

*The Chemical Reactions of Carbon Monoxide and Hydrogen
after Collision with Electrons.*

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In a previous communication* the authors described a method of measuring rates of reaction of molecules and atoms which were being activated by electron collision in suitably constructed triode tubes. The method has since been extended to study the decomposition of carbon monoxide and its interactions with hydrogen.

Carbon monoxide has long been known to undergo decomposition, chiefly into carbon and carbon dioxide in the silent discharge.† A mixture of solid oxides containing chiefly C_3O_2 is always observed.‡ Carbon monoxide and hydrogen yield an even greater diversity of products. Thus Losanitsch and Jovitschitsch§ and de Hemptinne|| noted the production of formaldehyde and its polymers and also some formic acid. Slosse and Nowak¶ and Löb** obtained formaldehyde and methyl alcohol, while the latter also found glycollic aldehyde. M. Berthelot†† stated that excess of hydrogen favours the production of $(CH_2O)_n$, whereas excess of carbon monoxide yields $(C_3H_4O_3)_n$.

Similar reactions occur when the gases are ionised by alpha particles. Cameron and Ramsay‡‡ found that carbon monoxide was decomposed into carbon, carbon dioxide and oxygen, while Lind and Bardwell§§ observed chiefly carbon and carbon dioxide but also some suboxide; mixed with hydrogen, carbon monoxide yields a white solid.

As regards the photochemical reaction, D. Berthelot and Gaudechon||| found traces of a solid polymer of formaldehyde when a mixture of carbon

* 'Roy. Soc. Proc.' vol. 115, p. 684 (1927).

† See, for example, Brodie, *ibid.*, vol. 21, p. 245 (1873), etc.

‡ See M. Berthelot, 'C. R.', vol. 82, p. 1360 (1878), etc.; Crespi and Lunt, 'J. Chem. Soc.', vol. 127, p. 2052 (1925), Ott; 'Ber. Deut. Chem. Ges.', vol. 58, p. 772 (1925).

§ 'Ber. Deut. Chem. Ges.', vol. 30, p. 135 (1897).

|| 'Bull. Acad. Roy. Belg.', vol. 34, p. 269 (1897).

¶ 'Bull. Acad. Roy. Belg.', vol. 35, p. 547 (1898).

** 'Z. Elektrochem.', vol. 11, p. 750 (1905).

†† 'C. R.', vol. 126, p. 609 (1898).

‡‡ 'J. Chem. Soc.', vol. 93, p. 966 (1908).

§§ 'J. Am. Chem. Soc.', vol. 47, p. 2675 (1925).

||| 'C. R.', vol. 150, p. 1690 (1910).

monoxide and hydrogen was exposed to ultra-violet light, but the existence of a direct photochemical reaction, *i.e.*, unsensitised by mercury vapour, is still in doubt.

The Research Staff of the General Electric Company* observed the disappearance of carbon monoxide in thermionic valves at pressures of about a thousandth millimetre, and potentials capable of sustaining an arc; the rate of "adsorption of ions" was shown to depend on the condition but not on the material of the surface.

The object of the present investigation was to study quantitatively the chemical behaviour of the various active species. By choosing a suitable range of pressures (about one-tenth to two-tenths millimetre for the electrode dimensions used), it was possible to collect quantities of products sufficient for chemical tests; whilst the method has the advantage over discharge-tube methods that the initial energies of the colliding electrons is known with sufficient accuracy to enable the breaks in the curves showing reaction-rate as a function of grid-potential to be correlated with the definite limiting electronic energies necessary to produce the various physically active molecules by collision.

Experimental.

The details of the method are similar to those described in the previous paper.† The main essentials consisted of the reaction system which included a quick-reading McLeod gauge and a cylindrical triode immersed to a constant level in liquid air; the electrodes were symmetrically placed, consisting of a straight wire filament, a helical wire grid and a cylindrical platinum anode; all could be removed by a ground-joint which held a vacuum with only a very fine ring of grease. The vessel V is shown with the lift by means of which the liquid-air level was kept constant. The products of several experiments were drawn into the cooled trap T, where chemical tests were applied. For exhaust, two hard-glass mercury diffusion pumps were used, backed by a Hyvac rotary oil pump.

Hydrogen was purified by slow passage over red hot copper and palladium. Carbon monoxide was made by running pure formic acid into concentrated sulphuric acid on the water bath and was passed through potash bulbs. Phosphoric anhydride was used for drying the gases and for lining the bulbs in which they were stored. The purity of the carbon monoxide was tested by the completeness of its absorption by ammoniacal cuprous chloride.

* 'Phil. Mag.', vol. 48, p. 553 (1924).

