An attempt was made to establish the position of the *tert.*-butyl groups in the naphthalene ring by means of boiling the di-*tert.*-butylnaphthalenes with dilute nitric acid, but no oxidation to the naphthalene-dicarbonic acids took place.

Very probably Wegscheider had already obtained these two isomeric di-*tert.*-butylnaphthalenes but his belief that his compounds of m. p. 80° and 146–147° were α,β-dinaphthyl and α,α-dinaphthyl was erroneous.

CONTRIBUTION FROM THE   WILLIAM GUMP
RESEARCH LABORATORY OF
DEHLS AND STEIN
NEWARK, N. J.
RECEIVED NOVEMBER 25, 1930
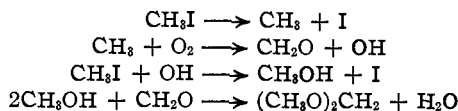PUBLISHED JANUARY 12, 1931

COMMUNICATIONS TO THE EDITOR

PHOTOCHEMICAL REACTIONS OF GASEOUS METHYL IODIDE

Sir:

In a recent communication to *Nature*, Iredale[1] has discussed the action of light upon gaseous methyl iodide. From a study of the short wave limit of the absorption spectrum, he calculates the energy of the C–H bond to be 65 Cal. and suggests, with Herzberg and Scheibe,[2] that the initial process is the dissociation of methyl iodide into CH_3 and I, since the absorption is continuous. Studies of the photochemical decomposition and oxidation of gaseous methyl iodide in progress in this Laboratory for some time past lend additional support to the idea that CH_3 and I are the initial products. The reaction behaves as though the process were actually that of the oxidation of free methyl groups. Formaldehyde, paraformaldehyde and methylal seem to be the products, while the iodine originally present in the methyl iodide can in all cases be recovered as free iodine.

A possible mechanism for the process is

$$CH_3I \longrightarrow CH_3 + I$$
$$CH_3 + O_2 \longrightarrow CH_2O + OH$$
$$CH_3I + OH \longrightarrow CH_3OH + I$$
$$2CH_3OH + CH_2O \longrightarrow (CH_3O)_2CH_2 + H_2O$$

Kinetic measurements are being made to determine the actual mechanism.

FRICK CHEMICAL LABORATORY   JOHN R. BATES
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RECEIVED DECEMBER 1, 1930
PUBLISHED JANUARY 12, 1931

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[1] Iredale, *Nature*, 604, Oct. (1930).

[2] Herzberg and Scheibe, *Trans. Faraday Soc.*, 25, 716 (1929).

THE THERMAL CHLORINATION OF METHANE BY A FLOW METHOD

Sir:

We have recently been investigating the thermal (non-catalytic) chlorination of methane by a flow method. The following conclusions as to the kinetics of the reaction may be of interest.

The reaction takes place readily in pyrex glass reaction tubes above about 200° at 1 atm. total pressure. The rate is unaffected if the reaction tube is packed with broken glass, or if the internal surface of the tube is coated with potassium chloride. The reaction is, therefore, homogeneous. The effects of changes in concentration of reactants indicate that it is also bimolecular.

At the lower temperatures (225–300°) the reaction is inhibited by oxygen. Thus at 225° and five minutes' heating, 30% of the chlorine reacts when the reaction mixture consists of 60% methane and 40% chlorine at 1 atm. With 5% of oxygen present there is no measurable reaction. At 300° the suppression by oxygen is still considerable, but at 375°, at which temperature the rate of the unsuppressed reaction is very high, 5% of oxygen has no measurable effect. This effect of oxygen points to a chain mechanism. This is borne out by a discrepancy between the observed reaction rate at any temperature and that calculated by the collision theory of bimolecular gas reactions. About 1000 more molecules react than the theory predicts. A recent study of the photochemical chlorination of methane by Coehn and Cordes [*Z. physik. Chem.*, Abt B, **9**, 1 (1930)] has demonstrated that a chain mechanism applies here also, chains being some 10^4 molecules in length at the maximum.

This work is being extended and will be later reported in full.

