

of simple alkenes. No reaction has been observed. Promoters such as chromium oxide and aluminum oxide which are suitable for activating the oxides for other reactions have failed to cause any manifestation of activity. On the other hand, the reaction proceeds smoothly when a metallic zinc or copper catalyst is employed. An active zinc-on-zinc oxide catalyst has been prepared by reducing zinc oxide in dry hydrogen.

Acetone has been hydrogenated over a zinc oxide-chromium oxide catalyst at atmospheric and elevated pressures, and other examples of the hydrogenation of compounds containing unsaturated oxygen atoms over oxide catalysts have been reviewed for the purpose of establishing the general proposition that oxide surfaces are capable of catalyzing the hydrogenation of compounds containing this kind of unsaturation while incapable of hydrogenating carbon-carbon unsaturation. Sodium carbonate has been found to be an effective agent for repressing the dehydration of isopropanol formed by the pressure hydrogenation of acetone.

An explanation of the specificity of catalytic oxides in the hydrogenation of organic compounds has been given, based on the idea that the degree of unsaturation of metal atoms in the surface of metallic compounds requisite for catalytic activity is conditioned not only by the degree of isolation of the active metal atoms but by the chemical nature of the surrounding atoms in the crystal lattice. Whether reaction is possible or not may depend likewise on the relative negativity of the unsaturated groups contained in the organic compound subjected to hydrogenation.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

KINETICS OF THE THERMAL CHLORINATION OF METHANE¹

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It is well established, more particularly in the patent literature, that methane-chlorine mixtures undergo reaction in the neighborhood of 400° without the intervention of contact agents.⁴ When methane is in excess the reaction is rapid but non-explosive, and a mixture of methyl chloride,

¹ This paper contains results of an investigation carried out as a part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

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⁴ For example, Lacy, U. S. Patent 1,111,842 (Sept. 29, 1914); Schleede and Luckow, *Ber.*, **55**, 3710 (1922). For bibliography, see Egloff, Schaad and Lowry, *Chem. Rev.*, **8**, 1 (1931).

methylene dichloride, chloroform and carbon tetrachloride, with equivalent amounts of hydrogen chloride, is formed by successive substitutions. When chlorine is in excess, the mixtures are explosive, and yield chiefly carbon and hydrogen chloride. In the latter case, contact agents have been used to prevent explosion, and guide the reaction along the substitution route. Whether certain contact agents also exert a positive catalytic effect as well is not definitely indicated, but this seems probable.⁵

No special study of the kinetics of these reactions has previously been made. That a homogeneous reaction is involved seems obvious, but the extent and nature of wall-action is unknown. Since the reactions are exothermic, it is logical to expect a chain mechanism but there is no evidence of this except in so far as the occurrence of explosions with excess of chlorine may be accepted as evidence. The probability of a chain mechanism is nevertheless the greater since the photochemical reaction has recently been shown to be of the chain type.⁶

In view of the current interest in thermal chain reactions, we have made a further study of the methane-chlorine reaction. Early in our investigation we were led to suspect that oxygen (introduced as an impurity in the chlorine) had a powerful inhibitory action. This was confirmed, and since inhibition of this sort is perhaps the most decisive evidence that can be obtained for the existence of reaction chains, we do not hesitate to say that a chain mechanism is involved.

Method and Apparatus.—The flow method was used, the extent of reaction being determined by estimating unreacted chlorine in the off-gas. The apparatus was such as has been used in similar experiments. The gases were led from cylinders through resistance-tube flowmeters and calcium chloride tubes into two tubes joining in a short capillary which led directly to a cylindrical Pyrex reaction tube. Another capillary conducted the off-gas from the reaction tube to a horizontal absorption tube 30 cm. long by 2 cm. in diameter which was half-filled with an aqueous potassium iodide solution. This solution could be titrated with alkali and thiosulfate. The reaction tube occupied the central half of an electric tube heater. The temperature of this was controlled by hand-regulation of the current during a run. The temperature was read with a double-junction chromel-alumel thermocouple placed in contact with the outside wall of the reaction tube near the center of the furnace.

