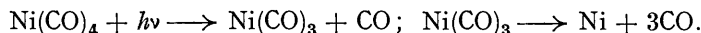


401. *The Spectra and Photochemical Decomposition of Metallic Carbonyls.*
Part II. Photochemical Data.

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SPECTRAL measurements already reported (this vol., p. 524) led to the suggestion of the following mechanism for the photochemical decomposition of nickel carbonyl:



The photochemical measurements to be described below substantiate this mechanism with the addition of a concurrent thermal recombination process: $\text{Ni(CO)}_3 + \text{CO} \longrightarrow \text{Ni(CO)}_4$. In the succeeding paper it will be shown that measurements on the thermal decomposition of nickel carbonyl indicate a precisely analogous sequence of processes for the "dark" reaction, and suggestions are made to explain such results as the discrepancy between thermal energy of activation and minimum effective photochemical quantum.

EXPERIMENTAL.

The nickel carbonyl was supplied as pure by The Mond Nickel Co., Ltd. It was stored in sealed glass tubes and filtered through glass wool before use. The source of light was a Hanovia Alpine Sun quartz mercury lamp taking 3.5 amps. at *ca.* 80 volts. The filters were as follows:

(i) 4360 Å. Copper sulphate solution [20 g. CuSO_4 in 300 c.c. of ammonia (*d* 0.880) made up to 1 litre], followed by potassium chromate solution [4 c.c. stock solution (3 g./l.) in 100 c.c. water, using 2 cm. layer] with plate glass to remove any ultra-violet light not cut out by the above.

(ii) 4360—4060 Å. Distilled water, followed by 2 cm. layer of a 1% solution of quinine hydrochloride + cuprammonium solution.

(iii) 3666 Å. Distilled water followed by 2 mm. of Chance's black glass.

(iv) 3010—3135 Å. Nickel chloride solution (70 g. nickel chloride free from cobalt and iron with 30 c.c. conc. hydrochloric acid made up to 1 litre).

(v) 2700—2400 Å. Nickel chloride solution, one-fifth of above concentration, followed by chlorine gas.

The solutions were contained in either one or two transparent spherical quartz flasks so as to produce a concentrated beam of almost parallel light as described by Bowen (J., 1932, 2236). Narrow layers of the solutions were contained in plane parallel-walled cells. The lamp was standardised at intervals by the method of Leighton and Forbes (*J. Amer. Chem. Soc.*, 1930, 52, 3139), the quantum efficiency of the decomposition of the uranyl oxalate solution being determined for different wave-lengths under standard conditions. The solution used here was $N/10$ with respect to oxalic acid and contained 8.6 g. of uranyl sulphate per litre. A plane-walled quartz cell 2.5 cm. thick was filled with a measured quantity of uranyl solution, emptied, rinsed, and the solution titrated against standard potassium permanganate. The cell was then filled with the same quantity of uranyl solution, which was exposed for a measured period, and again titrated. It was thus possible to determine the number of quanta emitted by the lamp per unit time. During the exposure the solution was shaken to prevent adhesion of bubbles to the vessel face.

Pure carbon tetrachloride and *cyclohexane* were redistilled from phosphoric oxide, and the hexane was supplied as spectroscopically pure by B.D.H. Ltd. Preliminary experiments to determine the fraction of light absorbed by the solvents showed that the last was completely transparent to all the frequencies used; the first was transparent to the 3666 line and to the 3000 group but absorbed much of the higher frequencies, and the second could similarly not be used for the region 2400—2790 Å.

Approximately standard solutions of nickel carbonyl were prepared by transferring the contents of a sealed tube of the substance (30 g.) into the solvent and making it up to 1 litre. Such a solution decomposed slowly, but before use it was filtered through glass wool. The progress of the reaction in solution was followed by measurement of the volume of carbon monoxide evolved. The quartz reaction cell was connected by flexible pressure tubing to a graduated gas burette filled with mercury, and the volume of gas liberated was measured at atmospheric pressure. The reaction cell was attached to a vigorous shaking apparatus, the amplitude of vibration being small. Light not absorbed by the nickel carbonyl solution was measured by means of a uranyl solution placed behind the reaction cell. Except with the very dilute solution, absorption was complete. In carbon tetrachloride, but not in the other solvents, a film of nickel gradually coated the front face of the reaction cell. An estimate of the light cut out by this was made separately at the conclusion of a run. The necessary corrections could then be made; for the purposes of initial rates this correction is unimportant, and in any case the linearity of the graph of c.c. evolved against time showed that light losses were not considerable.

An attempt was made to examine the photochemical decomposition in the gas phase manometrically. The quartz reaction cell was connected to a mercury manometer, and the entire apparatus could be evacuated by a Hyvac oil pump before introduction of the desired pressure of nickel carbonyl vapour.

