116. *The Spectra and Photochemical Decomposition of Metallic Carbonyls. Part I. Spectral Data.*

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THE study of the spectra of polyatomic molecules is interesting for two reasons. First, it helps in determining the energy levels and potential-energy curves of the molecules, and these matters are ultimately important in constructing theories of valency and molecule formation. Secondly, it is important to correlate the absorption spectra of molecules with the mechanism of their photochemical decomposition. This has already been emphasised by many workers (Mecke, *Trans. Faraday Soc.*, 1931, **27**, 359; 1934, **30**, 200; *Z. physikal. Chem.*, 1930, *B*, **7**, 108; Norrish *et al.*, J., 1932, 1518; 1933, 119, 1533; *Trans. Faraday Soc.*, 1931, **27**, 404; 1934, **30**, 103; Noyes, *Rev. Mod. Physics*, 1933, **5**, 280; Taylor, *J. Physical Chem.*, 1930, **34**, 2409). This correlation is most important in the case of many simple polyatomic molecules, the spectra of which have scarcely been examined. Broadly speaking, the absorption spectrum of a molecule in the gas phase belongs to one of three types: (i) there may be one or more systems of discrete bands showing rotational fine structure; (ii) there may be both discrete and diffuse regions in the spectrum, and these may overlap; (iii) the absorption may be continuous. The establishment of the connexion between diffuseness of one kind or another and some dissociation process occurring in the molecule, and the subsequent interpretation of such phenomena as predissociation in terms of molecular potential-energy curves, have been especially important. There are, however, many complications; *e.g.*, the rule, at first thought to be generally applicable, that a predissociation limit is to be identified with a photochemical " threshold " at which the quantum efficiency attains a saturation maximum value, does not always comply with the facts. Again, it is not at all certain that many diffuse banded spectra already attributed to predissociation processes are really to be explained in this way; for in the case of heavy-atom molecules the separation of rotation lines is often less than the breadth of the lines themselves, even under large dispersion (cf. Henri, *Proc. Roy. Soc.*, 1930, **128**, *A*, 178).

In particular, Norrish, studying carbonyl compounds, *e.g.*, aldehydes, ketones, and keten, found that in all cases absorption begins in approximately the same region, *viz.*, 2500—3400 Å., corresponding to absorption by the chromophoric carbonyl group; the mechanism by which aldehydes and ketones subsequently decompose is somewhat indefinite. He draws attention to the fact that the light energy enters the molecule at one point and is then transferred to another where it leads to chemical change. In the case of keten the primary change can be represented by the equation $h\nu + \mathrm{CH_2{:}CO} \longrightarrow \mathrm{CH_2} + \mathrm{CO}$; here again the energy absorbed by the carbonyl radical is transferred to the olefinic bond, which it breaks.

A subsidiary complication enters into the above processes due to the energy of reorganisation involved in the conversion of the free carbonyl radical into normal carbon monoxide $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$. A similar conversion of bivalent into quadrivalent carbon probably occurs with the methylene radical, $>\mathrm{CH_2}$ giving $\mathrm{CH_2}$.

The present investigation concerns the absorption spectra and mechanism of photochemical decomposition of nickel tetracarbonyl and of iron pentacarbonyl. There is a simplification here in the sense that the carbonyl groups probably already exist in the $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$ form, the molecular structure of nickel carbonyl being $\mathrm{Ni(\leftarrow C\overset{\leftarrow}{=}O)_4}$ (Sidgwick, " The Covalent Link," p. 189). Energy of reorganisation should not therefore be involved here.

Although kinetic measurements have been made on the rate of thermal decomposition

Fig. 1*b*.