The methane used in these experiments was put at our disposal by the Roessler and Hasslacher Chemical Company, Perth Amboy, N. J., through

⁵ See Jones, Allison and Meigham, U. S. Bur. of Mines Technical Paper No. 255 (1921).

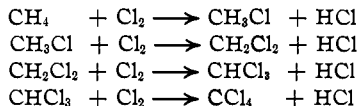
⁶ Coehn and Cordes, *Z. physik. Chem.*, Abt. B, 9, 1 (1930), by deviation from photochemical equivalence law. Whiston, *J. Chem. Soc.*, 117, 183 (1920); *J. Soc. Chem. Ind.*, 39, 384 (1920), finds that the photochemical reaction is powerfully inhibited by nitrosyl chloride.

the courtesy of Dr. B. S. Lacy to whom we give our best thanks. It had been specially prepared by fractionation of natural gas, and was substantially free from ethane, oxygen and carbon dioxide but contained a small amount of nitrogen. The chlorine was the ordinary material obtained in tanks. We found it wise to use a tank which had already been in intermittent use around the laboratory. Presumably this gets rid of the bulk of the dissolved oxygen. No other purification was attempted. That the gases were substantially free of oxygen is indicated by the sensitivity of the mixtures to additions of as little as 0.25% of this gas. When oxygen was wanted, it was generated electrolytically and run directly into the methane stream.

Results

Although 400° is usually mentioned as a suitable temperature for the methane-chlorine reaction, we have found that rate measurements are much more conveniently made in the neighborhood of 250°. We have further found that at these lower temperatures it is safe to work with mixtures containing excess of chlorine. These are subject to explosion at higher temperatures, but with ordinary care it is possible to study the slow non-explosive reaction.

Under the conditions of all of our experiments the only reactions occurring are



This is proved by the fact that within experimental error (less than $\pm 0.5\%$) a mole of hydrogen chloride is produced for every mole of chlorine reacting. Any other reactions, such as those forming carbon or chlorides of higher paraffins would lead to a discrepancy in this regard. We have not attempted to estimate the yields of individual chloromethanes in all cases, but we have satisfied ourselves that with excess of methane (*e. g.*, 3CH₄:1Cl₂) and small conversions of chlorine (*e. g.*, 25%), methyl chloride is the chief product. This was done by a series of fractional condensations. Doubtless as the chlorine ratio and the conversions are increased, there is a greater proportion of the more highly chlorinated products formed. We have systematically determined hydrogen chloride and chlorine in the off-gas by titration of the potassium iodide absorbing solution with standard alkali and sodium thiosulfate. The reported conversions are based directly on the data for chlorine.

Since there were evidences of "drift" in certain series of experiments, it has been made standard practice to "bracket" individual runs with a standard experiment with the results of which the particular run could be compared.

Experiments with "Oxygen-Free" Gases.—A series of experiments was conducted at 235° with methane-chlorine mixtures to which no oxygen had been added. The data for these appear in Table I. Experiments were carried out with an empty Pyrex reaction tube cleaned with nitric acid and water, with the same tube after rinsing with a 20% potassium chloride solution, and with a second tube which was filled with fragments of Pyrex (4-10 mesh). The latter had been washed with nitric acid and water. It was estimated that the glass surface had been increased over the empty tube by a factor of at least ten.

Since the rate was only moderately changed by coating the empty bulb, or by substituting the packed bulb for the empty bulb, it is evident that neither the character nor the extent of surface has any profound net effect.

In each set of experiments the percentage conversion of chlorine in a 2CH₄:1Cl₂ mixture was roughly twice that in a 1CH₄:2Cl₂ mixture, the total pressure being constant at 1 atm. This would be true of a second-order reaction

$$-\frac{d p_{\text{Cl}_2}}{dt} = k_2 p_{\text{Cl}_2} p_{\text{CH}_4}$$

or

$$-\frac{1}{p_{\text{Cl}_2}} \frac{d p_{\text{Cl}_2}}{dt} = k_2 p_{\text{CH}_4}$$

