

279. The Polymerisation of Gaseous Formaldehyde.

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PRELIMINARY to a physicochemical study of certain of the simpler reactions of formaldehyde with other substances, experiments have been carried out on the polymerisation of the gas at room temperature. The phenomenon was observed at an early date by Hofmann (*Ber.*, 1868, **1**, 200; 1869, **2**, 152), who found that formaldehyde returned to the polymerised state only very slowly. Further observations of a similar nature were made by van 't Hoff ("Studies in Chemical Dynamics," 1896, 37), the pressure of the vapour decreasing from an initial pressure of 23.6 mm. to less than 3 mm. during 5 months. On the other hand, according to Perdrix (*Ann. Inst. Pasteur*, 1906, **20**, 881), there is a mobile equilibrium between polymeride and gas. This view, however, is contrary to that of other investigators, particularly Auerbach and his collaborators (*Arb. Kais. Gesundh.*, 1907, **22**, 584; 1907, **27**, 183; 1914, **47**, 116), who showed that the vapour of different polyoxymethylenes (characterised as α , β , γ , and δ) does not attain complete equilibrium even after several months, and that at temperatures up to 218° molecules as large as $(\text{CH}_2\text{O})_8$ can exist in the gas phase.

The possibility of the reverse process of polymerisation occurring through intermediate formation of gaseous polymerised molecules appears to have been eliminated by the experiments of Trautz and Ufer (*J. pr. Chem.*, 1926, **113**, 105), who studied the pressure change accompanying the polymerisation of pure monomeric formaldehyde gas in a glass vessel and showed that the change followed a unimolecular law. This result, together with the fact that the amount of polymeride formed on a portion of the vessel which had previously been heated to remove adsorbed water was considerably less than that formed on the unheated portion, suggested that the process is essentially heterogeneous. Trautz and Ufer assumed, therefore, that the velocity is determined by the rate of diffusion to the surface, in accordance with the Nernst theory of heterogeneous reaction velocity. Their results are now confirmed and extended, but a somewhat different interpretation is advanced.

EXPERIMENTAL.

Gaseous formaldehyde was prepared by vaporisation of liquid monomeric formaldehyde, which is extraordinarily unstable and in certain circumstances polymerises with almost explosive velocity. The change from monomeric liquid to solid polymeride is markedly exothermic and possess characteristics which suggest the operation of some kind of chain mechanism. However, the addition of quinol, which is known to inhibit the polymerisation of, *e.g.*, styrene (Taylor and Vernon, *J. Amer. Chem. Soc.*, 1931, **53**, 2527), increased the stability of liquid formaldehyde only to a slight extent.

Liquid formaldehyde was prepared essentially according to the method of Trautz and Ufer (*loc. cit.*). The apparatus finally adopted was made of Pyrex glass and consisted of a vessel containing paraformaldehyde which could be heated to 110° in an oil-bath, and two liquid-air traps of the type recommended by those authors. The connecting tubing was heated electrically to about 80° to prevent polymerisation on the walls, there being no stop-cocks between the three vessels. The paraformaldehyde had previously been dried by standing in a desiccator over sulphuric acid, and a stream of dry nitrogen was passed through the apparatus while the traps and connecting tubing were heated with a blowpipe flame. The system was evacuated and again heated before a first fraction of liquid formaldehyde was collected through a side tube. The main fraction was condensed in the first trap, and carefully distilled in the manner recommended by Trautz and Ufer (*loc. cit.*) into the second trap, which was then sealed off. Pressure change in the first polymerisation experiments was followed with the aid of a constant-volume mercury manometer, but later a quartz spiral manometer was fitted, of the type employed by Bodenstein and Dux (*Z. physikal. Chem.*, 1913, **85**, 305). This instrument, supplied by the Thermal Syndicate Ltd., is readily sensitive to 0.1 mm. of mercury. It was used as a null-point instrument, but it is sufficiently robust to withstand sudden changes of several hundred mm. between the internal pressure and the external balancing pressure. The manometer was connected to the apparatus by quartz-pyrex graded seals, and the reaction system contained only one stop-cock, for the introduction or removal of formaldehyde. The quartz spiral and

1194 *Spence: The Polymerisation of Gaseous Formaldehyde.*

connecting capillary tubing comprised the total dead space, which was therefore negligibly small in comparison with a reaction vessel of 50 c.c. capacity, and polymerisation in this region was prevented as before by heating the tubing and the upper part of the manometer to 80°. Previous to each experiment, the apparatus was evacuated and tested for leaks.