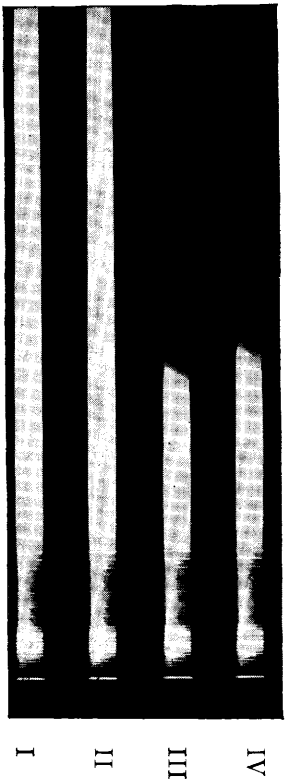
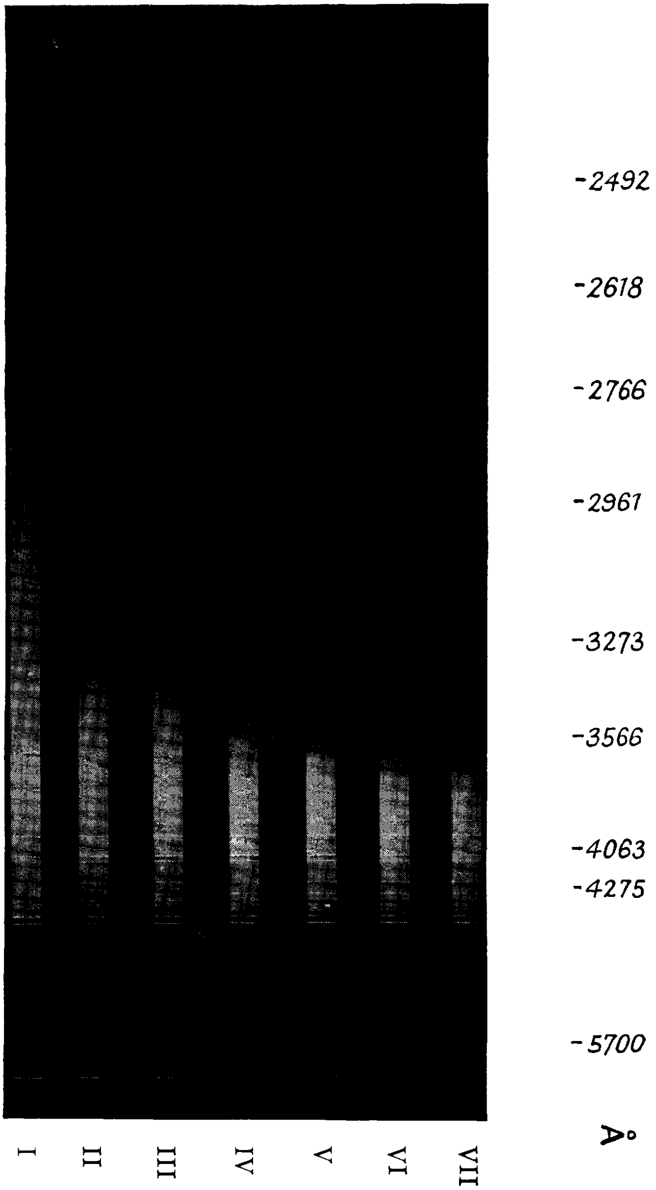


Fig. 1*a*.



[*To face p.* 525.

of nickel carbonyl and on the rate of its formation from the metal and carbon monoxide (Dewar and Jones, *Proc. Roy. Soc.*, 1903, **71**, *A*, 427; Mittasch, *Z. physikal. Chem.*, 1902, **40**, 1), no observations have been recorded on either its spectrum or its photochemical decomposition. The spectrum of iron carbonyl was measured by Eyber (*ibid.*, 1929, **144**, *A*, 1), and it appears that absorption by the vapour begins at about 4100 Å.; the absorption at shorter wave-lengths is continuous. With solutions in hexane, absorption begins at a rather longer wave-length, *ca.* 5500 Å., and, as before, is continuous. The difference between the threshold wave-lengths for absorption with the vapour and with the solution was thought to arise because of the presence of the orange diferrononacarbonyl, $Fe_2(CO)_9$, in the latter and its absence from the former.

Dewar and Jones (*Proc. Roy. Soc.*, 1905, **76**, *A*, 558; 1907, **79**, *A*, 66) showed that in visible light the pentacarbonyl is slowly converted into the nonacarbonyl with liberation of carbon monoxide. Eyber determined the quantum efficiency of this process, using light of wave-length 4000 Å., and found a value of *ca.* 1·1 mols. of carbon monoxide per quantum absorbed. Warburg and Negelein (*Biochem. Z.*, 1929, **204**, 4) have also found that 2 mols. of the pentacarbonyl decompose per quantum absorbed. Eyber accordingly suggested the following mechanism for the change:

