189. *The Influence of Hydrogen on Unimolecular Reactions involving Short Chains.*

By C. N. Hinshelwood and L. A. K. Staveley.

Hydrogen exerts a specific influence in preventing the falling off at low pressures of the velocity constants of unimolecular reactions (*Proc. Roy. Soc.*, 1927, *A*, **114**, 84; **115**, 215; **116**, 163). Three of the reactions thus affected have recently proved to involve short chains, namely, the decompositions of ethyl ether (Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1936, *A*, **154**, 335), propaldehyde (*idd.*, *Nature*, 1936, **137**, 29), and methyl ether (unpublished work). The reaction mechanism does not depend upon long chains as in the schemes devised by Rice and Herzfeld for the decomposition of organic compounds (*J. Amer. Chem. Soc.*, 1934, **56**, 284), but corresponds much more closely to the state of affairs shown by the work of Patat and Sachsse (*Z. physikal. Chem.*, 1935, *B*, **31**, 105), where a few exceptional molecules give chains, the average length being short. This length can be determined by the addition of small amounts of nitric oxide, which cuts off the chains, and reduces the reaction velocity to a well-defined limit, representing the rate of the primary process or processes. That the reactions taking place in the presence of the nitric oxide may be regarded as free from chains has been confirmed in this laboratory (see preceding paper, p. 812).

Experiments have been made to find out what the influence of hydrogen on the chain-free reactions will be. It proves to be the same as for the completely uninhibited reactions, at least with ethyl ether and propaldehyde. This shows that the hydrogen influences the primary process and not the propagation of such chains as may be present.

The measurements have been made exactly as described in the various papers dealing with the separate reactions. Pure hydrogen, carefully freed from oxygen by passage over a red-hot filament, was used.

Table I shows that the ratio of the low-pressure rate with and without hydrogen is almost independent of the presence of the nitric oxide, although the inhibition caused by the latter is considerable, being 2- or 3-fold.

Table II contains the results for ethyl ether, and Figs. 1 and 2, taken in comparison with those in the earlier publications, show that the characteristic phenomena appear unchanged by the suppression of the chains. The important facts are (1) that with increasing additions of hydrogen the rate approaches a limit which is the same as that reached at high partial pressures of the ether itself, (2) that hydrogen restores the fallen low-pressure rate, but does not influence the high-pressure rate. The simple interpretation of this is that the hydrogen maintains the Maxwell–Boltzmann distribution among the activated molecules, but exerts no other important influence. (To the arguments given in previous papers, that hydrogen does not act by reducing the ether, may be added the following: the only likely reduction products are ethane and ethyl alcohol, of which the latter is very much more stable than ether itself, so that if formed it would remain and be detected. This does not happen.)

The form of the curves in Fig. 1 calls for a further comment. Steacie and Solomon (*J. Chem. Physics*, 1934, **2**, 503) found the unimolecular constant for the ethyl ether decomposition to increase up to 200 atms. Thus, the curve for ether without hydrogen in Fig. 1 must retain a small negative slope even above several hundred mm., where it looks as though it would become horizontal. This is another example of the composite nature of many unimolecular reactions, in which the superposition of different activation mechanisms gives rise to a curve without discontinuities but of a definitely segmented form. The present results apply to the mode of unimolecular reaction predominating up to 1 atm. The common limits reached with high hydrogen and with high ether pressures are, of course, relative to the scale of pressures used. Several hundred atmospheres of ether will cause a different mechanism to predominate, and raise the rate beyond the limit we are dealing with now. So probably would the addition of several hundred atmospheres of hydrogen.

TABLE I.

Propaldehyde at 549°. *Initial pressure* 75 *mm.*

Press. of H_2, mm.		0	97	137	180	235	268	288	388	459	465	522
Ratio of rates of reaction with and without hydrogen	Without NO ...	1·00	1·10	—	1·26	—	1·38	—	1·48	—	1·47	—
	With 2 mm. NO	1·00	—	1·18	—	1·29	—	1·37	1·50	1·49	—	1·59

TABLE II.