that is, the fractional conversion of chlorine is directly proportional to the partial pressure of methane (for small conversions). In using this expression, some account must be taken of the fact that the methyl chloride first formed is also subject to chlorination, as are any methylene chloride and chloroform. We have determined the rate of chlorination of methyl chloride (Table I) to be about twice that of methane (and to be second-order also); and we have been informed that the rates of chlorination of methylene chloride and chloroform are somewhat less than that of methane. In order to take some account of these facts, the above equation has been integrated under the assumption that the partial pressure of methane—that is, of material subject to chlorination—remains constant. Thus

$$p_{\text{CH}_4} = p^0_{\text{CH}_4}$$

$$p_{\text{Cl}_2} = x p^0_{\text{Cl}_2}$$

where $100(1-x)$ = percentage of chlorine reacting. Then

$$-\frac{dx}{dt} = k_2 p^0_{\text{CH}_4} x$$

and

$$k_2 = \frac{2.303}{t p^0_{\text{CH}_4}} \log_{10} \frac{1}{x}$$

Values of $k_2 \times 10^3$ appear in Table I.

TABLE I

EXPERIMENTS AT 235° WITH "OXYGEN-FREE" MIXTURES OF METHANE AND CHLORINE (AND METHYL CHLORIDE AND CHLORINE)

Run	Initial part. press., CH ₄	atm. Cl ₂	Ratio CH ₄ /Cl ₂	Heating time, seconds	% Cl ₂ reacted	k ₂ × 10 ³
Empty Pyrex Tube: vol. 358 cc.; approx. 35 cm. long and 4 cm. diam.; washed with concd. HNO ₃ and H ₂ O						
122	0.329	0.659	1/2	260	19.3	2.51
121	.659	.329	2/1	260	32.8	2.32
123	.658	.329	2/1	261	34.6	2.47
Same Tube, coated with KCl: rinsed with 20% KCl soln.; drained and dried						
94	0.334	0.668	1/2	262	17.4	2.18
93	.668	.334	2/1	262	33.3	2.31
95	.668	.334	2/1	262	41.0	3.01
Packed Pyrex Tube: filled with broken Pyrex, 8 to 10 mesh; all washed concd. HNO ₃ and H ₂ O; tube approx. 35 cm. long and 5.5 cm. diam.; free vol., 360 cc.						
101	0.336	0.672	1/2	264	24.7	3.20
104	.335	.670	1/2	265	27.3	3.51
100	.672	.336	2/1	264	(28.2)	..
102	.672	.336	2/1	265	50.5	3.95
103	.670	.335	2/1	266	58.0	4.86
105	.670	.335	2/1	265	52.4	4.18
Methyl Chloride-Chlorine in Uncoated Empty Bulb (above)						
CH ₃ Cl						
MC8	0.330	0.660	1/2	261	37.2	5.40
MC7	.660	.330	2/1	261	60.5	5.39
MC9	.659	.330	2/1	261	57.6	4.99

Experiments with Added Oxygen.—The results of experiments in which small amounts of oxygen were added to the methane-chlorine mixture are summarized in Table II. The inhibitory effect of the oxygen is considerable. Thus at 250° with a 2CH₄:1Cl₂ mixture, 0.25% of oxygen produced more than a ten-fold decrease in rate. The relation between rate and concentration of methane and chlorine is fundamentally altered. Without added oxygen, the percentage of chlorine reacting in the un-packed tube was about twice as great in a 2CH₄:1Cl₂ mixture as in a 1CH₄:2Cl₂ mixture. With added oxygen, the relationship is exactly reversed—the percentage of chlorine reacting is the greater when chlorine is in excess. The inhibiting action of oxygen is about proportional to its concentration.