† *Loc. cit.*

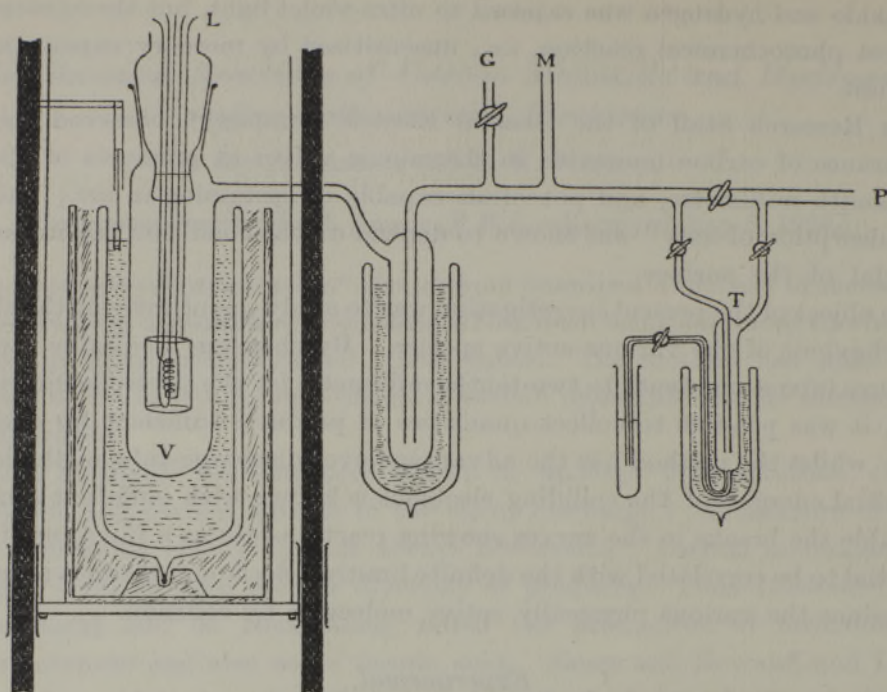
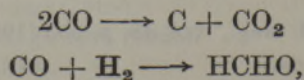


FIG. 1.—L, electrical connection. G, to gas mixtures. M, to gauge.

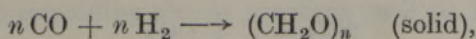
Measurements.

The determination of primary importance is that of reaction-rate for various voltages, *i.e.*, electron energies, the electron current being kept constant and measured. The rate is a complicated function of the gas pressure as, in addition to the effect of decreasing partial pressures of the reactants, there is the effect of the lengthening mean free path of the electrons. By plotting a series of pressure-time curves, it was possible, however, to compare the average rates over a standard range of pressure.

Measurements were also made of the initial pressure (P_1), the equilibrium pressure (P_2) after the liquid-air baths had been adjusted, the pressure (P_3) at the end of a reaction, the liquid-air baths being still in place, and the final pressure (P_4) at room temperature. The fraction $f = \frac{P_2}{P_1} \cdot \frac{P_1 - P_4}{P_2 - P_3}$ evidently gives a rough measure of the ratio of the decrease in the number of gas molecules by reaction to the number of molecules of reactants. Thus for the reactions



f should be 0.5, while for the reaction



f should be unity.

A further measurement was made in order to calculate the "efficiencies" defined as the number of molecules removed per electron. An effective current of C milliamperes is equivalent to the passage of $60 \times \frac{C}{e} \times 10^{-4}$ electrons per minute, where e is the electronic charge in e.m.u. If each electron causes the removal of n molecules, the decrease in pressure in millimetres of mercury per minute is

$$-\frac{dp}{dt} = 60 \times \frac{C}{e} \times 10^{-4} n \times \frac{22400}{V} \times \frac{760}{N},$$

where N is the Avogadro number and V the volume of the system, corrected for temperature. Inserting the values $e = 1.591 \times 10^{-20}$ e.m.u. and $N = 6.062 \times 10^{23}$, we obtain

$$n = -0.0944 \frac{V}{C} \frac{dp}{dt},$$

V being measured in cubic centimetres, C in milliamperes and $\frac{dp}{dt}$ in millimetres mercury per minute.

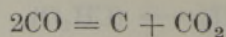
The Decomposition of Carbon Monoxide.

Langmuir* has shown that at very high temperatures tungsten combines with carbon monoxide to form the compound WCO. It was found, however, that the gas could be kept in the presence of glowing tungsten for several hours at a temperature high enough to give a suitable thermionic emission without appreciable decrease of pressure. Tungsten filaments were therefore used for the study of the decomposition of carbon monoxide by electrons.