Results.

A. *Reaction in the Gas Phase.*—The reaction was studied at room temperature. Nickel carbonyl vapour at various pressures was illuminated for long periods with light of two different wave-lengths (3666 and 3010—3135 Å.). Although a considerable fraction of the incident light energy was absorbed, it was surprising that a change of pressure was never recorded, and deposits of nickel were never obtained.

B. *Reaction in Solution.*—(i) *Calibration of light source.* The mercury lamp was first standardised for different wave-lengths. The 2.5 cm. cell containing uranyl oxalate solution absorbed all frequencies completely with the exception of the 3666 line and the group 4360—4060 Å. In Table I, the columns headed a, b, c, d, e, f, g, h, k, are :

- a. Wave-length of incident light in Ångström units.
- b. Exposure, in hours.
- c. $N/10$ -Potassium permanganate titre difference (c.c.) with no reaction cell between lamp and solution.
- d. Titre difference with empty reaction cell between lamp and solution.
- e. Titre difference with cell containing carbon tetrachloride interposed.
- f. " " " " hexane "
- g. " " " " *cyclohexane* "

- h. Fraction of light absorbed by 2.5 cm. cell (separately determined).
- k. Total efficiency of lamp in c.c. *N/10*-potassium permanganate per one hour's exposure allowing for losses.

TABLE I.

a.	b.	c.	d.	e.	f.	g.	h.	k.
4360—4060	2	8.4	8.0	8.0			0.78	5.1
3666	2	8.1	7.6	7.5	7.6	7.4	0.84	4.5
3010—3135	2	8.8	8.3	8.2	8.4		1.0	4.2
2700—2400	4	5.4	4.8		4.5		1.0	1.10

The efficiency of the lamp was checked several times during the course of the experiments but did not change appreciably.

According to Leighton and Forbes (*loc. cit.*), the quantum efficiency of the decomposition of the uranyl oxalate solution at different wave-lengths is as follows :

Å.....	4360—4060	3666	3135—3010	2700—2400
γ	0.5	0.45	0.54	0.58

The numbers of quanta effectively available from the lamp per second at the different wave-lengths are then :

Å.....	4360—4060	3666	3135—3010	2700—2400
$\nu \times 10^{-16}$	8.4	8.4	6.7	1.6

(ii) *Effect of shaking.* It was found that the rate of evolution of gas increased with more rapid movement of the cell up to a certain maximum. The influence of shaking is illustrated in Fig. 1. Extrapolation of the curve backwards indicates that shaking does not affect the actual rate of decomposition, but only the rate of evolution of bubbles of gas. In all the experiments given below, the "saturation" shaking rate was used.

FIG. 1.

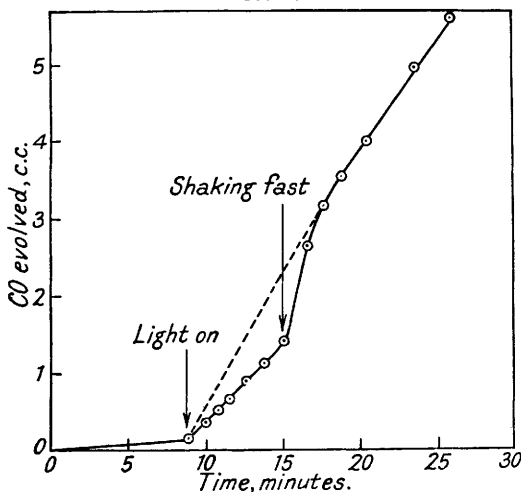
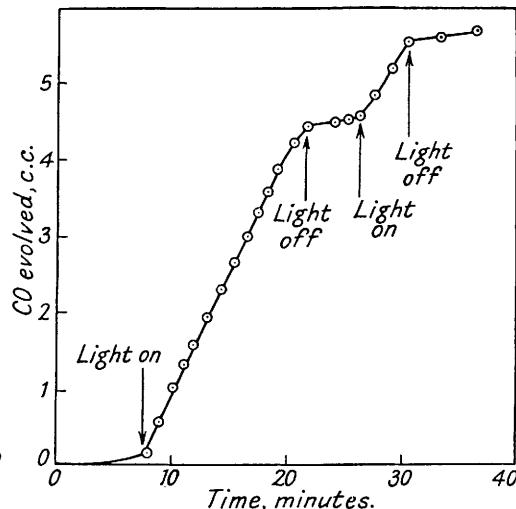


FIG. 2.



(iii) *Carbon tetrachloride solution.* As is to be expected from the nature of the absorption spectrum, light of wave-length greater than 4000 Å. does not cause decomposition. Two experiments which show this are summarised in Table II, the volume of carbon monoxide being reduced to *N.T.P.*

TABLE II.