In the empty reaction tube, the concentration-rate relation with added oxygen suggests that the rate is more nearly proportional to the square of the chlorine concentration, independent of the methane concentration, and inversely as the oxygen concentration. We might then write

$$-\frac{d\rho_{\text{Cl}_2}}{dt} = k' \frac{\rho_{\text{Cl}_2}^2}{\rho_{\text{O}_2}}$$

TABLE II
REACTION OF METHANE-CHLORINE MIXTURES CONTAINING OXYGEN

Run	CH ₄	Initial part. press., atm. Cl ₂	O ₂	Ratio CH ₄ /Cl ₂	Heating time, seconds	% Cl ₂ reacted	<i>k</i> ' × 10 ³
Empty clean reaction tube used (see Table I)							
Comparison of Rates with and without Oxygen at 250°							
136	0.663	0.331	0.0254	2/1	255	0.5	
137	.662	.331	.00259	2/1	254	5.8	
135	.664	.332	0	2/1	253	63.9	}
138	.663	.331	0	2/1	255	66.6	
Effect of Changing CH ₄ /Cl ₂ at 275°							
72	0.824	0.165	0.0104	5/1	269	16.2	4.16
71	.658	.329	.0103	2/1	269	19.7	}
73	.659	.330	.0103	2/1	269	24.0	
75	.660	.330	.0103	2/1	268	21.0	}
74	.330	.660	.0103	1/2	267	58.4	
56	.821	.164	.00518	5/1	271	39.9	}
57	.822	.165	.00519	5/1	269	38.7	
55	.657	.328	.00520	2/1	272	54.5	}
58	.658	.329	.00515	2/1	270	55.2	
Effect of Changing Oxygen Concentration at 275°							
54	0.653	0.327	0.0102	2/1	269	26.6	3.59
51	.657	.328	.00512	2/1	267	57.1	}
53	.657	.328	.00512	2/1	270	57.6	
55	.657	.328	.00520	2/1	272	54.5	}
52	.658	.329	.00257	2/1	268	85.1	
Packed reaction tube used (see Table I)							
Effect of changing CH ₄ /Cl ₂ at 275°							
81	0.951	0.325	0.0223	2/1	267	50.0	}
83	.649	.325	.0223	2/1	267	47.8	
82	.325	.650	.0223	1/2	268	61.2	5.55

We do not know how the oxygen enters into the reaction. It is assumed that it terminates reaction chains, and that it is consumed in this process. Assuming further that the chain length is equal to the chlorine-oxygen ratio, and that a molecule of oxygen disappears for every chain terminated, it follows that

$$-\frac{p_{\text{Cl}_2}}{p_{\text{O}_2}} dp_{\text{O}_2} = -dp_{\text{Cl}_2}$$

whence

$$\ln \frac{p_{\text{Cl}_2}}{p_{\text{O}_2}} = \ln \frac{p_{\text{OCl}_2}}{p_{\text{O}_2}}$$

or

$$\frac{p_{\text{Cl}_2}}{p_{\text{O}_2}} = \frac{p_{\text{OCl}_2}}{p_{\text{O}_2}}$$

and

$$p_{O_2} = p_{Cl_2} \frac{p_{O_{Cl_2}}}{p_{O_{Cl_2}'}}$$

Then

$$\begin{aligned} -\frac{dp_{Cl_2}}{dt} &= k' p_{Cl_2}^2 \frac{p_{O_{Cl_2}'}}{p_{Cl_2} \cdot p_{O_2}} \\ &= k' \frac{p_{Cl_2} \cdot p_{O_{Cl_2}'}}{p_{O_2}} \end{aligned}$$

Setting

$$p_{Cl_2} = xp_{O_{Cl_2}'}$$

where $100(1-x)$ = percentage chlorine reacting

$$-p_{O_{Cl_2}'} \frac{dx}{dt} = \frac{k' x p_{O_{Cl_2}'}}{p_{O_{Cl_2}'}}$$

or

$$-\frac{dx}{dt} = \frac{k' x p_{O_{Cl_2}'}}{p_{O_2}}$$

whence

$$k' = \frac{2.303 p_{O_2}}{p_{O_{Cl_2}'}} \log_{10} \frac{1}{x}$$

Values of k' appear in Table II.

The reaction of oxygen-containing gases appears to be somewhat different in a packed reaction tube (see bottom of Table II). The percentage conversion of chlorine is less affected by a change in the CH_4/Cl_2 ratio. The rates are noticeably greater than in the unpacked tube. Thus with a $2CH_4:1Cl_2$ mixture, the rate is twice as great in the packed tube even with twice as much oxygen present.