In order to ascertain whether the polymerisation of formaldehyde can be effected by ultra-violet light, as in the case of other aldehydes (cf. Leighton and Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165), and as seemed probable from previous work on the photo-oxidation of methyl iodide (Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689; *Trans. Faraday Soc.*, 1931, **27**, 468), some experiments were carried out in a quartz reaction vessel of 205 c.c. volume, having an internal surface of 196 cm.². The window was in the form of a small cell 1 cm. in thickness, which could be heated by a current of steam to prevent formation of polymeride on the inside. The body of the vessel was enclosed in a thermostat containing ice and water. Ultra-violet light, supplied by a straight-pattern mercury-vapour lamp, was switched on at intervals during the polymerisation of 385 mm. of formaldehyde, but no appreciable change in the rate could be observed. A water-cooled arc gave the same result. Further experiments carried out at lower pressures likewise gave no indication of photo-polymerisation; *e.g.*, initial pressure of formaldehyde, 25.3 mm. at 0°; pressure after 1160 mins. in ultra-violet light, 29.9 mm.; analysis showed that 5.9 mm. had polymerised, hence the 29.9 mm. left must have been composed of 8.9 mm. unchanged formaldehyde and 21 mm. of decomposition products, presumably hydrogen and carbon monoxide. These results do not altogether rule out the possibility of some photo-polymerisation occurring, since the rate is considerably greater than would be expected from the thermal data given below. The latter refer to surfaces of the polymeride, however, whereas the photo-experiments were carried out on clean quartz which gives a faster rate. It is evident, therefore, that there is practically no photo-polymerisation of formaldehyde at room temperatures, in agreement with the observations of Norrish and Kirkbride at 100° (*J.*, 1932, 1518).

When the surface of the vessel is clean and initially free from polymeride, the reaction proceeds rather rapidly for some minutes before attaining a reproducible rate. This is shown in the following tables. The unimolecular and bimolecular constants are calculated for each successive pair of figures from the equations $k_{\text{uni}} = (v \times 2.3026/\Delta ts) \log a/(a-x)$, $k_{\text{bi}} = (v/\Delta ts)x/a(a-x)$ where v is the volume of the reaction vessel, s its surface, and t the time (in mins.). In Expt. 1, Table I, the reaction clearly becomes unimolecular after an initial rapid period. However, when the pressure decreases below 200 mm., the unimolecular constant decreases and the bimolecular constant holds; below 75 mm. this in turn falls away. The existence of the first of these three phases is masked in most of the other experiments carried out under the same conditions, by the prolongation of the initial acceleration, but the approximate constancy of k_{bi} down to about 70 mm. is apparent in all cases.

When the walls of the vessel were already covered with polymeride from a previous experiment, no abnormally rapid rate was observed at the beginning, but rather a small induction period. Detailed study of this induction period was precluded owing to the varying times required for vaporisation of the formaldehyde, but it is hoped to obtain significant results with a modified apparatus. Measurements on polymeride surfaces are given in Table II: k_{uni} again decreases rapidly when p falls below *ca.* 250 mm., while k_{bi} holds from this region down to about 100 mm. Expts. 5, 6, and 7 were successive, the polymeride in Expt. 7 being the product of all three reactions. The data from these three experiments also show an appreciable decrease in the velocity of polymerisation with increasing thickness of deposit, amounting altogether to some 25%.

In an analogous manner to Auerbach's (*loc. cit.*) α , β , γ , and δ polyoxymethylenes, the polyoxymethylene obtained by direct polymerisation of the gas attains its vapour pressure equilibrium with extreme slowness. For instance, the apparatus was evacuated at the end of an experiment, and the polymeride kept at room temperature; after 52 hours a pressure of 1.8 mm. had developed, which increased to 2.5 mm. after 112 hours. This is in fairly good agreement with Auerbach's γ -polyoxymethylene, which attained 2.3 mm. after 72 hours and 2.5 mm. after 168 hours. Furthermore, when a system of polymeride and gas (120 mm.) was slowly heated during 3 hours, a position of equilibrium was reached at 89°. Below 89° the pressure decreased, but when this temperature was exceeded the pressure increased owing to depolymerisation. By analogy with Auerbach's polyoxymethylenes, it is presumed that the vapour consists almost entirely of polymerised molecules. Hence, the pressure increase above 89° is probably due to the liberation of large molecules by the solid and to the decomposition of these in the gas phase. However, the polymeride appears to undergo structural alteration

TABLE I.
Polymerisation of formaldehyde on Pyrex glass.

