079
53.6	18.0	2.63	.230	.0193	.00249	.00081
52.9	17.8	3.32	.160	.1074	.00225	.00070
				.0205	.00265	.00086

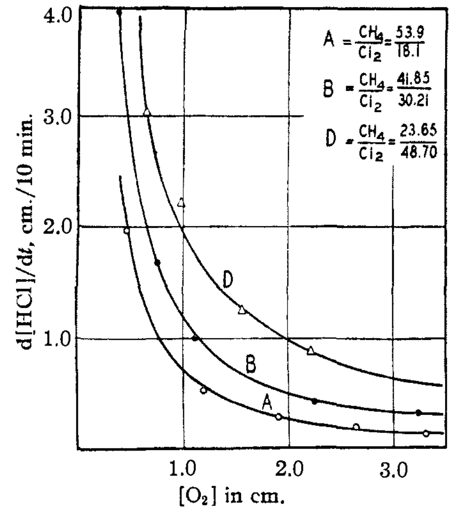

Fig. 1.

The values of K given in the table are calculated from Thon's equation, giving k values of 10, 1 and 0.1. As can be seen constancy of K with variations in the methane–chlorine ratio can be obtained only if $k = 1$, instead of 10 as in the hydrogen–chlorine reaction.

Since Thon's work was carried out in a static system, runs of the hydrogen–chlorine–oxygen reaction were made in our flow system to be sure that the equation might be applied to the present

TABLE III

	CH_4, cm.	Cl_2, cm.	O_2, cm.	HCl, cm.	O_2, cm.	HCl, cm.	K $k = 10$	$k = 1$	$k = 1/10$
				Reaction at 25°					
A	53.90	18.10	0.451	1.97	3.32	0.160	0.0205	0.00265	0.00086
B	41.85	30.21	.349	3.95	3.23	.331	.0139	.00228	.00109
C	37.05	35.35	.308	4.67	3.19	.518	.0145	.00255	.00139
D	23.65	48.70	.628	3.04	2.20	.888	.0096	.00245	.00173
				Reaction at 45°					
A	54.95	17.90	.441	2.12	2.42	.255	.0226	.00294	.00094
B	41.53	31.25	.431	4.33	3.68	.382	.0174	.00285	.00137
C	25.50	47.15	.735	3.40	2.27	.925	.0112	.00270	.00184
				Reaction at 5°					
A	54.0	18.7	.500	1.47	2.39	.255	.0195	.00249	.00083
B	43.2	29.5	.534	4.15	2.74	.853	.0157	.00243	.00113

work. The results of these are summarized in Table IV.

TABLE IV

H_2, cm.	Cl_2, cm.	O_2, cm.	HCl, cm.	*K*
44.0	30.0	0.32	17.8	0.067
43.6	29.7	1.048	5.44	.065
43.0	29.3	1.79	3.32	.073
42.3	28.6	3.08	2.02	.074

As can be seen, *K* is sufficiently constant to justify the use of this kinetic expression in flowing systems. A recent paper of Bodenstein and Schenk[5] confirms this.

The temperature coefficient of the reaction is 1.1 for the range from 5 to 45°, which is about the same as that of the hydrogen–chlorine reaction.[6]

The assurance given by these data that the methane–chlorine reaction takes place through a Nernst chain mechanism, made it of immediate interest to discover if a methyl group or a hydrogen atom were the intermediate (Scheme I or Scheme II). On theoretical grounds it would seem most probable that a chlorine atom, reacting with a methane molecule, would result in a methyl group and a hydrogen chloride molecule. In order to react to produce a hydrogen atom and methyl chloride, the chlorine atom must approach one of the triangular faces of the "carbon tetrahedron," where the residual bond forming power of the carbon atom has its greatest value.[7] Here it would be in interaction with the three hydrogen atoms situated on the apices of the triangle, resulting in a strong repulsion which would tend to necessitate a high activation energy. If, however, the chlorine atom approached along the line of the carbon hydrogen bond, it might react with the hydrogen atom with a much lower activation energy, since it would be separated by larger distances from the other three hydrogen atoms.

Experimentally, attempts to differentiate between the two possibilities failed. The hydrogen atoms, if formed, would undoubtedly yield hydrogen peroxide,[8] which may be detected in the presence of chlorine by the colorimetric method using titanium. No color was obtained after bubbling the off-gases, in which there was a large oxygen content, for an hour through an acidified solution of titanium chloride.

A number of different methods were used to try to remove the excess of chlorine which makes ineffective the usual tests for the extremely small amounts of formaldehyde which must be present. Fractional distillation, passing the gas over ascarite, mercury–zinc amalgam, and reducing the chlorine by a stannous chloride solution all failed to give a solution or a gas which would yield confirmatory evidence for the presence of formaldehyde. The tests employed were the resorcinal ring, formation of the *p*-nitrophenylhydrazone and the ultraviolet absorption spectrum of the gas.

Summary

The photoreaction between methane and chlorine obeys the equation of Thon for the inhibiting effect of oxygen. The reaction must therefore take place through a Nernst chain mechanism. Whether the methyl group or hydrogen atom is the chain carrier could not be verified experimentally, although simple considerations of the collision mechanism of a chlorine atom and a methane molecule make the former seem more probable.

ANN ARBOR, MICHIGAN RECEIVED JULY 24, 1934

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[5] Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

[6] Porter, Bardwell and Lind, THIS JOURNAL, **48**, 2603 (1926).

[7] Pauling, *ibid.*, **53**, 1367 (1931); Slater, *Phys. Rev.*, **37**, 381 (1931).

[8] Bates and Salley, THIS JOURNAL, **55**, 110 (1933).