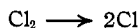
TABLE III
TEMPERATURE COEFFICIENT OF THE RATE

Run	Temp., °C.	Initial part. CH ₄	part. press., atm. Cl ₂	atm. O ₂	Heating time, seconds	% Cl ₂ reacted	k	Coeff., 10 ⁴	Energy of activation, cals./mole
With added oxygen—clean, empty reaction tube (see Table I)									
							$k' \times 10^5$		
65	265	0.656	0.328	0.0104	272	7.5	0.91	} 3.5	77,300
64	275	.656	.328	.0102	267	25.9	3.49		
66	275	.656	.328	.0102	267	21.7	2.85		
67	275	.651	.326	.0103	268	22.0	2.93	} 3.8	
69	275	.651	.326	.0103	268	20.7	2.73		
68	285	.651	.326	.0101	264	59.6	10.64		
Without added oxygen—clean, empty reaction tube (see Table I)									
							$k_2 \times 10^3$		
133	225	0.665	0.332	0	265	24.0	1.56	} 2.1	31,600
134	235	.664	.332	0	260	40.6	3.02		
132	235	.664	.332	0	260	44.2	3.38		
130	235	.664	.332	0	260	40.3	2.99	} 1.6	
131	245	.664	.332	0	255	58.6	5.21		

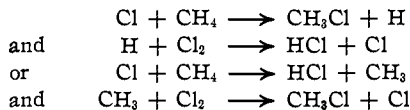
Temperature Coefficient and Heat of Activation.—Results of experiments to determine the temperature coefficient are given in Table III. The average value is 3.65 per 10° for $2\text{CH}_4:\text{Cl}_2$ mixtures containing 1% of oxygen, and 1.85 per 10° for such mixtures containing no added oxygen. The corresponding values of the activation energy are 77,300 cal. and 31,600 cal., respectively. Addition of oxygen thus alters the latter as well as the reaction kinetics.

Mechanism of the Process.—Although our results are neither precise enough nor sufficiently extensive to warrant general conclusions as to the mechanism, it is extremely interesting to find that what data we have indicate a close resemblance between the thermal chlorination of methane, and the photochemical hydrogen-chlorine reaction. For the latter it is well established that the rate in absence of oxygen is proportional to the product of the hydrogen and chlorine concentrations whereas in presence of oxygen the rate is approximately proportional to the square of the chlorine concentration and inversely as the oxygen concentration—precisely as in the case of the thermal methane-chlorine reaction.⁷

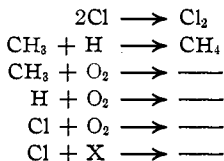
The photochemical hydrogen-chlorine reaction is generally believed to be of the atom-chain type. If we are to adapt this mechanism to the thermal methane-chlorine reaction, we will have as primary reaction a thermal (instead of a photolytic) dissociation of chlorine



followed by such reactions as



together with the chain-terminating reactions

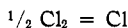


In view of the fact that there is no general agreement as to the details of the far more exhaustively studied hydrogen-chlorine reaction, there is not much point in entering on a prolonged discussion of possible mechanisms for the case in hand. There seems to be one rather serious drawback which will be briefly presented.

Since the homogeneous dissociation of chlorine is an essential to reaction, it is of interest to estimate the probable rate of this reaction for

⁷ Bodenstein and Unger, *Z. physik. Chem.*, **11B**, 253 (1931).

comparison with the observed rate of chlorination of methane. The free energy of the reaction



is about +30,000 cal. at 235°. ⁸ Thus

$$K_{508} = \frac{p_{\text{Cl}}}{p_{\text{Cl}_2}^{1/2}} = 10^{-13}$$

and for

$$p_{\text{Cl}_2} = 1, \quad p_{\text{Cl}} = 10^{-13}$$

The rate of recombination of chlorine atoms by collision at the equilibrium concentration would be, if every collision were effective

$$\frac{\sqrt{2}}{2} \pi \sigma^2 n^2 u = \frac{\sqrt{2}}{2} \pi (2 \times 10^{-8})^2 (10^6)^2 10^5 = 10^2$$

collisions forming a chlorine molecule per cc. per second.