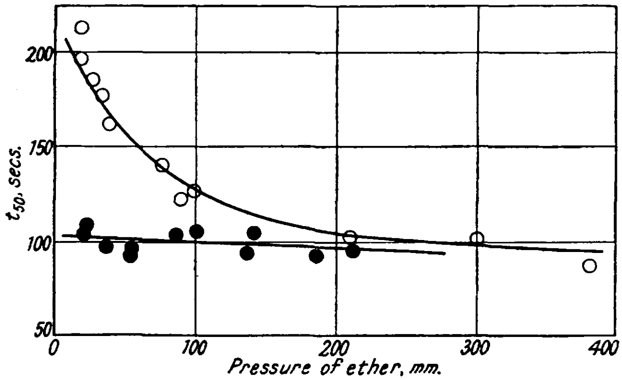
Ethyl ether and 5 *mm.* NO *at* 580°.

Ether, mm.	Hydrogen, mm.	t_{50}, sec.	Ether, mm.	Hydrogen, mm.	t_{50}, sec.	Ether, mm.	Hydrogen, mm.	t_{50}, sec.
378	0	87	211	403	96	35	0	180
300	0	102	186	392	93	42	86	147
210	0	103	136	396	95	35	174	130
142	0	105	100	388	107	35	214	111
99	0	128	88	394	105	37	359	102
90	0	123	56	421	97	33	546	93
77	0	142	54	432	94	(35	400	102)
42	0	163	23	409	110			
35	0	179	20·5	401	105			
29	0	186						
19·5	0	198						
19·5	0	215						

In Table II, t_{50} is the time required for the pressure to increase by 50% of the initial value. Correction of the results for change of end-point with pressure slightly exaggerates the curvature of the upper curve in Fig. 1 at low pressures, but does not change the general shape or affect the convergence of the two curves. The use of t_{50} instead of initial rates has been criticised. If, however, initial rates are plotted instead of t_{50}, essentially similar relationships are found. At the low pressures, initial rates cannot be measured as accurately as t_{50} values. The latter have accordingly been preferred.

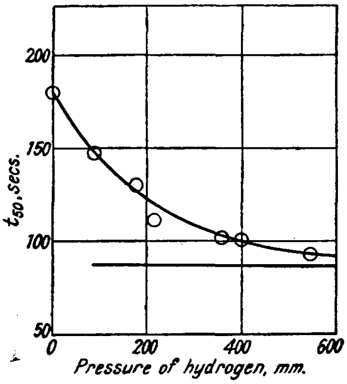
With methyl ether the average chain length proves to be longer (15—20 units), but nitric oxide is used up so quickly in chemical reactions that accurate measurements in presence of hydrogen are difficult. The behaviour of methyl ether with hydrogen is, however, so similar to that of ethyl ether that we may assume our conclusions about the latter to apply also to the former. In their work with para-hydrogen, Patat and Sachsse point out that the presence of hydrogen would not be expected to affect the concentration of free radicals, since for each radical removed a hydrogen atom would be formed which at once attacks an organic molecule with regeneration of a free radical. The present results support this idea.

FIG. 1.



Decomposition of ethyl ether at 580°. *Influence of hydrogen for different partial pressures of ether. Reaction inhibited by* 5 *mm. of nitric oxide. Open circles—no hydrogen present: shaded circles—*ca. 400 *mm. of hydrogen present. This figure should be compared with that for the uninhibited reaction (Fig.* 1 *of* Proc. Roy. Soc., 1927, *A*, **114**, 84).

FIG. 2.



Influence of various pressures of hydrogen on NO-*inhibited reaction of ethyl ether at* 580°. *Initial ether pressure* ca. 35 *mm. Horizontal line shows value for* 387 *mm. of ether without hydrogen.*

SUMMARY.

The influence of hydrogen on the unimolecular decompositions of propaldehyde and of ethyl ether has been investigated when all chains are suppressed by the addition of 2—5 mm. of nitric oxide. The hydrogen can increase the rate of reaction to the value characteristic of high partial pressures of the reactant, but no further. The effect is quantitatively similar to that found for the uninhibited reactions, showing that the hydrogen acts by maintaining the energy distribution among the molecules concerned in the primary process, and does not seriously influence such chains as may be present.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.
[*Received, April* 27*th*, 1936.]