On increase of the electron energy through carbon monoxide, pressure decreases were observed at potentials above the arcing potential. Carbon dioxide was shown to be a product by drawing baryta into the testing trap and comparing the cloudiness with the result of blank tests. After the tube was taken down, carbon was found on the electrodes. Traces of a grey deposit showed inside the valve after such experiment but disappeared during the baking which had to be performed between experiments. Under the conditions of experiment very little oxygen could have been left as the thinning of the filaments

* 'J. Am. Chem. Soc.,' vol. 37, p. 1139 (1915).

was extremely slow. That the main reaction can be represented by the equation



is shown by the following table of permanent pressure decreases :—

p_1 .	p_2 .	p_3 .	p_4 .	f .
mm.				
0.305	0.185	0.114	0.236	0.585
0.443	0.266	0.144	0.323	0.59
0.236	0.142	0.086	0.183	0.57
0.305	0.185	0.128	0.251	0.575

That f is slightly above 0.5 is in agreement with the production of a little solid, probably C_3O_2 .

Fig. 2 includes some typical pressure time curves. The rates were very

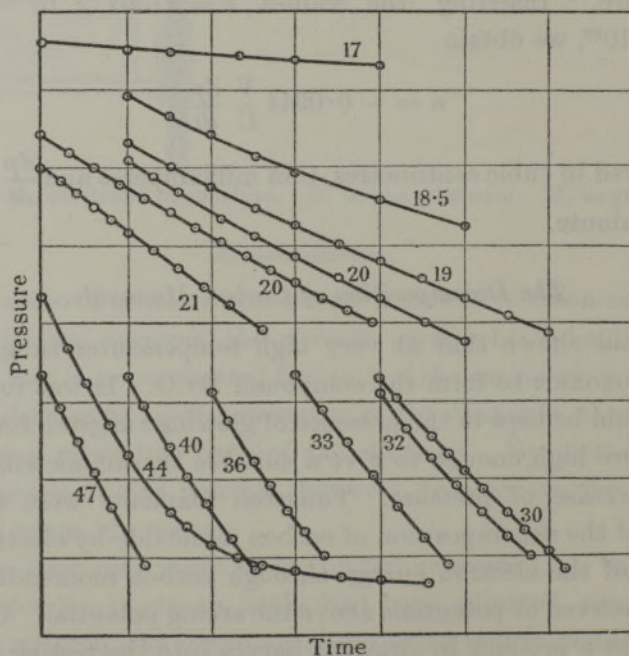


FIG. 2.—The numbers represent voltages (uncorrected). For convenience of representation a shifting scale has been employed. Two divisions of the ordinate represent 0.1 mm., one division of the abscissa represents 10 minutes. For each curve the range includes 0.2 to 0.1 mm., except for the lower voltages. V for this tube = 575 c.c. Emission = 1.62 milliamp.

nearly constant over the range 0.2 mm. to 0.1 mm., and the average rates over that range have been plotted against the uncorrected voltages in fig. 3.

It will be observed that reaction commences at electron speeds equivalent to ca. 14 v., the rate remaining almost constant until ca. 19 v., when a marked

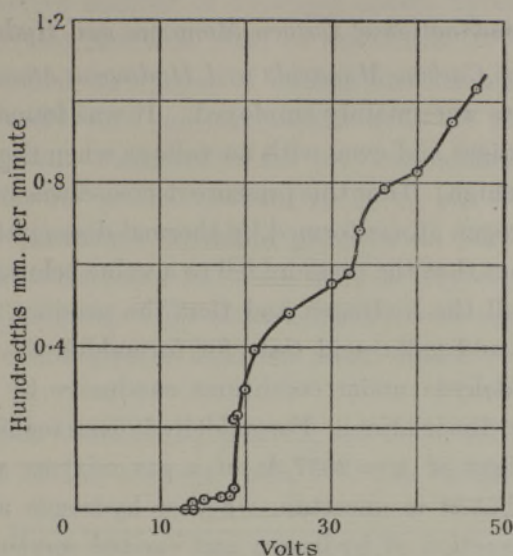


FIG. 3.—Reaction rate and electron energy in carbon monoxide.

rise in rate occurs. Less distinct breaks are noted at ca. 32 v. and 40 v. For the better elucidation of the changes in rate of reaction, three investigations were pursued. First, the slow rates between 14 v. and 19 v. were confirmed on several different samples of gas whose purity had been ascertained; moreover, the reaction in two cases was demonstrated to proceed almost to completion.

	mm.	mm.
Initial.....	0.168	0.155
Pressure after 8 hours.....	0.045	0.042

The decrease in pressure in the same time with no voltage was less than one-tenth as great.