t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.	t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.	t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.
Expt. 1. $v = 50$ c.c.; $s = 88$ cm. ² ; temp. = 23°.											
0	565.8	—	—	210	380.3	10.6	2.7	1320	87.6	5.4	4.7
10	530.0	37.0	6.9	240	359.9	10.4	2.8	1500	77.1	4.0	4.9
50	491.6	10.7	2.1	310	315.2	10.8	3.2	1710	70.4	2.5	3.5
90	464.1	8.2	1.7	530	200.2	11.7	4.7	2730	47.7	2.2	3.8
152	422.0	8.7	2.0	630	174.0	8.0	4.3	3210	43.5	1.1	2.4
180	402.1	9.8	2.4	720	155.0	7.3	4.5				
Expt. 2. $v = 50$ c.c.; $s = 250$ cm. ² ; temp. = 23°.											
0	567.9	—	—	270	119.5	6.4	5.1	690	59.3	2.8	3.8
40	420.5	15.0	3.1	300	109.7	5.7	5.0	1410	33.8	1.6	3.5
100	272.2	14.5	4.3	330	100.6	5.8	5.5	1920	29.3	0.6	1.9
150	200.1	12.3	5.3	360	94.6	4.1	4.2	2130	26.3	1.0	3.7
240	131.5	9.3	5.8								
Expt. 3. $v = 50$ c.c.; $s = 500$ cm. ² ; temp. = 18.5°.											
0	218.5	—	—	80	110.7	5.2	4.5	740	46.7	0.8	1.4
20	162.0	15.0	8.0	100	101.6	4.3	4.1	920	40.7	0.8	1.8
40	137.8	8.1	5.4	140	87.0	3.9	4.1	1280	33.9	0.5	1.4
60	122.8	5.8	4.4	200	72.0	3.2	4.0	2180	31.9	0.1	0.2
Expt. 4. $v = 50$ c.c.; $s = 500$ cm. ² ; temp. = 17.3°.											
0	468.5	—	—	30	288.3	12.6	4.1	60	212.9	8.8	3.9
5	413.7	24.9	5.7	40	257.3	11.4	4.2	80	182.3	7.8	3.9
10	380.1	17.0	4.3	50	232.4	10.2	4.2	100	160.1	6.5	3.8
20	327.0	15.1	4.3								

TABLE II.
Polymerisation of formaldehyde on Pyrex glass covered with polymeride.

t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.	t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.	t .	p , mm.	$k_{uni} \times 10^4$.	$k_{bi} \times 10^6$.
Expt. 5. $v = 50$ c.c.; $s = 500$ cm. ² ; temp. = 19°.											
0	508.0	—	—	50	275.7	10.9	3.8	180	115.7	4.7	3.7
5	479.7	11.5	2.3	60	249.9	9.8	3.7	200	106.6	4.1	3.7
10	447.3	14.0	3.0	80	209.8	8.8	3.8	220	99.3	3.6	3.5
20	391.7	13.2	3.2	100	180.2	7.6	3.9	750	49.4	1.3	1.9
30	345.7	12.5	3.4	120	157.4	6.8	4.0	760	49.0	0.8	1.7
40	307.5	11.8	3.6	140	139.8	5.9	4.0				
Expt. 6. $v = 50$ c.c.; $s = 500$ cm. ² ; temp. = 22°.											
0	501.3	—	—	50	296.2	10.2	3.3	140	158.2	5.0	3.0
10	450.7	10.6	2.2	60	269.4	9.5	3.4	230	112.3	3.8	2.9
20	405.7	10.5	2.5	80	228.3	8.3	3.3	290	100.4	1.9	1.8
30	364.3	10.8	2.8	100	197.2	7.3	3.5	310	97.9	1.3	1.3
40	328.0	10.5	3.0	120	175.0	6.0	3.2				
Expt. 7. $v = 50$ c.c.; $s = 500$ cm. ² ; temp. = 21.5°.											
0	496.3	—	—	40	340.1	9.0	2.5	150	169.8	4.3	2.4
10	450.3	9.8	2.1	50	312.6	8.4	2.6	210	141.4	3.1	2.0
20	408.7	9.7	2.3	60	288.3	8.1	2.7	290	108.0	3.4	2.7
30	372.2	9.4	2.4	120	193.1	6.7	2.9	360	94.7	1.9	1.9

at higher temperatures. A specimen of polyoxymethylene prepared at 50° gave less than 0.5 mm. of vapour in 4 hours at this temperature. When the temperature was raised to 85° the vapour pressure increased as follows :

Depolymerisation of polyoxymethylene at 85°.

t , mins.	0	10	20	30	50	70	110	125
p , mm.	2.5	3.5	4.8	6.2	7.8	9.7	11.9	12.6

Polyoxymethylene prepared at 23° showed slightly higher vapour pressures at 65° and 80°, but after standing at the latter temperature for 17 hours its rate of vaporisation at 85° was considerably reduced :

t , mins.	0	10	20	30	300	600
p , mm.	0	0.3	0.7	1.3	6.2	8.4

The rate of depolymerisation did not show a sharp increase above 89° as did the freshly prepared material, and even at 100°, only 11.9 mm. of vapour were liberated in 12 hours. This slow change in the character of the polymeride with temperature makes measurements of the temperature coefficient of the reaction uncertain. Experiments at 0° and 50° suggest that this is quite small, but further work is necessary before it can be determined with accuracy.