The observed velocity constant of the reaction without added oxygen at 235° is 10⁻³. This means that with 1 atm. each of methane and chlorine the fraction 10⁻³ of the chlorine reacts per second. Therefore, with 10¹⁹ molecules per cc., 10¹⁶ molecules of chlorine actually reacted per cc. per second at 235°. Since only 10² molecules of chlorine were calculated to dissociate thermally under these conditions, the chain length would have to be 10¹⁴. This seems entirely unlikely. Although the calculation is only approximate, it nevertheless appears that there will be difficulty in bringing the mechanism to conform with that of the photochemical hydrogen-chlorine reaction.

A curious coincidence emerges in connection with the temperature coefficient of the reaction without added oxygen. The reaction is second-order and homogeneous. The temperature coefficient gives 31,600 cal. for the activation energy by the conventional calculation. In view of the fact that the reaction is of the chain-type, this activation energy is undoubtedly a composite of several terms. Nevertheless, if it is assumed (ignoring the influence of oxygen) that the reaction is of the simple bimolecular collision type and the collision theory is applied, the rate calculated therefrom is in good agreement with that actually observed. This can hardly have any significance. The case is not unlike that of the dissociation of chlorine monoxide, which was accepted as one of the early examples of the bimolecular collision reaction,⁹ but which has recently been shown to have a much more complicated mechanism of the chain type.¹⁰

Summary

1. The kinetics of the homogeneous thermal reaction between methane and chlorine has been studied.

⁸ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 501.

⁹ Hinshelwood and Hughes, *J. Chem. Soc.*, **125**, 1841 (1925).

¹⁰ Beaver and Stieger, *Z. physik. Chem.*, **12B**, 93 (1931).

2. The reaction is rather powerfully inhibited by oxygen.
3. Without added oxygen, the rate of chlorination appears to be proportional to the product of the concentrations of methane and chlorine. In presence of oxygen the rate is more nearly proportional to the square of the chlorine concentration, independent of the methane concentration, and inversely proportional to the oxygen concentration.
4. The kinetics resemble that of the photochemical hydrogen-chlorine reaction. If the mechanism is the same, a thermal dissociation of chlorine would seem to be involved. Approximate calculations indicate that this can hardly proceed at a sufficient rate to give the observed reaction rate.

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[CONTRIBUTION NO. 66 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

THE REACTION BETWEEN OXYGEN AND ETHYLENE. I

By SAMUEL LENHER

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The oxidation of ethylene has been a subject of study for many years.¹ The present rather comprehensive investigation was undertaken with the object of studying the mechanism of the slow thermal oxidation of the olefins. The olefins offer a specific point of attack by oxygen at the carbon-carbon double bond, and as ethylene has but one such bond study of the oxidation of ethylene promised to throw light on the problem of the addition of oxygen at a simple olefin linkage, and accordingly to give data which could be applied generally to the oxidation of the mono-olefin hydrocarbons.

Especial attention was directed in the present work to the identification of the intermediate oxidation products, for the course of the oxidation can only be determined by analysis of all the products of the reaction. Bone and R. V. Wheeler^{1c} found that formaldehyde was the most prominent intermediate oxidation product and that its formation preceded that of carbon oxides and steam. They concluded that the reaction took place in a series of steps, and postulated the formation of vinyl alcohol and a hypothetical dihydroxyethylene as primary steps preceding the appearance of formaldehyde. The occurrence of carbon oxides and water was the final stage involving the decomposition and oxidation of formic acid which was derived from formaldehyde. Later, Blair and T. S. Wheeler^{1e} showed that acetaldehyde was an oxidation product of

¹ (a) Schützenberger, *Bull. soc. chim.*, 31, 482 (1879); (b) Phillips, *Trans. Am. Phil. Soc.*, 17, 149 (1893); (c) Bone and R. V. Wheeler, *J. Chem. Soc.*, 85, 1637 (1904); (d) Willstätter and Bommer, *Ann.*, 422, 36 (1920); (e) Blair and T. S. Wheeler, *J. Soc. Chem. Ind.*, 41, 303T (1922); 42, 415T (1923); (f) Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, A125, 277 (1929).