Secondly, it was confirmed that the reaction-rate scarcely rises at all between 15 v. and 18 v. but rises abruptly between 19 v. and 20 v., simultaneously with the intensification of the characteristic "sky-blue" radiation of carbon monoxide.

In the third place, attempts were made to fix the higher voltage breaks by measurements of average rates at intervals of half a volt near an apparent break, but it was found that the violent arcing prevented the repetition of results with sufficient accuracy. In the curve, rates have therefore been

inserted only when they have been repeated to an accuracy of 3 to 4 per cent. Very little reliance can be placed on apparent breaks above 20 v.

The Combination of Carbon Monoxide and Hydrogen.

A. *Combination of Carbon Monoxide and Hydrogen Atoms.*—Equimolecular mixtures of the gases were mainly employed. It was found that the pressure decreased at all voltages and even with no voltage when the filament temperature was sufficiently high. That this pressure decrease was not due solely to the freezing out of hydrogen atoms formed by thermal dissociation on the hot wire was shown by the fact that the pressure fell to a value below that corresponding to the removal of all the hydrogen and that the product frozen out readily gave the resorcinol and gallic-acid tests for formaldehyde. There is thus a synthesis of formaldehyde under conditions conducive to the production of hydrogen atoms by dissociation. Formaldehyde can readily be obtained by illumination with light of $\lambda = 2537 \text{ \AA.}$ of a gas mixture photosensitised by mercury vapour,* but it is uncertain whether hydrogen atoms are actually formed by the interaction of hydrogen and excited mercury atoms.† Since in the synthesis of ammonia from its elements it was found that hydrogen atoms combined with nitrogen molecules only in the presence of a metal catalyst or when activated by 13 v. electrons, it was of special interest to examine the formaldehyde synthesis from atoms in detail. Special precautions were taken to exclude reducible substances from the leads and glass walls, and it was found necessary to make all connections without solder and to coat the leads‡ with glass, the tube being also baked out until it fulfilled the requirement that after hydrogen atoms had been frozen out on the walls, the pressure returned to the initial pressure of hydrogen on allowing to stand at room temperature.

It was found that formaldehyde synthesis occurred readily with or without the large platinum anode, and this reaction thus differs from the ammonia synthesis in which the presence of a metal catalyst was necessary. Specimen pressure-time curves are included in fig. 6.

B. *Combination of Hydrogen Molecules with Carbon Monoxide.*—Preliminary experiments with oxide-coated filaments indicated that there was a ready reaction when the electron velocities exceeded 20 v., but after several hours use abnormally high rates were sometimes observed. Subsequent examination

* Taylor and Marshall, 'J. Phys. Chem.,' vol. 29, p. 1140 (1925).

† See Compton and Turner, 'Phil. Mag.,' vol. 48, p. 360 (1924); Phillips and Taylor, 'Phys. Rev.,' vol. 29, p. 309 (1927).

‡ Any cupric oxide on the leads is easily reduced in agreement with the observations of Bonhoeffer, 'Z. Phys. Chem.,' vol. 113, p. 199 (1924).

of the filaments showed that the oxide had become localised in spots, thus rendering a higher filament temperature necessary and consequent production of a small but effective number of hydrogen atoms by thermal dissociation. We are indebted to the Research Staff of the G.E.C. at Wembley for a fine suspension of the mixed carbonates of barium and strontium which could be deposited in extremely thin uniform layers both on platinum and (more effectively) on tungsten. As noted in the previous communication, the oxide coating is reduced by H^+ produced about 26–30 v., but these filaments (even with high rates of thermionic emission) produced in pure hydrogen scarcely any reduction of pressure below 30 v. and only a very slight reduction about 30 v. In these experiments only those emitters were employed which gave reaction rates not much greater than the mean values plotted in curve III, fig. 4.

Curve I, fig. 4, was obtained by plotting the mean values of two, three or four measurements of the average rates over the range 0.2 to 0.15 mm.,

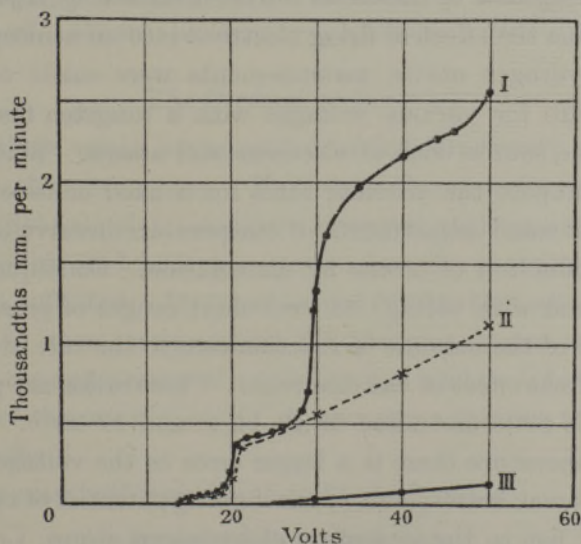


FIG. 4.—Reaction rate and electron energy over range 0.2 to 0.15 mm. I, Equimolecular mixtures of carbon monoxide and hydrogen. II, Carbon monoxide alone. III, Hydrogen alone.