An interesting feature of the reaction is the form in which the polymeride is deposited on the walls of the vessel. Portions of the glass which had recently been heated to softening point were usually comparatively free from it, and in most cases the deposit was of uneven thickness. Localised growths or nodules were also observed, roughly spherical in form and frequently as much as 2 mm. in diameter. In some cases a nucleus of dust or foreign material in the glass was noticed, the polymeride evidently having grown out from this point with greatly increased velocity.

DISCUSSION.

Trautz and Ufer (*loc. cit.*) give a scale diagram from which it has been possible to estimate the volume and internal surface of their reaction vessel. For purposes of comparison, the unimolecular and bimolecular constants have been calculated from their data in exactly the same way as in Tables I and II.

Polymerisation of formaldehyde in a glass vessel.

(Calculated from Trautz and Ufer's data.)

$v = 1120$ c.c.; $s = 700$ cm.²; temp. = 23.4°.

t , mins.	0	27	57	115	165	215
p , mm.	500.0	469.6	414.9	336.1	280.8	242.5
$k_{uni} \times 10^4$	—	37.1	66.2	58.1	57.5	46.9
$k_{bi} \times 10^6$	—	7.7	15.0	15.5	18.8	18.0

They did not carry out any measurements below 240 mm., but their results show that the reaction is approximately unimolecular, at least down to 280 mm. Below this pressure there is an appreciable decrease in the value of k_{uni} , whereas k_{bi} increases steadily up to 280 mm. and then remains stationary. This behaviour is entirely analogous to that cited above. The greater absolute values of the constant must be attributed to a more active glass surface, since the author has observed equally high velocities in soft-glass vessels and in Pyrex vessels which contained mercury or other foreign material or had not previously been heated in a vacuum.

Trautz and Ufer supposed that polymerisation took place on the surface, chiefly because the reaction appeared to be unimolecular. Although it is now evident that the process is not fundamentally unimolecular, the results indicate that it is entirely a surface phenomenon. Variations of extent of surface by a factor of six are accompanied by corresponding variations in the reaction velocity, while changes in the diameter of the vessel from about 14 mm. to 4 mm. do not appear to have any appreciable effect (see Tables I and II). Furthermore, the fact that reproducible results are only obtained after the formation of a deposit of polyoxymethylene, favours the view that the rate-determining process does not occur on the surface of the glass but on that of the polymeride itself. However, this does not rule out the possibility that the glass surface affects the rate indirectly by influencing the activity of the polyoxymethylene.

No definite conclusions can be drawn as to the significance of the invariable departure from unimolecularity, but a few important features are discussed. The deviation from unimolecular type occurs at various pressures in different vessels, but generally occurs between 200 mm. and 300 mm., the reaction becoming first bimolecular and then poly-molecular. Hence, it seems that the polymerisation is essentially a polymolecular reaction occurring either on the glass or on the polyoxymethylene surface. (i) In the former case, the gas would have to diffuse through a deposit of steadily increasing thickness, and if diffusion were rapid the course of the reaction would be independent of the thickness, whereas if it were slow, the velocity should be a function of the thickness; but if this view were correct, the reaction would be unimolecular at all pressures. Hence the slow decrease in velocity with increasing thickness of polymeride (Table II) must be attributed to some other cause, such as a reduction in the number of active centres. (ii) If it is assumed that

Notes on (a) a Case of Ketonic Activity of Acetic Anhydride, etc. 1197

after the initial fast reaction on the glass surface, the reaction takes place entirely on the polyoxymethylene surface, it must also be supposed that the active properties of the glass surface are transmitted through the long thread-like molecules of polyoxymethylene (cf. Mie and Hengstenberg, *Helv. Chim. Acta*, 1928, **11**, 1052; Staudinger, *Annalen*, 1929, **474**, 145), producing a polymeride surface of varying activity. The same effect could be achieved if the nature of the polyoxymethylene initially formed depended on the quality of the glass surface. In this way, the polymeride would be heterogeneous, each portion having a different heat of formation and a different energy of activation.

SUMMARY.

The polymerisation of gaseous formaldehyde in Pyrex-glass vessels at room temperatures is a surface reaction, unimolecular at high pressures and polymolecular below 200 mm.; it is not accelerated by ultra-violet light.

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