(a) 4360 Å. Concn. ca. 30 g./litre. Temp. 20° Bar. 762 mm.		(b) 4360—4060 Å. Concn. ca. 30 g./litre. Temp. 20°. Bar. 762 mm.	
Time, mins.	CO, c.c.	Time, mins.	CO, c.c.
0	0	0	0
4	0.19	light on → 8	0.33
light on → 8	0.33	11	0.50
11	0.43	15	0.69
14	0.56	light on → 17	0.79
light off → 16	0.67	19	0.88
18	0.77		

The reproducibility of the experiments is shown by three runs with light of wave-length 3666 Å. and initial concentration *ca.* 30 g./litre, summarised in Table III. The first of these is also shown graphically in Fig. 2.

TABLE III.

(a)	Time, mins.	CO, c.c.	Time, mins.	CO, c.c.	(b)	Time, mins.	CO, c.c.	(c)	Time, mins.	CO, c.c.
	0	0	20	4.24		0	0		0	0
light on →	8	0.19	light off →	21	4.48	5	0.13	light on →	8	0.21
	9	0.53		23	4.52	light on →	8	9	0.55	
	10	1.01		24	4.54		9	10	1.07	
	11	1.52	light on →	25	4.55		10	11	1.57	
	12	1.92		26	4.74		11	12	1.93	
	13	2.27		27	4.93		12	13	2.33	
	14	2.60		29	5.35		13	14	2.69	
	15	2.94	light off →	30	5.54		14	16	3.31	
	16	3.21		32	5.58		15	19	4.12	
	17	3.46		36	5.60		16	light off →	23	4.87
	18	3.72						25	4.97	

The above runs have an initial rate of approximately 0.4 c.c. of carbon monoxide/min.

The initial rate of a run with light of wave-length 3010—3135 Å. was 0.45 c.c./min. The initial concentration was, as before, *ca.* 30 g./l.

(iv) *Hexane solution.* With an initial concentration in each case of *ca.* 30 g./l. and light of wave-lengths 3666, 3010—3135, and 2700—2400 Å., the initial rates were approximately 0.04, 0.042, and 0.02 c.c./min.

(v) *cycloHexane solution.* With the same initial concentration and 3666 Å., the initial rate was approximately 0.055 c.c./min.

(vi) *Effect of initial concentration on the rate of decomposition.* With carbon tetrachloride as solvent and light of wave-length 3666 Å., three different initial concentrations were used (see Table IV). The initial rate was almost the same in the different experiments, *viz.*, 0.40, 0.36, and 0.31 c.c./min. With the lowest concentration, in which 12% of the incident light was not absorbed, the initial rate was correspondingly low.

TABLE IV.

(a) Concn. <i>ca.</i> 30 g./litre.	(b) Concn. <i>ca.</i> 15 g./litre.	(c) Concn. <i>ca.</i> 7.5 g./litre.						
Time, mins.	CO, c.c.	Time, mins.	CO, c.c.	Time, mins.	CO, c.c.			
	0	0	0	0	0			
light on →	8	0.21	light on →	8	0.28	light on →	8	0.03
	9	0.55		9	0.58		9	0.24
	10	1.07		10	1.0		10	0.62
	11	1.57		11	1.46		11	0.92
	12	1.92		12½	2.0		12	1.29
	13	2.33		14	2.39		13	1.61
	14	2.69		16	3.19		14	1.97
	16	3.31		17	3.57		15	2.31
	19	4.12		18	4.0		17	2.66
				20	4.41		19	3.11
				21	4.71		21	3.56
			light off →	22	5.0		23	4.08
				26	5.08		25	4.51

DISCUSSION.

On the basis of the mechanism given on p. 1817, the quantum efficiency should be 1, with the formation of 4 mols. of carbon monoxide per mol. of carbonyl. In carbon tetrachloride the quantum efficiency with respect to carbon monoxide has the following values, and is independent of initial concentration :

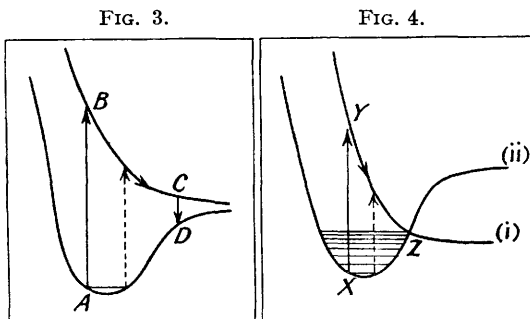
Wave-length, Å.	4360—4060	4060	3666	3010—3135
γ (mols. of CO)	0	0	2.2	2.8

It is seen that there is a threshold which corresponds in position to the limit of continuous absorption in the spectrum. Beyond this threshold towards the ultra-violet the quantum efficiency increases somewhat.