except for the smaller rates for which the middle of the range was used. In order to compare the efficiencies with those of the carbon monoxide decomposition, a few rates were also measured with carbon monoxide alone at the same total pressure and electron current in the same tube. These are shown in curve II, which is similar to fig. 3, except that the latter shows more detail.

The low filament temperatures used in this tube made possible a more accurate determination of the potential breaks. Thus, under the same conditions of pressure and filament current, the arc broke in carbon monoxide at 14.0 ± 0.3 v., as shown by current-potential curves, and the double point occurred at 28.5 ± 0.2 v. This agrees well with the known ionisation potential of carbon monoxide, viz., 14.3 v. The first rise in reaction rate both for carbon monoxide alone and for its mixture with hydrogen takes place in the interval 19.5 to 20.5 v. and can therefore be attributed to a break at about 20 v. A correction of about 1 v. should therefore be applied to the curve in fig. 3.

The second rise in reaction rate with hydrogen is likewise well defined at 29.5 to 30 v.

We thus obtain three critical potentials for the interaction of carbon monoxide and hydrogen in the absence of atoms formed by thermal dissociation, viz., 14.3 v., 20 v., and 29.7 v., the first two being coincident with those necessary for the decomposition of carbon monoxide.

C. Combination effected by Electrons in the Presence of Hydrogen Atoms.—In order to examine the effect of firing electrons into an atmosphere of carbon monoxide and hydrogen atoms, measurements were made on the rates of decrease of pressure for various voltages with a tungsten filament at a high temperature as the source both of electrons and atoms. When this is done, it is useless to compare the absolute rates for a fixed emission and different voltages, since the small adjustments of temperature involve large differences in the rate of production of atoms by dissociation. Consequently, the rates with voltage on and with voltage off over short ranges of pressure were compared. The ratio of the increase of reaction-rate to the rate at zero voltage is then a measure of the effect of the electrons. These ratios are plotted in fig. 5. Sharp rises in this ratio are noted at 13–14 v. and 19–20 v. Owing to the high filament temperature there is a larger error in the voltage measurement, but that the first break corresponds to the ionising potential of the CO molecule, i.e., 14.3 v., and not to the ionisation of hydrogen atoms, i.e., 13.5 v., was confirmed by measurement of the total current under identical conditions for a constant filament temperature, when the first break became evident at 12 v. (corresponding to $\text{H} \rightarrow \text{H}^+$ at 13.5 v.); and the second at 13.5 v. ($\text{CO} \rightarrow \text{CP}^+$ at 14.3 v.). We may conclude that the combination of hydrogen atoms and CO^+ ions is more rapid or effective than the combination of the atoms with unexcited molecules, and, in addition, either H^+ ions are not appreciably more reactive than H atoms or that they are not furnished in sufficient numbers to contribute greatly to the reaction.

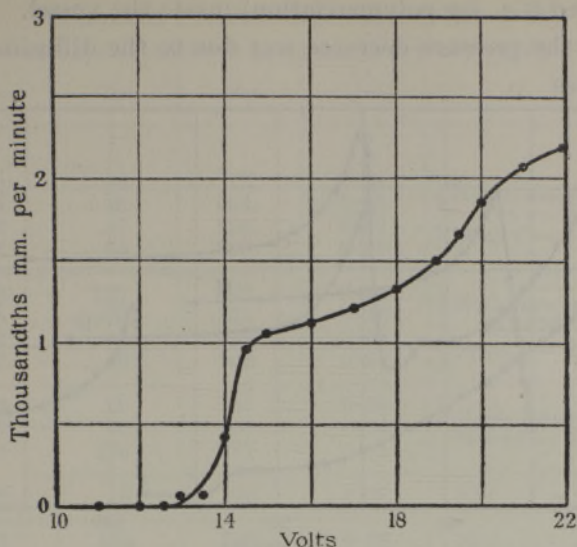


FIG. 5.—Rate of reaction of carbon monoxide and hydrogen atoms as a function of electron energy. The ordinates represent ratios of increase of rate with voltage on and rate with voltage off. Abscissæ are uncorrected voltages. Emission = 0.348 milliamp.

The Products of Reaction.

