402. *The Thermal Decomposition and Oxidation of Nickel Carbonyl.**

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MEASUREMENTS on the rate of thermal decomposition of nickel carbonyl vapour and on the rate of its formation from the metal and carbon monoxide have been made by Mittasch (*Z. physikal. Chem.*, 1902, **40**, 1) and by Dewar and Jones (*Proc. Roy. Soc.*, 1903, **71**, *A*, 427). They also studied the equilibria between these processes at different temperatures. No attempt has, however, been made to examine the data in the light of the modern theory of activation in gaseous systems. The decomposition might be expected to provide another example of a complex molecule decomposing in accordance with a quasi-unimolecular law. As might be anticipated, however, in view of the nature of the back reaction involving solid nickel, the measurements are very variable, and the simple process of decomposition is complicated, and masked by a variety of factors such as heterogeneous reactions.

The present work was carried out in conjunction with photochemical measurements reported in the preceding paper. Broadly, it can be concluded that the initial rate of decomposition of nickel carbonyl at about 100° is proportional to the first power of its concentration; in the later stages, the carbon monoxide formed has a retarding influence. The Arrhenius energy of activation of the homogeneous decomposition is probably somewhat greater than 12,000 cals. The facts can be well interpreted on the basis of the mechanism shown on p. 1824.

Peculiar phenomena of ignition are also recorded in the literature for mixtures of nickel carbonyl vapour and oxygen. Some experiments on this oxidation process are outlined below. The results can, in principle, be interpreted in terms of the theory of reaction chains; but as applied to other processes of this type where the phenomena are erratic, a study of the details would serve no purpose.

EXPERIMENTAL.

The glass reaction vessel was cylindrical, and was suspended in an oil-bath maintained at constant temperature. It was connected to a mercury manometer, and to vessels containing nickel carbonyl and oxygen, and the entire apparatus could be evacuated by means of a Hyvac

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* Since the completion of this work Dr. C. H. E. Bawn has kindly informed us that he also has obtained similar results in many respects.

oil pump. The capillaries leading to the reaction vessel were wound with electrically heated nichrome wire. The vessel containing nickel carbonyl had attached to it a drying tube containing anhydrous copper sulphate. In the experiments on the decomposition, nickel carbonyl vapour was introduced into the evacuated reaction vessel to the desired pressure, and the increase of pressure was followed. In the experiments on the oxidation, the carbonyl was introduced first, and oxygen immediately afterwards. At the temperatures involved, the decomposition of nickel carbonyl before addition of oxygen is slight. Vessels of different diameter were employed, and also a vessel packed with glass tubes giving a five-fold increase in surface area.

Fig. 1.

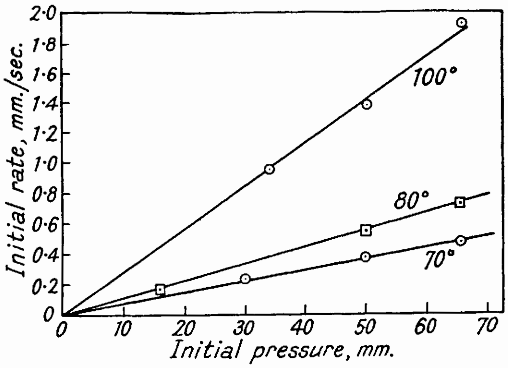
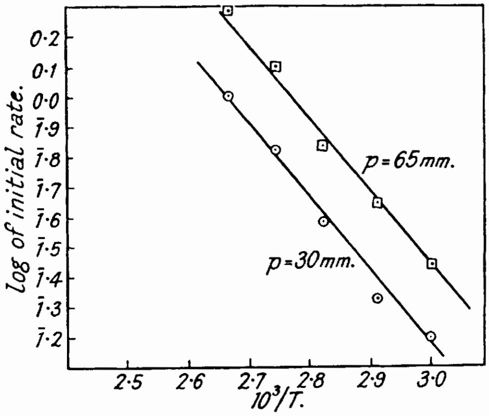


Fig. 2.