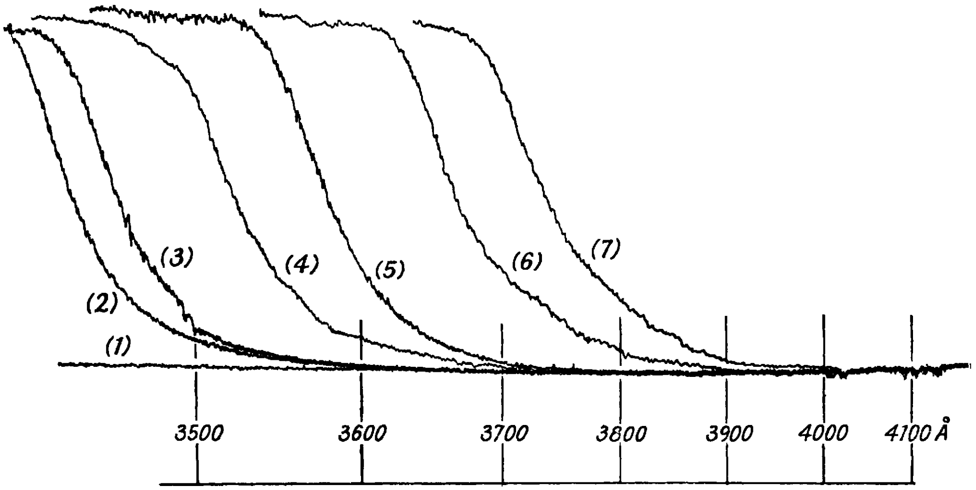
$$Fe(CO)_5 + h\nu \longrightarrow Fe(CO)_5^*, \quad Fe(CO)_5^* + Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO.$$

The present measurements indicate that in the gas phase, in hexane, or in carbon tetrachloride, nickel carbonyl absorbs continuously below about 3950 Å.; with iron pentacarbonyl our results agree essentially with those of Eyber, but we interpret them somewhat differently.

EXPERIMENTAL.

The nickel carbonyl was supplied as pure by The Mond Nickel Co., Ltd. The iron carbonyl was purified by distillation and was yellowish. The spectrograph used was a Hilger quartz instrument E 315, and the region studied 7000—2000 Å. The absorption cells were glass tubes with plane polished quartz ends cemented on, and varied in length from 2 to 50 cm. A series of photographs was taken, the length of absorbing column, pressure of vapour, and period of exposure being successively altered. Pressure was measured by a mercury manometer. The continuous sources used were a hydrogen discharge tube consuming *ca.* 3 kw., a tungsten Pointolite lamp, and the positive pole of a carbon arc.

FIG. 2.



Results.—Nickel carbonyl. (i) Gas Phase. Fig. 1*a* exhibits a typical series of photographs taken through the gas phase under the following conditions:

Absorbing column, 45·2 cm. Exposure, 1 min. Temp. 18°.

	I.	II.	III.	IV.	V.	VI.	VII.
Press. of $Ni(CO)_4$, mm.	1	2	8	36	85	155	200

It is seen that absorption is continuous beyond a certain wave-length under all the conditions used. The absence of bands just preceding the limit of complete absorption is most clearly brought out by the smooth nature of the spectrophotometer curves taken from different plates. Fig. 2 is a copy of seven such traces measured from spectra taken under the following conditions :

Absorbing column, 45·2 cm. Exposure, 5 min. Temp. 18°.

	I.	II.	III.	IV.	V.	VI.	VII.
Press. of $Ni(CO)_4$, mm..........	0	2	6	10	49	99	202

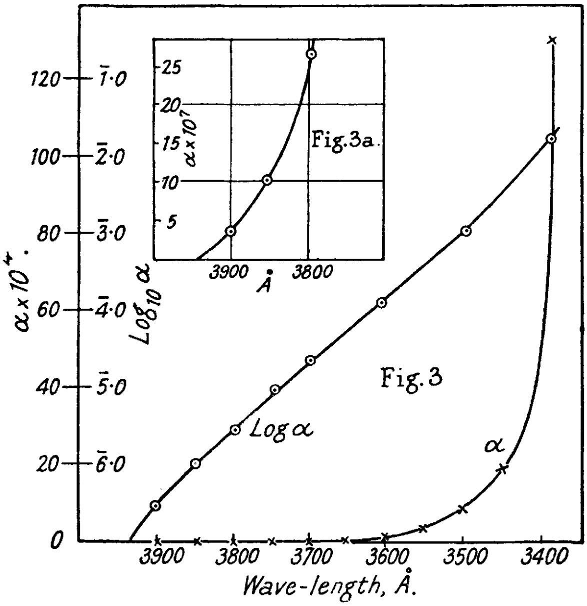
It is clear that a continuous transition occurs from the region of no absorption to that where absorption is complete. Values of the extinction coefficient $\alpha = (\log_{10}I_0/I)/pl$ (p in mm. Hg, l in cm.) have been determined at different wave-lengths from several such curves. A high degree of precision has not been attempted in determining these values, although the deviations are not, in view of the sensitivity of the quantity, serious. The values make it possible to extrapolate to the wave-length at which absorption begins. Table I gives the values of α determined from the second set of measurements above.