In all cases there was a permanent decrease of pressure and formaldehyde was detected in the testing trap. Neither methane, water, carbon nor methyl alcohol (as methyl salicylate) could be detected with equimolecular mixtures of carbon monoxide and hydrogen, even after the product of several experiments had been collected. It was observed further that after the product had been brought to room temperature the pressure began to decrease simultaneously with the appearance of a thin layer of white solid over the previously cooled surface of the reaction-tube. A few curves showing this "after effect" are included in fig. 6.

Eight curves examined were found to fit the formula

$$\log (p - p_0) = kt + \text{const.},$$

where p_0 = final pressure, and in every case the constant k did not differ greatly from $2 \times 10^{-3} \text{ sec.}^{-1}$. Such a low value precludes the possibility of a true unimolecular surface reaction, even if the rate of adsorption of molecules on the walls was limited by a diffusion layer. On the other hand, from the dimensions of the apparatus and the computed value of the diffusivity of formaldehyde at experimental pressures, the rate of diffusion from the McLeod gauge into the reaction-vessel was estimated to yield a rate of reduction of pressure of from $2 \times 10^{-3} p$ to $4 \times 10^{-3} p$, on the assumption that the formalde-

hyde was removed (*i.e.*, by polymerisation) inside the vessel. The alternative possibility, that the pressure decrease was due to the diffusion *into* the gauge

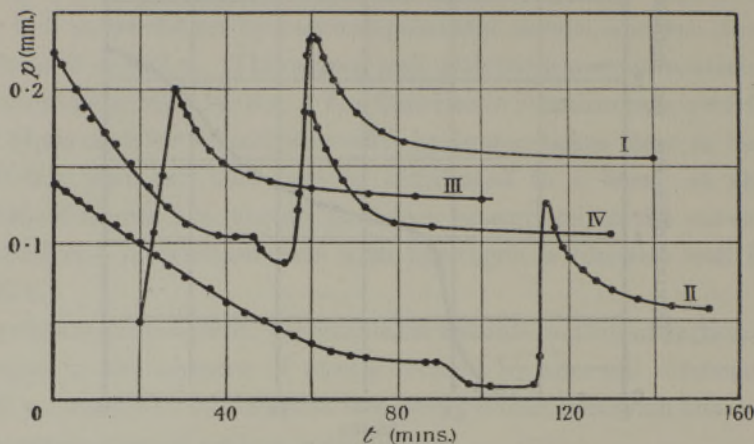


FIG. 6.—Specimen pressure-time curves. I, Reaction of hydrogen atoms with a metal catalyst. The first decrease is due to reaction, the second to cooling when the filament current was switched off, the rise is due to elevation to room-temperature, and the final lowering to polymerisation. II, Repeated with a platinum anode. III, Part of curve after reaction at 20 v. to show polymerisation. IV, The polymerisation curve after reaction at 50 v.

of a product of low vapour pressure, is precluded by the following values of the maximum and minimum pressures when the tube was immersed in liquid air and brought to room temperature a second time.

Experiment.	1.		2.	
	First.	Second.	First.	Second.
Pressure at liquid-air temperature	57	55	85	85
Highest pressure at room temperature	172	* 120	202	172
Lowest " " " "	106	105	160	159

The unit pressure is 10^{-3} mm.

It would seem, therefore, that there was a definite reaction, vapour $\rightarrow$ solid, at room temperature. This in accordance with the observed behaviour of liquid formaldehyde, which condenses to trioxymethylene on warming.

Further insight is gained by an examination of the permanent pressure decreases under varying conditions.

Permanent Pressure Decreases : $\text{CO} + \text{H}_2$.

p_1 .	p_2 .	p_3 .	p_4 .	f .	Remarks.
mm.					
0.178	110	38	72	0.91	} Hydrogen atoms but no electron current. Mean $f = 0.915$.
0.325	204	52	102	0.92	
0.278	175	57	106	0.92	
0.323	192	85	160	0.91	
0.503	303	187	322	0.94	} Hydrogen atoms and electrons up to 22 v. Mean $f = 0.95$.
0.373	225	100	177	0.95	
0.325	198	89	157	0.94	
0.310	197	60	102	0.96	
0.229	136	20	67	0.83	} Oxide emitter 20 v.-30 v. Mean $f = 0.83$.
0.330	207	40	107	0.84	
0.345	217	125	227	0.81	
0.313	202	5	36	0.91	50 v. $f = 0.91$.
0.258	157	106	186	0.86	} 35 v. Mean $f = 0.86$.
0.340	210	96	182	0.86	

The ratio f is seen to rise from 0.8, approaching unity. This is in accordance with the observation of a solid product and some formaldehyde in the gas phase.