A. *The Thermal Decomposition.*—(i) *Effect of concentration on initial rate.* In general, the initial rate is roughly proportional to the initial concentration, but the proportionality is only true when the vessel is in a steady state. Table I shows typical results, and Fig. 1 the proportionality.

Table I.

(1) Temperature, 70°.

Initial press., 30 mm.				Initial press., 50 mm.				Initial press., 65 mm.			
Δp.	Time, secs.	Δp.	Time, secs.	Δp.	Time, secs.	Δp.	Time, secs.	Δp.	Time, secs.	Δp.	Time, secs.
3	13	15	80	4	11	20	75	5	11	16	44
7	30	20	125	9	24	25	112	10	26	20	68
11	54			14	44	30	170				
Initial rate 0·23 mm./sec.				Initial rate 0·37 mm./sec.				Initial rate 0·44 mm./sec.			

(2) Temperature 80°.

Initial press., 16 mm.				Initial press., 50 mm.				Initial press., 65 mm.			
5	30	15	120	5	9	20	58	5	7	30	68
10	72	20	180	10	20	25	78	10	15	35	88
				16	40			20	36		
Initial rate 0·17 mm./sec.				Initial rate 0·52 mm./sec.				Initial rate 0·66 mm./sec.			

(3) Temperature 100°.

Initial press., 34 mm.				Initial press., 50 mm.				Initial press., 65 mm.			
6	6	24	33	8	6	35	33	10	5	35	22
14	16	29	45	21	15	40	42	19	10	45	31
19	24	34	60	28	23	48	57	27	15	55	40
Initial rate 0·95 mm./sec.				Initial rate 1·4 mm./sec.				Initial rate 1·9 mm./sec.			

The rate falls off very rapidly during an individual run, and much more so than is in accordance with the first-order law. This may be due, in part, to the existence of the back reaction and the equilibrium, but it seems very likely that carbon monoxide inhibits the decomposition. This effect has been confirmed but not studied in detail, and it seems definite that the expression for the rate of reaction is of the form : rate $= k_1[\mathrm{Ni(CO)_4}]/\{k_2 + k_3[\mathrm{CO}]\}$.

(ii) *Effect of vessel dimensions.* The effect of packing the reaction vessel is to retard the decomposition slightly. This might be taken to imply the presence of reaction chains which are broken on the vessel walls, but since the reaction velocity changes very markedly as the reaction vessel becomes coated with products, this is uncertain.

(iii) *Effect of temperature.* It is possible to make an estimate of the temperature coefficient of the decomposition by studying the initial rate at different temperatures for a given initial concentration. Typical results are given in Table II. In these experiments the entire sets of data at different temperatures with a given initial concentration were carried out on the same day as rapidly as possible with the vessel in a steady condition. Slight discrepancies in absolute rate in the different series are probably negligible for the present purpose.

TABLE II.

		(1) Initial press. of $Ni(CO)_4$, 65 mm.					(2) Initial press. of $Ni(CO)_4$, 30 mm.				
						Initial rate.					Initial rate.
60°	Δp	3	6	10	15	0·27	2	3	5	10	0·15
	Time, secs.	11	23	41	73		14	20	40	100	
70°	Δp	5	10	15	20	0·45	3	7	11	15	0·23
	Time, secs.	11	26	46	70		13	30	54	80	
80°	Δp	5	10	20	30	0·66	5	10	15	20	0·40
	Time, secs.	8	15	36	69		12	28	44	68	
90°	Δp	10	20	30	40	1·25	5	10	15	20	0·66
	Time, secs.	7	16	28	42		7	16	28	43	
100°	Δp	10	20	27	35	1·9	5	14	21	28	1·0
	Time, secs.	5	10	15	22		5	15	25	40	

The results are plotted in Fig. 2, from which the energy of activation deduced is *ca.* 12,000 cals. The presence of some heterogeneous reaction may mean that this value is too low.