The low value of the quantum efficiency here as compared with that expected is noticeable, but in the other solvents used a strikingly lower value is found. The results are as follows :

Wave-length, Å.	Hexane.					cyclo-Hexane.
	4360—4060	4060	3666	3010—3135	2700—2400	3666
γ (mols. of CO)	0	0	0.22	0.28	0.5	0.3

Two matters, therefore, require explanation : the low quantum yield, and the marked variation of quantum efficiency in the different solvents. An understanding of the quantum efficiency of less than 4 is suggested by the results on the gaseous decomposition. In view of the nature of the spectrum, it is certain that when the light is absorbed a dissociation must occur. No nickel is, however, deposited. In the gas phase therefore a rapid thermal back reaction must occur. It seems very unlikely that, if the primary process were $\text{Ni}(\text{CO})_4 + h\nu \longrightarrow \text{Ni} + 4\text{CO}$, a complete recombination and removal of nickel would occur at the temperature employed. On the other hand, if the primary process is $\text{Ni}(\text{CO})_4 + h\nu \longrightarrow \text{Ni}(\text{CO})_3 + \text{CO}$, it is not unlikely that the products might recombine thermally. There are good reasons for believing that this occurs in the thermal decomposition of nickel carbonyl (see following paper). It is also important to remember that with the reaction in solution the carbon monoxide is continuously removed, and back reactions may thereby be prevented, the decomposition proceeding more rapidly. Another mechanism for the recombination which has recently been suggested by Franck and Rabinowitsch (*Trans. Faraday Soc.*, 1934, 30, 120) and might be applicable to the present case is the following. The potential-energy curves of the lower and upper states might be relatively situated as in Fig. 3. Absorption of light from *A* to *B* will be followed by a dissociation along the curve *BC*. When the two potential-energy curves are near together, a collision may cause dissipation of energy and a transition between the two curves, *i.e.*, from *C* to *D*. The molecule will then return to a stable state.



This hypothesis might be presented in a slightly different manner which has other advantages. If the two potential-energy curves are relatively situated as in Fig. 4, absorption may occur from *X* to *Y*, followed by dissociation along *YZ*, and at *Z* there will be a definite possibility of the converse of predissociation, leading to recombination. If with nickel carbonyl the curves are really of this type, it becomes clear why the thermal decomposition can occur with a much lower energy of activation than is required photochemically. The vibration levels from *X* to *Z* will be excited thermally, giving a possibility of switch at *Z*. The infra-red spectrum of nickel carbonyl might afford valuable information in this connexion. The molecule has no dipole moment and may not absorb in this region, though nothing definite can be said about this. The mechanism outlined may also explain the increase in quantum efficiency with decrease in wave-length ; for the higher the frequency absorbed the more rapidly will the molecule in the dissociating state pass towards the switch position *Z*, and in consequence the chance of a transition back to the stable state will be diminished.

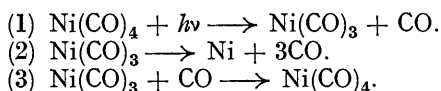
One detail of the mechanism suggested is, however, not yet clear. If the products of dissociation from the state (i) in Fig. 4 are $\text{Ni}(\text{CO})_3 + \text{CO}$, and those from state (ii) are $\text{Ni} + 4\text{CO}$, the energy difference between the horizontal parts of (i) and (ii) should be the energy of dissociation of the tricarbonyl. The latter has usually been taken as small, but now would have to be appreciable. It is possible that the tricarbonyl may be decomposed by collisions. On the other hand, it may be unjustifiable to discuss such hypotheses in detail until the potential-energy curves are more accurately defined.

The variation of quantum efficiency in different solvents may be due to one of two

causes : (i) the reaction is abnormally fast in carbon tetrachloride as the result of some ability of the carbon tetrachloride to catalyse the decomposition, whether it be by a physical process or by some chemical reaction involving the chlorine; (ii) the solvents hexane and *cyclohexane* are peculiarly able to bring about a recombination.

SUMMARY.

The rate of photochemical decomposition of nickel carbonyl has been measured in light of different wave-lengths, in the gas phase and in the solvents carbon tetrachloride, hexane, and *cyclohexane*. In the gas phase a thermal recombination balances the photochemical decomposition, so no change is observed. In the solvents, the quantum efficiency increases somewhat with frequency from a threshold value corresponding to the limit of continuous absorption in the spectrum. Taken as a whole the facts comply with the mechanism :



The several processes are discussed.

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