As regards the variation of f with the conditions of experiment, it was found that the lowest values (mean about 0.83) were obtained when atoms were not present, intermediate values (mean about 0.915) for the atom reaction without electrons and maximum values (mean about 0.95) for reactions into which atoms and electrons entered. Calling the highest pressure observed at room temperature p'_4 , the ratio, $f' = p_2(p_1 - p'_4)/p_1(p_2 - p_3)$, was calculated for several experiments. There was a large variation in the values obtained, as is only to be expected, since the true maximum cannot be known accurately. Two important general observations were that f' was never less than 0.5, agreeing with the view that simple formaldehyde molecules are the first product; also f' was greater for the larger values of f . This would seem to indicate that there is an actual synthesis in the first place of more complex molecules, the proportion of which varies with the conditions, being greatest when hydrogen atoms react with excited carbon monoxide molecules and least when atoms do not enter into the reaction.

The Electron Efficiencies.

The efficiencies for a few voltages calculated from the rates shown in figs. 3 and 4 are given in the following table :—

Volts corrected.	Efficiency, <i>i.e.</i> , molecules removed per electron (<i>n</i>).		
	Reaction. (1)	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$. (2)	$\text{CO} + \text{H}_2 \rightarrow \text{HCHO}$. (3)
17	0.013	0.016	0.018
21	0.10	0.127	0.14
31	0.19	0.21	0.61
40	0.28	0.29	0.79
50	—	0.40	0.93

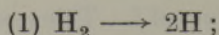
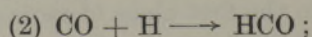
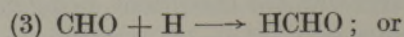
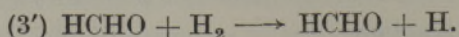
Column (1) tabulates the results with a tube for which $V = 575$ c.c. and an emission of 1.62 milliamp., while (2) and (3) are for an emission of 0.348 milliamp. in a tube with $V = 1340$ c.c.

The efficiencies obtained when hydrogen atoms are furnished by thermal dissociation are much higher, depending on the rate of production of atoms ; thus for fig. 4 at 20 v. under the conditions of experiment the rate of reaction was doubled by an emission of 0.348 milliamp., whilst the absolute rate was about 10 times the rate for that emission and voltage when hydrogen in the molecular form alone was present.

It must be concluded that with every ion produced, more than one molecule of carbon monoxide enters into reaction and that some type of chain or cluster mechanism is operative.

The Mechanism of the Reactions.

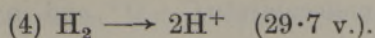
The synthesis of formaldehyde can be effected by a variety of processes. The simplest reaction is the direct union of carbon monoxide and hydrogen atoms produced by thermal dissociation.



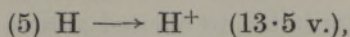
This reaction is similar to the sensitised photochemical reaction examined by Taylor and Marshall.* In addition there is an increase in reaction rate at

* 'Trans. Faraday Soc.,' March, 1926.

29.7 v., when only molecular hydrogen is originally present. This corresponds to the dissociation of hydrogen into atomic ions*

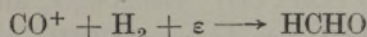


Since, however, there was no break at 13.5 v. corresponding to the reaction

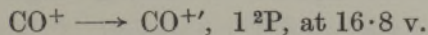
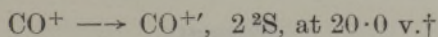


the H^+ ion does not appear to be more reactive than H and the break at 29.7 v. is merely due to the fact that this is the potential at which the actual dissociation of molecular hydrogen by electrons begins to become an efficient process.

In addition to the reactions involving modifications of molecular hydrogen, there are two others in which the excitation of the carbon monoxide alone causes combination with both molecular and atomic hydrogen. The observed critical reaction levels are 14.3 v. and 20 v. The lower level corresponds to the ionisation potential of the normal carbon monoxide molecule and we may infer either that the reaction



proceeds with small efficiency or that the carbon monoxide ions are raised by a subsequent electron collision to the more reactive 20 v. level. The transitions of the carbon monoxide positive ion to the 1^2P and 2^2S states occur at the following levels:—



We note no change in reactivity of the positive ion either on transition to the 1^2P state nor on excitation to levels between 14.3 v. and 20 v. ; indeed the reaction rate rose very little in that range both in the decomposition of carbon monoxide alone and in its union with hydrogen. In striking contrast is the increase in reactivity, in both cases, of the excited positive ion in the 2^2S state. The ion in this configuration may be expected to present a larger target area than the normal ion and consequently the efficiencies may be anticipated to be greater. If, indeed, the normal ion is reactive, the target area, to hydrogen molecules, of the ion in the 2^2S state must be about eight times that of the normal ion to account for the observed increase in reaction rate. It is interesting to

* See Compton and Mohler, 'National Research Council Bulletin,' No. 48, September, 1924.