TABLE I.

λ, Å.	(1).	(2).	(3).	(4).	(5).	(6).	Mean.
3950	0	0	0	0	0	0	0
3900	0	0	0	0	$1·3 \times 10^{-6}$	$0·6 \times 10^{-6}$	3×10^{-7}
3850	0	0	0	0	$3·9 \times 10^{-6}$	$1·9 \times 10^{-6}$	$9·0 \times 10^{-7}$
3800	0	0	0	0	$7·2 \times 10^{-6}$	$8·8 \times 10^{-6}$	3×10^{-6}
3750	0	0	$0·6 \times 10^{-5}$	$0·3 \times 10^{-5}$	$1·8 \times 10^{-5}$	$4·3 \times 10^{-5}$	$1·0 \times 10^{-5}$
3700	0	0	$0·6 \times 10^{-4}$	$0·1 \times 10^{-4}$	$0·5 \times 10^{-4}$	$1·3 \times 10^{-4}$	4×10^{-5}
3650	0	0	$0·8 \times 10^{-4}$	$0·2 \times 10^{-4}$	$2·6 \times 10^{-4}$		7×10^{-5}
3600	$0·6 \times 10^{-4}$	$0·2 \times 10^{-4}$	$1·0 \times 10^{-4}$	$0·6 \times 10^{-4}$	$3·8 \times 10^{-4}$		1×10^{-4}
3550	$2·6 \times 10^{-4}$	$1·5 \times 10^{-4}$	$3·2 \times 10^{-4}$	$8·5 \times 10^{-4}$			4×10^{-4}
3500	$3·7 \times 10^{-4}$	$2·7 \times 10^{-4}$	$23·0 \times 10^{-4}$				1×10^{-3}
3450	$2·0 \times 10^{-3}$	$1·8 \times 10^{-3}$					$2·0 \times 10^{-3}$
3400	$1·3 \times 10^{-2}$						$1·3 \times 10^{-2}$

In Fig. 3 the values of the extinction coefficient α and also of log α are plotted against λ. It is seen that the threshold for absorption lies at *ca.* 3950 Å., *i.e.*, 25320 cm.$^{-1}$ or 3·1 volts or 72 kg.-cals. per g.-mol.

FIG. 3.



(ii) Solution. The relationships with solutions in spectroscopically pure hexane (as supplied by B. D. H. Ltd.) or carbon tetrachloride are entirely similar to the above. Absorption begins at the same limit, *ca.* 3950 Å. The data are not given in detail. Fig. 1*b* shows four photographs : (1) the hydrogen continuum, (2) with 2·5-cm. layer of pure hexane, (3) with a solution of the tetracarbonyl in hexane 2·5 cm. thick, (4) with a more dilute solution of the same thickness.

Iron pentacarbonyl. The pressure of gaseous iron carbonyl used varied from 1 to 15 mm. The results were exactly similar to those for nickel carbonyl. The continuous absorption began at *ca.* 4100 Å., corresponding to 24390 cm.$^{-1}$ or 3·0 volts or 69 kg.-cals. per g.-mol.

The solution in hexane was orange-yellow, and continuous absorption began at *ca.* 5500 Å. It is very probable that the nonacarbonyl is present as impurity in the pentacarbonyl and causes a displacement of the limit to this extent. For the present purpose this matter is not relevant and was not examined further.

DISCUSSION.

In view of the continuous absorption there can be no doubt that the primary act in the absorption of light by nickel carbonyl involves a dissociation process, *viz.*, the formation of nickel and carbon monoxide. This dissociation is, however, not the climax of the absorption of a series of vibrational quanta, *i.e.*, following a " convergence " limit; nor is it connected with a predissociation process of any kind, for no diffuse bands are observed. The upper molecular state must be unstable, having either a pure repulsion potential-energy curve or one showing a shallow minimum at large internuclear separation. In the latter case increase of temperature might bring about excitation of bands by absorption from higher vibrational levels in the ground state. The ease with which nickel carbonyl decomposes thermally makes it difficult to examine this. At 50° no bands were detected, and on the whole, and having regard to the complete nature of the absorption and the failure to retransmit at any higher frequencies, it seems likely that the upper potential-energy curve is a purely repulsive one rising steeply with decreasing nuclear separation.