(iv) *Discussion.* If the mechanism of the thermal decomposition of nickel carbonyl is similar to that of its photochemical decomposition, the reaction scheme would be :

$$
\begin{aligned}
&(1)\ Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO\\
&(2)\ Ni(CO)_3 \longrightarrow Ni + 3CO\\
&(3)\ Ni(CO)_3 + CO \longrightarrow Ni(CO)_4
\end{aligned}
$$

Hence, for a stationary concentration of tricarbonyl :

$$
\begin{aligned}
k_1[Ni(CO)_4] &= k_2[Ni(CO)_3] + k_3[Ni(CO)_3][CO]\\
\textit{i.e.},\ [Ni(CO)_3] &= k_1[Ni(CO)_4]/\{k_2 + k_3[CO]\}\\
\therefore\ \text{Rate} &= k_1[Ni(CO)_4] - k_3[Ni(CO)_3][CO]\\
&= k_1[Ni(CO)_4] - k_1k_3[Ni(CO)_4][CO]/\{k_2 + k_3[CO]\}\\
&= k_1[Ni(CO)_4]\{1 - k_3[CO]/(k_2 + k_3[CO])\}\\
&= k_1[Ni(CO)_4]/\{1 + k_3[CO]/k_2\}
\end{aligned}
$$

This expression agrees with the results described above. The initial rate in the absence of carbon monoxide will be proportional to the initial concentration of nickel carbonyl, and carbon monoxide will exert an inhibiting effect. The results therefore appear to fall into line with the photochemical work and hypotheses outlined in the preceding paper.

If the theory of activation is correct, different reactions of the same type should proceed at equal absolute rates when the quantity E/T is the same. The value of $E = 12{,}000$, and the measured rates at *ca.* 100° are in fair agreement with this, though exact concordance cannot be expected in view of the back reaction and other complicating factors.

B. *The Oxidation.*—(i) *General.* Mixtures of nickel carbonyl and oxygen appear either to explode or not to react at all. Below certain pressures, no pressure change is observed over long periods and there is a transition from no reaction to explosion with a slight increase in pressure. This result suggests that a limit phenomenon is involved. The investigation consists essentially, therefore, in a study of the effect of different factors upon this lower critical pressure limit. It is difficult to give precise details owing to the lack of reproducibility, and absolute values of the pressure limit are without significance. The matter is also complicated by the presence of an induction period which is variable but appears to be longest in a clean reaction vessel. Again, the rate of introduction of the gases into the clean reaction vessel noticeably affects the subsequent reaction. As far as possible, a constant and slow rate of introduction was maintained in the following experiments. Results showing the general trend of the phenomena are given.

(ii) *Effect of temperature on the critical pressure limit.* In the following table the approximate lowest pressure of nickel carbonyl vapour which will inflame on introduction of excess oxygen at the slow rate mentioned above is given for different temperatures in a vessel 7 cm. in diameter.

Temp.	60°	50°	40°
Press., mm.	45	80	100

It is seen that the critical pressure limit decreases with increasing temperature; the alteration is probably more marked than with most other lower critical limits (cf. Hinshelwood, " Kinetics of Chemical Change," 3rd Edn., Chap. 7).

(iii) *Effect of vessel dimensions on the critical pressure limit.* Decrease of the vessel diameter increases the critical pressure required for explosion. The results are not suitable for testing the theory in detail. At 60°, in a vessel of 7 cm. diameter the limit is 45 mm., whereas in one of 4 cm. diameter it is greater than 140 mm. The influence of inert gases upon the lower limit was not studied.

(iv) *Discussion.* It is clear that reaction chains are involved in the oxidation of nickel carbonyl. The phenomenon of a lower critical limit of explosion and the effect of different factors upon it suggest the occurrence of branching chains. A hypothetical scheme of elementary processes cannot be constructed at present, and it is uncertain to what extent the nuclei of nickel or of nickel oxide are important in the inflammation. The occurrence of an induction period and the erratic nature of the process, together with the effect of vessel dimensions, suggest that the reaction chains are broken on the wall.

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