† See Birge, 'Nature,' vol. 116, p. 170 (1925), vol. 117, p. 229 (1926); Duffendack and Fox, 'Science,' vol. 64, p. 277 (1926), and 'Astroph. J.,' vol. 65, p. 214 (1927).

note that no abrupt changes in rate either of the decomposition of carbon monoxide or its union with hydrogen occur at 24 v., the approximate dissociation potential of the molecule into $C + O^+$, and, in addition, that the mean time between collisions in these experiments of the order of 10^{-6} second, an indication that the molecular ion in the 2^2S state must have a somewhat larger life than that generally attributed to excited atoms.

The parallelism between the reactions of CO^{+} (2^2S) with normal carbon monoxide, hydrogen molecules and hydrogen atoms suggests that the various reactions may be interpreted with the aid of the theory of ionic clusters advocated by Langevin,* J. J. Thomson,† and Lind.‡ On this view the enhanced reactivity of the CO^{+} in the 2^2S state would be due, not merely to its larger collision area, but also to the fact that after radiating part of its energy, it leaves a positive ion with more energy in the vibrational or "chemical" degree of freedom than the normal ion.§ By virtue of this energy, it is enabled to form clusters with CO, H_2 and H, the clusters reacting with one another, with electrons and with the original molecules. Thus, the cluster ion $(CO \cdot CO)^+$ yields $CO_2 + C$, $(CO \cdot CO \cdot CO \cdot CO)^+$ yields C_3O_2 and CO_2 , $(H_2 \cdot CO)^+$ gives HCHO, $(CO \cdot CO)^+ + 2H_2 + e$ could give $2HCHO$ and so on. The observations that CO^{+} (2^2S) ions combine with hydrogen atoms with great avidity, and that the first product in this case is not simple formaldehyde molecules but contains also polymers, find a ready explanation on the view that the original $(HCO)^+$ cluster is capable of forming longer clusters of the type $(H_2CO)_n$.

Summary.

The decomposition of carbon monoxide into carbon and carbon dioxide (also some suboxide) and its union with hydrogen to form formaldehyde (and polymers) under excitation by electron impact have been examined. It is shown that hydrogen atoms produced by thermal dissociation react directly with carbon monoxide molecules, and also react with enhanced efficiency with carbon monoxide positive ions. It is believed that this increase in reactivity is to be attributed to either a chain or a cluster mechanism. Hydrogen molecules react with carbon monoxide positive ions, but much more readily with ions excited to the 2^2S level; this may be due either to the larger target area

* 'Ann. Chim. Phys.,' vol. 5, p. 245 (1905).

† 'Phil. Mag.,' vol. 47, p. 337 (1927).

‡ 'Science,' vol. 64, p. 1 (1926).

§ See Franck, 'Trans. Faraday Soc.,' vol. 21, p. 540 (1925); Birge, 'Nature,' vol. 117 p. 350 (1926); and Birge and Sponer, 'Phys. Rev.,' vol. 28, p. 259 (1926).

of the ion in the 2^2S state or to its greater tendency to form clusters with CO, H_2 and H. Excitation of the normal CO^+ ion and transition to the 1^2P state do not affect the reaction rate. No indication of direct decomposition into carbon and oxygen was noted at the dissociation potential. The subsequent polymerisation of formaldehyde has been shown to follow a unimolecular law, but this is due merely to slow diffusion of the simple molecules from the pressure gauge. The reaction products have been obtained in quantities sufficient for chemical tests.

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*The Velocity Distribution of Photoelectrons produced
by Soft X-Rays.*

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1.—*Introduction.*

In the literature published on the subject of soft X-rays, there are two papers* to be found, which deal particularly with the velocity of the photoelectrons produced by such rays. Both authors of these papers state, that they have found a photoelectric emission built up of homogeneous groups of electrons with characteristic velocities, giving rise to very sharp and steep jumps in the curves obtained by P. Lukirsky with retarding electric fields, and to equally sharp lines on the photographic plates in J. A. Becker's magnetic deflection apparatus. There were scarcely any electrons with low velocities present. In the autumn, 1925, the writer engaged himself in an investigation on the same problem at King's College, London, as a direct continuation of experiments which Prof. O. W. Richardson had been carrying out, chiefly

* Lukirsky, 'Phil. Mag.,' vol. 47, p. 466 (1924), and 'Z. f. Physik,' vol. 22, p. 351 (1924); Becker, 'Phys. Rev.,' vol. 24, p. 478 (1924).