The absorption limit at 3950 Å. corresponds to absorption of 72 kg.-cals./g.-mol. The region of absorption usually found for the carbonyl group lies, as stated above, at shorter wave-lengths. It seems unlikely, therefore, that absorption occurs *via* this group. Moreover, in this case, bands, even if diffuse, should be detected. Absorption by normal carbon monoxide first occurs in the far ultra-violet, so that this also is not applicable. If then the light enters the $Ni \leftarrow C$ link, 72 kg.-cals. should on the above interpretation be an upper limit for the energy of this bond, some energy disappearing as kinetic energy of the products of dissociation. Thermochemical data by which this may be checked are not available, but in other compounds the energy of a co-ordinate link may be about this value; for instance, the energy of dissociation of $C \equiv O$ is 235 kg.-cals., that of $C{=}O$ 163 kg.-cals., the difference being 72 kg.-cals. It is clear that a strict addition of bond energies in this way is not legitimate, but it will be correct as regards order of magnitude. The exact agreement is fortuitous but nevertheless striking.

Since the lowest known excited level of carbon monoxide is not lower than 4·8 volts (109 kg.-cals.) and is probably 5·98 volts (136 kg.-cals.) (Birge, *Physical Rev.*, 1926, **28**, 1157), it is probable that in the primary dissociation normal carbon monoxide molecules are formed. The most likely mechanism is then $Ni(CO)_4 + h\nu \longrightarrow Ni(CO)_3 + CO$, the $Ni(CO)_3$ later decomposing spontaneously to give nickel and carbon monoxide. Energy may be liberated in this spontaneous process, leading to some excitation of the products.

Nickel carbonyl, however, decomposes relatively easily below *ca.* 100°, although the rate is erratic and may depend to a considerable extent on surface factors (cf. Mittasch, *loc. cit.*). It is possible, though not probable, that the energy of activation of the " gaseous " decomposition is less than 20 kg.-cals. Presumably this is introduced into the molecule as energy of vibration of the $Ni \leftarrow C$ linkages. It might then be supposed that in the photochemical decomposition the 72 kg.-cals. are absorbed by one $Ni \leftarrow C$ linkage and then distributed among all four, giving to each approximately the amount suggested by the thermal process. For various reasons this is unlikely. It is, moreover, not uncommon to find the energies required for photochemical change higher than those for the corresponding thermal reactions.

On the above basis the quantum efficiency should be 1 mol. of nickel carbonyl decomposing per quantum, with formation of 4 mols. of carbon monoxide. Difficulties of various kinds are inherent in the measurements, but preliminary experiments in carbon tetrachloride (to be reported later) give a value of the correct order.

To comply with the quantum efficiency of 2 in the decomposition of iron carbonyl, Eyber suggested the mechanism given on p. 525. The continuous nature of the absorption shows, on the other hand, that the primary act is a dissociation, and it is more likely that the changes are to be represented as follows:

$$Fe(CO)_5 + h\nu \longrightarrow Fe(CO)_4 + CO, \quad Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9.$$

This mechanism was suggested by Dewar and Jones, who also demonstrated the greater stability of iron tetracarbonyl than of nickel tricarbonyl. It agrees with a quantum efficiency of 2 and covers the other facts. The limit at 4100 Å. implies absorption of 69 kg.-cals. by the Fe←C link, a rather smaller value than in the case of Ni←C. This difference is not unreasonable: iron carbonyl decomposes thermally only at much higher temperatures than those needed for the decomposition of nickel carbonyl. The energy of activation for the change $Fe(CO)_5 \longrightarrow Fe(CO)_4 + CO$ may be of the order 30 kg.-cals. Here, too, therefore, the photochemical quantum exceeds the thermal critical energy.

SUMMARY.

(1) The absorption spectrum of nickel carbonyl vapour or its solution in hexane or carbon tetrachloride is continuous from 3950 Å. towards shorter wave-lengths.

(2) The absorption spectrum of iron pentacarbonyl vapour is continuous from 4100 Å. towards shorter wave-lengths. In hexane or carbon tetrachloride the continuum begins at 5500 Å.; the difference is probably due to the presence of diferrononacarbonyl as impurity.

(3) In both cases the primary act in the absorption of light must be a dissociation.

(4) The mechanism suggested for the photochemical decomposition of nickel carbonyl is $Ni(CO)_4 + h\nu \longrightarrow Ni(CO)_3 + CO$, $Ni(CO)_3 \longrightarrow Ni + 3CO$.

(5) Previous theories of the mechanism of the photochemical decomposition of iron carbonyl are amended to the following: $Fe(CO)_5 + h\nu \longrightarrow Fe(CO)_4 + CO$, $Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9$.

We are grateful to the Government Grant Committee of the Royal Society for a grant, to The Mond Nickel Co. Ltd. for the gift of nickel carbonyl, and to Prof. H. H. Plaskett of the University Observatory for enabling us to make the photometric measurements.

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