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RECEIVED DECEMBER 10, 1930
PUBLISHED JANUARY 12, 1931

ADSORPTION AND PROMOTER ACTION IN CATALYSIS

Sir:

The results of Elissafoff's experiments [*Z. Electrochem.*, **21**, 352 (1915)] have been quoted by Hugh S. Taylor in his "Treatise upon Physical Chemistry" and also by Rudel and Haring [*Ind. Eng. Chem.*, **22**, 1234–1237 (1930)] as an example of adsorption in catalysis. The first investigator found that copper sulfate in the presence of glass wool decomposed hydrogen peroxide more rapidly than either substance alone, and that the effect was greater than the sum of the individual effects. Since separate experiments showed that a glass powder, of the same composition as the

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glass wool, removed copper from solution, Elissafoff concluded that the copper was adsorbed at the interface and that the increased concentration of copper was responsible for the increase of rate. This conclusion was justified by close parallelism between the increased rate of reaction when the copper concentration was increased tenfold, and the increased amount of copper removed from a solution of similarly increased copper concentration.

At the time my attention was called to this article, I conducted a few brief tests with results incompatible with those of Elissafoff. The experiments could not be amplified for lack of time, and therefore it seems best to indicate them briefly now. Hydrogen peroxide solutions were decomposed in quartz vessels by freshly prepared copper sulfate solutions containing one millimole per liter of copper sulfate. It was found that the velocity constant was nearly first order and not easily reproduced in the presumably neutral solutions employed. It is felt that the data from one series of experiments may be compared among themselves, however. It was also found that the addition of glass wool to a solution containing hydrogen peroxide and copper sulfate did increase the rate of decomposition but to a less extent than Elissafoff observed. The reaction velocities for the promoted reaction increased appreciably with time, which points to a dependence of rate upon an adsorbed catalyst. However, it was found that a filtered extract of the glass wool increased the rate quite as much as the solid material. Also it was found that increasing the amount of glass wool ten-fold increased the rate of reaction very little. From these observations it was concluded that the glass wool no doubt removed copper from solution as Elissafoff says, but not as copper sulfate. The copper probably formed a basic salt upon the surface of the glass wool, and then solid copper peroxide, a reaction which is favored by the alkali from the glass. The reaction in the absence of glass wool can be and probably is homogeneous; thus it seems probable that the mechanism of the reaction is different under "promotion" conditions than otherwise, and that this reaction is not an example of the effect of adsorption upon catalytic reaction rates.

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THE OXIDATION OF CARBON MONOXIDE BY DISSOCIATED WATER VAPOR

Sir:

In a recent publication Harteck and Kopsch[1] have shown that atomic oxygen, from a discharge tube, has very little effect on carbon monoxide;

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[1] Harteck and Kopsch, *Z. Elektrochem.*, **36**, 714 (1930).

only 5% reacted. At the suggestion of Professor Hugh S. Taylor we have carried out experiments on the action of dissociated water vapor on carbon monoxide. It seems entirely probable that in the water vapor discharge tube[2] we have a source of hydroxyl, also the reaction[3] $OH + CO = CO_2 + H$ is 24,000 cal. exothermic. That we do get oxidation is shown by the results given in Table I.

TABLE I

RESULTS OF EXPERIMENTS

Water through tube, mole	CO, mole	CO converted to CO_2, %
0.039	0.005	21.60
.059	.005	26.30

We have also passed a constant quantity of oxygen through the tube and then varied the water vapor concentration. It is to be pointed out that the exit of the tube did not become very warm, which means that the water vapor was not decreased to such an extent that recombination of the atomic oxygen took place on the walls. Also, there was no back diffusion to the discharge tube in any of the experiments. The results are given in Table II.

TABLE II

EXPERIMENTAL DATA

Water through tube, mole	Oxygen, mole	CO, mole	CO converted to CO_2, %
0.003	0.028	0.005	5.90
.012	.028	.005	24.30
.059	.028	.005	37.10

Since Copeland[4] has found that water vapor is essential for the production of atomic oxygen, we can attribute the oxidation in Harteck and Kopsch's experiment to the presence of a small quantity of water.

Further details will be published shortly.

DEPARTMENT OF CHEMISTRY   G. I. LAVIN
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[2] Lavin and Stewart, *Proc. Nat. Acad. Sci.*, **15**, 829 (1929); Taylor and Lavin, THIS JOURNAL, **52**, 1910 (1930).

[3] Bonhoeffer and Haber, *Z. physik. Chem.*, **A137**, 263 (1928).

[4] Copeland, *Phys. Rev.*, **36**, 1221 (1930).